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Solution Processed Solar Cells

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SOLUTION PROCESSED SOLAR CELLS

A Dissertation
Presented to
the Graduate School of
Clemson University

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

by
Yi Jin
December 2016

Accepted by:
George Chumanov, Committee Chair
Jeffrey N. Anker
Brian Dominy
Modi Wetzler
ABSTRACT

Photovoltaics have experienced a rapid development in the device structure, material process and efficiency in the past decade. Here, uniform, fully converted CH$_3$NH$_3$PbI$_3$ films were synthesized at room temperature by converting PbI$_2$ in a saturated solution of CH$_3$NH$_3$I in 2-propanol/hexane (cyclohexane). Solar cells with a structure of ITO/ZnO/CH$_3$NH$_3$PbI$_3$/graphite/carbon black electrode were fabricated by spin coating at ambient conditions. The best device yielded 10.2% power conversion efficiency. PbI$_2$-based photovoltaic devices having ITO/ZnO (or WO$_3$)/PbI$_2$/graphite (or without graphite)/carbon black structure were fabricated by spin coating at ambient conditions. The best devices yielded 0.32% power conversion efficiency. Pure 2H CuFeO$_2$ nanoplates with a thickness of about 100 nm were synthesized at temperatures as low as 100 °C. 2H CuFeO$_2$ has a band gap of 1.33 eV, high absorption coefficient, and highly photostability. The material appears promising for solar applications. A new method based on the cation exchange reaction for the synthesis of Cu$_x$Zn$_y$Sn$_2$S$_{4-0.25x-0.5y}$ with the crystallite size more than 85 nm was developed. This method appears promising for facilitating the development of Cu$_2$ZnSnS$_4$ based devices.
DEDICATION

To

my parents, wife, and daughter

a little girl with a smiling and curious face brings in a new passion for discovering
ACKNOWLEDGMENTS

I would like to express my gratitude to my advisor, Dr. George Chumanov, for his expert guidance, full support, and encouragement through my study and research. In addition, I express