DEVELOPMENT AND EVALUATION OF CARBON-BASED QUANTUM DOTS FOR CARBON DIOXIDE PHOTOCONVERSION

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DEVELOPMENT AND EVALUATION OF CARBON-BASED QUANTUM DOTS FOR CARBON DIOXIDE PHOTOCONVERSION

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
Sushant Sahu
September 2014

Accepted by:
Dr. Ya-Ping Sun, Committee Chair
Dr. Brian Dominy
Dr. Andrew G. Tennyson
Dr. Bruce Gao
ABSTRACT

World energy consumption has increasingly grown over the past several decades. Because of its potential in photochemical energy conversion, photocatalysis has been the subject of much recent research. Recently, carbon or graphene-based quantum dots have attracted growing attention in solar energy conversion applications, because of its unique optoelectronic properties, broad-band optical absorption, bright fluorescence emissions, favorable photoinduced electron transfer properties, reliable chemical inertness and stability, cost-effectiveness, and non-toxicity. While nanosized wide band gap semiconductor-based systems were largely at the center of attention in such studies, carbon-based quantum dots have recently emerged as a new class of semiconductor like photoactive materials, due to some of its excellent optical figures of merit suited for light harvesting applications.

In this dissertation, we have demonstrated the possibility of using quantum-sized carbon particles as chromophores for photosensitized energy conversion and visible-light photocatalysts for carbon dioxide conversion to organic acids as well as results supporting photoinduced redox properties in carbon nanodots. Metal- and semiconductor-doped carbon nanodots in various configurations have been developed for their utility in photocatalytic conversion of carbon dioxide. Our results demonstrate that nanoscale carbon dots represent a promising new alternative platform for light-driven energy conversion applications, competitive to conventional nanoscale semiconductor-based photocatalytic systems.
DEDICATION

Dedicated to my father Mr. Prabhakar Sahu and my wife Sumati.
ACKNOWLEDGMENTS

First and foremost, I would like to thank my advisor Professor Ya-Ping Sun for providing this research opportunity and for his continuous support, rigorous guidance, and constructive criticisms as well as his patience during my Ph.D. program at Clemson. His passion, dedication, focus along with his diligent approach towards research has had a significant impact on me during my graduate school journey. His clear and firm vision has helped me to overcome my frustration on numerous occasions during this research process.

My sincere thanks also go to my Ph.D. committee members, Dr. Brian Dominy, Dr. Andrew Tennyson and Dr. Bruce Gao, for their time, expertise, suggestions and critiques during the completion of this dissertation. I am grateful for their support and understanding in my research pursuits.

I want to thank the past and present members of Dr. Sun’s lab for their assistance, cooperation, discussions and companionship during my time here at Clemson. Specifically, my thanks go to past members Dr. Mohammed Meziani, Dr. Li Cao, Dr. Anilkumar Parambath, Dr. Sumit Sonkar, Dr. Xin Wang, and Dr. George Luo and the current group, especially Gregory Lecroy for his insightful discussions, Fan Yang and Yamin Liu. I would particularly like to thank Mrs. Ping Wang for her assistance and support in the lab whenever I needed it.

I also want to express my appreciation to Dr. Christopher Huebner at COMSET for providing access to the fluorescence lifetime instrument facility at Clemson.
University, and I would like to acknowledge the Chemistry Department and its associated staff for their useful tools and resources when required during my graduate studies.

Last but not least, I would like to thank my friends and family. My eternal thanks go to my wife and my parents back home in India for their unconditional love and care. I would not have achieved this without their understanding, belief and support.
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CHAPTER ONE

CARBON “QUANTUM” DOTS FOR PHOTOINDUCED ENERGY CONVERSION

1.1 Introduction

Because of its potential in photochemical energy conversion, photocatalysis has been the focus of much recent research.\(^1-3\) Solar energy is the most abundant, environmentally clean, effective, safe and sustainable energy source, providing approximately 120,000 TeraWatt (TW) annually to the Earth.\(^4, 5\) However, several difficult technical issues need to be addressed before it and other renewable sources of solar energy can be effectively used to meet global energy needs, primarily efficient harvesting, conversion, and storage. Currently, the global consumption of power is approximately 16.0 TW, of which roughly 85% comes from burning fossil fuels (oil, natural gas and coal), and it is estimated that by 2050, the average demand for primary power will be on the order of 30 TW,\(^4, 5\) meaning to make a significant impact on a global scale, technological advances and materials for energy harvesting, conversion or storage for a sustainable future should be able to scale to the TW level.

The increasing demand for clean energy technology has generated much research in the development of nanostructured materials for efficient solar harvesting to address current global energy related concerns, in particular CO\(_2\) conversion to hydrocarbon fuels and solar water splitting for hydrogen (H\(_2\)) generation, both of which were recently identified as key emerging energy applications.\(^6-14\) The aim of these studies is to discover
new material systems that enable conversion efficiencies beyond 10%, the U.S. Department of Energy’s (DOE’s) target for a commercially viable photocatalyst.\textsuperscript{15} In addition, the increasing demand for renewable energy sources requires the development of inexpensive, nontoxic, stable catalysts with a capability of retrieval and extended use without substantial loss of activity for efficient solar light-harvesting materials. The global potential of solar energy to power the world is an attractive alternative, one that can mitigate problems caused by the climate shift due to global warming resulting from CO\textsubscript{2} emissions. Moreover, photocatalytic conversion of solar energy to chemical energy or electricity provides a variety of possible options for local, off-the-grid power. In addition, traditionally photocatalytic reactions on the catalyst surface (e.g. TiO\textsubscript{2}) are also seen as a promising approach for addressing air pollution and environmental remediation including water purification and developing self-cleaning surfaces for building materials or coatings.\textsuperscript{16-20} However, the primary challenge is the lack of active, stable multifunctional catalysts that can efficiently harvest abundant solar energy as well as promote interfacial charge separation and CO\textsubscript{2} activation to facilitate proton-coupled electron transfer to generate value-added solar fuels and produce hydrogen energy from water splitting reactions.\textsuperscript{7,11}

It is estimated that the total solar energy intercepted by the earth in one hour is more than the world’s total energy consumption in an entire year.\textsuperscript{4} The ability to harvest this potential resource comes down to a number of technological challenges that are primarily synthetic in nature. Of critical importance is the design of materials that efficiently absorb solar light and convert its energy into long-lived charge-separated
states, transfers and subsequent photoredox reactions. The majority of the solar photodriven reactions are currently focused on water splitting and the conversion of CO₂. The ideal process would involve the simultaneous reduction of CO₂ and water to yield hydrocarbons and value-added fuels.

Materials extensively used for photoinduced energy conversion include nanoscale semiconductors, such as metal oxide-based semiconductors and semiconductor quantum dots (QDs). The semiconductors usually function as photocatalysts because of their narrow energy gap between the valence and conduction bands. In order for photocatalysis to occur, they need to absorb energy equal to or more than their energy gap, resulting in the promotion of an electron (e⁻) from the valence band (VB) to the conduction band (CB), leaving a positive hole (h⁺) in the VB. The photogenerated e⁻/h⁺ pair separate and migrate to react with electron donors or acceptors adsorbed on the catalyst surface. They can take different paths, either recombining non-radiatively as heat or radiatively by emitting light, generating phonons, or becoming trapped in shallow or deep traps or through the back transfer of charge carriers from an adsorbed molecule to the semiconductor photocatalyst (Figure 1.1).³

For a specific photoreaction to occur, the photocatalyst must have an energy band-gap and band-edge positions as well as appropriate physicochemical properties. The band-edge structure indicates the ability for light harvesting and the thermodynamic limitations of the photoreactions that can be carried out by the charge carriers. Variations in physicochemical properties, such as size, morphology, surface area, and crystallinity, have also been found to play a role in the adsorption ability of the catalyst and the charge
Figure 1.1 (a) Schematic representation of a photocatalytic reaction mediated by a semiconductor nanocrystal. Photoexcited electrons migrate to the surface and reduce an electron acceptor (A), while the holes oxidize an electron donor (D). This process is in competition with electron-hole recombination pathways. (b) Energy level diagram for a photocatalytic reaction, indicating energetic requirements for valence and conduction band edges ($E_{VB}$ and $E_{CB}$) with respect to reduction potentials of the donor and acceptor ($E (D^+/D)$ and $E (A/A^-)$). (c) Schematic illustration of surface trap sites with their electronic energy states localized within the semiconductor band gap. (From Ref. [3].)
carrier separation and transfer in photocatalytic reaction.\textsuperscript{7, 11} Smaller particles (very high surface to volume ratios) without aggregation are the preferred photocatalysts because of their high specific surface areas and their number of surface reactive sites, both of which increase the probability of photogenerated charge carriers reaching the interface without recombination. However, nanostructures of semiconducting particles exhibit quantization effects when the electronic particles (negative electrons and positive holes) of these materials are confined to very small spaces, usually sizes below the Bohr exciton radius.\textsuperscript{21, 22} This quantum confinement results in unique optical and electronic properties with the potential for inexpensive photon harvesting and solar energy conversion to useful hydrocarbons.

One and two dimensional single-crystalline nanostructures such as nanorods, nanowires, nanotubes and nanosheets have been found to have higher specific surface areas and lower charge carrier recombination rates than nanospheres. The high crystallinity of these nanostructures is also advantageous for reducing the density of the defects caused by grain boundaries, which often act as recombination sites for photogenerated carriers.\textsuperscript{2, 7, 11}

Some of the other commonly adopted practices for improving overall photochemical efficiency include the addition of sacrificial agents in the reaction medium to selectively trap one of the photogenerated charges, the inclusion of a noble metal co-catalyst, and coupling with other semiconductors.\textsuperscript{7, 11} Sacrificial electron donors and metal doping (Au, Pt, Ag, Rh, Pd, Cu, etc.) are often used to achieve measurable product yields, where metal nanoparticles are believed to retard electron-hole recombination by
serving as electron sinks/traps and to facilitate interfacial electron transfer, while sacrificial agents such as aliphatic alcohols (e.g. isopropanol, methanol) are generally used as electron donors to enhance overall reaction kinetics, apparent quantum yields and product yields.\textsuperscript{7, 11} The formation of heterojunction structures by coupling two nanostructured semiconductors with different band gaps and matching band potentials are used to extend light absorption, improve charge separation, and enhance the interfacial charge-transfer efficiency.\textsuperscript{7, 11, 14}

More recently, carbon-based nanostructures have seen increasing attention in photocatalysis research because of their unique optoelectronic properties, efficient visible-light photoactivity, rich photoinduced electron transfer properties, reliable chemical inertness and stability, cost-effectiveness, and non-toxicity.\textsuperscript{14, 23, 24} This chapter provides a brief overview of the state of photocatalysis research on these carbon-based nanostructures. More specifically, carbon-based quantum dots and graphene-based nanoarchitectures will be reviewed from the standpoint of photocatalytic solar energy conversion applications with a special emphasis on CO\textsubscript{2} photoconversion. After a brief discussion of their optical and photophysical characteristics, the chapter goes on to explore and summarize recent progress on the potential of using carbon-based nanostructures and carbon-based quantum dots as building blocks in solar energy conversion applications. With a focus on the recent advancement in their use as photocatalysts, optoelectronic devices and solar cells will be highlighted, along with a discussion on the potential and the challenges of these fields.
1.2 Synthetic Strategies and Optical Properties of Carbon Quantum Dots

1.2.1 Carbon Dots: An Overview

The discovery of photoluminescent carbon nanoparticles, referred to as “carbon dots” in an original report in 2006 by Sun et al., led to much research on the development of luminescent carbon-based nanoparticles. They are often synthesized through laser ablation of graphite, arc discharge of graphitic rods, plasma treatment, electrochemical oxidation of graphite, electrochemical soaking of carbon nanotubes, thermal oxidation of suitable molecular precursors, hydrothermal and solvothermal routes, vapor deposition of soot, proton-beam irradiation of nanodiamonds, pyrolysis of food precursors, microwave/ultrasonic synthesis and bottom-up methods.

In the original study, Sun et al. found that nanoscale carbon particles exhibited strong, colorful photoluminescence in both the solution and the solid state upon surface passivation with soft polymeric amines. The resulting photoluminescence spectra were generally broad and excitation wavelength dependent (Figure 1.2). These nanoscale carbon particles were initially synthesized through laser pyrolysis (Nd: YAG laser, 1064 nm, 10 Hz) of a graphitic target, followed by acid treatment and surface passivation with organic molecules such as PEG1500N (diamine-terminated oligomeric polyethylene glycol, \( \text{H}_2\text{NCH}_2(\text{CH}_2\text{CH}_2\text{O})_{35}\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \)) or PPEI-EI (polypropionylethyleneimine-co-ethyleneimine). Both PEG1500N and PPEI-EI-functionalized samples were found to disperse well in an aqueous solution with particles measuring sub-10 nm diameter as confirmed by TEM and AFM analyses.
Figure 1.2 Top: PEG$_{1500}$N attached carbon dots excited at the indicated wavelengths and photographed directly and Bottom: The absorption (ABS) and photoluminescence (PL) emission spectra (with progressively longer excitation wavelengths from 400 nm on the left in 20 nm increment) of PPEI-EI carbon dots in an aqueous solution. The emission spectral intensities are normalized to quantum yields (normalized to spectral peaks in the inset). (From Ref. [28a].)
Carbon dots possess excellent optical figures of merit suited for light harvesting applications that are competitive with semiconductor quantum dots and far superior to a typical dye molecule.\textsuperscript{34, 35} Some relevant optical figures of merit for carbon nanoparticles include high molar absorptivity (50 M\textsuperscript{−1}C\textsubscript{atom} cm\textsuperscript{−1} at around 450 nm),\textsuperscript{36} high fluorescence quantum yields (~55-60\% through gel column separation),\textsuperscript{38} high radiative rates (~ 1 x 10\textsuperscript{8} s\textsuperscript{−1}),\textsuperscript{38} high multiphoton absorption cross-sections (~39000 Goeppert-Mayer unit or GM),\textsuperscript{28b} tunable emission, non-blinking and photostability.\textsuperscript{23, 29}

1.2.2 Optical Absorption and Photoluminescence Properties:

Most carbon quantum dots and/or crystalline graphene-based quantum dots usually exhibit well-established optical absorption bands in the UV region, with a long tail extending into the visible region.\textsuperscript{23, 24} The absorbance of carbon dots was found to slightly increase and become more prominent towards longer wavelengths, exhibiting a weak shoulder in the visible range (around 400-450 nm) upon surface passivation with soft polymeric species.\textsuperscript{38, 39} Small aqueous suspended carbon nanoparticles have been found to be strongly absorptive over the UV/vis spectral region (Figure 1.3), with the estimated molar absorptivity at 400-450 nm around 50 M\textsubscript{C-atom} cm\textsuperscript{−1} (M\textsubscript{C-atom} denotes molar concentration in terms of carbon atoms in the suspension of carbon nanoparticles). The optical absorption of nanoscale carbon particles can be attributed primarily to the π-plasmon absorption broadly covering the UV/vis and near-IR spectral regions (Figure
1.3), likely originating from the collective excitation of π-electron density (similar to the π to π*-like transition states of C=C) that probably arise from sp² graphitic domains (π-domains) or sp² islands as found in nano-sized graphitic particles. In addition, the UV-visible absorption spectrum of carbon dots, although featureless, overlaps well with the solar spectrum around the visible to near-IR spectral range (Figure 1.3).
Figure 1.3 Left: A representative UV/vis absorption spectrum of aqueous suspended carbon nanoparticles. Right: The observed absorption spectrum of broadly distributed carbon dots (solid line) compared with the solar spectrum around the visible spectrum at sea level (dashed line).
There have been many reports on the observation of fluorescence emissions in carbon quantum dots. This fluorescence has been tentatively suggested to result from excitons (electron-hole pairs) in photoexcited carbon nanoparticles, emissive traps, aromatic conjugate structures, oxygen-containing groups, free zig-zag sites having carbene-like triplet ground state and edge defects. In addition, one of the interesting features of fluorescence in carbon dots (C-dots) is the excitation wavelength dependence of the emission and its intensity, whether it arises due to quantum confinement effects because of varying sizes of nanoparticles and/or different emissive traps on the C-dots surface or a mechanism that is not yet entirely understood. This size-dependent photoluminescence (PL) behavior of C-dots has been observed by many researchers. As evident from X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectroscopic studies by several groups worldwide, synthesized carbon dots have various functional groups including C=O, C-O-C, C=O, and C–H on the surface which may result in a series of diverse emissive traps between the π and π* states of C=C or the sp² domains. The oxygen-containing groups on the surface of C-dots may form “surface states”, which may affect the energy gap of the surface trap. Hence, the different kinds and the relative population of the functional groups on the surface of C-dots probably cause such changes in their emission as intensity and the position of the PL peaks. Experimentally, when a certain excitation wavelength is used to photoexcite carbon dots, a surface energy trap dominates the emission, with another corresponding surface state emissive trap becoming dominant as
the excitation wavelength is changed. Hence, the photoluminescence (PL) mechanism is probably controlled by both size and surface defects.

The widely accepted mechanism of fluorescence emission in carbon dots is attributed to the radiative recombination of the carbon particle surface-trapped electrons and holes, phenomenologically resembling those found in nanoscale semiconductors. The exciton migration may occur to surface traps (trap states), resulting in non-radiative relaxation pathways without emission to the original ground state, consequently acting as quenching sites leading to lower PL quantum yields in naked carbon nanoparticles (without any deliberate surface passivation).\textsuperscript{61-66} Particles with greater surface to volume ratios, and thus smaller carbon nanoparticles, with more diverse surface trapping sites and with their in-particle interactions stabilized by the surface passivation agents apparently result in stronger fluorescence emissions in carbon dots (surface-passivated carbon nanoparticles). This surface passivation effect/phenomenon was observed while studying the fluorescence quenching of naked carbon nanoparticles by aliphatic amines (e.g. ethyl amine), exhibiting reverse Stern-volmer quenching behavior with increasing luminescence intensities at very low quencher concentrations (~ sub mM regime) of aliphatic amines (Figure 1.4).\textsuperscript{64}
Figure 1.4 Stern-volmer plots of the quenching of luminescence intensities (400 nm excitation) of carbon nanoparticles by ethyl amine. (From Ref. [64].)
As reported in the literature, photoexcited carbon dots not only serve as excellent electron acceptors \(^{23, 67, 68}\) but also as electron donors to be responsible for the observed photoinduced energy conversion.\(^{52, 69, 70}\) The photoluminescence spectra of carbon dots (C-dots), which are generally broad with substantial stokes shifts, are dependent on excitation wavelength, indicating spectral heterogeneity (Figure 1.2) and dominant emission in the blue-green region with fluorescence quantum yields at 400 nm usually approaching more than 10%.\(^{23, 29}\) Luminescence decays from laser-ablation produced C-dots excited at 407 nm have multi-exponential PL decays with average excited-state lifetimes of 5 ns for emissions at 450 nm and 4.4 ns for emissions at 640 nm, suggesting different emissive sites.\(^{28a}\) Sun and coworkers also explored the effects of passivation of small carbon nanoparticles using a combination of surface-doping with nanoscale semiconductors such as TiO\(_2\), ZnS, and ZnO and organic functionalization coupled with gel column fractionation to harvest fluorescent carbon dots exhibiting fluorescence emission quantum yields of up to 78%.\(^{37, 39}\)

1.3 Photocatalytic CO\(_2\) Reduction, Hydrogen Generation and Degradation of Organic Pollutants: Recent Progress

1.3.1 CO\(_2\) Photoreduction

In the photocatalytic conversion of CO\(_2\) on a semiconductor photocatalyst, the photogenerated electrons and holes are transferred to CO\(_2\) and H\(_2\)O through a series of
reactions, leading to the formation of hydrocarbons such as formic acid, carbon monoxide, formaldehyde, methanol and methane: 7

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{HCOOH} \quad E_{\text{Redox}}^0 = -0.61 \text{ V} \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{CO} \quad E_{\text{Redox}}^0 = -0.53 \text{ V} \\
\text{HCOOH} + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E_{\text{Redox}}^0 = -0.48 \text{ V} \\
\text{HCHO} + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{CH}_3\text{OH} \quad E_{\text{Redox}}^0 = -0.38 \text{ V} \\
\text{CH}_3\text{OH} + 2\text{H}^+ + 2\text{e}^- &\rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad E_{\text{Redox}}^0 = -0.24 \text{ V} \\
2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- &\rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \quad E_{\text{Redox}}^0 = -0.31 \text{ V} \\
2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- &\rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \quad E_{\text{Redox}}^0 = -0.33 \text{ V} \\
2\text{H}^+ + 2\text{e}^- &\rightarrow \text{H}_2 \quad E_{\text{Redox}}^0 = -0.41 \text{ V} \\
\text{H}_2\text{O} + \text{h}^+ &\rightarrow \cdot\text{OH} + \text{H}^+ \quad E_{\text{Redox}}^0 = +2.32 \text{ V} \\
2\text{H}_2\text{O} + 2\text{h}^+ &\rightarrow \text{H}_2\text{O}_2 + 2\text{H}^+ \quad E_{\text{Redox}}^0 = +1.35 \text{ V} \\
2\text{H}_2\text{O} + 4\text{h}^+ &\rightarrow \text{O}_2 + 4\text{H}^+ \quad E_{\text{Redox}}^0 = +0.82 \text{ V} \\
\end{align*}
\]

(Note: The potentials are in reference to a Normal Hydrogen Electrode at pH 7.)
Figure 1.5 Schematic illustration of a photocatalytic CO$_2$ reduction on a semiconductor photocatalyst.
Thus, in principle, in order to reduce the CO$_2$ to fuel such as methane, electrons in the conduction band should have more negative potential than the redox potential of CO$_2$/CH$_4$ (-0.24V Vs NHE) to provide the driving force for the reaction.$^7$ Although the specific photochemical mechanisms are not well understood, it is proposed they involve shared intermediates through multiple complex reaction pathways.$^7, 71$ The concept of a semiconductor-mediated photocatalytic reduction of CO$_2$ is illustrated in Figure 1.5. Thermodynamically, this reaction is an uphill one, with a large positive change in the Gibbs free energy.

Large band-gap semiconductors are the most suited photocatalysts for CO$_2$ reduction because they provide sufficient negative and positive redox potentials in their conduction bands and valence bands, respectively.$^7$ However, a significant disadvantage of using wide band-gap (UV absorbing) semiconductors is their inability to use visible-light efficiently. Moreover, the solar spectrum contains only a small proportion of UV ($\sim 4-5\%$), a condition that limits the application of widely used wide band-gap semiconductors for photocatalytic solar energy conversion.$^6-14$ In addition, achieving selectivity in CO$_2$ reduction is more problematic than in water splitting where H$_2$ and O$_2$, are the only possible final products. Additionally, CO$_2$ is a very stable molecule, with a low aqueous solubility ($\sim 33$ mM under ambient conditions i.e. at 1 atm and $\sim 25^0$C) resulting in a low photoconversion efficiency.$^7$

The low photochemical quantum yields are the current challenge in the photocatalysis process. Often, the catalytic efficiency for CO$_2$ photoreduction is measured in terms of production rates ($\mu$mol h$^{-1}$ or $\mu$mol g$^{-1}$ h$^{-1}$), with photocatalytic
activity usually depending on the specific amount of the photocatalyst, the illumination
time, the illumination intensity and the illumination area; thus, it can be measured by
estimating the apparent quantum yields calculated by quantified photoproducts and the
incident number of photons absorbed by the catalyst based on the following equation:

\[
\text{Apparent Quantum Yield (AQY \%)} = \frac{\text{Number of Reacted Electrons}}{\text{Number of Photons Absorbed}} \times 100
\]

As mentioned before, the efficiency of a photocatalytic reaction on a catalyst is
driven by the ratio of the surface charge carrier transfer rate \(k_{\text{redox}}\) to the photoexcited
charge carrier recombination rate \(k_{\text{recombination}}\). Time resolved spectroscopic studies\(^{72,73}\)
have found that most of the photogenerated electron-hole pairs (~90%) recombine very
quickly after photoexcitation, with only a fraction (~5%) of these charges able to be
accessed for redox reactions at the interface before they undergo this rapid
recombination\(^{74}\), leading to relatively low quantum efficiency for a majority of the
semiconductor-based photocatalytic reactions.

Semiconductor nanomaterial-based systems have been extensively studied in solar
energy conversion applications\(^ 3, 6-15\) since the discovery of the Honda-Fujishima effect
in 1972.\(^ {75}\) Titania (TiO\(_2\)) constitutes the most common benchmark photocatalysts due to
its electronic structure and appropriate physicochemical properties.\(^ 7\) However, the most
significant disadvantage of this wide band-gap semiconductor is that its range of light is
limited to the UV spectrum.\(^ 7, 10, 76, 77\) This issue can be addressed through metal ion
(cation or anion) doping including transition metal ions, thereby extending the
photoactivity towards the visible range by introducing newly occupied electronic levels near the top of the original valence band.\textsuperscript{78,79} However, the reason for this modification is often not sufficiently clear, suggesting that the conditions required for doping and its influence on photocatalytic activity needs further clarification to support its use in the rational improvement of photocatalytic materials.\textsuperscript{2,7} To date a number of semiconductor-based photocatalysts, both metal oxide and non-oxide semiconductors (e.g. TiO\textsubscript{2}, ZrO\textsubscript{2}, Ta\textsubscript{2}O\textsubscript{5}, Ga\textsubscript{2}O\textsubscript{3}, ZnO, WO\textsubscript{3}, GaP, GaN, SiC, CdS, ZnS, Bi\textsubscript{2}WO\textsubscript{4}, ZnGa\textsubscript{2}O\textsubscript{4}, and NaTaO\textsubscript{3}), that include nitrides, sulfides, oxynitrides, and oxysulfides have been developed for photocatalytic applications based on the advances already made in this area.\textsuperscript{6-10}

More recently, because of the cost-effectiveness of carbon-based nanomaterials, including those made of pure carbon, their use as semiconducting nanocomposites in photocatalytic reactions has been rapidly growing in the research community.\textsuperscript{8,14,23,24,80-90} Carbon-based nanostructures exhibit unique and novel optical properties.\textsuperscript{14,23,24,29,89} For example, graphene as a single layer graphite with close-packed conjugated hexagonal lattices forming a 2D honeycomb structure exhibits superior properties such as high electrical and thermal conductivity (electron mobility ~ 200000 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} and thermal conductivity ~ 5000 W m\textsuperscript{-1} K\textsuperscript{-1}), good transparency (97.7%), good mechanical strength, flexibility, and a large specific surface area (2630 m\textsuperscript{2} g\textsuperscript{-1}).\textsuperscript{14} It is usually described as a zero band-gap semiconductor as the $\pi^*$-state conduction band and the $\pi$-state valence band touch each other at the Dirac point. The band structure of graphene is symmetric about this point with the Fermi level located between the valence band and the conduction band.\textsuperscript{14}
Also of particular interest is graphene oxide (GO), which is typically prepared through the chemical exfoliation of graphite by strong oxidants via the widely used Hummer’s method.\textsuperscript{91} GO can be considered as an individual sheet of graphene with oxygen-containing functional groups (such as hydroxyl, epoxy, and carboxyl) on both the basal plane and the edges.\textsuperscript{92} In graphene-based composites, graphene acts either as a functional component or a substrate for immobilizing the other components. The large specific surface area coupled with its high conductivity usually facilitates charge transfer, transport and subsequent redox reactions, as well as provides the mechanical strength of the resulting composites and extends the light absorption range. Hence, anchoring photocatalysts and redox active materials on graphene has the potential to improve the performance of the resulting composites in photocatalytic applications in which graphene serves as an electron collector and transporter as it efficiently hinders electron-hole recombination and lengthens the lifetime of the photo-generated charge carriers from semiconductor nanoparticles.\textsuperscript{14, 80, 85}

The most common approaches for the synthesis of exfoliated graphene sheets are the mechanical cleavage of highly pyrolytic graphite, which results in low production yields; the chemical vapor deposition (CVD) method; and the oxidation-exfoliation-reduction of graphite powder via chemical treatment resulting in reduced graphene oxide with partly restored graphitic structure and conductivity.\textsuperscript{85, 87, 88}
1.3.2 CO₂ Photoconversion with Carbon-based Catalysts

Cao et al. used surface-functionalized small carbon nanoparticles (sub-10 nm size) for the absorption of visible photons to drive photocatalytic processes. Similar to the method traditionally used in the development of conventional nanoscale semiconductor-based photocatalysts, in the photoreduction of CO₂, the carbon dots were surface-doped with a small amount of gold or platinum metal (Figure 1.6), which was designed to act as a reservoir for photoexcited electrons, thus preventing them from recombining with holes and promoting an interfacial charge-transfer. The photoconversion of CO₂ was analyzed by quantifying the formation of formic acid as a significant main product, the results indicating that the estimated quantum efficiency of the photoreduction was substantial from that achieved in past research using semiconductor nanoparticles as photocatalysts. More importantly, given that the primary purpose of the study was to understand the photoinduced redox properties in small carbon nanoparticles, these results confirmed the presence of photoinduced charge separation in carbon dots as previously suggested by the fluorescence quenching behavior of carbon dots with either electron donors or acceptors.
Figure 1.6 Top: Aqueous soluble PEG-functionalized carbon nanoparticles before (left, fluorescent) and after (right, photocatalyst for CO$_2$ reduction in aqueous solution) coating with metal (Au or Pt). Bottom: Schematic diagram of photocatalytic CO$_2$ reduction employing aqueous carbon dots in a CO$_2$ saturated optical glass reactor. (From Ref. [70].)
The photoexcited carbon dots in aqueous solution acted as electron donors, reducing the platinum (IV) and gold (III) compounds into their corresponding metals to be deposited on the dot surface, probably primarily at the surface defect-derived energy trapping sites. The deposited metals, even in very small amounts, effectively quenched FL to the degree of almost eliminating the fluorescence emissions (Figure 1.7) in the carbon dots but with essentially no effect on fluorescence decays (essentially the same FL lifetime). The exclusive near-neighbor static quenching can be attributed to the disruption of the electron-hole radiative recombinations, responsible for the fluorescence emissions in carbon dots. The results provide important evidence for the availability of photogenerated electrons that can be harvested for productive purposes, in turn supporting the current mechanistic framework describing the fluorescence emission and photoinduced redox properties of carbon dots.
Figure 1.7 Top: A schematic illustration of the photoreductive deposition of Pt metal on to the carbon dot surface and the subsequent fluorescence quenching. The rainbow “shell” indicates that the fluorescence is likely from the passivated carbon particle surface. Bottom: Observed fluorescence quantum yields ($\Phi_F$, 440 nm excitation, normalized against the value at time zero $\Phi_F^0$) of the carbon dots in aqueous solution without (□) and with the Pt (IV) compound (○) after visible-light photoirradiation for various periods of time. The corresponding spectral intensity changes for the first few (○) data points (with increasing photoirradiation times in the arrow direction) are shown in the inset. (From Ref. [69].)
Naked carbon nanoparticles without any surface passivation have also been used to demonstrate the chromophore-equivalent functions of aqueous suspended small carbon nanoparticles in harvesting visible photons for the reductive coating of the nanoparticles with silver and gold.\textsuperscript{36} In this study, the photoreductive conversion process was monitored by progressive increases in the plasmon absorption (Figure 1.8 A),\textsuperscript{36} and, as a result, the preparation of unique carbon-noble metal core-shell nanostructures that may find potential applications as molecular imaging agents and catalysts.\textsuperscript{36} A similar photodeposition approach was used recently to prepare carbon dot supported silver nanoparticles (CD-Ag nanoparticles) using the carbon dots, both as reducing agents and templates, resulting in a metal-nanoparticle-decorated surface on the dot that improved the performance of organic optoelectronic devices.\textsuperscript{93} Polyethylene glycol (PEG) passivated carbon dots (derived from the decomposition of \(\alpha\)-cyclodextrin) were photoexcited with UV irradiation in the presence of AgNO\textsubscript{3}, which reduced the Ag\textsuperscript{+} ions to silver nanoparticles via electron transfer from the photoexcited carbon dots to obtain CD-Ag nanoparticles with a sub-10 nm size as seen in HR-TEM images (Figure 1.8 B)\textsuperscript{93} consistent with earlier report of carbon dots with other noble metals.\textsuperscript{70}
Figure 1.8 A) UV/visible absorption spectra (0.2 cm optical path-length) of the aqueous suspended carbon nanoparticles with progressively increasing levels of Ag$^0$ coating (upper, with increasing photolysis time in the arrow direction of 0, 1, 2, 3, 4, 6 and 9 h) and Au$^0$ coating (lower, 0, 1, 2.5, 5, 8 and 10 h). (From Ref. [36].)
Figure 1.8 B) (a) Photographs and schematic illustration of AgNO$_3$ and carbon dot (CD) + AgNO$_3$ blend solutions before (left) and after (right) ultraviolet irradiation. (b) HR-TEM image of CD-Ag nanoparticles (NPs). Yellow and red circles indicate the presence of carbon dots and silver nanoparticles, respectively. The red and yellow parallel lines show the distinguishable lattice fringes (3.2 Å and 2.1 Å) of the carbon dots and the silver nanoparticles, respectively. Scale bar, 5 nm. (c) Comparison of UV-vis absorption spectra of CD-Ag nanoparticles in solution and in a film, and carbon dot and AgNO$_3$ solutions after ultraviolet irradiation. (From Ref. [93].)
Photoexcited carbon dots not only behave as electron donors but also serve as excellent electron acceptors\textsuperscript{67,68} as Wang \textit{et al.} demonstrated in their study showing that carbon dots efficiently quench the luminescence of known electron donors such as N, N-diethylaniline (DEA)\textsuperscript{67}. This behavior, which was found to be solvent-dependent, is more efficient in polar solvents, yielding Stern-volmer quenching constants $K_{SV}$ of 19 M\textsuperscript{-1} and 5.1 M\textsuperscript{-1} in methanol and chloroform, respectively (Figure 1.9 A and 1.9 B)\textsuperscript{67}, results indicating a photoinduced electron transfer quenching mechanism. They also found that the PL emission of carbon dots in toluene was quenched by the known electron acceptors 4-nitrotoluene and 2,4-dinitrotoluene, resulting in Stern-volmer quenching constants of 38 M\textsuperscript{-1} and 83 M\textsuperscript{-1} respectively, indicating the latter to be the more effective quencher as expected because of its stronger electron acceptor capability (Figure 1.9 A)\textsuperscript{67}. A similar photoinduced electron transfer property of carbon dots (C-dots) obtained through alkali-assisted electrochemical synthesis was studied by Kang \textit{et al.}\textsuperscript{68} The luminescence decay (485 nm excitation, monitored with a 550 nm narrow band-pass filter) of C-dots in toluene was quenched by known electron acceptor 2,4-dinitrotoluene and electron donor N,N-diethylaniline, resulting in the observation of Stern-volmer quenching constants ($K_{SV} = k_{q} \tau$) of 18.2 M\textsuperscript{-1} and 20.1 M\textsuperscript{-1}, respectively (Figure 1.9 C)\textsuperscript{68}. 
Figure 1.9 A) Stern-Volmer plots for the quenching of luminescence quantum yields (425 nm excitation) of the carbon dots by 2,4-dinitrotoluene (○) and 4-nitrotoluene (△) in toluene; and plots for the quenching of luminescence lifetimes (407 nm excitation) by 2,4-dinitrotoluene (●) and 4-nitrotoluene (▲). The lines represent the best fits (the least-square regression) of the respective data.

Figure 1.9 B) Stern-volmer plots for the quenching of luminescence quantum yields (400 nm excitation) of the carbon dots by DEA in methanol (○, the line from fitting the data points up to 0.05 M) and chloroform (□, the line from fitting the data points up to 0.08 M), and for the quenching of luminescence lifetimes (407 nm excitation) in methanol (●). The low-concentration portion of the same plot for diethylamine as the quencher in methanol (- - - -) is also shown for comparison. (From Ref. [67].)
Figure 1.9 C) Luminescence decays (485 nm excitation, monitored with 550 nm narrow band pass filter) of C-dots in toluene (a) 2,4-dinitrotoluene and (b) DEA (N, N-diethylamidine). Inset: Stern-volmer plot for the quenching of luminescence QY (485 nm excitation) of the C-dots in (a) 2,4-dinitrotoluene and (b) DEA. (From Ref. [68].)
Because of their photoinduced electron transfer characteristics, carbon dots have also been used as an effective photocatalyst for fabricating gold nanoparticles-reduced graphene oxide (AuNPs-rGO) nanocomposites. After UV irradiation in a mixture of graphene oxide (GO) and HAuCl₄ aqueous solution, carbon dots served as an effective photocatalyst for GO and Au (III) complex reduction through photogenerated electrons in carbon dots.⁹⁴

Considering the importance of nano-sized carbons in photocatalysis and energy conversion applications, a number of studies applying various forms of carbons, including graphene-based nanomaterials, have been explored for CO₂ photoconversion in the production of solar fuels.⁸,⁸¹,⁸⁵ For example, graphene oxide (GO), a close relative of carbon nanodots in which a substantial portion of the sp²-hybridized carbons are converted to sp³ hybridization (up to 60% according to Ruoff and coworkers),⁹² was used as a photocatalyst for CO₂ photoreduction to methanol.⁹⁵ A CO₂ to methanol conversion rate of 0.172 µmol g⁻¹ h⁻¹ was achieved using graphene oxide as a photocatalyst synthesized via the modified Hummer’s method under visible-light irradiation, the findings indicating an approximately 6 fold more active catalyst towards CO₂ photoconversion than the pure TiO₂ employed in that study (Figure 1.10).⁹⁵
Figure 1.10 Schematic illustration of the photocatalytic CO$_2$ reduction mechanism on graphene oxide (GO). (From Ref. [95].)
In further research in this area, Li et al. investigated a hydrothermal route for synthesizing ZnO-reduced graphene oxide nanocomposites for CO₂ reduction to methanol at a production rate of 4.58 µmol g⁻¹ h⁻¹ under simulated sunlight,⁹⁶ while Tan et al. obtained reduced graphene oxide-TiO₂ nanocomposites prepared via a solvothermal route for CO₂ photoreduction to methane with a formation rate of 0.135 µmol g⁻¹ h⁻¹ under visible-light.⁹⁷

The effect of the different defect densities of graphene on the photocatalytic reduction of CO₂ to methane was studied by Hersam and coworkers by preparing graphene-TiO₂ nanocomposite thin films.⁹⁸ They found that graphene-TiO₂ nanocomposites with low graphene defect densities showed approximately a 7-fold enhancement over bare TiO₂ for CO₂ photoreduction to methane under visible illumination. This increase was attributed primarily to the enhanced electrical mobility of the graphene that resulted in a longer mean free path for electrons on its surface, thus facilitating the CO₂ photoreduction reactions by allowing photoexcited electrons to more effectively diffuse to reactive sites.⁹⁸ They also demonstrated that the dimensions of the carbon nanomaterial plays a key role in determining the spectral response as does the reaction specificity of carbon-titania nanosheet composite photocatalysts in CO₂ photoreduction.⁹⁹ Non-covalently bound SWCNT-1D-TiNS-2D and graphene-2D-TiNS-2D nanocomposites with low carbon defect densities were synthesized and evaluated for CO₂ photoreduction to methane in the presence of CO₂ saturated water vapor under UV (λ ~365 nm) and visible-light irradiation (λ > 380 nm).⁹⁹ Both systems showed higher photocatalytic rates for methane formation in comparison to pure 2D titania nanosheets
(TiNS). However, the resulting 2D-2D graphene-titania nanosheet composites yielded stronger optoelectronic coupling than the 1D-2D carbon nanotube-titania nanosheet composites, resulting in enhanced photoactivity in the former for CO₂ photoreduction under UV-light, while the 1D carbon nanotubes were found to be more effective titania photosensitizers, absorbing longer wavelengths of light leading to greater photoactivity enhancement under visible-light.⁹⁹

Tu et al. fabricated hollow spheres consisting of molecular-scale alternating Ti₀.₉₁O₂ nanosheets and graphene nanosheets via the combination of the layer-by-layer assembly technique and a microwave irradiation technique to investigate the photocatalytic activity involved in CO₂ conversion.¹⁰⁰ Although CO was the primary photoproduct, a relatively small amount of CH₄ was detected on the graphene-Ti₀.₉₁O₂ hollow spheres with a production rate of 8.91 μmol g⁻¹ h⁻¹ (CO) and a rate of 1.14 μmol g⁻¹ h⁻¹ (CH₄), respectively. The sufficiently compact stacking of ultrathin Ti₀.₉₁O₂ with graphene nanosheets resulted in a 9 times improvement in photocatalytic activity relative to the commercial P25 (TiO₂) catalyst, an increase attributed to the fast photogenerated electron transport to the graphene leading to the spatial separation of electrons and holes and thus the enhanced lifetime of charge carriers in such hybrid nanocomposites.¹⁰⁰

In a subsequent study, an in situ simultaneous reduction-hydrolysis (SRH) technique was used to fabricate 2D sandwich-like graphene-TiO₂ hybrid nanosheets in a binary ethylene diamine (En)/H₂O solvent to serve as photocatalysts for CO₂ conversion to hydrocarbons (CH₄ and C₂H₆) in the presence of water vapor.¹⁰¹ The highest production rate of 8 μmol g⁻¹ h⁻¹ for CH₄ and 16.8 μmol g⁻¹ h⁻¹ for C₂H₆ was achieved.
with a graphene content of 2.0 wt%.\textsuperscript{101} Wang \textit{et al.} obtained graphene-WO\textsubscript{3} nanobelt composites prepared by the hydrothermal method for photoreduction of CO\textsubscript{2} to methane (production rate $\sim$ 0.11 $\mu$mol/h) under visible-light irradiation.\textsuperscript{102} In the absence of graphene, TiO\textsubscript{2} and WO\textsubscript{3} showed unappreciable photocatalytic activity towards methane production, suggesting that graphene can elevate the conduction band of WO\textsubscript{3} for the photoreduction of CO\textsubscript{2} into hydrocarbon fuels.\textsuperscript{102} Lv \textit{et al.} used a Ni/NiO-loaded reduced graphene-modified Ta\textsubscript{2}O\textsubscript{5} composite (NiOx-Ta\textsubscript{2}O\textsubscript{5}-rG) photocatalyst prepared via the hydrothermal method for selective photoreduction of CO\textsubscript{2} or CO\textsubscript{2}/NaHCO\textsubscript{3} and H\textsubscript{2}O to methanol and H\textsubscript{2} under UV-light.\textsuperscript{103} NiOx-Ta\textsubscript{2}O\textsubscript{5}-rG containing 1\% graphene showed the highest reduction of CO\textsubscript{2} to CH\textsubscript{3}OH, producing approximately 3.4 times more CH\textsubscript{3}OH than the corresponding photocatalyst with no graphene under otherwise identical experimental conditions. These findings were explained in terms of the excellent charge separation and transfer characteristics of graphene, both of which hindered the recombination of excited charge carriers in the composite photocatalyst with graphene.\textsuperscript{103}

More recently, carbon materials with stacked 2D graphite-like structures, such as graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) as a metal free organic semiconductor with carbon and nitrogen,\textsuperscript{104} have been explored as photocatalysts for CO\textsubscript{2} conversion. For example, Dong \textit{et al.} demonstrated photoreduction of CO\textsubscript{2} to CO at a 1.9 mM/h production rate in the presence of water vapor using graphitic carbon nitride as a photocatalyst under visible-light ($\lambda > 420$ nm) photoirradiation,\textsuperscript{105} while Mao \textit{et al.} synthesized graphitic carbon nitride through a pyrolysis of urea, demonstrating its selective photocatalytic activity towards CO\textsubscript{2} photoreduction to methanol ($6.28 \mu$mol g\textsuperscript{-1} h\textsuperscript{-1}) and ethanol.
(4.51 μmol g⁻¹ h⁻¹) with an overall quantum efficiency of 0.18%, also under visible-light photoirradiation.¹⁰⁶ In further research, Wang et al. used mesostructured TiO₂/graphitic carbon nanocomposite photocatalysts to serve as catalysts for the conversion of CO₂ and water to CH₄ (1.53 μmol g⁻¹ h⁻¹) and CO (10.05 μmol g⁻¹ h⁻¹) under simulated solar irradiation.¹⁰⁷ More recently, Maeda et al. developed a visible-light responsive hybrid photocatalyst consisting of carbon nitride (C₃N₄) and a small fraction of ruthenium complex for selective photoreduction of CO₂ to formic acid (~ 431 μmol g⁻¹ h⁻¹) with an apparent quantum efficiency of up to 1.5% at 400 nm and a high turnover number in the presence of triethanol amine (TEOA) as electron donor.¹⁰⁸a In addition to a Ru-based complex, a cobalt-based complex (Co-(bpy)₃Cl₂) has also been used to form hybrids with graphitic carbon nitride for selective photoconversion of CO₂ to CO (~ 1.85 μmol/h) using triethanol amine (TEOA) as the electron donor and hydrogen source.¹⁰⁸b

As an emerging material, carbon nanotubes (CNTs) have attracted much attention for use in photocatalytic applications because of their structural features, excellent electronic and mechanical properties, high surface area (~1600 m² g⁻¹), chemical inertness, and stability.⁸⁹, ⁹⁰ Several studies have recently focused on investigating CNTs as scaffolds for anchoring semiconductor nanoparticles and enhancing the selectivity and efficiency of the photocatalytic process.⁸⁹, ⁹⁰ It has been reported that CNTs appear to function in three roles in composite photocatalysts. First, CNTs as an electron acceptor may induce an efficient charge transfer, retarding the charge recombination.¹⁰⁹, ¹¹⁰ Second, as a photosensitizer, CNTs may extend the visible-light absorption of the photocatalyst, enhancing the visible-light harvesting efficiency.¹¹¹, ¹¹² Third, the presence
of CNTs may help enlarge the specific surface area of the photocatalysts, leading to their higher adsorptive ability and their protection from photocorrosion.\textsuperscript{113}

Additional research conducted by Xia \textit{et al.} studied the reduction of CO\textsubscript{2} with H\textsubscript{2}O using MWNT-supported TiO\textsubscript{2} prepared by both sol-gel and hydrothermal methods.\textsuperscript{114} In the sol-gel method, the MWNTs were coated with anatase TiO\textsubscript{2} nanoparticles, and for the hydrothermal method, rutile TiO\textsubscript{2} nanorods were uniformly deposited on the MWNTs. The selectivity of the product depended on the method used in material preparation: formic acid was obtained from the hydrothermal synthesis and ethanol from the sol-gel synthesis.\textsuperscript{114} More recently, Chai and coworkers found that carbon nanotube-Ni doped TiO\textsubscript{2} nanocomposite photocatalysts prepared by the co-precipitation method followed by chemical vapor deposition (CVD) were active in the photocatalytic reduction of CO\textsubscript{2} to methane under visible-light with a production rate of 0.145 \textmu mol g\textsuperscript{-1} h\textsuperscript{-1}, with the photocatalytic CO\textsubscript{2} reduction activity following the order CNT@Ni/TiO\textsubscript{2} > Ni/TiO\textsubscript{2} > TiO\textsubscript{2} under visible-light illumination (Figure 1.11).\textsuperscript{115a} Likewise, Gui \textit{et al.} developed MWCNT@TiO\textsubscript{2} core-shell nanocomposites for the photoreduction of CO\textsubscript{2} to methane at a formation rate of 0.1375 \textmu mol g\textsuperscript{-1} h\textsuperscript{-1} under visible-light irradiation under ambient conditions.\textsuperscript{115b}
Figure 1.11 Schematic illustration of the charge transfer for the photoreduction of CO$_2$ with H$_2$O using CNT@Ni/TiO$_2$ nanocomposites under visible light irradiation with the introduction of a new energy level, Ev. (From Ref. [115a].)
Table 1.1 Summary of the literature on photoreduction of CO\(_2\) using carbon-based catalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Loadings Or Co-catalysts</th>
<th>Primary Photoproducts</th>
<th>Product Yields (\mu\text{mol g}^{-1} \text{h}^{-1})</th>
<th>Quantum Efficiency</th>
<th>Light Source and Light Intensity</th>
<th>Experimental Conditions ( Reactants, Time, T(^{\circ})C)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dots</td>
<td>Au or Pt</td>
<td>HCOOH</td>
<td>-</td>
<td>0.3%</td>
<td>450 W Xe Arc Lamp with 425 nm cut-off filter</td>
<td>CO(_2) saturated aqueous solution in an optical cell under ambient conditions, 5 h irradn., 25(^{\circ})C; roughly order of magnitude higher than DegussaP25 (TiO(_2))</td>
<td>70</td>
</tr>
<tr>
<td>Graphene-titania Nanocomposite</td>
<td>None</td>
<td>CH(_4)</td>
<td>-</td>
<td>-</td>
<td>100 W Hg vapor lamp for UV-light (~ 100 W/m(^2)) and 60 W day light bulb for visible-light (~ 31 W/m(^2))</td>
<td>H(_2)O saturated CO(_2) in 25 ml teflon reactor 3 h irradn. under ambient conditions, 25(^{\circ})C; 4.5 time higher CH(_4) than titania under UV and 7.2 times higher than titania under visible-light</td>
<td>98</td>
</tr>
<tr>
<td>Ti(_{0.91})O(_2) and graphene Nanocomposite</td>
<td>None</td>
<td>CH(_4), CO(_2)</td>
<td>8.91, 1.14</td>
<td>-</td>
<td>300 W Xe lamp</td>
<td>CO(<em>2) saturated water vapor in 230 ml reactor under ambient conditions, 6 h irradn.; Overall conversion ~ 5 times higher than pure Ti(</em>{0.91})O(_2) and 9 times higher than commercial P25</td>
<td>100</td>
</tr>
<tr>
<td>TiO(_2)-graphene 2D sandwich like hybrid nanosheets</td>
<td>None</td>
<td>CH(_4), C(_2)H(_6)</td>
<td>8, 16.8</td>
<td>-</td>
<td>300 W Xe lamp</td>
<td>CO(_2) saturated water vapor in 230 ml reactor under ambient conditions, 4 h irradn.</td>
<td>101</td>
</tr>
<tr>
<td>2D–2D graphene-titania nanosheet</td>
<td>None</td>
<td>CH(_4)</td>
<td>-</td>
<td>-</td>
<td>100 W Hg-vapor lamp for UV-light (~ 100 W/m(^2)) and 60 W day light bulb for visible light (~ 31 W/m(^2))</td>
<td>H(_2)O saturated CO(_2) in 25 ml teflon reactor 3 h irradn. under ambient conditions, 25(^{\circ})C; 3.5 times higher CH(_4) than titania under UV and 3.7 times higher than titania under visible-light</td>
<td>99</td>
</tr>
<tr>
<td>1D–2D carbon nanotube-titania nanosheet</td>
<td>None</td>
<td>CH(_4)</td>
<td>-</td>
<td>-</td>
<td>2 times higher CH(_4) than titania under UV and 5.1 times higher than titania under visible-light</td>
<td>2 times higher CH(_4) than titania under UV and 5.1 times higher than titania under visible-light</td>
<td>99</td>
</tr>
<tr>
<td>TiO(_2)-graphitic carbon composite</td>
<td>None</td>
<td>CH(_4), CO</td>
<td>1.53, 10.05</td>
<td>-</td>
<td>300 W Xe Arc lamp</td>
<td>CO(_2) saturated water vapor in a stainless steel reactor (1500 ml capacity) at 30(^{\circ}) C and 110 kPa</td>
<td>107</td>
</tr>
<tr>
<td>Graphene Oxide (GO) by modified Hummer’s method</td>
<td>None</td>
<td>CH(_2)OH</td>
<td>0.172</td>
<td>-</td>
<td>300 W halogen lamp as simulated solar source</td>
<td>Continuous gas flow reactor, 0.2 gm catalyst, CO(_2) and water vapor under ambient conditions, 25(^{\circ})C; GO showed 6 fold higher activity than pure TiO(_2)</td>
<td>95</td>
</tr>
<tr>
<td>Photocatalyst</td>
<td>Loadings Or Co-catalysts</td>
<td>Primary Photoproducts</td>
<td>Product Yields ( \mu \text{mol g}^{-1} \text{h}^{-1} )</td>
<td>Quantum Efficiency</td>
<td>Light Source and Light Intensity</td>
<td>Experimental Conditions (Reactants, Time, ( T^\circ\text{C} ))</td>
<td>Comments</td>
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<tr>
<td>ZnO-reduced graphene oxide(RGO) nanocomposite</td>
<td>None</td>
<td>CH(_{3})OH</td>
<td>4.58</td>
<td>-</td>
<td>500 W Xe lamp</td>
<td>CO(_2) saturated glass reactor ZnO-RGO (1gm/L) in 100 ml of 0.0025M NaHCO(_3)</td>
<td></td>
</tr>
<tr>
<td>Multiwalled Carbon nanotube supported TiO(_2) composites</td>
<td>None</td>
<td>HCOOH, C(_2)(_2)OH, CH(_4)</td>
<td>18.67, 29.87, 11.74</td>
<td>-</td>
<td>15 W UV lamp 365 nm light</td>
<td>Stainless-steel reactor, H(_2)O and CO(_2) with mole ratio (5:1) under ambient conditions, 5h irradiation, 25°C</td>
<td></td>
</tr>
<tr>
<td>CNT@Ni/TiO(_2) composite</td>
<td>Ni</td>
<td>CH(_4)</td>
<td>0.145</td>
<td>-</td>
<td>75 W visible daylight lamp</td>
<td>Photoreactor purged with pure CO(_2) flowing through a water bubbler at atmospheric pressure, 10 h irradiation.</td>
<td></td>
</tr>
<tr>
<td>MWCNT@TiO(_2) core-shell nanocomposites</td>
<td>None</td>
<td>CH(_4)</td>
<td>0.1375</td>
<td>-</td>
<td>15 W energy saving light bulb (Philips)</td>
<td>Quartz photoreactor with CO(_2) saturated water under ambient conditions, 8 h irradiation</td>
<td></td>
</tr>
<tr>
<td>Graphene-WO(_3) nanobelt composite</td>
<td>None</td>
<td>CH(_4)</td>
<td>0.11 ( \mu \text{mol/h} )</td>
<td>-</td>
<td>300 W Xe lamp 400nm long pass filter</td>
<td>Glass reactor with CO(_2) saturated water vapor, 0.1gm catalyst under ambient conditions (25°C, 1atm), ( \sim ) 8 h irradiation</td>
<td></td>
</tr>
<tr>
<td>graphene-modified NiO(_x)TaO(_5) composite</td>
<td>Ni/NiO</td>
<td>CH(_2)OH, H(_2)</td>
<td>1.04 ( \mu \text{mol/h} )</td>
<td>-</td>
<td>400 W metal Halogen lamp, UV-Vis light</td>
<td>10ml quartz cuvette with 2.5 mg/ml of catalyst CO(_2) saturated aqueous solution under ambient conditions; 3.4 times more CH(_3)OH than sample without graphene</td>
<td></td>
</tr>
<tr>
<td>Reduced Graphene Oxide-TiO(_2) nanocomposite</td>
<td>None</td>
<td>CH(_4)</td>
<td>0.135</td>
<td>-</td>
<td>15 W daylight bulb</td>
<td>CO(_2) saturated water vapor in a continuous gas flow reactor under ambient conditions</td>
<td></td>
</tr>
<tr>
<td>Graphitic Carbon Nitride (g-C(_3)N(_4)) from Melamine</td>
<td>None</td>
<td>CO</td>
<td>1.9 mM/h</td>
<td>-</td>
<td>300 W Xe lamp With 420 nm cut-off filter</td>
<td>CO(_2) saturated water vapor in a glass reactor under ambient conditions</td>
<td></td>
</tr>
<tr>
<td>Mesoporous C(_3)N(_4)-Ru complex hybrid photocatalyst</td>
<td>8% Ru and triethanol amine as sacrificial donor</td>
<td>CO, H(_2), HCOOH</td>
<td>431</td>
<td>1.5%</td>
<td>450 W Xe lamp with NaNO(_2) solution filter ( \lambda &gt; 400 \text{ nm} )</td>
<td>CO(_2) saturated pyrex test tube reactor under ambient conditions</td>
<td></td>
</tr>
<tr>
<td>g-C(_3)N(_4) from Urea</td>
<td>None</td>
<td>CH(_2)OH, C(_2)(_2)OH, O(_2)</td>
<td>6.28, 4.51, 21.33</td>
<td>0.18%</td>
<td>300 W Xe lamp and 267 mW/cm(^2)</td>
<td>CO(_2) saturated pyrex glass reaction cell with 0.2 g catalyst in 100 ml of 1.0 M NaOH under ambient conditions, 20°C, 1 atm</td>
<td></td>
</tr>
<tr>
<td>C(_2)N(_4)-Co(bpy)(_2)Cl(_2) hybrid photocatalyst</td>
<td>Triethanol amine as sacrificial agent</td>
<td>CO, H(_2)</td>
<td>1.85 ( \mu \text{mol/h} )</td>
<td>0.25%</td>
<td>300 W Xe lamp with 420 nm cut-off filter</td>
<td>Schlenk flask (80 mL) under an atmospheric pressure of CO(_2) with 50 mg of catalyst in acetonitrile solvent under visible-light, 60°C, 1 atm</td>
<td></td>
</tr>
</tbody>
</table>
1.3.3 Photocatalytic Hydrogen (H₂) Generation

The past decade has seen much research emphasis on the development of highly active visible-light responsive photocatalysts for hydrogen generation from water and sunlight, though with limited success.\(^8, 11-14\) In the photocatalytic water splitting reaction, the photogenerated electrons and holes act as reducing and oxidizing agents, producing H₂ and O₂, respectively. Thermodynamically, this uphill reaction results in a large positive change in the Gibbs free energy ΔG\(^0\) of 237.2 kJ/mol. A schematic representation of the principle behind photocatalytic water splitting is depicted in Figure 1.12.\(^12\) To achieve overall water splitting, the bottom level of the conduction bands must be located at a more negative potential than the reduction potential of H\(^+\) to H₂ (0 V vs NHE at pH 0 or -0.41 V at pH 7), while the top of the valence bands must be positioned more positively than the oxidation potential of H₂O to O₂ (1.23 V vs NHE at pH 0 or 0.82 V vs NHE at pH 7). Therefore, the minimum photon energy thermodynamically required to drive the reaction is ~1.23 eV, corresponding to a wavelength of approximately 1010 nm in the near infrared region. However, in practice, the ideal minimum band gap energy should be higher (close to about 1.35 eV) due to the energy loss associated with the over-potentials required for the two chemical reactions and the driving force for charge carrier transportation.\(^11\)
Figure 1.12 Schematic illustration of photocatalytic water splitting over semiconductor photocatalyst. (From Ref. [12].)
While photocatalytic hydrogen generation via solar radiation is a promising approach for obtaining carbon-free fuel and a sustainable energy system, the practical applications of this technique are primarily limited by the lack of active catalysts that can efficiently harvest the visible-light, the relatively low quantum efficiency and the photocorrosion of the catalysts. Since the earliest report of photocatalytic splitting of water on TiO$_2$ semiconductor electrodes upon UV illumination aided by a small electrochemical bias, semiconductor nanomaterial-based photocatalysts have received much attention in the photogeneration of hydrogen from water. Recently, inexpensive carbon-based nanocomposites, including pure carbon nanomaterials as alternatives to traditional semiconductor-based photocatalysts, have been developed for use in photocatalytic hydrogen generation; however, the progress in this areas has been limited.

Carbon quantum dots have recently emerged as a new class of semiconductor-equivalent photoactive materials as well as visible-light sensitizers because their optical figures of merit are suitable for photocatalytic applications and because of their low cost. Suitable photosensitizers for efficient hydrogen production need a visible-light response, appropriate electronic energy levels for the injection of photoexcited electrons into the conduction band of a semiconductor catalyst, and simultaneously, holes in the valence band that can oxidize the reducing species adsorbed on the surface. In addition, they should have appropriate functional groups on their surfaces to facilitate easy, robust coupling with the semiconductor photocatalyst as well as be resistant to photodegradation or photocorrosion under operating conditions.
Recent research has demonstrated that carbon quantum dots (CQDs) play a dual role in improving photocatalytic performance towards hydrogen evolution in CQDs/TiO$_2$(P25) nanocomposites. On one hand, under UV excitation CQDs act as electron reservoirs, improving the efficient separation of photogenerated electron-hole pairs on P25(TiO$_2$), which is phenomenologically similar to graphene, and CNTs in their nanohybrid photocatalysts. On the other, under visible-light illumination ($\lambda > 450$ nm), CQDs act as visible-light photosensitizers, sensitizing P25, in which the photoinduced electron transfer from excited CQDs to P25 occurs, followed by subsequent reactions with protons to produce hydrogen (Figure 1.13 a). The highest hydrogen production rate (9.1 $\mu$mol/h), which was observed for a composite photocatalyst, was approximately ~ 4 times higher than that for pure P25 (TiO$_2$) under UV-light with no co-catalysts.
Figure 1.13 a) Schematic illustration of the photocatalytic H\textsubscript{2} production mechanism over carbon quantum dots/TiO\textsubscript{2} (CQDs/P25) under UV and visible-light (\(\lambda > 450\) nm) irradiation. (From Ref. [116].)

Figure 1.13 b) The schematic diagram of the sensitization mechanism of the CQDs deposited on the surface of TiO\textsubscript{2} nanotubes. (From Ref. [117].)
Kang et al. used TiO$_2$ nanotube arrays loaded with carbon quantum dots as a photoanode for efficient hydrogen generation in a photoelectrochemical cell with a coiled Pt wire as the counter electrode in an aqueous solution consisting of Na$_2$S (0.25 M) and Na$_2$SO$_3$ (0.35 M) as an electrolyte (pH $\sim$ 9.5) under visible-light.$^{117}$ Under the illumination of simulated sunlight (AM 1.5 G, 100 mW cm$^{-2}$), the photocurrent density of the CQDs/TiO$_2$ NT photoanode was found to be four times greater than the TiO$_2$ NT photoanode. Upon visible-light photoexcitation, the excited electrons in the LUMO level of the CQDs were transferred to the conduction band of the TiO$_2$ NTs in contact. These electrons were then transported to the counter electrode for the hydrogen evolution reaction along the TiO$_2$ NTs axial direction, and leftover holes in the HOMO level of the CQDs were consumed by the sacrificial reagent to complete the galvanic circle (Figure 1.13 b).$^{117}$ The estimated hydrogen evolution rate was 14.1 μmol h$^{-1}$ for the CQDs/TiO$_2$ NT photoanode, with a faradic efficiency of nearly 100%.$^{117}$ Yu et al.$^{118a}$ observed a similar photoelectrochemical hydrogen generation property in CQD/TiO$_2$ composites. Likewise, Ho and coworkers used hydrothermal approach for the synthesis of TiO$_2$/carbon dots (TiO$_2$/CDs)$^{118b}$ and ZnS/carbon dots (ZnS/CDs)$^{118c}$ heterostructures to enhance the photocatalytic hydrogen evolution rate.

In addition to the carbon quantum dots (CQDs), the photocatalytic activities for hydrogen production has the potential to be enhanced by loading graphene quantum dots (GQDs) onto semiconducting catalysts.$^{119}$ In their study, Meng and coworkers prepared inversely structured TiO$_2$ nanotubes-array (TiO$_2$-NA) and CdS-modified TiO$_2$ nanotubes-array (CdS/TiO$_2$-NA) with graphene quantum dots (GQDs) anchored into them via an
impregnation method as photoanodes for their evaluation in photoelectrochemical hydrogen production under simulated sunlight.\textsuperscript{119} The photocatalytic performance order for different catalysts was found to be GQD/CdS/TiO\textsubscript{2}-NA > CdS/TiO\textsubscript{2}-NA > GQD/TiO\textsubscript{2}-NA > TiO\textsubscript{2}-NA. The enhanced hydrogen generation activity of the GQDs-modified catalysts is ascribed to the improved charge separation and transfer characteristics promoted by the GQDs.\textsuperscript{119}

Graphene-based hybrid catalysts with semiconductors have been found to exhibit better photocatalytic performance than pure semiconductors primarily due to their role as charge collectors and co-catalysts. While most photocatalysts studied are based on graphene/semiconductor nanohybrids,\textsuperscript{80-85} graphene oxide (GO) as a semiconductor alone has been explored for photocatalytic hydrogen generation\textsuperscript{120} as well as CO\textsubscript{2} reduction\textsuperscript{95} due to its appropriate physicochemical properties. The total evolution of H\textsubscript{2} from GO in an aqueous methanol (20 vol %) solution after 6 h was measured to be 17000 μmol (QE ~ 2.7 % under UV-light), far exceeding the amount of hydrogen obtained from pure water (280 μmol). This increase was attributed to the role of methanol as a sacrificial electron donor, consuming the photogenerated holes and thereby facilitating the charge carrier separation.\textsuperscript{120}

Graphene and its composites with semiconductors such as metal oxides (e.g. TiO\textsubscript{2}) and metal sulfides (e.g. CdS) have been widely implemented in photocatalytic water splitting to produce hydrogen.\textsuperscript{8, 14} For example, in one of the well-received studies, classical CdS nanoclusters were grown on a graphene oxide support via the solvothermal method followed by the deposition of Pt nanoparticles as co-catalysts (Figure 1.14 A).\textsuperscript{121}
The CdS-graphene hybrid photocatalysts exhibited H$_2$ production rate of 1.12 mmol/h (approximately 4.87 times higher than that of pure CdS nanoparticles) at a graphene content of 1.0 wt % and a Pt loading of 0.5 wt % under visible-light irradiation with an estimated apparent quantum efficiency (QE) of 22.5% at a wavelength of 420 nm.\textsuperscript{121} Based on similar conceptual approaches, many other emerging applications of graphene-based semiconductor photocatalysts for H$_2$ generation have been developed, including graphene-semiconductor binary and trinary systems, dye-sensitized graphene-based systems, graphene as co-catalysts and even a potential role as a photosensitizer in various hybrid photocatalysts.\textsuperscript{14} Moreover, recently polymeric graphitic carbon nitride (g-C$_3$N$_4$) has been found to exhibit good photocatalytic activity for hydrogen and oxygen evolution from water in the visible range.\textsuperscript{104, 122, 123} In addition, coupling g-C$_3$N$_4$ with graphene sheets (graphene/g-C$_3$N$_4$ composites) has led to increased conductivity and photocatalytic response for hydrogen evolution using a methanol aqueous solution with Pt as a co-catalyst.\textsuperscript{124} Thus obtained all carbon graphene/g-C$_3$N$_4$ composites have shown a H$_2$ evolution rate ($\sim$ 451 $\mu$mol h$^{-1}$ g$^{-1}$) 3 times higher than that of pure g-C$_3$N$_4$ under visible-light irradiation due to their efficient charge carrier separation characteristics (Figure 1.14 B).\textsuperscript{124}
Figure 1.14 A) a) Schematic illustration of the charge separation and transfer in the graphene-CdS system under visible-light. The photoexcited electrons transfer from the conduction band of the semiconductor CdS to both the located Pt and to the carbon atoms on the graphene sheets, which are accessible to protons that readily transform to H₂. b) H₂ production rate dependence for different graphene content. (From Ref. [121].)

B)

Figure 1.14 B) Proposed mechanism for the enhanced electron transfer in graphene/g-C₃N₄ composites. (From Ref. [124].)
1.3.4 Photocatalytic Degradation of Organic Pollutants

China generates approximately 1.6 x10^9 m^3 dye-containing waste water annually, usually originating from its printing, textile, and photographic industries, water that is difficult to biodegrade or oxidize using chemicals. As an advanced oxidation process, photocatalysis has generated growing interest among researchers in the field of waste water treatment due to its ability to completely mineralize organic matter usually to CO_2 and water.\(^{16, 17, 20}\) However, one of the primary concerns is the optimization of the interaction between the organic pollutants or contaminant dyes, the photocatalyst and the light-irradiation essential for enabling the degradation reaction. Carbon quantum dots including graphene- and CNT-based hybrid photocatalysts exhibit potential for use in practical environmental remediation applications involving photocatalytic degradation or the photooxidization of common organic pollutant dyes like methyl orange (MO), methylene blue (MB), and rhodamine B (Rh B).\(^{23, 24, 82-85, 90, 129, 130}\) Reactant dyes must be effectively adsorbed on the semiconducting catalyst surface in order to be mineralized by photoinduced electron transfer reactions. In general, the photocatalytic degradation of organic contaminants proceeds via generation of reactive oxygen species such as ‘O_2’, ‘OH radicals which participate in the oxidization of organic pollutants or dyes.\(^{125, 126}\) The most widely accepted mechanistic framework for dye degradation via the generation of hydroxyl radicals in semiconductor photocatalysis is the following: \(^{57, 80, 125-128}\)

Semiconductor + light (hv) → Semiconductor (e^- + h^+)

Semiconductor (e^-) + O_2 → Semiconductor + O_2^-
Semiconductor (h\(^+\)) + OH\(^-\) → Semiconductor + 'OH

Semiconductor (h\(^+\)) + H\(_2\)O → Semiconductor + 'OH + H\(^+\)

Semiconductor (h\(^+\)) + 'OH + dye/pollutants → CO\(_2\) + H\(_2\)O or degradation products

Lee and coworkers demonstrated the one-step, alkali-assisted electrochemical fabrication of carbon quantum dots (CQDs) with upconversion PL, using graphite rods as both the anode and cathode with NaOH/EtOH as the electrolyte at a current density of 10-200 mA/cm\(^2\), obtaining CQDs with size-dependent photoluminescence in the size range of 1.2-3.8 nm.\(^{57}\) Extending their research, they designed TiO\(_2\)/CQDs and SiO\(_2\)/CQDs nanocomposites via the traditional sol-gel method to investigate their photocatalytic activity towards methylene blue (MB) dye degradation.\(^{57}\) Upon photoexcitation with a longer wavelength of light, CQDs emitted at shorter wavelengths (325-425nm) as a result of upconversion luminescence, which, in turn, excited TiO\(_2\) or SiO\(_2\) to generate charge carriers (e\(^-\)/h\(^+\)) pairs that can generate active oxygen radicals such as 'O\(_2\)^-\), 'OH, which subsequently can result in MB dye decomposition.\(^{57}\) Using a similar conceptual approach, they designed photocatalysts (rutile TiO\(_2\)/GQD and anatase TiO\(_2\)/GQD composite systems) for harvesting the visible spectrum of sunlight based on the upconversion luminescence properties of graphene quantum dots (GQDs) at 407 nm (3.05 eV).\(^{129}\) Under visible-light illumination, MB photodegradation efficiency up to 97% in 60 min with the rutile TiO\(_2\)/GQD complex and 31% with anatase TiO\(_2\)/GQD complex photocatalysts was achieved because the upconversion PL of GQD excited only the
former (Rutile TiO$_2$ with a band gap of $\sim$ 3.02 eV) to generate the electron-hole pairs to
drive the photocatalytic processes, resulting in highly efficient photodegradation.$^{129}$

Although the nanocomposites of carbon quantum dots (CQDs) and other
inorganic materials have shown good photocatalytic activity, limited research has been
focused on CQDs alone.$^{130,131}$ One such study was conducted by Hu et al. who explored
carbon quantum dots (CQDs) alone (derived from the combustion of wood) for the
photocatalytic degradation of methylene blue (MB) under visible-light (Figure 1.15 a).$^{130}$
Their results suggested CQDs alone did indeed exhibit high photocatalytic activity
towards MB oxidative degradation, thereby confirming that the photoinduced charge
separation in CQDs drives the photoredox processes, findings consistent with previous
research.$^{52,70,130}$

The doping of non-metal impurities has been a popular strategy for band gap
tuning of semiconductors towards the visible range through the creation of new electronic
states in semiconductor materials.$^{78,79}$ Qu et al. used the hydrothermal method to
synthesize N-doped graphene quantum dots (GQDs) and S, N co-doped GQDs with citric
acid as the carbon source and urea or thiourea as the N and S sources.$^{132}$ In addition, they
investigated N:GQD/TiO$_2$ and S, N:GQD/TiO$_2$ nanocomposites as visible-light
photocatalysts towards enhanced degradation/oxidization of Rhodamine B (RhB), where
GQDs functioned as the photosensitizer by injecting electrons into the TiO$_2$ nanocrystals,
promoting the formation of reactive oxygen species ('O$_2^-$, 'OH radicals) responsible for
the degradation of RhB (Figure 1.15 b).$^{132}$ Similarly, N-doped carbon quantum dots (N-
CQDs)-rutile TiO$_2$ with enhanced photocatalytic performance for RhB degradation were
demonstrated under visible-light.\textsuperscript{133} Based on similar concepts, various C-dots based hybrid photocatalysts with excellent photocatalytic activity have been studied, specifically C-dots/ZnO, C-dots/Fe\textsubscript{2}O\textsubscript{3}, C-dots/Ag/Ag\textsubscript{3}PO\textsubscript{4}, C-dots/BiVO\textsubscript{4}, graphitized C-dots/P25, C-dots/TiO\textsubscript{2} nanosheets, and C-dots-TiO\textsubscript{2} nanotubes, among others.\textsuperscript{134-138}

Much research has focused on graphene-based photocatalysts in photocatalytic degradation or oxidization for the removal of organic pollutants/contaminants, with the associated photodecomposition mechanism proposed being similar to other carbon-based photocatalysts (carbon nanotubes, activated carbon, etc.).\textsuperscript{82-85} For example, Zhang \textit{et al.} demonstrated a facile hydrothermal route for obtaining a chemically bonded TiO\textsubscript{2} (P25)-graphene composite (P25/GR) via one-step hydrothermal reaction.\textsuperscript{126} Because of the unique properties of graphene,\textsuperscript{14} the P25/graphene composite showed increased adsorptivity of pollutants, extended light absorption range, and facile charge transportation and separation, leading to a decreased recombination probability of electron-hole pairs, resulting in the enhanced photooxidation of MB dye in comparison to bare P25.\textsuperscript{126} Moreover, compared to P25/CNTs composites, P25/graphene composites exhibited higher photocatalytic activity towards MB photodegradation. The enhancement of P25/graphene over P25/CNTs was largely ascribed to its large, two-dimensional planar structure favorable for dye adsorption through $\pi-\pi$ conjugation and its superior charge transportation features.\textsuperscript{126} Other metal oxide semiconductors (ZnO) and metal chalcogenides (CdS, ZnS) including polymeric graphitic carbon nitrides (g-C\textsubscript{3}N\textsubscript{4}) as semiconductors have also been employed to obtain hybrid photocatalysts with graphene for extensive application in the photocatalytic degradation of dyes.\textsuperscript{80, 82, 139}
Figure 1.15 a) The photocatalytic mechanism of carbon quantum dots (CQDs) with oxygen-containing surface groups. (From Ref. [130].)

Figure 1.15 b) The possible photocatalyst mechanism of graphene quantum dots/TiO$_2$ (GQD/TiO$_2$) under visible-light. (From Ref. [132].)
1.4 Carbon Quantum Dots in Photovoltaics

1.4.1 Bulk Heterojunction (BHJ) Solar Cells

A BHJ solar cell typically consists of an electron-donating conjugated polymer such as poly (3-hexylthiophene) (P3HT) or poly (3-octylthiophene) (P3OT) with strong light absorption and a widely used fullerene derivative, [6, 6]-phenyl C$_{61}$-butyric acid methyl ester (PCBM), with electron-accepting properties as the active layer between two electrodes.\textsuperscript{140} Light absorption leads to the generation of excitons, or closely bound electron-hole pairs, which need to dissociate into free electrons and holes at a donor/acceptor (D/A) interface before these free charges can be transported to the electrodes.\textsuperscript{141} The key requirements for a BHJ include not only strong absorption across the solar spectrum, donor and acceptor with HOMO/LUMO matching for a high open circuit voltage ($V_{oc}$), and high charge carrier mobility but also a morphology of the active layer and a device structure to ensure that the excitons can reach the D/A interface within their effective diffusion length, which is typically on the order of 10 nm.\textsuperscript{141, 142}

In photovoltaics, graphene derivatives such as graphene oxide and graphene quantum dots have been used as active acceptor materials in organic-inorganic hybrid solar cells as well as sensitizers in nanocrystalline quantum dots (QD)-sensitized solar cells; however, they are limited by low power conversion efficiency.\textsuperscript{23, 24, 30, 83, 85, 88} In one of the earliest studies, hydrophilic graphene oxide (GO) was functionalized with phenyl isocyanate to enable solubility in organic solvents to be used as an electron accepting material in bulk heterojunction organic solar cells with P3HT or P3OT as the electron
The unique 2D structure of graphene improved the donor/acceptor interfaces between it and the P3OT or P3HT, facilitating the charge separation and transfer. A best power conversion efficiency of 1.4 %, an open circuit voltage ($V_{oc}$) of $\sim 0.92$ V, a short-circuit current density ($J_{sc}$) of $\sim 4.2$ mA.cm$^{-2}$, and a fill factor (FF) of $\sim 0.37$ were achieved for P3OT-based bulk heterojunction solar cells with 5% graphene content under simulated sunlight (100 mW cm$^{-2}$ AM 1.5G light illumination).\textsuperscript{143}

Based on a similar concept, electrochemically derived 0 D graphene quantum dots (size $\sim$ 3-5 nm) were used as new acceptor materials and conventional P3HT as a donor in polymer photovoltaic devices.\textsuperscript{144} Polymer photovoltaic cells with the structure of ITO/PEDOT: PSS/P3HT: GQDs/Al were fabricated, where ITO, PEDOT, PSS and P3HT refer to indium tin oxide, poly (3,4-ethylenedioxythiophene), poly (styrene sulfonate) and poly(3-hexylthiophene), respectively (Figure 1.16).\textsuperscript{144} As seen from the $J$-$V$ characteristic curves in the figure 1.16, a low photocurrent was obtained for the device based on the pure P3HT due to the poor electron mobility of the polymer and the lack of interfaces for the dissociation of the photogenerated excitons, whereas in the P3HT:GQD composite device, a substantial increase in the photocurrent is observed.\textsuperscript{144} The GQDs provide a large surface area for the formation of p-n interfaces for charge transportation and as a pathway for electron transport resulting in an enhanced photocurrent with an overall power conversion efficiency approaching $\sim 1.28\%$ in the P3HT: GQD composite device configuration\textsuperscript{144} (Figure 1.16).
Figure 1.16 Schematic (a) and energy band (b) diagrams of the ITO/PEDOT:PSS/P3HT:GQDs/Al device. c) J-V characteristic curves for the ITO/PEDOT:PSS/P3HT/Al, ITO/PEDOT:PSS/P3HT:GQDs/Al and ITO/PEDOT:PSS/P3HT:GQDs/Al devices after annealing at 140° C for 10 min, single log scale. (From Ref. [144].)
In similar research, Gupta et al. investigated aniline-functionalized GQDs and aniline-functionalized graphene sheets (GS) as the electron acceptor material blended with P3HT or MEH-PPV conjugated polymer in BHJ solar cells in an optimized device configuration. Their results found that the GQDs dispersed in conjugated polymers exhibited enhanced organic photovoltaic (OPV) and organic light emitting diode (OLED) characteristics compared to the GS due to improved morphological and optical characteristics in the case of former.

1.4.2 Dye-sensitized Solar Cells (DSSCs)

Dye-sensitized solar cells, invented by Michael Grätzel, are inexpensive, highly efficient devices rivaling Si-based photovoltaics. The traditional device consists of a nanocrystalline dye-anchored TiO$_2$ photoanode, an electrolyte redox mediator (I$_3^-$/$I^-$) and a cathode or counter electrode. After photoexcitation of the dye (usually ruthenium bipyridine or zinc porphyrin complexes), an electron is injected from the LUMO of the dye to the conduction band of the semiconductor TiO$_2$. It is then carried from the photoanode to the platinized counter electrode, with the regeneration of the oxidized dye resulting from a redox couple like iodide/triiodide which reduces the dye through a continuous supply of electrons.

Yan et al. designed nanocrystalline TiO$_2$ solar cells with graphene quantum dots substituting for the traditionally used ruthenium complex as the sensitizer in dye-sensitized solar cells. A short-circuit current density ($J_{sc}$) of 200 μA/cm$^2$ and an open-
circuit voltage \((V_{oc})\) of 0.48 V were obtained with a fill factor of 0.58 under a simulated AM 1.5 global light. The lower current density was attributed to the low affinity of the GQDs with the oxide surfaces as a result of physical adsorption without chemical covalent binding and subsequent poor charge injection (Figure 1.17).\textsuperscript{149} Similarly, Dutta \textit{et al.} used a combination of GQDs with ZnO NWs to demonstrate their potential as solar harvesting material in photovoltaic cells exhibiting \(J_{sc} = 0.45\) mA cm\(^{-2}\) with an open-circuit voltage of \(V_{oc} = 0.8\) V and an FF = 0.5, leading to an estimated power conversion efficiency of 0.2\%, significantly higher (~75 times) than the control device without the GQDs displaying a short-circuit current, \(J_{sc} = 5.9\) \(\mu\)A/cm\(^2\) and \(V_{oc} = 0.1\) V. In addition, the excited state interaction between the photoexcited GQDs and the ZnO NWs from the charge-transfer process were verified by both emission spectroscopy and photovoltaic measurements.\textsuperscript{150}

More recently, GQDs-polypyrrole conducting polymer composites (PPG) with different compositions of GQDs were employed to fabricate DSSCs.\textsuperscript{151} A maximum PCE of 2.09\% was observed in PPG composites with 0.03 mol\% (w/v) of GQDs.\textsuperscript{151}
Figure 1.17 Absorption spectrum of GQD and its application as a sensitizer in nanocrystalline solar cells. (a) Absorption spectrum (molar extinction coefficient $\epsilon_m$) of GQD in dichloromethane. (b) The calculated HOMO and LUMO energy levels of GQD (1), band levels of TiO$_2$, and reduction potential of I$_3^-/I^-$. All values are below the vacuum level in electron volts. The calculated band gap of GQD is 0.1 eV larger than that measured optically. It nevertheless suffices to illustrate the possible sensitizing effect of GQD on TiO$_2$. (c) The current-voltage characteristics of a typical nanocrystalline TiO$_2$ solar cell sensitized by GQD, in the dark and under illumination, respectively. (From Ref. [149].)
Carbon dots have also been recently explored as potential candidates for quantum dot (QD) or dye-sensitized solar cells due to their versatility in nature coupled with their electron transfer behavior and unique optoelectronic properties.\textsuperscript{23, 24, 29} Mirtchev \textit{et al.} employed carbon quantum dots as sensitizers in nanocrystalline TiO\textsubscript{2}-based solar cells. The current-voltage characteristic curves ($J$-$V$) displayed a short-circuit current density ($J_{sc}$) of 0.53 mA cm\textsuperscript{-2} and an open-circuit voltage ($V_{oc}$) of 0.38 V, with a fill factor (FF) of 0.64 and a power conversion efficiency of 0.13\% (Figure 1.18 A).\textsuperscript{152} Solar cells designed from MeOH CQD solutions and aqueous CQDs refluxed in HNO\textsubscript{3} to ensure complete surface oxidation exhibited a similar performance, while a non-sensitized nanocrystalline TiO\textsubscript{2} gave an efficiency of 0.03\% under simulated AM 1.5 irradiation (Figure 1.18 A).\textsuperscript{152} Similar solar cell performance was achieved using N-doped carbon quantum dots (N-CQDs) as sensitizers in DSSCs (Figure 1.18 B).\textsuperscript{133} The solar cell exhibited the open-circuit voltage, short-circuit current density and fill factor values of 0.46 V, 0.69 mA/cm\textsuperscript{2} and 0.43, respectively, achieving a power conversion efficiency of 0.13\% for TiO\textsubscript{2}-based DSSCs, whereas undoped CQDs sensitized TiO\textsubscript{2} resulted in an overall power conversion efficiency of 0.03\% (Figure 1.18 B).\textsuperscript{133}
Figure 1.18 A) (a) CQD-sensitized TiO$_2$ nanoparticle and the proposed CQD-TiO$_2$ bonds, (b) UV-Vis-NIR absorption spectrum of CQD thin film on quartz substrate, (c) Current-voltage characteristics of CQD-sensitized solar cells prepared from a MeOH CQD solution and from an aqueous solution of CQD refluxed in nitric acid to ensure complete surface oxidation and (d) Current-voltage characteristics of aqueous CQD-sensitized solar cell. (From Ref. [152].)
Figure 1.18 B) The schematic device structure of an N-doped CQDs-sensitized TiO$_2$ solar cell. (From Ref. [133].)
Recently, several researchers have explored a new mechanism of plasmon-enhanced semiconductor photocatalysis for improving the efficiency of photocatalytic processes by exploiting the strong plasmon resonance of plasmonic nanoparticles (Ag, Au), generating intense local electric fields near the surface referred to as “hot spots”; however, the overall photoconversion efficiencies are still very low. In a recent study, Kim and coworkers demonstrated that the surface plasmon resonance effect of carbon dot-supported silver nanoparticles promoted significant radiative emission and greater light absorption, resulting in an enhanced current efficiency of 27.16 cd A$^{-1}$, a luminous efficiency of 18.54 lm W$^{-1}$ and an external quantum efficiency (EQE) of 9.07%, approximately more than 2 times higher than control devices without CD-Ag nanoparticles (current efficiency ~11.65 cd A$^{-1}$, luminous efficiency ~ 6.33 lm W$^{-1}$ and EQE ~ 4.26%) in polymer light-emitting diodes (PLEDs) as well as a power conversion efficiency (PCE) of 8.31% and an internal quantum efficiency of 99% in polymer solar cells (PSCs) compared with control devices without CD-Ag nanoparticles (power conversion efficiency ~ 7.53% and internal quantum efficiency ~ 91% in polymer solar cells) (Figure 1.19).
Figure 1.19 Device structure and characteristics of polymer optoelectronic devices incorporating CD-Ag nanoparticles: a) polymer light-emitting diodes (PLEDs) and b) polymer solar cells. (From Ref. [93].)
In addition to plasmonic carbon dots with metal (Ag) coating, carbon nanoparticles (CNP) alone have been applied as an interfacial layer between TiO$_2$-coated ZnO nanorod arrays and P3HT polymer, resulting in substantially improved performance in these hybrid solar cells.$^{155}$ The current-voltage ($J$-$V$) characteristic curves of photovoltaic devices with the configuration ITO/ZnO-TiO$_2$-CNP/P3HT-Au resulted in a short-circuit current density ($J_{sc}$) and a power conversion efficiency (PCE) of 8.69 mA/cm$^2$ and 0.68%, respectively, substantially higher in performance in reference to control devices ($J_{sc}$ ~ 1.20 mA/cm$^2$ and PCE ~ 0.02%) without CNP with an ITO/ZnO-TiO$_2$/P3HT-Au device configuration (Figure 1.20).$^{155}$ In addition, a recent study found that the incorporation of carbon dots into a conventional P3HT:PCBM-based BHJ solar cell resulted in a 12% improvement in the power conversion efficiency of polymer solar cells, probably due to the effective light conversion of the near UV and blue-violet portions of sunlight by the carbon dots.$^{156}$
Figure 1.20 (a) Device structure and (b) energy level diagram of the solar cells of ITO/ZnO/ZnO-TiO$_2$-CNP/P3HT/Au. (c) Absorption spectra of the films of ZnO-TiO$_2$, ZnO-TiO$_2$-CNP, ZnO-TiO$_2$/P3HT and ZnO-TiO$_2$-CNP/P3HT on ITO glass substrates. (d) $J$-$V$ characteristics (empty: dark; filled: illuminated) of the photovoltaic devices of ITO/ZnO-TiO$_2$/P3HT/Au and ITO/ZnO-TiO$_2$-CNP/P3HT/Au. (From Ref. [155]).
1.4.3 Organic Light Emitting Diodes (OLEDs)

Carbon dots and/or graphene quantum dots have been the focus of considerable research attention in organic light emitting diode (OLED) applications due to their relatively high PL quantum yields, particularly after surface passivation and multicolor emission coupled with good electron mobility.\(^{23, 24, 29, 30}\) Carbon dot based light emitting diode (LED) devices consist of a carbon dot emissive layer sandwiched between an organic hole transport layer and an organic or inorganic electron transport layer fabricated via solution-processing technology. Wang et al. first demonstrated a white light-emitting device using highly fluorescent carbon dots (purified through column chromatography, size \(\sim\) 5 nm, PL QY \(\sim 60\%\)) derived from carbonizing citric acid in a hot non-coordinating solvent.\(^{157}\) A maximum brightness output of 35 cd m\(^{-2}\) corresponding to a current efficiency of 0.022 cd A\(^{-1}\) was achieved at a current density of 160 mA cm\(^{-2}\) at 9 V.\(^{157}\) A maximum external quantum efficiency of 0.083% at a current density of 5 mA cm\(^{-2}\) with a color-rendering index of 82 was also achieved, indicating that carbon dots have the potential to act as new class of phosphor materials for fabricating high-performance white light electroluminescent devices.\(^{157}\)

More recently, Zhang et al. reported the observation of multicolor electroluminescence (EL) from carbon dots (CDs) (size \(\sim\) 3.3 nm), investigating the current density and luminance curves as a function of the applied voltage of the carbon dot-LEDs (CD-LEDs) by tuning the device structure and the injecting current density (by changing the applied voltage) (Figure 1.21).\(^{158}\) Depending on the injection conditions for
the respective device structures, the CD-LEDs displayed steady light (blue or white) or tunable light (blue, cyan, magenta, and white) from the same carbon dots. The recorded maximum brightness of the devices was 24 cd/m$^2$ for blue light and 90 cd/m$^2$ for white light, the highest values of brightness reported to date at $>2.5$ times brighter than the 35 cd/m$^2$ from a white light CD-LED made by Wang et al.$^{157,158}$

Tang et al. prepared glucose-derived water-soluble crystalline graphene quantum dots (GQDs) (PL QY 7-11%) with an average diameter of 1.65 nm ($\sim$ 5 layers) using the microwave-assisted hydrothermal method. The ability of GQDs to serve as efficient light converters for converting blue light into white light was demonstrated by coating them onto a blue light emitting diode, the results indicating a weakening in the emission intensity of blue light and the appearance of a broad peak in the spectrum at 510 nm. When excited by a blue LED of 410 nm, the GQDs emit a broad band (fwhm = 104 nm) centered at 510 nm. Due to the mixing of 410 nm (blue light) and a broad emission peak centered at 510 nm, the blue light is converted to white light.$^{159}$ They also developed an easy method for fabricating a graphene quantum dot (GQD)-agar composite (QY~ 12%) for use in a WLED.$^{160}$ A white GQD-agar LED (WLED) was fabricated by coating the GQD-agar composite as color converting material onto the blue LED. The luminous efficiency and light conversion efficiency of the white LED was 42.2 lm W$^{-1}$ and 61.1%, respectively, and the light conversion efficiency of the WLED was found to be stable for more than 100 hours of continuous operation.$^{160}$
Figure 1.21 (a) Current density and brightness of the CD-LEDs emitting blue, cyan, magenta, and white light, with the inset showing a device structure comprised of ITO/PEDOT:PSS (anode), poly-TPD (Hole transport layer), CDs (active layer), TPBi (Electron transport layer), and LiF/Al (cathode); (b) the luminous and power efficiencies vs current density; (c) electroluminescence (EL) spectra and true color photographs of blue, cyan, magenta, and white emissions; (d) CIE1931 coordinates of the blue, cyan, magenta, and white emission from the same CD-LEDs under different voltages. (From Ref. [158].)
In similar study, Chen and coworkers reported the synthesis of multicolor fluorescent carbon dots (QY up to 47%) from the chemical unzipping of epoxy-enriched polystyrene (PS) photonic crystals via a one-step pyrolysis approach. They further explored blue, orange and white LEDs (by coating carbon dots on ultraviolet InGaN LED chips) based on the photoluminescence of these carbon dots to demonstrate their potential applications in optoelectronic devices. The same group used a plasma-induced method to fabricate photoluminescent carbon dots (QY~ 6%) using acrylamide as the precursor. They further explored fabricating a white LED by combining a carbon dot/CdTe QDs/silicone mixture with a UV-LED chip as the excitation source. Compared with the conventional YAG: Ce phosphor-based white LEDs, this resulting LED emitted white light with a higher color rendering index (CRI) up to 87, indicating that the incorporation of a carbon dot and highly fluorescent CdTe QD mixture into an UV-LED may be a promising solution for white light sources with high CRI. Similarly, Son et al. synthesized ZnO-graphene hybrid quasi-core-shell quantum dots (~ 15.8 nm size) for use in a white-light-emitting diode (WLED), the results indicating improved performance. These white light graphene quantum dot-based LEDs displayed a remarkable brightness of 798 cd /m² in addition to exhibiting new blue emissions which have not been seen before in pure ZnO quantum dots.

1.5 Concluding Remarks and Future Perspectives:

Despite recent accomplishments in photocatalytic energy conversion using carbon
dots, research on their use for CO$_2$ conversion is still at an early stage, and far from being commercially feasible, even when combined with other semiconductor-based photocatalysts. Fundamental investigations are needed on a number of issues concerning the design of more effective photocatalysts for CO$_2$ photoconversion and other solar energy conversion applications. For example, more research is needed to more fully understand photoinduced charge carrier generation, charge separation and transport behavior in carbon dots using sophisticated spectroscopic tools such as transient absorption and time-resolved spectroscopic measurements to explain the complex charge transfer dynamics in such systems.

However, efficient light harvesting ability across the solar spectrum, along with rich photoinduced electron transfer properties, makes carbon dots a promising candidate for photocatalytic and photovoltaic applications. Nanoscience research can significantly impact the development of novel and more potent catalysts through the design and control of photocatalyst properties, primarily in terms of band gap engineering for preferential redox potentials of the photoinduced charge carriers, chemical composition, and surface tuning. Both the photocatalytic activities and optical properties of carbon dots can be tuned by their surface states.$^{130}$ Manipulations of surface defects in carbon nanodots and their composites with tailored properties may find potential applications as the next generation of optoelectronic and energy-storage devices. Therefore, the availability of various physical, chemical or electrochemical approaches for the preparation and evaluation of their photochemical robustness/stability provides the
opportunity to engineer both the intrinsic and the surface nature of carbon dots required for specific applications.

While past research has shown that carbon-based photocatalysts have been extensively employed as photooxidation catalysts for the photocatalytic degradation of organic pollutants, limited studies have been conducted on CO$_2$ photoreduction to value-added fuels, probably due to the cost and the difficulties involved in isotope-labeling experiments to clarify the origin of low yield CO$_2$ reduction products, rarely exceeding tens of μmol g$^{-1}$ h$^{-1}$. In addition, while artificial electron donors can be used to consume the photogenerated holes to prevent photooxidation reactions and/or photocorrosion of catalysts, these photocatalytic reactions are inherently short term, lasting only until the donor is depleted. Currently, the majority of studied systems are predicated on half reactions of CO$_2$ reduction only; however, in the future, full cycle studies with a stronger focus on oxidation half reactions (e.g. O$_2$ evolution, H$_2$O$_2$) are necessary to understand redox reactions. Another related concern in photocatalytic redox reactions is the separation of oxidation and reduction half reactions to avoid reverse processes. Photoelectrochemical cells may provide solution to this problem through effective separation of two half-cell reactions, an approach already being practiced by a number of researchers$^{117-119}$ and one that may receive more attention in future.

Recent research has led to the development of a new mechanism for improving the efficiency of photocatalytic processes, one involving the strong plasmon resonance of Ag and Au nanoparticles.$^{153, 154}$ While the introduction of metal-enhanced fluorescence of carbon nanodots on Ag island films has been found to demonstrate a near field
distance dependent phenomenon in carbon nanodots, more recently, the surface plasmon effect of Ag-coated carbon dots was found to enhance the performance of polymer optoelectronic devices. Moreover, plasmon-enhanced photocatalysis has been reported in several photocatalytic processes, including water splitting, CO₂ reduction to methane, and the decomposition of organic molecules. Hence, it is important to understand the mechanistic role of plasmonic metal (Ag, Au) co-catalysts in improving the photocatalytic product yields in the photoreduction of CO₂ involving multi-electron reductions. For example, Kamat et al. have reported that metal nanoparticles can act as reservoirs for photogenerated electrons in semiconductors supporting the charge transfer mechanism, a phenomenon also found in noble metals such as Pt. On the other hand, surface plasmon-enhanced photocatalysis associated with local electric field enhancement at the interface has been demonstrated by several research groups. These conflicting results indicate the need for further research in the field.

It has been demonstrated that graphene-based photocatalysts are promising candidates in solar energy conversion applications, primarily CO₂ conversion to chemical fuels and photocatalytic water splitting as well as photosensitized oxidation of organic contaminants. The improved photocatalytic performance in graphene-based semiconducting nanocomposites is primarily driven by the improved charge separation and transfers, thereby hindering the recombination of electron-hole pairs, creating more surface reactive sites and resulting in increased absorption and extension of the light absorption range as well as improved stability of the photocatalysts. The coupling interaction of graphene with the semiconductor often opens a band gap, probably
inducing a doping effect in the carbon monolayer; however, the semiconducting properties of graphene are usually ignored when it is used as an electron acceptor and transporter, even when reduced graphene oxide functions as the scaffold.

More research is needed in the design and synthesis of graphene with the desired morphology, composition, size, edge structure and dimensionality for superior photocatalytic activity. Despite its potential applications in photocatalysis, the underlying mechanism of photocatalytic enhancement by graphene-based nanocomposites is not fully understood. Questions involve whether graphene composites are different from other carbonaceous (activated carbon, fullerenes or carbon nanotubes) composite materials. For example, a study conducted by Zhang et al. suggested that graphene-TiO$_2$ composites are essentially the same as other carbon-TiO$_2$ (activated carbon, fullerenes and carbon nanotubes) composite materials with respect to the enhancement of the photocatalytic performance of TiO$_2$ in methylene blue (MB) decomposition.

Future research includes characterizing carbon-based catalysts through spectral sensitivity towards visible light and control over their photoactivity and selectivity towards value-added solar fuels (e.g. methanol, methane) from CO$_2$ photoreduction. New approaches for using heterojunctions to drive electronic processes in the desired direction, selective photoexcitation of localized electronic states to gain better selectivity via band gap/surface engineering (e.g., appropriate true metal ion doping) and control over the synthesis of photoactive carbon nanomaterials with tailored properties may also receive more attention.
References


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CHAPTER TWO

CARBON NANOPARTICLES AS VISIBLE-LIGHT PHOTOCATALYSTS FOR EFFICIENT CO₂ CONVERSION AND BEYOND

This work has been published as:


The significant rise in atmospheric CO₂ levels due to the combustion of hydrocarbon fuels has generated much concern. Among various CO₂ sequestration options, a compelling approach is photocatalytic conversion to recycle CO₂ back to hydrocarbon fuels, for which the use of solar irradiation may represent an ultimate solution. However, there are major challenges in finding potent photocatalysts for such a task.¹⁻³ Nanoscale wide-band-gap semiconductors such as titanium dioxide (TiO₂) and cadmium sulfide (CdS) were originally used and have since been quite popular in CO₂ photoreduction and related photocatalytic reactions,¹⁻⁴ but their limitations in terms of the requirement for UV excitation and generally low conversion efficiencies have also become evident.²⁻³ Various improvement strategies, including the use of TiO₂ nanotubes and dye sensitization to extend the absorption of the photocatalysts into the visible region, have been developed.⁵⁻⁶ Here we report a new approach involving the use of surface-functionalized small carbon nanoparticles to harvest visible photons for subsequent charge separation on the particle surface in order to drive the photocatalytic process. The aqueous solubility of the catalysts enables photoreduction under essentially
homogeneous reaction conditions. Beyond CO$_2$ conversion, the nanoscale carbon-based photocatalysts are also useful to the photogeneration of H$_2$ from water under similar experimental conditions.

It is now known that small carbon nanoparticles can be covalently functionalized to give them strong absorption and emission in the visible spectral region that may also extend into the near-IR.$^7$, $^8$ The fluorescence emissions are attributed to radiative combinations of electrons and holes confined on the carbon nanoparticle surface (Figure 2.1),$^7$, $^9$, $^{10}$ phenomenologically resembling those found in nanoscale semiconductors. In this study, the carbon particle surface was also doped with gold or platinum to concentrate the photogenerated electrons to enable more efficient CO$_2$ reduction.

Carbon powders containing sub-10 nm nanoparticles were refluxed in aqueous nitric acid (2.6 M) for 12 h, dialyzed in membrane tubing (pore size equivalent to M$_W$ ~1000) against fresh water, and then centrifuged to retain the supernatant as an aqueous suspension of small carbon nanoparticles bearing surface carboxylic acid moieties.$^7$ The particles recovered from the suspension were functionalized with oligomeric poly(ethylene glycol) diamine (PEG$_{1500N}$; Figure 2.1) in a classical amidation reaction that involved the acylation of the particle-surface carboxylic acids in neat thionyl chloride as an intermediate step.$^7$, $^{10}$ The functionalized carbon nanoparticles were readily dissolved in water to form stable aqueous solutions of various concentrations, with solution colors ranging from yellow at low concentrations to black at very high concentrations. A UV-vis absorption spectrum of the solution used in subsequent photolysis for gold coating is shown in Figure 2.2.
Figure 2.1 Aqueous soluble PEG-functionalized carbon nanoparticles before (left, fluorescent) and after (right, photocatalytic for CO₂ reduction in aqueous solution) coating with metal.
The functionalized particles were coated with gold or platinum by simple solution-phase photolysis, as these metals are known in the literature for their photocatalytically enhanced reduction reactions. The photoexcited carbon particles acted as electron donors to reduce the gold or platinum salt (HAuCl₄ or H₂PtCl₆, respectively) to the corresponding metal on the particle surface, similar to what was observed in the photoreduction of aqueous silver cation into silver metal. The photolysis conditions were such that only the functionalized particles were allowed to get photons (405-720 nm for gold and 425-720 nm for platinum, to exclude not only the metal salts but also any residual impurities in the salt samples from photoexcitation), thus eliminating the possibility of any “free” (i.e., not associated with carbon nanoparticles) gold or platinum nanoparticles. For gold, the progressive photoreductive coating of the carbon particles was monitored by the emergence and rapid increase of the surface plasmon absorption of the coated nanoscale gold (Figure 2.2, corresponding to a gold-to-core carbon molar ratio of ~1:38). No gold formation was found in repeated control experiments in the absence of the functionalized carbon nanoparticles, as expected.
Figure 2.2 Absorption spectra of the functionalized carbon nanoparticles in aqueous solution before (dashed line) and after (solid line) coating with gold.
Transmission electron microscopy (TEM) imaging, which took advantage of the high electron density and crystalline fringes of the coated metal, confirmed the gold coating (Figure 2.3), as did results from energy-dispersive X-ray (EDX) analyses. The average diameter of the gold-coated particles was ~ 9 nm according to statistical analysis of multiple TEM images, and the size distribution standard deviation was ~ 3 nm.

For platinum coating of the functionalized carbon nanoparticles, the convenient monitoring of a plasmon absorption was not possible (such an absorption was absent in the concerned wavelength region; see Figure 2.4), so the coating was again confirmed by TEM imaging (Figure 2.4) and the associated EDX results.
Figure 2.3 TEM images (inset: high-resolution) of the functionalized carbon nanoparticles with gold coating.
Figure 2.4 Absorption spectra of the functionalized carbon nanoparticles in aqueous solution before (solid line) and after (dashed line) platinum coating. Inset: TEM images of the coated particles.
The functionalized carbon nanoparticles with gold or platinum coating were used as photocatalysts for the reduction of CO$_2$. In a typical experiment, an aqueous solution of the gold coated particles (corresponding to the UV-vis absorption spectrum in Figure 2.1) was added to an optical cell in the photolysis setup, after which the solution was purged with CO$_2$ gas toward saturation at ambient temperature. The resulting solution in the optical cell was photoirradiated with visible light (425-720 nm) for 5 h. As known in the literature, the photoreduction of CO$_2$ generally yields formic acid as a significant product.$^{1-3}$ In this study, the formic acid formed as a volatile photoproduct in the aqueous solution post-photoirradiation was harvested by simple distillation, from which a new aqueous solution containing formic acid was collected and then basified to pH 12 with aqueous NaOH to convert the acid to sodium formate. Upon the evaporation of water, the salt was analyzed by $^1$H and $^{13}$C NMR spectroscopy to confirm and quantify the amount of formate using sodium acetate as an internal standard (Figure 2.5).

The formation of formic acid from CO$_2$ photoconversion was confirmed by $^{13}$C-labeling experiments using aqueous NaH$^{13}$CO$_3$ (at the saturated CO$_2$-equivalent concentration) as the feed under neutral and acidic pH conditions (mimicking aqueous CO$_2$). The $^{13}$C-labeled formic acid thus obtained from the same photocatalytic reduction was readily detected by $^{13}$C NMR spectroscopy with only a few hundred scans (vs >20 000 scans required for regular formic acid from aqueous CO$_2$ or NaHCO$_3$).

The quantification of the photoproduct was used to estimate quantum yields for photocatalytic reactions of CO$_2$ under the specific experimental conditions.$^6$ For the reduction to formic acid only, the estimated quantum yield was $\sim 0.3\%$, which was likely
lower than the overall quantum yield for the CO$_2$ conversion (because of conversion to other photoproducts such as methanol,$^{13}$ see Figure 2.1). Nevertheless, even for the production of formic acid alone, the observed quantum yield is already at the higher end of the available literature values for reactions with a variety of photocatalysts under many different conditions.$^3$ As a more direct comparison, the use of suspended TiO$_2$ nanoparticles (Degussa P25) as photocatalysts with UV light irradiation (through a 350 nm cutoff filter) in the same photolysis setup resulted in quantum yields that were an order of magnitude lower (also for formic acid only).

For the platinum-coated photocatalysts in the CO$_2$ conversion reaction under otherwise identical experimental conditions, the results were generally similar to those with the gold-coated ones described above, though more quantitative comparisons, including those for effects of varying amounts of metal coating, are still being pursued.
Figure 2.5 $^1$H NMR spectra of (a) HCOONa harvested from the CO$_2$ photocatalytic reduction and (b) CH$_3$COONa as an internal standard in D$_2$O.
Mechanistically, photoexcitation of the surface-passivated small carbon nanoparticles likely results in charge separation to form surface-confined electrons and holes (Figure 2.1),\textsuperscript{9, 10} on which significant experimental evidence has already become available. For example, the bright fluorescence emissions, which can be attributed to radiative recombinations on the particle surface, could be quenched by both electron donors and acceptors in an equally efficient fashion.\textsuperscript{9} The emissions were also essentially diminished by the gold or platinum coating, as the coated metal was designed to soak up the surface-confined electrons, disrupting the radiative recombinations. Therefore, the functionalized carbon nanoparticles apparently served the function of harvesting visible photons to drive the photoreduction process, with the particle surface defects facilitating the charge separation by trapping the separated electrons and holes, phenomenologically similar to what occurs for metal-coated semiconductor nanoparticles (e.g., platinum-coated CdS or TiO\textsubscript{2}).\textsuperscript{11-13} In addition to the obviously important advantage of strong visible absorption, other distinctive features of the nanoscale carbon-based photocatalysts include their aqueous solubility for the photoconversion under homogeneous reaction conditions and the confinement of the photoinduced charge separation to the particle surface, thus facilitating more efficient electron harvesting by the coated gold or platinum as the cocatalyst in the CO\textsubscript{2} conversion.

Beyond CO\textsubscript{2} photoreduction, the same functionalized carbon nanoparticles with gold or platinum coating could be used as photocatalysts for H\textsubscript{2} generation from water.\textsuperscript{4, 14, 15} Experimentally, the same aqueous solution of the gold- or platinum-coated nanoparticles in the absence of CO\textsubscript{2} was irradiated under the same conditions as those
described above. The top of the sealed optical cell for the photoirradiation was connected to a H₂ indicator containing an aqueous CuSO₄ solution (bright blue color) (Figure 2.6). H₂ generation in the photocatalytic reaction of water was detected by a color change and precipitation in the H₂ indicator (due to reduction of Cu²⁺ to Cu⁺ and Cu by H₂ at 30 °C). A more quantitative determination of the amount of photogenerated H₂ from water and the associated reaction quantum yields is in progress. According to literature results, there are overlaps in terms of the configuration in photocatalysts for CO₂ reduction and water splitting.²-⁴,¹²,¹⁴ In fact, one of the mechanistic explanations for CO₂ reduction in aqueous solution is based on a two-step process, namely, initial photocatalytic generation of atomic H followed by reduction of CO₂.¹²
Figure 2.6 Schematic diagram of the setup used for the detection of photocatalytically generated H$_2$. 
In summary, surface-modified small carbon nanoparticles represent a highly promising new platform for visible-light photocatalysis of CO$_2$ conversion and beyond. The photocatalysts are stable in the photoreduction reactions. The photoconversion efficiencies likely benefit from the solubility of the catalysts (which allows for homogeneous reaction conditions in solution), surface confinement of the photoinduced charge separation and trapping, and the straightforward doping of metal cocatalysts. There is obviously more room for improvement in the further development of these carbon-based photocatalysts.
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CHAPTER THREE

VISIBLE-LIGHT PHOTOCONVERSION OF CARBON DIOXIDE INTO ORGANIC ACIDS IN AN AQUEOUS SOLUTION OF CARBON DOTS

This work has been published as:

3.1 Introduction

The level of carbon dioxide (CO₂) in the atmosphere and its significant environmental implications have generated much concern, promoting the development of various carbon sequestration strategies. Photocatalytic conversion is obviously a compelling approach in this regard, in which CO₂ is reduced back to hydrocarbon fuels. Even more desirable is the use of solar energy for the photoreduction, which presents a major challenge for the effective photon-harvesting by the catalysts across the solar spectrum.¹ ² Among widely employed photocatalysts for the purpose of CO₂ reduction have been nanoscale wide-bandgap semiconductors such as titanium dioxide (TiO₂) and cadmium sulfide (CdS) nanoparticles.¹ ³ ⁴ However, as limited by their bandgap transitions, these nanomaterials are generally ineffective in harvesting visible photons over a broad spectral range. Thus, various enhancement approaches including the use of doped TiO₂ nanotubes and/or dye sensitization to extend the absorption of the photocatalysts into the visible have been developed, with some significant successes. For example, Feng et al. prepared TiO₂ nanotube arrays via anodic oxidation of titanium foil
in an electrolyte. The arrays under sunlight could catalyze the reduction of CO$_2$ into methane, and the reduction efficiency could be enhanced substantially after the arrays were "coated" with ultrafine platinum nanoparticles. Woolerton, et al. used enzyme-modified TiO$_2$ nanoparticles (Degussa P25) with ruthenium bipyridyl complex as visible-light photosensitizer for the CO$_2$ photoconversion. Asi et al. synthesized nanocomposite of TiO$_2$ with silver bromide for the visible-light (420 nm and longer) photoreduction of CO$_2$. More recently, Cao et al. took a rather different approach to use surface-functionalized small carbon nanoparticles, dubbed “carbon dots” (Figure 3.1), for the absorption of visible photons to drive photocatalytic processes. In the photoreduction of CO$_2$, the carbon dots were surface-doped with a small amount of gold or platinum metal, which was designed to concentrate the photogenerated electrons, similar to what was widely practiced in the development of conventional nanoscale semiconductor-based photocatalysts. The photocatalytic conversion of CO$_2$ was probed by quantifying the formation of formic acid as a significant product, from which the estimated quantum yields for the photoreduction were substantial in reference to those achieved in the literature with the use of semiconductor nanoparticles as photocatalysts. More importantly in terms of a primary purpose in that study to understand the photoexcited state processes in small carbon nanoparticles, the photocatalytic reduction results served to confirm the presence of photoinduced charge separation in carbon dots, as already suggested by the fluorescence quenching results of carbon dots with either electron donors or acceptors.
Beyond mechanistic implications, (with some other carbon-based photocatalytic systems\textsuperscript{12-14}) the previous study opened the possibility for carbon dots to serve as a new platform of potent photocatalysts for more efficient CO\textsubscript{2} photoreduction. However, because it is a new platform, there is naturally the demand for more experimental results for further validation. In the work reported here, we used gold-doped carbon dots from better-controlled synthesis as aqueous soluble catalysts for a closer examination on the visible-light photoconversion of CO\textsubscript{2} into small organic acids, including acetic acid (whose formation requires many more electrons than that of formic acid),\textsuperscript{15} and more interestingly on the significantly enhanced photoconversion with higher CO\textsubscript{2} pressures over aqueous solution of the catalysts. The results from the pressure-dependent (and thus CO\textsubscript{2} concentration-dependent) study under otherwise the same experimental conditions are particularly valuable in terms of confirming the participation of CO\textsubscript{2} in the reaction as the source of the converted organic acids and also the photocatalytic functions of the carbon dots.
3.2 Experimental Section

**Materials.** Carbon nanopowder (purity >99%) was purchased from Sigma-Aldrich, bis-(3-aminopropyl)-terminated oligomeric poly(ethylene glycol) of average molecular weight ~1,500 (PEG$_{1500N}$) from Anvia Chemicals, CO$_2$ gas (purity >99.5%) from Airgas, and hydrogen tetrachloroaurate (HAuCl$_4$•3H$_2$O) and sodium hydroxide (NaOH) were purchased from Alfa-Aesar. Imidazole and fumaric acid were obtained from Aldrich Chemicals, thionyl chloride (purity >99%) from Alfa Aesar, nitric acid was obtained from VWR, and $^{13}$C-enriched sodium bicarbonate (NaH$^{13}$CO$_3$, purity 97% and $^{13}$C content 99%) and D$_2$O from Cambridge Isotope Laboratories. HPLC grade solvents isopropanol, methanol, and phosphoric acid were supplied by Fisher Scientific, and dialysis membrane tubing (MWCO ~ 500) was supplied by Spectrum Laboratories. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

**Measurements.** A Baxter Megafuge (model 2630), Eppendorf (model 5417 R), and Beckman-Coulter ultracentrifuge (Optima L90K with a type 90 Ti fixed-angle rotor) were used for centrifugation at various $g$ values. Optical absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer. NMR measurements were carried out on Bruker (500 MHz and 300 MHz) and JEOL (500 MHz) NMR spectrometers. GC-MS analyses were performed on a Shimadzu GC-MS instrument (model QP 2010) with an Rxi-XLB/or Rt-5MS column and an electron ionization (EI) MS detector. Transmission
electron microscopy (TEM) images were obtained on Hitachi 9500 TEM and HD-2000 scanning-TEM systems.

**Photocatalysts.** In the synthesis of PEG_{1500N}-functionalized carbon dots, an as-supplied carbon nanopowder sample (1 g) was refluxed in an aqueous nitric acid solution (5 M, 90 mL) for 48 h. The reaction mixture back at room temperature was dialyzed against fresh water, and then centrifuged at 3000g to retain the supernatant. The recovered sample containing primarily small carbon nanoparticles was refluxed in neat thionyl chloride for 12 h, followed by the removal of excess thionyl chloride under nitrogen. The post-treatment carbon particle sample (100 mg) was mixed well with carefully dried PEG_{1500N} (1 g) in a flask, heated to 140 °C and stirred at the constant temperature under nitrogen for 72 h. The reaction mixture was cooled to room temperature, dispersed in water, and then centrifuged at 20,000g to retain the dark supernatant as an aqueous solution of the as-prepared carbon dots.

For the metal doping of carbon dots, an aqueous dispersion of the carbon dots was mixed with an aqueous solution of gold compound (HAuCl₄), and the mixture was irradiated with visible light. The doping level was monitored in terms of the gold plasmon absorption band.³⁶,³⁷

**Photocatalytic Reactions.** The CO₂ photocatalytic reduction experiments under different CO₂ pressures were performed on a setup consisting of a 1 kW xenon arc source coupled with a "hot filter" to eliminate both infrared and UV irradiations (transparent only in the 405-720 nm spectral region). Two stainless steel cylindrical optical cells with flat front and back sapphire windows (2.5 cm in diameter, sealed with teflon O-rings)
were used as photochemical reactors with the pressure limit of at least 2,000 psia.\textsuperscript{28} The short-path cell had an optical path-length of 16 mm (~4 mL in reactor volume) and the long-path cell of 80 mm (~20 mL in reactor volume). In a typical experiment, the cell was first loaded (not completely full) with an aqueous dispersion of the photocatalysts, purged with high-purity nitrogen gas under ambient condition, and then sealed. Pressurized CO\textsubscript{2} (in a syringe pump) was introduced into the sealed cell through metal tubing and valve until the desired pressure in the cell was achieved, and the actual pressure upon stabilization of the system was measured and recorded by using a precision pressure gauge (Heise).

Some CO\textsubscript{2} photocatalytic reduction experiments under ambient pressure were carried out by using an ACE Glass immersion-well photochemistry apparatus equipped with a 450 W medium-pressure Hanovia lamp, coupled with a cycling water filter and a glass or solution filter. An aqueous dispersion of the photocatalysts in the photochemistry apparatus was purged first with high-purity nitrogen gas and then with CO\textsubscript{2} gas (for about 60 min) for saturation, followed by photoirradiation.

Aqueous NaHCO\textsubscript{3} or NaH\textsuperscript{13}CO\textsubscript{3} solution (up to 80 mM, mimicking mildly acidic conditions of pH ~ 4.5-5.5) was used as CO\textsubscript{2} or \textsuperscript{13}C-enriched CO\textsubscript{2} in the same photocatalytic reactions.

**Photoproduct Characterization and Analysis.** The aqueous reaction mixture post-photoirradiation was collected via slow depressurization from the high-pressure optical cell into a cooled flask, followed by short-path distillation into an aqueous NaOH solution (pH ~ 11) for the organic acids in the reaction mixture to be trapped as salts.
Upon the removal of water via evaporation, the resulting solid sample was characterized by using NMR and GC-MS methods. Formic acid and acetic acid (or formate and acetate in some measurements) were identified, confirmed, and quantified. Imidazole and fumaric acid were used as internal standards in the \( ^1 \)H NMR quantification measurements.

### 3.3 Results and Discussion

The photocatalytic reactions were carried out in aqueous solutions under pressurized \( \text{CO}_2 \) conditions. In the catalyst preparation, the fluorescent carbon dots with the core carbon nanoparticles functionalized by oligomeric poly(ethylene glycol) diamine (PEG\(_{1500N}\), Figure 3.1) were synthesized under more controlled conditions for more effective carbon particle surface passivation and the associated bright fluorescence emissions, as reported previously.\(^{16}\) These carbon dots in aqueous solution exhibited fluorescence quantum yields around 20\% at 400-450 nm excitation, comparable with or better than what were observed in other batches of the similarly synthesized PEGylated carbon dots in previous studies.\(^{16}\) For the photochemical doping of the carbon dots by gold metal, the aqueous solution of the carbon dots was irradiated in the presence of the gold salt \( \text{HAuCl}_4 \), where the electrons from the photoinduced charge separation in the carbon dots were likely responsible for the reductive formation of gold metal (Figure 3.2).\(^ {17, 18}\) Since the radiative recombination of the surface-confined electrons and holes is believed to be responsible for the observed fluorescence emissions in carbon dots,\(^9\) the
Figure 3.1 Cartoon illustration of the PEG$_{1500N}$-functionalized carbon dot, with the rainbow-colored “shell” signifying that the fluorescence is from the passivated surface of the dot. The shell illustration does not imply a true core-shell structure for the carbon dot, as the passivation molecules covering the carbon particle surface likely form a structurally random soft layer that is significantly different from the kind of shell found in conventional semiconductor QDs.
metal doping was accompanied by rapidly diminishing fluorescence intensities in the solution (Figure 3.2), as expected.\textsuperscript{17}

The doping level of gold on carbon dots was monitored by the emergence of the gold plasmon band in optical absorption spectra (Figure 3.3). The association of the nanoscale gold and carbon dots, namely the doping, could be confirmed directly by the transmission electron microscopy (TEM) imaging comparatively in both transmission and Z-contrast modes (Figure 3.3) and also indirectly by the observed complete fluorescence quenching due to the doped gold interfering with the emissive processes in carbon dots (Figure 3.2).\textsuperscript{17} The gold-doped carbon dots used as photocatalysts in this study were generally of a gold-to-carbon (in the nanoparticle core) molar ratio around 1:100.
Figure 3.2 Cartoon illustrations of (upper) the high-pressure optical reactor. (Lower left) Photoreductive doping of the carbon dot with gold, completely quenching the dot-surface-based fluorescence (illustrated as the change in the dot surface from rainbow to gray) and (lower right) the gold-doped carbon dot as a photocatalyst for CO$_2$ conversion, where the doped gold (in yellow) was small in quantity, insufficient to form a shell, and likely random in terms of size and shape. The sacrificial electron donor was isopropanol added in some experiments or PEG$_{1500}$N molecules on the surface of the carbon dots in the absence of isopropanol.
The photocatalytic reduction of CO$_2$ in an aqueous solution of the gold-doped carbon dots was carried out at ambient temperature (25 °C) in high-pressure cylindrical optical cells (Figure 3.2) capable of taking the CO$_2$ pressure up to at least 2,000 psia, corresponding to the aqueous CO$_2$ concentration up to 1.37 M (calculated according to data available in the literature). Small organic acids in the reaction mixture were targeted for detection and analyses quantitatively. The acids were harvested by distilling the reaction mixture into a basic aqueous solution (pH ~ 11), followed by recovering the salts thus formed for NMR characterization and other analyses.

The $^1$H- and $^{13}$C-NMR results suggested a substantial presence of formic acid as a significant product from the CO$_2$ photoreduction, as generally known in the literature, and also acetic acid. Separately, the solution used in the NMR measurements was acidified (pH ~ 3) to convert the salts to corresponding acids for GC-MS analyses, from which the results also identified formic acid and acetic acid, as expected.

In the literature, acetic acid has been identified as a product in CO$_2$ photoreduction with the use of other photocatalysts, though quantity-wise from minor to negligible in almost all studies. Therefore, since the photocatalytic activities of carbon dots are due to the photochemical processes in the core carbon nanoparticles, the concern was a potential involvement of the carbon in the core as a source for the observed acetic acid. In control experiments, $^{13}$C-labeled CO$_2$ (NaH$^{13}$CO$_3$ with 99% $^{13}$C as a source) was used in the same photoreduction reactions. The $^{13}$C-NMR results for the formic acid and acetic acid suggested major enhancement effect in both, with the corresponding $^{13}$C-NMR signals readily detected in many fewer scans than what was required for samples
Figure 3.3 (Upper) TEM images of the gold-doped carbon dots (left, in transmission mode; right, in Z-contrast mode, where Z refers to the atomic number so that the contribution of the doped gold is emphasized). (Lower) Optical absorption spectra of the carbon dots without (——) and with gold (— —) and recovered postreaction (— • • —).
without the $^{13}$C enrichment, due to the products from $^{13}$C-labeled CO$_2$ (or more specifically H$^{13}$COOH and $^{13}$CH$_3^{13}$COOH).

Other experimental evidence against any potential involvement of the carbon atoms in carbon dots included the observation that the use of the same carbon dots without gold coating for the photocatalytic conversion of CO$_2$ resulted in much lower yields for both formic acid and acetic acid. Mechanistically, it is believed that the photoexcitation of carbon dots results in efficient charge separation, with the generated electrons and holes trapped at surface sites on the carbon dots. The electrons and holes would otherwise recombine radiatively for the fluorescence emissions in carbon dots, but the metal doping interrupted the radiative recombination by scavenging the electrons (Figure 3.2). Here the doped gold could apparently harvest and concentrate the photogenerated electrons in the carbon dots, thus more effective in the photocatalytic activities for the CO$_2$ reduction, as generally understood in the literature.

In a further examination of the involvement of water as a source of hydrogen in the formed organic acids, the photocatalytic reduction of CO$_2$ was performed in a deuterated water solution under the same experimental conditions, followed by the same product collection and isolation procedures. In the subsequent $^2$H-NMR characterization (regular water as solvent), the expected DCOO$^-$ and CD$_3$COO$^-$ NMR signals could readily be detected at 8.47 ppm and 1.89 ppm, respectively, suggesting the participation of D$_2$O in the photoreduction. A mechanism known in the literature is such that the involvement of water in the photocatalytic conversion of CO$_2$ might be associated with a two-step reduction process, first the photocatalytic splitting of water for atomic hydrogen
and then the addition of the hydrogen to CO$_2$. The observed deuteration of both formic acid and acetic acid from the reaction in D$_2$O is consistent with such a mechanism and also reaffirms the mechanistic connection between formations of the two organic acids in the photocatalytic reduction of CO$_2$.

There are several ways to evaluate the performance of catalysts in the CO$_2$ photoreduction reaction, among which a more popular one has been the R value measuring the amount of products produced per hour of light illumination for a specific amount of the photocatalyst:

$$R = \frac{W_P}{tW_C} \quad (1)$$

where $W_P$ is the amount of photoproducts in millimoles (mmol), t is the photoirradiation time in hours (h), and $W_C$ is the amount of photocatalyst used in grams (g). For the gold-doped carbon dots as photocatalysts in this work, quantitatively the amounts of the small organic acids produced in the photoreduction were subject to some variations with experimental conditions such as different batches or quantities of catalysts and reactor setups, which also affected relative populations of the two acids in the reaction mixtures. Nevertheless, with the short-path optical cell as a high-pressure photoreactor under a specifically controlled condition (CO$_2$ pressure of 700 psia and photoirradiation in the 405-720 nm wavelength range for 4 h), the observed R values for formic acid and acetic acid were 1.2 mmol h$^{-1}$g$^{-1}$ and 0.06 mmol h$^{-1}$g$^{-1}$, respectively. The performance for the former compares favorably to what have been reported in the literature for other photocatalysts. For example, in the study by Zhao, et al. on CO$_2$ photoreduction with cobalt phthalocyanine-TiO$_2$ nanocomposite as the photocatalyst and
visible-light irradiation, the best R value for formic acid was about 0.15 mmol h\(^{-1}\) g\(^{-1}\).\(^{22}\) Johne and Kisch used ZnS nanoparticles loaded on a silica matrix as photocatalysts for the CO\(_2\) reduction with 2, 5-dihydrofuran as a reducing agent and UV-light irradiation, achieving a formate production rate of about 0.29 mmol/h (or approximately 0.6 mmol h\(^{-1}\) g\(^{-1}\) in terms of the R value).\(^{21}\)

The significant acetic acid production with the use of gold-doped carbon dots as photocatalysts is somewhat unique, as this is generally a very minor product in the CO\(_2\) photoreduction with other catalysts.\(^{15, 25-30}\) The previously highest R value for acetic acid in the literature was from the work of Pathak \textit{et al.}, where well-dispersed TiO\(_2\) nanoparticles were used as photocatalysts for UV-light reduction in supercritical CO\(_2\) under high pressure, though the estimated R value was still rather small (on the order of 0.006 mmol h\(^{-1}\) g\(^{-1}\)).\(^{28}\) Irvine, \textit{et al.} also observed a significant amount of acetic acid in their colloidal CdS-based photocatalytic CO\(_2\) reduction in aqueous NaHCO\(_3\) with sulfite or hydroquinone as a hole acceptor (320-580 nm photoirradiation), with an estimated acetic acid production rate of about 0.00125 mM/h (or an R value of about 0.004 mmol h\(^{-1}\) g\(^{-1}\)).\(^{26}\) The relatively more efficient formation of acetic acid in the work reported here reflects upon the effectiveness of the gold-doped carbon dots as photocatalysts for visible-light-driven CO\(_2\) conversion, as the reduction to acetic acid requires overall eight electrons, regardless of any detailed mechanisms.\(^{15}\)

\[
2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} \quad (2)
\]

Again in studies already reported in the literature,\(^{15, 25-30}\) acetic acid has generally been a very minor or negligible product in the CO\(_2\) photoconversion. Therefore, the
formation mechanism for the product is poorly understood, except for a general acknowledgment of the mechanistic complexity. Among the three proposed mechanisms in the literature, two assumed the dimerization of initially reduction-generated radical or radical anion species as a key step toward the formation of acetic acid, specifically OHC• or CO$_2$• dimerized into OHC-CHO or OOC-COO•, respectively, followed by further photoreduction. The other mechanism on the acetic acid formation called for the reductive coupling of methanol and •COOH, both of which from initial steps in the CO$_2$ photoreduction process. A common theme is such that acetic acid shares intermediates with formic acid and/or reacts further from the latter, signifying the important role of formic acid in the understanding of the photocatalytic CO$_2$ conversion.
Figure 3.4 Results in terms of formic acid concentrations in the reaction mixtures from a series of photoconversion reactions in aqueous solutions of the carbon dots under different CO$_2$ pressures (in the long-path optical cell as the high-pressure reactor).
For a more systematic evaluation on the photoconversion under different CO$_2$ pressures, the reactions were carried out in the long-path high-pressure optical cell (thus a larger reactor volume for more samples/product quantities and thus relatively improved accuracy) under otherwise the same experimental conditions for all CO$_2$ pressures. The formic acid production obviously increased with the increasing CO$_2$ pressure (Figure 3.4), mainly because the CO$_2$ concentration in aqueous solution increases with increasing pressure. At 1,900 psia, the amount of formic acid was about an order of magnitude higher than that produced under ambient CO$_2$ pressure, which should correspond roughly to the same magnitude of increase in the photocatalytic reaction quantum yield for the formic acid formation (around 0.3% in the CO$_2$-saturated aqueous solution under ambient pressure,$^{10}$ estimated by using the method of Mallouk and coworkers$^{33, 34}$). The strong CO$_2$ pressure dependence might be understood in terms of the importance of the initial interactions between the photoexcited catalysts and CO$_2$ molecules in the conversion to formic acid, with more CO$_2$ molecules in the aqueous solution under a higher CO$_2$ pressure in the optical cell and/or the involvement of more complex multistep processes in the photoconversion reaction. Shown in Figure 3.5 is a comparison of the R values for formic acid and acetic acid from the experiments at different CO$_2$ pressures.
Figure 3.5 Comparison of R values for the photoconversion to formic acid (o) and acetic acid (□) in reactions under different CO₂ pressures.
The gold-doped carbon dots as photocatalysts were apparently stable in terms of their optical properties and catalytic activities. For example, upon continued photoirradiation for 6 h or longer in the photocatalytic reaction for CO\textsubscript{2} conversion, the optical absorption spectrum of the photocatalysts post-reaction exhibited no significant changes from that pre-reaction (Figure 3.3). The photocatalysts could also be recovered from the reaction mixtures and reused in the subsequent photoreduction reactions of CO\textsubscript{2}. The difference between the use of new and recovered photocatalysts is generally within the typical experimental variation (the changes in the results with the use of new catalysts in several experiments under the same conditions).

In summary, carbon dots with gold coating, thus diminished fluorescence emissions, are potent photocatalysts for the conversion of CO\textsubscript{2} to small organic acids. The formation of a significant amount of acetic acid, which requires many electrons in the photoreduction, reflects upon the effectiveness of the carbon dots as photocatalysts. The photocatalytic functions are apparently not limited to the carbon dots synthesized in this study, as even those prepared with carbon soot from overcooked barbequed meat exhibited similar activities.\textsuperscript{35} The substantially enhanced photoconversion in aqueous solution of the catalysts under higher CO\textsubscript{2} pressures is not only important mechanistically, suggesting the role of CO\textsubscript{2} concentration in the harvesting of photogenerated electrons and thus the photoconversion quantum yield, but also valuable technologically, with pressurized CO\textsubscript{2} as a more favorable reaction condition for larger quantities of the photoproducts.
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CHAPTER FOUR
CARBON DIOXIDE PHOTOCONVERSION DRIVEN BY VISIBLE-LIGHT EXCITATION OF SMALL CARBON NANOPARTICLES IN VARIOUS CONFIGURATIONS

4.1 Introduction

World energy consumption has grown over the past several decades. As we have become aware of the depletion in our sources of energy such as oil or their detrimental impact on our planet through the greenhouse effect, it has become increasingly more important to develop clean and sustainable energy systems based on solar energy, potentially a sustainable energy source which is not only environmental friendly but also economically viable. Though solar energy may address many of the problems with existing sources, it has proven difficult to efficiently capture, store, and harness it as a cost-effective source of power. As a result, efficient conversion of solar energy to more usable forms such as chemical energy is attracting much interest in the scientific community.

The solar spectrum contains only a small proportion of UV (~ 4-5%), limiting the applications of widely used wide-bandgap (UV absorbing) semiconductors for photocatalytic solar energy conversion, leading to the recent interest in developing new photoactive materials that absorb in the visible range of the spectrum. The efficient photoconversion of CO₂ and water into value-added fuels using visible light is a
challenge in photocatalytic systems, primarily because of the fast electron-hole recombination rates in photocatalysts. In addition to physical sequestration and long term storage, there is a renewed interest in the photocatalytic reduction of CO$_2$ into C1 to C3 hydrocarbons upon photoirradiation with visible light. Our previous work reported C1 carboxylic acid (HCOOH) as the primary CO$_2$ photoreduction product using surface-functionalized nanoscale carbon particles referred to as “carbon dots.” The photocatalytic reduction results obtained indicated the presence of a photoinduced charge separation in photoexcited small surface-functionalized carbon nanoparticles.

However, it would be interesting to determine whether carbon nanoparticles without any surface functionalization by organic or other molecules could also be used for the same photocatalytic purpose. This chapter reports that aqueous-suspended bare (naked without any surface passivation) carbon nanoparticles could catalyze the CO$_2$ photoconversion into formic acid, although with very low efficiency, thus establishing a baseline in the use of nanoscale carbon particles for harvesting visible photons to drive CO$_2$ photoreduction. Results obtained with various catalyst configurations including surface-doped metal as well as semiconductor-doped carbon nanoparticles as photocatalysts and their respective experimental conditions are presented and discussed here.
4.2 Experimental Section

**Materials.** Graphite rods (purity >99.9%) for arc-discharge were supplied by Graphite Store, Inc., and carbon dioxide (CO₂, purity >99.5%) by Airgas. Silver nitrate (AgNO₃), hydrogen tetrachloro aurate trihydrate (HAuCl₄·3H₂O), and sodium hydroxide (NaOH) were purchased from Alfa-Aesar, and anhydrous sodium acetate (CH₃COONa), sodium bicarbonate (NaHCO₃), and formic acid (99%) from Acros Organics. NaH¹³CO₃ (99% in ¹³C, 97% purity) and D₂O were obtained from Cambridge Isotope Laboratories, Inc., and titanium dioxide (TiO₂) nano-powders (Degussa P25) from Degussa Corp. The oligomeric poly(ethylene glycol) diamine (PEG₁₅₀₀₅) was obtained from Anvia Chemicals, 2, 2’-(ethylenedioxy)bis(ethyamine) of average molecular weight ~ 148 and Titanium (IV) ethoxide, Ti(OC₂H₅)₄ (97%) were purchased from Sigma-Aldrich. Thionyl chloride (>99%), zinc acetate dihydrate Zn(CH₃COO)₂·2H₂O (>98%) and sodium sulfide nonahydrate Na₂S·9H₂O (>98%) were supplied from Alfa Aesar; and nitric acid (60-70%), ethanol (>99%), N, N-dimethylformamide (DMF, 99%), and sodium dodecyl sulfate (SDS, 99%) were obtained from VWR. HPLC-grade isopropanol, methanol and chloroform were obtained from Fisher-Scientific and used as received. The dialysis membrane tubing (MWCO ~ 500) was supplied by Spectrum Laboratories. Water was deionized and purified using a Labconco WaterPros water purification system.

**Measurements.** A conventional arc-discharge chamber was used for the production of carbon soot from the high-purity graphite rods. The discharge chamber was
situated in a floating helium atmosphere (101.325 k Pa), and the discharge conditions were 70 A direct current at 28 V.

Baxter Megafuge (model 2630) and Beckman-Coulter ultracentrifuge (Optima L90K with a type 90 Ti fixed-angle rotor) were used for centrifugation at various g values. Optical absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer. NMR analyses were performed on Bruker Avance (500 MHz or 300 MHz) and JEOL (500 MHz) NMR spectrometers. The GC-MS characterization was carried out on a Shimadzu (QP 2010) GC-MS instrument equipped with a SHR5XLB column and an electron ionization (EI) MS detector.

Transmission electron microscopy (TEM) images were obtained using a Hitachi HD-2000 S-TEM system in both transmission and Z-contrast modes, and atomic force microscopy (AFM) analyses were conducted in the acoustic AC mode on a Molecular Imaging PicoPlus system equipped with a multipurpose scanner and a NanoWorld Pointprobe NCH sensor.

Fluorescence spectra were recorded on a Jobin-Yvon emission spectrometer equipped with a 450 W Xenon source, Gemini-180 excitation and Triax-550 emission monochromators, a photon counting detector (Hamamatsu R928P PMT at 950 V) and a commercial fluorimeter (Quantamaster, Photon Technology International, Inc.) using 1 cm quartz cuvettes. 9, 10-Bis(phenylethynyl)-anthracene in cyclohexane and quinine sulfate in 0.1 M H₂SO₄ were used as standards in the determination of the fluorescence quantum yields using the relative method, i.e., matching the absorbance at the excitation wavelength between the sample and standard solutions and comparing their
corresponding integrated total fluorescence intensities. The fluorescence lifetimes were measured using a Fluorolog®-Tau-3 Lifetime System (Horiba Jobin Yvon Inc., France), with 400 nm being chosen as the excitation wavelength, and emissions were collected at an emission maximum of EDA-carbon dots (458 nm) and PEGylated carbon dots (464 nm) as well as for doped carbon dots at 464 nm with Ludox (colloidal silica solution) as the scattering reference. The data were fitted using the DataMax software fitting module using non-linear least square fit. X-ray diffraction measurements were carried out on a Rigaku Ultima IV X-ray diffractometer, with the diffraction patterns being collected at room temperature using Cu Kα radiation (\( \lambda = 1.54 \text{ Å} \)) at an accelerating voltage of 40 kV and an emission current of 40 mA. The angle range was scanned from 5° to 85° (2θ) with a step size of 0.02° or 0.05°. Raman spectra were obtained on a Renishaw Raman spectrometer equipped with a 50 mW diode laser source set at 785 nm excitation and a CCD detector. Fourier transform-infrared (FT-IR) spectra were collected on a Nicolet iS5 FT-IR instrument (Thermo Scientific) equipped with an iD5 ATR diamond module in the spectral range of 500-4000 cm\(^{-1}\) on transmission mode.

Photolysis experiments were conducted primarily on a set-up consisting of a 450 W or 1 kW xenon arc source, coupled with the use of filters to eliminate infrared irradiation and to select the excitation wavelength ranges. An ACE Glass immersion-well photochemistry apparatus with a 450 W medium-pressure Hanovia lamp, coupled with a cycling water filter and a glass or solution filter, was also used in some experiments. The photon flux determination was achieved using power meters, Power Max 5100
(Moletron Detector Incorp.) with a thermopile sensor and Ophir Nova II (Ophir Photonics) with a PD300R-3W photodiode sensor.

**Photocatalysts.** As-produced carbon soot from arc-discharge was refluxed in aqueous nitric acid (2.6 M) for 24 h, dialyzed in membrane tubing (pore size equivalent to \( M_w \sim 500 \)) against fresh water for 48 h, and then centrifuged in several steps, the last being at 80,000 rpm in the ultracentrifuge for 1 h to retain the supernatant as an aqueous dispersion of carbon nanoparticles (CNPs). The dispersion without or with the addition of isopropanol and PEG\(_{1500N}\) was used for the CO\(_2\) photocatalytic conversion.

**Carbon Dots.** In the synthesis of EDA- or PEG\(_{1500N}\)-functionalized carbon dots, an as-supplied carbon nanopowder sample (1 g) was refluxed in an aqueous nitric acid solution (5 M, 90 mL) for 48 h. The reaction mixture was dialyzed against fresh water at room temperature and then centrifuged at 3000 g to retain the supernatant. The recovered sample containing primarily small carbon nanoparticles was refluxed in neat thionyl chloride for 12 h, followed by the removal of the excess thionyl chloride under nitrogen. The post-treatment carbon particle sample (100 mg) was mixed well with carefully dried EDA or PEG\(_{1500N}\) (1 g) in a flask, heated to 128 °C and stirred at a constant temperature under nitrogen for 72 h. The reaction mixture was cooled to room temperature, dispersed in water, and then centrifuged at 20,000 g to retain the dark supernatant as an aqueous solution of the as-prepared carbon dots.

ZnS-and TiO\(_2\)-doped carbon dots were obtained using the precipitation method and sol-gel processes similar to a previously reported procedure.\(^46\)
**ZnS-doped carbon dots.** The surface-oxidized carbon nanoparticles (300 mg) harvested from the nitric acid oxidation (2.6 M, 24 h) of carbonized polypyrrole nanoparticles were dispersed in DMF (100 mL) via sonication for 1 hour. Zn(CH₃COO)₂·2H₂O (330 mg, 1.50 mmol) was added to the suspension under vigorous stirring, followed by slow dropwise addition of an aqueous Na₂S.9H₂O solution (0.62 M, 2.5 mL) at room temperature under continuous stirring. The mixture was centrifuged at 3000g, and the residue was retained and repeatedly washed with distilled water to obtain the ZnS-doped carbon nanoparticles (480 mg).

ZnS-doped carbon nanoparticles (250 mg) were suspended in an aqueous SDS solution (1 wt%, 180 ml) via sonication for 1 hour. Upon filtration, the filter cake was washed repeatedly with water and then dried under nitrogen. The solid ZnS-doped carbon nanoparticle sample (100 mg) obtained was mixed carefully with dry PEG₁₅₀₀₀ (0.5 g), and the mixture was heated to 110 °C and stirred for 72 h under a nitrogen atmosphere. After being cooled to room temperature, the reaction mixture was dispersed in water and then centrifuged at 20000g to retain the supernatant as an aqueous solution of ZnS-doped carbon dots.

**TiO₂-doped carbon dots.** The surface-oxidized small carbon nanoparticles (200 mg) obtained from the nitric acid oxidation (2.6 M, 24 h) of commercially supplied Aldrich carbon nanopowder were mixed with a sol-gel solution containing Ti(OC₂H₅)₄, ethanol, water, and nitric acid at a molar ratio of 1:70:1.9:0.2, followed by refluxing at 80 °C with constant stirring for 1 h, followed by further stirring for 12 h and then filtered.
The filtered cake was dried, ground and subsequently annealed at 250 °C for 1 h to obtain the TiO\textsubscript{2}-doped carbon nanoparticles (225 mg).

The same procedure and conditions discussed above were used for the functionalization of TiO\textsubscript{2}-doped carbon nanoparticles with PEG\textsubscript{1500N}, except the functionalization reaction with PEG\textsubscript{1500N} was carried out at a relatively higher temperature (180\textdegree C) under nitrogen protection.

**Photolysis.** An aqueous dispersion of carbon nanoparticles with a selected optical density of 450 nm was prepared, with aqueous HAuCl\textsubscript{4} being added until the desired concentration was reached (up to 1 mM). The optically transparent mixture in a cylindrical optical cell with flat front and back windows was photoirradiated in the photolysis set-up through a hot filter (720 nm cut-on) and a 425 nm cut-off filter for a varying time period, during which the progress of the Au\textsuperscript{0} coating of the carbon nanoparticles was monitored in terms of the plasmon absorption band. The same procedure and conditions were used for the photolysis of the aqueous carbon nanoparticles with aqueous AgNO\textsubscript{3} for the coating of Ag\textsuperscript{0}. Control experiments were conducted using the same photolysis set-up with aqueous AgNO\textsubscript{3} and HAuCl\textsubscript{4} solutions in the absence of carbon nanoparticles.

The naked, Ag\textsuperscript{0}-coated or Au\textsuperscript{0}-coated carbon nanoparticles acting as photocatalysts in an aqueous dispersion (with or without 0.2 M isopropanol and with or without 5 mM PEG\textsubscript{1500N}) were taken in an optical cell and was purged with CO\textsubscript{2} gas toward saturation and then photoirradiated through the hot filter (720 nm cut-on) and 425 nm cut-off filters. In addition to the exclusion of infrared irradiation, the absence of
thermal effects was ensured by circulating cold nitrogen gas through the reaction chamber. Post-photoirradiation, the dispersion was distilled under reduced pressure to harvest the photoproduct formic acid, and the collected solution was trapped as a basic solution of pH ~ 11 by using an aqueous NaOH solution. Sodium formate was obtained after the removal of water, and confirmed and quantified by using NMR and GC-MS methods. Imidazole and fumaric acid were used as internal standards for the $^1$H-NMR quantification measurements.

Some of the CO$_2$ photocatalytic reduction experiments under ambient conditions were carried out using an ACE Glass immersion-well photochemistry apparatus equipped with a 450 W medium-pressure Hanovia lamp, coupled with a cycling water filter and a pyrex glass ($\lambda > 365$ nm) or solution filter. An aqueous dispersion of the photocatalysts in the photochemistry apparatus was purged first with high-purity nitrogen gas and then with CO$_2$ gas (for approximately 60 min.) for saturation, followed by photoirradiation.

For the labeling with $^{13}$C, NaH$^{13}$CO$_3$ (up to 0.36 M) mimicking a mildly acidic pH (pH ~ 4.5-5.5) or approximately neutral pH was used in the place of CO$_2$ gas while the other experimental conditions remained the same. In the control experiment, with all conditions the same except for no photoirradiation, no reactions or any formic acid were detected, as expected. Commercially supplied TiO$_2$ nano-powders (Degussa P25) at a concentration of 0.5 gm/L were dispersed in water, and the suspension was used in the photocatalytic reactions for comparison.
4.3 Results and Discussion

Carbon soot containing small nanoparticles was prepared by an arc-discharge of high-purity graphite rods in a helium atmosphere. While the conditions were similar to those used in the production of multiple-walled carbon nanotubes (MWNTs), the applied arc-discharge condition (such as the electric currents) applied here did not result in the formation of nanotubes, so no MWNTs were detected in the as-produced carbon soot.

For the preparation of aqueous-suspended carbon nanoparticles, the carbon soot from the arc-discharge was refluxed in aqueous nitric acid to convert some of the particle surface carbons into oxygen-containing moieties such as epoxy, alcohols and carboxylic acids (Figure 4.3), thus making the carbon particles more dispersible in polar solvents. The aqueous dispersion of the nitric acid-treated carbon soot was dialyzed in membrane tubing (MW cut-off 500) against fresh water to remove all salts and lower molecular weight species, followed by vigorous centrifuging at a high speed to retain the supernatant as a stable aqueous suspension of small carbon nanoparticles (generally less than 10 nm based on atomic force microscopy as seen in Figure 4.1).

The X-ray diffraction pattern (XRD) of oxidized carbon nanoparticles exhibited a broad peak centered at $2\theta \sim 25.5^0$ (lattice spacing $d = 0.34$ nm) resembling a graphitic carbon structure (Figure 4.2 a). In the Raman spectrum clear signatures of carbon, primarily the D band at $\sim 1324$ cm$^{-1}$ attributed to the disorder-induced stretching modes of graphite resulting from the presence of structural defects (sp$^3$-hybridized carbon
Figure 4.1 AFM images on the specimens prepared from the aqueous suspended carbon nanoparticles (left) and those surface-coated with Ag⁰ (right).
Figure 4.2 a) X-ray diffraction (XRD) pattern and b) Raman spectrum of oxidized carbon nanoparticles obtained from arc-discharge method.
content) and the G band at ~1589 cm\(^{-1}\) resulting from the \(E_{2g}\) mode corresponding to the stretching mode of \(sp^2\)-bonded carbon atoms in the graphite plane, indicate that carbon nanoparticles are composed of graphitic structures (Figure 4.2 b).

In the FTIR spectrum, several functional groups are found, including C=O (1699 cm\(^{-1}\)) and C-O-C (1211 cm\(^{-1}\)) consistent with the incorporation of oxygen containing moieties, thus enabling good solubility in water. The broad peak at 1548 cm\(^{-1}\) can be attributed to graphitic C=C stretching vibrations (Figure 4.3). A weak broad band centered around 2886 cm\(^{-1}\) can be ascribed to C-H stretching mode while small peaks centered at 1416 cm\(^{-1}\) and 1346 cm\(^{-1}\) can be assigned to C-H bending mode vibrations. Additionally, a broad IR band in the region ~3100-3650 cm\(^{-1}\) can be attributed to -OH bonds.

The aqueous-suspended small carbon nanoparticles were found to be strongly absorptive over the UV/vis spectral region (Figure 4.4), with the estimated molar absorptivity at 400-450 nm around 50 M\(_{\text{C-atom}}\) cm\(^{-1}\) (compared with ~16 M\(_{\text{C-atom}}\) cm\(^{-1}\) for \(C_{60}\) at the first absorption band maximum),\(^{16}\) where M\(_{\text{C-atom}}\) denotes molar concentration in terms of carbon atoms in the suspension of carbon nanoparticles, or up to 370,000 and \(3 \times 10^6\) M\(_{\text{C-particle}}\) cm\(^{-1}\) for the particles of 5 and 10 nm in diameter, respectively.
Figure 4.3 FTIR spectrum of oxidized carbon nanoparticles.
Figure 4.4 A representative UV/vis absorption spectrum of aqueous suspended carbon nanoparticles. Inset: the appearance of a typical suspension.
The aqueous suspended carbon nanoparticles (typically approximately 0.3 mg/mL) were used as photocatalysts for the reduction of CO₂. For the experiments, the suspension in a photolysis cell was purged with CO₂ gas toward saturation at ambient temperature, followed by photoirradiation with visible-light (425-720 nm) for up to 12 h. During the reaction the ambient temperature was maintained via the circulation of cold nitrogen gas through the reaction chamber. The characterization of the photolysis products was based on the detection of formic acid, known as a significant product (though not the only product according to previous studies in the literature) in the photocatalytic reduction of CO₂.²⁻⁷, ¹⁷, ¹⁸ The obvious decrease in the pH in the reaction mixture was consistent with the formation of formic acid. For its detection and quantification, formic acid as a volatile compound was distilled from the reaction mixture into a basic aqueous solution (pH ~ 11). The formate salts thus obtained were harvested from the basic solution upon the removal of water, and then analyzed by ¹H and ¹³C NMR in D₂O (Figure 4.5). Further confirmation of the identity of formic acid (acidified from the formate) was achieved through GC-MS analysis (m/e of 46 for the molecular ion).

The same photolysis experiment was conducted with NaH¹³CO₃ as the ¹³C-labeled CO₂ source. Results from the characterization of the photoproduct formic acid were similar, except that the signal in ¹³C NMR was much more intense and readily detectable with fewer NMR scans. Blank experiments conducted with naked carbon nanoparticles in the absence of light irradiation under the same experimental conditions showed no detectable formic acid or formate, thus supporting the essential
Figure 4.5 a) $^1$H NMR characterization results of formic acid as formate ($\delta \sim 8.49$ ppm) harvested from photocatalytic CO$_2$ reduction with fumaric acid ($\delta \sim 6.54$ ppm) as internal standard in D$_2$O with the use of naked carbon nanoparticles as catalysts and b) $^{13}$C NMR results on formate ($\delta \sim 171.25$ ppm) characterization with the use of gold coated naked carbon nanoparticles as photocatalysts.
photosensitized conversion of CO₂ into formic acid by the catalysts. These experimental results collectively suggested that aqueous-suspended carbon nanoparticles could serve as photocatalysts in harvesting visible photons for the conversion of CO₂ into formic acid. The photoconversion quantum yields based on the formation of formic acid were only in the order of 0.001-0.003% (Table 4.3), roughly comparable with those observed with the use of commercially supplied TiO₂ nano-powders (Degussa P25) in aqueous suspension as photocatalysts under similar experimental conditions (UV excitation up to 360 nm). In the literature, the quantum yield numbers associated with Degussa for CO₂ photoconversion varied widely, though generally low (10⁻⁶ – 10⁻⁴).⁴, ⁶, ⁷ However, a significant difference is that the carbon nanoparticles harvest visible photons for the CO₂ conversion, while the TiO₂ nano-powders require UV excitation, as was also used in this study.

Mechanistically, the photoexcitation of the aqueous-suspended carbon nanoparticles likely results in a charge separation for the formation of surface-confined electrons and holes (Figure 4.6), which may undergo radiative recombination resulting in fluorescence emissions.¹⁹-²³ However, the emissions observed from the naked carbon nanoparticles (without any surface functionalization molecules like in the carbon dots) in aqueous or other solvent suspensions have generally been weak,¹⁵ due at least in part to the photogenerated electrons and holes not being stable in the absence of any particle surface passivation. The same effect probably makes them less effective photocatalysts for the relatively low quantum yields in the photocatalytic conversion of CO₂.
Figure 4.6 A cartoon illustration on photocatalytic processes in the carbon nanoparticles (CNPs) without (upper) and with (lower) the metal coating for CO$_2$ conversion.
These experiments on CO₂ photoconversion were conducted in an aqueous media in the presence of isopropanol (up to 0.2 M) as a sacrificial electron donor, as commonly used in many studies already reported in the literature. Interestingly, however, the same experiments with the naked carbon nanoparticles as photocatalysts in an aqueous dispersion without isopropanol were not obviously less efficient in terms of the conversion to formic acid.

An oligomeric polyethylene glycol compound, H₂NCH₂CH₂CH₂(OCH₂CH₂)ₙCH₂NH₂ (n ~ 35, PEG₁₅₀₀N) was added to the aqueous suspension of carbon nanoparticles to improve the nanoparticle dispersion (potentially reducing the light scattering by the particles). The same photocatalytic experiments in the aqueous dispersion of carbon nanoparticles with PEG₁₅₀₀N and saturated CO₂ gas or NaH¹³CO₃ similarly yielded formic acid or ¹³C-labeled formic acid, respectively, with the photoconversion being found to be approximately 6 times more efficient.

In many reported studies on the use of semiconductor (such as TiO₂) nanoparticles as photocatalysts, an approach widely used for enhanced CO₂ photoconversion has involved the coating of the nanoscale semiconductors with a metal, often a noble metal such as platinum, silver or gold. The mechanistic explanation for the significant improvements in product quantum yields is generally that the coated metal concentrates the photogenerated electrons in the nanoscale semiconductor to make the photoreduction of CO₂ more efficient. The same approach has been employed in the use of noble metal-doped carbon dots as photocatalysts. In this study, the naked carbon nanoparticles in an aqueous suspension were coated with silver (Ag⁰) or gold (Au⁰) by
simple photolysis, the resulting metal-coated carbon nanoparticles serving as more effective photocatalysts.

For the Au$^0$ coating, a stable aqueous dispersion of the carbon nanoparticles in the presence of HAuCl$_4$ was photoirradiated with visible light (425-720 nm). The photogenerated electrons in the carbon nanoparticles reduced the gold cations (Au$^{+3}$) into Au$^0$ on the particle surface (likely at defect sites), as monitored by progressive increases in the Au$^0$ plasmon absorption (Figure 4.7). As a control, no such absorption was observed after photolysis in the absence of carbon nanoparticles under otherwise the same experimental conditions. Figure 4.8 shows representative transmission electron microscopy (TEM) images of Au$^0$-coated carbon nanoparticles, with the imaging in the Z-contrast mode particularly sensitive to Au$^0$ on the carbon particle surface due to the high Z-number of the metal. Crystal lattice fringes were observed in the high-resolution TEM images, the lattice spacing determined to be 0.29 nm, consistent with that of the face-centered-cubic Au$^0$ (110).$^{27}$

More quantitatively, the molar absorptivity value known from previous studies ($2 \times 10^3$ M$_{\text{Au-atom}}^{-1}$ cm$^{-1}$ at around 530 nm, where M$_{\text{Au-atom}}$ denotes molar concentration in terms of gold atoms) was used to estimate the amount of coated Au$^0$.$^{28}$ Nanoparticles with a gold-to-carbon ratio of approximately 1% were used as photocatalysts in the CO$_2$ conversion experiments.
Figure 4.7 UV/vis absorption spectra of the aqueous suspended carbon nanoparticles with progressively increasing levels of Au$^0$ coating (in the direction of the arrow).
Figure 4.8 TEM images on the Ag$^0$-coated carbon nanoparticles in Z-contrast mode (upper, with the inset showing a particle image in high-resolution transmission mode) and on the Au$^0$-coated carbon nanoparticles in transmission mode (lower-left) and Z-contrast mode (lower-right).
The experimental conditions were the same as those for the naked carbon nanoparticles functioning as photocatalysts described above as were the collection and characterization of the significant product, formic acid. As expected, the photoconversion of CO$_2$ to formic acid was much more efficient with the Au$^0$-coated carbon nanoparticles as photocatalysts in an aqueous suspension, with a more pronounced decrease in pH (down to 3 or lower) in the reaction mixture, indicative of a higher formic acid concentration. The estimated quantum yields for the formation of formic acid were higher by an order of magnitude than those with naked carbon nanoparticles as photocatalysts (Table 4.3), yet lower than those found previously with the use of metal-coated carbon dots.$^{12}$

The carbon nanoparticles in an aqueous suspension were also coated with silver (Ag$^0$) using the same photolysis procedure as with the silver salt AgNO$_3$, the coating level also being monitored in terms of the Ag$^0$ plasmon absorption (Figure 4.9). The Ag$^0$ coated on the carbon nanoparticles was similarly detected in the TEM imaging, as shown in (Figure 4.9). At high resolution, the spacing observed in the crystal lattice fringes was determined to be 0.235 nm, consistent with that of the face-centered-cubic Ag$^0$ (111).$^{29}$ The Ag$^0$-coated carbon nanoparticles were used as photocatalysts in the CO$_2$ conversion in an aqueous suspension under the same photoirradiation conditions, the estimated quantum yields for the conversion of CO$_2$ to formic acid being similar to those with the Au$^0$-coated carbon nanoparticles as photocatalysts as discussed above.
Figure 4.9 UV/vis absorption spectra of the aqueous suspended carbon nanoparticles with progressively increasing levels of Ag$^0$ coating (in the direction of the arrow).
To gain further insight into the photocatalytic reduction mechanism, more specifically the role of solvent molecules, CO$_2$ photoreduction experiments were performed in deuterated water (D$_2$O) under identical experimental conditions using the same product collection and characterization procedures. As seen in the $^2$H-NMR characterization (regular water as solvent) shown in Figure 4.10, the expected DCOO$^-$ NMR signals were readily detected at 8.43 ppm, suggesting the participation of the D$_2$O solvent in the photoreduction, consistent with the photocatalytic CO$_2$ conversion mechanism found in the literature.$^6$

In addition, we studied the effect of $^{13}$C enriched bicarbonate concentration as a source for $^{13}$CO$_2$ at neutral pH on $^{13}$C enriched product yields for formic acid under different initial $^{13}$C enriched bicarbonate concentration using gold-coated naked CNPs under the same experimental conditions and photolysis set-up. The product yields observed for formic acid increased with the increase in the $^{13}$C enriched bicarbonate concentration (Figure 4.11), suggesting that the observed photocatalytic $^{13}$C labeled bicarbonate or $^{13}$CO$_2$ conversion was dependent on the initial concentration of the $^{13}$CO$_2$ source, with an obvious increase in formic acid product yields at higher $^{13}$C enriched bicarbonate concentrations (Figure 4.11). Furthermore, the photocatalysts were stable in their aqueous solutions and could be recycled in subsequent CO$_2$ or $^{13}$CO$_2$ photoreduction experiments. However, the photocatalytic performance of the catalyst was found to be $\sim$ 1.5 times lower in terms of formic acid production yield.
Figure 4.10 Deuterium ($^2$H) NMR characterization (regular water as solvent) of deuterated formic acid as DCOO$^-$ (δ ~ 8.43 ppm) collected from CO$_2$ photoconversion experiment using gold coated naked carbon nanoparticles (CNPs) dispersed in deuterated water (D$_2$O) as solvent.
Figure 4.11 Observed formic acid production yields with different concentration of $^{13}$C enriched bicarbonate as $^{13}$CO$_2$ feed/source.
Thus, aqueous-suspended carbon nanoparticles upon visible-light excitation appear to drive the CO$_2$ photoconversion process without any other substances or aids (Figure 4.6), despite the relatively low quantum yields (though still comparable to those obtained using aqueous-suspended Degussa as photocatalysts with UV-light excitation).

These results are also significant mechanistically, suggesting that the photoinduced redox properties of carbon nanoparticles resemble, at least phenomenologically, those found in traditional nanoscale semiconductors.

While the aqueous suspensions of carbon nanoparticles (without or with metal coating) used in the photocatalytic reactions were stable with respect to precipitation and appeared solution-like (Figure 4.4), they were different from true solutions in terms of their significant light scattering. This scattered light did not contribute appreciably to the photocatalytic conversion, thus representing wasted photons. The effort to reduce the light scattering by adding oligomeric PEG diamine (PEG$_{1500N}$, also serving as a sacrificial electron donor) to improve the dispersion of the nanoparticles was successful, resulting in the higher (~ 6 times higher) photocatalytic activity of the carbon nanoparticles observed in the photoconversion results.

Surface-passivated small carbon nanoparticles (carbon dots) with various surface passivation agents were also employed as photocatalysts in regular CO$_2$ or $^{13}$C enriched bicarbonate as a source of $^{13}$CO$_2$ in the photocatalytic studies in order to examine their CO$_2$ photoreduction efficiency. The carbon dots with the core carbon nanoparticles functionalized by 2,2’-(ethylenedioxy)bis(ethylamine) (EDA, $\text{H}_2\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NH}_2$) molecules or oligomeric poly(ethylene glycol)
diamine (PEG$_{1500}$N, H$_2$NCH$_2$(CH$_2$CH$_2$O)$_{35}$CH$_2$CH$_2$CH$_2$NH$_2$) were synthesized to obtain EDA-carbon dots and PEGylated carbon dots, respectively, and were used as photocatalysts (corresponding to the optical absorption spectra shown in the Figure 4.12) under similar experimental conditions. These carbon dots samples exhibited photoluminescence quantum yields in excess of 10% around 400-440 nm. Fluorescence lifetimes of carbon dots were measured by frequency-domain lifetime measurements.$^{31}$ Both PEGylated and EDA-carbon dots exhibited multi-exponential decays (Table 4.2), indicating the distribution of diverse emissive sites on each passivated carbon dot as frequently seen in similar such systems.$^{32,33}$

Table 4.1 shows the formic acid product yield distribution from $^{13}$C enriched bicarbonate (used as the $^{13}$CO$_2$ source) photoconversion obtained with carbon dots with various surface passivation agents (Scheme 4.1). Table 4.1 shows that the photocatalytic activity of the EDA-carbon dots was found to be relatively higher (~ 2 times higher) than the PEGylated carbon dots, a result perhaps attributed to the overall carbon nanodot structural profiles attained via the respective functionalization reactions (Scheme 4.1). Using relatively smaller EDA molecules as the surface passivation agent (hence smaller shell around the carbon core) probably results in greater interaction in the case of EDA-carbon dots with CO$_2$ molecules in comparison to those with PEGylated carbon dots, leading to the higher photocatalytic product yield observed in the former.
Scheme 4.1 A cartoon illustration of EDA-or PEGylated-carbon dot as a surface passivated small carbon nanoparticle.
Figure 4.12 Absorption (ABS) and fluorescence (FLSC, excitation wavelengths at 400 nm, solid line and 440 nm, dotted line) spectra of the as-synthesized a) PEGylated carbon dots in aqueous solution b) EDA-carbon dots in aqueous solution.
For overall comparative purposes, Table 4.3 summarizes the product yields and apparent photoconversion quantum yields for formic acid obtained from the CO$_2$ photoconversion using naked carbon nanoparticles, metal (Au)-coated naked carbon nanoparticles and surface-functionalized small carbon nanoparticles under visible light illumination. As this table shows, the photoconversion quantum yields with different carbon nanoparticle photocatalysts are as follows:

PEGylated-carbon dots ~ Au coated naked CNPs > Naked CNPs.

This photocatalytic trend can be explained in terms of the photoinduced charge separation and structural characteristics achieved in the nanocatalyst configurations mentioned previously as well as from their estimated CO$_2$ photoconversion quantum yields (Table 4.3).

Moreover, photoreduction results were dependent on the optical properties of carbon dots used in terms of their bright photoluminescence (PL) emission or fluorescence quantum yields. In a series of experiments, two batches of PEGylated carbon dots A and B exhibiting PL quantum yields of ~ 12 % and ~ 6 %, respectively, at approximately 400-450 nm were used for the photodeposition of a small amount of gold (typical Au to carbon molar ratio ~ 1%) to obtain gold-doped carbon dots as reported in our prior studies. The resulting gold-doped carbon dots catalysts were used in high pressure CO$_2$ photoreduction experiments under different CO$_2$ pressures, with increasing CO$_2$ concentration at higher CO$_2$ pressures. As seen in Figure 4.13, the photocatalytic performance of gold-doped carbon dots obtained from carbon dots exhibiting greater
Table 4.1 Comparison of formic acid production yields from NaH$^{13}$CO$_3$ photoconversion for EDA-carbon dots and PEGylated carbon dots under similar experimental conditions.

<table>
<thead>
<tr>
<th>Photocatalyst used for NaH$^{13}$CO$_3$ conversion</th>
<th>Photoirradiation time (h)</th>
<th>Formic Acid Production Rate ($\mu$mol g$^{-1}$ h$^{-1}$)</th>
<th>Formic Acid Product yield (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDA C-dots for NaH$^{13}$CO$_3$ (39 mM) Conversion</td>
<td>6 h</td>
<td>102.32</td>
<td>10.45</td>
</tr>
<tr>
<td>PEGylated C-dots for NaH$^{13}$CO$_3$ (44 mM) Conversion</td>
<td>6 h</td>
<td>43.66</td>
<td>4.47</td>
</tr>
</tbody>
</table>
Table 4.2 Fluorescence lifetime results on carbon dots with different surface passivation excited at 400 nm.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEGylated Carbon Dots</td>
<td>9.62</td>
<td>9.56</td>
<td>1.69</td>
<td>4.95</td>
</tr>
<tr>
<td>EDA-Carbon Dots</td>
<td>8.57</td>
<td>10.28</td>
<td>2.50</td>
<td>7.69</td>
</tr>
</tbody>
</table>

The percentage of $\tau_1$, $\tau_2$, and $\tau_3$ is about 22.65%, 48.26% and 29.09% for PEGylated carbon dots and the percentage of $\tau_1$, $\tau_2$, and $\tau_3$ is about 14.51%, 44.44% and 41.05% for EDA-carbon dots respectively. ($\chi^2$ represents goodness of a fit parameter)
Table 4.3 Formic acid production rates and photochemical quantum yields in CO$_2$ photoreduction for carbon nanoparticles as photocatalysts in various configurations.

<table>
<thead>
<tr>
<th>Photocatalyst used for CO$_2$ Photoconversion</th>
<th>HCOOH Formation Rates (µmol g$^{-1}$ h$^{-1}$)</th>
<th>Apparent Quantum Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naked CNPs,</td>
<td>3.66</td>
<td>0.0011%</td>
</tr>
<tr>
<td>Gold coated naked CNPs</td>
<td>38.66</td>
<td>0.111%</td>
</tr>
<tr>
<td>PEGylated carbon dots</td>
<td>43.66</td>
<td>0.013%</td>
</tr>
</tbody>
</table>
Figure 4.13 Effect of carbon dots catalyst photoluminescence quantum yields with carbon dots A (○) and carbon dots B (□) on formic acid production yields (in mM) in CO₂ photoconversion reactions under different CO₂ pressures using gold doped carbon dots in aqueous solution as photocatalysts.
Table 4.4 Fluorescence lifetime measurements on different batches of PEGylated carbon dots used as photocatalysts excited at 400 nm.

<table>
<thead>
<tr>
<th>Carbon Dot Samples</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEGylated C-Dots (A)</td>
<td>7.56</td>
<td>9.56</td>
<td>2.35</td>
<td>5.06</td>
</tr>
<tr>
<td>PEGylated C-Dots (B)</td>
<td>6.73</td>
<td>8.52</td>
<td>1.24</td>
<td>7.19</td>
</tr>
</tbody>
</table>

The percentage of $\tau_1$, $\tau_2$, and $\tau_3$ is about 22.45%, 45.09% and 32.46% for PEGylated C-dots (A) and the percentage of $\tau_1$, $\tau_2$, and $\tau_3$ is about 20.02%, 47.95% and 32.03% for PEGylated C-dots (B) respectively.
PL quantum yield (C-dots A) showed substantially improved photocatalytic activity compared to the ones exhibiting lower PL quantum yields (C-dots B) (Figure 4.13). This behavior is probably attributed to the better photoinduced charge separation and charge transfer characteristics expected in the carbon dot catalysts with relatively higher PL quantum yield as supported by their average excited-state lifetime measurement results (Table 4.4). This study also supports the importance of the superior optical properties (in terms of high PL quantum yields) of the catalysts in photocatalytic reactions.

Metal chalcogenide semiconductors, e.g. zinc sulfide (ZnS)- or cadmium sulfide (CdS)-based systems, have been well documented as good candidates for photocatalytic CO$_2$ reduction due to their electronic band structure, which is appropriate for photogenerated charge carriers.$^5$ $^{35-39}$ Likewise, its counterpart TiO$_2$ (band gap ~ 3.2 eV), ZnS absorbs in the UV region (constituting about 4-5% of the entire solar spectrum) because of its wide bandgap of ~ 3.66 eV, which considerably limits its light harvesting capability across the solar spectrum.$^5$ $^6$ $^7$ $^{35-37}$

To date numerous efforts have been attempted to improve the photocatalytic efficiency via incorporation with other materials, including metal ion doping strategies,$^{40}$ loading with Au$^{41}$ and visible-light sensitization approaches through the creation of heterojunctions with other narrow band gap semiconductors or dyes in order to drive the electronic processes in the desired direction.$^6$ $^7$ $^{42}$ $^{43}$ Despite good performances, these approaches involve complex synthetic procedures, instability in aqueous solutions under irradiation and the use of toxic elements, thus limiting their use in a wide range of
practical applications. Thus, there is a need for the development of inexpensive, high performance and non-toxic visible-light sensitizers for photocatalytic systems.

Recently, carbon nanodots have received increased attention as potential alternatives in photocatalysis due to their excellent optoelectronic properties such as broadband optical absorption, bright photoluminescence (PL) emissions, favorable photoinduced electron transfer characteristics, good chemical stability, non-toxicity and facile scalable production at lower cost.\textsuperscript{21, 22} For example, Kang and coworkers used carbon quantum dots as visible light photosensitizers to promote the photoelectrochemical hydrogen generation on TiO\textsubscript{2} nanotube arrays.\textsuperscript{43} Similarly, Ho and coworkers developed the hydrothermal synthesis of TiO\textsubscript{2}/carbon dots (TiO\textsubscript{2}/CDs) and ZnS/carbon dots (ZnS/CDs) heterostructures to enhance the photocatalytic hydrogen evolution rate.\textsuperscript{44, 45} However, limited research has focused on the photocatalytic reduction of CO\textsubscript{2} using semiconductor/carbon dots nanocomposite photocatalysts.

In this work, we developed a surface doped semiconductor, specifically TiO\textsubscript{2}- and ZnS- doped carbon dot nanohybrids, for utilization in photocatalytic CO\textsubscript{2} reduction to formic acid under visible light illumination. The semiconductor (ZnS, TiO\textsubscript{2})-doped carbon dots were synthesized via precipitation or sol-gel methods, similar to previously reported protocols.\textsuperscript{46} These semiconductor-doped carbon dots (Scheme 4.2) show improved photocatalytic performance towards CO\textsubscript{2} photoreduction over bare/or undoped carbon dots without any other aids or co-catalysts. Moreover, the photocatalytic activities of doped carbon dots were found to be substantially higher (more than an order of
magnitude higher) in comparison to classical Degussa P25 (TiO$_2$) based catalysts, indicating doped carbon dots are a promising platform for photocatalytic CO$_2$ conversion.

ZnS- and TiO$_2$-doped carbon dots were obtained following the procedure reported previously.$^{46}$ Surface-oxidized small carbon nanoparticles harvested from the nitric acid oxidation of precursor carbon nanopowder were dispersed in relatively stable aqueous or other organic suspensions. Carbon nanoparticles serve as nucleation centers and subsequent growth sites for ZnS and TiO$_2$ nanocrystals in a titration of their precursor solutions under appropriate conditions to yield ZnS- and TiO$_2$-doped carbon nanoparticles. Briefly, in the synthesis of ZnS-doped carbon nanoparticles, acid-treated carbon nanoparticles (obtained from the carbonization of polypyrrole)$^{47,48}$ in aqueous solutions with Zn(CH$_3$COO)$_2$ (zinc acetate) were precipitated with a dropwise addition of Na$_2$S (sodium sulfide) solution followed by repeated washings with water and centrifugation to recover the ZnS-doped carbon nanoparticles. For TiO$_2$ doping, acid-treated carbon nanoparticles (obtained from commercially supplied carbon nanopowder from Aldrich) were mixed with a sol-gel solution containing titanium ethoxide, ethanol, water and nitric acid and refluxed at 80 °C for 1 h for the adsorption of Ti condensate on the carbon nanoparticle surface followed by annealing at 250°C to obtain the TiO$_2$-doped carbon nanoparticles. The doped carbon nanoparticles were functionalized by PEG$_{1500N}$ molecules to yield ZnS- and TiO$_2$-doped carbon dots, respectively (Scheme 4.2). The semiconductor doped carbon dots used as prepared were usually less than 10 nm in size as per AFM analyses of their height profiles (Figure 4.14). The doped carbon nanoparticles were further characterized and confirmed by X-ray diffraction and Raman.
Scheme 4.2 Schematic representation of semiconductor-doped carbon dots.
Figure 4.14 AFM imaging results on ZnS-doped carbon dots.
spectroscopy analyses. The powder X-ray diffraction (XRD) pattern of the ZnS-doped carbon nanoparticles exhibited broad peaks resembling a cubic-zinc blende crystal structure, a stable phase for room temperature bulk ZnS.\textsuperscript{49, 50} The diffraction peaks observed have been assigned to the 111 ($2\theta \sim 29^0$), 220 ($2\theta \sim 48^0$) and 311 ($2\theta \sim 57^0$) planes of the cubic crystal of ZnS (Figure 4.15) consistent with previous research.\textsuperscript{49, 50} Additionally, the XRD diffraction pattern observed matched well with the standard XRD pattern of the cubic zinc blende structure (Figure 4.15).

In the TiO$_2$-doped carbon nanoparticles, diffraction peaks were observed at $25.95^0$, $38.43^0$, $48.58^0$, $54.76^0$, $62.99^0$, $70.0^0$ and $75.47^0$, which can be indexed to the (101), (004), (200), (211), (204), (220), and (215) crystal planes of the TiO$_2$ anatase phase.\textsuperscript{51} Furthermore, the XRD diffraction pattern observed matched well with the standard XRD pattern of the TiO$_2$ anatase phase (Figure 4.15).
Figure 4.16 Raman spectra of a) TiO$_2$-doped carbon nanoparticles and b) ZnS-doped carbon nanoparticles prefunctionalization.
The Raman spectrum of both the ZnS-and TiO$_2$-doped carbon nanoparticles exhibited the characteristic D and G bands for carbon, indicating a graphitic carbon structure in doped carbon nanoparticles, as expected (Figure 4.16). In addition, in the Raman spectrum of the TiO$_2$-doped carbon nanoparticles, typical modes of anatase could be observed,\textsuperscript{51} i.e., the E$_{g(1)}$ peak (152 cm$^{-1}$), the B$_{1g(1)}$ peak (390 cm$^{-1}$), the E$_{g(2)}$ peak (632 cm$^{-1}$), and the A$_{1g}$ + B$_{1g(2)}$ modes centered at 508 cm$^{-1}$, consistent with the XRD results (Figure 4.15 and Figure 4.16). Hence, the XRD and Raman data both suggested the doping of ZnS and TiO$_2$ on the carbon nanoparticles. Doping levels found in terms of C: ZnS and C: TiO$_2$ molar ratios in ZnS-doped carbon dots and TiO$_2$-doped carbon dots are typically 20:1 and 40:1 as estimated by thermogravimetric (TGA) analyses from our prior studies.\textsuperscript{46}

The measured FL quantum yield of the doped carbon dots used in this study were ~ 5\% and ~ 8\% around 400-440 nm for TiO$_2$-doped and ZnS-doped carbon dots, respectively. Fluorescence lifetimes of doped carbon dots were measured by frequency-domain lifetime measurements as mentioned previously.\textsuperscript{31} These doped carbon dots exhibited multi-exponential decays (three-exponential decays). The lifetime results of doped carbon dots used in this study excited at 400 nm are tabulated in Table 4.5, which shows that the average excited-state lifetime of ZnS-doped carbon dots (~ 6 ns) was relatively higher than that of the TiO$_2$-doped carbon dots (~ 5 ns), consistent with the higher photocatalytic activity exhibited by the former.
Table 4.5 Fluorescence lifetime measurements of doped-carbon dots excited at 400 nm.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS-doped Carbon Dots</td>
<td>8.30</td>
<td>8.52</td>
<td>1.54</td>
<td>11</td>
</tr>
<tr>
<td>TiO$_2$-doped Carbon Dots</td>
<td>4.29</td>
<td>8.59</td>
<td>0.76</td>
<td>12.1</td>
</tr>
</tbody>
</table>

The percentage of $\tau_1$, $\tau_2$, and $\tau_3$ is about 20%, 44.32% and 35.68% for ZnS-doped carbon dots and the percentage of $\tau_1$, $\tau_2$, and $\tau_3$ is about 26.05%, 43.09% and 30.86% for TiO$_2$-doped carbon dots respectively, used in this study.
The photocatalytic activity of doped carbon dots in aqueous solutions was investigated using an immersion-well photochemistry apparatus with a pyrex glass filter ($\lambda > 365$ nm) and a solution filter. Some experiments were also conducted under visible light illumination. Experimentally, in the photoreduction of CO$_2$, the doped carbon dots as photocatalysts in their aqueous dispersion in an immersion-well photochemistry reactor were bubbled with CO$_2$ gas until saturation. The photoirradiation was achieved using a 450 W medium-pressure Hanovia lamp through cycling water filter and glass filter for up to 10 h. The evaluation of the photocatalytic CO$_2$ conversion was based on the detection of formic acid as a primary product. More specifically for evaluation, the reaction mixture from the photoreduction was distilled, with the volatile portion being collected in a basic aqueous solution (NaOH, pH ~ 11), where the formic acid was trapped as a formate. The sodium formate salt was harvested from the basic solution by removing the water, and then re-dissolved in deuterated water for $^1$H and $^{13}$C NMR measurements. The NMR results confirmed the presence of formate, with a distinctive $^1$H peak at 8.49 ppm ($\text{HCOO}^-$) and a $^{13}$C peak at 171.07 ppm ($\text{HCOO}^-$). The product yields of formic acid were determined and quantified in terms of its formation rates in $\mu$mol g$^{-1}$ h$^{-1}$ using different doped catalysts (Table 4.6).
Table 4.6 a) Formic acid product yields and formation rates from CO$_2$ or NaH$^{13}$CO$_3$ photoconversion with various catalysts under identical experimental conditions.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Photoirradiation Time (h)</th>
<th>Formic acid Yield ($\mu$mol)</th>
<th>Formic acid Formation Rates ($\mu$mol g$^{-1}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS-doped carbon dots for CO$_2$ conversion</td>
<td>10 h</td>
<td>4.38</td>
<td>83.42</td>
</tr>
<tr>
<td>TiO$_2$-doped carbon dots for CO$_2$ conversion</td>
<td>10 h</td>
<td>2.67</td>
<td>50.85</td>
</tr>
<tr>
<td>Degussa P25 for CO$_2$ conversion</td>
<td>10 h</td>
<td>0.057</td>
<td>0.57</td>
</tr>
<tr>
<td>ZnS-doped carbon dots for NaH$^{13}$CO$_3$ (66 mM) conversion</td>
<td>10 h</td>
<td>4.52</td>
<td>86</td>
</tr>
</tbody>
</table>

Table 4.6 b) Formic acid product yields and rates from $^{13}$C enriched bicarbonate (NaH$^{13}$CO$_3$) photoconversion with undoped and semiconductor-doped carbon dots in a specific photoreactor under similar experimental conditions.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Photoirradiation Time (h)</th>
<th>Formic acid Yield ($\mu$mol)</th>
<th>Formic acid Formation Rates ($\mu$mol g$^{-1}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped carbon dots for NaH$^{13}$CO$_3$ (78 mM) photoconversion</td>
<td>8 h</td>
<td>1.71</td>
<td>41.80</td>
</tr>
<tr>
<td>ZnS-doped carbon dots for NaH$^{13}$CO$_3$ (58 mM) photoconversion</td>
<td>8 h</td>
<td>5.44</td>
<td>119.56</td>
</tr>
</tbody>
</table>
Table 4.6 shows the formic acid production yields and its formation rates with the use of different photocatalysts. Semiconductor doped carbon dots (TiO$_2$/C-dots or ZnS/C-dots) were found to be more efficient in the photoreduction of CO$_2$ to formic acid compared to the undoped/bare carbon dots under similar conditions. The photocatalytic activity of ZnS-doped carbon dots was found to be approximately 3 times higher than that of bare/undoped carbon dots in terms of the formic acid production yield under similar experimental conditions (Table 4.6 b). As can be seen in Table 4.6 a, ZnS-doped carbon dots were found to be more efficient photocatalysts than the TiO$_2$-doped carbon dots. This result may be attributed not only to their relatively lower FL quantum yield and shorter lifetime but also because of the low doping levels typically found in such nanocatalyst configurations. Nonetheless, the photocatalytic performance of doped carbon dots were found to be substantially higher (more than an order of magnitude higher with respect to Degussa P25, more specifically, ~ 77 times higher than Degussa P25 with the use of ZnS-doped carbon dots and ~ 47 times higher than Degussa P25 with the use of TiO$_2$-doped carbon dots as photocatalysts) than to the commercially supplied TiO$_2$ nanopowder (Degussa P25) photocatalysts under identical experimental conditions (Table 4.6 a).

In addition, to investigate the origin of the formic acid (HCOOH) generated during the photocatalytic reaction, experiments were conducted with $^{13}$C labeled bicarbonate as the $^{13}$CO$_2$ source using the same isolation, characterization and quantification procedures. The quantified product yields observed in the photocatalytic experiments were similar (Table 4.6 a). However, as seen in the Figure 4.17, for $^{13}$C enriched bicarbonate as the
$^{13}$CO$_2$ source, the $^{13}$C NMR spectrum of the product shows a readily detectable enhanced $^{13}$C NMR peak assigned to H$^{13}$COO$^-$ whereas regular CO$_2$ (unlabeled $^{12}$CO$_2$) shows a very weak appearance of the signal, one that is barely detectable, probably due to non-enriched or H$^{12}$COO$^-$ signal contribution (Figure 4.17). These experimental results suggest the formic acid (HCOOH) observed during the photocatalytic reaction is produced from CO$_2$ reduction.

Mechanistically, the fluorescence emissions in carbon dots may be attributed to the radiative recombinations of the electrons and holes from the photoinduced charge separation, which are likely confined/trapped at the surface sites of the core carbon nanoparticles and stabilized by the surface passivation in carbon dots.$^{22, 23}$ The doping of semiconductors (TiO$_2$, ZnS) apparently provides secondary surface passivation in carbon dots$^{46}$, resulting in improved photoinduced charge separation and transfer in doped carbon dots along with a synergic effect between the doped semiconductor (ZnS, TiO$_2$) and the carbon dot, might be responsible for the enhancement of the photocatalytic performance of doped carbon dots in comparison to undoped carbon dots.

Since ZnS (band gap ~ 3.66 eV) and TiO$_2$ (band gap ~ 3.2 eV) does not absorb in the visible range of spectrum, the observed visible light photocatalytic activity in doped carbon dots may be attributed to the photocatalytic functions of carbon dots. Figure 4.18 represents an illustration of the proposed photosensitized conversion of CO$_2$ in semiconductor doped carbon dots.

Upon visible light photoexcitation, photogenerated electrons in carbon dots may favorably migrate to the conduction band (C.B.) site of the semiconductor nanocrystals
(ZnS or TiO$_2$) followed by the subsequent photoreduction of surrounding CO$_2$ molecules (Figure 4.18). A similar photosensitization mechanism in carbon quantum dots (CQDs) is used to explain the enhanced hydrogen evolution rate in carbon quantum dot/TiO$_2$ nanotube composites under visible light.$^{43}$

In conclusion, this study found that semiconductor (TiO$_2$, ZnS) doped carbon dots can be utilized as effective photocatalysts towards CO$_2$ photoreduction to formic acid. The photocatalytic performance of doped carbon dots is significantly higher compared to classical Degussa P25 (TiO$_2$) based photocatalysts under similar experimental conditions. Furthermore, semiconductor doped carbon dots were found to be more efficient than undoped or bare carbon dots in CO$_2$ photoreduction. Doping with semiconductors apparently provides passivation of the surface defects on carbon dots, probably resulting in improved photogenerated charge carrier separation and transportation in such nanocatalyst configurations, potentially benefiting the photoreduction efficiency. However, further improvement of the photoactivity and refinement of the structure of each component is necessary in such nanocomposite heterostructures for further validation of the results and wide-scale practical application. In addition, further research could emphasize the detection and quantification of other products from the photocatalytic conversion of CO$_2$, in particular methanol as it is expected to be more abundant in the presence of coated noble metal as a co-catalyst.$^{4,6,7}$
Figure 4.17 $^{13}$C NMR results for ZnS-doped carbon dots used for $^{12}$CO$_2$ and $^{13}$CO$_2$ photoreduction with similar concentration of observed formic acid product yields under identical experimental conditions (up to 2048 NMR scans).
Figure 4.18 A cartoon illustration of the proposed photocatalytic CO$_2$ reduction mechanism in semiconductor doped carbon dots under visible light illumination.
Carbon nanoparticles (surface-oxidized for facile solvent dispersion resulting in a more stable suspension), even when naked without any other substances or aids, could harvest visible photons to drive the photocatalytic conversion of CO\textsubscript{2} in an aqueous medium. The surface-doping of the carbon nanoparticles with a metal that concentrates electrons could substantially improve the CO\textsubscript{2} photoconversion efficiency. The performance of suspended carbon nanoparticles as visible-light photocatalysts is already competitive with the conventional nanoscale semiconductor-based systems, with a potential for further development of the nanoscale carbon-based photocatalysts for CO\textsubscript{2} conversion and beyond.
References


APPENDICES
# Appendix A

## Glossary of Terms

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SY</td>
<td>Super Yellow</td>
</tr>
<tr>
<td>LiF</td>
<td>Lithium fluoride</td>
</tr>
<tr>
<td>PTB7</td>
<td>Poly ([4, 8\text{-bis [(2-ethylhexyl) oxy]} \text{benzo} [1, 2-b: 4, 5b'] dithiophene-2, 6-diyl}] [3-fluoro-2-[(2-ethylhexyl) carbonyl] thieno-[3, 4-b]thiophenediyl] )</td>
</tr>
<tr>
<td>PC(_{71})BM</td>
<td>([6, 6])-phenyl-C(_{71}) butyric acid methyl ester</td>
</tr>
<tr>
<td>PolyTPD</td>
<td>Poly-(N, N’-bis (4-butylphenyl)-N, N’-bis(phenyl) benzidine)</td>
</tr>
<tr>
<td>TPBi</td>
<td>1, 3, 5-tris (N-phenylbenzimidazol-2-yl) benzene</td>
</tr>
<tr>
<td>CIE</td>
<td>International Commission on Illumination</td>
</tr>
</tbody>
</table>
Appendix B

Coauthored Publications During My Graduate Study


16 Carbon Nanotubes for Photoinduced Energy Conversion Applications

Ge Peng, Sushant Sahu, Mohammed J. Meziani, Li Cao, Yamin Liu, and Ya-Ping Sun

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16.1 INTRODUCTION

Photoinduced energy conversion processes are at the center of many green and renewable energy technologies.¹⁻⁷ Materials widely used for photo-energy conversion are classic semiconductors, especially those at the nanoscale, such as silicon nanoparticles, semiconductor quantum dots (QDs), or nanorods.³,⁴,⁸⁻¹⁵ Since the discovery of fullerenes,¹⁶ carbon nanomaterials have been widely pursued for their photon-harvesting and photoinduced redox characteristics relevant to energy conversion applications.¹⁷⁻²⁰ In fact, fullerene derivatives are among the most popular materials used in organic or related photovoltaic devices.²¹⁻²⁷

Carbon nanotubes (CNTs) are also photoactive, with high optical absorption cross-sections (for both one- and multiphoton excitations),²⁸⁻³¹ rich excited state properties,³²⁻³⁶ and efficient photoinduced charge-transfer processes.³⁵,³⁷,³⁸ CNTs have been investigated extensively for potential applications in photo-energy conversions.³⁹⁻⁴² For example, CNTs have been integrated successfully into organic photovoltaic devices as part of the photoactive layer, and as highly prospective materials to replace counter electrodes and transparent conductive oxide (TCO) layers. The first use of CNTs as electron acceptors in bulk-heterojunction solar cells was reported in 2002, when researchers blended single-walled carbon nanotubes (SWCNTs) with polythiophenes and observed an increase in the photocurrent by two orders of magnitude.⁴³ In another report, the use of CNTs in dye-sensitized solar cells (DSSCs) has doubled the efficiency of such photoelectrochemical solar cells.⁴⁴ It has also
been demonstrated that SWCNT can be an efficient photovoltaic diode device material with impressive electrical characteristics, including the generation of multiple electron–hole pairs when light is focused on an individual CNT. The current trend is to use a new kind of all carbon photovoltaic device, in which all the functional layers are made of graphitic nanomaterials.

For example, solar cells made with C₆₀/SWCNTs/reduced graphene oxide as the active layer and an additional evaporated C₆₀ blocking layer have yielded a power conversion efficiency of 0.21%, and a significant increase to 0.85% was reported when replacing C₆₀ with the better absorber C₇₀. Recently, Strano and coworkers have demonstrated a polymer-free carbon-based photovoltaic device capable of harnessing light in the infrared region, which relies on exciton dissociation at the SWCNT/C₆₀ interface. In their device assembly, only highly purified single chirality (6,5) semiconducting SWCNTs were used, allowing for the distinction between intrinsic losses and those caused by impurities in SWCNT chirality. Although device efficiency was limited (~0.10%), it is interesting to note that it is comparable to many polymer-SWCNT bulk-heterojunction (BHJ) devices. They also found that the presence of 20 wt% of a second chirality of semiconducting SCWCNT (6,4) could result in more than 30 times decrease in power conversion efficiency. This effect clearly demonstrates the negative effects of multi-chirality present in an SWCNT active layer on photovoltaic device performance.

CNTs also offer distinctive properties that are not found in fullerenes, such as the very broad spectral coverage with band-gap electronic transitions well into the near-IR spectral region, the ballistic electron transport that may facilitate charge transfer and/or separation over an extended distance, and CNTs can be used as linear semiconductors of extremely large aspect ratios. Unlike fullerenes, CNTs are capable of accommodating structural defects, which on one hand might be negative to some of the desired properties but on the other present excellent and possibly unique opportunities, from the functionalization for much improved dispersion or solution-phase processing to defect-derived photoluminescence and to the manipulation of photoinduced redox processes.

In recent years, graphene has emerged to become a center of attention in the field of carbon nanomaterials. However, when considering the unique properties of graphene, there are still distinct advantages for the use of CNTs in energy conversion applications. In this chapter, we will highlight the fundamental optical and electronic properties of CNTs, including their optical absorption, band-gap and defect-derived photoluminescence emissions, and photoinduced charge separation and transfers. The effect of their geometric structures, such as diameter and chiral indices, dispersion and chemical functionalization on these properties will be also discussed. Also, we will review the potential of CNTs as building blocks in solar energy conversion applications with a focus on the recent progress of water splitting, CO₂ conversion, and BHJ devices and DSSCs, along with some discussion on the challenges and perspectives in these exciting fields.

16.2 OPTICAL ABSORPTION

CNTs have unique cylindrical hollow structures of extremely large aspect ratios, and one may conceptually visualize their structures by taking single or multiple graphene sheets and rolling them into seamless tubes. Depending on the number of the graphene layers, CNTs are further categorized into SWCNT and multiple-walled (MWCNT) CNTs. Owing to this quasi-one-dimensionality, the electronic and optical properties of CNTs are very sensitive to their geometric structure, such as diameter and chiral indices, providing the possibility to tune these properties within a wide range of band gaps from metallic to semiconducting. The situation in MWCNTs is complicated as their electronic properties are determined by the contribution of all individual shells which have different structures. In general, because of the synthesis, MWCNTs usually show a higher defect concentration than SWCNTs. Often, measurements of optical absorption of MWCNT can be difficult and yield inaccurate results and the few studies that have been carried out on CNTs have almost exclusively involved SWCNTs.
Carbon Nanotubes for Photoinduced Energy Conversion Applications

For SWCNTs, the rolling of a graphene sheet will need to match carbon atoms on the edges, which can be described by a chiral vector, \( \mathbf{C}_h \), consisting of two primitive vectors \( \mathbf{C}_h = n \mathbf{a}_1 + m \mathbf{a}_2 \), to match the graphene carbon atoms from edge to edge (Figure 16.1).\(^{66,68,69}\) The chiral vector, also commonly referred to as the chiral index \((n,m)\) (or chirality, helicity), uniquely defines the diameter \((d)\) and chiral angle \((\theta)\) of an SWCNT:

\[
d = \frac{\sqrt{3}a_{cc}}{\pi} \sqrt{n^2 + nm + m^2} \tag{16.1}
\]

\[
\theta = \tan^{-1}\left[\sqrt{3}m/(2n + m)\right] \tag{16.2}
\]

where \(a_{cc}(\sim 0.142 \text{ nm})\) is the nearest-neighbor C–C distance.

Depending on its chiral vector, an SWCNT can either be semiconducting or metallic (including semi- or quasi-metallic), which is often referred to as “metallicity.” When \(n-m \neq 3q\) \((q\) is an integer), the electronic density of states (DOS) in the SWCNT exhibits a significant band gap near the Fermi level, and the nanotube is thus semiconducting; when \(n-m = 3q\), the conduction and valence bands in the SWCNT overlap, and the nanotube becomes metallic (or semi-metallic when \(n \neq m\)). Statistically, there are twice as many ways for rolling graphene sheet into a semiconducting SWCNT as ways for rolling the same sheet into a metallic SWCNT. Therefore, the semiconducting-to-metallic nanotube ratio of 2:1 should generally be expected in an as-grown mixture of SWCNTs.

The electronic structures of both semiconducting and metallic SWCNTs are characterized by several pairs of van Hove singularities in the DOS, inducing unique optical features of SWCNTs, as illustrated in Figure 16.2.\(^{64,70–73}\) Each van Hove singularity is labeled with the index of the subband to which it belongs. The peaks related to transitions between the first and second pairs of DOS singularities in semiconducting nanotubes, designated as \(S_{11}\) and \(S_{22}\), are observed at about 0.9 and 1.5 eV, whereas the position of the feature because of the transitions between the first pair of DOS singularities in metallic nanotubes, designated as \(M_{11}\), is at about 2 eV. The optical absorption peaks are superimposed on a significant background, which is attributed to the tail of the inter-band \(\pi\)-plasmon resonance that exhibits a broad peak in the optical absorption at around 5 eV.\(^{74}\) The \(\pi\)-plasmon represents a collective oscillation of \(\pi\)-electrons polarized along the tube axis, which is induced by a \(\pi\)--\(\pi^*\) inter-band excitation, and its experimentally observed energy range agrees well with values predicted by theory for bundled SWCNTs.\(^{75}\)

FIGURE 16.1 The conceptual SWCNT formation by rolling up a graphene sheet. As an example, the dashed lines represent the two edges that will merge in the rolling up of a \((7,3)\) semiconducting SWCNT. (Adapted from Liu, X. et al., Phys. Rev. B: Condens. Matter, 66, 045411, 2002.)
Carbon Nanomaterials

For the evaluation of electronic and optical features in SWCNTs, the nanotubes must be dispersed very well to minimize inter-nanotube quenching effects. In this regard, O'Connell et al. developed a method to isolate individual SWCNTs in surfactant micelles through strong ultrasonic treatment and ultra-high-speed centrifugation, yielding relatively short tube fragments (~80–200 nm in length). Optical absorption spectra of these isolated nanotubes exhibited more resolved and sharpened near-infrared absorption peaks. Within each transition region, the observed peaks were attributed to individual tubes, and the variation in the peak intensity originated from differences in both the relative abundance and the absorption cross-section of the tube species. Spectra of samples containing many species, including bundled tubes, typically showed broad, undifferentiated optical absorption features arising from strongly overlapped transitions, rather than sharp, resolved absorption bands.

Experimental work on the implication of chemical functionalization of SWCNTs on the electronic and optical properties has also been investigated. It has been found that with an increasing degree of functionalization, the extended π-network is increasingly disrupted, leading to a significant electronic perturbation in the nanotubes. At lower functionalization degrees, the S_{11}, S_{22}, and M_{11} transitions can still be discerned in the UV–vis–NIR spectrum but with less intensity. For example, such behavior has been reported for oxidized SWCNTs, and for SWCNTs modified by the addition of nitrenes. At higher functionalization degrees, the S_{11}, S_{22}, and M_{11} features were no longer visible, as demonstrated for nanotube ozonolysis, fluorination, as well as the addition of various types of organic residues. The weakening or loss of all of the inter-band transitions in both the semiconducting and metallic tubes was attributed to the saturation of the delocalized partial C–C double bonds by the attachment of functional groups, which leads to new bonds at the expense of the π-electrons in the highest occupied molecular orbitals (HOMOs) in the nanotubes.

Metallic and semiconducting SWCNTs have also been readily characterized by resonance Raman spectroscopy. The radial breathing mode (RBM) in the Raman spectrum of SWCNTs

![FIGURE 16.2](https://example.com/figure16.2.png)

(a) Optical absorption spectrum of an SWCNT sample with an average diameter of 1.3 nm. The inset shows the same spectrum after subtraction of the surface π-plasmon. (Adapted from Liu, X. et al., Phys. Rev. B: Condens. Matter, 66, 045411, 2002.) (b) Absorption spectra of films of purified HiPCO, purified laser, and soluble Arc produced SWCNTs after baseline correction. The inset shows the corresponding inter-band transitions in the DOS diagram showing van Hove singularities and the levels/bands involved. (Adapted from Hamon, M.A. et al., J. Am. Chem. Soc., 123, 11292, 2001.)
is useful for determining the diameter and the \((n, m)\) values of the nanotubes. Based on the RBM bands, electronic properties of the nanotubes can be predicted by using the so-called Kataura plots. The Raman band of SWCNTs centered at around 1580 cm\(^{-1}\) (G-band) also exhibits a feature at approximately 1540 cm\(^{-1}\) that is characteristic of metallic SWCNTs. The G-band can be deconvoluted to allow a determination on the relative proportions of metallic and semiconducting species.

## 16.3 PHOTOEXCITED STATE PROPERTIES

### 16.3.1 Photoluminescence Emissions

CNTs were found to display both band-gap fluorescence and defect-derived photoluminescence emissions, which are obviously different in origin, but complementary in certain properties. A shared requirement between the two kinds of emissions is that they are both highly sensitive to the nanotube dispersion. For the band-gap emission, the dispersion is often assisted by the use of surfactants or polymers with the CNTs and also ultra-high-speed centrifugation.\(^{76–78,96–101}\) The functionalization is effective in the exfoliation of nanotube bundles to the level of individual nanotubes and very thin bundles, but it is hardly applicable to the investigation of band-gap fluorescence. For example, isolated SWCNTs in surfactant micelles, reported by O’Connell et al.,\(^{76}\) displayed a series of band-gap fluorescence peaks in the near infrared (~800–1600 nm) that were attributed to fluorescence across the band gap of semiconducting nanotubes, as illustrated in Figure 16.3. The data showed that the sample contained many light-emitting species, with each displaying one dominant transition in this spectral range and a very small Stokes shift between its absorption and emission peaks. SWCNT emission was observed exclusively for E\(_{11}\) transitions and not for E\(_{22}\) or higher transitions, a result that is in accordance with the predictions of Kasha’s rule that molecular electronic luminescence originates entirely from the lowest-lying electronic state within a spin multiplicity manifold.\(^{102}\) Clearly, the many distinct spectral features in the E\(_{11}\) region correspond to different \((n,m)\) species of semiconducting SWCNTs in the structurally heterogeneous sample. The mapping of SWCNTs with various diameters by using fluorescence spectroscopy has been accomplished, as shown in Figure 16.3. Such distinct features cannot be achieved with SWCNT bundles because of strong luminescence quenching by neighboring metallic tubes. Recently, there were reports on the detection of band-gap fluorescence for suspended SWCNTs in an ambient environment\(^{99}\) and also for nanotubes produced by the laser ablation method.\(^{96,97,100,101}\)

An accurate quantum yield value for the band-gap fluorescence is still being determined or decided, with current numbers ranging from 0.001% to 1.5%, presumably depending on several factors, such as nanotubes diameter \((d)\), diameter distribution, the degree of nanotube bundling/aggregation, and surface doping or chemical treatment.\(^{76–78,96–98,103,104}\) For example, it has been reported that the quantum efficiency of SWCNTs from the arc-discharge production \((d \sim 1.5\) nm) is weaker in band-gap fluorescence because the average diameter is larger than that of SWCNTs produced by following the HiPco method \((d \sim 0.7–1.2\) nm).\(^{96}\) The band-gap emission is more prominent in the small-diameter nanotubes with an upper diameter limit of 1.5 nm. For example, the observed quantum yield of SWCNTs from the laser ablation production \((d \sim 1.4\) nm) is of the order of \(1 \times 10^{-5}\); this is two orders of magnitude lower than that of the HiPco nanotubes. The band-gap emission was also found to be suppressed strongly after chemical functionalization and in the line of this observation, the emission spectrum of dispersed SWCNTs after the acid treatment was found to be weak and poorly structured.\(^{96,102}\) In another investigation, Cognet et al.\(^{105}\) reported reversible stepwise quenching of individual SWCNTs by acid and irreversible quenching of individual SWCNT exposed to diazonium salts.

Initially, both SWCNTs and MWCNTs on their surface modification or functionalization were found to be strongly luminescent in homogeneous organic or aqueous solution, exhibiting broad luminescence emission bands in the visible and well extending into the near-IR region.\(^{54}\) In that report, Sun et al. found strong defect-derived photoluminescence emissions in CNTs purified by nitric acid treatment and then functionalized with amino or other polymers or oligomers, such as
polyethylene glycol (PEG\textsubscript{1500N}) or an aminopolymer poly(propionylethylenimine-co-ethylenimine) (PPEI-EI) (Figure 16.4), where the functionalization targeted and passivated selectively defects on the nanotube surface. The luminescence excitation spectra of these functionalized CNTs monitored at different emission wavelengths were consistent with the broad UV–vis absorption spectra. However, the emission spectra were strongly dependent on excitation wavelengths in a progressive fashion. The excitation wavelength dependence indicated the presence of significant inhomogeneity or a distribution of emitters in the sample (nanotubes of different diameters) or emissive excited states (trapping sites of different energies).\textsuperscript{54,106–108} Defect-derived luminescence has also
been observed in other well-functionalized CNT samples of diverse functional groups.\textsuperscript{54,55,106–108} For example, Guldi et al. reported that the luminescence was associated with CNT samples from different production methods, including laser ablation and arc discharge, and with heavily oxidized nanotubes.\textsuperscript{108} Similarly, Wong et al. reported strong visible luminescence from CNTs that are functionalized with Wilkinson’s catalyst.\textsuperscript{106}

The observed defect-derived luminescence quantum yields are generally high. As shown in Figure 16.4, for example, the luminescence quantum yields of PPEI-EI-functionalized SWCNTs (PPEI-EI-SWCNT) and PEG\textsubscript{1500N}-functionalized SWCNTs (PEG\textsubscript{1500N}-SWCNT) at 450 nm excitation are 4.5\% and 3\%, respectively.\textsuperscript{55} Generally speaking, the luminescence quantum yields of SWCNTs and MWCNTs are of the same order of magnitude. The luminescence decays of functionalized nanotubes are relatively fast and nonexponential, with average lifetimes of the order of a few nanoseconds. The nonexponential nature of the luminescence decays is consistent with the presence of multiple emissive entities in the sample and the observed excitation wavelength dependence of luminescence.

Mechanistically, Sun et al. suggested that the broad visible luminescence could be attributed to the presence of passivated surface defects on CNTs, which serve as trapping sites for the excitation energy.\textsuperscript{54} The passivation as a result of the surface modification and functionalization with oligomeric and polymeric species stabilizes the emissive sites in their competition with other excited state deactivation pathways.\textsuperscript{54,55,107}

There was also other experimental evidence suggesting that the defect-derived luminescence is sensitive to the degree of functionalization and dispersion of the CNTs. The higher observed luminescence quantum yield is generally associated with better functionalized CNTs, as supported by results from the experiments of repeated functionalization and the defunctionalization of functionalized CNTs.\textsuperscript{55,109} For example, Lin et al.\textsuperscript{55} demonstrated this sensitivity by comparing nonfunctionalized and functionalized SWCNTs, with the former dispersed in dimethylformamide (DMF) with the assistance of polyimide under sonication and the latter functionalized with polyimide and dissolved in DMF. At the same equivalent nanotube content, the two solutions had comparable optical density at the same excitation wavelength (450 nm). However, the luminescence measurements of the two solutions revealed that the latter was much more luminescent than the former (Figure 16.5). This strongly supports the conclusion that the dispersion of CNTs plays a critical role in their luminescence.

Despite the extensive effort on the elucidation of the two kinds of emissions, there are still significant technical and mechanistic issues for both. For example, the accurate determination of the
quantum yield for the band-gap fluorescence remains difficult because of the wavelength region, whereas the nature and properties of the emissive excited states for the defect-derived luminescence require further investigation.

### 16.3.2 Charge Separation and Transfers

Studies of photoinduced electron transfer processes of CNTs hybridized with electron-donating or other electron-accepting molecules have provided evidence for donor–acceptor interactions. Such studies have played a key role in utilizing CNTs in solar energy conversion devices. In fact, it is well known that fast transfer of photoinduced charges from the donor to the acceptor level is very essential for an efficient photovoltaic device. If the electron is not transferred within few femtoseconds in a photovoltaic device, the photogenerated exciton will decay to the ground state, emitting photoluminescence and resulting in a device with poor efficiency. Depending on the redox properties of its counterpart, CNT in the composites can act as either electron acceptor or electron donor. For example, CNTs act as electron acceptors in combination with porphyrins, phthalocyanines, tetrathiafulvalene (TTF) derivatives, semiconducting nanoparticles, and conjugated polymers, or as an electron donors when combined with fullerenes. In these systems, the donors or acceptors have been linked to nanotubes by either covalent or noncovalent coupling. In both approaches, the removal of impurities from CNTs must be done carefully because the use of strong oxidation agents (such as a mixture of sulfuric acid and hydrogen peroxide) hinders the photogeneration of free carriers at the donor–acceptor interface.

The most widely examined photoactive components bound to CNTs have been porphyrin molecules, because they are excellent visible light-harvesting chromophores, electron donors, and are also photostable with tunable redox properties. For example, Sun et al. first developed an efficient covalent tethering of SWCNTs with porphyrin through the esterification of SWCNT-bound carboxylic groups and explored their photoexcited state properties via steady-state and time-resolved fluorescence methods (Figure 16.6). Interestingly, the rates and efficiencies of the excited state transfer were found to depend on the length of the tether that links the porphyrins with the SWCNTs. Intramolecular excited state energy-transfer quenching of porphyrin fluorescence by the tethered nanotube occurred in the sample with a longer tether, but no fluorescence quenching was observed in the sample with a shorter tether. The observed fluorescence decays before and after the attachment to SWCNTs were essentially the same resembling static quenching behavior. Not only SWCNT but also MWCNT when covalently linked with porphyrin molecules can act as electron acceptors.

![Structure of porphyrin decorated SWCNTs I and II.](image)

**FIGURE 16.6** Structure of porphyrin decorated SWCNTs I and II. (Adapted from Li, H. et al., *Adv. Mater.*, 16, 896, 2004.)
The same strategy was successful in integrating very strong electron donors like tetrathiafulvalene (TTF), extended TTF, and ruthenium(II) bipyridine, which all supported the occurrence of photoinduced electron transfer processes.\textsuperscript{120–122,127,128} Similarly, in most of these studies inserting spacers of different length was found to control the rate of the electron transfer. For example, the lifetime of the charge-separated states (typically of the order of several hundreds of nanoseconds) was appreciably extended when longer linkers and π-extended TTF were used.\textsuperscript{122} Another popular concept was to utilize CNT networks as support to anchor light-harvesting metallic and/or semiconductor nanoparticles, which endowed CNTs with specific optoelectronic activities. Research efforts along these lines include organizing these nanoparticles on oxidized CNTs with the aid of crosslinking agents, such as thiol–amine and amine–carboxylic acid crosslinking agents.\textsuperscript{129–132} For example, the interactions and the charge-transfer efficiencies between QDs (such as CdS, CdSe, and CdTe) and CNTs have been evaluated by studying the changes in the photoluminescence and using transient absorption (TA) spectroscopy.\textsuperscript{133} The photoluminescence behaviors of these nanohybrids were found to be strongly dependent on how the QDs were attached to the CNTs. However, in most of these studies, the QD emission upon visible light excitation was strongly quenched when it was bound to the CNT, suggesting a fast electron transfer to the nanotubes.\textsuperscript{133}

Overall, the absorption and fluorescence of these complexes showed that the CNTs are efficient electron acceptors, thus, paving the way to construct novel photovoltaic devices and light-harvesting systems using various configurations.\textsuperscript{134,135} For example, porphyrin, ruthenium(II) bipyridine, and QDs when linked to SWCNTs allowed their integration for DSSCs.\textsuperscript{134,135}

Considerable efforts have also been dedicated to understand the photoinduced electron transfers at the interface between conjugated polymers and CNTs because of their known potential in organic photovoltaic applications. Among the polymers, poly(3-hexylthiophene) (P3HT), poly(p-phenylene vinylene), and polyindenofluorene are important because of their solubility, high conductivity, and photoluminescence property, which can be tuned in their nanocomposites prepared by different procedures. An important consideration when associating CNTs with these polymers is to avoid a high density of structural defects to preserve the electronic structure. Defects on the CNT surfaces are known to markedly disrupt electron transfer from photoexcited polymer to the CNTs.\textsuperscript{35} A versatile approach for the solubility of these nanocomposites often involved the wrapping of CNTs with polymer through noncovalent stacking interaction by sonication and ultracentrifugation cycles in different solvents.\textsuperscript{103,136} Electron diffraction studies of these nanocomposites showed that the polymer backbone forms crystalline polymer monolayers wrapped around the nanotube to yield highly ordered polymer:SWCNT nanocomposites. These studies also showed that polymer crystallinity increases with the amount of SWCNT in the composite, and this could explain the improvement of exciton diffusion as well as of charge mobility in these nanocomposites.\textsuperscript{137} In these nanocomposites, high photoluminescence quenching of polymers was often observed even in the presence of very minor quantities of CNTs, indicating the occurrence of photoinduced electron transfer. For example, based on photoluminescence quenching, Ferguson et al. demonstrated conclusively that charge transfer occurs in addition to the previously observed energy transfer mechanism.\textsuperscript{138} They selectively excited either P3HT or SWCNTs in composite films and probed the free carrier generation with time-resolved microwave conductivity (TRMC). In this study, it was shown that photoexcitation of the polymer gives rise to long-lived carriers, due to spatial separation of the charges across the donor–acceptor interface. However, no charge transfer to the polymer was observed after photon absorption by the SWCNTs, and the carriers were short lived because of their confinement inside the tube along when we consider the electron acceptor character of SWCNTs. Detailed spectroscopic analyses in solution showed an intense redshift for the SWCNT transition energies, consistent with the formation of a type II (staggered band line-up) heterojunction at the P3HT/SWCNT interface,\textsuperscript{136,139,140} where the charge separation occurs. Nicholas et al. showed that photoexcitation of P3HT forming a monolayer around an SWCNT leads to ultrafast (~430 fs) electron transfer between the materials using a combination of femtosecond spectroscopy.\textsuperscript{141} The addition of excess P3HT leads to long-term charge separation in
Carbon Nanotubes for Photoinduced Energy Conversion Applications

which free polarons remained separated at room temperature. Their time-correlated single-photon counting studies showed that the photoluminescence decay of P3HT was shortened from 1.7 to 0.43 ps when 1% of SWCNTs individually wrapped with P3HT were added to a blend.

Recent theoretical and experimental studies of P3HT/SWCNT interfaces demonstrated that in fact only semiconducting SWCNTs with a small diameter form favorable type-II heterojunctions with P3HT (Figure 16.7). Metallic SWCNTs act as recombination sites either by electron transfer from the LUMO of the conductive polymers to empty states in the conduction band of metallic SWCNTs or by electron transfer from the valence band of metallic SWCNTs to the HOMO of P3HT. Time-resolved microwave conductivity experiments revealed that the long-lived carrier population can be significantly increased up to three orders of magnitude by incorporating highly enriched semiconducting SWCNTs into semiconducting polymer composites. Recently, the utilization of semiconducting SWCNTs coated with an ordered P3HT layer was found to enhance the charge separation and electron transport in the active layer of BHJ solar cells. A strong photoluminescence quenching was observed for the P3HT/s-SWCNT nanofilaments than in the case of the random P3HT/s-SWCNT mixture spin cast from solution (Figure 16.7), suggesting that well-ordered P3HT layers in the nanofilament configuration form an intimate contact with the semiconducting SWCNTs and can improve the dissociation of excitons generated in the polymer.

However, it is also energetically possible for CNTs to act as electron donors in donor–acceptor nanohybrids when combined with good electron acceptors exhibiting excellent light-harvesting ability. For example, such trend was successfully demonstrated by D’Souza et al. in a self-assembled

![Figure 16.7](image-url)
SWCNT-C\textsubscript{60} hybrids, in which SWCNT acted as an electron donor and the fullerene as an electron acceptor (Figure 16.8). Toward this attempt, SWCNTs were first noncovalently functionalized using alkyl ammonium functionalized pyrene (Pyr-NH\textsubscript{3}\textsuperscript{+}) to form SWCNT/Pyr-NH\textsubscript{3}\textsuperscript{+} hybrids, which was further utilized to complex with benzo-18-crown-6 functionalized fullerene, crown-C\textsubscript{60}, via ammonium-crown ether interactions to yield stable SWCNT/pyrene-NH\textsubscript{3}\textsuperscript{+}/crown-C\textsubscript{60} nanohybrids. Studies of steady-state and time-resolved fluorescence and nanosecond transient absorption revealed efficient quenching of the singlet excited state of C\textsubscript{60} in the nanohybrids and confirmed electron transfer as the quenching mechanism resulting in the formation of SWCNT/pyrene-NH\textsubscript{3}\textsuperscript{+}+/crown-C\textsubscript{60} charge-separated states (with a relatively longer lifetime of the order of 100 ns). The rates of charge separation, $k_{CS}$, and charge recombination, $k_{CR}$, were found to be $3.46 \times 10^9$ and $1.04 \times 10^7$ s\textsuperscript{-1}, respectively.

A similar conclusion was also derived by Guldi et al. when studying sapphyrin (a pentapyrrolic “expanded porphyrin” macrocycle)-functionalized SWCNT complexes obtained through donor–acceptor stacking interactions. These complexes showed rapid decay of sapphyrin-excited states, something that does not occur for sapphyrin solutions in the absence of nanotubes. Upon photoexcitation of the nanotube material, the presence of a signal ascribable to the sapphyrin radical anion was observed at 840 nm in the transients, a finding that is consistent with electron transfer from the nanotubes to the sapphyrin. The same group recently reported that water-soluble perylenediimide dye with reasonably sized \pi-system behaved as a strong electron acceptor when mutually interfaced with semiconducting SWCNTs. Detailed spectroscopic studies of these nanohybrids confirmed the occurrence of distinct ground and excited-state interactions and the formation of radical ion pair states within a few picoseconds. Such donor–acceptor nanohybrids may prove useful in the generation of nanotube-based electron transfer ensembles for light-harvesting and photovoltaic applications.

The combination of CNT with donors or acceptors upon illumination seems to give a fast charge separation and a slow charge recombination, which is expected to open up opportunities to a new generation of donor–acceptor nanohybrids. The long lifetimes of the charge-separated species make these systems excellent candidates for the fabrication of photovoltaic devices.
16.4 PHOTOINDUCED ENERGY CONVERSION

Numerous efforts have been made to take advantage of the outstanding optoelectronic and structural properties of CNTs in solar energy conversion, such as water splitting, CO$_2$ conversion, and organic solar cells. Highlighted below are some interesting recent contributions and achievements dealing with the above needs, along with some discussion on the challenges and perspectives in this exciting field.

16.4.1 CNTs in Photocatalytic Water Splitting and CO$_2$ Conversion

The past few years saw a renewed interest in photocatalytic water splitting and conversion of CO$_2$. The aim is to find new material systems that enable conversion efficiencies beyond 10% which has been set as target for a commercially viable catalyst by the U.S. Department of Energy. The majority of research focuses on the design of suitable materials (typically semiconductors) that are able to efficiently harvest sunlight for the generation of electrons. In general, when a semiconductor is illuminated with photons having energies greater than that of the band gap, electron–hole pairs are generated and separated in a space-charge layer in the material. The pairs, if not recombined, travel to the surface of a semiconductor, and split water to produce oxygen and hydrogen, or reduce CO$_2$ to yield hydrocarbons (e.g., alcohols). A schematic representation of the principle for these photocatalytic reactions is given in Figure 16.9. To produce hydrogen from water or to reduce CO$_2$ to fuel, the electrons in the conduction band must have a potential that is more negative than the redox potential of H$^+$/H$_2$ (0 eV versus normal hydrogen electrode (NHE)) or CO$_2$/CH$_3$OH (~0.03 eV versus NHE) to provide the driving force for the reaction. However, water oxidation occurs when the hole potential is more positive than the redox potential of O$_2$/H$_2$O (+1.23 eV versus NHE). On this basis, the minimum band-gap energy required to drive the reaction is 1.23–1.27 eV, which corresponds to absorption of solar photons of wavelengths below about 1000 nm. In practice, the ideal minimum band-gap energy should be higher (close to about 1.35 eV) because of energy losses associated with the over-potentials required for the two chemical reactions and driving force for charge carrier transportation.

For a combination of cost, nontoxicity, chemical stability, and performance, nanoscale TiO$_2$ has been one of the most attractive photocatalysts among conventional semiconductors. However, the use of nanoscale titania remains limited in terms of the requirement for UV excitation and generally low conversion efficiencies. The major drawback in using TiO$_2$ is its large band-gap

![FIGURE 16.9](https://example.com/figure16.9.png)
energy (3.2 eV), which limits its photocatalytic activity to photons with wavelengths below 385 nm, leading to only approximately 4% effectiveness of the solar radiation, while 43% of light in visible region is wasted. Semiconductors with small band gaps, such as CdS (bandgap of ~2.2 eV), have been successfully used as visible-light photocatalysts because of their high activity and sufficiently negative flat-band potential. However, there are still some major problems such as the serious photocorrosion under long-term light irradiation, which hinders its broad applications. The other major limiting factors that also need to be dealt with are the high charge recombination rate of the photogenerated electrons and holes, and low surface area, which is detrimental for the forward reaction and adsorbance of reactants. In response to these limitations, several approaches have been employed by incorporating suitable atoms such as N and S into their nanostructures, loading nanoscale co-catalysts (e.g., Cu, Ag, Pt, Ru) or other semiconductors on their surfaces, and changing their nanoscale geometrical shapes (e.g., rods, tubes, wires, sheets).\textsuperscript{2–4} In addition, to take full advantage of these nanocatalysts, their immobilization and dispersion have also been a major focus as it offers several advantages, such as increasing the specific surface area and facilitating the catalyst reusability.\textsuperscript{3,4,147,148} For example, the agglomeration of the nanoparticles has been a critical problem associated with several photocatalyst platforms.\textsuperscript{3,147,148}

As an emerging material, CNTs have attracted considerable attention for photocatalytic applications because of their special structures, excellent electronic and mechanical properties, high surface area (\(\sim 1600 \text{m}^2\text{g}^{-1}\)), chemical inertness, and stability. In fact, several works have recently been directed toward investigating CNT as a scaffold to anchor semiconductor nanoparticles and assist in promoting selectivity and efficiency of the photocatalytic process. It has been reported that CNTs may have three main roles in the composite photocatalysts. First, CNTs as an electron acceptor could induce an efficient charge transfer and retard the charge recombination.\textsuperscript{149,150} Second, as a photosensitizer, CNTs could expand the visible-light absorption of the photocatalyst and enhance the visible light usage efficiency.\textsuperscript{151,152} Third, the presence of CNTs could help to enlarge the specific surface area of the photocatalysts, leading to their higher adsorptive ability and their protection from photocorrosion.\textsuperscript{153}

Earlier, Ou et al. impregnated anatase (TiO\(_2\)) particles with small Ni clusters and used them as a catalyst to grow MWCNTs via chemical vapor deposition (CVD) at 550°C.\textsuperscript{154} The hybrid materials were found to be active for \(\text{H}_2\) evolution from a methanol/water solution under visible light illumination. The addition of organic alcohols as reducing agents considerably enhanced the reaction efficiency by preventing gasous \(\text{H}_2\) and \(\text{O}_2\) from recombining on the surface of TiO\(_2\). In contrast to the completely inactive TiO\(_2\)-Ni catalyst, the addition of 4.4 wt% MWCNTs produced significant amounts of hydrogen, with a reaction rate of 38 \(\text{mol/(h\cdotg)}\) (5 \(\mu\text{mol/(h\cdotg)}\) in pure water). Increasing the amount of CNTs above 4.4 wt%, however, led to a decrease in the absorption of light and, thus, in the activity of water splitting. This effect was explained in terms of MWCNTs acting as a photosensitizer, which made the absorption of the catalyst cover the whole range of the UV–vis spectrum. In another report, obvious improvement of the photocatalytic activity for hydrogen generation was achieved by assembling functionalized MWCNTs with Eosin Y dye and Pt and using triethanolamine (TEOA) as the electron donor.\textsuperscript{155} The MWCNTs were treated with HNO\(_3\) to form \(-\text{COOH}\) and \(-\text{OH}\) groups, which provided anchoring sites for Eosin Y. The highest hydrogen generation rate of 3.06 mmol/(h\cdotg) and the apparent quantum yield of 12.14% were reached when the pH value was 7, the mass ratio of Eosin Y:MWCNT was 5:4, the Pt-loading content was 1 wt%, and the wavelength of incident light was longer than 420 nm. In a similar study, the same photocatalytic system was used but instead of Pt, mixed metal oxides CuO/NiO were used as efficient active center of \(\text{H}_2\) evolution.\textsuperscript{156} A rate of \(\text{H}_2\) evolution of approximately 1.0 mmol/(h\cdotg) was achieved under optimal conditions.

MWCNT–TiO\(_2\) nanocomposites were also synthesized hydrothermally via the direct growth of titania nanoparticles on the surface of functionalized MWCNTs and then loaded with Pt for \(\text{H}_2\) production from splitting water.\textsuperscript{151} A quantity of 1 wt% Pt loaded 5 wt% MWCNT–TiO\(_2\) nanocomposites showed the highest hydrogen generation rate (235.1 or 8092.5 \(\mu\text{mol/(h\cdotg)}\), respectively) with TEOA as the electron donor under visible light (\(\lambda > 420\) nm) or full spectral irradiation from a xenon
lamp, whereas no capacity to split water was found on the Pt-loaded pristine TiO$_2$ and MWCNTs. In a similar study, hydrothermal technique was used to synthesize MWCNTs/CdS nanocomposites, and it was found that 10 wt% MWCNTs/CdS had the maximum photocatalytic H$_2$ production up to 2882.8 μmol after 10 h of photoreaction and better photostability than pure CdS, which was 2.25 times less. In both studies, the enhanced photocatalytic activity was attributed to the excellent light absorption and charge separation on the interfaces between the modified MWCNTs and TiO$_2$ or CdS. In a separate report, Wang et al. studied the effect of the mass ratio of CdS/CNT in the nanocomposites on the photocatalytic activities. Significant band-gap narrowing was observed due to the incorporation of CNT into CdS, indicating the strong interactions between CdS and CNT. The optimum rate of H$_2$ evolution for these CdS–CNT nanocomposites was obtained with a mass ratio of 1:0.05, which was found to be approximately four times higher than that of CdS alone. To further enhance the catalytic effect of CNT/CdS, Park et al. explored the ternary hybrids of CdS, MWCNT, and metal catalyst under visible light in the presence of electron donor (Na$_2$S and Na$_2$SO$_3$). When hybridized with CdS and Pt, acid-treated CNT had the largest amount of hydrogen production (up to 3276 μmol/g). In such ternary hybrids, Pt, Ni, and Ru were found to be effective in catalyzing proton/water. Other metals (Pd, Au, Ag, Cu) showed very low activities with the following order: Pt > Ni > Ru > Pd > Au > Ag > Cu. The positive effect of SWCNTs on TiO$_2$ as photocatalyst for water splitting has been demonstrated by Ahmmad et al. A drastic synergy effect was found with an increase in the amount of H$_2$ gas by a factor of ca. 400 simply by mixing SWCNTs with TiO$_2$.

Besides TiO$_2$ and CdS, other semiconductors with visible-light responses have also been investigated for water splitting by other researchers. For example, Yu et al. demonstrated enhanced photocatalytic hydrogen production by MWCNTs modified Cd$_{0.1}$Zn$_{0.9}$S prepared by hydrothermal treatment (Figure 16.10). The optimal MWCNT loading was determined to be about 0.25 wt% and the corresponding H$_2$-production rate using Na$_2$S and Na$_2$SO$_3$ as sacrificial agents was 1563.2 μmol/h·g with an apparent quantum efficiency of 7.9% at 420 nm even without any noble metal co-catalysts, exceeding that of pure Cd$_{0.1}$Zn$_{0.9}$S by more than 3.3 times, and also higher than that (2.16%) of CNTs/CdS nanocomposites reported before. The composites also exhibited good stability and recycling performance of photocatalytic H$_2$ production.

Chai et al. have reported a hydrothermal synthesis of MWCNTs/ZnIn$_2$S$_4$ composites and examined their photocatalytic H$_2$ production under visible-light irradiation. In their study, 3 wt% MWCNTs/ZnIn$_2$S$_4$ composite reached the maximum photocatalytic hydrogen production rate (about 684 μmol/h) with an apparent quantum efficiency as high as 23.3% under 420 nm light irradiation. Recently, MWCNTs and metal-free graphitic carbon nitride (g-C$_3$N$_4$) composites have been

![FIGURE 16.10](image-url)  
**FIGURE 16.10** Proposed mechanism for the enhanced electron transfer in the CNT/Cd$_{0.1}$Zn$_{0.9}$S composites under visible-light irradiation. (Adapted from Yu, J., Yang, B. and Cheng, B., Nanoscale, 4, 2670, 2012.)
Carbon Nanomaterials demonstrated to be a good visible light photocatalyst for \( \text{H}_2 \) evolution in aqueous methanol solutions.\(^{163}\) Mesoporous g-C\(_3\)N\(_4\) was found to possess unique semiconductor properties with a narrow band-gap energy of 2.7 eV along with an open crystalline pore wall and a large surface area (about 200 m\(^2\)/g). The optimal MWCNT content was determined to be 2.0 wt\% and corresponding \( \text{H}_2 \) evolution rate was 7.58 \( \mu \text{mol/h} \) which was about 3.7-fold higher than that of pure g-C\(_3\)N\(_4\). It was suggested that MWCNTs have a higher capture electron capability and can promote electron transfer from g-C\(_3\)N\(_4\) toward their surface, leading to the improvement of photocatalytic performance.

Very recently, the enrichment of larger diameter semiconducting SWCNTs was found to be useful for improvement in the performance of photocatalytic water splitting.\(^{164}\) A CO\(_2\)-assisted arc-discharge method was developed to directly synthesize enriched semiconducting SWCNTs with content of \( >90\% \), and a majority having diameters of \( >1.5 \text{nm} \). Results showed that enriched semiconducting SWCNTs combined with TiO\(_2\) have much better photocatalytic enhancement. The optimal enriched semiconducting SWCNTs content was determined to be 10 wt\% and corresponding \( \text{H}_2 \) evolution rate was 2.0 \( \mu \text{mol/h} \). It was proposed that more allowable transitions from van Hove singularities of semiconducting SWCNTs between the conduction and valance band of TiO\(_2\) make semiconducting SWCNTs more energetically favorable for the charge transfer and, thus, improve the water-splitting efficiency.

In contrast to water splitting, only one example has been reported for CO\(_2\) photoconversion. Although CO\(_2\) photoconversion has a similar mechanism, it requires two to eight electrons to reduce one CO\(_2\) molecule to the desired product. In other words, more free electrons are required in the photocatalyst, which is often accompanied by a dramatic increase in the recombination rate. Xia et al.\(^{165}\) studied the reduction of CO\(_2\) with H\(_2\)O using MWCNTs-supported TiO\(_2\) that were prepared by both sol–gel and hydrothermal methods. In using the sol–gel method, the MWCNTs were coated with anatase nanoparticles, and by the hydrothermal method, rutile nanorods were uniformly deposited on the MWCNTs. The selectivity of the product depended on the method used in material preparation: formic acid was obtained from hydrothermal synthesis and ethanol was produced from sol–gel synthesis.

These original studies provided a valid proof of concept for the successful integration of CNTs within a photocatalytic system and their ability to enhance \( \text{H}_2 \) production and CO\(_2\) reduction, although the improvements seen so far are quite modest. The results demonstrate that the unique features of CNT make it an excellent supporting material for semiconductor nanoparticles as well as an electron collector and transporter to separate photogenerated electron–hole pairs. There exists still a large range of research opportunities to further enhance the performance in carefully designed hybrid assemblies. Fundamental research on exploring how electrons and holes move and react in these photocatalytic systems will also provide a better understanding of the factors that control photocatalytic activity.

16.4.2 CNTs in Solar Cells

The direct conversion of solar radiation into electricity using photovoltaic devices is currently viewed as an urgent component to meet our demand for clean energy. Generally, this process includes three successive procedures: (i) generation of excitons (photogenerated electron and hole pair) induced by photon absorption by semiconductor materials with the proper electronic band gap, (ii) separation of the electrons and holes from each other, and (iii) their migration through donor and acceptor molecules to the electrodes, generating a photocurrent in an external circuit (Figure 16.11).\(^{166}\) The wavelength dependence of the power density of ambient sunlight on the Earth’s surface is shown in Figure 16.11. The challenge for photovoltaic cell designers is to optimize energy conversion of this incident solar flux to electrons in an external circuit. The theoretical maximum efficiency from a Schockley–Queisser analysis for a solar cell was reported to be about 31%.\(^{167}\) Advances in this technology continue to bring to the market different semiconductor materials and configurations to achieve thinner applications and improved efficiency.
in converting light into electricity (Figure 16.12). Currently, the best single crystal silicon with a band gap of 1.1 eV can be used to make a photovoltaic device with about 25% efficiency, but such systems suffer from high cost of manufacturing and installation. Cheaper solar cells (Figure 16.12) can be made from other materials, but their efficiency needs to be enhanced for making them practically viable. Among all the alternative technologies to silicon-based solar cells, organic photovoltaics have attracted significant attention because of their low costs, flexibility, and lightweight ability. Most of the research focus for organic photovoltaics has been on...
either BHJ devices or DSSCs. Currently, there are at least four major fundamental aspects in moving these organic photovoltaics toward commercial applications, including low charge mobility, lack of absorbance in the red/NIR spectral range, poor chemical stability, and excitonic character of photocarrier generation.

Recent trends suggest that the successful utilization of CNTs, in particular SWCNTs, could potentially overcome many of the above-mentioned deficiency and lead to the realization of high-efficiency and low-cost solar cells. SWCNTs exhibit several unique properties that make them possibly attractive candidates. Remarkably, they offer a wide range of band gaps to match the solar spectrum, enhanced optical absorption, a charge mobility of the order of $10^5$ cm$^2$/V s for individual nanotubes, and approximately 60 cm$^2$/V s for CNT films. This provides an opportunity for charge carrier dissociation and transport because of their large surface area (above 400 m$^2$/g) and electron-accepting properties. In addition, they also exhibit good chemical stability, and can be easily doped or functionalized; thus, tuning the Fermi level to the favorable position when forming heterojunction with semiconductors. In recent years, various strategies and designs for the integration of CNTs in organic photovoltaics have been developed. These include the direct integration of CNTs inside the BHJ and DSSC photoactive layers, and their use as highly prospective materials to replace counter electrodes and TCO layers.

### 16.4.2.1 CNTs in Bulk Heterojunction

BHJ typically consists of an intimate blend of two semiconductors, an electron-donating conjugated polymer, strongly light absorbing, and usually a soluble fullerene derivative with electron-accepting properties, placed as the active layer between two electrodes (Figure 16.13). With suitable offsets between the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the blend forms a donor–acceptor system which is suitable to separate photogenerated electron–hole pairs at the interface. The probability that an exciton reaches the interface and dissociates is high if the length scale of the network features is consistent with the exciton diffusion length (10–30 nm). One of the most widely examined material systems consisted of poly(3-hexylthiophene) (P3HT) as the electron donor and 6,6-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) as the electron acceptor. Such a combination has led to power conversion efficiencies between 6% and 9%, although efficiencies exceeding 10% should be possible according to theoretical calculations. Nevertheless, the efficiency in this kind of devices was found to be limited by the small charge mobility, due to the hopping transport, and the clustering of fullerenes. To prevent this problem, CNTs have often been proposed as an alternative to the fullerenes.
A common strategy to implement CNTs in BHJs involved the dispersion of CNTs in a solution of an electron donating conjugated polymer, such as P3HT or poly(3-octylthiophene) (P3OT) (Figure 16.13). The conjugated polymers act as the photoactive material and CNTs act as the acceptor of the dissociated electrons or holes and their transport path. These blends are then spin-coated onto a transparent conductive electrode with a thickness that varies from 60 to 120 nm. These conductive electrodes are usually glass covered with indium tin oxide (ITO) and a 40 nm sublayer of poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(styrenesulfonate) (PSS). The latter two help to smooth the ITO surface, decreasing the density of pinholes and stifling current leakage that occurs along shunting paths. Through thermal evaporation or sputter coating, a 20–70 nm thick layer of aluminum and sometimes an intermediate layer of lithium fluoride are then applied on the photoactive material.

SWCNTs were first proposed as electron acceptor in the BHJ cells by Kymakis et al. who spin casted composite films of P3OT and 1 wt% SWCNTs onto transparent ITO-coated quartz substrates. Compared with the pristine P3OT device, the composite exhibited current densities several orders of magnitude higher under AM1.5 (100 mW/cm²) illumination. The power efficiency of the blend device was dramatically increased from $2.5 \times 10^{-5}$ to 0.04% with respect to the pristine one. The same authors were able to reach a maximum of 0.22% power efficiency after annealing the device to a temperature higher than the glass transition temperature of the polymer (120°C for 5 min). The improved device performance was attributed to the introduction of internal polymer–nanotube junctions, which allowed for a better charge carrier transport in the polymer matrix and more effective charge separation and collection.

Doping a higher percentage of SWCNTs to the polymer matrix was often avoided because of the possibility that it may cause short circuits as the CNT lengths are comparable to the total thickness of photovoltaic films. The design of new donor materials with optimized properties (chemical...
stability and extended light absorption) was also found to improve the photovoltaic performances. For example, Lanzi et al. employed new thiophene derivatives bearing a u-methoxy-functionalized hexamethylene side chain as donor, blended with SWCNTs (3 wt%) as the acceptor. This new class of polythiophenes is more soluble and resistant to atmospheric oxygen and led to solar cells with an efficiency of 0.53%. MWCNTs and SWCNTs integrated into the photoactive material were investigated, too, but most of the results indicate a very low power efficiency in the cells. This poor performance has been, in part, associated with the presence of metallic SWCNTs that short circuit the cell (reducing the shunt resistance), impurities (mostly metal catalyst residue), SWCNT aggregation, and low-charge carrier mobility in the polymer matrix. As mentioned earlier, metallic SWCNTs lack a true band gap and can, therefore, act as an efficient recombination pathway for excitons in polymer-SWCNT blends, lowering charge-separation efficiency. By contrast, semiconducting SWCNTs display ultrafast photoinduced energy and charge transfer with conjugated polymers such as P3HT, and they can act as efficient acceptors at the interface with P3HT. Through theoretical calculation, Kanai et al. proposed that the ground state interaction between P3HT and metallic SWCNTs substantially redistributes charge density, resulting in a potential well for holes on the metallic SWCNT and electrons on the polymer, thus seriously hindering charge-separation efficiency. Experimentally, Holt et al. produced blends enriched with either metallic or semiconducting SWCNTs dispersed in a P3HT, and presented conclusive evidence that charge separation is significantly enhanced by at least threefold as the concentration of metallic SWCNTs is reduced, suggesting that composites of P3HT and semiconducting SWCNTs may be promising as the active layer in organic photovoltaic devices. Recently, Ren et al. used enriched semiconducting SWCNTs coated with an ordered P3HT layer to enhance the charge separation and transport in the active layer and demonstrated an AM1.5 efficiency of 0.72%. Contrary to previous prediction, both semiconducting and metallic SWCNTs were also found to function as efficient hole acceptors probably because of the heavy p-doping of P3HT, making selective omission of metallic SWCNT unnecessary. In this regard, Dissanayake et al. reported a surprising external quantum efficiency exceeding 90% for a millimeter-scale P3HT/SWCNTs device, irrespective of whether semiconducting or metallic SWCNTs were used. Instead of BHJs, they used a bilayer heterojunction, depositing on a quartz substrate horizontally aligned arrays of SWCNTs (metallic and/or semiconducting ones) and directly contacting each of them at the extremes by metal electrodes (Al or Pd). Then, P3HT was deposited onto nanotubes and top-contacted by an ITO layer. Another parameter that was also found to crucially influence the charge and exciton transport in the active layer was the SWCNT diameter. The optimal conditions suggested a nanotube diameter between 1.3 and 1.5 nm. Recently, C60-encapsulated semiconducting SWCNTs were used to fabricate p–n heterojunctions with n-type Si. The Si substrate was found to dominate the power-conversion efficiency of SWCNT/Si solar cells at wavelengths less than 1100 nm, whereas semiconducting SWCNTs played a critical role in transforming the infrared light (1550 nm) into the electrical energy. Although the power efficiency was low (~0.01%), the performance of this device was found to be much better than that observed in solar cells fabricated by C60-encapsulated SWCNTs containing both metallic and semiconducting SWCNTs. It was found that when the light photon energy exceeds two times the band-gap energy of semiconducting SWCNTs, the efficiency suddenly increases, suggesting the occurrence of multiple exciton generation.

The other major issue limiting the device performance of CNT solar cells is the bundling/aggregation of nanotubes during polymer dispersion, which reduces the amount of interface available for charge separation, alters the properties of the isolated tubes, and allows only for low concentrations of SWCNTs to be achieved. Nogueira et al. covalently functionalized SWCNT with thiophene moieties to improve their dispersion in a P3OT matrix. The best BHJ solar cell was obtained using 5 wt% of the modified SWCNTs and showed an efficiency of 0.184%. The same group further improved the efficiency to 1.48% under 15.5 W/m² light by using a polybithiophene layer between fluorine-doped tin-oxide (FTO) and a P3OT/SWCNT composite to collect and transport the holes and also avoid nanotube contact with the FTO. To supply additional dissociation sites, Pal et al.
physically blended functionalized MWCNTs into P3HT polymer and then deposited a C$_{60}$ layer to create a P3HT-MWCNT-C$_{60}$ double-layered device. However, the power efficiency was still relatively low at 0.01% under 100 mW/cm$^2$ white illumination. Recently, Ham et al. reported a high charge transfer ability on nano-planar heterojunction structures consisting of highly oriented and isolated SWCNTs grown by CVD parallel to the substrate on which was deposited a P3HT layer. Their photovoltaic efficiencies per nanotube ranging from 3% to 3.8% were attributed to the absence of CNT aggregation.

To expand the absorption range of BHJs to the infrared region, several groups anchored QDs, such as CdSe and PbSe, onto the sidewalls of SWCNTs by functionalized thiol groups. For example, the organic photovoltaic devices based on blend films of poly(vinyl carbazole)/PbSe QD-grafted SWCNTs exhibited an incident photon-to-current conversion efficiency of 2.6% upon infrared light illumination, which was two times larger than the control device without SWCNTs. SWCNTs or MWCNTs also served as efficient charge transporters, as a scaffold for fullerenes in conducting polymer-BHJ cells. Under these conditions, the electrons captured by C$_{60}$ molecules are transferred to SWCNTs or MWCNTs, facilitating fast transport rather than slow hopping between C$_{60}$ molecules. The current density of such device was greatly increased when 0.1 wt% MWCNTs were introduced to an 1:1 P3HT:PCBM solution; as a consequence, the power efficiency of the devices was improved to around 2.0%, and this efficiency was nearly three times larger than that of the device without MWCNT addition. In another report, a photovoltaic device from C$_{60}$-modified SWCNTs and P3HT was made by first microwave irradiating a mixture of SWCNT–water solution and C$_{60}$ solution in toluene, followed by adding P3HT. The best power conversion efficiency of 0.57% under solar irradiation (95 mW/cm$^2$) was achieved on the cell annealed at 120°C for 10 min. Sadhu et al. recently improved the efficiency of P3HT:PCBM to 2.5% by functionalizing the MWCNTs with thiophene groups. The improved efficiency was attributed to the well-dispersed MWCNTs, resulting in an extension of the exciton dissociation volume and charge transport properties through the nanotube percolation network in P3HT/MWCNT, PCBM/carbon nanotube (CNT), or both phases. The highest power conversions reported to date with the use of CNTs were obtained by depositing an SWCNT layer on the cathodic side, either between the ITO and the PEDOT:PSS or between the PEDOT:PSS and the photoactive blend in a modified ITO/PEDOT:PSS/P3HT:PCBM/Al solar cell (Figure 16.14). SWCNTs were deposited by dip coating from a hydrophilic suspension, after an initial nondestructive argon plasma treatment to achieve a power conversion efficiency of 4.9%, compared to 4% without SWCNTs.

Another effective way to further enhance the charge mobility of BHJ cells has been through the use of nitrogen- or boron-doped CNTs in active layers, as highly selective electron- or hole-transport enhancement materials. The work function of N- and B-doped MWCNTs was found to match well with the LUMO of PCBM and the HOMO of P3HT, respectively, because of the excess or lack of electrons created during the doping. In particular, the incorporation of 1.0 wt% B-MWCNTs in P3HT/PCBM BHJ solar cells resulted in balanced electron and hole transport, and accomplished a power conversion efficiency improvement from 3.0% (conventional control cells without CNTs) to 4.1%.

### 16.4.2.2 CNTs in Dye-Sensitized Solar Cells

DSSCs have emerged as an alternative to solid-state $p$–$n$ junction photovoltaic devices, primarily because of its potential to harvest visible light quite efficiently and generate electricity on resource-abundant raw materials and energy-saving device processing. DSSCs operate in terms of a process (Figure 16.15) that is similar in many respects to photosynthesis, the process by which green plants generate chemical energy from sunlight. Central to these cells is a thick film of nanometer-sized wide-band-gap semiconductor (such as TiO$_2$ or ZnO) that provides a large surface area for the adsorption of light-harvesting organic dye molecules. Upon illumination, the photoexcited dye injects an electron into the conduction band of the semiconductor, which carries the electron to the transparent electrodes. This process is accompanied by a reduction of the oxidized dye
**FIGURE 16.14** (a) Schematic of various BHJ solar cells, in which SWCNTs were precisely placed at different hierarchical levels in the device structure. (b) $J$–$V$ curves for these cells (structures from 1 to 5) under AM 1.5 G illumination. (Adapted from Chaudhary, S. et al., *Nano Lett.*, 7, 1973, 2007.)

**FIGURE 16.15** Schematic illustration for the operation of the DSSCs. (Adapted from Grätzel, M., *Nature*, 414, 338, 2001.)
by a redox-active electrolyte usually iodide/triiodide (I⁻/I₃⁻), which transports the resulting positive charge to the platinized counter-electrode.

In terms of quantum efficiency, the maximum attainable efficiency has remained in the range of 11−12%, 220 which are far lower than that predicted theoretically (~20%). 221,222 Several strategies have been proposed to boost the performance of DSSCs, including efficient light harvesting in the visible region, the promotion of electron transport from the adsorbed dyes to the TiO₂ electrode to avoid charge recombination, and efficient hole transport to the counter electrode through the liquid or solid electrolytes. To this end, CNTs have been demonstrated to be promising materials in addressing some of these issues by incorporating them in TiO₂ active layers to improve charge separation and transport and directly using them as counter electrode in replacement of conventional platinum.

CNT networks have been used in TiO₂ active layers, with the purpose of promoting the charge collection and transport in TiO₂ films. 134,223−228 However, the enhancement of device performance is still limited, due to the insufficient contact between TiO₂ and the CNTs and the serious CNT aggregation. Lee et al. 228 fabricated a DSSC using TiO₂-coated MWCNTs, produced by sol–gel method, achieving an increase of 50% in the conversion efficiency with respect to conventional DSSC. Kamat et al. demonstrated the beneficial role of SWCNT network in improving the charge separation, as the rate of back electron transfer between the oxidized sensitizer (Ru(III)) and the injected electrons becomes slower in the presence of the nanotube scaffold (Figure 16.16). 134 It was found that the photoinduced electrons in TiO₂ survive about 50% longer when embedded within the SWCNT network, thus, reducing the charge recombination rate. The authors also noticed an improvement in the photocurrent generation, but this improvement was found to be neutralized at a lower photovoltage as the apparent Fermi level of the TiO₂ and SWCNT composite becomes more positive than that of pristine TiO₂. The beneficial aspect of CNT dispersion was demonstrated by Zhang et al., who improved the dispersion property of CNTs by introducing oxygen-containing groups using O₂ plasma, and then incorporating them within a TiO₂ matrix. 229 The resulting composite provided a better attachment of TiO₂ particles and greater degree of dye adsorption and lower levels of charge recombination. The authors demonstrated a conversion efficiency of 6.34% in DSSCs, 75% higher than that in conventional TiO₂-based devices.

For further improvement of the photoanode performance in DSSCs, it is highly desirable to use semiconducting SWCNTs with a suitable position of conduction band that would facilitate electron transport from mesoscopic TiO₂ particles to ITO electrode through the SWCNTs. Recently, Belcher et al. developed a new method to disperse and template compact core/shell SWCNT/TiO₂ nanocomposites using a genetically engineered M13 virus (Figure 16.17). 230 Using this method, SWCNTs

FIGURE 16.17 Schematic diagram of virus-enabled SWCNT/TiO$_2$ DSSCs. (a) Process of virus/SWCNT complexation, and biomineralization of TiO$_2$ on the surface of the virus/SWCNT complex. (b) Scheme of DSSCs incorporating the SWCNT/TiO$_2$ complex. Energy diagrams of DSSCs incorporating semiconducting SWCNTs (c) and metallic SWCNTs (d). The dye absorbs photons and generates electron–hole pairs, and instant charge separation then occurs at the dye/TiO$_2$ interface. Semiconducting SWCNTs improve electron collection at FTO electrodes, whereas incorporation of metallic SWCNTs results in recombination and back reaction. (Adapted from Dang, X. et al., Nat. Nanotech., 6, 377, 2011.)
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were stabilized without surfactants and surface modifications, and their electronic properties were preserved. By using these nanocomposites as photoanodes in DSSCs, the authors demonstrated that well-dispersed semiconducting SWCNTs can be used to improve the power conversion efficiency of DSSCs to 10.6%. They also demonstrated that metallic and semiconducting SWCNTs affect device performance in opposite ways, and aggregation states of SWCNTs affect device performance, guiding further studies in incorporating SWCNTs in photovoltaic devices.

A large number of studies have focused on the use of CNTs as effective counter electrodes because of their good catalytic activity, good conductivity, high surface area, environmental stability, flexibility, and comparatively lower cost. Although Pt has been the preferred material for counter electrode, its high cost and tendency to degrade over time when in contact with the commonly used electrolytes are serious drawbacks for large-scale and cost-effective DSSC fabrication. In recent developments, it has been proposed that higher performing counter electrodes can be achieved with defect-rich CNT species and vertically aligned CNTs. For example, Lee et al. found that defect-rich edge planes of bamboo-like-structure MWCNTs can ensure low charge-transfer resistance and an improved fill factor. The device performed well and achieved an efficiency of 7.67%, compared to 7.83% for the Pt-based cell. The high catalytic activity has been attributed to the high surface area and the defect-rich basal plane of CNTs. It has also been debated that this may also be attributed to residual catalyst particles located in the nanotubes.

Aligned CNTs have proved to be a very useful material because electrons can directly transfer through individual tubes, instead of hopping between the different carbon structures within this film which significantly increases their abilities for charge separation and transport. For example, it was found that aligned MWCNT sheet in DSSCs has efficiencies higher than the randomly dispersed CNT film and comparable with platinum. The resulting cell showed an efficiency of 6.6%, compared with 5.27% of the platinum-based cell under the same conditions. In another study, an efficiency of 6.05% was achieved by using vertically aligned MWCNTs grown on graphene paper. With respect to MWCNTs, even higher catalytic activity can be achieved with SWCNTs because of their higher surface area. For example, gel-coated SWCNTs-DSSCs exhibited good stability and reached an efficiency of 8% in conjunction with iodine electrolyte. More recently, vertically aligned SWCNTs have been successfully implemented as efficient counter electrode in DSSCs, featuring notably improved electrocatalytic activity toward a noncorrosive thiolate/disulfide redox shuttle over conventional Pt counter electrodes (Figure 16.18). Any iodine-based electrolyte was

![FIGURE 16.18](image_url)

**FIGURE 16.18**  Photocurrent–voltage characteristics of DSCs using vertically aligned SWCNTs or Pt counter electrodes under 1 sun illumination (AM 1.5 G, 100 mW cm⁻²). (Adapted from Hao, F. et al., Sci. Rep., 2, 368, 2012.)
avoided because it tends to corrode metallic current collectors and has the tendency to absorb light in the visible wavelengths, which means fewer photons can be utilized. The device with vertically aligned SWCNTs counter electrode demonstrated power conversion efficiency up to 5.25%, lower than the DSSC record of 11% with iodine electrolytes and a platinum electrode, but significantly higher than 3.49% for a control test that combined the new electrolyte with a conventional Pt electrode.

To further improve the performance of the counter electrode in DSSCs, it is highly desirable to use enriched long and smaller diameter metallic SWCNTs. The long tubes should reduce the inter-tube connections, increasing the conductivity of the cathode and small diameter to enhance the chemical reactivity. The use of these high conductive metallic SWCNTs would improve the rate transfer of the electrons arriving from the external circuit to the redox system.

16.4.2.3 CNTs in Transparent Electrodes

ITO has been the predominant material used to create transparent conductive electrodes in organic photovoltaic devices of BHJs and DSSCs, and other optoelectronic devices (e.g., displays, touch screens, organic light emitting diodes (OLEDs)) due to its superior combination of environmental stability, relatively low electric resistivity, and high optical transparency (70 Ω/sq at 90% transmittance). However, this material suffers from significant deficiencies, including processing expense involving high temperature deposition, limited availability of indium, incompatibility with plastic substrates, and lack of flexibility, which make it completely unsuited for future flexible electronic devices. Thus, the use of CNTs as potential replacements of ITO transparent electrodes, especially those requiring high flexibility, has been a research endeavor of great interest ever since the discovery of SWCNTs. The huge intrinsic charge mobility of an individual CNT, the high optical transparency over a wide range of frequencies, and the amenability to solution processing are attractive enough to design electrically conductive, flexible, transparent, and low-cost networks.

Recent investigations have demonstrated organic photovoltaics incorporating SWCNT films as a conductive transparent anode, with the primary barrier to greater efficiencies being the relatively high sheet resistance of the SWCNT film. There has always been a trade-off between conductivity and transparency as the film thickness increases, the sheet resistance and optical transmittance decrease. To meet minimum industry standards, a nearly ideal SWCNT-based transparent conductive film should have a sheet resistance of <50 Ω/sq at 85% transparency, or 100 Ω/sq at 90% (generally taken at 550 nm). Current state-of-the-art SWCNT transparent conductive films have sheet resistances of the order of 300 Ω/sq at 90% transmittance and 100 Ω/sq at 80% transmittance with some variations depending on the methods used. In spite of their great potential, the widespread use of SWCNTs in electronic materials remains stalled by issues with unbundling and purifying them to obtain much greater precision over their electronic properties. For example, it is well known that the high electrical conductivity of SWCNTs is associated only with metallic SWCNTs, which generally represent the minority fraction in the mixture with the available synthesis methods for SWCNTs. In addition, experimental evidence has pointed out that the conductivity in nanotube films is also dominated by resistance at the tube–tube junctions. Indeed, the contact resistance at metallic–semiconducting junctions is three orders of magnitude higher than that at the metallic–metallic junctions. One of the common methods employed to overcome this obstacle has been chemical doping and functionalization of the films prior to device fabrication. In particular, the adsorption of electron-withdrawing species was found to both lower the SWCNT film sheet resistance and bleach the primary peaks in the optical absorption spectrum, thereby increasing the film transparency. The nanotube films’ post-fabrication were often doped via treatment with a strong acid HNO$_3$, SOCl$_2$, and AuCl$_3$ to metallize semiconducting nanotubes and to decrease the inter-tube resistance at the junctions (the mitigation of Schottky barrier), thus significantly enhancing the electrical conductivity in the films. For example, Feng et al. demonstrated that an acid treatment of few-walled CNTs (FWCNTs) can produce both a 10-fold decrease in resistance and a 1.5-fold increase in transparency. Their FWCNTs ($T = 70\%$, $R_s = 86 \, \Omega/sq$/
P3HT:PCBM/Al device showed a maximum efficiency up to 0.61%, which was comparable to ITO (0.68%) with almost identical operation. Hecht et al. prepared CNT transparent conducting film using a chlorosulfonic acid dispersion of CVD-grown few-walled CNTs (from Unidym, Inc.) (predominantly single-walled and double-walled tubes grown by CVD with greater than 95% purity) and measured a sheet resistance of 60 $\Omega$/sq at a transmittance of 90.9%, almost matching the performance of ITO films on plastic substrates. In another interesting work, Barnes et al. prepared organic photovoltaic devices by spray deposited oxidized-SWCNTs electrodes giving lower resistance and increased power conversion efficiency from 3.5% to 4.1% with respect to ITO-based devices. Although enhanced optoelectronic performance was achieved, these doped films are generally less stable thermally and chemically, often degrading in performance over time. Other studies have also recognized the importance of the geometry of aligned CNTs to further improve thermal conductivity (TC) performance. Vertically aligned CNTs were found to provide a larger electrical and thermal conductivity along the tube axis than randomly dispersed ones.

Nevertheless, the demonstrated effect of metallization does point to the great potential of transparent conductive films from separated metallic SWCNTs where there is no need for metallization. Metallic SWCNTs have extremely high electrical conductivity (estimated theoretically as high as $10^6$ S/cm) with a ballistic propagation of electrons, largely free from scattering over a distance of thousands of atoms. With their resistance approaching the theoretical lower limits, metallic nanotubes may, in principle, carry an electrical current density of $4 \times 10^9$ A/cm$^2$, which is more than 1000 times greater than that in metals such as copper. Sun et al. recently highlighted major achievements in the development of postproduction separation methods, which are now capable of harvesting separated metallic SWCNTs from different production sources, and their use in transparent electrodes in various device nanotechnologies. According to a direct comparison by Sun et al., the electrical conductive performance in the films from the separated metallic SWCNTs was consistently much better than that in the films from as-purified SWCNTs. The results thus obtained suggested that at approximately 80% transmittance (550 nm) the surface resistivity of the film from metallic SWCNTs was less than 100 $\Omega$/sq (Figure 16.19), a performance level already competitive to that of ITO coatings for some applications.

![FIGURE 16.19](a) Films of SWCNTs on alumina filters from the as-purified sample (left) and the separated metallic fraction (right). (b) A direct comparison of surface resistivity values in films of SWCNTs (fabricated via vacuum filtration) from the as-purified sample (⧫) and the separated metallic fraction (⧫). (Adapted from Lu, F. et al., Chem. Phys. Lett., 497, 57, 2010.)
The separated metallic SWCNTs were also found to enhance transparent conductive performance in composite films with conductive polymers, particularly the poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) blend as it is optically transparent in the visible spectral region (Figure 16.20). In such composites, the conductive polymer blend served the function of dispersion agents, so no surfactants were necessary in the film fabrication. In the work by Wang et al., suspensions of nanotubes (enriched metallic or nonseparated SWCNTs) in DMSO were mixed with aqueous PEDOT:PSS in various compositions, and the resulting mixtures were sprayed onto an optically transparent substrate. The sheet resistance results demonstrated that the composite films with enriched metallic SWCNTs were consistently and substantially better in performance than those with nonseparated SWCNTs (and both better than films with neat PEDOT:PSS). Aqueous PEDOT:PSS is not as effective as commonly used surfactants in the dispersion of SWCNTs, which

![FIGURE 16.20](image)

**FIGURE 16.20** Electrical conductivity results of P3HT/SWCNT composite films depending on (a) different amounts of pre-separation (□) and separated metallic (○) nanotube samples, and (b) their corresponding effective metallic SWCNT contents in the films (dashed line: the best fit in terms of the percolation theory equation). (c) Surface resistivity results of PEDOT:PSS/SWCNT films on glass substrate with the same 10 wt% nanotube content (○: pre-separation purified sample and ▼: separated metallic SWCNTs; and for comparison, ●: blank PEDOT:PSS without nanotubes) but different film thickness and optical transmittance at 550 nm. Shown in the inset are representative films photographed with tiger paw print as background. (Adapted from Wang, W. et al., *J. Am. Chem. Soc.*, 130, 1415, 2008.)
is negative to the performance of the resulting nanocomposite films. Appropriate structural modifications to PEDOT:PSS for derivatives of improved dispersion characteristics may be pursued to optimize the composite films. It should be pointed out that the use of conductive polymers in transparent electrodes may yield other benefits not reflected in the performance of low surface resistivity. For example, to adjust and improve the interfacial work function in electronic devices such as OLEDs, PEDOT:PSS is often coated as an additional thin layer on a nanotube film or ITO coating in transparent electrodes.\textsuperscript{291,292}

For photovoltaic applications, Tyler et al. recently used SWCNTs sorted via the density-gradient ultracentrifugation (DGU) method as transparent anode material and showed that a composition in metallic SWCNTs >70\% affords a power conversion efficiency 50-fold higher than monodisperse semiconducting SWCNTs thin films (Figure 16.21).\textsuperscript{293} Again, this result points out the necessity to use highly enriched metallic CNTs as electrodes with very low resistance.\textsuperscript{294,295}

There is sufficient evidence to validate, in principle, the long-held expectation that metallic SWCNTs may ultimately be used in transparent electrodes, or at least alternatives to the ITO technology. In practice, however, many technical issues from materials (separated metallic SWCNTs)

![Graph showing J-V curves and sheet resistance](image.png)

**FIGURE 16.21** (a) $J-V$ curves of representative devices show a trend of increasing performance with metallic SWCNT content, and nearly identical performance in devices fabricated with 80\% and 99.9\% metallic SWCNT anodes. (b) The sheet resistance of SWCNT films, plotted here in the inverse, shows a clear dependence on metallic SWCNT content. After nitric acid treatment (left axis), doped semiconducting films have lower sheet resistance than metallic films. After PEDOT:PSS treatment (right axis), the sheet resistance of all films is increased, but the metallic films show greater conductivity than semiconducting films. (Adapted from Tyler et al., *Adv. Energy Mater.*, 1, 785, 2011.)
Carbon Nanomaterials to fabrication have yet to be addressed. Beyond transparent electrodes, metallic SWCNTs may find other applications in which extremely high electrical conductivity and excellent optical properties are both required, or even some in which optical transparency is not necessary.

16.5 CONCLUSIONS AND PERSPECTIVES

During the past several years, exciting progress has been made in the research on the integration of CNTs into photo-energy conversion systems as exemplified in the solar-driven water splitting for H\textsubscript{2} fuels, photoreduction of CO\textsubscript{2}, and in the uniquely configured light-weight and low-cost photovoltaic devices of BHJs and DSSCs. SWCNTs in particular have shown a rich, unique, and useful array of optical and electronic properties. For example, each structural species of semiconducting nanotube displayed not only a set of intense and distinct absorption transitions ranging from near-infrared to ultraviolet wavelengths, but also well-defined fluorescent band-gap photoluminescence in the near infrared. Their combination with electron acceptors or donors favored a fast and long charge separation and a slow charge recombination, by providing a high electric field at the polymer/nanotube interfaces and allowing the electrons to transport efficiently along their length. CNTs are also capable of accommodating structural defects, which present in many cases unique opportunities, from the functionalization for much-improved dispersion or processing to defect-derived photoluminescence and to the manipulation of photoinduced redox processes.

Because of these unique features, CNTs have demonstrated great potential for the emerging energy conversion applications by playing several roles. For example, when converting water into H\textsubscript{2}, or converting CO\textsubscript{2} into hydrocarbon fuels, besides providing a high surface area support and immobilization for semiconductor nanoparticles, their presence induced enhanced photocatalytic activity through one or all of the three primary mechanisms: minimization of electron–hole recombination, band-gap tuning/photosensitization, and provision of high-quality adsorptive active sites. Their incorporation into organic photovoltaic devices as components of the photoactive layer and as alternative materials for counter electrodes and transparent conductive films have also been very promising, enabling the development of cheaper, flexible, and more robust devices.

Although performance remains the major barrier for CNTs, the prospect for improvement is great in every step of CNT integration, from growth, purification, separation, dispersion, alignment, doping, to coating. One of the most important areas to explore is chiral selective growth and separation of SWCNTs. Metallic SWCNTs are more suited to replace counter electrodes and TCO layers because their conductivity is much higher than that of the mixture, whereas semiconducting SWCNTs are highly desired for the BHJ and DSSC photoactive layers because they display ultrafast photoinduced charge transfer with conjugated polymers. The separated SWCNTs will likely continue to find use in a variety of energy conversion devices, though higher metallic and semiconducting purity seems necessary for more high-end applications. Significant improvement may also be achieved by developing better dispersion and alignment processes and new stable dopants. High level of dispersion and vertical alignment will allow for even more surface space and for CNT–CNT junction resistance reduction, resulting in greater solar absorption and charge collection and therefore high power efficiency. Besides all these parameters, systematic evaluations of the device performance as a function of various film processing parameters such as concentrations within the composite, active layer film thickness, and film annealing temperature, as well as deeper understandings of the structure–function relationship are still lacking and need to be addressed before fully realizing the extraordinary properties of CNTs in energy conversion systems.

Finally, the recent emergence of graphene nanosheets and related materials may offer other great opportunities for the development of carbon tube–sheet hybrid nanotechnologies, which may speed up their applications for advanced energy conversion.
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Carbon Nanotubes for Photoinduced Energy Conversion Applications

Versatility with carbon dots – from overcooked BBQ to brightly fluorescent agents and photocatalysts

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Carbon soot from overcooked barbecue meat was used as a precursor for brightly fluorescent carbon dots and for their serving as potent visible-light photocatalysts, similar to those from other nanoscale carbon sources, thus demonstrating the versatility of carbon dots in terms of structure, composition, and properties.

Since the original report,\textsuperscript{1,2} carbon-based “quantum” dots or carbon dots have been widely pursued as potentially performance-wise competitive yet nontoxic alternatives to the presently dominating semiconductor quantum dots (QDs).\textsuperscript{3} The number of reported studies on carbon dots has seen rapid increases, with topics ranging from improvements in their synthesis to the exploration on their variety of application potentials.\textsuperscript{3–5} For example, Yang, \textit{et al}. reported the use of carbon dots as fluorescence imaging agents in live mice.\textsuperscript{6} Li, \textit{et al}. used conjugates of carbon dots with transferrin as optical probes to target tumor cells for cancer diagnostics.\textsuperscript{7} Cao, \textit{et al}. doped carbon dots with gold or platinum metal for their photocatalytic activities in the visible light-driven photoreduction of carbon dioxide (CO\textsubscript{2}).\textsuperscript{8}

Carbon dots are generally small carbon nanoparticles with the particle surface passivated by the functionalization of organic molecules or other soft materials (Scheme 1, almost a special kind of “core-shell” nanostructure with a nanoscale carbon core and a shell of soft materials) for bright fluorescence emissions. While naked carbon nanoparticles without deliberate surface functionalization in relatively stable aqueous or other suspensions may also exhibit colorful fluorescence, the observed emission quantum yields have been low or very low, for which an explanation is such that the solvent molecules might be responsible for the relatively weak surface passivation effect.\textsuperscript{3,9} Therefore, a typical structure for brightly fluorescent carbon dots is “core-shell”, namely a carbon nanoparticle core covered with a soft shell of organic materials (Scheme 1).

In the originally reported carbon dots,\textsuperscript{1,2} the carbon core was from nanoparticles produced in the laser ablation of a carbon target containing pure graphite powders and cement. Since then, a variety of carbon sources or precursors have been used in the synthesis of carbon dots, including stepwise approaches and direct one-pot preparation, yielding dots of wide-varying optical properties and performance parameters. Organic and bioorganic materials such as sugars, celluloses, and proteins have been among more popular precursors.\textsuperscript{10–11} Recently there have also been several reports on the use of household and food products as starting materials for carbon dots, including, for example, orange juice\textsuperscript{14} and bread, jaggery, corn flakes, or biscuits.\textsuperscript{15} These results demonstrated the versatility with respect to the core structure and composition in carbon dots, as well as potentially abundant and/or renewable sources in eventually their scale-up production.

Here we report the use of char from overcooked barbecue (BBQ) for precursor carbon nanoparticles in the synthesis of carbon dots. The optical and related properties of the carbon dots thus prepared were found to be largely similar to those of the dots from other carbon sources, including similarly high fluorescence quantum yields and the photocatalytic activities with the harvesting of visible photons. The results further illustrate the versatile nature of carbon dots with respect to their rather diverse and flexible precursor sources and their intrinsic robustness in performance capabilities.

Scheme 1  A cartoon illustration of a carbon dot as a surface-passivated small carbon nanoparticle.
Regular ground-beef available at a typical grocery store was cooked on a conventional outdoor grill until char could be harvested. The char sample was washed with acetone and then evaporated to remove the solvent completely. For thermal annealing, the sample was heated under flowing argon atmosphere in a laboratory tube-furnace for 5 h. The resulting soot-like material was refluxed in aqueous nitric acid (2.5 M), followed by centrifugation to retain the supernatant and then dialysis in a membrane tubing (cut off molecular weight ~ 500) against fresh water. The stable aqueous dispersion of carbon nanoparticles thus obtained appeared similar to those from other carbon sources, exhibiting an featureless UV/vis spectrum and weak fluorescence emissions (on the order of 1–2% in observed quantum yields). The powder X-ray diffraction (XRD) pattern of the carbon nanoparticles consisted of a broad peak centered at 2θ ~ 26° (d = 3.45 nm), consistent with mostly disordered carbon in the sample. In the observed Raman spectrum of the sample, both D-band and G-band (centered at about 1350 cm⁻¹ and 1580 cm⁻¹, respectively) were very broad, also largely similar to those of the previously used carbon nanoparticles from other sources. Representative atomic force microscopy (AFM) images of the carbon nanoparticles are shown in Fig. 1.

The precursor carbon nanoparticles were functionalized with oligomeric polyethylene glycol diamine of an average molecular weight ~ 1500 (denoted as PEG₁₅₀₀N) via the classical amidation reaction in the PEG₁₅₀₀N melt, as reported previously.¹⁶ The resulting PEGylated carbon dots (Fig. 1) in aqueous solution exhibited similarly featureless UV/vis absorption spectrum (Fig. 2). The fluorescence spectra were excitation wavelength dependent, also similar to what were reported for carbon dots from other sources. At 440 nm excitation, for example, the observed fluorescence spectrum of the carbon dots from the BBQ precursor (Fig. 3) was similar to that of the previously reported carbon dots (the core carbon nanoparticles from other sources), with the corresponding fluorescence quantum yield (measured by the relative method in reference to the fluorescence standard 9,10-bis(phenylethynyl)-anthracene) of about 14% in the former vs. typically 15–20% in the latter.¹⁶

The as-synthesized sample of carbon dots is generally a mixture of dots with different fluorescence quantum yields, likely reflecting the various levels of surface passivation effectiveness in the carbon dots. Aqueous gel column separation has been demonstrated as a relatively convenient method for the isolation of more fluorescent fractions.¹⁶,¹⁷ In this work, the as-synthesized sample was fractionated on a Sephadex G-100 gel column, from which the most fluorescent fraction was found to exhibit a quantum yield of close to 40% in the green (emissions centered around 520 nm with 440 nm excitation, Fig. 3). While not quite as bright as the highly fluorescent carbon dots from fractionating samples synthesized with other carbon nanoparticle sources in previous studies,¹⁶ the performance of these carbon dots from overcooked BBQ precursors is still substantial, demonstrating the versatility and robustness such that brightly fluorescent carbon dots are not narrowly associated with specific carbon sources.

Mechanistically with respect to the photoexcited state processes and fluorescence emissions, there must be photoinduced charge separations in the core carbon nanoparticles, resulting in electrons...
and holes being immobilized at various sites on the nanoparticle surface (Fig. 4). Similar to what are known in conventional semiconductor QDs, radiative recombinations of the electrons and holes in photoexcited carbon dots are likely responsible for the observed fluorescence emissions. The particle surface passivation apparently plays a major role in stabilizing the charge separated states for the emissions to be much brighter. In fact, the photo-generated electrons in carbon dots could be used for the reduction of silver and gold cations into their corresponding metals, as also confirmed in this work for the carbon dots from BBQ-derived nanoscale carbon precursors. The reduced gold metal deposited on the dot surface, responsible for the observed gold plasmon absorption (Fig. 4), and at the same time diminishing the fluorescence emissions by disrupting the radiative recombination processes. Associated with the disrupting function of the gold on the carbon dot surface is such that the metal could concentrate the photo-generated electrons, further enhancing the photoreduction (such as in CO₂ photoconversion, Fig. 4).

The same concentration of electrons in gold-doped carbon dots could be used for some of the more challenging photoreduction purposes, including the photocatalytic conversion of CO₂ into formic acid (Fig. 4). Experimentally with the gold-doped carbon dots (corresponding to the absorption spectrum shown in Fig. 4) as photocatalysts, their aqueous dispersion in an immersion-well photochemistry apparatus was bubbled with CO₂ gas until saturation. The photoirradiation was by the use of a 450 W medium-pressure Hanovia lamp through cycling water filter and saturation. The photoirradiation was by the use of a 450 W formic acid (Fig. 4). The control experiments with carbon dots under the same conditions in the absence of CO₂ resulted in no detectable formate, thus reaffirming that the photoproduct must be from the CO₂ reduction (Fig. 4).

In summary, brightly fluorescent carbon dots (with quantum yields up to 40%) could be synthesized from BBQ char. Since the char-derived precursor was obviously complicated in terms of chemical composition, the high performance found in the resulting carbon dots supports the argument that carbon dots are intrinsically versatile in the core structure and composition and performance-wise robust. In addition to those already available in the literature, the results reported here suggest that high-performance carbon dots can be sourced from a variety of abundant and renewable precursor materials, amenable to a much broader range of applications.

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Notes and references


Carbon “quantum” dots for optical bioimaging

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Carbon dots, generally referring to small carbon nanoparticles with various levels of surface passivation, have emerged as a new class of quantum dot-like fluorescent nanomaterials. Since the original report in 2006, carbon dots have been investigated by many research groups worldwide, with major advances already made in their syntheses, structural and mechanistic understandings, and evaluations for biocompatibilities and potential bio-applications. In this article, representative studies responsible for these advances in the development and understanding of carbon dots are reviewed, and those targeting the use of carbon dots as high-performance yet nontoxic fluorescence agents for optical bioimaging in vitro and in vivo are highlighted and discussed.

1 Introduction

Quantum dots (QDs) are generally semiconductor nanocrystals of physical dimensions smaller than the exciton Bohr radius.1–7 Because of the quantum-confinement effect, the electronic and optical properties of QDs exhibit characteristic dependencies on the nanoparticle sizes and composition, especially the infamous display of beautiful fluorescence colors for QDs of varying semiconductor nanoparticle sizes.8 Among well-established semiconductor QDs are the size-wise narrowly distributed CdSe nanoparticles, whose quantum yields were found to be 10–15% with the original synthesis in a high temperature organometallic reaction by Bawendi and coworkers.9 The capping of CdSe nanoparticles by a wide-bandgap semiconductor in later studies substantially improved both the optical performance and the photochemical stability,10–13 with the QDs represented by CdSe–ZnS core–shell nanoparticles, now commercially available in aqueous or organic compatible versions (corresponding to different surface functionalizations), exhibiting fluorescence quantum yields of more than 50%.10

The high optical performance of QDs has captured the imagination of researchers in biomedical fields, with the exploration for a wide variety of potential bio-applications already producing exciting results.14–18 The rationale for the use of QDs over organic dyes is terms of much enhanced

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performance is now generally accepted in the literature. However, the obvious performance advantages of QDs for bioimaging applications are challenged by some significant shortcomings, among which the most serious is the toxicity issue. The presently dominating semiconductor QDs are limited by their containing heavy metal elements such as cadmium, whose potential health and environmental hazards are well-documented. For example, the existing data suggest that the cadmium-based QDs are toxic to vertebrate systems at relatively low concentrations, and there may also be risks with the bioaccumulation of these toxic materials in organs and tissues. Therefore, there has been much effort in the research community on searching for alternative QD-like photoluminescent materials.

Among more promising candidates for the alternative QDs are nanosized silicon (and germanium to some extent) particles, though it does not appear that the development of silicon QDs is on track to compete with the cadmium-based QDs in bioimaging and related applications. Interestingly, carbon in the same group as silicon in the periodic table apparently provides a more effective solution in the development of alternatives to the semiconductor QDs, with the discovery of brightly fluorescent carbon-based QDs or carbon dots (also referred to as C-Dots). In this article we highlight the structural characteristics and optical properties of carbon dots, and their rapid advances toward serving as high-performance yet nontoxic advance-agent agents for bioimaging and related biomedical applications.

2 Carbon dots

Carbon dots in a broad definition generally refer to small carbon nanoparticles in aqueous or other suspensions. The original hint on nanoscale carbon particles being photoluminescent could be traced back to the observation that the surface defects in both single-walled and multiple-walled carbon nanotubes became brightly emissive under some specific conditions, especially when the nanotubes were functionalized for the purpose of dispersion at the individual nanotube level without bundling or aggregation. In a conceptually and experimentally similar fashion, Sun and coworkers functionalized small carbon nanoparticles with various oligomeric species to target an effective passivation of the particle surface, resulting in bright and colorful fluorescence emissions (Fig. 1), thus the finding of carbon dots. It was subsequently found that carbon dots are also strongly multi-photon fluorescent, with extremely large two-photon cross-sections on pulsed laser excitation (800–900 nm).

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The effective carbon particle surface passivation has apparently been a necessary condition for carbon dots of high fluorescence performance, despite the rather broad definition on carbon dots. “Naked” carbon nanoparticles without deliberate surface functionalization in relatively stable aqueous or other suspensions may also exhibit colorful fluorescence emissions, as reported by many research groups, but with generally low to very low emission quantum yields. Since the presence of solvents around the naked particles has been necessary for the fluorescence emissions, it may be argued that the solvent molecules provide relatively weak but nevertheless meaningful surface passivation for the suspended carbon nanoparticles. Therefore, there seems no need to differentiate conceptually carbon dots with and without deliberate surface functionalization (or other forms of more effective passivation effects), as the surface passivation simply alters the fluorescence performance, dramatically may be, of the various carbon dots.

The carbon nanoparticles in carbon dots may come from a variety of sources, some even from really unconventional ones. In the original study, carbon soot from laser ablation of a graphitic target, which typically has a higher population of smaller carbon nanoparticles, was used as a precursor for surface passivation in the preparation of brightly fluorescent carbon dots. Since then, many different production strategies have been practiced, including the use of commercially available carbon nanopowders as the starting material to harvest the desired smaller nanoparticles. Among representative syntheses of carbon dots in one-pot was the work by Hu et al. to use direct laser irradiation of graphite powder in an organic solvent (diamine hydrate, diethanolamine, or PEG$_{1500}$ (polyethylene glycol oligomers of 1500 average molecular weight)) under ultrasonication. The carbon dots produced in the solvent diethanolamine exhibited fluorescence quantum yields as high as 7.8% at 420 nm excitation. Bourlinos et al. used thermal carbonization of suitable small molecule precursors, including various ammonium citrate salts, for carbon dots. For example, the citric acid salt was heated in air at 10 °C min$^{-1}$ until it reached 300 °C, held at that temperature for 2 h, to result in water-soluble carbon dots of 7 nm average diameter and a fluorescence quantum yield of 3% at 495 nm excitation. Similarly, Wang et al. synthesized carbon dots via thermal oxidation of a molecular precursor, citric acid specifically, in a molten lithium nitrate salt in an argon atmosphere, followed by the surface passivation reaction with PEG$_{1500}$ (polyethylene glycol oligomers of 1500 average molecular weight). The same approach of thermally carbonizing polymeric nanoparticles into carbon nanoparticles was used by Sun and coworkers. Upon functionalization for effective surface passivation, the resulting carbon dots were found to be similar to those with core carbon nanoparticles from another source (such as laser ablation) in terms of fluorescence performance and related spectroscopic properties.

Liu et al. reported a rather unusual way to harvest carbon nanoparticles in soot from smoldering candles. The soot was treated with a nitric acid solution (5 M), followed by purification with polyacrylamide gel electrophoresis, and the resulting carbon nanoparticles in an aqueous suspension exhibited photoluminescent emissions over a broad color range (Fig. 2), despite their generally low quantum yields (up to 1.9% at 366 nm excitation). Other carbon nanoparticles from somewhat unconventional sources for carbon dots included those from the soot produced by natural gas combustion, or even from food caramels. For the latter by Chattopadhyay and coworkers, amorphous carbon nanoparticles of 4–30 nm size
were obtained by heating bread, jaggery, corn flakes, or biscuits, and the nanoparticles in suspension exhibited photoluminescent emissions (quantum yield of about 1% at 365 nm excitation). These results demonstrated the versatility with carbon dots in terms of their primary structure, namely the core carbon nanoparticle. In other words, photoluminescent emissions represent an intrinsic property of surface-passivated carbon nanoparticles regardless of their origins and precise structures or compositions. However, the effectiveness of the surface passivation does affect the optical performance of carbon dots in a dramatic fashion.

Wang et al. reported that the as-synthesized sample of carbon dots with surface functionalization by oligomeric PEG diamine (PEG1500N, with 1500 denoting average molecular weight of the oligomers) was a mixture, which could be separated on a conventional gel column to obtain fractions of different fluorescence quantum yields. Some of these fractions were found to be highly fluorescent, with quantum yields of 60% or higher for excitation around 450 nm (compared with the quantum yields of 16–20% in the as-synthesized mixture), and their fluorescence brightness could be appreciated by naked eyes (Fig. 3). In fact, the high fluorescence quantum yields coupled with large optical absorptivities make these carbon dots 2–3 times brighter than the corresponding commercially supplied green CdSe–ZnS QDs (Invitrogen “QD525PEG”) at the individual dot level (Fig. 4). It was rationalized that the more fluorescent fractions contained carbon dots of better PEG1500N functionalization and thus more effective surface passivation.

The effective surface passivation to improve the fluorescence performance in carbon dots was also reflected in the work by Sun et al., who doped the core carbon nanoparticle surface with inorganic salts (ZnO, ZnS, or TiO2) in combination with the organic functionalization. The resulting carbon dots (denoted as CZnO-Dots, CZnS-Dots, or CTiO2-Dots) exhibited much brighter fluorescence emissions than those from the corresponding carbon dots without the doping, with the observed quantum yields up to 50%. The inorganic salts have

![Figure 3](image3.png)

**Fig. 3** The absorption and fluorescence (440 nm excitation) spectra of the ultrabright PEGylated carbon dots. Inset: photos under sunlight for solutions of the carbon dots in water and fluorescein in ethanol with matching optical density at 440 and 490 nm, respectively (from ref. 53).

![Figure 4](image4.png)

**Fig. 4** Fluorescence microscopy images (458 nm excitation) of carbon dots in the “as-prepared” sample (left-top) and in the most fluorescent fraction (left-bottom), and images of Invitrogen QD525PEG CdSe–ZnS QDs (right-top). The bar-chart comparison was based on averaging the 300 most fluorescent dots in each of the three samples (from ref. 53).

![Figure 5](image5.png)

**Fig. 5** Top: absorption (ABS) and fluorescence (FLSC, 440 nm excitation) spectra of the “as-prepared” (dash lines) and the most fluorescent fraction (solid lines) of the carbon dots in an aqueous solution (from ref. 55). Bottom: the excitation and emission spectra of the green fluorescent protein (E. coli-generated) (from ref. 56).
augmented the passivation effect of the subsequent organic functionalization.29 In a further effort, Anilkumar et al. fractionated the as-prepared sample of C\textsubscript{ZnS}-Dots on the conventional gel column to obtain carbon dots of observed fluorescence quantum yields up to 78\% at 440 nm excitation. The fluorescence emissions (centered at 540 nm) cover a spectral region similar to that covered by green fluorescence proteins (Fig. 5).56

For the emission mechanism in carbon dots, it was proposed28 and is now increasingly adopted in the research community27,28 that radiative recombinations of the carbon nanoparticle surface-confined electrons and holes (Fig. 6) are responsible for the observed bright fluorescence. The electrons and holes are likely generated by efficient photoinduced charge separations in the carbon nanoparticles, and the role of surface passivation by the organic or other functionalization is probably to make the surface sites more stable to facilitate more effective radiative recombinations. Experimental evidence in support of the mechanistic framework included the fluorescence quenching results with both electron donors and acceptors, which could apparently scavenge the surface-confined holes and electrons in carbon dots, respectively (Fig. 6), to result in efficient and effective quenching of the emissions (diffusion-controlled with additional static contributions).57 Recently, it was also demonstrated that the photogenerated electrons in carbon dots could be used for reduction purposes59,60 and more importantly the electrons could be concentrated into the gold or platinum metal doped on the carbon particle surface (Fig. 6) for the photocatalytic conversion of carbon dioxide and also the photocatalytic splitting of water for hydrogen generation.60,61 These results have reinforced the view that carbon dots essentially resemble nanoscale semiconductors in terms of photoinduced redox processes, in which the radiative recombinations in the absence of quenchers result in bright fluorescence emissions.

### 3 Optical bioimaging

Carbon dots have been evaluated for optical bioimaging applications,28,30,62–66 including their cellular uptakes and the fluorescence brightness in the cellular environment, and their in vivo imaging in mice models in reference to the commercially available CdSe–ZnS QDs in the same models. The results have been very promising.28,30,64,66 Beyond the competitive performance in cellular and in vivo imaging, carbon dots have also been found to be nontoxic from cytotoxicity and in vivo toxicity evaluations.27,61–68

#### Cellular imaging

Carbon dots have been demonstrated for successful uses in the fluorescence imaging of cells,28,63–65 taking advantage of their visible excitation and emission wavelengths, their fluorescence brightness at the individual dot level, and their high photostability. In the original study of carbon dots by Sun et al.,28 the PEGylated carbon dots were incubated with Escherichia coli for the fluorescence staining of the bacteria cells, so were the oligomeric aminopolymer-functionalized carbon dots with Caco-2 cells for internalization (Fig. 7). The confocal microscopy imaging revealed that the endocytosed carbon dots were mostly in the cytoplasm, with only minor penetration into the cell nucleus (Fig. 7).28 The same approach was applied in several...
subsequent studies, including the one by Liu et al. on the labeling of E. coli cells and also murine P19 progenitor cells.44

There have been a number of other studies on using fluorescence to monitor the cellular uptake of various carbon dots.61,65,69–72 For example, Qiao et al. reported the fluorescence detection of carbon dots with surface-passivation by 4,7,10-trioxa-1,13-tridecanediamine (TTDDA) in COS-7 cells.65 After incubation of COS-7 cells with the carbon dots for 24 h, the cell membrane and cytoplasm became brightly fluorescent.65 Similarly, Wang et al. incubated silica-encapsulated carbon dots with BGC823 cells for 24 h, and observed fluorescence in the cytoplasmic area due to the expected penetration of the dots into the cells but not into the nuclei.66 Liu et al. incubated HepG-2 cells with the TTDDA-passivated carbon dots and examined multicolor fluorescence emissions of the dots under different excitation conditions under a laser scanning confocal microscope (LSCM). The carbon dots taken up by HepG-2 cells exhibited bright blue, green, and red emission colors at 405 nm, 488 nm, and 543 nm excitations, respectively.66 Zhu et al. prepared carbon dots from graphene oxide precursors for the imaging of MG-63 cells. Bright fluorescence emissions from the cytoplasm were observed with both 405 and 488 nm excitations.70 Yang et al. synthesized carbon dots by hydrothermal carbonization of chitosan.71 In the imaging of A549 cells with the carbon dots, the fluorescence spots were observed only in the cell membrane and cytoplasmic area, with much weaker signals in the cell nucleus region. Jaiswal et al. used carbon dots from the microwave-mediated caramelization of PEG oligomers to label cells under UV excitation.72 However, the magnification in the imaging was not high enough to determine the dot locations inside the cell.

The available cell imaging results generally suggest that carbon dots taken up by cells are mostly localized in the cytoplasm. However, there were a couple of reports on the internalization of carbon dots in the cell nucleus. According to Ray et al.,69 small carbon nanoparticles from candle soot without any particle surface functionalization (except for the oxidation by 5 M nitric acid) could be endocytosed by EAC cells to be in both cytoplasm and nucleus. After the incubation with the carbon nanoparticles for only 30 min, the EAC cells could be lighted to bright blue-green under UV excitation and yellow under blue excitation. In the former the whole cells were lighted, while in the latter the cytoplasm was brighter than the nucleus (though it was still brighter than in the control cells). Chandra et al. reported that carbon dots tagged with organic molecules (α-naphthylamine, fluorescein, and rhodamine B) were distributed in the whole human red blood corpuscles (RBC), as suggested by results from confocal microscopy.73 For mechanistic explanations on various carbon dots targeting different compartments in cells, which are presently not available, high-resolution imaging experiments are needed to determine more precisely the intracellular distribution of the carbon dots.

Carbon dots are brightly multiphoton fluorescent, with the two-photon cross-sections in the near-IR (800–900 nm) orders of magnitude larger than those in the benchmark organic dyes.74 Therefore, carbon dots are excellent multiphoton fluorescence agents for optical cell imaging, as demonstrated by Cao et al.75 In that reported study, aminopolymer-functionalized carbon dots were taken up by MCF-7 cells after the incubation for 2 h at 37 °C (likely via endocytosis, as no uptake for the same incubation at 4 °C). The internalized carbon dots exhibited bright fluorescence emissions under two-photon excitation with a femtosecond pulsed laser at 800 nm (Fig. 8). Similarly in the imaging of HeLa cells by Li et al.,62 carbon dots were found in lysosome and endosome of the cells.

The presence of surface passivation molecules on the carbon nanoparticles in carbon dots has made it easier for their

![Fig. 8 Two-photon fluorescence microscopy images (pulsed femtosecond laser for 800 nm excitation) of MCF-7 cells with internalized carbon dots (from ref. 29).](Image 3)

![Fig. 9 (a) HeLa cells incubated with carbon dots; (b) the cells incubated with transferrin-coupled carbon dots; and (c) the cells incubated with transferrin-coupled carbon dots after transferrin pre-treatment (from ref. 74).](Image 4)
conjugation with bioactive species for specific applications.\textsuperscript{74} For example, Li \textit{et al.} coupled carbon dots with human transferrin through carbodiimide chemistry, and used the conjugates to target HeLa cells.\textsuperscript{74} The demonstration was such that the carbon dots with the grafted PEG polymer were not able to penetrate the cell membrane, while the conjugates with transferrin exhibited selectivity toward the cancer cells (overexpressed with transferrin receptors) (Fig. 9).

Zhu \textit{et al.} developed a carbon dot-based dual emission hybrid for imaging cellular copper ions.\textsuperscript{75} Carbon dots were functionalized with \textit{N}-\textit{N},\textit{N}′,\textit{N}″-tris(pyridin-2-ylmethyl)ethane-1,2-diamine (abbreviated as AE-TPEA) and then coated with CdSe@SiO\textsubscript{2} QDs. The idea was that Cu\textsuperscript{2+} could quench the fluorescence of carbon dots but not that of CdSe@SiO\textsubscript{2} QDs; thus the latter was used as an internal reference. The hybrid probe was used in the imaging of Cu\textsuperscript{2+} in HeLa cells. Upon the addition of Cu\textsuperscript{2+}, the green fluorescence from carbon dots was significantly inhibited in reference to that of the QDs.\textsuperscript{75} Liu \textit{et al.} used PEI-functionalized carbon dots for gene delivery and bioimaging.\textsuperscript{76} These carbon dots were found to have positive charges on the surface, thus were poly-electrolyte-like to condense DNA. The gene expression of plasmid DNA delivered by the carbon dots was competitive to that by PEI25k in COS-7 cells and HepG2 cells.\textsuperscript{76} Beyond the delivery, the carbon dots were also used for optical imaging. The COS-7 cells were stained by carbon dots after 3 h transfection, and the stained cells exhibited blue, green, and red fluorescence emissions with 405, 488, and 543 nm excitations, respectively. Inside the cells the carbon dots were mostly trapped in endosomal compartments, without any meaningful penetration into the cell nucleus.\textsuperscript{78} In another drug delivery study by Lai \textit{et al.},\textsuperscript{77} carbon dots with PEG functionalization were used for the delivery of the anti-cancer drug doxorubicin (DOX). The DOX loaded on the dots exhibited more toxicity to HeLa cells than free DOX, and the fluorescence imaging results seemed to suggest that the release of DOX from the carrier carbon dots occurred inside the cells.\textsuperscript{77}

The reported studies highlighted above have demonstrated that carbon dots are amenable to various uses in optical cell imaging, with the same or similar protocols as those originally developed and validated for conventional semiconductor QDs. In fact, the brighter carbon dots already exhibited the same or better performances as those achieved by commercially available CdSe-ZnS QDs in imaging comparison at the individual dot level. More evaluations on carbon dots for potential applications such as fluorescence labeling of cells, high-resolution and/or high-sensitivity cellular imaging, drug delivery (especially for the delivery and imaging on the same platform), and single-particle tracking of live cells may be expected.

**Biocompatibility and toxicity**

A distinct advantage of carbon dots is their containing no heavy metal elements, unlike those in presently dominating semiconductor QDs. In fact, carbon nanoparticles have a history of being used in some commercial products, such as automobile tires. With the surface functionalization of the precursor carbon nanoparticles, the resulting carbon dots become soluble (or strictly speaking to form a solution-like dispersion), exhibiting excellent biocompatibility. The available toxicity evaluation results suggest that carbon dots are generally nontoxic or at least no more toxic than the selected oligomeric or polymeric species used as surface passivation agents in the carbon dots.\textsuperscript{37,66–68}

Yang \textit{et al.} performed cytotoxicity evaluations on PEGylated carbon dots and found that these dots were generally nontoxic to the selected cell lines.\textsuperscript{37} In the evaluations, the carbon dots were introduced to HT-29 and MCF-7 cells, with the corresponding free PEG molecules as the control, and the cell proliferation, mortality, and viability were subsequently determined. No meaningful cytotoxicity was found with both carbon dots and the PEG control at relatively lower concentrations, and at higher concentrations the free PEGs were apparently somewhat more toxic to the cells than the PEGylated carbon dots (Fig. 10). The latter was explained in terms of free PEGs similar to surfactants molecules being more damaging to the cell membrane.\textsuperscript{67} Carbon dots with the carbon particle surface functionalized by poly(propyleneethyleneimine-co-ethyleneimine) (PPEI-EI) copolymers, on the other hand, were somewhat more cytotoxic than the PPEI-EI control at relatively higher concentrations.\textsuperscript{45} In that case the carbon dots were considered more as being a delivery vehicle for PPEI-EI into the cells.\textsuperscript{46} In the study by Liu \textit{et al.}, the cytotoxicity of carbon dots with surface-functionalized PPEI-EI of different EI fractions was evaluated, again in terms of determining the proliferation, mortality, and viability of HT-29 and MCF-7 cells.\textsuperscript{67} These results suggested that the cytotoxicity of carbon dots was dependent on the EI fraction in PPEI-EI on the dot surface. The significant role of the
surface passivation molecules in carbon dots in the observed cytotoxicity was further confirmed in the study by Wang et al., on the basis of a direct comparison between carbon dots of different surface passivation agents. However, the good news from these studies is that meaningful cytotoxicity of carbon dots could only be detected at higher concentrations, much beyond those required for optical cell imaging under a conventional fluorescence microscope.

There have been a number of other studies collectively concluding that carbon dots are of no or low toxicity to various cell lines. Chandra et al. evaluated the toxicity of carbon dots to red blood cells by measuring the hemolysis rate. At a concentration of 330 μg mL⁻¹, the carbon nanoparticles with surface carboxyl groups exhibited some toxic effect, but after the coupling with organic molecules the carboxyl groups were converted into amide bonds, with the resulting carbon dots being significantly less toxic. The results again support the notion that the surface functionalization of the core carbon nanoparticles plays a critical role in determining the cytotoxicity of the carbon dots.

For in vivo toxicity evaluation of carbon dots, Yang et al. used a mice model. In the experiment, an aqueous solution of the carbon dots with oligomeric PEG diamine (PEG1500N) on the dot surface was administrated into mice via intravenous injection. Post-administration, the carbon dots did not lead to any clinical symptoms in the mice during the observation period of up to 28 days. These PEGylated carbon dots were ¹³C-labeled in such a way that the carbon nanoparticle core was substantially enriched with ¹³C, which was designed to enable the quantification of carbon dots in various organs in dissected mice by using isotope-ratio mass spectroscopy. Some carbon dots were found in liver, spleen, and kidneys according to the experimentally determined ¹³C/¹²C ratios, though the levels of accumulation were generally low. Serum biochemical parameters such as hepatic (ALT and AST) and renal (UA, BUN and Cr) toxicity indicators were found to be at normal levels (Fig. 11). Histopathological examinations on liver, spleen, and kidneys yielded results consistent with the conclusion that the PEGylated carbon dots are nontoxic in vivo (Fig. 11). At a relatively lower injection level sufficient for optical imaging in vivo, the PEGylated carbon dots post-administration into mice (injection via the tail vein) were cleared via renal excretion within about 24 h. In the liver and kidney specimens from the dissection around that time point, essentially no fluorescent carbon dots were detected in the imaging by confocal fluorescence microscopy.

In a more recent in vivo study by Tao et al., carbon dots synthesized from multi-walled carbon nanotubes as starting materials were radioactively labeled with ¹²⁵I for blood circulation and biodistribution evaluation in mice. The blood circulation of carbon dots followed a two-compartment model, with the first- and second-phase circulation half-lives around 0.1 h and 2 h, respectively. In biodistribution, the intravenously injected carbon dots mainly accumulated in the reticuloendothelial system (RES) organs such as liver and spleen. The kidney uptake of carbon dots was high at early time points, indicating that carbon dots could pass the glomerulus and be excreted by urine. These results were in general agreement with those found in the earlier in vivo study by Yang et al.

Tao et al. also investigated the in vivo toxicology of carbon dots in female Balb/c mice over 90 days. Neither death nor significant body weight change was observed in the treated group of mice, and no obvious signs of toxic effects from the carbon dots were observed at the injected dosage of 20 mg kg⁻¹. Blood biochemistry results based on liver (ALT, AST, ALP and A/G) and renal (BUN) function tests suggested that carbon dots were nontoxic to liver and kidneys in the observation period of

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**Fig. 11** Results from the in vivo (mice) toxicity evaluation of carbon dots: (a) serum biochemistry (the black bars for control mice; top: 1 day, middle: 7 days, and bottom: 28 days post-exposure). (b) Histopathology results (from ref. 37).
up to 90 days. Hematology analyses on various parameters (including white blood cells, red blood cells, hemoglobin, mean corpuscular volume, mean corpuscular hemoglobin, mean corpuscular hemoglobin concentration, platelet count, and mean corpuscular hemoglobin) yielded normal readings in comparison with those of the control. The nontoxic nature of carbon dots was further confirmed by histopathology analyses of liver, spleen, kidney and heart samples.

A conclusion based on the currently available toxicity data is that the intrinsic configuration of carbon dots, namely surface-functionalized small carbon nanoparticles readily aqueous soluble, is nontoxic in vitro and in vivo. Therefore, when considering toxicity issues of carbon dots for specific bio-applications, the emphasis should be on the selection of appropriate nontoxic molecules or species for the carbon particle surface functionalization, as their toxicity profile may dictate that of the resulting carbon dots.

**Optical imaging in vivo**

There have already been demonstrations of the use of carbon dots for fluorescence imaging in vivo.\textsuperscript{30,62,66} Yang et al. were the first to explore the feasibility of carbon dots as a fluorescence contrast agent in mice.\textsuperscript{66} In the experiment, PEGylated carbon dots in an aqueous solution were injected subcutaneously into mice, and the fluorescence images at different excitation wavelengths were collected. There was sufficient contrast for the imaging in both green and red emission colors.\textsuperscript{66} In a more recent study, Tao et al. applied the same protocol to nude mice and obtained similar results.\textsuperscript{66} More specifically, an aqueous solution of carbon dots was injected subcutaneously into the mice, followed by fluorescence imaging with excitations at seven different wavelengths from 455 nm to 704 nm. The best fluorescence contrast was found at 595 nm excitation (Fig. 12).\textsuperscript{66}

Carbon dots have also been explored for fluorescence imaging in mice via other injection modes.\textsuperscript{66} For the sentinel lymph node imaging, the PEGylated carbon dots were injected intradermally into the front extremity, and fluorescence images at 470 nm excitation were collected continuously. Following the injection, carbon dots migrated along the arm to the axillary lymph node (sentinel lymph node, Fig. 13). The observed migration of the carbon dots was slower in comparison with that of the semiconductor QDs, probably due to the smaller sizes of the carbon dots (around 5 nm) and/or the surface PEG functionalization. The axillary lymph nodes were harvested and dissected at 24 h post-injection, and in the specimen fluorescence from the carbon dots could readily be detected (Fig. 13).
In the study by Yang et al., carbon dots were also intravenously injected into mice for whole-body circulation. The mouse abdomen was shaved for fluorescence detection of carbon dots in organs during the circulation. The organs with bright fluorescence emissions readily observed (even by naked eyes, Fig. 14) in about an hour post-injection was the bladder, which must have accumulated a large amount of the intravenously injected carbon dots. At about 3 h post-injection, the urine became brightly fluorescent, consistent with the expected renal excretion of the carbon dots. For other organs including liver, spleen and kidneys, the fluorescence imaging was performed ex vivo. The organs were harvested at 4 h post-intravenous injection, in which the observed fluorescence was generally weak, suggesting a rather low accumulation level of the carbon dots. Between the dissected liver and kidneys, brighter fluorescence was detected in the latter (Fig. 14), consistent with the urine excretion pathway for the carbon dots.

Under the imaging conditions, the carbon dots were photochemically stable, without any significant signal degradation in repeated excitations for the continuous collection of fluorescence images. Li et al. performed a similar ex vivo imaging evaluation on carbon dots. In the evaluation, the blue fluorescent carbon dots were detected in spleen, liver, small intestine, heart, lungs, kidneys, and also brain. The detection of carbon dots in brain was significant, suggesting that the dots might be able to cross the blood–brain barrier.

In a more recent study, Cao et al. made a direct comparison between carbon dots and commercially available CdSe–ZnS QDs for fluorescence imaging in mice. These carbon dots were specifically prepared for relatively higher fluorescence quantum yields, about 60% at 440 nm excitation. In vitro under a confocal fluorescence microscope, the fluorescence brightness was similar between images of the carbon dots and the CdSe–ZnS QDs. In mice following the subcutaneous injections, the fluorescence images were also similar, as illustrated in Fig. 15, suggesting comparable performance of the carbon dots to that of the presently dominating semiconductor QDs for in vivo fluorescence imaging in the specific visible wavelength region.

The evaluation of carbon dots in vivo has only had a good beginning, with much remaining to be explored. However, one conclusion from the still limited body of experimental evidence is that the optical performance of carbon dots is preserved under in vivo imaging conditions. Further investigations on application potentials such as the coupling of carbon dots with bioactive molecules for specific targeting in vivo and their uses in cancer diagnostics and angiography may be expected.

4 Summary and perspectives
Carbon dots have apparently emerged as a new class of fluorescent nanomaterials, already competitive in many respects to conventional semiconductor QDs. As fluorescence agents for optical bioimaging in vitro and in vivo, carbon dots are advantageous in terms of their ready aqueous solubility, physicochemical and photochemical stabilities, high optical performance and non-blinking, and more importantly excellent biocompatibility. A proliferation of more investigations on potential bio-applications of carbon dots in imaging and beyond may be expected. For the further development of carbon dots, the synthesis of carbon dots with bright fluorescence emissions emphasized in the red/near-IR spectral regions, thus more effective in tissue penetration, is desired. Also in need are more studies on the exploitation of the surface functionalization in carbon dots for controlled coupling with bioactive species to enable specific targeting in cellular and in vivo imaging and related biomedical applications. The recent effort on a more unified understanding of fluorescence emissions in carbon dots and other carbon nanomaterials, especially in modified graphene materials, is likely to continue, which should be highly beneficial to the overall development and mechanistic understanding of fluorescent carbon nanomaterials for their serving as more competitive alternatives to conventional semiconductor QDs.

Acknowledgements
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References

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Carbon-core silver-shell nanodots as sensitizers for phototherapy and radiotherapy

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Abstract
Spherical carbon nanoparticles (carbon nanodots) with a silver shell were investigated as potential sensitizing agents. The cytotoxicity of the combination of ultraviolet radiation or x-rays with the nanodots was examined in cancer cells in vitro. The cell viability decreased following the exposure to the radiation. The carbon nanodots enhanced the radiation effects by significantly reducing the amount of surviving cells compared to that of the cells exposed only to the radiation. Carbon-core silver-shell nanodots can be proposed as a bimodal sensitization platform for biological and medicinal applications employing non-ionizing or ionizing radiation.

(Some figures may appear in colour only in the online journal)

1. Introduction
Photodynamic therapy (PDT) is a kind of phototherapy using a combination of non-ionizing radiation and light-sensitive (sensitizing) compounds. Radiotherapy (RT) employs high energy ionizing radiation (x-rays, gamma rays, electrons, protons, light ions) that acts directly on DNA and cellular compartments without sensitizing substances. Both PDT and RT are conventional well-established cancer treatment modalities with their own advantages and disadvantages [1, 2]. While PDT is superior for treatment of skin lesions, RT is used to eradicate tumors inside the body. In PDT a combination of a photosensitizer and optical radiation (visible light) is used. In the absence of radiation the photosensitizer is nontoxic, making PDT a safe method with practically no serious side effects for the patient. However, the tissue penetration of the optical radiation is shallow [1]. Although the clinical potential of PDT is now recognized, the treatment is not fully optimized and more efficient photosensitizers are needed. The ionizing radiation used in RT has the ability to penetrate much deeper into tissues depending on the type and energy of the radiation used (photons, charged particles). Nevertheless, RT is not selective and requires high accuracy in radiation delivery to increase energy deposition in the target tumor, minimizing damage to the surrounding normal tissues. Management of cancer has progressed during recent decades due to improving radiation dose delivery by technological advancement [2]. Nevertheless, despite the fact that RT is one of the most effective cancer treatments many patients still suffer from radiation side effects. One of the possibilities to make RT more effective is to apply the photosensitization concept employed in PDT. A photosensitizer/radiosensitizer would...
selectively absorb the radiation, thus increasing the amount of intracellularly generated free radicals. Conventional porphyrin-type photosensitizers have been evaluated for this purpose but without great success [3, 4]. Nanomedicine is a new rapidly developing area giving promising opportunities in this field [5]. Nanoparticles (NPs) are suitable for this purpose due to their ability to absorb both ionizing and non-ionizing radiation. They could allow improvement of the therapeutic efficacy and minimization of negative effects on healthy surrounding tissues.

Photocatalytic titanium dioxide (TiO$_2$) NPs have been shown as potential photosensitizers in vitro and in vivo [6–8]. Bioconjugation of monoclonal antibodies with TiO$_2$ NPs was demonstrated to improve the photokilling selectivity in cancer cells in vitro [9]. Doping of TiO$_2$ with gold enhances PDT efficacy in vitro [10]. These semiconductor particles are good photocatalytic agents acting according to the first type of photochemical mechanism (through free radicals). Conventional organic (porphyrin-type) photosensitizers act through the second type of photochemical mechanism (through singlet oxygen), which is considered to be the main reaction pathway in PDT. This is probably one of the reasons why NPs have not been considered as good photosensitizers for PDT. The short wavelength (ultraviolet, UV) radiation necessary to excite semiconductor NPs has a very shallow penetration depth in tissues, giving another reason why PDT with TiO$_2$ NPs has not been developed further. However, this obstacle can be bypassed now with new lower bandgap nanomaterials or with other modalities like two-photon PDT, which employs deeper penetrating near infrared radiation [11, 12].

The interaction of photons with matter depends on its density and atomic number. Thus, NPs made of higher atomic number materials are expected to act as x-ray radiosensitizers. Gold NPs are most widely explored as RT agents. Depending on the particle surface coating and radiation source energy they exhibit from modest [13–16] to significant [17, 18] radiosensitizing effect in vitro. Several promising studies with NPs and RT in vivo have been reported [19–21]. Semiconductor NPs represent another group of potential radiosensitizers. The mechanism of radiocatalysis is similar to that of photocatalysis [22, 23] (figure 1). However, semiconductors cannot be as effective as noble metals because the former scatter less ionizing radiation due to their lower atomic number. However, it has been reported that TiO$_2$–Al$_2$O$_3$ or TiO$_2$–BaF$_2$ and ceramic composites can be used as radiocatalysers even with a low dose of ionizing irradiation [22, 24]. The radiosensitizing effect of CdSe semiconductor NPs has also been shown in vitro [25]. Therefore, it is not straightforward to determine in advance which NPs, composed of high or low atomic weight materials, would be efficient radiosensitizers.

In this work we have investigated novel carbon nanodots coated with a silver shell [26]. Such metal-coated carbon nanodots have recently been shown to be effective photocatalysts [27]. Moreover, carbon nanodots are more attractive than TiO$_2$ NPs since the bandgap of the carbon nanodots can be tuned down to lower energies, while the TiO$_2$ bandgap corresponds to the UV region even for a bulk crystal [26]. To the best of our knowledge, this is the first demonstration of the bimodal therapeutic effect of carbon nanodots, which can be applied in both PDT and RT.

2. Experimental and methods

2.1. Nanoparticle synthesis

PEGylated carbon nanodots (carbon nanoparticles with the particle surface functionalized by oligomeric polyethylene glycol diamine, PEG$_{1500}$N) were synthesized according to previously reported procedures [28], with minor modification. Briefly, a carbon nanopowder sample (3 g) was refluxed in an aqueous nitric acid solution (2.6 M, 240 ml) for 24 h. The reaction mixture back at room temperature was dialyzed against fresh water, and then centrifuged at 1000 g to retain the supernatant. The recovered surface-oxidized small carbon nanoparticles were refluxed in neat thionyl chloride for 6 h,
followed by the removal of excess thionyl chloride under nitrogen. The treated carbon particle sample (100 mg) was mixed well with carefully dried PEG1500 (1 g) in a flask, heated to about 180 °C and stirred under nitrogen for 72 h. The reaction mixture was cooled to room temperature, dispersed in water, and then centrifuged at 25 000 g to retain the dark supernatant as an aqueous solution of the as-prepared carbon nanodots.

Carbon-core silver-shell nanodots (C–Ag–PEG) were prepared in an aqueous solution from the PEGylated carbon nanodots. To 9 ml of the solution, AgNO₃ was added to the desired final molar concentration (1.5 mM). To obtain a silver coating on the carbon nanodots the optically transparent initial C–Ag–PEG solution was photoirradiated up to 135 minutes in a photolysis set-up, which included a 450 W Xe lamp and a 425 nm cut-off filter coupled with a bandpass 405–720 nm filter. The Ag-to-C molar ratio was about 0.03. Such stock solution of the ‘as manufactured’ carbon nanodots was further used in cell experiments.

2.2. Transmission electron microscopy

The morphology and size of the C–Ag–PEG NPs were characterized by transmission electron microscopy (TEM) using a JEOL JEM-1230 (Tokyo, Japan) electron microscope (operated at 60–80 kV) equipped with a Morada digital camera (Olympus, Tokyo, Japan). The particle suspension (5 µl) was placed on formvar–carbon grids and allowed to adsorb for 5 min. The grids were washed at least three times with ultrapure water and dried with a paper filter before visualization with the microscope. The images were analyzed with iTEM SIS (Olympus) software.

2.3. Nanoparticle size measurements

The hydrodynamic size of the C–Ag–PEG NPs was measured in PBS (pH 7.4) solution at 25 °C by the dynamic light scattering (DLS) method using a Zetasizer particle analyzer (Nano ZS, Malvern Instruments, Worcestershire, UK). To determine particle size the instrument measures the signal correlation in time of the light scattered at 173° from the sample.

2.4. Spectroscopic measurements

For spectroscopic measurements the NPs were suspended in PBS (7.4 pH) buffer. Absorbance was measured with a UV–vis spectrophotometer (model UV-2550, Shimadzu, Kyoto, Japan) and fluorescence with a fluorescence spectrophotometer (Cary Eclipse, Varian Inc., Mulgrave, Australia). The recorded spectra were fitted with a Gauss function and normalized at the peak maxima.

2.5. Cell viability assay

To evaluate the photosensitizing ability of the NPs in vitro prostate adenocarcinoma cell lines (LNCaP and Du145) and immortalized fibroblasts (F11-hTERT) were used as cancer and normal cell models, respectively. The cells were maintained in 25 cm² dishes (EasyFlask, Nunc, Roskilde, Denmark). The LNCaP and Du145 cells were subcultured twice a week supplementing them with a fresh RPMI-1640 (Sigma Aldrich) growth medium with 10% fetal bovine serum (FBS), 1% penicillin/streptomycin and 1% L-glutamine. The F11-hTERT cells were grown in a DMEM (Lonza) growth medium with 20% FBS, 1% penicillin/streptomycin and 1% L-glutamine.

For irradiation experiments, the cells were harvested from their culture dishes using a routine trypsinization method. For the Du145 line around 3000 cells per well were seeded in 96-well culture plates (Costar, Corning Inc., NY, USA) with 200 µl of growth medium per well. For the LNCaP and F11-hTERT lines around 10 000 cells per well were seeded in 24-well plates (Costar) with 1 ml of growth medium per well. After 24 h the growth medium was changed for a fresh one containing 1 or 2 µl of the nanodot stock solution per 1 ml of growth medium. The wells, which were replaced with a fresh medium without NPs, served as the control group. After 20 h incubation, the cells were washed one time with fresh medium and 200 µl of fresh medium was added to each well. After 2 h the plates were irradiated at different irradiation doses of UV or x-rays. Non-irradiated wells served as the control group. After irradiation, the cells were grown for 24 h in the case of x-ray or 72 h in the case of UV radiation. Afterwards the medium was carefully aspirated from each well and the cells were fixed with ethanol for 15 min. Then the plates were washed several times with distilled water and the cells were stained with 10% methylene blue (MB) in 0.01% NaOH solution for 15 min and washed again with distilled water, to remove the excess of MB. Gradually the plates were dried in air. Finally, 0.1% HCl solution was added to extract MB from the cells to the solution. The optical density at 650 nm was measured for each well with a PowerWave XS2 (BioTek US, Vinooski, VT, USA) plate reader. The cell survival (S) was then assessed as follows:

\[
S = \frac{A_{\text{Control}}}{A_{\text{Treated}}} \cdot 100
\]

where \( A_{\text{Control}} \) and \( A_{\text{Treated}} \) are the optical densities of MB extracted from control and treated cells, respectively.

2.6. Irradiation of cells

For non-ionizing radiation experiments, an in-house built UV lamp emitting 375–410 nm with a peak at 375 nm was used. The lamp fluence rate was 7 mW cm⁻². The fluence rate of the lamp was measured using a SOLO 2 power meter with a PH100-SiUV photodetector (Gentec-EQ, Québec, Canada). Each plate was placed exactly in the same marked area in the middle of the plate, where the fluence rate measurements gave similar readings within this position.

For ionizing radiation experiments, the cells were irradiated with 160 kV x-rays (current 6.3 mA) using a CP 160 x-ray cabinet (Faxitron Bioptics, Tucson, AZ, USA). This x-ray cabinet is designed for irradiation of small rodent animals and cells in a suspension [29]. The instrument has been calibrated for different source-to-sample distances.
In our experiments the SSD was 22.9 cm (shelf position 8), at which the dose rate is 1 Gy min$^{-1}$. One plate at a time for each radiation dose was placed within the center of the indicated area on the tray.

The survival curves were fitted using the multitarget survival probability model [30, 31]

$$\text{Survival(%) = 100 \cdot \left[1 - \left(1 - \exp\left(-\frac{D}{D_0}\right)\right)^n\right]}$$

where $D$ is the delivered radiation dose, $D_0$ is the radiation dose presuming each target is hit at least once, and $n$ is the extrapolation factor showing the number of critical targets necessary to be hit (inactivated) before the cell is killed. From this the quasi-threshold $D_q$ can be calculated as

$$D_q = D_0 \cdot \ln n$$

also known as the survival curve shoulder or quasi-sublethal threshold. The calculations were performed using the SigmaPlot version 11.0 program (Systat Software, Inc., Chicago, IL, USA).

The enhancement ratio of UV or ionizing radiation-induced cell killing by the carbon nanodots was calculated using the following formula:

$$ER_1 = \frac{100 - S_{R+\text{[C]}}}{100 - S_R}$$

where $S_R$ is cell survival after radiation alone, $S_{R+\text{[C]}}$ is cell survival after radiation with the carbon nanodots.

In addition, the potentiation of radiation-induced reduction in cell survival was assessed as follows:

$$ER_2 = \frac{S_R}{S_{R+\text{[C]}}}.$$  

3. Results

In an attempt to find a better photosensitizer and/or radiosensitizer we have studied novel silver-coated carbon nanodots. The investigated carbon nanodots are spherical with an average diameter of 26 nm with a standard deviation of 12 nm as observed by TEM (figure 2). The DLS measurements show that the NPs are quite monodisperse with a hydrodynamic size of about 60 nm (figure 3). These carbon nanodots exhibit fluorescence emission with a peak at about 455 nm under photoactivation at their excitation wavelength of 340 nm (figure 4). The plasmonic band at 405 nm caused by a collective movement of loose electrons differs from the excitation spectrum, which is the characteristic of the nanocrystal due to the quantum confinement effect.

The nanodots were further investigated in cultures of three different human cell lines (prostate adenocarcinoma Du145 and LNCaP, and immortalized fibroblasts F11-hTERT). The tested concentrations of the ‘as manufactured’ carbon nanodots show dose-dependent cytotoxicity to the...
Table 1. Fitting parameters of the PDT survival curves. $R^2$ values are 0.999 (±0.889).

<table>
<thead>
<tr>
<th>Cells</th>
<th>$n$ targets per cell</th>
<th>$D_q (J \text{ cm}^{-2})$ inverse slope</th>
<th>$D_q (J \text{ cm}^{-2})$ curve shoulder</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV +C–Ag</td>
<td>UV +C–Ag</td>
<td>UV +C–Ag</td>
</tr>
<tr>
<td>Du145</td>
<td>∗8 ± 5</td>
<td>4 ± 2</td>
<td>2.6 ± 0.9</td>
</tr>
<tr>
<td>LNCaP</td>
<td>71 ± 11</td>
<td>10 ± 5.0</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>F11-hTERT</td>
<td>3 ± 0.4</td>
<td>1 ± 0.2</td>
<td>4.4 ± 0.4</td>
</tr>
</tbody>
</table>

Figure 5. Cytotoxicity of the C–Ag–PEG nanodots in three different cell lines. Two concentrations were tested: the cells were incubated for 20 h with the growth medium containing 1 µl (C1) or 2 µl (C2) of ‘as manufactured’ nanodots per 1 ml of medium. The cell survival assay was performed 72 h after the incubation.

Figure 6. Survival of the adenocarcinoma cells (Du145, LNCaP) and normal fibroblasts (F11-hTERT) after photodynamic treatment with the C–Ag–PEG nanodots. The cells were incubated with the C1 concentration of the carbon nanodots for 20 h and then exposed to the UV lamp (peak at 375 nm, fluence rate 7 mW cm$^{-2}$). The cell survival assay was performed 72 h after the irradiation.

75 ± 5% survival for the Du145 cells measured 24 h after the incubation.

Exposure of the cells to the UV radiation potentiated cytotoxicity of the carbon nanodots. The survival curve shoulder, the point where cell killing becomes exponential, is smaller for the cells preincubated with the carbon nanodots and then exposed to the UV radiation compared to the cells exposed only to the UV radiation (table 1). The photodynamic efficacy of the nanodots varied in different cell lines (figure 5). The effect was weaker for the LNCaP cells than that for the Du145 cells. About 95% of the cancer cells were photokilled at the UV dose of 7 J cm$^{-2}$ for the LNCaP cells and 5 J cm$^{-2}$ for the Du145 cells. The F11-hTERT cells used as a normal cell model were less sensitive to the therapy: about 75% of the normal cells were photokilled at the UV dose of 8 J cm$^{-2}$. For the Du145 cells optimal cell killing effect is achieved at 2–3 J cm$^{-2}$ while the reduction in cell survival augments with increasing radiation dose (figure 7). The LNCaP and F11-hTERT cells were significantly less responsive than the Du145 cells to the combined effects of the UV radiation and carbon nanodots (figure 7).

Since the Du145 cells were most responsive to the photodynamic treatment, they were chosen for further study of the effects of ionizing radiation. During x-ray irradiation the carbon nanodots also sensitize the cancer cells (figure 8). The carbon dots potentiate RT-induced cell killing by about
Table 2. Fitting parameters of the RT survival curves. $R^2$ values are 0.999.

<table>
<thead>
<tr>
<th>Factor</th>
<th>$n$ targets per cell</th>
<th>$D_0$ (Gy) inverse slope</th>
<th>$D_q$ (Gy) curve shoulder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>RT + C–Ag</td>
<td>RT + C–Ag</td>
<td>RT + C–Ag</td>
</tr>
<tr>
<td>Du145</td>
<td>3 ± 0.1</td>
<td>24.2 ± 0.4</td>
<td>25.7 ± 1.0</td>
</tr>
<tr>
<td>Du145</td>
<td>2 ± 0.1</td>
<td>22.2 ± 1.2</td>
<td>14.5 ± 2.1</td>
</tr>
</tbody>
</table>

Figure 7. Enhancement ratio of UV radiation-induced cell killing ($ER_1$) and radiation-induced survival reduction ($ER_2$) by the carbon nanodots.

Figure 8. Survival of the Du145 cells after RT with the C–Ag–PEG nanodots. The cells were incubated with the C2 concentration of the carbon nanodots for 20 h prior to irradiation with the 160 kV x-rays (dose rate 1 Gy min$^{-1}$). The cell survival assay was performed 24 h after the irradiation.

Figure 9. Enhancement ratio of ionizing (160 kV) radiation-induced cell killing ($ER_1$) and radiation-induced survival reduction ($ER_2$) by the carbon nanodots.

4. Discussion

The mechanism of photocatalysis in semiconductors is well known, and also applies for NPs (figure 1). After light absorption an exciton is formed. An electron in a conduction band can be involved in oxidation processes with adsorbed molecules while a hole from a valence band can participate in reduction processes. It should be noted that on the surface of a small NP both a hole and an electron can be present [23]. This feature is not available on a bulk semiconductor surface where only one species, hole or electron, is present [32]. Due to this exciton relaxation mechanism, free radicals and reactive oxygen species (ROS) can be generated. Usually these are superoxide anion $O_2^-$ and hydrogen peroxide $H_2O_2$.

Deposition of metal islands on the semiconductor NPs can significantly increase the photocatalytic efficacy [33, 34]. This is in general due to a better charge separation because excited electrons accumulate in metal sites while holes in the semiconductor. Due to the high electron density in the coated metal, TEM images of the C–Ag–PEG nanodots show that the silver forms no islands but a uniform layer (figure 2). It is not clear how charges separate and interact in this metal and semiconductor junction. Moreover, noble metals themselves and metal NPs can act as photocatalyzers [35, 36]. Spectroscopy shows that the UV radiation is absorbed by the plasmonic band of the silver layer and the semiconductor-like carbon core (figure 4). Thus the silver coating itself can absorb UV radiation and act as a photocatalyst. Therefore, it is hard to tell which part of the C–Ag–PEG is more responsible for the photocatalytic behavior. Action spectra can give answers...
on the photocatalytic mechanism of the carbon core and metal layer.

The photocatalytic efficiency of the C–Ag–PEG was studied using a UV lamp (375–410 nm, peak emission at 375 nm). UV radiation has very poor penetration in tissues, and in clinical practice its use is thus limited to superficial layers of biological tissues. However, the carbon nanodots used in our study are a good model not limiting its biological applications. By increasing the size of the carbon core we can decrease the band gap and increase the wavelength, thus meeting the needs for deep tissue penetration of the radiation. Decreasing the band gap to some extent reduces the photocatalytic efficacy. Another solution is the use of other modalities like two-photon excitation, which gains the advantage of deep tissue penetration of near infrared radiation [11, 12]. C–Ag–PEG NPs have quite good perspectives as photocatalysts and photosensitizers. By comparing the viability of the cells incubated with free C–Ag–PEG as the control group to that of the cells incubated with the NPs and irradiated with the UV lamp, the NPs were considerably more cytotoxic under irradiation (figure 6). This is, to the best of our knowledge, the first attempt to demonstrate the photocatalytic activity of C–Ag–PEG in vitro. The PDT effect was significantly stronger in cancer cells than in the non-cancer cell line F11-hTERT (figure 6).

Encouraged by these results we have further studied whether these carbon nanodots can be used to increase the biological effects of ionizing radiation. For this purpose we have chosen the Du145 cell line, which was the most responsive cell line in the photosensitization experiment (figure 6). Indeed, the viability of the Du145 cells incubated with free C–Ag–PEG and irradiated with 160 kV x-rays was significantly lower than that of the cells only irradiated with x-rays (figure 7). The mechanism of radiocatalysis in semiconductors is similar to that of photocatalysis (figure 1). The only difference is that in the first case electron(s) can leave the nanocrystal. Such electron ejection depends on the energy that the electron gains after the collision with a high energy photon. If the electron does not leave the nanocrystal the mechanism is basically the same as in photocatalysis (figure 1). If the electron leaves the nanocrystal such an ejected electron in the biological environment close to the NPs can generate ROS like $O_2^-$ such an ejected electron in the biological environment close to the NPs can generate ROS like $O_2^-$. The ejected electrons can generate free radicals and damage vital biomolecules. This quality is achievable only for high Z elements and low energy (keV) radiation. The interaction cross section of photon radiation with matter is dependent on atomic number Z. The photoeffect is proportional to Z$^3$ being dominant for low keV energies, while Compton scattering depends on Z prevailing for high keV energies [38]. Pair or triplet production depends on Z$^2$ being dominant for energies above 1.022 MeV. Thus, the theory predicts that for therapeutic purposes only low energy x-ray radiation together with NPs composed of elements with high Z can ensure radiosensitization. Isotopes like $^{109}$Pd, $^{125}$I, $^{169}$Yb or $^{192}$Ir are examples of radiation in the keV range used in brachytherapy [39]. Gold nanoparticles are the most studied NPs using x-ray sources in the tens to hundreds of keV range [40].

Radio sensitization can be achieved relying on two aspects. Firstly, the photoeffect cross section is higher than that of Compton scattering or pair (triplet) production. According to the ‘Photon Cross Section Database’ of the National Institute of Standards and Technology (NIST) the photon total cross section for silver at 25 keV is about $1.65 \times 10^3$ barn/atom and at 1 MeV only about 1 barn/atom. Therefore, with low energy x-rays more electrons can be ejected from the silver-coated carbon nanodots after the primary event, i.e. the interaction of the photon with an electron. Also, the probability of Auger electron ejection increases when the x-ray energy is lower than the binding energy of a K-shell electron in the target atom [39]. Thus, for low energy photons more electrons are ejected from a single NP and more vacancies (holes) are induced. Secondly, photo or Auger effects generate low energy electrons, which can only travel short distances outside the NPs [41]. The migration distances of such slow energy electrons are comparable to the size of a live cell [42]. This means that the ejected electrons can generate free radicals and damage vital biomolecules without escaping the cell. They can also minimize damage outside cancer cells, increasing therapeutic selectivity. While photo and Auger electrons play a significant role in radiosensitization, it should be noted that the holes produced after electron ejections can also be effective redox centers and beneficial in the radiosensitization process too.

The mechanism of radiosensitization by NPs is a complex and interdisciplinary issue. It cannot be fully understood in terms of radiophysics, cell biology or chemistry alone. One of the aspects is the concept of dose deposition (absorption of radiation) enhancement, a so-called contrast-medium enhanced radiation therapy (CERT) [43]. The concept predicts increase of radiation energy deposition in tumor cells by a contrast agent. A number of theoretical studies have been published on simulation of radiation effects in the presence of NPs within the framework of this aspect. The theory of dose deposition enhancement by gold nanoparticles predicts that about 1% gold NP concentration is necessary to increase kV energy dose deposition by a factor of two [39]. For MV energies the required concentration of gold NPs (∼1500 mg per 1 g of tissue) is not clinically achievable [39]. However, an orders of magnitude lower concentration of gold NPs induces radiosensitizing effects [40]. For such low concentrations the energy absorption consideration predicts tumor dose enhancement by only 1–7% [44]. These simulations assuming non-uniform distribution of NPs in the tissues predict even
lower radiosensitizing effects [45]. When using the energy deposition model a similarly misleading conclusion can be made that the MV energy range is not suitable for NP radiosensitization due to a lack of contrast between tissue and gold for high energies [46]. However, radiosensitization by gold NPs has also been demonstrated for MV energies [13, 47].

The calculated energy dose deposition does not completely describe the experimentally observed biological effects. Therefore, for this purpose it may be necessary to take into account biological factors such as microlocalization of NPs and distribution of molecular targets in a cell. For example, microscopic dose enhancement factors have been calculated for various distances around gold nanoparticles. Within the distance of $5 \mu m$ from a gold NP the enhancement could be about 2–20-fold while for distances further than 30 $\mu m$ the predicted enhancement is only about 5% [48]. Some theories like the local effect model (LEM) [40] and the AuNP radiosensitization predictive model (APR) are available considering cell biology [49]. These calculations predict an increase in low energy photo and Auger electron cascade around NPs for 160 kV and 300 kV radiation, respectively. The simulated decrease in cell survival due to radiosensitization fits well with the experimental data for the two adenocarcinoma cell lines MDA-MB-231 and PC-3 in vitro [40, 49]. It is important to see the biological relevance of these models tailored to different cell lines, nanomaterials and radiation energies.

From the physical point of view, higher atomic number metals have larger radiation interaction cross sections and can scatter more radiation than surrounding biomolecules and, in our case, the carbon core. Therefore, at this moment we do not know which component, silver coating or carbon core, and to what extent gives the radiocatalytic activity, and how charges dissipate and interact in the junction between the metal shell and the carbon core. In this case we can only conclude that the C–Ag–PEG NPs generate ROS and work as radiosensitizers in the Du145 cell line.

NPs are internalized by cells via endocytosis [50, 51]. They can be entrapped in early endosomes, then in late endosomes and finally in lysosomes. We can suggest that the C–Ag–PEG NPs generate free radicals and ROS, which can cause lysosomal rupture and release their contents into cytosol. It has been reported that lysosomes contain proteases that may cause apoptosis [52]. It can also happen that the free radicals generated by the C–Ag–PEG NPs can escape from the endosomes and lysosomes causing damage to vital biomolecules in the cytosol and leading to cell death.

5. Conclusions

In this work a photocatalytic and radiocatalytic system was studied based on pegylated spherical carbon nanodots with a carbon core and a silver shell (C–Ag–PEG). Upon stimulus with external radiation these carbon nanodots sensitize living cells. Comparison of the cell viability before and after exposure to UV radiation suggests that the C–Ag–PEG nanodots are considerably more cytotoxic under irradiation. The viability of cells incubated with the C–Ag–PEG nanodots and irradiated with 160 kV x-rays was significantly lower than that of cells irradiated only with the ionizing radiation. The investigated unique C–Ag–PEG nanodots can be exploited as an activatable system for radiation applications. These results warrant further studies on the intracellular action mechanisms of carbon nanodots.

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Efficient Fluorescence Quenching in Carbon Dots by Surface-Doped Metals - Disruption of Excited State Redox Processes and Mechanistic Implications

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ABSTRACT: The carbon dots in this study were small carbon nanoparticles with the particle surface functionalized by oligomeric poly(ethylene glycol) diamine molecules. Upon photoexcitation, the brightly fluorescent carbon dots in aqueous solution served the function of excellent electron donors to reduce platinum(IV) and gold(III) compounds into their corresponding metals to be deposited on the dot surface. The deposited metals even in very small amounts were found to have dramatic quenching effects on the fluorescence emission intensities, but essentially no effects on the observed fluorescence decays. The obviously exclusive near-neighbor static quenching could be attributed to the disruption of electron−hole radiative recombinations (otherwise responsible for the fluorescence emissions in carbon dots). The results provide important evidence for the availability of photogenerated electrons that could be harvested for productive purposes, which in turn supports the current mechanistic framework on fluorescence emission and photoinduced redox properties of carbon dots.

INTRODUCTION

Small semiconductor nanoparticles and related core−shell nanostructures, generally referred to as quantum dots (QDs) due to the presence of quantum confinement effects, have attracted much attention for their excellent optical properties and a variety of potential applications.† Among well-established QDs are those based on insoluble cadmium salts, especially the popular and now commercially available CdSe/ZnS core−shell nanoparticles with various surface coatings.1−5 However, there have also been some significant concerns on these presently dominating QDs, especially with respect to their toxicity associated with the heavy metal content.6,7 Therefore, the search for alternative QD-like optical nanomaterials that are nontoxic yet still high performance has continued.8−11

Nanoscale carbon particles have recently emerged as a unique class of optical nanomaterials targeting both biomedical and energy conversion applications.11−30 Small carbon nanoparticles upon surface functionalization by organic molecules were found to exhibit bright and colorful fluorescence emissions. These strongly fluorescent nanoparticles, dubbed “carbon dots” (Scheme 1),11 have been demonstrated for their competitive optical performance to that of well-established semiconductor QDs.16,19,30 Carbon dots have also been evaluated for their potential bioimaging applications in vitro and in vivo.15,21,30 For energy conversion, carbon dots are apparently capable of harvesting visible photons to drive catalytic processes to reduce carbon dioxide into formic acid.

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Supporting Information

Scheme 1
and in a similarly photocatalytic process to split water for the generation of hydrogen molecules.29

Mechanistically, the fluorescence emissions in carbon dots are attributed to radiative recombinations of the photoinduced electrons and holes that are confined to the carbon nanoparticle surface,11,19 phenomenologically resembling those found in nanoscale semiconductors. In such a mechanistic framework, more favorable to stronger fluorescence emissions in carbon dots would be a larger ratio of the carbon particle surface to the particle volume, thus carbon nanoparticles of smaller sizes. Also favorable would be diverse energy trapping sites on the carbon nanoparticle surface stabilized more effectively by the passivation agents. The available experimental results are generally in support of the mechanistic framework, including especially those concerning the photoinduced redox properties of carbon dots.18,29 As reported in the literature, carbon dots upon photoexcitation can serve as not only excellent electron acceptors,18 but also electron donors to be responsible for the observed visible-light photocatalytic energy conversion.29 In this regard, small carbon nanoparticles are dramatically different from fullerences as size-wise comparable carbon clusters, since the latter are incapable of donating electrons even in the photoexcited states.31 It is therefore interesting to examine more closely the somewhat unique photoinduced electron donating characteristics in carbon dots, which is particularly relevant to their photocatalytic and other applications.

Fluorescence quenching has been used extensively in the investigation of photoinduced redox processes in fullerenes and other carbon nanomaterials. In this study, we examined the efficient and effective quenching of fluorescence emissions in carbon dots by noble metals on the dot surface, for which the progressive metal coating was achieved in the photoreduction of the corresponding aqueous metal salts. The fluorescence quenching was determined to be exclusively static in nature, as one might predict, attributable to the metallic species deposited on the dot surface interrupting the radiative recombination processes. Thus, the results further support the existing mechanistic framework for the fluorescence emissions and the photoinduced redox properties in carbon dots.

RESULTS AND DISCUSSION

The carbon dots with oligomeric poly(ethylene glycol) diamine (PEG1500N, Scheme 1) as surface functionalization agent were synthesized as previously reported.19 Aqueous solutions of the carbon dots were very stable, with solution colors from yellow at a low concentration to nearly black at a high concentration. The observed optical absorption spectrum was generally broad, so were fluorescence spectra at different excitation wavelengths (Figure 1). As known in the literature, the fluorescence quantum yields in carbon dots are generally dependent on excitation wavelengths, with the highest yield found in the green. For the sample of PEG1500N-functionalized carbon dots in this study, the observed fluorescence quantum yields were about 20% at 440 nm excitation and about 6% at 500 nm excitation (Figure 1).

Optical absorption and fluorescence spectra of the carbon dots in aqueous solution were both stable with respect to photoirradiation (450 W xenon source coupled with filters for the 425–720 nm spectral range and for up to 10 h), with the observed fluorescence spectral profiles and intensities essentially unchanged (within experimental uncertainties generally expected in the photophysics community on measurements of fluorescence quantum yields, Figure 2). The results suggested that there were no meaningful photochemical reactions in the aqueous solution of carbon dots without any other substances. In the presence of a metal salt, however, specifically the platinum(IV) compound H2PtCl6 or gold(III) compound HAuCl4 in the aqueous solution, the same photoirradiation resulted in dramatic decreases in observed fluorescence intensities (or relative quantum yields) over a relatively short period of time (Figure 2), namely substantial quenching of the fluorescence emissions (Figure 2 inset). The minor spectral shifts or changes with the quenching probably reflected the fact that the quenching efficiencies for the various emissions in the fluorescence spectrum of carbon dots were slightly different.

In the experiment for a more systematic examination, an aqueous solution of carbon dots with 0.3 mM of H2PtCl6 was irradiated with visible light (425–720 nm) for various time intervals, and effects of the photoirradiation were monitored by optical absorption and fluorescence measurements on the solution immediately after the photoirradiation. While the absorption of the carbon dots was insensitive to the photoirradiation, the observed fluorescence intensities (thus fluorescence quantum yields) were highly sensitive at all
excitation wavelengths (Figure 3). At 440 or 500 nm excitation of the solution that was photoirradiated with the visible light for only about 10 min, the decrease in fluorescence quantum yields was around 90% (Figure 3), and somewhat less dramatic decrease at 400 nm excitation but still more than 50% (Figure 3). The relationship between the decrease in fluorescence intensities in the photoirradiated solution and the duration of the photoirradiation was apparently dependent on the initial H2PtCl6 concentration in the solution. When a lower H2PtCl6 concentration of 0.012 mM was used, for example, the fluorescence quenching as a function of the photoirradiation time was less dramatic, although still highly efficient (Figure 3).

The replacement of the platinum(IV) compound by HAuCl4 in the aqueous solution of carbon dots for the same photoirradiation resulted in similar but somewhat less efficient fluorescence quenching after the photoirradiation. As shown in Figure 4, the decrease in fluorescence quantum yield in the photoirradiated solution was again more significant for 440 or 500 nm excitation than at 400 nm excitation. Interestingly, however, at 550 nm excitation, the fluorescence quenching as a result of the photoirradiation was overall obviously less significant (Figure 4).

The observed dramatic quenching of fluorescence emissions in carbon dots could not be due to the presence of H2PtCl6 or HAuCl4 in the aqueous solution. In control experiments, the observed fluorescence quantum yields of carbon dots in aqueous solution with 0.3 mM of the Pt(IV) compound after visible light photoirradiation for various periods of time. Shown in the inset are the results (Φf/Φf0 with 500 nm excitation) for different concentrations of the Pt(IV) salt used in the photoirradiation (0.3 mM: △, 0.06 mM: ○, and 0.012 mM: ◊).

Figure 3. The normalized fluorescence quantum yields (Φf/Φf0 with excitation at 400 nm: ○, 440 nm: □, and 500 nm: △) of the carbon dots in aqueous solution with 0.3 mM of the Pt(IV) compound after visible light photoirradiation for various periods of time. Shown in the inset are the normalized fluorescence quantum yields (Φf/Φf0 with excitation at 400 nm: ○, 440 nm: ◊, and 500 nm: △) of the same solution after visible light photoirradiation for various periods of time.

Figure 4. The emergence and increases of the gold plasmon absorption band (around 550 nm) after aqueous solution of the carbon dots with the Au(III) compound was photoirradiated for 15, 270, 330, and 390 min. Shown in the inset are the normalized fluorescence quantum yields (Φf/Φf0 with excitation at 400 nm: ○, 440 nm: ◊, and 500 nm: △) of the same solution after visible light photoirradiation for various periods of time.

The emergence and increases of the gold plasmon absorption band (around 550 nm) after aqueous solution of the carbon dots with the Au(III) compound was photoirradiated for 15, 270, 330, and 390 min. Shown in the inset are the normalized fluorescence quantum yields (Φf/Φf0 with excitation at 400 nm: ○, 440 nm: ◊, and 500 nm: △) of the same solution after visible light photoirradiation for various periods of time.

The deposition of platinum or gold metal on the carbon dot surface due to the dot-catalyzed photoreduction of the corresponding metal salt was confirmed in transmission electron microscopy (TEM) imaging experiments, especially in terms of the Z-contrast mode to take advantage of the significant difference in electron density between carbon and platinum or gold metal (Figure 6). Electron dispersive X-ray spectroscopy (EDX) analyses performed on individual particles in randomly selected regions of the TEM specimen also confirmed the platinum or gold coating, with the observed EDX spectra exhibiting platinum or gold peaks, respectively, in addition to those of carbon, silicon (due to the holder), and copper (from the TEM grid). For even longer photoirradiation times, the amount of deposited metal on carbon dots became sufficient for the resulting samples to be characterized by using X-ray diffraction (Figure 7). The broadness in the diffraction peaks signified the nanoscale nature of the deposited metals on the carbon dot surface.

All of the results described above are consistent with the mechanistic framework of several key features: (1) There is photoinduced charge separation in the small core carbon nanoparticles in carbon dots; (2) The electrons and holes are confined to the surface sites in the dots; (3) The radiative recombinations of the electrons and holes are responsible for the observed fluorescence emissions in carbon dots; (4) The
electrons are capable of reducing platinum or gold salt into the corresponding metal, resulting in the deposition of the metal on the dot surface; and (5) The surface-deposited metal even in small amounts (far below the threshold for the observation of plasmon absorption in case of gold) can effectively quench or almost diminish the fluorescence emissions in the dots. This is probably understandable because the metal deposition is expected to be primarily or at least to initiate at the surface sites that host the electrons, thus particularly effective in interrupting the subsequent photoinduced charge separation and/or radiative recombinations. In such a mechanistic framework, the fluorescence quenching must be static in nature, as confirmed experimentally in terms of the complete decoupling between quenchings in fluorescence quantum yields and lifetimes.

Fluorescence decay measurements on an aqueous solution of carbon dots with surface-deposited platinum or gold metal were performed by using the time-correlated single photon counting (TCSPC) technique. Shown in Figure 8 are the observed fluorescence decays compared with those of neat carbon dots (without any photoirradiation and thus no metal deposition) in aqueous solutions. While the decay curves could not be deconvoluted from the corresponding instrumental response functions by using a monoexponential decay function, the direct comparison between the curves obviously suggests no meaningful quenching effects on the fluorescence decays of carbon dots by the surface-deposited metal. However, the corresponding observed fluorescence quantum yields were reduced dramatically (Figures 3 and 4). The complete decoupling between the effects on fluorescence intensities and decays is classical for pure static quenching, namely that the quenchers are near-neighbors to the emissive species. In this case, the near-neighbor configuration must be absolute with the platinum or gold metal (the quencher) right at the emissive sites on the carbon dot surface, thus the observation of exclusively static fluorescence quenching.

The fluorescence emissions in carbon dots are generally dependent on excitation wavelengths. The different excitation wavelengths might affect the subsequent excited state energy distribution, the charge separation, and/or the confinement of electrons and holes on the dot surface and their radiative decay.
The same data are plotted on linear scale in the insets. and with \( \text{fi} \) intensities, excited at 407 nm, and monitored with 470 nm narrow photogenerated platinum metal deposited on the dot surface, few minutes might be due to contributions beyond the separation processes in carbon dots made the dot surface, which did result in a significant rebound in fluorescence quantum yields and decays toward the presence of the quenchers. The results add more and important support to the current mechanistic framework for fluorescence emissions and their associated photoinduced charge separation and recombination processes in carbon dots.

**EXPERIMENTAL SECTION**

**Materials.** Carbon nanopowder (>99%) was purchased from Sigma-Aldrich, and gold chloride trihydrate (HAuCl₄·3H₂O) and chloroplatinic acid hexahydrate (H₃PtCl₆·6H₂O) from Alfa Aesar. The oligomeric poly(ethylene glycol) diamine (PEG₁₅₀₀₅) was supplied by Anvia Chemicals, and thiouyl chloride (SOCl₂) from Alfa Aesar. Dialysis membrane tubing was acquired from Spectrum Laboratories. Water was deionized and purified by being passed through a Labconco WaterFors water purification system.

**Measurements.** Baxter Megafuge (model 2630) and Beckman-Coulter ultracentrifuge (Optima L-90K with a type 90 Ti fixed-angle rotor) were used in the synthesis of carbon dots. UV–vis absorption spectra were recorded on a Shimadzu UV2501-PC spectrophotometer. Fluorescence spectra were acquired on a Jobin-Yvon emission spectrometer equipped with a 450 W xenon source, Gemini-180 excitation and Tirax-550 emission monochromators, and a photon counting detector (Hamamatsu R928P PMT at 950 V). 9,10-Bis(phenylethynyl)-anthracene in cyclohexane and quinine sulfate in 0.1 M H₂SO₄ were used as standards in the determination of fluorescence quantum yields by the relative method (matching the absorbance at the excitation wavelength between the sample and standard solutions and comparing their corresponding integrated total absorbance intensities). Fluorescence decays were measured on a time-correlated single photon counting (TCSPC) setup with a Hamamatsu stabilized picosecond light pulser (PLP-02) for 407 nm excitation (<100 ps pulses at 1 MHz repetition rate), coupled with a Phillips XP2254/B PMT in a thermoelectrically cooled housing as detector for an overall instrument time resolution better than 500 ps.

**Figure 8.** Observed fluorescence decays (log scale for the fluorescence intensities, excited at 407 nm, and monitored with 470 nm narrow bandpass filter) of the carbon dots in aqueous solution without (—) and with (---) the photodeposited platinum metal (upper) or gold metal (lower). The same data are plotted on linear scale in the insets.
1 000 g to retain the supernatant. The recovered surface-oxidized small carbon nanoparticles were refluxed in neat thionyl chloride for 6 h, followed by the removal of excess thionyl chloride under nitrogen. The treated carbon particle sample (300 mg) was mixed well with carefully dried PEG1000 (3 g) in a flask, heated to 180 °C and stirred under nitrogen for 76 h. The reaction mixture was cooled to room temperature, dispersed in water, and then centrifuged at 25 000 g to retain the dark supernatant as an aqueous solution of the as-prepared carbon dots.

**Photolysis and Fluorescence Quenching.** An aqueous solution of the PEG1000-functionalized carbon dots (observed fluorescence quantum yield about 20% at 440 nm excitation) with targeted optical density was prepared, and to the solution was added H2PtCl6 to the desired final molar concentration. The optically transparent mixture in a cylindrical optical cell with a front and back windows was photoirradiated in the photoysis setup through a 425 nm cutoff filter coupled with a hot filter (405–720 nm transmission) for a varying period of time, followed immediately by absorption and fluorescence measurements of the solution for the monitoring of spectral changes and the determination of fluorescence intensity (quantum yield) quenchings. The same photoysis procedure and conditions were the evaluation on the evaluation on the fluorescence measurements of the solution for the monitoring of spectral changes and determination of fluorescence intensity (quantum yield) quenchings. The same photoysis procedure and conditions were applied to an aqueous solution of the carbon dots with HAgCl4 of the targeted concentration for a varying period of time, followed by the same absorption and fluorescence measurements of the solution for the evaluation on the effect of photoysis. Aqueous solutions of the carbon dots without and with H2PtCl6 or HAgCl4 but no photoradiation were used as controls or references.

**ASSOCIATED CONTENT**

Supporting Information
EDX results of Pt- and Au-coated carbon dot specimens on silicon-based grids, with their corresponding imaged areas (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

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Photoluminescence Properties of Graphene versus Other Carbon Nanomaterials

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CONSPектУS

Photoluminescent nanomaterials continue to garner research attention because of their many applications. For many years, researchers have focused on quantum dots (QDs) of semiconductor nanocrystals for their excellent performance and predictable fluorescence color variations that depend on the sizes of the nanocrystals. Even with these advantages, QDs can present some major limitations, such as the use of heavy metals in the high-performance semiconductor QDs. Therefore, researchers continue to be interested in developing new QDs or related nanomaterials. Recently, various nanoscale configurations of carbon have emerged as potential new platforms in the development of brightly photoluminescent materials.

As a perfect π-conjugated single sheet, graphene lacks electronic bandgaps and is not photoluminescent. Therefore, researchers have created energy bandgaps within graphene as a strategy to impart fluorescence emissions. Researchers have explored many experimental techniques to introduce bandgaps, such as cutting graphene sheets into small pieces or manipulating the π electronic network to form quantum-confined sp2 “islands” in a graphene sheet, which apparently involve the formation or exploitation of structural defects. In fact, defects in graphene materials not only play a critical role in the creation of bandgaps for emissive electronic transitions, but also contribute directly to the bright photoluminescence emissions observed in these materials. Researchers have found similar defect-derived photoluminescence in carbon nanotubes and small carbon nanoparticles, dubbed carbon “quantum” dots or “carbon dots”. However, they have not systematically examined the emissions properties of these different yet related carbon nanomaterials toward understanding their mechanistic origins.

In this Account, we examine the spectroscopic features of the observed photoluminescence emissions in graphene materials. We associate the structural characteristics in the underlying graphene materials with those emission properties as a way of classifying them into two primary categories: emissions that originate from created or induced energy bandgaps in a single graphene sheet and emissions that are associated with defects in single- and/or multiple-layer graphene. We highlight the similarities and differences between the observed photoluminescence properties of graphene materials and those found in other carbon nanomaterials including carbon dots and surface defect-passivated carbon nanotubes, and we discuss their mechanistic implications.

I. Introduction

Graphene and related materials have been studied extensively for their interesting and in many cases unique properties and application potentials.1 While much effort has been focused on electronic characteristics in single- and few-layer graphene sheets, their optical properties including especially photoluminescence emissions have attracted growing recent attention. It is now widely acknowledged that graphene materials could be made photoluminescent over the visible spectral region, extending into the near-IR, though mechanistically various emissions observed experimentally might have different origins. A “perfect” (that found in computer simulations) or nearly perfect single-layer graphene sheet is not photoluminescent for a lack of electronic bandgaps. Therefore, the creation of energy bandgaps has been a popular strategy to impart fluorescence emissions in graphene.2–7 There are obviously many different ways to create or induce the bandgaps, such as cutting graphene...
sheets into small pieces (or producing the pieces directly) or manipulating the $\pi$ electronic network to form sp$^2$ "islands" in a graphene sheet (Figure 1), though most of these are associated with structural defects as well. In fact, one may argue that the formation of islands is in itself a result of specifically engineered defects in the graphene sheet (Figure 1).

Defects and their effects on electronic transitions are apparently at the center of both opportunities (for bright photoluminescence emissions) and complications relevant to the optical properties of graphene and related materials. Some in the carbon nanomaterials research communities have complained about confusions associated with how the observed photoluminescence is attributed or defined, such as how to differentiate fluorescence emissions found in specifically engineered graphene sheets and in "graphene quantum dots". Adding to the complications and confusions is the fact that similar (at least phenomenologically and likely also mechanistically) photoluminescence emissions have been found in carbon nanotubes$^8$ and small carbon nanoparticles (dubbed carbon "quantum" dots or "carbon dots", Figure 1).$^9,10$

In those carbon nanomaterials, bandgap transitions and especially the critical role of structural defects and their passivation by various means have been explored extensively. Thus, there is a need for a systematic examination on photoluminescence emissions in these different yet related carbon nanomaterials toward a global view on the shared or distinctive mechanistic origins.

Here we begin with a classification of the widely reported photoluminescence emissions in graphene materials into two primary categories, followed by an examination on the phenomenological and/or mechanistic similarities and differences between the observed photoluminescence properties in graphene materials and those found in other carbon nanomaterials. The emphases will be on cross references to the emissions in carbon dots and surface defect-passivated carbon nanotubes.

II. A Classification of Observed Photoluminescence Emissions

There have been many literature reports on the observation of photoluminescence emissions in graphene materials, which have been assigned to various origins.$^2,7,11-21$ A closer examination on the spectroscopic features of the emissions and the associated structural characteristics in the underlying materials would suggest that most of the observed photoluminescence emissions could be divided roughly into two categories. One is due to bandgap transitions corresponding to conjugated $\pi$-domains, and the other with more complex origins that are more or less associated...
with defects in the graphene structures. The two categories may be interconnected in many cases, as the creation or induction of the $\pi$-domains is often based on the exploitation or manipulation of defects in graphene sheets.

**Bandgap Fluorescence of Conjugated $\pi$-Domains.** A graphene sheet is characterized by the extended $\pi$-network, which is structurally analogous to an infinitely large planar aromatic molecule, but fundamentally different in terms of electronic transitions. The lack of bandgaps in graphene is on one hand widely considered as being of unique advantages in applications such as nanoelectronics, but on the other hand presents challenges to the community that is more interested in the optical properties of graphene materials. Therefore, much effort has been devoted to making the $\pi$-network in graphene from infinite to finite for the creation of electronic bandgaps. In simplistic terms, this is essentially to isolate conjugated $\pi$-domains that are structurally the same as large aromatic molecules in the graphene sheet, regardless of whether the isolation is through creating $sp^2$ islands in a large sheet or cutting a graphene sheet into small pieces or through other fundamentally similar means or configurations. A popular approach for the creation of $sp^2$ islands has been the reduction of graphene oxides (GOs), which are typically obtained from exhaustively oxidizing graphite under harsh conditions (Hummers method), followed by exfoliation into predominantly single-layer sheets.22 GOs have been used as precursors for the conversion to reduced GOs (rGOs), which possess some of the basic structures found in single-layer graphene sheets. Generally the conversion chemistry for the rGOs with fluorescent $\pi$-domains is controlled to such a degree that there are no $\pi$-connections between the $sp^2$ islands, as that would otherwise result in interisland quenching of the targeted fluorescence emissions.2,16 Among more representative illustrations for such an approach is the one shown in Figure 2 due to Eda et al.2 In that study, GOs were reduced via exposure to hydrazine to recover only partially the graphene $\pi$-network that was destroyed under the extreme oxidation conditions in the reaction for GOs, so that the isolated nanosized $sp^2$ islands were immersed in the $sp^3$ carbon-oxygen matrix (Figure 2), conceptually and phenomenologically equivalent to large aromatic molecules dispersed in nonconjugated carbon-oxygen polymers. These conjugated $\pi$-domains could localize electron-hole pairs, with the created energy bandgaps dependent on domain sizes (Figure 2), as expected.2

A critical requirement for the bandgap fluorescence is that the single-layer configuration must be preserved in the partial conversion to rGOs or in other strategies for creating or inducing isolated $sp^2$ islands in order to avoid any interlayer quenching effects. For example, in the work by Gokus et al., graphene sheets were treated with oxygen plasma etching to impart fluorescence emissions, which were found to be strong in the single-layer sheets but essentially none in the multiple-layer sheets due to significant interlayer quenching.12

Several nomenclatures have been used to describe such an approach of making graphene materials fluorescent by creating or inducing electronic energy bandgaps, capturing various aspects or features of the observed fluorescence emissions. In essence, the approach may be considered as reflecting more of a molecular view on graphene, namely, that a single-layer graphene sheet is used as a precursor for being electronically sliced into isolated $\pi$-conjugated nanoparticles, each of which resembles a large aromatic molecule of a distinctive energy bandgap for both optical absorption and fluorescence emission. Issues that may complicate such a molecular view include the role and consequence of $\pi$-plasmon absorption (common in carbon nanomaterials) into those percolated $sp^2$ islands that are nonemissive, and effects of defects in the graphene sheets, especially in the commonly used ones from partial conversion of GOs. Experimentally, the observed bandgap fluorescence has not
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been so bright in terms of quantum yields (Table 1), generally lower than those of defect-derived photoluminescence emissions in graphene materials.

**Photoluminescence of Defect-Derived Origins.** The creation of electronic energy bandgaps in graphene has been a popular approach to impart fluorescence, but many other observed photoluminescence emissions can hardly be assigned to any bandgap origins. In the bandgap-based fluorescence discussed above, the single-layer configuration and nonpercolation between sp² islands are necessary in order to avoid any significant interlayer and interisland fluorescence quenching effects, respectively. Therefore, the photoluminescence emissions observed in multiple-layer graphene sheets could obviously not be originated from the same kind of conjugated π-domains. An early example for such photoluminescence was in the chemical functionalization of few-layer graphene sheets, where there was significant luminescence interference in Raman characterization of the functionalized samples (Figure 3), similar to what were encountered in the chemical modification or functionalization of carbon nanotubes (Figure 3). In a number of studies on small graphene pieces, including multiple-layer ones, similar photoluminescence emissions were observed (Table 1).

Defects in graphene sheets are loosely defined, probably as a necessary due to a variety of possible structural details.

<table>
<thead>
<tr>
<th>TABLE 1. Photoluminescence Parameters for Selected Graphene Materials</th>
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<tr>
<td>sample source</td>
</tr>
<tr>
<td>from GOs mostly single-layer sheets</td>
</tr>
<tr>
<td>from poly cyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>from GOs small graphene pieces</td>
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<td>from GO-like material</td>
</tr>
<tr>
<td>from GOs butylamine functionalization</td>
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FIGURE 3. Raman results on poly(vinyl alcohol) (PVA) functionalization of few-layer graphene (left, ref 23) and SWNTs (right, ref 24). Adapted from refs 23 and 24 with permission. Copyright 2009 The Royal Society of Chemistry and Copyright 2003 American Chemical Society.

There are sp² and sp³ carbons in the sheets that are not perfect, so that defects are really any sites other than the perfect sp² domains. Many seemingly distinctive photoluminescence emissions in graphene materials have been found, which could not be explained in terms of fluorescent sp² islands or the like. Among representative examples were emissions proposed as being originated from functionalized surface defect sites, those ascribed to CO-related localized electronic states at the oxidation sites after oxygen plasma treatment of graphene, and “quasi-molecular fluorescence” in oxidized graphene arising from carboxylic acid groups electronically coupled with nearby atoms in polycyclic aromatic compound-like moieties. These nonbandgap emissions apparently share a common attribute for their relationships to or even dependence on defects in the graphene materials, though mechanistic details are probably more complex. A characteristic feature in many of the observed photoluminescence emissions was a lack of substantial interlayer quenching, contrary to the critical requirement for being single-layer only for the bandgap fluorescence discussed above. The defect-derived photoluminescence emissions are also generally much brighter, corresponding to higher observed quantum yields (Table 1). For at least those emissions that are sensitive to the passivation of defects in graphene materials, with those well-passivated ones
exhibiting much enhanced emission intensities,\textsuperscript{4,20,21} the observed photoluminescence properties are generally similar to those found in surface-passivated carbon nanoparticles and nanotubes,\textsuperscript{8–10,26–28} thus likely for their sharing the same or similar mechanistic origins.

III. “Graphene Quantum Dots” versus Carbon “Quantum” Dots

Quantum dots (QDs) were originally referred to semiconductor nanoparticles of sizes in the quantum-confined regime (less than the exciton Bohr radius typically in a few nanometers), namely, that excitons in the small particles are confined in the spatial dimensions with quantized energy states. Typical semiconductor QDs are nanocrystals of inorganic compounds from the group II–VI elements in the periodic table. As a result of the quantum confinement, QDs often exhibit unique size- and composition-dependent optical and electrical properties. For example, semiconductor QDs such as CdS or CdSe are well-known for their predictable energy bandgaps at different nanocrystal sizes, corresponding to beautiful fluorescence color variations.\textsuperscript{29}

Surface defects in conventional QDs of semiconductor nanocrystals are generally considered as being undesirable, causing energy "leaks" and other negative effects on the bandgap fluorescence emissions. Therefore, a number of strategies have been developed to minimize the defect-related effects, such as the capping of a semiconductor nanocrystal by another wider-bandgap semiconductor (the particularly famous CdSe/ZnS core–shell nanostructures, for example) to achieve much enhanced fluorescence properties.\textsuperscript{29}

There are obvious similarities between electrons being confined in the conjugated $\pi$-domains in graphene and in nanoscale semiconductor particles, with similar size (dimension) dependent electronic energy bandgaps (Figure 2) and corresponding variations in fluorescence colors. Therefore, the former is conceptually similar to the latter, perhaps logical to be named as graphene quantum dots (GQDs), even though the isolated $sp^2$ islands are structurally not "dots" at all. As for the small graphene pieces, they appear closer to dots, but issues such as effects on or possible contributions to the observed fluorescence emissions by the edges and/or defects still need to be addressed. In fact, the fluorescence color variations with the $\pi$-domain sizes in graphene sheets are less pronounced in comparison with those found in classical semiconductor QDs due to the intrinsic properties of the created or induced energy bandgaps (Figure 2),\textsuperscript{2} and also likely to the expected "contamination" by the defect-derived photoluminescence emissions.
GQDs have also been used in many reports to refer to graphene materials of photoluminescence emissions that are not associated with isolated sp$^2$ islands and thus cannot be assigned to bandgap transitions, but with a somewhat different version of emission color variations (Figure 4). Many of the observed emission properties resemble those found in surface-passivated small carbon nanoparticles (Figure 4), dubbed carbon “quantum” dots or carbon dots (Figure 5),9,10 where the word quantum is in quotation marks for the lack of the same kind of classical quantum confinement found in semiconductor QDs. The only quantum effect in carbon dots seems to be associated with the requirement for the carbon nanoparticles to be small enough to achieve an extremely large surface-to-volume ratio.9

Carbon dots have recently emerged as a new class of brightly photoluminescent (or fluorescent if the proposed electronic transition character is ultimately proven correct) nanomaterials,9,10,26–28,30 with their photophysical properties resemble in many respects those commonly found in semiconductor QDs. A typical carbon dot is a small carbon nanoparticle with the particle surface functionalized by organic molecules or coated with polymers or other species (Figure 5). Spectroscopically, carbon nanoparticles are rather effective in photon-harvesting, with the optical absorptions covering a broad spectral region, which are primarily $\pi$-plasmon in nature.31 Upon the near-UV or visible photoexcitation of even bare carbon nanoparticles without any surface functionalization, relatively weak emissions have been observed in aqueous and other suspensions (Figure 6, where the solvent molecules might have provided some relatively minor surface passivation effect).32,33 With the surface passivation, carbon dots are strongly emissive in the visible, extending into the near-IR (Figure 6). So far the ultrabright carbon dots are those with emissions in the green, marching surprisingly well the spectral coverage of green fluorescence proteins, with experimentally determined emission quantum yields up to more than 75%.27 The observed emission decays in carbon dots are generally not single-exponential, but on average not fast, with averaged lifetimes on the order of 4–5 ns.26 Therefore, in another way to look at the strong optical transitions in carbon dots, the radiative rate constants for the emissions, which are known to reflect on the electronic transition probability, are around $10^8$ s$^{-1}$, much larger than those found in any organic chromophores.

As alluded to above, many of the observed photoluminescence emissions in graphene materials are similar to those in carbon dots in almost all aspects of the spectroscopic properties, including especially the passivation effect for significantly enhanced emission quantum yields (Table 1) and characteristic spectral changes with excitation wavelengths (Figure 4). For example, Shen and co-workers used a mixture of different sized graphene pieces for surface-passivation by polyethylene glycol (PEG). The resulting materials exhibited excitation wavelength dependent photoluminescence.
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emissions that are comparable with those found in carbon dots (Figure 4).21

Structurally, defects in graphene sheets involving sp³ carbons are really no difference in any fundamental fashion from what are on the surface of a small carbon nanoparticle with an extremely large surface-to-volume ratio (Figure 1). It is therefore logical to expect their sharing the same photoluminescence mechanism. For the emission mechanism in carbon dots, it was proposed9,10 and is now increasingly adopted in the relevant research community that radiative recombinations of the carbon nanoparticle surface-confined electrons and holes (Figure 7) are responsible for the observed bright photoluminescence (or simply called fluorescence in such a mechanistic framework). The electrons and holes are generated likely by efficient photoinduced charge separations in the carbon nanoparticles, and the role of surface passivation by the organic or other functionalization is probably to make the surface sites more stable to facilitate more effective radiative recombinations. Experimental evidence in support of the mechanistic framework includes the photoluminescence quenching results with both electron donors and acceptors, which could apparently scavenge the surface-confined holes and electrons in carbon dots, respectively (Figure 7), to result in efficient and effective quenching of the emissions (diffusion-controlled with additional static contributions).34 Recently, it was also demonstrated that the photogenerated electrons in carbon dots could be used for reduction purposes,31,35 and more importantly the electrons could be concentrated into the gold or platinum metal doped on the carbon particle surface (Figure 7) for the photocatalytic conversion of carbon dioxide and also the photocatalytic splitting of water for hydrogen generation.35 These results have reinforced the view that carbon dots essentially resemble nanoscale semiconductors in terms of photoinduced redox processes, in which the radiative recombinations in the absence of quenchers result in bright photoluminescence. For the defect-derived photoluminescence emissions in graphene materials, similar redox-driven quenching processes with both electron donors and acceptors have been reported.14,21 The results are further evidence for the obvious similarities between defect-derived photoluminescence emissions in the different carbon nanomaterials.

In the final analysis of GQDs versus carbon dots, the former has essentially been used loosely in the literature to refer to two rather different categories of photoluminescent graphene materials, those fluorescent due to created or induced electronic energy bandgaps and others that are associated with defects. The defect-derived photoluminescence
emissions in graphene materials are phenomenologically and likely also mechanistically no different from those in carbon dots. Since the emissions due to defects are generally much brighter, with significantly higher quantum yields (Table 1), there is thus the question on how much they contaminate the relatively weaker bandgap emissions in quantized sp² islands (probably more legitimate mechanistically for their being designated as GQDs), as defects obviously play a significant role in the creation or induction of conjugated π-domains in graphene. One might even argue that some of the reported bandgap fluorescence emissions in graphene were actually combinations with defect-derived photoluminescence emissions.

IV. Relevance to Photoluminescence Emissions in Carbon Nanotubes

Carbon nanotubes are a related class of carbon nanomaterials in which both bandgap fluorescence and defect-derived photoluminescence emissions have been found and studied in detail, and thus may serve as references in the understanding of similar emissions in graphene materials. Unlike the created or induced bandgaps in graphene, there are intrinsic energy bandgaps in semiconducting single-walled carbon nanotubes (SWNTs) due to the van Hove singularity in the electronic density of states. The bandgap energies are dependent on nanotube diameters, but generally well into the near-IR spectral region. The mapping of SWNTs with various diameters by using fluorescence spectroscopy has been accomplished. For both SWNTs and their multiple-walled counterparts (MWNTs), the as-produced sootlike samples often contain carbon and other impurities such as residual catalysts, which thus require purification by using oxidative acids or the like. The purification process exaggerates the existing defects and induces new defects in the nanotube structure. These defects become brightly emissive under some specific conditions, especially when functionalized for the purpose of dispersion at the individual nanotube level without bundling or aggregation. For example, Sun and co-workers found strong photoluminescence emissions in carbon nanotubes purified by nitric acid treatment and then functionalized with amino or other polymers or oligomers (Figures 4 and 8), where the functionalization targeted and passivated defects on the nanotube surface. This is both conceptually and practically similar to the passivation effect used in the preparation of carbon dots and also found in graphene materials of enhanced defect-derived photoluminescence emissions (Table 1).

The passivated defects-based photoluminescence emissions in graphene materials, carbon dots, and carbon nanotubes likely share the same mechanistic framework, namely, that the emissions are due to radiative recombinations of trapped electrons and holes. In fact, the photoluminescence emissions in carbon nanotubes are indiscriminative between SWNTs and MWNTs, similar to the same indiscrimination between single- and few-layer graphene sheets for the defect-derived emissions. Unique to SWNTs, however, is the observed strong intertube quenching in nanotube bundles that effectively diminishes both bandgap and defect-derived emissions. This is interesting because MWNTs are essentially tubes that are coaxially stacked, but no “intertube” quenching effects on the defect-derived photoluminescence. It seems that the presence and absence of quenching effects may be understood in terms of the emissive entities in these carbon nanomaterials. The bandgap fluorescence in graphene is associated with the sp² island (the emissive entity)
on a single sheet (Figures 1 and 2), which is quenched by \( \pi \)-domains in neighboring sheets in a few-layer configuration, whereas the defect-derived emissions are associated with the defect site (the emissive entity) across several sheets in a similar few-layer configuration (Figure 1), and thus little affected by the interlayer interactions. The same is true in carbon nanotubes, with SWNTs and MWNTs corresponding to single- and few-layer graphene sheets, respectively, except for no bandgap fluorescence in MWNTs. The photoluminescence emissions from defects (the emissive entity) in both SWNTs and MWNTs are similarly little affected by the rest of the nanotube electronic structures. As for the observed intertube quenching in nanotube bundles, it is mechanistically different, due to the close association of at least two nanotubes, equivalent to interactions between two separate pieces of graphene (either single- or few-layer). Therefore, the quenching behavior in these photoluminescent carbon nanomaterials may be valuable to mechanistic understanding or classification of the observed emissions.

There have been no reports in the literature on interactions between two or more graphene species that result in significant quenching of either bandgap fluorescence or defect-derived photoluminescence emissions. However, the quenching of this kind has been used successfully in probing the debundling of layer graphene sheets, including especially their dispersion in polymeric and other nanocomposite materials.\(^{39,40}\) Obviously, the better the dispersion, the stronger the observed emissions due to the reduction or elimination of any intertube quenching effects. Similar applications for the photoluminescence properties of graphene materials may be expected.

V. Summary

The widely observed photoluminescence emissions in graphene materials may roughly be classified into two primary categories, those originated from created or induced energy bandgaps in a single graphene sheet and others that are one way or another associated with defects in single- and/or multiple-layer graphene. The former conceptually resembles conventional semiconductor QDs, and thus is more appropriately designated as GQDs. However, there seems to be a fundamental difference between these GQDs and conventional semiconductor QDs with respect to effects of structural (surface and/or edge) defects. The defects in QDs of semiconductor nanocrystal particles often act essentially as fluorescence quenchers, so that the passivation in terms of capping the particle surface with another wider-bandgap semiconductor greatly enhances the intrinsic fluorescence emissions in the semiconductor QDs. In GQDs referring to isolated sp\(^2\) islands in a single graphene sheet, the edge or other defects are photoluminescent themselves, with high sensitivity to passivation. In fact, the same defect passivation strategy as used successfully for conventional semiconductor QDs may actually substantially enhance the defect-derived photoluminescence emissions to the extent that would overwhelm the desired bandgap fluorescence in the GQDs. Therefore, because the defect-derived photoluminescence emissions are relatively brighter, there may be a general risk for their contaminating the observed bandgap fluorescence in the GQDs, though a more precise differentiation between the bandgap and defect-derived emission contributions in the GQDs is hardly a trivial task spectroscopically.

The defect-derived photoluminescence emissions in graphene materials, generally bright and enhanced significantly when the defects are effectively passivated, are similar to those found in carbon dots and functionalized carbon nanotubes, and they likely share mechanistic details. The bright emissions in these carbon nanomaterials are valuable to a number of potential technological applications, especially those in biology and medicine. Unlike some presently dominating semiconductor QDs that contain heavy metals such as cadmium, the carbon nanomaterials are generally nontoxic or less toxic, though further evaluations are still needed.

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FOOTNOTES
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REFERENCES
Introduction

Graphene, as a two-dimensional nanoscale sheet with an extended $sp^2$ carbon network, has attracted much recent attention for both fundamental investigations and potential technological applications. The optical properties of graphene and related carbon nanomaterials and nanocomposites have also been widely explored. Graphene sheets are generally produced either top-down by exfoliation of graphite, including an indirect route through oxidation into exfoliated graphene oxides (GOs) followed by reduction, or bottom-up by techniques such as vapor deposition. Pristine graphene is a zero-bandgap material, but to manipulate and control its optical and electronic properties, researchers have devoted much effort to producing non-zero bandgaps. Various approaches for opening energy gaps have been used in graphene materials by creating either defects or isolated nanoscale islands of graphene-like material. These approaches can be separated into two categories, depending on whether this modification is achieved by manipulating the π-electronic network to form $sp^2$ domains in a graphene sample or breaking large graphene sheets into nanoscale pieces.

Linear and nonlinear optical properties of graphene-based materials offer the potential for highly attractive applications in photonics and optoelectronics. For example, photoluminescence associated with induced bandgaps in graphene has been pursued as an alternative to fluorescent quantum dots (QDs). In addition, because of its extended π network, graphene exhibits an excellent nonlinear optical response. Among the various nonlinear optical properties of graphene materials, one of the most widely pursued has been optical limiting, which is important in a number of technologies, from passive manipulation of optical beams to protection against intense laser pulses. In this article, the optical absorption characteristics and photoluminescence properties due to various induced energy gaps and, in some cases, the formation of graphene quantum dots (QGDs) in graphene-based materials are highlighted. Nonlinear optical properties of these materials are reviewed with an emphasis on optical limiting through both nonlinear absorption and scattering mechanisms.

Absorption

Graphene sheets with $sp^2$-hybridized carbon atoms and associated π networks exhibit optical absorption over a broad spectral range from the ultraviolet to the near-infrared, although their insolvability has made solution-phase studies of optical absorption difficult. As with other carbon nanomaterials, including carbon nanotubes and even carbon nanoparticles, π-plasmon absorption plays a major role in photon harvesting by graphene-based materials.

Graphene oxides (GOs) are graphene “derivatives” in which a substantial fraction of the $sp^2$-hybridized carbons are...
converted to \( sp^3 \) hybridization (up to 60% according to Ruoff and coworkers)\(^{20} \) upon typically harsh oxidative treatment such as the Hummers method.\(^{21} \) Aqueous suspensions of GOs (solution-like, Figure 1a) are readily prepared to allow quantitative optical absorption measurements.\(^{17,40,52} \) The solubilized GOs (with primarily single-layer sheets) also serve as excellent precursors in various conversion schemes for the preparation of graphene sheets containing different ratios (purposely or by default) of \( sp^2 \) and \( sp^3 \) carbons.\(^{22,53} \) As a typical example, gradual changes in optical absorption can be used to monitor the transformation of a GO film at various stages of reduction (by hydrazine, in the case of Figure 1b).\(^{22} \) The same strategy was applied to follow the conversion of GOs in a thermal treatment in supercritical fluids at relatively low temperatures.\(^{55} \)

Many other methods of altering the ratios between \( sp^2 \) and \( sp^3 \) carbons have been explored, including the formation of isolated \( sp^3 \) islands in graphene sheets and/or the manipulation of defects (associated with \( sp^3 \) carbons), for the creation and tuning of electronic energy gaps. These nanoscale (often quantum-confined) domains in graphene materials, also referred to as graphene quantum dots (GQDs),\(^{9,22,28,29,54} \) offer distinctive optical absorption and photoluminescence characteristics, as discussed in more detail in the next section. They also generally serve as the basis for nonlinear optical properties in graphene materials. For nonlinear absorption, as an example, GOs in \( N,N \)-dimethylformamide were investigated using 532-nm nanosecond and picosecond pulses in a Z-scan setup, where the nonlinear response is monitored as the sample is moved through the focus of a laser beam.\(^{55} \) The results suggested significant two-photon absorption, especially with picosecond laser pulses. Other studies on nonlinear optical properties in graphene materials are highlighted and discussed later in this article.

**Emission**

Photoluminescence emission from graphene sheets has been reported and classified into several mechanism-based categories.\(^{13,22,24,29,30,34,56–59} \) Among the more classical are those associated with bandgap transitions, where the bandgaps are mostly created by various theoretically established approaches. In fact, opening bandgaps has been a popular way to impart photoluminescence emission to graphene-based materials, for which several strategies have been developed.\(^{9,10,22–31,54,60–63} \)

One of the two primary approaches to opening bandgaps is to physically or chemically treat graphene sheets to reduce the connectivity in the \( \pi \)-electronic network,\(^{24–26} \) including the formation of electron-confined \( sp^2 \) islands in GOs.\(^{7,22,27} \) The other approach is to break graphene sheets into nanoribbons or even small dots.\(^{28–31} \) Because of the expected confinement of electrons in these purposely created nanoscale domains, they are often called GQDs, as discussed above.

A typical example of the first approach is photoluminescence in GOs and reduced GOs (RGOs).\(^{22} \) Specifically, GOs prepared using the Hummers oxidation method were reduced by exposure to hydrazine into RGOs, in which the graphene \( \pi \) network was disconnected, equivalent to the formation of isolated \( sp^2 \) domains (about 3 nm in size edge-to-edge) in the carbon–oxygen \( sp^3 \) matrix (Figure 2a–c). These quantum-sized \( sp^2 \) islands could localize electron–hole pairs and create energy bandgaps, resulting in fluorescence emission through radiative recombination of excitons (Figure 2d). The fluorescence intensities were found to depend on the degree of the reduction treatment in the conversion to RGOs, with significant quenching after extensive treatment. This quenching probably reflects the facilitation of nonradiative excited-state processes by some percolation among the \( sp^2 \) domains.

For a typical example of the second approach, micron-sized graphene sheets were prepared by thermal reduction of GOs, followed by oxidation treatment in concentrated \( H_2 SO_4 \) and \( HNO_3 \) and then hydrothermal processing to yield GQDs of one to three layers and an average lateral size of 9.6 nm.\(^{29} \) Such small dots are known to have strong edge effects due to free zigzag sites commonly with a carbene-like triplet ground state.\(^{30} \) The observed photoluminescence in these GQDs was attributed to bandgap transitions associated with the free zigzag sites in the dots.\(^{13,29} \) Such a mechanism was supported experimentally by the pH dependence of the photoluminescence emission. The emission intensities were enhanced under alkaline conditions but almost completely quenched under acidic conditions as a result of the protonation of the free zigzag sites.

Photoluminescence due to induced bandgaps can also be excited by nonlinear optical processes.\(^{64–67} \) The multiphoton photoluminescence of GO nanoparticles (average sizes around 40 nm) was investigated using laser pulses at 810 nm (~160 fs) and 1215 nm (~160 fs) for two- and three-photon excitation, respectively.\(^{46} \) The photoluminescence spectra were similar to those observed for linear excitation, suggesting

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**Figure 1.** (a) Absorption spectrum of graphene oxides (GOs) in aqueous dispersion. Inset: Photographs of dispersions with low (0.05 mg/ml, left) and high (0.75 mg/ml, middle) GO concentrations and of a GO film on a quartz slide (right). Reproduced with permission from Reference 52. ©2011, Elsevier. (b) Absorption spectra of GO thin films progressively reduced by exposure to hydrazine for total times noted in the legend. Reproduced with permission from Reference 22. ©2010, Wiley-VCH.
that multiphoton excitation also caused electron–hole recombination with energies reflecting quantum confinement in graphitic islands in the GQDs.

Shen et al. reduced GOs with hydrazine hydrate and then surface-passivated the reduced GOs with diamine-terminated oligomeric poly(ethylene glycol) to yield GQDs with sizes of 5–19 nm. They attributed the up-conversion fluorescence in these GQDs to the anti-Stokes process, such that the π electrons are photoexcited to a higher-energy state (lowest unoccupied molecular orbital) and then transition back to a lower-energy state (σ orbital). Nanocomposites of GQDs with TiO$_2$ were investigated for their photocatalytic activities based on up-conversion and down-conversion fluorescence emission. It was proposed that the fluorescence was associated with bandgaps in tiny nanoribbons from the protruding edges in the GQDs.

Photoluminescence observed in GQDs with average lateral diameters of 3–5 nm and an average height of 0.95 nm (thus mostly single- or double-layer species), including that from up-conversion by multiphoton excitation, was attributed to surface energy traps and zigzag sites in the dots.

Other photoluminescence mechanisms in graphene-based materials that are associated with nonlinear optical processes include plasmon emission, nonequilibrium electron-energy distributions, and hot-carrier recombination. It has been suggested that the nonlinear up- and down-converted luminescence emission in graphene and thin graphite species in response to picosecond infrared laser pulses can be attributed to laser-created electron–hole plasmas in these nanomaterials. The nonlinear nature of the observed optical properties was confirmed by the quadratic power dependence of the luminescence emission before saturation at higher laser powers.

As an example of the nonequilibrium electron distribution mechanism, observation of unusually strong broadband nonlinear photoluminescence in graphene upon femtosecond pulsed laser irradiation has been reported. The broad distribution of nonequilibrated electrons and holes, whose radiative recombination was responsible for the photoluminescence emission, was attributed to rapid (within tens of femtoseconds after optical excitation) scattering between photoexcited carriers. The photoluminescence following excitation of single-layer graphene (exfoliated from graphite) by ultrafast laser pulses (30 fs) was found to exhibit a nonlinear dependence on laser excitation power with an exponent of 2.5. The non-linear process was rationalized mechanistically in terms of the electron distribution being driven strongly out of equilibrium by the ultrafast laser excitation.

Hot carriers in graphene-based materials can be generated under intense pulsed laser irradiation, with their recombination resulting in luminescence emission. For example, two-photon...
luminescence emission (peaking at ~590 nm) from GO nanoparticles (around 30 nm) with ultrafast laser excitation has been observed. The emission intensity was found to vary with the incident laser power on a logarithmic scale, and the slope from curve fitting was around 2, as expected (Figure 4).

**Optical limiting**

Optical-limiting materials, or optical limiters, exhibit linear transmittance at low incident light fluences but become opaque at high incident light fluences.37,69–71 Widely pursued limiting mechanisms have included nonlinear absorption (multiphoton, reverse-saturable, or free-carrier absorption) and nonlinear scattering.37,69–72 Various carbon nanomaterials have been developed as optical limiters using both mechanisms, with examples of fullerenes for nonlinear absorption and carbon black suspensions for nonlinear scattering.37,73–78 The recent exploration of graphene-based materials for optical limiting can also be categorized in terms of these mechanisms.35,39,71,79–86

Excellent broadband (450–1064 nm) optical-limiting properties were found for graphene sheets prepared from substoichiometric GOs (sub-GOs, obtained by partially oxidizing graphite using a modified Staudenmaier method).35 When dispersed in heavy-atom solvents such as chlorobenzene or film matrices, these graphene sheets exhibited optical-limiting thresholds down to 10 mJ/cm² at 70% linear transmittance for nanosecond laser pulses. These thresholds are well below the pulse fluences required for microbubble or microplasma formation. Unlike fully oxidized stoichiometric GOs, sub-GOs contain a significant fraction of sp² carbon atoms known to be responsible for bandgap opening and related optical properties and, thus, for the observed nonlinear absorption.35 Mechanistically, this optical limiting was apparently related to the environment surrounding the graphene sheets rather than being an intrinsic property of the absorbing domains in the sheets, according to a comparison between two film matrixes, namely, poly(methyl methacrylate) and polycarbonate. The formation of localized and highly absorbing triplet-like states due to solvent/matrix effects in sub-GOs was proposed.35

Graphene dispersions in organic solvents that were populated by single- and few-layer sheets were prepared for studies of their optical-limiting properties.39 Using open-aperture Z-scan measurements, which show the transmittance decrease arising from nonlinear loss when the focus of a probe laser is moved through a sample, broadband optical-limiting responses to nanosecond laser pulses at 532 nm and 1064 nm were observed. The limiting mechanism was primarily nonlinear scattering associated with the formation of solvent bubbles and microplasma in the graphene dispersions, so the performance was affected by the solvent surface tension, with lower surface tension corresponding to higher scattering intensity and a lower limiting threshold. The solvent surface tension effect was similar to that reported previously for the optical-limiting performance of dispersed carbon nanotubes.71 Another study also suggested that the solvent polarity could affect the optical-limiting performance of graphene materials, by modifying their bonds to solvent molecules.79

Optical-limiting properties of various graphene nanostructures, including GO nanosheets (GONSs) and nanoribbons (GONRs) and graphene nanosheets (GNSs) and nanoribbons (GNRs), were investigated using an open-aperture Z-scan system with nanosecond laser pulses at 532 nm and 1064 nm.80 The optical-limiting performances of the GNSs, GONRs, and GNRs were exceptional, and chemical reduction of these nanostructures to enhance the integrated crystalline structure and electronic conjugation was found to improve their performances even further. The results were explained in terms of both two-photon absorption and nonlinear scattering in the graphene nanostructures.80

Graphene-based nanocomposites have also been explored for optical-limiting applications.80–85 For example, graphene–porphyrin composite materials were examined for their limiting responses toward nanosecond laser pulses at 532 nm, in comparison with those of porphyrin and of graphene.81,82 The improved performance in the nanocomposites was rationalized in terms of enhanced excited-state absorption and multiphoton absorption, as well as nonlinear scattering.81,82 In a pair of similar studies,83,84 optical-limiting properties of graphene–porphyrin and graphene–fullerene nanohybrids were probed using the open-aperture Z-scan technique. The results showed that both nanohybrids performed better than porphyrin, fullerene, or GOs alone, with the graphene–fullerene nanohybrid exhibiting the best performance (Figure 5).84

The proposed optical-limiting mechanism in the nanohybrids was a combination of photoinduced electron and/or energy transfer, reverse saturable absorption, two-photon absorption, and strong nonlinear scattering (the fast growth of hot carbon vapor bubbles

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![Figure 4](https://example.com/figure4.png)  
**Figure 4.** Characterization of graphene oxide nanoparticles (GONs). (a) Two-photon luminescence (TPL) spectrum of GONs (cut off at 660 nm by cascading filters), (b) base-10 logarithmic plot of TPL intensity as a function of laser power (P), giving a slope of approximately 2. Reproduced with permission from Reference 59, ©2012, Wiley-VCH.
due to incandescence and sublimation of graphitic particles) (Figure 5). 84

In another study, GNSs were decorated with CdS quantum dots, and the resulting nanocomposites were investigated for their optical-limiting properties. 85 Limiting thresholds of \( \sim 0.88 \text{ J/cm}^2 \) at 532 nm and \( >6.4 \text{ J/cm}^2 \) at 1064 nm were obtained. Similarly, it has been reported that, in GO–Fe\(_3\)O\(_4\) nanocomposites, the two-photon coefficients and nonlinear refraction coefficients were enhanced by about a factor of three in comparison with those in pristine GOs. 86 The observed optical-limiting threshold of 3.7 \text{ J/cm}^2 at 87% linear transmittance was also better than those of pristine GOs and C\(_{60}\) at high input fluence, which was attributed to strong nonlinear scattering in combination with negative nonlinear refraction and two-photon absorption.

Other nonlinear optical properties

Beyond their use for optical limiting, nonlinear optical absorption and scattering in graphene-based materials have also been investigated with respect to other nonlinear optical phenomena, including nonlinear refraction, spatial self-phase modulation, four-wave mixing, and second-harmonic generation.\(^{36,87-92}\) For example, GOs synthesized from graphite with a controlled degree and location of oxidation were found to have spatially heterogeneous nonlinear optical responses. 86 In Z-scan measurements, the increased pump power resulted in enhanced two-photon absorption of the sp\(^2\) domains in the GOs. It was suggested that the nonlinear optical properties could be altered by changing the relative sp\(^2\) and sp\(^3\) fractions in the GO sheets. 86 Composites of GOs with the sodium salt of poly\{2-(3-thienyl)ethoxy-4-butylsulfonate\} (TPP) were also studied for their nonlinear optical response to femtosecond laser pulses at 800 nm in Z-scan measurements. 87 The results suggested enhanced nonlinear absorption (20 \text{ cm}^3/(\text{GW}^2)) and nonlinear refraction coefficients (0.05 \text{ cm}^2/(\text{GW})) in the GO–TPP composite films. Negative nonlinear refraction due to the self-defocusing effect was also observed. These nonlinear optical enhancements in the GO–TPP films were attributed to multiphoton absorption, excited-state absorption, and charge transfer. 87

Spatial self-phase modulation (SSPM) was observed in a dispersion of exfoliated graphene sheets in organic solvents using various laser sources (ultraviolet, visible, and near-infrared). 88 The apparently coherent light-scattering phenomenon was attributed to the large broadband and ultrafast third-order nonlinearity (\(\chi^{(3)}\)) originating from the Dirac-cone band structure in graphene sheets.

Four-wave mixing measurements were performed to study the coherent nonlinear response of single- and few-layer graphene flakes. 89 An exceptionally large third-order optical susceptibility (\(\chi^{(3)} \approx 10^{-7} \text{ esu}\)) was observed in the near-infrared region, which might be due to interband electron transitions in the graphene sheets, as in SSPM. In a comparison of optical microscopy images of graphene flakes by reflection and four-wave mixing, the nonlinear optical contrast increased with the number of layers (up to six, Figure 6), which was explained in terms of constructive interference of the radiated fields from different graphene layers. Dark nonlinear images were also obtained for graphene flakes with many more layers (\(\gg 20\)), which can be ascribed to the reflection of the incident light and the reabsorption of the nonlinear signals in the thick graphene flakes.

Finally, graphene-based materials have also been explored both theoretically and experimentally for second-harmonic generation (SHG). 90-92 For example, SHG signals (400-nm light) were observed from exfoliated graphene and multilayer graphite films on an oxidized silicon surface when an incident pump pulse laser (800 nm, 150 fs) was applied. 90

Conclusions

In summary, optical properties of graphene sheets and related nanomaterials are mostly associated with induced energy
bandgaps. Therefore, relevant research efforts have been centered on the creation and, in some cases, the manipulation of the bandgaps. Mechanistically, however, further understanding is necessary to clarify the roles of and relationships between isolated (or quantum-confined) π-electronic islands and defects in graphene sheets and derivatives for the observed linear and nonlinear optical responses, as well as the similarities and any fundamental differences in optical properties among graphene materials, carbon nanotubes, and carbon dots. The investigation of the linear and nonlinear optical properties of these graphene-based carbon nanomaterials will facilitate the study of their potential applications in photonics and optoelectronics.

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References
Research Paper

Competitive Performance of Carbon “Quantum” Dots in Optical Bioimaging

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Abstract

Carbon-based “quantum” dots or carbon dots are surface-functionalized small carbon nanoparticles. For bright fluorescence emissions, the carbon nanoparticles may be surface-doped with an inorganic salt and then the same organic functionalization. In this study, carbon dots without and with the ZnS doping were prepared, followed by gel-column fractionation to harvest dots of 40% and 60% in fluorescence quantum yields, respectively. These highly fluorescent carbon dots were evaluated for optical imaging in mice, from which bright fluorescence images were obtained. Of particular interest was the observed competitive performance of the carbon dots in vivo to that of the well-established CdSe/ZnS QDs. The results suggest that carbon dots may be further developed into a new class of high-performance yet nontoxic contrast agents for optical bioimaging.

Key words: Carbon dots, fluorescence, optical bioimaging, quantum dots.

1. Introduction

Small carbon nanoparticles have been shown as versatile precursors for brightly fluorescent nano-dots [1-15], with the observed optical properties in solution phenomenologically similar to and performance-wise comparable with those of the well-established semiconductor quantum dots (QDs) [9,16-19]. Structurally, the fluorescent carbon-based “quantum” dots (or often referred to as carbon dots) are small carbon nanoparticles with relatively simple particle surface functionalization [1,2,7,10,11]. Carbon dots with oligomeric polyethylene glycol diamine (PEG1500, Scheme 1/Figure S1) [20] as the surface functionalization agent were shown to be nontoxic [21], amenable to fluorescence bioimaging applications in vitro and in vivo [10,11,22,23]. More recently, highly fluorescent carbon dots with emission quantum yields more than 50% were obtained by surface-doping the core carbon nanoparticles with an inorganic salt such as ZnS (Scheme 1/Figure S1) or TiO$_2$ [20,24], and/or by applying a gel-column fractionation scheme to the as-synthesized carbon dots samples [9,20]. The brighter dots thus harvested promise more and better opportunities for fluorescence bioimaging, especially for uses in vivo to improve the contrast against tissue background. Here we report an experimental validation on the use of these highly fluorescent carbon dots for imaging in mice, with especially a demonstration on the competitive performance of these dots to that of the well-established semiconductor QDs under purposely matching experimental conditions.

2. Experimental Section

2.1. Materials

Carbon nano-powders, $O,O'$-bis(3-aminopropyl) polyethylene glycol ($M_W \sim 1,500$, PEG$_{1500N}$) and thionyl chloride (>99%) were purchased from Aldrich, zinc acetate dihydrate (Zn(OOCCH$_3$)$_2$•2H$_2$O, >98%) and sodium sulfide (Na$_2$S•9H$_2$O, >98%) from Alfa,
and nitric acid, N,N-dimethylformamide (DMF, 99%), and sodium dodecyl sulfate (SDS, 99%) from VWR. The aqueous CdSe/ZnS quantum dots solution (Qdot® 525 ITK™ amino (PEG) QDs) was acquired from Invitrogen. Millipore Durapore membrane filters (pore size 0.22 μm) and dialysis membrane tubing were supplied by Spectrum Laboratories. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

![Cartoon illustrations of non-doped (left) and doped (right) carbon dots](image)

**Figure S1. (Scheme 1)** Cartoon illustrations of non-doped (left) and doped (right) carbon dots [20].

### 2.2. Measurement

Baxter Megafuge (model 2630) and Beckman-Coulter ultracentrifuge (Optima L90K with a type 90 Ti fixed-angle rotor) were used. UV/vis absorption spectra were recorded on a Shimadzu UV2101-PC spectrophotometer. Fluorescence spectra were measured on a Jobin-Yvon emission spectrometer equipped with a 450 W xenon source, Gemini-180 excitation and Tirax-550 emission monochromators, and a photon counting detector (Hamamatsu R928P PMT at 950 V). Quinine sulfate and 9,10-bis(phenylethynyl)-anthracene were used as standards in the determination of fluorescence quantum yields by the relative method (matching the absorbance at the excitation wavelength between the sample and standard solutions and comparing their corresponding integrated total fluorescence intensities). Atomic force microscopy (AFM) images were acquired in the acoustic AC mode on a Molecular Imaging PicoPlus AFM system equipped with a multipurpose scanner and a NanoWorld point probe NCH sensor. Transmission electron microscopy (TEM) characterization was carried out on Hitachi 9500 TEM and Hitachi HD-2000 S-TEM systems. Confocal fluorescence images were obtained on a Leica laser scanning confocal fluorescence microscope (DM IRE2, with Leica TCS SP2 SE scanning system) equipped with an argon ion laser (JDS Uniphase). The fluorescence imaging in mice was performed on a MAG Biosystems Lumazone FA in vivo Imaging System equipped with an Asahi Max-301 xenon arc source for excitation through a liquid light guide and a Princeton Instruments PIXIS:1024B digital CCD camera system as detector. Band-pass and cut-off filters were used for the selection of excitation and emission wavelengths.

### 2.3. Carbon Dots

A carbon nano-powder sample (2 g) was refluxed in an aqueous nitric acid solution (2.6 M, 200 mL) for 12 h. The mixture back at room temperature was dialyzed against fresh water, followed by centrifuging at 1,000 g to retain the supernatant. The surface-oxidized small carbon nanoparticles recovered from the supernatant (100 mg) were refluxed in neat thionyl chloride for 6 h. Upon the removal of excess thionyl chloride on a rotary evaporator with a vacuum pump, the sample was mixed well with PEG1500N (1 g) in a flask. The mixture was heated to 110 °C, and vigorously stirred at that temperature under nitrogen protection for 3 days. The sample back at room temperature was dispersed in water, followed by centrifuging at 25,000 g to retain the supernatant as an aqueous solution of the as-prepared carbon dots. The sample solution was concentrated and then loaded onto a Sephadex G-100™ gel-column packed in house for fractionation [9]. Fluorescence quantum yields of the fractions were determined, and those more fluorescent were combined into a single aqueous solution of carbon dots (40% in fluorescence quantum yield) for further characterization and bioimaging.

For the surface-doping with ZnS, the surface-oxidized carbon nanoparticles (600 mg) were dispersed in DMF (200 mL) *via* sonication for 30 min, and to the suspension was first added Zn(OOCCH₃)$_2$·2H₂O (680 mg, 3.1 mmol) under vigorous stirring and then slow dropwise addition of an aqueous Na₂S solution (0.62 M, 5 mL) at room temperature. The mixture was centrifuged at 3,000 g, and the precipitate was retained and repeatedly washed with distilled water to obtain the ZnS-doped carbon nanoparticles (881 mg).

The ZnS-doped carbon nanoparticles (200 mg) were dispersed in an aqueous SDS solution (1 wt%, 120 mL) *via* sonication for 30 min. Upon filtration, the filter cake was washed repeatedly with water and then dried. The solid sample was mixed thoroughly with PEG1500N (1.9 g), and the mixture was heated to 110 °C and stirred at that temperature for 72 h under nitrogen protection. The reaction mixture back at...
room temperature was dispersed in water, followed by centrifuging at 25,000g to retain the supernatant as an aqueous solution of as-prepared C$_{ZnS}$-Dots. The sample solution was similarly concentrated and then fractionated on the same Sephadex G-100$^{TM}$ gel-column [20]. Fluorescence quantum yields of the fractions were determined, and those more fluorescent were combined into a single aqueous solution of C$_{ZnS}$-Dots (60% in fluorescence quantum yield) for further characterization and bioimaging.

2.4. Imaging in Mice

All of the animal experiments were performed at Clemson University by strictly following the IACUC (Institutional Animal Care and Use Committee) approved protocols. Female DBA/1 mice (~25 g, acquired from Harlan) were housed in plastic cages (three mice/cage) at the Godley-Snell Research Center at Clemson University and kept on a 12 h light/dark cycle, with food and water provided ad libitum. Following the acclimation of one week, the mice were randomly divided into groups of 3 mice per group for imaging evaluations. Throughout the imaging experiments the mice were kept under anaesthesia (3% isoflurane flow). Two injection modes (subcutaneous and front extremity) were used for the in vivo imaging. Before subcutaneous injection, the back area surrounding the injection point on the mouse was shaved to minimize autofluorescence. The control group in both injection modes was injected with equivalent volume of phosphate buffered saline (PBS). For the front extremity injection, the mice 24 h post-injection were sacrificed by CO$_2$ treatment under anaesthesia. The axillary lymph nodes were dissected for fluorescence imaging. All images were processed and analyzed by using the NIH-commissioned and supplied ImageJ software (http://rsbweb.nih.gov/ij/).

3. Results and Discussion

Small carbon nanoparticles (mostly less than 10 nm in diameter) were harvested from the commercially supplied carbon nano-powders (Aldrich) by first the aqueous nitric acid treatment and then a combination of dialysis to remove impurities and vigorous centrifuging to retain the supernatant. These nanoparticles were functionalized with PEG$_{1500N}$ in classical amidation reaction to yield PEGylated carbon dots (Scheme 1/Figure S1). The as-prepared sample was fractionated on a gel-column (Sephadex$^{TM}$ G-100) to harvest the more fluorescent portion of the sample [9], with the corresponding fluorescence quantum yield in the green of 40% (440 nm excitation, figure 1).

The sample solution was diluted for the preparation of specimens for characterization by microscopy techniques. Both AFM and TEM results showed dot-like images (figure 2), agreeing well with those for carbon dots reported previously [9].

![Figure 1. Absorption (ABS) and fluorescence (FLSC, 440 nm excitation) spectra of the carbon dots without (upper) and with the ZnS doping (lower) in aqueous solutions, with fluorescence quantum yields of 40% and 60%, respectively. In the insets are photos of the corresponding solutions (excitation at 440 nm and emissions monitored through a 530 nm cut-off filter).](http://www.thno.org)
The carbon nanoparticles could be suspended in aqueous solution in a relatively stable fashion, thus serving as nucleation centers in the titration of zinc acetate with sodium sulfide for the formation of ZnS to yield ZnS-doped carbon nanoparticles [24]. The surface-doping level likely varied from particle to particle, so that a surfactant (sodium dodecyl sulfate or SDS)-assisted dispersion procedure in favor of the carbon nanoparticles with more ZnS doping was used to exclude those with no or a negligible level of doping. Subsequently, those nanoparticles with the surface completely covered by ZnS (thus no accessible carboxylic acid moieties on the particle surface for reactions with amino molecules) were discriminated in the functionalization chemistry with PEG$_{1500}$N [20]. The functionalization reaction conditions were similar to those used for carbon dots without the surface doping, resulting in ZnS-doped carbon dots (denoted as C$_{ZnS}$-Dots). According to thermogravimetric analysis (TGA), the estimated core composition in terms of C:ZnS molar ratio in the C$_{ZnS}$-Dots was about 20:1. The as-prepared sample was similarly fractionated on the gel-column to harvest more fluorescent C$_{ZnS}$-Dots [20], with the observed fluorescence quantum yield in the green of 60% (440 nm excitation, figure 1). These dots were diluted for the preparation of specimens for characterization by AFM and TEM, and the representative results are shown in figure 3. The vigorously diluted solution was also used to disperse the dots on cover-glass surface for confocal fluorescence imaging under the same specimen and measurement conditions as those for commercially supplied CdSe/ZnS QDs (Invitrogen Qdot® 525 ITK™ amino (PEG) QDs, fluorescence quantum yield ~60% verified). As shown in figure 4, the well-dispersed C$_{ZnS}$-Dots and the CdSe/ZnS QDs are quite similar in fluorescence brightness at essentially the individual dot level.
The highly fluorescent carbon dots without and with the ZnS doping (quantum yields 40% and 60%, respectively) were evaluated in terms of fluorescence imaging in mice [23]. The animal experiments were performed by strictly following the IACUC (Institutional Animal Care and Use Committee) approved protocols. Female DBA/1 mice (~25 g) were housed in plastic cages (three mice/cage) at the Godley-Snell Research Center for animal research at Clemson University on a 12 h light/dark cycle and provided with food and water ad libitum. Following the acclimation of one week, the mice were randomly divided into groups of three mice per group. For the injection and subsequent imaging, the mice were kept under anesthesia with 3% isoflurane flow.

Before the subcutaneous injection, the back area surrounding the injection point on the mouse was shaved to avoid autofluorescence. The injection volume was kept at 20 µL, with the solution concentration adjusted to match the targeted optical density at the excitation wavelength. As shown in figure 5, fluorescence emissions from the subcutaneously injected dots could readily be detected in a Lumazine FA in vivo imaging system (MAG Biosystems), with a relatively shorter fluorescence collection time and improved imaging contrast in comparison with those in the use of as-prepared less fluorescent carbon dots [23]. The image brightness was obviously higher for the C\textsubscript{ZnS}-Dots sample, consistent with the corresponding higher fluorescence quantum yield in solution. In mice the subcutaneously injected carbon dots diffused relatively slowly, with the gradual fading of fluorescence signals in about 24 h post-injection.

Figure 5. Top: Subcutaneously injected carbon dots (upper spot) and C\textsubscript{ZnS}-Dots (lower spot) of similar optical densities in mice (470 nm and 525 nm band-pass filters for excitation and emission, respectively). Bottom: Subcutaneously injected C\textsubscript{ZnS}-Dots (upper spot) and Invitrogen Qdot\textsuperscript{®} 525 ITK\textsuperscript{TM} amino (PEG) QDs (lower spot) of similar optical densities in mice (434 nm band-pass filter for excitation and 474 nm cut-off filter for emission collection). The color-coded images (right) were processed with ImageJ from NIH.
In a comparison of fluorescence imaging performance with commercially supplied CdSe/ZnS QDs (Invitrogen Qdot® 525 ITK™ amino (PEG) QDs), the concentration of the subcutaneously injected QDs was adjusted such that the optical density was approximately the same as that of the carbon dots \textit{in vivo}. The resulting fluorescence images for C\textsubscript{ZnS}-Dots and the CdSe/ZnS QDs in mice were of similar brightness (figure 5), consistent with their similar fluorescence quantum yields in solution and comparable fluorescence imaging results at the individual dot level (figure 4).

For potential uses of carbon dots for fluorescence imaging \textit{in vivo}, a relatively straightforward demonstration is on tracking the migration of the dots through lymph vessels in mice following the paw injection [23,25,26]. For the highly fluorescent carbon dots without and with ZnS doping (quantum yields 40% and 60%, respectively), they could both migrate along the arm upon their intradermal injection into the front extremity (figure 6). However, the migration of the C\textsubscript{ZnS}-Dots was apparently less pronounced, with the relative brightness in the fluorescence images (figure 6) of the migrated dots suggesting less C\textsubscript{ZnS}-Dots (more fluorescent) migrated. The axillary lymph nodes were harvested and dissected at 24 h post-injection, where strong fluorescence emissions from the carbon dots were observed (figure 6), further confirming the migration of the dots and the preservation of their fluorescence properties \textit{in vivo}.

The improved optical imaging performance of these more fluorescent carbon dots in mice further confirms that the excellent fluorescence properties of carbon dots observed in solutions and on surface at the individual dot level are preserved \textit{in vivo}, suggesting significant application potentials of carbon dots. Particularly encouraging is the fact that the \textit{in vivo} performance of the carbon dots is competitive to that of the well-established CdSe/ZnS QDs, beyond the obvious advantage of carbon dots being nontoxic according to available experimental evaluations [10,11,21,27-29]. The results from this study justify the further development of carbon dots into a new class of high-performance yet benign contrast agents for optical bioimaging.

Figure 6. Intradermally injected carbon dots (upper) and C\textsubscript{ZnS}-Dots (lower) of similar optical densities in mice, with images of dissected lymph nodes in the insets (470 nm and 525 nm band-pass filters for excitation and emission, respectively). The color-coded images (right) were processed with ImageJ from NIH.
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Conflict of Interest

The authors have declared that no conflict of interest exists.

References

Carbon nanoparticles as Chromophores for Photon Harvesting and Photoconversion


1. Introduction

Carbon nanomaterials have generated a tremendous amount of attention in the scientific community. While most of the research and development efforts have been on fullerenes, carbon nanotubes, and graphene sheets, carbon nanoparticles, which are often considered as impurities or unwanted complications in the other carbon nanomaterials, have recently emerged as a unique class of highly fluorescent nano-dots. However, little or no attention has been paid to potential uses of carbon nanoparticles as chromophores in photochemical reactions or for photon harvesting and photoconversion in general. In the study reported herein we demonstrate the chromophore-equivalent functions of aqueous-suspended small carbon nanoparticles in harvesting visible photons for the reductive coating of the nanoparticles with silver and gold and, as a result, the preparation of unique carbon–noble-metal core–shell nanostructures.

2. Results and Discussion

Carbon nanopowders produced from arc-discharge of pure graphite rods were refluxed in aqueous nitric acid (2.6 M) for 12 h, dialyzed in membrane tubing (pore size equivalent to $M_w \sim 500$) against fresh water, and then centrifuged to retain the supernatant as an aqueous suspension of small carbon nanoparticles (generally less than 10 nm according to atomic force microscopy).[13] The oxidative acid treatment converted some of the particle surface-carbons into oxygen-containing moieties, such as alcohols and carboxylic acids, that made the carbon particles more dispersible and thus the aqueous suspension formed more stable.

Herein we demonstrate the chromophore-equivalent functions of small carbon nanoparticles in harvesting visible photons for the reductive coating of the nanoparticles with silver and gold and, as a result, the preparation of unique carbon–noble-metal core–shell nanostructures.
The suspended small carbon nanoparticles were found to be strongly absorptive over the UV/Vis spectral region (Figure 1), with an estimated molar absorptivity at 400–450 nm of around $\varepsilon_{\text{C}_0} = 50 \, \text{M C}_0 \text{cm}^{-1}$ (compared with $\varepsilon_{\text{C}_0} = 16 \, \text{M C}_0 \text{cm}^{-1}$ for $\text{C}_{60}$ at the first absorption band maximum). Therefore, the suspended carbon nanoparticles are indeed excellent chromophores over the UV/Vis spectral region (Figure 1). The stable aqueous dispersion of the nanoparticles was also weakly fluorescent, as reported previously.

The photon-harvesting and photoconversion capabilities of the aqueous suspended carbon nanoparticles were evaluated in terms of their usability as photoreduction agents for the conversion of metal salts to metals. In the reduction of $\text{Ag}^+$ to $\text{Ag}^0$, a stable aqueous dispersion of the carbon nanoparticles in the presence of $\text{AgNO}_3$ (2 mM) was photo-irradiated (450 W xenon arc lamp through a 425 nm cut-off filter to exclude the silver salt and any possible trace impurities in the sample from photoexcitation, and a 720 nm cut-on thermal filter to prevent the sample from being heated) for up to 9 h. Since the reduction due to the photogenerated electrons proceeds on the carbon nanoparticle surface, the surface was coated by the produced $\text{Ag}^0$. The photoelectrochemical process was monitored by the progressive increase in the silver plasmon absorption (Figure 1). No such absorption was observed after photolysis in the absence of carbon nanoparticles under experimental conditions otherwise the same. Quantitatively, the molar absorptivity values for the plasmon absorption peak in different samples (with different $\text{Ag}^0$-coating levels, Figure 1) of the coated carbon nanoparticles were determined by classical inductively coupled plasma (ICP) analyses, and the results were similar between the samples, averaging $1.5 \times 10^6 \, \text{M C}_0 \text{cm}^{-1}$ (where $M_{\text{Ag}_0}$ denotes the molar concentration in terms of silver atoms), suggesting a relative insensitivity of the molar absorptivity to the $\text{Ag}^0$ coating level on the carbon nanoparticles.

The literature provides molar absorptivity values for $\text{Ag}^0$ nanoparticles of different sizes (Figure 2). An interpolation on the plot for the experimentally determined molar absorptivity value given herein for the $\text{Ag}^0$ in coated carbon nanoparticles would correspond to $\text{Ag}^0$ nanoparticles of 2–3 nm in diameter (Figure 2). The overall $\text{Ag}^0$-coated particles though, were larger, but still mostly less than 10 nm with a somewhat broad size distribution, as confirmed by the results from electron microscopy characterization (Figure 3). Therefore, the $\text{Ag}^0$ core–shell nanoparticles obtained from the photolysis were significantly different from neat $\text{Ag}^0$ nanoparticles of the same size in terms of plasmon-absorption properties. However, the electron microscopy results were not consistent with a structure of small (2–3 nm) $\text{Ag}^0$ nanoparticles attached to a larger carbon particle. Instead $\text{Ag}^0$ covers the carbon particle surface in large random patches (Figure 3). Mechanistically, the photoreduction is likely due to electrons confined or trapped at the carbon-particle surface defects, so it may be expected that the surface defect sites are coated with more $\text{Ag}^0$. In this regard, the photoelectroductive coating of a carbon nanoparticle by $\text{Ag}^0$ would make the surface of the resulting core–shell particle smoother.

Transmission electron microscopy imaging of the coated carbon nanoparticles was performed in both the transmission and Z-contrast modes, with the latter being more sensitive to $\text{Ag}^0$ on the carbon-particle surface due to the high Z-number of the metal (Figure 3). The $\text{Ag}^0$-coated carbon nanoparticles
were generally smaller than 10 nm, little affected by the coating level as the variation in the amount of coating was insignificant in terms of changing the overall core–shell particle size. Electron dispersive X-ray spectroscopy (EDX) analyses of individual particles of different sizes confirmed the silver coating, showing the silver peak in addition to those of carbon, silicon (from the holder), and copper (from the TEM grid).

The amount of Ag\textsuperscript{0} coating on carbon nanoparticles could be determined from the plasmon absorption bands (on top of the carbon particle absorption) by using the molar absorptivity value of 1.5 × 10\textsuperscript{4} M\textsubscript{Ag}/atom\textsuperscript{-1} cm\textsuperscript{-1}. For the samples corresponding to the absorption spectra in Figure 1, the Ag\textsuperscript{0}-to-carbon molar ratios varied in a range centered around 0.5%, so the coating level was generally low.

The formation of Ag\textsuperscript{0} was also confirmed by X-ray powder diffraction results (Figure 4), where the diffraction pattern for the face-centered cubic (fcc) phase of Ag\textsuperscript{0} could be identified on top of the pattern for the carbon nanoparticles. Interestingly, the observed diffraction peaks were not so broad, with the Scherrer equation\textsuperscript{34} calculation suggesting particle sizes up to 10 nm. This is likely a result of the Ag\textsuperscript{0} shell shielding X-rays which let the core–shell structures appear as solid Ag\textsuperscript{0} species in the X-ray diffraction measurement. Similar phenomena and results have already been reported in the literature, as those on magnetite nanoparticles with a silver or gold shell.\textsuperscript{35, 36}

Similarly, the reduction of a Au salt to Au\textsuperscript{0} was readily accomplished with photoexcited carbon nanoparticles in aqueous solution, resulting in a gradual coating of the carbon-particle surface with Au\textsuperscript{0}. The photo-irradiation of the aqueous-suspended carbon nanoparticles proceeded in the presence of HAuCl\textsubscript{4} (2 mM) using the same photolysis setup for up to 10 h. The progressive formation of Au\textsuperscript{0} was again monitored by the plasmon absorption (Figure 1). The X-ray diffraction results further confirmed the formation of Au\textsuperscript{0} during the photolysis of carbon nanoparticles (Figure 4), with the observed pattern again corresponding to the fcc phase. The diffraction peaks also not being as broad as expected could be attributed to the shielding effect of the Au\textsuperscript{0} shell.\textsuperscript{34, 35} The molar absorptivity value for the Au\textsuperscript{0} absorption peak (around 530 nm in Figure 1) was determined to be about 2000 M\textsubscript{Au}/atom\textsuperscript{-1} cm\textsuperscript{-1}, which was also largely independent of the coating level in the Au\textsuperscript{0}-coated carbon nanoparticles. According to the size-dependent plasmon absorptivity results already available in the literature (Figure 2),\textsuperscript{21,22–33} this experimentally determined absorptivity value would then correspond to Au\textsuperscript{0} nanoparticles of 2–3 nm in diameter. However, the carbon–Au\textsuperscript{0} core–shell nanoparticles were just as large as the carbon–Ag\textsuperscript{0} ones discussed above, as confirmed by results from electron microscopy characterization (Figure 3). Again the plasmon absorption properties of the Au\textsuperscript{0}-coated nanoparticles (overall less than 10 nm in diameter) are different from those of solid Au\textsuperscript{0} nanoparticles of similar sizes.

The amount of Au\textsuperscript{0} coating on carbon nanoparticles was calculated from the molar absorptivity value, with the estimated Au\textsuperscript{0}-to-carbon molar ratios varying in a range centered around 0.7% for the core–shell structures corresponding to the absorption spectra in Figure 1. Thus the Au\textsuperscript{0}-coating level was also generally low. As discussed above for Ag\textsuperscript{0}-coated carbon particles, the Au\textsuperscript{0} coating should also favor the surface defect sites in the carbon nanoparticles, thus making the shell non-uniform yet smoothing the surface of the overall core–shell structure. The electron microscopy results (Figure 3) were consistent with such a nanoscopic picture, and so were those
from EDX analyses of individual Au\textsuperscript{0}-coated carbon nanoparticles of different sizes.

The fluorescence emissions from small carbon nanoparticles have been attributed to radiative recombinations of surface-confined electrons and holes, generated through charge separation following the photoexcitation of the nanoparticles.\textsuperscript{[9]} The electrons on the carbon nanoparticle surface are likely responsible for the reduction of Ag and Au salts into their corresponding metals, subsequently coating the carbon nanoparticle surface. The reductive coating efficiencies for Ag and Au were rather similar, except for the slower increase in the Au\textsuperscript{0} absorption band upon increased photo-irradiation time (Figure 1), as the per-atom equivalent peak absorptivity is smaller for Au.

3. Conclusions

The results reported here suggest that small carbon nanoparticles serve the function of typical chromophores to harvest visible photons for energy conversions, though the associated coating by the products thus generated (Ag and Au metals in this study) is not a necessary consequence. Nevertheless, this photo-induced redox processes in suspended carbon nanoparticles may also be exploited for other conversions associated with soluble products. The reductive coating of carbon nanoparticles with the metals enables the preparation of unique carbon-metal core–shell nanostructures, whose various potential applications, such as in catalysis or as imaging agents, are currently explored.

Experimental Section

Materials: Graphite rods (purity > 99.9\%) for arc-discharge were supplied by Graphite Store. Silver nitrate (AgNO\textsubscript{3}) and hydrogen tetrachloroaurate trihydrate (HAuCl\textsubscript{4}·3H\textsubscript{2}O) were purchased from Sigma–Aldrich. Dialysis membrane tubing was obtained from Spectrum Laboratories. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

Measurements: Optical absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer. X-ray powder diffraction measurements were carried out on a Scintag XDS-2000 powder diffractometer system. Transmission electron microscopy (TEM) analyses were performed on Hitachi 9500 TEM and Hitachi HD-2000 S-TEM equipment. The quantitative determination of Ag\textsuperscript{0} and Au\textsuperscript{0} contents in various samples in terms of ICP analyses was performed with aqueous solutions of AgNO\textsubscript{3} and HAuCl\textsubscript{4}.

Photolysis: An aqueous dispersion of the carbon nanoparticles with a targeted optical density at 450 nm was prepared, followed by the addition of AgNO\textsubscript{3} to the desired final concentration. The optically transparent mixture was photo-irradiated in a cylindrical optical cell with flat front and back windows in the photolysis setup through a 425 nm cut-off filter for various time periods. The same procedure and conditions were used in the photolysis of aqueous carbon nanoparticles with HAuCl\textsubscript{4}. Control experiments were performed with aqueous solutions of AgNO\textsubscript{3} and HAuCl\textsubscript{4} in the absence of any carbon nanoparticles.

Acknowledgements

This work was supported by the Air Force Research Laboratory through the nanoenergetics program. Additional supports from NSF (Y.-P.S.) and ACS-PRF (Y.-P.S.) are also acknowledged. J.X. was on leave from Changzhou University in Changzhou (China) with a visiting scholarship provided by the National Science Foundation of China (21003015) and the Abroad Scholarship of Jiangsu Province. L.C. was supported by a Susan G. Komen for the Cure Postdoctoral Fellowship. H.Q. was affiliated with and supported by Clemson University Electron Microscope Facility. A.P. was a participant in the Palmetto Academy, an education-training program managed by South Carolina Space Grant Consortium.

Keywords: carbon nanoparticles · chromophores · core–shell nanostructures · photon harvesting · redox chemistry


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Toward quantitatively fluorescent carbon-based “quantum” dots

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Carbon-based “quantum” dots (or “carbon dots”) are generally defined as surface-passivated small carbon nanoparticles that are brightly fluorescent. Apparently, the carbon particle surface passivation in carbon dots is critical to their fluorescence performance. An effective way to improve the surface passivation is to dope the surface of the precursor carbon nanoparticles with an inorganic salt, followed by the typical functionalization with organic molecules. In this work we passivated small carbon nanoparticles by a combination of the surface-doping with nanoscale semiconductors and the organic functionalization, coupled with gel column fractionation to harvest the most fluorescent carbon dots, which exhibited fluorescence emission quantum yields of up to 78%. Experimental and mechanistic issues relevant to potentially further improve the performance of carbon dots toward their being quantitatively fluorescent are discussed.

Introduction

Among optical materials, those that are strongly fluorescent have attracted much attention for their variety of applications from display technologies to biology and medicine. In the development of fluorescent nanomaterials, a major milestone was the discovery of semiconductor quantum dots (QDs), which are defined in general as nanoscale semiconductor particles with physical dimensions smaller than the exciton Bohr radius for the quantum-confinement effect.1–4 It seems that the rationale for the use of QDs over organic dyes is now generally accepted in the literature.5,6 However, despite the many widely acknowledged advantages of QDs, such as bright fluorescence, high photostability, and resistance to metabolic degradation in bio-applications,7–10 most of the high-performance QDs require the use of heavy metal elements such as cadmium, whose known toxicity may prove to be a major disadvantage.11–13 In fact, a number of studies have suggested that QDs containing heavy metals are toxic to vertebrate systems at relatively low concentrations,14,15 and that there may also be risks with the bioaccumulation of these toxic materials in organs and tissues.15,16 Extensive efforts have been made on encapsulating QDs in benign delivery vehicles to minimize their harmful biological and environmental effects, as well as on the development of non-toxic or much less toxic fluorescent nanomaterials as alternatives to the semiconductor QDs. In this regard, the recent finding17 and subsequent development of carbon-based “quantum” dots (dubbed “carbon dots”) are particularly encouraging, with their known optical properties and already available performance demonstrations suggesting great application potentials.18–24

Carbon dots are surface-passivated small carbon nanoparticles (Scheme 1),17 from which the fluorescence is likely due to surface energy trapping sites and their associated radiative recombinations.20,25 Therefore, despite the absence of the traditional quantum confinement effect in carbon dots, the requirement for particles to be “quantum-sized” in semiconductor QDs is also applicable to the core carbon particles in order to ensure a very large surface-to-volume ratio for bright fluorescence emissions.17 Carbon dots are highly stable photochemically, exhibiting no optical blinking.17 According to available results from biological evaluations in vitro and in vivo, carbon dots are non-toxic to cells and mice,23,26,27 amenable to serving as fluorescence probes in optical bioimaging.18,28

The carbon particle surface passivation in carbon dots is apparently critical to their fluorescence performance. For carbon dots with the surface passivation by oligomeric poly(ethylene
results relevant to potentially further improving the performance of carbon dots are discussed.

Results and discussion

Neat carbon nanoparticles were refluxed in aqueous nitric acid to oxidize some of the surface carbons into carboxylic acids. The resulting particles in aqueous suspension were fractionated gravimetrically for the harvesting of those mostly smaller in size (5 nm or less). These small carbon nanoparticles could be suspended in aqueous solutions in a relatively stable fashion, thus serving as nucleation centers in the titration for the formation of ZnS or TiO2 to yield ZnS- or TiO2-doped carbon nanoparticles, respectively. The surface-doping was probably not uniform among different nanoparticle samples, more likely with varying doping levels from particle to particle. A surfactant-assisted dispersion procedure in favor of the precursor carbon nanoparticles with inorganic salts such as ZnS or ZnO, followed by the same functionalization with PEG1500N molecules to obtain surface-doped carbon dots (denoted as C\textsubscript{ZnS}-dots or C\textsubscript{ZnO}-dots, respectively, Scheme 1). These dots with their core carbon nanoparticles surface-passivated by a combination of inorganic and organic moieties exhibited significantly enhanced fluorescence performance. A logical question was then how much the surface passivation could be further improved toward quantitatively fluorescent carbon dots. In the work reported here, we passivated small carbon nanoparticles by a combination of doping (surface coating but not to the level of forming a shell) with nanoscale semiconductors and organic functionalization, coupled with gel column fractionation to harvest the most fluorescent carbon dots, which exhibited fluorescence emission quantum yields of up to 78%. Experimental and mechanistic issues relevant to potentially further improving the performance of carbon dots are discussed.

UV/vis absorption spectra of the as-prepared C\textsubscript{ZnS}-dots and C\textsubscript{TiO2}-dots samples in aqueous solutions are shown in Fig. 1. The spectra are characterized by a similar shoulder in the blue (420–450 nm), which has been observed in other surface-doped carbon dots and also in some non-doped carbon dots (Fig. 1). The excitation into the absorption shoulder resulted in strong fluorescence emissions around 510 nm for both C\textsubscript{ZnS}-dots and C\textsubscript{TiO2}-dots solutions, again similar to those observed previously for other carbon dots (Fig. 1). There were some variations in fluorescence quantum yields for the as-prepared C\textsubscript{ZnS}-dots and C\textsubscript{TiO2}-dots samples from batch to batch, due likely to the inhomogeneity in each sample (containing various fractions of dots with different surface morphologies in terms of the surface-doping and organic functionalization chemistry), but all consistently higher than 30%.

The as-prepared C\textsubscript{ZnS}-dots and C\textsubscript{TiO2}-dots samples in aqueous solutions were fractionated on a gel column (Sephadex\textsuperscript{TM} G-100) to harvest the most fluorescent fraction from each of the samples. As shown in Fig. 1, the blue shoulder in the absorption spectra of these fractions is more pronounced than that in the as-prepared C\textsubscript{ZnS}-dots and C\textsubscript{TiO2}-dots samples, though the corresponding fluorescence spectra remain similar. However, the observed emission quantum yields for the most fluorescent C\textsubscript{ZnS}-dots and C\textsubscript{TiO2}-dots were much higher than those for the as-prepared samples, up to 78% for C\textsubscript{ZnS}-dots and 70% for C\textsubscript{TiO2}-dots. In fact, the bright fluorescence from these solutions could be appreciated visually under natural light. Shown in Fig. 2 are comparisons of the C\textsubscript{ZnS}-dots and C\textsubscript{TiO2}-dots solutions with the nearly quantitatively fluorescent fluorescein solution under sunlight and with the excitation of monochromated light from a xenon arc source.

Fluorescence decays of C\textsubscript{ZnS}-dots and C\textsubscript{TiO2}-dots were measured by using the time-correlated single photon counting (TCSPC) technique. For the most fluorescent C\textsubscript{TiO2}-dots, as an example, the observed decay curve was similar to that of the
highly fluorescent non-doped carbon dots reported previously (Fig. 3). The decay could only be fitted by a multi-exponential function with an average lifetime of about 6 ns. On average, therefore, the fluorescence lifetimes are not long, despite the observed high fluorescence quantum yields. The corresponding average fluorescence radiative rate constant $k_F$ is more than $1 \times 10^8$ s$^{-1}$, which is considerably larger than those typically found in organic fluorophores, suggesting extraordinarily high electronic transition probabilities in these carbon-based fluorescent dots.

The highly fluorescent samples of $C_{\text{ZnS}}$-dots and $C_{\text{TiO}_2}$-dots were characterized by microscopy techniques for an understanding of their structural parameters. As shown in Fig. 4 for results from the transmission electron microscopy (TEM) analysis of the $C_{\text{ZnS}}$-dots sample, the individual dots were well-dispersed, with an average particle size of about 5 nm. The ZnS doping in the dots was visible in the high-resolution TEM images (Fig. 4), so was the TiO$_2$ doping in $C_{\text{TiO}_2}$-dots (Fig. 5). The sizes of $C_{\text{TiO}_2}$-dots were also around 5 nm according to atomic force microscopy (AFM) imaging results (Fig. 5).

Mechanistically, the fluorescence emissions in carbon dots are attributed to radiative recombinations of the carbon particle surface-trapped electrons and holes, where the large surface (relative to the particle volume) and diverse surface energy trapping sites in the small carbon nanoparticles are stabilized by the surface passivation agents. Within such a mechanistic framework, the enhanced fluorescence performance in nanoscale semiconductor-doped carbon dots (more specifically $C_{\text{ZnS}}$-dots and $C_{\text{TiO}_2}$-dots in this study) may be rationalized in terms of improved surface passivation by a combination of inorganic surface-doping and organic functionalization, as well as probably more diverse surface sites as a result of the doping (thus facilitating more effective trapping of electrons and holes on the particle surface). There seem to be several issues (or opportunities at the same time) for further investigations to improve the presently highly fluorescent carbon dots toward being quantitatively fluorescent (quantum yields close to one hundred percent). One is on the selection of the dopant, for which nanoscale semiconductors are advantageous but apparently not necessary. Structural and/or material parameters such as the compatibility of the selected inorganic salt with the carbon nanoparticle surface may play major roles in determining the fluorescence performance of the resulting carbon dots. Another issue is on the relative quantities of the inorganic and organic surface passivation moieties, or perhaps even their mutual
compatibility on the carbon nanoparticle surface. These are obviously not easy issues, but nonetheless potentially explored for carbon dots of further enhanced fluorescence properties.

Again within the same mechanistic framework, the increase in fluorescence quantum yields as a result of surface-doping the carbon nanoparticles with ZnS or TiO₂ in carbon dots may be rationalized in terms of two possible effects. One is more effective energy trapping and radiative recombinations (essentially a more effective formation of emissive states), and the other is the suppression of processes competing with the fluorescence emissions (namely less “quenching”). According to the comparison between the most fluorescent carbon dots with and without the inorganic doping, the fluorescence decays in the doped carbon dots did not slow in parallel to the increases in fluorescence quantum yields (Fig. 3), suggesting that the doping effect primarily enhances the formation of emissive states. Interesting further studies may include a probing of such formation processes by using picosecond or femtosecond optical spectroscopy techniques.

**Experimental section**

**Materials**

$$O, O’\text{-Bis}(3\text{-aminopropyl})\text{ polyethylene glycol } (M_w \approx 1500, \text{PEG}(_{1500N}), \text{thionyl chloride}>99\%), \text{and Ti(OC}_2\text{H}_5)_2(97\%) \text{were purchased from Aldrich; Zn(OOCCH}_3)_2\cdot 2\text{H}_2\text{O} (>98\%) \text{and Na}_2\text{S} \cdot 9\text{H}_2\text{O} (>98\%) \text{from Alfa; and nitric acid (60–70\%), ethanol (>99\%), } N,N\text{-dimethylformamide (DMF, 99\%), sodium dodecyl sulfate (SDS, 99\%) from VWR; and Sephadex G}-100\text{TM gel from GE Healthcare. Carbon-coated copper grids were supplied by Electron Microscopy Sciences; Millipore Durapore membrane filters (0.22 μm pore size) by Fisher Scientific; and the dialysis membrane tubing (molecular weight cutoff } \approx 1000\text{) by Spectrum Laboratories. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.**

**Measurements**

Baxter Megafuge (model 2630), Beckman Coulter ultracentrifuge (Optima L-90K), and VWR bath sonicator (model 250D) were used. Thermogravimetric analysis (TGA) measurements were performed on a TA Instruments Q500 TGA analyzer. Transmission electron microscopy (TEM) images were obtained on Hitachi 9500 TEM and Hitachi HD-2000 S-TEM systems. Atomic force microscopy (AFM) analysis was carried out in the acoustic AC mode on a Molecular Imaging PicoPlus AFM system equipped with a multipurpose scanner and a NanoWorld Pointprobe NCH sensor. The height profile analysis was assisted by using the SPIP software distributed by Image Metrology.

UV/vis absorption spectra were recorded on a Shimadzu UV2101-PC spectrophotometer. Fluorescence spectra were obtained on a Spex Fluorolog-2 emission spectrometer equipped with a 450 W xenon arc source and a detector consisting of a Hamamatsu R928P photomultiplier tube (PMT) operated at 950 V. Fluorescence quantum yields were determined by the relative method, with the use of quinine sulfate and 9,10-bis(phenylethynyl)-anthracene as well-characterized fluorescence standards. Fluorescence decays were measured on a time-correlated single photon counting (TCSPC) setup with a Hamamatsu stabilized picosecond light pulser (PLP-02) for 407 nm excitation (<100 ps pulses at 1 MHz repetition rate), coupled with a Phillips XP2254/B PMT in a thermoelectrically cooled housing as a detector for an overall instrument time resolution better than 500 ps.

**Doped carbon nanoparticles**

A carbon nanopowder sample (2 g) obtained from laser ablation was refluxed in an aqueous nitric acid solution (2.6 M, 200 mL) for 24 h. After being cooled to room temperature, the sample was dialyzed against fresh water, followed by centrifuging at 1000 g to retain the supernatant, from which surface-oxidized carbon nanoparticles were recovered (about 1 g).

The surface-oxidized carbon nanoparticles (600 mg) were dispersed in DMF (200 mL) via sonication for 30 min. To the suspension was added Zn(OOCCH₃)₂·2H₂O (680 mg, 3.1 mmol) under vigorous stirring, followed by slow dropwise addition of an aqueous Na₂S solution (0.62 M, 5 mL) at room temperature. The mixture was centrifuged at 3000 g, and the precipitate was retained and repeatedly washed with distilled water to obtain the ZnS-doped carbon nanoparticles (881 mg).

In a typical experiment for the TiO₂ doping, a sol–gel solution was prepared by mixing Ti(OC₃H₇)₄, ethanol, water, and nitric acid in the ratio of 1/70/1.9/0.2, followed by refluxing at 80 °C with constant stirring for 1 h. To the solution (32 mL) was added the surface-oxidized carbon nanoparticles (200 mg), and the mixture was sonicated for 1 h, stirred for 12 h, and then filtrated. The filter cake was grounded and annealed at 250 °C for 1 h to obtain the TiO₂-doped carbon nanoparticles (230 mg).
**C\textsubscript{ZnS}-dots and C\textsubscript{TiO\textsubscript{2}}-dots**

ZnS-doped carbon nanoparticles (200 mg) were dispersed in an aqueous SDS solution (1 wt\%, 120 mL) via sonication for 30 min. Upon filtration, the filter cake was washed repeatedly with water and then dried. The solid sample was mixed thoroughly with PEG\textsubscript{1500N} (1.9 g), and the mixture was heated to 110 °C and stirred for 72 h under nitrogen protection. Upon being cooled to room temperature, the reaction mixture was dispersed in water, and then centrifuged at 25 000g to retain the supernatant as an aqueous solution of C\textsubscript{ZnS}-dots.

The same procedure and reaction conditions were used for the functionalization of TiO\textsubscript{2}-doped carbon nanoparticles with PEG\textsubscript{1500N} to obtain C\textsubscript{TiO\textsubscript{2}}-dots.

The as-prepared C\textsubscript{ZnS}-dots and C\textsubscript{TiO\textsubscript{2}}-dots samples were further processed in terms of gel column fractionation to harvest the most fluorescent dots. For the gel column, Sephadex G-100 was soaked in water for 3 days. The supernatant (including the suspended ultrafine gel) was discarded, and the remaining gel was washed until no changes in conductivity were observed. The gel (15 g) was soaked in water for 3 days. The supernatant was retained as an aqueous solution of the as-prepared sample. The gel precipitation reaching about an inch in height, the column was opened for the continuous addition of the gel suspension. The gel-filled column was washed until no changes in conductivity were observed. Air bubbles were removed with vacuum. Separately, a glass column was filled with water to remove air bubbles, and then closed. The gel suspension was poured into the column, and as the gel precipitation reaching about an inch in height, the column was opened for the continuous addition of the gel suspension. The gel-filled column was washed until no changes in height, followed by the testing and calibration of the column. In the fractionation experiment, an aqueous solution of the as-prepared sample was added to the gel column and eluted with water. Fractions (typically 5–10) were collected and evaluated for their absorption and fluorescence properties.

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**References**

Reverse Stern–Volmer behavior for luminescence quenching in carbon nanoparticles

Li Cao, Parambath Anilkumar, Xin Wang, Jia-Hui Liu, Sushant Sahu, Mohammed J. Meziani, Ethan Myers, and Ya-Ping Sun

Abstract: Photoluminescence properties of carbon nanoparticles from different treatments in various suspensions were evaluated, and the results were in general agreement with those available in the literature. An interesting observation was that the quenching of luminescence emissions in the aqueous suspended carbon nanoparticles by aliphatic amines deviated from the classical Stern–Volmer behavior in a somewhat unusual fashion, exhibiting reversed quenching (increasing luminescence intensities) at very low quencher concentrations. The implication of the observation to the mechanistic framework that may account for photoluminescence emissions in both functionalized and naked carbon nanoparticles is proposed and discussed.

Key words: carbon nanoparticles, luminescence, quenching, surface passivation, Stern–Volmer.

Introduction

Quantum-sized semiconductor nanoparticles or quantum dots (QDs) have attracted much attention for their excellent optical properties and many related potential applications.1–6 Among well-established QDs are those based on cadmium selenide nanoparticles and associated core–shell nanostructures.7,8 However, since cadmium is a heavy metal known for its significant toxic effects and environmental hazards,9–12 there has been extensive effort on the search for alternative QD-like photoluminescent materials. For example, nanosized silicon as an indirect bandgap semiconductor has been modified and (or) processed specifically for much improved fluorescence quantum efficiencies.13–15

Carbon is hardly considered as a member of the “semiconductor family”, but it was found and demonstrated unambiguously by Sun and co-workers16,17 that nanoscale carbon particles could be made brightly fluorescent with both one- and two-photon excitations. There have since been a large number of studies on fluorescent carbon nanoparticles from many different sources and processing or functionalization schemes and conditions.18–24 While the bright fluorescence (with yields up to 50% and, performance-wise, competitive with that of the well-established semiconductor QDs)18 has generally been associated with surface-functionalized carbon nanoparticles, there have been a number of reports on the detection of luminescence emissions in “naked” carbon nanoparticles.21,25–30 For example, photoluminescence was found in acid-treated candle soot in aqueous suspension,25,26 and subsequently many other suspended soot-like carbon materials (such as natural gas soot27 or carbonized sugars21). Among other naked carbon nanoparticles found to be photoluminescent were those from electrochemical decomposition and (or) oxidation of carbon-based or carbon-rich nanomaterials suspended in water or other solvents.28–30 These carbon nanoparticles were generally small (less than 10 nm), and their luminescence quantum yields were generally low (mostly less than 1%).

In the work reported here, we examined carbon nanoparticles from different treatments for evaluation and confirmation of their photoluminescence properties in suspensions.
under various experimental conditions. An interesting observation was that the quenching of luminescence emissions in the aqueous suspended carbon nanoparticles by aliphatic amines deviated from the classical Stern–Volmer behavior in a somewhat unusual fashion, exhibiting reversed quenching (increasing luminescence intensities) at very low quencher concentrations. The implication of the results to the mechanistic framework that may account for photoluminescence emissions in both functionalized and naked carbon nanoparticles is proposed and discussed.

Results and discussion

The aqueous suspension of the as-purified carbon nanoparticles (produced in the arc discharge of pure graphite rods) was centrifuged at 3,500 g to yield a colored supernatant. Upon dialysis against pure water, the apparently homogeneous particle suspension was still colored (denoted as fraction S, Fig. 1), with the observed absorption spectrum of a featureless curve (Fig. 1). The excitation at various visible wavelengths resulted in significant luminescence emissions (Fig. 1), in general agreement with what has been reported in the literature for suspended carbon nanoparticles from different sources and preparations.21,25–30 The observed emission quantum yields (for example, 0.24% at 440 nm excitation) were at the lower end of the values already in the literature.

The carbon nanoparticles in the homogeneous suspension were, size-wise, broadly distributed according to atomic force microscopy imaging (Fig. 2). The results from transmission electron microscopy (TEM) analysis of the same sample were generally consistent with such an assessment, though the relatively low contrast between the smaller carbon nanoparticles and the carbon coating on the TEM grid hindered a more quantitative determination of size distributions.

The carbon nanoparticles could also be suspended in polar organic solvents, in which the luminescence emission properties were somewhat different. The luminescence spectra remained very broad, with some variations in the spectral peak and band width (Fig. 3), and the observed emission quantum yields were clearly solvent dependent, obviously more luminescent in the solvent dimethyl sulfoxide (DMSO) (Table 1).

The presence of solvent was apparently necessary for the observation of luminescence emissions from carbon nanoparticles. No luminescence could be detected for the same particles under solvent-free conditions (for example, deposited on solid substrate). This has generally been the case for other naked carbon nanoparticles from different sources and preparations. Thus, it seems logical to assume that the solvent molecules may passivate the particle surface, similar to but understandably less effective than the surface passivation agents in the much more fluorescent functionalized carbon nanoparticles (dubbed “carbon dots”).16–18 In this regard, the higher luminescence quantum yields of the carbon nanoparticles suspended in DMSO (Table 1) might simply be due to relatively more effective particle surface passivation by DMSO molecules (conceptually similar to weak surface noncovalent “functionalization” of the carbon nanoparticles). Therefore, the photoluminescence in all small carbon nanoparticles (naked or functionalized carbon dots) could have the same origin: the emissive energy trapping sites on the passivated surface of carbon nanoparticles.16

The effect of surface passivation on luminescence properties of the carbon nanoparticles was also reflected in the unusual quenching results with aliphatic amines as quenchers. Specifically for diethylamine (DEA) in aqueous suspension of the carbon nanoparticles, as a representative example, the observed luminescence intensities increased with an increasing amount of quencher molecules at low DEA concentrations, namely the reversed Stern–Volmer quenching behavior (Fig. 4). Beyond the low concentration region (~4 mmol/L for DEA in aqueous solution), the normal quenching took over, though the Stern–Volmer plot was curved downward at higher DEA concentrations (Fig. 4). The absorption and luminescence emission spectra of the carbon nanoparticles remained largely unchanged with DEA.
concentration in both the reversed and normal Stern–Volmer quenching regions.

The reversed Stern–Volmer quenching behavior at low quencher concentrations might be explained by the same mechanistic framework as that for the functionalized carbon nanoparticles, namely that the DEA molecules in initially low population could be “adsorbed” onto the carbon nanoparticles to improve the surface passivation, phenomenologically similar to weak noncovalent functionalization, to result in higher luminescence intensities. The effect of improved passivation might be overtaken by the normal Stern–Volmer quenching at higher quencher concentrations. Interestingly, similarly different quenching behaviors in low and high DEA concentration regions were observed for the carbon nanoparticles in methanol (Fig. 5), but not in DMSO (Fig. 5). The latter was a solvent in which the carbon nanoparticles were found to be significantly more luminescent (Table 1). The absence of the reversed quenching behavior in DMSO was consistent with the argument that the

Table 1. Luminescence quantum yields of the carbon nanoparticles in different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Phi_F$ for excitation at 440 nm (400 nm) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>0.84 (0.73)</td>
</tr>
<tr>
<td>DMF</td>
<td>0.29 (0.25)</td>
</tr>
<tr>
<td>Water</td>
<td>0.24 (0.16)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.2 (0.14)</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.14 (0.09)</td>
</tr>
</tbody>
</table>

Fig. 3. Luminescence spectra (400 nm excitation, normalized in the inset) of the carbon nanoparticles (fraction S) in DMSO (—), DMF (· · ·), water (— —), ethanol (— · —), and methanol (— —).
observed higher luminescence quantum yields in DMSO could be attributed to the more effective surface passivation by the solvent molecules, with which the similar passivation effect by the low-concentration DEA molecules was apparently not competitive.

Other water-soluble amines such as ethylamine and methoxy polyethylene glycol amine (CH₃O(CH₂CH₂O)₁₁CH₂CH₂NH₂, PEG₅₅₀N) exhibited similar reversed quenching behavior at lower quencher concentrations (Fig. 6). The subsequent turnover in Stern–Volmer plots could again be attributed to the competition between the initial enhancement in luminescence intensities due to the improving particle surface passivation and the normal luminescence quenching. The latter was likely due to photoinduced electron transfer processes.³¹

The dispersion of purified carbon nanoparticles in aqueous solution was dependent on the solution pH, being more stable under neutral than acidic conditions. Therefore, the centrifugation at 3500 g to obtain the supernatant for the experiments described above was performed with the as-purified (nitric acid-treated, thus acidic) sample, followed by dialysis of the supernatant to result in an even more stable aqueous suspension at neutral pH (fraction S, as compared below with the other fractions). The residue from the same centrifugation was also dialyzed against deionized water to neutral pH (as fraction R), and the fraction was subdivided into various fractions (fraction R₁, R₂, R₃, and R₄, Table 2) via sequential centrifugation at different g values, as described in more details in the Experimental section. The fractions thus obtained were characterized and evaluated for their luminescence properties, in reference to those of the sample (fraction S) described above.

The atomic force microscopy results for these fractions suggested no major differences from fraction S (Fig. 2), except for the observation of some larger particles in low population (insignificant statistically). The absorption and luminescence properties of these fractions were also found to be mostly similar among fractions R (Fig. 7), though the luminescence spectra were somewhat shifted from that of fraction S (Figs. 1 and 7), and the observed luminescence quantum yields were also lower (Table 2). Nevertheless, for such inhomogeneous samples of suspended carbon nanoparticles, the changes in spectroscopic results across all samples could hardly be considered as dramatic, or they are actually qualitatively similar.

**Table 2.** Luminescence quantum yields of different fractions in water.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Φₑ for excitation at 440 nm (400 nm) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction S</td>
<td>0.24 (0.16)</td>
</tr>
<tr>
<td>Fraction R₁</td>
<td>0.14 (0.11)</td>
</tr>
<tr>
<td>Fraction R₂</td>
<td>0.15 (0.11)</td>
</tr>
<tr>
<td>Fraction R₃</td>
<td>0.16 (0.13)</td>
</tr>
<tr>
<td>Fraction R₄</td>
<td>0.14 (0.11)</td>
</tr>
</tbody>
</table>

Fig. 6. Stern–Volmer plots for the quenching of luminescence intensities (400 nm excitation) of the carbon nanoparticles (fraction S) by ethylamine (top) and PEG₅₅₀N (bottom) in aqueous solution.

Fig. 7. Normalized luminescence spectra (400 nm excitation) of the carbon nanoparticles in water: fraction S (—), fraction R₁ ( · · · ), fraction R₂ ( — — ), fraction R₃ ( — — — ), and fraction R₄ ( — — — ).
The results from this study, in general agreement with those reported in the literature, confirmed that neat carbon nanoparticles in aqueous and other solvent suspensions were photoluminescent, though with much lower emission quantum yields than those found in functionalized carbon nanoparticles or carbon dots. The fractionation aimed at size selection in terms of different centrifugation fields was apparently not so effective, probably because the gravimetric properties of the suspended carbon nanoparticles were affected by not just the particle sizes, but also surface characteristics such as the presence and population of oxidized groups (carboxylic acids, especially). Nevertheless, the general insensitivity of the observed spectroscopic properties to the fractionation seemed to suggest that the photoluminescence emissions were qualitatively similar across all of the suspended carbon nanoparticles. Mechanistically, the luminescence in these nanoparticles likely has the same origin as that in the functionalized carbon nanoparticles, both due to passivated surface energy trapping sites. A major difference is that the suspended carbon nanoparticles are passivated by solvent molecules (so the naked particles are not so naked after all), whereas the nanoparticles in brightly emissive carbon dots are passivated by surface functionalization. The significance for the observation of reversed Stern–Volmer quenching behavior in this study is that it helps to illustrate the importance of surface passivation to the luminescence emissions in carbon nanoparticles.

**Experimental section**

**Materials**

Fine-extruded graphite rods (carbon content > 99.9%) were purchased from Graphitestore.com, Inc. Dialysis membrane tubing was supplied by Spectrum Laboratories. Water was deionized and purified by being passed through a Labconco WaterPro water purification system.

**Measurements**

A Baxter Megafuge (model 2630) and Beckman-Coulter ultracentrifuge (Optima L90K with a type 90 Ti fixed-angle rotor) were used for centrifugation at various g values. Atomic force microscopy analyses were conducted in the acoustic AC mode on a Molecular Imaging PicoPlus system equipped with a multipurpose scanner for a maximum imaging area of 10 μm × 10 μm and a NanoWorld Pointprobe NCH sensor (125 μm in length). Transmission electron microscopy (TEM) studies were performed on Hitachi 9500 TEM and Hitachi HD-2000 S-TEM systems. Optical absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer. Luminescence emission spectra were measured on a Jobin-Yvon fluorescence spectrometer equipped with a 450 W xenon source, Gemini-180 excitation monochromator and Tirax-550 emission monochromator, and a single-photon counting detector (Hamamatsu R928P PMT at 950 V). Quinine sulfate and 9,10-bis(phenyl-ethynyl)-anthracene were used as the fluorescence standard.

**Carbon nanoparticles**

The carbon soot containing nanoparticles was produced in the arc discharge of graphite rods. The discharge chamber was in a floating helium atmosphere (1 atm; 1 atm = 101.325 kPa) while the rods wereburned with a direct current of 70 A (28 V). The as-produced carbon soot was dispersed in dimethylformamide (DMF) with ultrasonication (Crest Ultrasonics, Model 950DA, 50–60 Hz) for 24 h. The dispersion was then evaporated to remove DMF for the recovery of carbon particles.

The particle sample (3 g) in aqueous nitric acid solution (2.6 mol/L, 240 mL) was refluxed for 12 h. The resulting acidic suspension at room temperature was centrifuged at 3500g for 5 min to collect the supernatant. It was then neutralized with sodium carbonate, followed by dialysis (membrane molecular weight cutoff ~500) against fresh deionized water for 3 days. The resulting stable dispersion of carbon nanoparticles, denoted as fraction S, was used in most of the measurements, including those that required a transfer from aqueous to another solvent.

The residue from the centrifugation above, denoted as fraction R, was added to water for the same dialysis to result in an aqueous suspension at neutral pH. Upon settling after 12 h, the sediment was harvested as fraction R1, and the supernatant was centrifuged at 55 000g for 1 h to obtain the residue as fraction R2. The new supernatant was again centrifuged in a higher field of 393 000g for 1 h to yield the residue as fraction R3 and the final supernatant as fraction R4.

Concentrations of the carbon nanoparticles in suspensions were generally low, less than 10 mg/L. At such low concentrations, the particle concentration effect on spectroscopic results was negligible.

**Acknowledgements**

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**References**

Carbon dots of different composition and surface functionalization: cytotoxicity issues relevant to fluorescence cell imaging
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What is This?
Carbon dots of different composition and surface functionalization: cytotoxicity issues relevant to fluorescence cell imaging

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Abstract
Nanoscale carbon particles have emerged as versatile precursors for a new class of highly fluorescent nanomaterials that resemble semiconductor quantum dots. The surface-passivated fluorescent carbon nanoparticles, dubbed 'carbon dots', were already demonstrated for their potential optical bioimaging applications in vitro and in vivo. In this study, we conducted a systematic cytotoxicity evaluation on the carbon dots prepared by various combinations of precursor carbon nanoparticles and molecules for the particle surface functionalization. The results suggested that the cytotoxicity of carbon dots was dependent on the selection of surface passivation molecules. Those dots showing more significant cytotoxicity at higher concentrations were also evaluated for their effects on the fluorescence imaging of live cells. The implications of the results on the eventual use of carbon dots as cell imaging agents are discussed.

Keywords: fluorescence, carbon dots, quantum dots, cytotoxicity, cell imaging


Introduction
Nanoscale carbon particles have emerged as versatile precursors for a new class of highly fluorescent nanomaterials that resemble semiconductor quantum dots (QDs). As originally reported by Sun and co-workers, small carbon nanoparticles (less than 10 nm) could be treated in aqueous nitric acid to impart carboxylic acid moieties on the particle surface, followed by their functionalization with organic molecules to result in soluble particles of bright and colorful fluorescence emissions. These surface-passivated fluorescent carbon nanoparticles, dubbed 'carbon dots', have been demonstrated for their potential optical bioimaging applications in vitro and in vivo. A variety of nanoscale carbon precursors and different surface passivation agents have been used for the synthesis of carbon dots or structurally and property-wise similar nanoscale configurations. Mechanistically, the fluorescence emissions in carbon dots are attributed to radiative recombinations of the carbon particle surface-trapped electrons and holes, where the large surface (relative to the particle volume) and diverse surface energy trapping sites in the small carbon nanoparticles are stabilized by the surface passivation agents. According to more recent studies, carbon dots with fluorescence quantum yields more than 50% in the green could be prepared, with their optical performance competitive to that of the well-established semiconductor (CdSe/ZnS) QDs, while for carbon dots emissive in the red, substantial improvements in fluorescence performance still present challenges. An important advantage of carbon dots is that, unlike the semi-conductor QDs containing heavy metals such as cadmium, carbon is generally not considered as a toxic element. Carbon powders containing nanoparticles or their aggregates are presently used in many commercial products (automobile tires, for example). In the laboratory, carbon dots with oligomeric poly(ethylene glycol) diamine (PEG1500N) as the surface passivation agent in an aqueous solution were injected into mice for toxicity evaluation over a period of up to 28 d, and the results suggested no significant toxic effects in vivo. There have also been several cytotoxicity studies on carbon dots of specific configurations. For example, luminescent carbon nanoparticles synthesized by the electrochemical treatment of graphite were evaluated in terms of established cytotoxicity assay with a human kidney cell line, in which the cell viability was not negatively affected by the particles. The PEG1500N-functionalized carbon dots were also found to be non-toxic to several human cancer cell lines, as measured by the cell proliferation, mortality and viability.
Carbon dots have been shown to internalize into various cells, amenable to being used as fluorescence probes in cellular imaging applications. While carbon dots in terms of their nanoscale configuration are not intrinsically cytotoxic, nor are the precursor bare carbon nanoparticles, and there are some indications on the surface passivation molecules being somewhat different in their cytotoxicity profiles when free in solution versus being attached to the carbon nanoparticle surface. In the study reported here, we conducted more systematic cytotoxicity evaluations on the carbon dots prepared by various combinations of precursor carbon nanoparticles and molecules for the particle surface functionalization (Scheme 1). The results suggested that the cytotoxicity of carbon dots was dependent on the selection of surface passivation molecules. Those dots showing more significant cytotoxicity at higher concentrations were also evaluated for their effects on the fluorescence imaging of live cells.

Materials and methods

Materials
Carbon nanopowders (produced by laser ablation), pyrrole and thionyl chloride were purchased from Sigma-Aldrich (Atlanta, GA, USA), O,O’-bis(3-aminopropyl) polyethylene glycol (PEG1500N; average molecular weight ~1500) from Frontier Chemicals (Oak Creek, WI, USA), ferric chloride hexahydrate, decyltrimethylammonium bromide (DeTAB) and poly(propionylethyleneimine) (PPEI; average molecular weight ~5000, partially hydrolyzed to yield poly(propionylethyleneimine-co-ethyleneimine [PPEI-EL]) from Alfa Aesar (Ward Hill, MA, USA), and polyethyleneimine (PEI; average molecular weight ~1200) and polyallyl amine (PAA; average molecular weight ~1000) from Polysciences Inc (Washington, PA, USA). Membrane tubing for dialysis was supplied by Spectrum Laboratories Inc (Rancho Dominguez, CA, USA). Water was deionized and purified by being passed through a Labconco Water Pros water purification system.

Precursor carbon nanoparticles
For the synthesis of polymeric nanoparticles, an aqueous solution of the surfactant DeTAB (0.4 mol/L, 40 mL) was stirred at 3°C, and to the solution was added pyrrole (1 g) drop-wise to result in a microemulsion. An aqueous ferric chloride solution (6.9 mol/L, 5 mL) was added, and the mixture was stirred at 3°C for three hours. The polymerization reaction was quenched by excess methanol, followed by harvesting the polypyrrole nanoparticles via centrifugation. Upon drying in a vacuum oven at room temperature for 12 h, the polymeric nanoparticles in a crucible were carbonized in a furnace under inert atmosphere (heated to 800°C at a rate of 5°C/min and then held at 800°C for 5 h).

The commercially supplied carbon nanopowder sample and the sample obtained from carbonizing polypyrrole nanoparticles were both refluxed in aqueous nitric acid (2.6 mol/L) for 12 h, followed by dialysis (membrane pore size equivalent to molecular weight ~1000) against fresh water, and then the removal of water to obtain the precursor carbon nanoparticle samples.

Scheme 1  Structure of carbon dots with various surface passivation agents used. PEG1500N, O,O’-bis(3-aminopropyl) polyethylene glycol; PPEI-EL, poly(propionylethyleneimine-co-ethyleneimine); PEI, polyethyleneimine; PAA, polyallyl amine (A color version of this scheme is available in the online journal)
Carbon dots

The functionalization of carbon nanoparticles with PEG1500N for PEGylated carbon dots was reported previously, and so was the gel-column fractionation of the as-synthesized sample to harvest the more fluorescent dots. A similar procedure to the one for PPEI-El-functionalized carbon dots was used for the PEI- and PAA-functionalized carbon dots. Briefly, the precursor carbon nanoparticles from the carbonization experiment were refluxed in neat thionyl chloride for 12 h. Upon the removal of excess thionyl chloride, the sample (100 mg) was mixed well with carefully dried PEI (1 g) in a flask. The mixture was heated to 110°C, and the melt thus formed was vigorously stirred under nitrogen protection for 72 h. The reaction mixture was brought back to room temperature and dispersed in water, followed by high-speed centrifugation to retain the supernatant (a colored aqueous solution). It was dialyzed against fresh water to eliminate any residual impurities (such as reagents used in the synthesis, including thionyl chloride, for example), and then water was removed to obtain the carbon dots. The same procedure was applied to the synthesis of the PAA-functionalized carbon dots.

Cytotoxicity assays

The human breast cancer cell line MCF-7 (American Type Culture Collection [ATCC]; Manassas, VA, USA) and human colon adenocarcinoma grade II cell line HT-29 (ATCC) were grown at 37°C with 5% CO2 in Eagle’s minimum essential medium (ATCC, with non-essential amino-acids, 1 mmol/L sodium pyruvate, 2 mmol/L L-glutamine and 1.5 g/L sodium bicarbonate) supplemented with 10% (v/v) fetal bovine serum (ATCC) and 1% of penicillin–streptomycin (Cambrex Bio Science, East Rutherford, NJ, USA). In assays, cells were plated in 96-well plates at an initial density of 1 x 10^4 cells per well in 100 μL of growth medium for 24 h incubation. Separately, the selected carbon dots or corresponding free surface passivation agents in aqueous solutions were diluted to the final exposure concentrations with fresh culture medium and sterilized with a 0.2-μm Acrodisc syringe filter just prior to the cell exposure, and the samples were introduced to the cells. Cells cultured in the free medium were taken as the control. The exposure was for 24 h or another specific time period, followed by the cytotoxicity determination in terms of established protocols: the cell mortality as (the total cell number of the control group)/(total cell number) in percentage; and the cell proliferation as (the total cell number of the exposed group)/(total cell number of the control group) in percentage. The cell viability was evaluated by the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay (measuring the ability of mitochondrial reduction of the tetrazolium salt MTT to formazan by succinic dehydrogenase).

Cell imaging

HT-29 and MCF-7 cells at an initial density of 1 x 10^4 per well were seeded in each well of a four-chambered Lab-Tek coverglass (Thermo Scientific, Rockford, IL, USA) and cultured at 37°C until reaching approximately 80% confluence. The separately prepared aqueous solution of carbon dots was filtered (0.2-μm Acrodisc syringe filter), and then diluted with fresh culture medium to the specific concentrations before being added to the glass slide chamber. Cells without exposing to carbon dots were taken as the control. Upon incubation for 24 h or another specific time period, the cells were washed three times with phosphate-buffered saline (PBS; 500 μL each time) and kept in PBS for fluorescence imaging (458 nm excitation and 470–820 nm emission collection). The images were processed and analyzed with the NIH ImageJ software (National Institutes of Health, Bethesda, MD, USA).

Results and discussion

The oligomeric PEG diamine, PEG1500N (Scheme 1), has been used as a surface passivation agent for carbon nanoparticles since the original finding of carbon dots; hence, the toxicity profile of the PEGylated carbon dots has received more attention. Free PEG1500N molecules are generally non-toxic to cells according to all available cytotoxicity evaluation results. In their corresponding carbon dots, different sources of precursor carbon nanoparticles have been used. For laser ablation-produced carbon nanoparticles (in house or acquired commercially), the resulting carbon
dots were found to be non-cytotoxic, as reported previously. Subsequently, a gel-column fractionation method was developed to harvest more fluorescent carbon dots from the as-prepared mixture (Figure 1). The much higher fluorescence quantum yields in the dots thus harvested were attributed structurally to improved passivation on the carbon particle surface by PEG1500N molecules. Because of their bright fluorescence, which is competitive in performance to that observed in the well-established CdSe/ZnS QDs for the comparable spectral region, the fractionated carbon dots have been targeted for cell imaging applications, with an expectation that their cytotoxicity behavior should be similar to that of the as-prepared carbon dots sample. In this study, the expectation was confirmed experimentally, with results from the cytotoxicity assays on the fractionated highly fluorescent carbon dots (observed emission quantum yields all larger than 40%) exhibiting no significant cytotoxicity (Figure 2).

Precursor carbon nanoparticles for carbon dots were also produced by carbonizing polymeric nanoparticles, which were obtained from the emulsion polymerization of pyrrole. The carbon nanoparticles thus produced were similarly processed with aqueous nitric acid, and then functionalized by PEG1500N for carbon dots (Figure 3). As compared in Figure 1, the absorption and fluorescence spectra of PEGylated carbon dots with different core carbon nanoparticles are similar. Since the synthesis of polymeric nanoparticles involved the use of metal catalysts and the subsequent carbonization might produce unwanted impurities, extra effort including dialysis with small pore-size membrane tubing was made to remove any residual catalysts and/or impurities from the as-prepared carbon dots. The resulting sample was evaluated in terms of the cell viability assay, from which the results again suggested no significant cytotoxicity in comparison with that of free PEG1500N (Figure 2).

The PEGylated carbon dots in all available configurations are apparently non-cytotoxic up to concentrations much higher than what is necessary for optical cell imaging and related applications. The highly fluorescent dots harvested from gel-column fractionation, equally benign to cells, are

![Figure 2](image1.png)

**Figure 2** Results from cytotoxicity evaluations of PEG1500N-functionalized carbon dots (black) and free PEG1500N (white) with MCF-7 and HT-29 cell lines (concentrations of PEG1500N in terms of the carbon core-equivalent in the carbon dots). (a–f) With carbon nanoparticles from laser ablation. (g) With those from the carbonization of polypyrrole particles. Data presented as mean ± SD (n = 4). PEG1500N, O,O′-bis(3-aminopropyl) polyethylene glycol.

![Figure 3](image2.png)

**Figure 3** A representative atomic force microscopy topography image of PEG1500N-functionalized carbon dots (carbon nanoparticles from the carbonization of polypyrrole particles) on mica, with the height profile analysis along the line. PEG1500N, O,O′-bis(3-aminopropyl) polyethylene glycol (A color version of this figure is available in the online journal).
particularly promising for potentially fluorescence imaging and/or labeling at a very high sensitivity.

Oligomeric aminopolymers (Scheme 1) represent another class of surface passivation agents for carbon nanoparticles in the preparation of carbon dots, with the fact that PPEI-EI (Scheme 1) was used in the original finding of carbon dots.\textsuperscript{1,2} The PPEI-EI-functionalized carbon dots were also found to be readily internalized into cells.\textsuperscript{2} As reported previously,\textsuperscript{17} the cytotoxicity of PPEI-EI-functionalized carbon dots was meaningfully higher than that of free PPEI-EI beyond a threshold concentration, and the increased cytotoxicity was apparently associated with a larger ethyleneimine (EI) fraction in the PPEI-EI copolymer. In this study, PPEI-EI was used with precursor carbon nanoparticles from the route of carbonizing polymeric nanoparticles (Figure 1). The results from the cytotoxicity evaluation of the resulting carbon dots further confirmed that below a relatively high threshold of carbon core-equivalent PPEI-EI concentration, the carbon dots were mostly non-toxic to the cells (Figure 4).

Equivalent to the extreme of high EI mole fraction in PPEI-EI copolymer is the oligomeric PEI homopolymer (EI only without PPEI units, Scheme 1). PEI has found many biomedical applications, for which there have been a number of toxicity evaluations of PEI based on different cell lines and assays.\textsuperscript{23–26} According to the MTT assay (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide reduced to purple formazan in living cells) in this study on free PEI in aqueous solution, the sample was apparently non-toxic to HT-29 cells even at relatively high concentrations (on the order of 50 $\mu$g/mL). As shown in Figure 5, the PAA-functionalized carbon dots were generally comparable to free PAA at the same carbon particle core-equivalent concentrations, both obviously more toxic to the cells with an exposure time of 24 h, but less so when the exposure time was shortened to four hours.

Overall, the results presented above suggest that the cytotoxicity of carbon dots is dependent on the selection of the surface passivation agent. The oligomeric aminopolymers are generally more cytotoxic than PEG\textsubscript{1500N}, and somewhat more so are their corresponding carbon dots. Except for PAA, however, the threshold concentrations for significant

![Figure 4](https://example.com/figure4.png)

**Figure 4** Results from cytotoxicity evaluations of carbon dots (black) and corresponding surface functionalization agents (white) with MCF-7 and HT-29 cell lines (concentrations of the polymers in terms of their carbon core-equivalent in the carbon dots): PPEI-EI with EI mole fraction in the copolymer of $\approx$ 20\% (upper), and PEI (lower). Data presented as mean ± SD ($n = 4$). PEI, polyethyleneimine; PPEI-EI, poly (propionylethyleneimine-co-ethyleneimine); EI, ethyleneimine
cytotoxicity are still relatively high, thus limiting any negative impact on the eventual use of carbon dots (such as for the optical imaging of live cells).

For potential cell imaging applications, carbon dots of the various surface functional groups (hydrodynamic sizes significantly less than 50 nm even for those functionalized with the polymers) could be internalized into cells (HT-29 and MCF-7) for ready detection in confocal fluorescence microscopy. Since the PEG1500N-functionalized carbon dots are generally benign to cells up to relatively high concentrations, there should not be concerns in terms of cytotoxicity issues for their uses in live cell imaging. For carbon dots with PPEI-EI or especially PEI functionalization, it is probably necessary to keep concentrations of the dots below the threshold corresponding to significant cytotoxicity (Figure 4). As shown in Figure 6, the internalized PPEI-EI-functionalized carbon dots were very bright. Even at a rather low concentration (used for the incubation with cells), the PEI-functionalized carbon dot uptaken by the cells could still be readily detected under a confocal fluorescence microscope (Figure 6).

The PAA-functionalized carbon dots being more cytotoxic was manifested in the cell imaging results, with obvious cell damage by the dots at concentrations near the threshold for significant cytotoxicity (Figure 7). However, similarly guided by the cytotoxicity results (Figure 5), the use of lower concentrations for the same incubation time (24 h) or higher concentrations for a much shorter incubation time (1 h) caused no apparent cell damage, and the internalized carbon dots could still be readily detected in confocal fluorescence microscopy imaging (Figure 7). The results seem to suggest that the cellular uptake of PAA-functionalized carbon dots is rather efficient, requiring only a short incubation time.

The results from this study provide some new insights into the cytotoxicity issues on carbon dots as related to

Figure 5  Results from cytotoxicity evaluations of PAA-functionalized carbon dots (black) and free PAA (white) with MCF-7 and HT-29 cell lines at different incubation times (left: 4 h, and right: 24 h). Data presented as mean ± SD (n = 4). PAA, polyallyl amine

Figure 6  Results from confocal fluorescence imaging (458 nm excitation) of PPEI-EI-functionalized (upper) and PEI-functionalized (lower) carbon dots internalized in HT-29 cells (incubation for 24 h). PPEI-EI, poly (propionylethylenimine-co-ethyleneimine); PEI, polyethyleneimine (A color version of this figure is available in the online journal)
Figure 7 Results from confocal fluorescence imaging (458 nm excitation) of PAA-functionalized carbon dots internalized in HT-29 cells, corresponding to different carbon core-equivalent concentrations of the dots and incubation times: 50 μg/mL and 24 h (upper), 10 μg/mL and 24 h (middle), and 50 μg/mL and 1 h (lower). PAA, polyallyl amine. (A color version of this figure is available in the online journal.)

their potential cell imaging applications. It remains true that carbon dots in terms of their nanoscale structures and configurations are not intrinsically cytotoxic, with any observed cytotoxicity due exclusively or primarily to the particle surface passivation molecules. For those molecules, their cytotoxicity is largely similar when free versus being functionalized on the particle surface. Therefore, the cytotoxicity consideration in the selection of surface passivation agents for carbon dots targeted for uses with live cells may be readily accomplished by looking at the cytotoxicity profiles of the free agents. According to the results presented above, surface passivation molecules of no or low cytotoxicity even at high concentrations are available for carbon dots of similarly no or low cytotoxicity, suitable for uses in live cell imaging. Even for those molecules that are more cytotoxic, their corresponding carbon dots may still be used with live cells if their concentrations are kept low enough and/or the incubation time is short enough. Therefore, it seems reasonable to conclude that carbon dots are promising fluorescence agents for optical imaging of live cells.

**Author contributions:** All authors participated in the design, interpretation of the studies and analysis of the data and review of the manuscript. YW, PA, J-HL and LC contributed more to bio-evaluations and cell imaging, and KNT, SS, PW and XW more to synthesis and characterization. PGL and Y-PS were responsible for the overall project.

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Fullerenes for Applications in Biology and Medicine

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Abstract: Fullerenes as a unique class of carbon allotropes have been studied extensively for their distinctive material properties and potential technological applications, including those in biology and medicine [1-6]. The functionalization chemistries have also enabled the modification of fullerene cages of different sizes (C₆₀, C₇₀, and so on) and ratios. C₆₀, the most abundant fraction in as-produced mixtures, has understandably received most attention [7]. The fullerene cages, their sizes and shapes, have been exploited for bio-applications, such as plugging "holes" in viruses for inhibition purposes [8-10]. Beyond their ball-like structures, fullerenes are rich in electronic properties, especially known for their high affinity toward electrons, with the ability to accept multiple electrons. Their related excellent radical scavenging capability has been exploited for various uses in biological systems [1,11-13]. The cavity in a fullerene cage has proven useful in terms of encapsulating medically relevant materials, such as magnetic metals for diagnostic and therapeutic applications [14]. Fullerenes, with the presence of 5-member rings in particular, are readily functionalized, for which a large number of chemistry has been developed to result in a variety of fullerene derivatives, polymers, self-assembled macromolecules, among others [7,15]. The functionalization chemistries have also enabled the modification and to some extend the control of hydrophobicity-hydrophilicity in derivatized fullerenes.

Fullerenes are generally poor in terms of solubility in commonly used organic solvents, let alone in aqueous solutions. For example, upon vigorous sonication of a C₆₀ sample in water, large aggregates are found in the suspension [16]. The hydrophobicity of fullerene cages has been advantageous in some specific cases, such as their compatibility with hydrophobic domains in biological systems [17]. However, for bio-applications of fullerenes in general, the insolubility in aqueous media has been considered as a major obstacle. Among various strategies for improved aqueous solubility or compatibility [18], one uses simple dispersion with the aid of a surfactant, such as poly(N-vinylpyrrolidone) or cyclodextrins [19,20], and another involves chemical modification of the fullerene cage with hydrophilic units such as amino acid, carboxylic acid, polyhydroxyl groups, or amphiphilic polymers [1,21-25].

The functionalization and the resulting aqueous soluble or compatible fullerene derivatives have also contributed to the study and understanding of fullerene toxicology. Despite some uncertainties and debates on whether fullerene cages are toxic, it seems relatively safe to assume that the cages modified with nontoxic species for aqueous solubility or compatibility pose no acute toxicity [26,27].

Since a major focus in the pursuit for potentially using fullerenes in biology and medicine has been on drug development and formulation, in this paper we highlight some representative studies related to such a focus, including the use of fullerenes for drug-like functions and for their improving the formulation of established drugs. Also discussed are some other potential medically relevant applications of fullerenes, such as their serving as potent agents in photodynamic therapy and magnetic imaging.

FULLERENES AS “DRUGS”

HIV Inhibitor

A well-publicized case on potentially having fullerenes as drugs was the use of C₆₀ cage to inhibit human immunodeficiency virus or HIV protease (HIVP) and HIV transcriptase (HIVTP) [1]. The inhibition exploits the shape, size, and hydrophobic nature of the fullerene cage, impeding the ability of HIV to replicate as well as infect more cells [1,7]. Since HIV is known to easily undergo quick mutations, which present problems for other inhibitors that are based mostly on peptide molecules, the fullerene inhibition has proposed to be advantageous [1]. In the first reported work by Wudl and coworkers [28,29], their specifically synthesized water-soluble fullerene derivative was found to be active against HIV-1 and HIV-2 in vitro. The compound was otherwise non-cytotoxic (up to 100 μM) in uninfected peripheral blood mononuclear cells, H9, Vero, and CEM cells [30]. The work inspired the subsequent development of conceptually similar water-soluble fullerene derivatives as HIVP inhibitors [1,7]. The basic idea behind the design of these inhibitors was to have the fullerene cage target the hydrophobic cavity of HIVP, with additional functionalities on the cage to enhance electrostatic interactions with the aspartate units [31].

Prato and coworkers synthesized amphiphilic fullerene bis-adducts (different isomers) as HIV inhibitors [32]. The antiviral evaluation results showed various levels of inhibitory activities against HIV-1, but no activities against HIV-2. Among different isomers of the bis-adducts, the observed inhibitory activities were different, depending on the functionalization sites on the fullerene cage [32,33]. A significant issue with these fullerene derivatives was their significant toxicity to human CEM cells due to the strong
amphiphilicity, which might disrupt the balance of the cell membrane to cause cell death [32].

Another strategy in anti-HIV drug development has been on the inhibition of HIV-reverse transcriptase (HIV-RT), which is essential for the retroviruses to reproduce [1,34]. In a recent study, Mashino and coworkers evaluated a series of pyrrolidino-fullerene derivatives for their HIV-RT inhibition activities, as compared with nevirapine (a commercial HIV-RT inhibitor) [34]. It appeared that the fullerene derivatives were more effective than nevirapine, particularly for the fullerene derivatives bearing carboxylic acid groups. Similarly, Troshin and coworkers synthesized fullerene derivatives of multiple carboxylic acid moieties to test their inhibition of virus-induced cytopathicity (giant cell formation) using HIV-1 or HIV-2 infected lymphocyte CEM cells [35]. Anti-HIV activities were found for these fullerene derivatives with respect to both HIV-1 and HIV-2.

Toshima and coworkers reported an interesting approach to use fullerene-sugar hybrid for photo-degradation of HIV-1 protease (HIV-1P) [36]. The use of sugar was for enhanced interactions between the hybrid and HIV-1 protease through hydrogen bonding.

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**Scheme 1.**

**Fig. (1).** Photo-degradation of proteins using the hybrid upon UV irradiation. Each protein (1.5 μM) was incubated with the hybrid in 10% dimethyl formamide/PBS buffer (pH 7.0, 50 mM) at 25 °C for 2 h under irradiation with a UV lamp (365 nm, 100 W) placed 10 cm from the sample, and the products were analyzed by tricine-SDS-PAGE. Gels (a)–(c) and (d) represent HIV-1 protease, BSA, Lyso and HIV-1 protease + BSA, respectively. Lane 1, size marker; lane 2, protein alone; lane 3, protein upon UV irradiation; lane 4, protein + the hybrid (1.5 μM) without UV irradiation; lanes 5–8, protein + the hybrid (concentrations 1.5, 0.5, 0.15 and 0.05 μM, respectively) upon UV irradiation. [36] Reprinted with permission from ref 36 (Copyright 2008, The Royal Society of Chemistry).
Regioisomer pionic acid (AMPA), or oxygen-glucose deprivation, though the reaction steps with relatively low activation barriers [39]. The enhanced protective effect of the fullerenes against cell damage and death [1, 7] was more effective [38]. The presence of free radical species in human body is natural, but their overproduction may be harmful and cause serious diseases. Therefore, there has been extensive research on the development of free radical scavengers for biomedical applications [1, 11]. Fullerenols are known for their excellent free radical scavenging capabilities [1, 7, 11, 13], considerably more effective than conventionally used antioxidants [11]. In biological systems, fullerenes may be used to terminate free radical species for the protection against cell damage and death [1, 7].

Dugan, et al. synthesized two regioisomers (C_3 and D_3) of tris-malonyl C_{60} with carboxylic acids to serve as radical scavengers (Scheme 2) [37]. Both regioisomers inhibited excitotoxic death of cultured cortical neurons induced by the exposure to N-methyl-D-aspartate (NMDA), α-amino-3-hydroxy-5-methyl-4-isoxazolepro-pionic acid (AMPA), or oxygen-glucose deprivation, though the regioisomer C_3 was more effective than the regioisomer D_3 [37]. Specifically for the comparison between the two regioisomers, the neuronal death associated with NMDA was prevented almost completely in a solution of C_3 (100 µM), but only reduced by about 20% in a D_3 solution of the same concentration. The results for the inhibition of AMPA-induced neuronal death were similar, with reductions of 80% and 40% by C_3 and D_3, respectively, at the same 100 µM concentration (Fig. 2). Separately, in the use of regioisomers C_3 and D_3 as antioxidants to prevent lipid peroxidation by superoxide and hydroxyl radical, the former was also found to be more effective [38]. The enhanced protective effect of the regioisomer C_3 was attributed to its being more polar, which increases its ability to penetrate lipid membranes [38].

Computational studies on the tris-malonyl C_{60} derivative (C_3) as a model system suggested a high affinity of the compound toward unpaired electrons [39]. According to the results, an important step in radical scavenging by fullerene cage is the conversion of the superoxide anion (O_2^-) to the neutral oxygen (O_2) species, which is followed by the reaction of fullerene anion radical with another superoxide to result in the eventual formation of hydrogen peroxide (H_2O_2). The overall process is exothermic and mainly involves reaction steps with relatively low activation barriers [39].

Other fullerene derivatives, such as the C_{60} adduct with α-alanine [40], were synthesized and found to be active in eliminating superoxide anion and hydroxyl radical [40]. Fullerenols were also functionalized by steroids, which are found in almost all living things, for improved biocompatibilities of the resulting radical scavengers [41]. The fullerene-steroid adducts were demonstrated for their antioxidant activity in β-carotene/linoleic acid model system [41].

Fullerenols refer to a class of fullerene derivatives with the cage functionalized by a large number of hydroxyl groups [42]. Because of the functionalities, fullerenols are readily aqueous soluble. They are excellent free-radical scavengers, reacting with superoxide anion radicals, hydroxyl radicals, and nitrous oxide radicals in chemical and biological systems [43]. According to a recent report, fullerenols were found to be more effective scavengers than fullerene derivatives with carboxylic acids [44]. Specifically, several fullerenols derivatized from C_{60} and the gadolinium endohedral fullerene, C_{60}(C(COOH)_2)_2, C_{60}(OH)_22, and Gd@C_{82}(OH)_22, were studied for their scavenging superoxide radical anion (O_2^-), singlet oxygen, hydroxyl radical (HO·), and the nitrogen-centered 2,2-diphenyl-1-picrylhydrazyl free radical (DPPH) [44, 45]. In the cellular experiment, the human lung adenocarcinoma cell line A549 and rat brain capillary endothelial cell line rBCECs were treated with one of the fullerenols (10-100 µM) prior to incubation with various concentrations of the particular free radical species under investigation. The radical-scavenging activity of the fullerenols for the protection of A549 and rBCECs cells treated with the superoxide radical anion and hydroxyl radical was examined by using electron spin resonance (ESR) spectroscopy, so was the effectiveness of the fullerenols in inhibiting lipid peroxidation. The observed ESR signal decreased against the control for each of the free radicals, indicating a lower population of the radicals. Among the three compounds, the relative potencies in terms of radical-scavenging to protect the cells from oxidative damage were found to be in the order of Gd@C_{82}(OH)_22 > C_{60}(C(OH))_22 > C_{60}(C(COOH))_22 [44].

Beyond the in vitro evaluations discussed above, Gharbi, et al. investigated the effects of C_{60} in vivo, for its ability to reduce the radical-related toxicity of carbon tetrachloride (CCL_4) in rats [46]. Experimentally, a C_{60} sample was dispersed with the assistance of surfactant molecules to form a surfactant-stabilized aqueous suspension. The suspended C_{60} species exhibited no acute or subacute toxicity in rodents, even at large intakes of 2.5-5.0 g C_{60} per kg body weight. For the evaluation of C_{60} in vivo, rats were treated with C_{60} suspension and cultured for various periods, 3, 7, or 14 days before CCL_4 intoxication. Twenty-four hours after CCL_4 intoxication, the livers of all rats pretreated with C_{60} exhibited normal morphology with the same features as those observed for the animals treated with C_{60} only (Fig. 3). In contrast, rats...
administered with CCl₄ only (without the C₆₀ pre-treatment) exhibited severe liver damage. The results were explained such that the C₆₀ species in pre-treated animals scavenged majority of CCl₃· and CCl₃OO· radicals (generated during metabolization of CCl₄) and thus limited their harmful effects [46].

FULLERENE AS DRUG CARRIERS

The fullerene cage is structurally stable, but readily functionalized, thus serving as versatile three-dimensional scaffolds for carrying various drugs. Among desirable properties relevant to drug delivery, fullerenes have generally exhibited no acute toxicity in a number of in vivo and in vitro studies [47,48]. Fullerenes have also been found to go to tissues rather quickly [49,50], amenable to their being used to carry drugs to certain hydrophobic tissues, such as those in the liver [51-53]. In addition, the ability of fullerenes to effectively scavenge free radicals and other reactive species in vivo has made their conjugates with some well-established drugs unique systems in drug delivery, with the fullerenes serving the protection function in situ to mitigate side effects of the administered drugs [7,37].

Wilson and coworkers reported the synthesis of a C₆₀-paclitaxel conjugate (Scheme 3) designed as a slow-release drug-delivery system [54]. The conjugate was examined for its ability to form stable dilauroylphosphatidylcholine (DLPC) liposome formulations and its anti-tumor activity against human epithelial lung carcinoma A549 cells. The mean IC₅₀ values for conjugate-DLPC and paclitaxel-DLPC formulations were 410 and 253 nM, respectively, suggesting similar potencies for these formulations [54].

Doxorubicin (DOX) is a broad-spectrum antineoplastic drug, commonly used in the treatment of a wide range of cancers. However, doxorubicin has several acute and chronic side effects; and it is believed that oxidative stress and the formation of free radicals is a major contributor to the damage caused by this drug. Fullerenes have been shown to effectively scavenge free radicals and other reactive species, thus protecting the cells from the toxic effects of doxorubicin.

Fig. (2). (A) C₃ attenuated neuronal death and (B) dihydrorhodamine oxidation induced by serum deprivation. Cell death was determined by manual cell counts of trypan-stained neurons 48 h after onset of serum deprivation. *, P < 0.05 vs. serum deprivation, using ANOVA followed by Student–Newman–Keuls test for multiple comparisons. Values are mean ± SEM, n = 4–8 per condition. Figure is representative of two additional replicates. (B) Confocal images of cortical neurons showing Nomarski images (upper) of neurons before (CTL) and 8 h after the onset of serum deprivation (SD). Neurons in the SD condition demonstrate typical apoptotic features, including membrane blebbing and condensation of nuclear contents. (lower) Concurrent photomicrographs show increased fluorescence due to oxidation of preloaded, nonfluorescent dihydrorhodamine to fluorescent rhodamine 123. Rhodamine fluorescence is quantified with a linear pseudocolor scale corresponding to arbitrary fluorescence intensity units. [37] Reprinted with permission from ref 37 (Copyright 1997, The National Academy of Science of USA).
Fig. (3). Macroscopic and microscopic effects of C60 on rat livers: (A) control liver; (B) liver after 7 days of pretreatment with C60 (2.0 g/kg of body weight); (C) liver of a rat intoxicated with CCl4 (1 mL/kg of body weight); (D) liver after 14 days of pretreatment with C60 before CCl4-treatment. Trichrome staining of liver sections (magnification = 100x) from: (E) C60 treated rat; (F) magnification of E; (G) CCl4 treated rat; (H) an example of C60 pretreated rat before CCl4 treatment showing a few necrotic areas limited to some cords of hepatocytes. The liver sections of the other C60 pretreated rats (5/6) showed only a slight steatosis. [46] Reprinted with permission from ref 46 (Copyright 2005, The American Chemical Society).

Scheme 3.
radicals play crucial roles in the mechanism of DOX toxicity. A relatively popular strategy in the delivery of DOX has been the use of agents that would mitigate side effects of the drug [55-57]. Fullerenes have naturally become candidates for such agents, including their conjugation with DOX to exploit the excellent radical-scavenging and antioxidative characteristics of the fullerene cage [58]. However, a major issue in the use of fullerene-DOX conjugates for improved drug formulation is their aqueous solubility or biological compatibility. DOX in its natural form is marginally soluble in water. The fullerene cage is even less hydrophilic, hardly helpful to DOX in terms of biocompatibility with physiological media. Therefore, special considerations are necessary in the conjugation of fullerene with DOX to impart sufficient hydrophilicity into the conjugates in order to achieve the desired bioavailability [59].

Sun and coworkers conjugated methano-C₆₀ derivatives with DOX through covalent linkages, in which the use of hydrophilic (oligomeric polyethylene glycol) tethers (Scheme 4) was found as effective in terms of improved aqueous compatibility [59]. The tethers, in addition to being hydrophilic, provided structural flexibility in the conjugates, which was also beneficial to the solubility. The fullerene-DOX conjugates were both stoichiometrically and structurally defined, as confirmed unambiguously by using nuclear magnetic resonance (NMR) and other techniques [59]. Spectroscopically for the aqueous compatible C₆₀-DOX₂ conjugate in Scheme 4, the observed absorption spectrum was close to a superposition of those of free DOX and the methano-C₆₀ (Fig. 4). As the absorption near the observed spectral peak was due primarily to that of the DOX moieties in the conjugate, the molar absorptivity at the spectral maximum was used to estimate the conjugate concentration in solution. The aqueous compatible conjugate (C₆₀-DOX₂ in Scheme 4) was bio-evaluated in the MTT assay. For human breast cancer MCF-7 cells used in the assay, the exposure to the conjugate decreased the cell viability in a dose-dependent fashion, to about half of the control at the DOX-equivalent concentration of 25 μg/mL (Fig. 5). Interestingly, the observed antineoplastic activities of the fullerene-conjugated DOX and free DOX toward the breast cancer cell line were rather similar [59], despite the fact that the cellular uptake and distribution were different between the conjugate and free DOX [57].

In a conceptually similar approach, Chaudhuri, et al, covalently attached DOX and polyethylene glycol onto fullerol for aqueous soluble conjugate [60]. With fullerol, the multiple hydroxyl groups on the fullerene cage not only provided the aqueous solubility but also enabled a high loading of drugs. In the cell viability MTS assay, the cytotoxicity of the fullerol-DOX conjugate against mouse melanoma cell line B16-F10, mouse lung carcinoma (LLC1), and metastatic human breast cancer cell line MDA-MB-231 was found to be in a time dependent fashion,
consistent with a slow cleavage of DOX from the conjugate. In comparison with free DOX, however, the conjugate was less effective for all three cancer cell lines, particularly poor for MDA-MB-231 cells. For evaluation of the fullerol-DOX conjugate in vivo, its therapeutic efficacy against a melanoma-tumor model was determined in reference to that of free DOX. The conjugate was as effective as free DOX in inhibiting the tumor growth, but resulted in less DOX-induced hematopoietic toxicity and cardiotoxicity (Fig. 6) [60]. Interestingly, following the treatment with the fullerol-DOX conjugate, there was an elevated level of DOX in the tumor as compared with that post-treatment with free DOX. This was rationalized as being consistent with the preferential passive accumulation of nanoparticles in the tumor through enhanced permeability and retention (EPR) effect [60]. The observation that the fullerol-DOX conjugate was similarly effective as free DOX in inhibiting tumor growth was attributed to slow cleavage of the carbamate bond in the conjugate, resulting in sustained release of active DOX.

Fullerene-drug conjugates may differ significantly from the corresponding free drug molecules in cellular uptake and distributions, as suggested by experimental results [57]. For DOX-containing conjugates, Sun and coworkers exploited the strong absorption and fluorescence of DOX in the visible spectral region for their tracking with optical imaging techniques [57]. The spectroscopic results suggested that the fluorescence emissions of DOX were quenched by the conjugated fullerene cage (Scheme 4) due to excited state energy transfers. Nevertheless, the remaining fluorescence from the conjugate was still sufficiently bright for optical imaging, even in cells. As made evident in confocal fluorescence images, both free DOX and the fullerene-DOX conjugate (C60-DOX2 in Scheme 4) could readily be internalized by MCF-7 cells (Fig. 7). In the cells the fluorescence intensities of the conjugated DOX were in general relatively lower than those of free DOX, consistent with the solution-phase results on the presence of intra-conjugate fluorescence quenching [57]. According to the imaging results, the cellular distribution of the conjugate was quite different from that of free DOX. For the latter, there was clearly a substantial accumulation in the cell nucleus, with only relatively weak fluorescence observed in the cell membrane or cytoplasm. In contrast, the internalized fullerene-DOX conjugate was found mostly in the cytoplasm, with much weaker fluorescence from the cell nucleus.

DOX is strongly two-photon active, namely excited with two near-IR photons to be fluorescent in the visible [61]. Two-photon fluorescence imaging offers advantages such as deeper tissue penetration by the near-IR light, low light absorption by tissues, and generally non-invasive in nature [62]. The internalization of both free DOX and the fullerene-DOX conjugate (C60-DOX, in Scheme 4) into MCF-7 cells was confirmed by the two-photon fluorescence imaging results, which were also generally similar to those from the confocal fluorescence imaging (Fig. 8). Therefore, DOX moieties could indeed serve as excellent two-photon fluorescence probes for bioimaging and/or tracking in drug delivery.

Fullerenes were also used to conjugate with other species such as nitroxide radicals for the modification of biological reactions and protection of normal cells and tissues in anticancer chemotherapy, where the fullerene cage and nitroxide fragments were used as both radical traps and spin-labels [13,63]. For example, the anticancer drug cyclophosphamide was evaluated in combination with nitroxide methanofullerene in a leukemia P-388 tumor model for therapeutic efficacy [64]. When cyclophosphamide or nitroxide methanofullerene was injected individually, no tumor-bearing mice survived. However, the treatment of mice with the combination of cyclophosphamide and nitroxide methanofullerene resulted in a survival rate of 70% for the animals, suggesting the important role of the fullerene-nitroxide conjugate in modifying biological reactions for improved tumor chemotherapy [64].

The fullerene conjugation approach was further extended to include those with metal complexes [60,65]. For example, cisplatin, a metal-containing drug used as a first line chemotherapy agent for most cancers, was complexed with acid-terminated fullerol [60]. The fullerol-cisplatin complex formed clusters of sizes in the range of 30–100 nm. The treatment of Lewis lung carcinoma cells with the fullerol-cisplatin clusters improved antiproliferative effect on the cancer cells as compared to that with free cisplatin [60]. In a separate study, a fullerene-porphyrin conjugate was prepared for targeted delivery of the paramagnetic 25Mg2+ isotope to the heart muscle [65]. Upon a single injection, about 80% of the tissue hypoxia symptoms was recovered in less than 24 h. Mechanistically, the paramagnetic 25Mg2+ released from the conjugate may selectively stimulate the ATP overproduction in the oxygen-depleted cells. The resulting positive changes in energy metabolism of the heart cells may help to prevent and/or treat the local myocardial hypoxic disorders and, hence, protect the heart muscle from serious damages in a variety of the hypoxia-caused clinical situations [65].

In addition to the conjugation through covalent chemical bonding, drugs could also be loaded onto fullerenes or fullerene-based delivery vehicles through physical adsorption [66]. For example, some amphiphilic fullerene derivatives were found to self-assemble into new spherical buckysome structures of 100-200 nm in sizes [66]. These water-soluble buckysomes were used to encapsulate anticancer drug paclitaxel, known as being hydrophobic, with a maximum percentage encapsulation of 53% loading of paclitaxel. According to results from in vitro cell viability assays, though still considered as preliminary [66], the formulation of paclitaxel encapsulated in buckysomes was comparable with Abraxane (albumin-bound formulation of paclitaxel) in suppressing the growth of MCF-7 breast cancer cells [66].

OTHER RELEVANT USES
Photodynamic Effect and Therapy

Fullerenes are in general of very weak fluorescence emissions. For C60 and derivatives, the observed fluorescence quantum yields
in vivo efficacy of nanoparticle drug conjugates studied in a mice melanoma tumor model. Melanoma bearing animals were injected with three doses of DOX or carbon nanostructure conjugated DOX equivalent to a dose of 6 mg/kg DOX at days indicated by the arrows. Graphs show the effects of treatment on (a) tumor growth as a function of time and (b) body weight of the animals as a measure of systemic toxicity. The top panel shows representative tumors from each treatment group. Both DOX and Ful-DOX induced statistically significant tumor growth inhibition (P < 0.05, ANOVA). (c) Graph shows weights of excised spleen and heart following drug treatment. Inset shows representative images of heart and spleen from each treatment group. (d) Graph shows the DOX distribution profiles in different organs after the animals were dosed thrice at 6 mg/kg. All data shown are mean ± SE of n = 4–5 per treatment group and were subjected to statistical analysis (*, P < 0.05; **, P < 0.001 ANOVA followed by Newman Keul post hoc test). (e) Epifluorescence images showing the effect of treatment on tumor apoptosis. Tumor sections probed for apoptosis using TUNEL assay. The cryosections were probed with fluorescent (TMR-red) terminal deoxynucleotidyl transferase-mediated dUTP nick end labeling (TUNEL) staining. Images were obtained using a Nikon Eclipse TE2000 fluorescence microscope equipped with red filter. [60] Reprinted with permission from ref 60 (Copyright 2009, The American Chemical Society).

are mostly on the order of 0.1% [67]. The dominating excited singlet state process is intersystem crossing to the triplet state, which is essentially quantitative in C_{60} [68]. As a result, C_{60} and derivatives are excellent triplet sensitizers, which have been used to generate highly reactive oxygen species (ROS) for the photodynamic effect [69,70]. These species are capable of reacting with a wide range of biological targets and killing cancer cells [11]. Therefore, fullerenes have been used as effective photosensizers in vitro and in vivo, contributed to the rapid advances in photodynamic therapy for the treatment of multiple diseases [71].

In an early study, Tokuyama and coworkers demonstrated the phototoxicity of some water-soluble C_{60} derivatives against cancer cells [21]. Upon photoirradiation with low-energy visible light, the fullerences exhibited inhibitory activity against human HeLa cancer cells, whereas in the dark no measurable inhibitory activity could be detected. Interestingly, however, the same compounds showed no phototoxic activity against Raji cells (B lymphocytes) [72].

There have been some studies on the phototoxicity of fullerenes potentially affected by the number of additions on the cage [73-76]. For example, C_{60} mono-adduct and tris-adduct were evaluated for their difference in phototoxicity against human T-lymphocytes (Jurkat cells) [73]. Both of them were found to be phototoxic when irradiated with a fluorescent lamp, though the tris-adduct was more so, as reflected in the more effective inhibition of cell growth. Interestingly, the opposite was observed in the absence of light, only the mono-adduct exhibited inhibition effect [73]. The
functional groups in the mono- and tris-adducts were different, so there could be other effects in addition to those due to the number of additions to the cage. In a more direct comparison of the photoinduced cytotoxicity among three C₆₀ adducts with one to three cationic (quaternary pyrrolidinium) groups [75]. Mroz et al. found that the fullerene mono-adduct was more phototoxic to cells than their corresponding multi-adducts, which was attributed to the relative hydrophobic characteristics, with the higher hydrophobicity of the mono-adducts enhancing their cellular uptake [75]. The influence on phototoxicity due to different number of functional groups on fullerene cage is still under debate or even contradictory sometime. For example, in a previous study on the phototoxicity against microbes by the same compounds, an opposite trend was found, namely that C₆₀ multi-adducts were more phototoxic [76].

Photosensitizers currently in clinical investigations are based mostly on molecules with a tetrapyrole structure (porphyrins, chlorines, and related molecules) [77]. There have been efforts on combining fullerene and porphyrin structures in the development of photodynamic therapy agents [77-79]. For example, hybrids covalently linking C₆₀ cage with free-base porphyrin (P-C₆₀) and zinc porphyrin complex (ZnP-C₆₀) were synthesized and evaluated for their phototoxicity against Hep-2 human larynx carcinoma cells.
In the dark as control, no cytotoxicity was observed for the hybrids in concentrations of less than 1 μM for 24 h. However, with photoirradiation majority (80%) of the tumor cells were inactivated due to singlet oxygen (\(^1\text{O}_2\))-mediated photo-damage. The proposed mechanism for the cell death was that the C\(_{60}\) hybrids upon photoirradiation induced apoptosis by a caspase-3-dependent pathway [79].

In addition to chemically modified fullerenes, pristine fullerenes were also dispersed by non-covalent methods for their application in photodynamic therapy. For example, C\(_{60}\) and C\(_{70}\) were dispersed in water by the solvent exchange method or using dispersion agents such as \(\gamma\)-cyclodextrin (\(\gamma\)-CD) and poly(vinylpyrrolidone) [80-82]. The dispersed fullerenes were examined for their phototoxicity against rat fibroblast cell line (5RP7) [80], human keratinocytes (HaCaT) [81], and human lens epithelial cells (HLE B-3) [82]. Significant photoinduced cytotoxicity was observed in reference to the control of no toxicity in the dark [80-82]. Mechanistically, the phototoxicity was due primarily to singlet oxygen, with minor contribution from superoxides [80-83]. Beyond the aqueous dispersion strategy, Ikeda and coworkers employed lipid membrane to incorporate C\(_{60}\) and C\(_{70}\) (LMIC\(_{60}\) and LMIC\(_{70}\), respectively) for photodynamic therapy [84-86]. In the experiments with HeLa cells, LMIC\(_{60}\) with a cationic surface exhibited some low toxicity in the dark, but much higher toxicity upon photoirradiation (Fig. 9) [84]. LMIC\(_{70}\) was found to be more effective than LMIC\(_{60}\) in single oxygen generation, with higher phototoxicity against HeLa cells, which was attributed to the stronger light absorption by C\(_{70}\) in the visible spectral region [85]. A recent improvement to these systems was to solidify the liposome structure by covering the surface with siloxane network for increasing the residence time of the incorporated fullerenes [86].

The use of fullerenes for photodynamic therapy in vivo has also been explored [87]. For example, Tabata and coworkers chemically modified C\(_{60}\) with polyethylene glycol (PEG), and intravenously injected the PEGylated C\(_{60}\) (C\(_{60}\)-PEG) into mice carrying a tumor mass in the back subcutis [87]. The C\(_{60}\)-PEG compound exhibited higher accumulation and more prolonged retention in the tumor tissue than in normal tissue. Upon exposure of the tumor site (with C\(_{60}\)-PEG from circulation post-injection) to visible light, the tumor growth was dramatically suppressed without any damages to the overlying normal skin according to histological examination [87]. In further investigation, the terminal group of PEG in C\(_{60}\)-PEG was coupled with diethylenetriaminepentaacetic acid (DTPA) as chelating ligand to complex with Gd\(^{3+}\) [88]. The resulting C\(_{60}\)-PEG-Gd was used for enhanced magnetic resonance imaging (MRI) to monitor the tumor during the photodynamic therapy [88].

[Fig. (9).] Scheme of the LMI[60]fullerene structure, and photodamage from LMI[60]fullerenes in HeLa cells. The cells were exposed to light (350–500 nm) for 2 h at 19 mW cm\(^{-2}\) and observed using microscopy: phase contrast images (a–c), exclusion of propidium iodide (d–f) and staining with Hoechst 33342 (g–i). [84] Reprinted with permission from ref 84 (Copyright 2007, The Royal Society of Chemistry).
Endofullerenes as MRI Contrast Agents

The endohedral metallocomplexes of fullerenes, especially with paramagnetic lanthanides like gadolinium (Gd) inside the fullerene cage (Scheme 5), have been widely pursued for applications as contrast agents in magnetic resonance imaging (MRI) [89-91]. MRI, an imaging technique used primarily for living tissues, currently relies on contrast agents based on gadolinium poly(aminocarboxylate) chelates. There are many issues with these agents, including low contrast, less flexible, lack of specific targeting, and limited chelate-site interaction with water [92]. As proposed and to some extent demonstrated in the literature, the use of endohedral metallofullerenes with encapsulated Gd may help to address these issues. Much progress has been made in the development of the fullerene-based MRI contrast agents for higher sensitivity (relaxivity) and specific targeting in enhanced molecular/cellular diagnosis.

Wilson, et al. synthesized many lanthanide endofullerenes and derivatives and they used the water-soluble derivatives for biodistribution and metabolism studies in mice [93]. Since the pioneering work, many research groups have developed endohedral metallofullerenes as MRI contrast agents. For example, Dorn and coworkers reported a series of endofullerenes encapsulated with mixed metal species (Gd/Lu and Ho/Lu) to be used as contrast agents in MRI and X-ray [94]. Endofullerenes with Gd are considered as particularly promising for their high relaxivity and low toxicity under conditions in metabolic processes [95]. For example, Bolskar and coworkers prepared water-soluble Gd-endofullerene derivatives, Gd@C_{60}[C(COOH)_{2}]_{10}, whose relaxivity (4.6 mM⁻¹s⁻¹) is comparable to that in commercially available Gd(III) chelate-based MRI contrast agents (Magnevist and ProHance) [95]. The potential of Gd@C_{60}[C(COOH)_{2}]_{10} was demonstrated in MRI experiments in vivo with a rodent model at a dosage of about 35 mg/kg (Fig. 10). Similar to the commercial Gd chelate-based MRI contrast agents, the administrated Gd@C_{60}[C(COOH)_{2}]_{10} moved rapidly to the kidneys, with only minimal uptake by the liver [95].

Tóth, et al. measured water-proton relaxivity values for the endofullerene derivatives Gd@C_{60}(OH)_{k} and Gd@C_{60}[C(COOH)_{2}]_{10} at variable temperatures and as a function of the magnetic field [96]. The results from such experiments were consistent with an outer sphere relaxation mechanism. Interestingly, the proton relaxivity values for both compounds increased strongly with decreasing pH, probably a result of pH-dependent aggregation of Gd@C_{60}(OH)_{k} and Gd@C_{60}[C(COOH)_{2}]_{10}. It was suggested that the pH dependency of the proton relaxivity in these compounds might make them candidates for potentially pH-responsive MRI contrast agent applications [96].

Higher fullerenes with encapsulated magnetic elements have also been pursued for their serving as MRI contrast agents [97,98]. For example, Gd@C_{82}O_{2}(OH)_{10}C(P(O)Et_{2})_{2}H_{10} derivatized from Gd@C_{82} exhibited larger relaxivity than that in the carboxylated Gd@C_{82} under the same conditions [98]. A rationale was that Gd@C_{82}O_{2}(OH)_{10}C(P(O)Et_{2})_{2}H_{10} with the organophosphonate might aggregate via strong hydrogen bonds, resulting in larger and slower tumbling entities and correspondingly higher relaxivity values. It was also suggested that the phosphonate substituents for their high affinity to bone surfaces might have additional advantages as MRI contrast agents for bone targeting [98]. The same group reported that the relaxivity value of another derivative, Gd@C_{82}O_{6}(OH)_{16}(NHCH_{2}CH_{2}COOH)_{6}, was higher than that of the commercial MRI contrast agent Magnevist [97].

Recently, new metallofullerenes encapsulating trimetallic nitride were produced and derivatized for their serving as high-performance contrast agents [99-103]. For example, Dorn and coworkers derivatized Gd,N@C_{80} with acyl peroxide to produce the highly water-soluble Gd,N@C_{80}(OH)_{16}(CH_{2}CH_{2}COOM)_{16} (M = H or Na) in high yield [103]. The versatile method would allow the functionalization of the carbon cage with a variety of functional groups through carbon-carbon bonds, with the terminal carboxyl groups enabling further conjugation with species for the specific targeting purpose. According to results from in vitro evaluations, Gd,N@C_{80}(OH)_{16}(CH_{2}CH_{2}COOM)_{16} exhibited equivalent contrast enhancement at dosage levels 1/50 of that of the commercial MRI contrast agent Omniscan. The in vivo study revealed that this new MRI agent of derivatized Gd,N@C_{80} could provide high contrast enhancement at a very low concentration and work as a long-term diagnostic agent for its slow diffusion behavior in reference to Omniscan [103]. Similarly, MacFarland, et al. synthesized a series of aqueous soluble Gd,N@C_{80} derivatives bearing a variety of glycol methyl ethers ranging from monoethylene glycol to hexaethylene glycol [102]. These compounds were evaluated to visualize tissue architecture in vivo with standard MRI techniques.
In a conceptually similar approach, endohedral metallofullerenes encapsulating mixed-metal species such as Sc₂GdN@C₈₀ and ScGd₂N@C₈₀ have also been synthesized and evaluated as MRI contrast agents [101].

SUMMARY AND OUTLOOK

In summary, fullerene cages as unique carbon nanostructures apparently offer great opportunities for the exploration of their biological and biomedical applications. As highlighted above, there have already been many successes in the exploration, which should inspire more fundamental studies and technological development. One significant issue not covered in any detail in this article is on the potential toxicity or bio-safety of fullerenes, which has been and is still being extensively investigated and intensively debated. Nevertheless, it seems that similar to what have been found in other carbon nanomaterials such as carbon nanotubes and nanoparticles, the well-functionalized and soluble derivatives of fullerenes are generally less toxic or nontoxic in vitro and/or in vivo.

Since the discovery of carbon nanotubes and more recently graphene sheets, fullerenes to some have become somewhat an “old story”. However, while the nanotubes and sheets are competitors with advantages for some applications, fullerenes remain unique, as they are not only carbon nanomaterials but also molecules, with stoichiometrically defined structures and compositions. These characteristics, among others, make fullerenes particularly valuable for at least drug-related biomedical uses. A strong case can be made for further investigations on various configurations of fullerenes for their applications in biology and medicine.

Fig. (10). Upper: a ball-and-stick depiction of Gd@C₆₀[C(COOH)₂]₁₀, illustrating a possible arrangement of 10 C(COOH)₂ addends on a single C₆₀ cage (light blue, C; red, O; white, H; dark blue, Gd). Lower: representative in vivo rodent MR images focusing on a cross section containing a portion of one kidney. (a) Baseline image without contrast agent; (b) image of the same cross section 16 min after administration of Gd@C₆₀[C(COOH)₂]₁₀ with increased signal intensity in the kidney. [95] Reprinted with permission from ref 95 (Copyright 2003, The American Chemical society).
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Noncovalent Interactions of Derivatized Pyrenes with Metallic and Semiconducting Single-Walled Carbon Nanotubes

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ABSTRACT: Pyrene has been a popular molecular structure in the noncovalent functionalization of single-walled carbon nanotubes (SWNTs), and the selectivity between metallic and semiconducting SWNTs for the underlying interactions has been exploited for the postproduction metallic—semiconducting nanotube separation. Two pyrene derivatives, 1-ptyreneacetic acid (PyAA) and 1-docosyloxymethylpyrene (DomP), which are hydrophilic and hydrophobic, respectively, were evaluated on their noncovalent interactions with SWNTs, as relevant to their selectivity and applicability to the postproduction separation. The results suggested that the interactions were not only dependent on molecular structures but also sensitive to solvent conditions and that a relatively lower solvent strength environment (solutions of less polar solvents) might be more favorable to the realization of the selectivity between interactions with metallic and semiconducting SWNTs. The surprising differences for the two pyrene derivatives in terms of their doping effects on the band gap transitions in semiconducting SWNTs are also reported and discussed.

INTRODUCTION

Single-walled carbon nanotubes (SWNTs), while grown mostly spontaneously in various productions, may be considered conceptually as being rolled from a graphene sheet into cylindrical structures. Depending on the chiral vector on which the rolling is based, an SWNT is either metallic or semiconducting. Statistically there are twice as many ways for rolling graphene sheet into a semiconducting SWNT as those for rolling the same sheet into its metallic counterpart, and therefore a metallic-to-semiconducting nanotube ratio of 1:2 should generally be expected in an as-grown mixture of SWNTs. Metallic and semiconducting SWNTs differ not only in electrical conductivity but also in many other physical and chemical properties, including especially optical absorption and Raman spectroscopic characteristics, static polarizability, doping effects, and chemical reactivities. For example, semiconducting SWNTs are known to be extremely sensitive to electrical gating and capable of conductance changes by orders of magnitude under various electrostatic gate voltages. Conversely, metallic SWNTs are less sensitive to molecular adsorption and chemical gating, since charge transfer does not significantly affect the charge density at the Fermi level. In the widely pursued use of SWNTs in transparent conductive coatings to compete with the currently predominant indium tin oxide (ITO) technology, as a technologically important example, metallic SWNTs are required, as semiconducting SWNTs are more absorptive in visible/near-IR spectral regions, and thus their presence in the coatings is negative to the performance requirements for low electrical resistivity and high optical transparency. Obviously, the availability of SWNTs that are either metallic or semiconducting is much desired by the research community, with significant effort and progress already made in the development of methodologies for harvesting metallic and semiconducting SWNTs postproduction.

The noncovalent functionalization of SWNTs with planar aromatic molecules has been popular in the effort on introducing the nanotubes into solution. The selectivity in various degrees between metallic and semiconducting SWNTs in the noncovalent functionalization has been exploited for the postproduction separation. The interactions of aromatic molecules with nanotubes, on which the noncovalent functionalization and solubilization are based, are apparently dependent sensitively on the molecular structures as well as experimental conditions. In the work reported here we examined the structurally analogous pyrene derivatives, 1-ptyreneacetic acid (PyAA) and 1-docosyloxymethylpyrene (DomP) illustrated in Scheme 1, on their significant differences in the noncovalent functionalization and solubilization of SWNTs, especially for what was manifested in the selectivity between metallic and semiconducting nanotubes in different solvent environments. The sharp contrast between the two pyrene derivatives in terms of doping effects on the electronic transitions associated with the van Hove...
The pyrene derivative PyAA is hydrophilic, capable of noncovalently attaching to SWNTs in an aqueous solution. At a more basic pH (~12), the noncovalent functionalization was found to be nonselective between metallic and semiconducting SWNTs, so that the aqueous solubilization of the nanotubes as result of the functionalization was exploited for the removal of impurities from the nanotube sample to result in highly pure SWNTs. In this work, PyAA was used in aqueous solutions of lower pH values to functionalize SWNTs in the sample purified by the widely used nitric acid treatment, with the purpose of evaluating the selectivity for potentially metallic–semiconducting nanotube separation. At pH ~9, for example, PyAA could similarly solubilize SWNTs, leaving behind residues containing few nanotubes (according to resonance Raman spectroscopy characterization) and mostly impurities, largely the same as the results obtained at pH ~12. The aqueous supernatant (still pH ~9) was fractionated in various centrifugation fields, and the resulting sediments were characterized spectroscopically. The Raman G-band and RBM (radial breathing mode) band for the precipitates remained little changed from those of the pretreatment mixture (Figure 1), suggesting no significant enrichment of metallic SWNTs.

In aqueous solutions of even lower pH values, PyAA became much less soluble, making the functionalization and solubilization of SWNTs practically impossible. Thus, polar organic solvents were used for further evaluation on the selectivity of PyAA toward metallic or semiconducting SWNTs. In DMF, PyAA was still capable of noncovalently functionalizing and dispersing SWNTs, with the subsequent centrifugation to result in a more soluble fraction in the supernatant and the rest in the residue. As also shown in Figure 1 on a comparison of Raman spectra, the Raman G-band for the fraction in the residue from centrifugation exhibited some contribution of the Breit–Wigner–Fano (BWF) profile, which is known as characteristic of a sample enriched with metallic SWNTs, and the corresponding G-band for the fraction in the supernatant was more symmetric, with the bandwidth narrower than that of the preseparation mixture. These results suggested that the noncovalent functionalization by PyAA in DMF was somewhat selective toward semiconducting SWNTs, resulting in fractions enriched with either metallic or semiconducting SWNTs. While the selectivity was not high and the separation not effective, the significant difference between the results in aqueous and organic solutions pointed to a major role played by the solvent in the targeted separation of metallic and semiconducting SWNTs via the noncovalent functionalization by the pyrene derivative. It seems reasonable to rationalize that the tougher requirement for aqueous solubilization of the extremely hydrophobic nanotubes probably overwhelms the relatively weaker differences in pyrene–nanotube interactions between metallic and semiconducting SWNTs, thus essentially no separation in basic aqueous solutions. The same rationale may be applied to the observed real yet relatively less effective metallic–semiconducting separation in DMF. As an extrapolation, noncovalent functionalization by the pyrene derivative in less polar organic solvents should be favorable to more effective metallic–semiconducting separation. In those solvents (such as THF), however, the solubility of PyAA is not high enough for the noncovalent functionalization and solubilization. The pyrene derivative with a long alkyl tail (DomP, Scheme 1) is more suitable to those solvent conditions.

As reported previously, the lack of selectivity for PyAA in the noncovalent functionalization between metallic and semiconducting SWNTs in a basic aqueous solution could be exploited for removing residual metal catalysts and carbonaceous impurities from the nanotube sample. In addition, the purification with PyAA may also serve another important purpose of making the highly pure nanotube sample more suitable for the metallic–semiconducting separation. Generally in the solubilization of SWNTs through various noncovalent or covalent functionalization reactions, there is always a portion of the sample that is insoluble under whatever conditions, as found, for example, in sequentially repeated functionalization reactions with the same nanotube sample. The composition of this “special” insoluble portion of the sample may be complex, though...
it does contain mostly SWNTs according to Raman and other characterization results. While the reasons behind these SWNTs being obviously different in their response to functionalization agents and solubilization reaction conditions are not so clear, logical speculations might include the bundling of nanotubes in such a way that morphologically prevents their being accessed by the functionalization agents or the presence of some intertwining or even cross-linking between the nanotubes. Regardless, a negative consequence of such a special portion of the sample to the postproduction separation based on preferential solubilization of semiconducting SWNTs is that these never-soluble nanotubes, a mixture of metallic and semiconducting, would remain in the residue to interfere with the mass balance of the separation. Therefore, beyond the sample purification reported previously,18 the PyAA noncovalent functionalization and solubilization in basic aqueous solution also eliminated the always-insoluble portion from the nanotube sample to yield highly pure SWNTs that could be “split” into metallic and semiconducting fractions in the postproduction separation.

DomP is structurally similar to PyAA, except for a long alkyl tail which makes the molecule more soluble in organic solvents, including those that are less polar. In the noncovalent functionalization, DomP is selective toward semiconducting SWNTs, thus an excellent agent for postproduction separation of SWNTs into metallic and semiconducting fractions.22–24 Experimentally, the separation is such that the DomP-functionalized semiconducting SWNTs are solubilized in an organic solvent like THF, leaving in the residue metallic SWNTs. As a result, the separation is sensitive to the nanotube sample purity, as impurities may interfere with the noncovalent functionalization of SWNTs by DomP and the distribution of the impurities between the two separated fractions is not predictable. In this work, the highly pure sample of SWNTs from the PyAA purification was used for the DomP separation. In the separation experiment, about two-thirds of the nanotube sample could be solubilized by DomP into THF as the fraction in the supernatant, leaving behind the other fraction in the residue. Upon the removal of DomP, the two fractions from the supernatant and residue were found to be dominated by semiconducting and metallic SWNTs, respectively, according to results from resonance Raman (Figure 2) and near-IR optical absorption (Figure 3) characterizations. The noncovalent nature in the DomP functionalization of SWNTs was confirmed by the fact that DomP could be washed off the nanotubes and recovered quantitatively (according to the quantitative NMR characterization). The separated nanotubes after the removal of DomP molecules were morphologically similar to the preseparation highly pure sample, as suggested by electron microscopy results (Figure 4).28

For the separated semiconducting fraction, the observed absorption spectrum consists of a weak feature around 700 nm (14 300 cm−1) in addition to the prominent S11 and S22 bands (Figure 3). The assignment of this absorption feature is of significant interest because this is the region where M11 absorption is expected (thus potential contradiction to the notion that the fraction is dominated by semiconducting SWNTs).25 However, a more likely assignment for the weak feature is S33 absorption, which according to literature results is strongly dependent on the nanotube diameter. Shown in Figure 5 are collections of literature data on the nanotube diameter dependencies of the S11 and M11 absorption bands.26–28 The S33 and M11 are both higher in energy for smaller diameter SWNTs, with the absorptions gradually red-shifting with increasing nanotube diameters. However, the S33 obviously red-shifts faster than does the M11, with the two absorption bands apparently converging at about 14 500 cm−1 (690 nm) for SWNTs of around 1.4 nm in diameter (Figure 5). Interestingly, the arc discharge-produced SWNTs used in this work for postproduction separation are rather narrowly distributed in diameter, with an average diameter of 1.4 nm according to the Raman radial breathing mode (Figure 2). Therefore, it is understandable that the S33 and M11 absorptions appeared in the same wavelength region for the separated metallic and semiconducting arc-discharge SWNTs. On the basis of the estimated peak positions in the absorption spectrum of the separated semiconducting SWNTs (Figure 3),

![Figure 2. Raman spectra (expanded G-band and RBM-band in insets) of the separated metallic (---) and semiconducting (---) SWNTs from the DomP separation of a highly pure nanotube sample.](image1)

![Figure 3. Optical absorption spectra (on wavenumber scale, with the same on wavelength scale in the inset) for neat nanotube films of the separated metallic (---) and semiconducting (---) SWNTs.](image2)
the energy gaps for $S_{22} - S_{11}$ and $S_{33} - S_{22}$ are around 4600 and 4200 cm$^{-1}$, respectively.

Noncovalent functionalizations of SWNTs with planar aromatic molecules are commonly attributed to interactions similar to $\pi - \pi$ stacking found in many aromatic systems. The interactions typically have significant effects on the nanotube $\pi$ electronic structure, resulting in decreased or even diminished band gap electronic transitions, which is referred to in the literature as the nanotube surface doping effect. For the DomP functionalization of the separated semiconducting SWNTs in THF, the effect on both $S_{11}$ and $S_{22}$ bands was obviously extreme, essentially diminishing the absorptions in THF solution and also in the thin film made from the solution (Figure 6). The effect was reversible, however, with both $S_{11}$ and $S_{22}$ absorption bands restored upon the removal of DomP from the nanotube surface.

The doping effect associated with the PyAA functionalization was clearly different. As compared in Figure 6, both $S_{11}$ and $S_{22}$ absorption bands in thin films prepared from the basic aqueous solution or DMF solution of PyAA-functionalized semiconducting SWNTs were largely preserved, suggesting that there was no significant doping effect. The observation, readily producible in repeated experiments, was somewhat surprising as stronger interactions with the nanotubes were expected for PyAA (capable of solubilizing both metallic and semiconducting SWNTs). Nevertheless, a rationalization on the results might be that the functionalization action of PyAA for nanotube solubilization was driven more significantly by the solvent conditions, due less to $\pi - \pi$ stacking-like interactions that induce the doping effect. Alternatively, the strong effect with DomP might be attributed to possible secondary functionalization of the complex-like configuration of pyrenes-on-nanotube by the long alkyl chain. Further investigations with more variations of planar aromatic molecules and solvent and other experimental conditions are required for an improved understanding of the doping effect.

In summary, the noncovalent interactions of the derivatized pyrenes (representing more broadly planar aromatic molecules) with SWNTs are apparently complex, depending not only on molecular structures but also on solvent conditions. Consequently, the selectivity of such interactions between metallic and semiconducting SWNTs is similarly or more affected, which further complicates the use of the selectivity for metallic–semiconducting nanotube separation. However, the complications also bring opportunities, enabling potentially exploitations of the different molecular structures and experimental conditions.
for more effective separation and harvesting of purer metallic and/or semiconducting SWNTs. The results from this work seem to suggest that the selectivity in pyrene—nanotube interactions is relatively weak between the metallic and semiconducting SWNTs, so that an environment of relatively lower solvent strength (less polar solvents) should be more favorable to the realization of the selectivity. These findings may provide some guidance in the further pursuit of postproduction bulk separation of metallic and semiconducting SWNTs by using planar aromatic molecules as fully recyclable separation agents.

**EXPERIMENTAL SECTION**

**Materials.** The SWNT samples (arc-discharge production) were produced in house or acquired from Carbon Solutions, Inc. (“AP-SWNT”, carbonaceous purity 40–60%). 1-Pyreneacetic acid (PyAA) and pyrene methanol were purchased from Aldrich. Nitric acid was obtained from Fisher Scientific, concentrated hydrochloric acid (HCl, 37%) and sodium hydroxide (NaOH) from Acros, and tetrahydrofuran (THF), ethyl acetate, and dimethylformamide (DMF) from Mallinckrodt. The organic solvents were distilled prior to use. Membrane filters (PVDF, 0.22 μm pore size) were supplied by Fisher Scientific. Water was deionized and purified by being passed through a Labconco WaterPros water purification system.

**Measurements.** A Fisher Scientific centrifuge (Model 228) and homogenizer (PowerGen 125) and VWR bath sonicator (Model 250D) were used in the purification and separation experiments. Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/SDTA851e instrument or a TA Instruments Q500 TGA analyzer. Electron microscopy images were obtained in the SE mode on a Hitachi HD-2000 scanning transmission electron microscope. Optical absorption spectra were recorded on Shimadzu UV-3100 and UV-3600 spectrophotometers. Raman spectra were obtained on a Jobin Yvon T64000 Raman spectrometer equipped with a Melles-Griot He–Ne laser (35 mW) for 632.8 nm excitation, a triple monochromator, a liquid-nitrogen-cooled symmetry detector, and an Olympus BX-41 microscopy for sampling.

**Sample Purification.** The as-produced samples of SWNTs were purified in terms of an established procedure involving nitric acid treatment. Briefly, a sample (1 g) was heated at 300 °C with air in a furnace for 30 min, then suspended in aqueous nitric acid (2.6 M, 500 mL), and refluxed for 24 h. The mixture back at room temperature was centrifuged to retain the residue, followed by repeated washing with deionized water until neutral pH. The purified sample was recovered by removing water and drying in a vacuum for 12 h.

For further purification with PyAA, an above purified sample (150 mg) and PyAA (200 mg) were mixed in an aqueous NaOH solution (0.1 M, 100 mL) with homogenization for 30 min and then sonicated for 12 h. The resulting suspension was centrifuged at 14000g for 30 min to retain the dark-colored supernatant. For the precipitation of nanotubes, the supernatant was acidified with aqueous HCl to pH ~ 3. Upon filtration with a PVDF membrane filter (0.22 μm pore size), the nanotube sample was washed with deionized water and ethyl acetate in repeated dispersion—centrifugation cycles and then refluxed in ethyl acetate for 12 h. The purified SWNTs were precipitated and collected (105 mg), and from the solution PyAA was recovered nearly quantitatively. TGA results suggested that the purity in the nanotube sample was higher than 95%.

**Separation with PyAA.** A purified nanotube sample (150 mg) was added to an aqueous PyAA solution (pH ~ 9, 100 mL). The mixture was homogenized for 30 min and then sonicated for 24 h, followed by centrifuging at 3000g for 30 min to collect the precipitate. It was washed with dilute acid solution, refluxed in THF for 24 h, and then washed repeatedly with THF until no PyAA was detected in the washing solution.

For separation in organic solvent, a purified nanotube sample (150 mg) was added to a solution of PyAA in dry DMF (150 mg, 60 mL). The mixture was homogenized for 30 min and sonicated for 24 h, followed by centrifuging at 50000g to collect the precipitate. It was refluxed in THF for 24 h and then washed repeatedly with THF until no PyAA was detected in the washing solution.

**Separation with DomP.** DomP (Scheme 1) was synthesized and fully characterized as previously reported. In the separation, a purified nanotube sample (150 mg) was added to a solution of DomP in dry THF (10 mg/mL, 60 mL), and the mixture was homogenized for 1 h and sonicated for 24 h, followed by centrifuging at 14000g for 15 min. The supernatant was collected, and the residue was used for another round of the same separation. After two repeats, the three supernatants were combined and evaporated to remove THF for the soluble fraction and the final residue as the other fraction. Both fractions were washed repeatedly with THF, refluxed in THF for 24 h, and then washed repeatedly with THF again to ensure a complete removal of DomP from the samples.

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Abstract: Small (~15 nm diameter), highly fluorescent conjugated polymer nanoparticles were evaluated for nanoscale 2D and 3D tracking applications. Nanoparticles composed of conjugated polymers possess high absorption cross sections, high radiative rates, and low or moderate aggregation quenching, resulting in extraordinarily high fluorescent brightness. The bright fluorescence (~200 000 photons detected per particle per 20 ms exposure) yields a theoretical particle tracking uncertainty of less than 1 nm. A lateral tracking uncertainty of 1–2 nm was determined from analysis of trajectories of fixed and freely diffusing particles. Axial (Z) position information for 3D particle tracking was obtained by defocused imaging. Nanoscale tracking of single particles in fixed cells was demonstrated, and a range of complex behaviors, possibly due to binding/unbinding dynamics, were observed.

Introduction

Nanoscale 2D and 3D single particle tracking methods have proven to be extraordinarily useful for investigating a wide variety of cellular processes such as molecule transport, membrane dynamics, and the motion of motor proteins.1–6 There is considerable interest in improving the spatial and temporal resolution of tracking methods. While the positions of isolated, tethered single dye molecules can be determined with ~1.5 nm accuracy,1 the low brightness and fluorescence emission rates of a single dye molecule place severe constraints on time resolution and intracellular studies. Strategies for improving the spatiotemporal resolution of particle tracking experiments include the use of multiple labeling with dyes or fluorescent proteins,7 fluorescent nanoparticles such as colloidal semiconductor quantum dots and dye-loaded nanospheres,8,9 and highly scattering metal nanoparticles. However, dye-loaded nanoparticles and metal nanoparticles are typically larger than 20–30 nm, which can affect biological function, and their hydrodynamic drag places an effective limit on temporal resolution. Individual colloidal semiconductor quantum dots yield limited resolution at acquisition rates above 50 Hz due to saturation effects.3,6 Based on these considerations, it appears that the development of more highly luminescent nanoparticles with diameters in the range of 5–20 nm is needed to improve the spatial and temporal resolution of particle tracking methods.

We recently developed brightly fluorescent nanoparticles, here referred to as CPNs, that consist of one or more π-conjugated polymer molecules.9–12 In contrast to dye-doped polymer or silica beads, which are typically limited to a few percent dye loading due to aggregation and self-quenching effects,13 CPNs are entirely composed of fluorescent polymer, resulting in markedly higher absorption cross sections. In addition, conjugated polymers exhibit minimal self-quenching, with reported fluorescence quantum yields of 70% for pure solid films,14 while CPN fluorescence quantum yields as high as 40% have been determined.12 CPNs can be prepared with diameters ranging from 4 nm (a single polymer molecule) to >50 nm, with particle brightness scaling approximately linearly with nanoparticle volume over this size range, which permits the optimization of the particle size–brightness trade-off for a...
particular application. In addition, the excitation wavelength is readily tailored to a specific application by choosing from a wide variety of commercially available π-conjugated polymers, and highly red-shifted emission can be achieved by energy transfer to dopant dyes or polymers. For particles in the 5–50 nm range, CPNs can achieve arguably the highest fluorescence brightness to volume ratio of any nanoparticle reported to date; a fluorescence cross section of $2.2 \times 10^{-13}$ cm$^2$ and saturated emission rates of 10$^9$ photons per particle per second were observed for CPNs $\sim$15 nm in diameter. CPN encapsulation and functionalization have been demonstrated, indicating the possibility of nanoparticle conjugation to specific biomolecules. Additionally, highly photostable CPNs, $\sim$1000 times more photostable than conventional dyes, have been demonstrated. Furthermore, CPNs do not contain toxic heavy metals, which are a concern for some applications.

In this study, we evaluate the use of single $\sim$15 nm diameter CPNs for 2D and 3D tracking at an acquisition rate of 50 Hz. From the signal levels of isolated nanoparticles, a theoretical tracking uncertainty of better than 1 nm is estimated. An experimental tracking uncertainty of 1–2 nm is obtained from tracking analysis performed on stationary particles. 2D and 3D tracking of particles undergoing Brownian motion in glycerol is demonstrated, and an estimated tracking uncertainty of less than 5 nm in the $xy$ plane and $\sim$20 nm along the $z$ axis is determined. Intracellular particle tracking is also demonstrated, and particle trajectories are found to be consistent with expected phenomena such as partially confined diffusion and reversible and irreversible binding to the cell components. The tracking results indicate that CPNs are promising for measuring the local diffusivity and nanoscale motion of individual biomolecules and subcellular structures in cells.

**Experimental Section**

**Nanoparticle Preparation and Characterization.** The polyfluorene derivative PFBT (MW 10,000, polydispersity 1.7) was purchased from ADS Dyes, Inc. (Quebec, Canada). Tetrahydrofuran (THF, HPLC grade, 99.9%) and glycerol (99.5%) were purchased from Sigma-Aldrich (Milwaukee, WI). All chemicals were used without further purification. For preparation of PFBT nanoparticles, 10 mg of the conjugated polymer PFBT were dissolved in 10 g of HPLC grade tetrahydrofuran (THF) by stirring overnight under an inert atmosphere. The solution was then filtered through a 0.7 μm glass fiber filter to remove any insoluble material. Then 200 μL of the solution were injected by pipet into 8 mL of water under mild sonication. The THF was removed by partial vacuum evaporation, and aggregates were removed by filtration through a 220 nm PTFE membrane filter. Typically, less than 10% of the polymer was removed by filtration, as determined by UV–vis, indicating that most of the polymer formed nanoparticles. A suspension of PFBT nanoparticles in glycerol was prepared by mixing the aqueous nanoparticle suspension with glycerol, followed by partial vacuum evaporation at 70 °C to remove the water. For the determination of particle size by AFM, one drop of the nanoparticle dispersion was placed on a freshly cleaved mica substrate. After evaporation of the water, the surface topography was imaged with an Ambios Q250 AFM in AC mode, yielding a size range of 14.9 ± 4.9 nm (histogram provided in the Supporting Information). A zeta potential of $-46.7$ mV was determined by electrophoretic light scattering (Zetasizer Nano ZS, Malvern Instruments). UV–vis absorption spectra of PFBT in THF and aqueous suspensions of PFBT nanoparticles were recorded with a Shimadzu UV-2101PC scanning spectrophotometer using 1 cm quartz cuvettes, and fluorescence spectra were recorded using a commercial fluorometer (Quantamaster, PTI, Inc.). Nanoparticle optical absorption cross sections were estimated from the absorbance of solutions at a known weight fraction, and estimates of the nanoparticle mass were based on the nanoparticle diameter and polymer density. Nanoparticle fluorescence quantum yields were determined from UV–vis and fluorescence spectra using Coumarin 6 as a standard.

**Cell Culture.** For the cell imaging experiments, mouse macrophage-like J774.A1 cells (ATCC, Manassas, VA) were plated at $2 \times 10^5$ cells/dish onto 35 mm glass-bottom microplate dishes (Matek, Ashland, MA) and allowed to incubate overnight (5% CO$_2$, 37 °C). The culture medium was then removed, and the cells were washed three times with phosphate buffered saline (PBS). The cell fixation and permeabilization were carried out as described by Pathak et al.$^{15}$ A 1.5 mL aliquot of a solution of 4% paraformaldehyde in PBS was added to cells for 10 min at room temperature, followed by rinsing three times with PBS, incubation with a 0.2% Triton solution in PBS for 10 min, and washing with PBS. After fixation, the cells were stored in PBS at 4 °C until use.

**Single Particle Imaging and Tracking.** Single particle imaging and tracking were performed on a customized wide-field epifluorescence microscope described as follows. The 488 nm laser beam from an argon laser is guided onto the epi-illumination port of an inverted fluorescence microscope (Olympus IX-71). Inside the microscope, the laser beam is reflected by a 500 nm long-pass dichroic mirror (Chroma 500 DCLP) and focused onto the rear aperture of a high numerical aperture objective (Olympus Ach, 100×, 1.25 NA, Oil). The laser excitation at the sample focal plane exhibits a fairly Gaussian profile with a full width at half-maximum of $\sim$5 nm. Typical laser intensities employed were $\sim$500 W/cm$^2$ in the center of the laser spot in the sample plane, as estimated based on the measured laser power, size of the excitation spot, and transmission of the objective. Nanoparticle fluorescence is collected by the objective lens, filtered by the combination of two 500 nm long-pass filters, and then refocused by an achromat lens onto a back-illuminated frame transfer CCD camera (Princeton Instruments, PhotonMAX: 512B), yielding a pixel resolution of 105 nm/pixel. An xyc piezoelectric scanning stage (P-517.3CL, Polytak PI) was used to center particles within the laser focal spot and for fine adjustment of focus. Acquisition rates of 33 or 50 images per second were employed. An overall microscope fluorescence detection efficiency of 3–5% was determined using nile red loaded poly-styrene spheres (Invitrogen) as standards. Single nanoparticle fluorescence cross sections were determined by comparison of single nanoparticle fluorescence intensity to that of nile red loaded latex beads (Invitrogen). Determination of the lateral ($x,y$) position, width, and integrated intensity of the fluorescence spots was performed using custom scripts written for Matlab (Mathworks, Natick, MA). For the single particle tracking of PFBT nanoparticles undergoing Brownian motion in glycerol, a drop ($\sim$50 μL) of nanoparticles suspended in glycerol at a concentration of 15 pM was placed between two cleaned microscope coverslips. For tracking of individual PFBT nanoparticles in a cell, 0.5 mL of a 4:1 glycerol/PBS solution, containing bovine serum albumin (BSA) (1 mg/mL) and PFBT nanoparticles (20 μM), was added into the prepared microscope dishes containing fixed cells and allowed to incubate for 12 h prior to imaging.

**Results and Discussion**

An aqueous suspension of nanoparticles roughly 15 nm in diameter was prepared from the conjugated polymer PFBT. AFM images, polymer chemical structure, UV–vis absorption and fluorescence spectra, and fluorescence microscopy of single particles are shown in Figure 1. PFBT was selected due to its excellent photostability and high absorption cross section at the 488 nm excitation wavelength employed in the tracking experiments. An estimated optical absorption cross section (per 15 nm diameter particle) of $2.8 \times 10^{-13}$ cm$^2$ at 488 nm was

determined. The fluorescence quantum yield of the nanoparticles was determined to be 7%, corresponding to a fluorescence intensity trajectory yielding an average of \( \sim 10^9 \) detected photons per particle per image. Based on the measured 315 nm width (fwhm) of the single particle fluorescence spot, typical number of detected photons per image \( N = 2 \times 10^8 \), \( \sigma = 105 \text{nm} \), and \( b = 17 \), an estimated tracking uncertainty of better than 0.3 nm is obtained. The second and third terms in the above expression contribute less than 10% of the estimated tracking uncertainty, indicating that the expected contribution of pixel size and background noise to the tracking uncertainty is minimal.

Particle tracking resolution was experimentally determined by performing 2D tracking measurements of stationary particles deposited on a glass coverslip. A representative 2D trajectory and analysis are shown in Figure 2. Several hundred sequential fluorescence microscopy images were acquired at an acquisition rate of 50 images per second, and the particle position was determined by nonlinear least-squares fitting of the fluorescence intensity trajectories. Photobleaching trajectory (photons detected per 20 ms exposure time) of a single PFBT nanoparticle (blue line) and 20 nm nile red loaded polystyrene bead (red line).

The tracking uncertainty is largely determined by the saturated emission rate. An initial estimate of the tracking uncertainty based on per-particle fluorescence intensity levels was obtained as follows. Assuming the tracking uncertainty is due to a combination of photon counting noise and the photostability of the single particle level under conditions employed for single particle tracking, particles were dispersed on a glass coverslip and imaged with a CCD-equipped inverted fluorescence microscope at an acquisition rate of 50 Hz. Bright, near-diffraction-limited fluorescence patterns were observed, and the detected photons per particle per image typically ranged between \( 1 \times 10^8 \) and \( 1 \times 10^9 \) for several hundred consecutive images (Figure 1c, d). Analysis of 20 typical single particle fluorescence intensity trajectories yielded an average of \( \sim 10^8 \) total photons emitted per particle (roughly \( 5 \times 10^7 \) photons detected), with some particles emitting more than \( 10^{10} \) photons, and a per particle emission rate of \( \sim 1 \) GHz (corresponding to nearly saturated emission), in agreement with prior results. These figures of merit are encouraging for improving the spatialtemporal resolution of fluorescence-based particle tracking, since, at high acquisition rates, the tracking uncertainty is largely determined by the saturated emission rate.

An initial estimate of the tracking uncertainty based on per-particle fluorescence intensity levels was obtained as follows. Assuming the tracking uncertainty is due to a combination of photon counting noise and the photostability of the imaging setup, the tracking uncertainty \( \delta \) is given by the expression:

\[
\delta = \sqrt{\frac{\sigma^2}{N} + \frac{a^2/12}{N} + \frac{8\pi\sigma^4b^2}{a^2N^3}}
\]


and then plateaus (Figure 2c). This result was confirmed repeatedly and could be indicative of internal dynamics of the nanoparticle, such as intermittent quenching of the fluorescence in regions of the nanoparticle by reversibly photogenerated defects in the conjugated polymer, as has been observed in the fluorescence intensity trajectories of single conjugated polymer chains. The 1–3 nm tracking resolution determined at a temporal resolution of 20 ms is consistent with the estimated resolution based on signal level. Based on literature values, the saturated emission rate of the PFBT nanoparticles is roughly 20 times higher than that of the dye-loaded nanoparticle. Since each polystyrene bead contained 200 dye molecules, the brightness of the PFBT dots is roughly equivalent to 200 dye molecules under these imaging conditions.

2D particle tracking was demonstrated on CPNs undergoing Brownian motion in a glycerol/water solution. A small amount of glycerol/water solution (>98% glycerol) containing 1 nm diameter PFBT nanoparticles was sandwiched between two microscope coverslips and imaged at a rate of 50 Hz as described above. An $xyz$ piezoelectric scanning stage was translated in the $xy$ plane until a particle was located and roughly centered in the laser beam, followed by adjustment of the $z$ position to bring the particle approximately into focus, at which time the CCD was set to acquire 1000 sequential images at a rate of 50 Hz. Typically, >300 images were acquired before the particle drifted too far above or below the focal plane to permit accurate determination of particle position. For the cases in which the particle remained in the focal plane for 1000 images (20 s), the photons detected per nanoparticle per image typically remained above 100 000 for the entire experiment, as required for high resolution, long-term tracking. The particle trajectories (Figure 2b) were obtained from the images by fitting to Gaussian functions as described above. Fitting a 2D Gaussian to the per-frame displacement histogram (Figure 2e) yielded $\sigma = 12$ nm, which is primarily due to diffusion. To determine the diffusion constant, MSD as a function of lag time (Figure 2d) was fit to the equation

$$\text{MSD}(\tau) = 4\pi D \tau + (\nu \tau)^2$$  \hspace{1cm} (2)

where $D$ is the diffusion constant and $\nu$ is the drift velocity. The results were analyzed for several particles, yielding a negligible drift velocity and diffusion constants ranging from 4 × 10$^{-4}$ to 2 × 10$^{-3}$ μm²/s (Figure 2f), which is somewhat smaller than the theoretical diffusion constant obtained from the Stokes–Einstein relation. The discrepancy may be due to some particle swelling by the glycerol as well as the additional hydrodynamic drag known to occur for charged colloids at low ionic strength. The MSD curve can be extrapolated to zero lag time to estimate the tracking uncertainty, yielding a value ranging between 1 and 4 nm. This estimate of the tracking uncertainty is consistent with the 1–2 nm tracking uncertainty obtained based on the rms displacement per frame for stationary particles.

Tracking of particles in 3D was performed, employing a variant of defocused imaging to determine the axial ($z$) position of the nanoparticle. Trajectories and analysis are shown in Figure 3. The objective focal plane was displaced several hundred nanometers from the particle of interest, and particles were imaged as described above. The lateral positions and widths of the fluorescence spots were determined by Gaussian fitting, as described above. The width of the fluorescence spot was analyzed to determine the axial position as follows. To experimentally determine the relationship between the width of the defocused point spread function and nanoparticle axial position, the PFBT nanoparticles were immobilized on a coverslip and the axial position was systematically varied using an $xyz$ piezoelectric stage, which was driven with a staircase waveform generated by a programmable function generator. The sample was then displaced in 20 nm steps, and the resulting spot widths were analyzed using the particle tracking routine (Figure 3a). The fluorescence spot width $W$ as a function of axial position $z$, in units of nanometers, was fit to a parabola,

$$W = az^2 + bz + c$$  \hspace{1cm} (3)

yielding a good fit for the parameters $a = 3.9 \times 10^{-4}$, $b = 2.5 \times 10^{-3}$, $c = 330$. Using this equation, the axial position was
determined from the width of the fluorescence spot. Based on the standard deviation of 2.4 nm in the ~350 nm average width obtained for a fit for a spot roughly 240 nm from the focal plane, error propagation analysis applied to the above equation yields an uncertainty in axial position of 25 nm. The estimation of the axial position of a defocused particle from the fluorescence spot width was combined with lateral position measurements to determine the 3D trajectory of a particle undergoing Brownian motion (Figure 3c). The axial and the lateral MSD exhibited a linear dependence on lag time, as expected for Brownian motion. The axial diffusion coefficient, \( D_x \), and the lateral diffusion coefficient, \( D_y \), were obtained from their respective MSD curves, resulting in \( 3.8 \times 10^{-3} \) and \( 1.9 \times 10^{-3} \) \( \mu m^2/s \), respectively (Figure 3d). Extrapolation of the axial MSD to the zero lag time shows an estimated tracking uncertainty of 19 nm, consistent with the result obtained by error propagation. Figure 3e shows the histogram of per-frame displacements, which is fit to a Gaussian function, giving \( \sigma = 14.3 \pm 0.3 \) nm, which is largely attributable to axial tracking uncertainty. These results indicate that, for 3D tracking of the ~15 nm diameter PFBT nanoparticles, a lateral \((x,y)\) resolution of <5 nm and an axial \((z)\) resolution of ~20 nm can be achieved at an acquisition rate of 50 Hz using a conventional fluorescence video microscopy apparatus. It is expected that further improvements in temporal and axial resolution could be obtained using more advanced tracking methods.  

Tracking of PFBT nanoparticles was performed in the vicinity of fixed and permeabilized mouse macrophage-like J774 cells, at an acquisition rate of 33 Hz, in 4:1 glycerol/phosphate buffered saline (PBS) solution. In the absence of bovine serum albumin (BSA), the nanoparticles accumulated on the surface of the cell membrane within a few minutes. Addition of 1% BSA was found to greatly reduce nonspecific binding to the membrane, likely due to adhesion of the protein to the nanoparticle surface. Figure 4 shows a brightfield transmission image of the cell, together with nanoparticle trajectories and analysis. When the edge of the cell was placed near the center of the imaging area, particles were visible in the interior of the cell, adhered to the membrane, and outside the cell, and a sequence of images was acquired. As compared to the results obtained in nearly pure glycerol, the reduced viscosity of the 80% glycerol resulted in higher per-frame displacements of the particles. The motion of the particles during each acquisition interval resulted in variable spot shapes that reduced the accuracy of Gaussian fitting, so a centroid algorithm was used to track the particles.  

In the trajectories and MSD curves (Figure 4b–d), several distinct phenomena are observed. The particle inside the cell (Figure 4a, b) switches between free Brownian motion, with a corresponding linear increase in the MSD curve, and confined or bound behavior resulting in a relatively flat MSD. Additional, longer trajectories would be needed to differentiate between confined diffusion behavior and binding–unbinding behavior. Another particle apparently adhered to the cell membrane and exhibited low amplitude (15 nm) oscillatory motion, while the particle outside the cell exhibited free Brownian motion.  

**Conclusion**

In conclusion, we have demonstrated that small (~15 nm diam) PFBT nanoparticles exhibit intense fluorescence that permits 3D tracking with nanometer lateral spatial resolution and video rate temporal resolution. The saturated per particle emission rate is typically \( 10^9 \) photons/s, roughly 2–3 orders of magnitude higher than that of other luminescent nanoparticles of similar size, resulting in a factor of 10–30 improvement in spatial resolution for emission rate-limited tracking experiments. The high fluorescence cross section of the particles is useful for tracking in complex environments exhibiting high auto-fluorescence and scattering that often drowns out the signal of dyes and other small nanoparticle labels. Free Brownian motion of the nanoparticles in glycerol was observed with nanoscale resolution at a 50 Hz acquisition rate, and complex motion in cells was observed. Based on these results, we conclude that the extraordinary brightness of CPNs under one-photon and two-photon excitation should be useful for a broad range of particle tracking applications requiring small particles, video rate or higher temporal resolution, and nanometer spatial resolution. It is likely that additional efforts to improve particle brightness and photostability by employing improved polymers or by encapsulation could yield further improvements in tracking resolution.  

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**Supporting Information Available:** Additional figures providing experimental details and a particle tracking video. This material is available free of charge via the Internet at http://pubs.acs.org.  

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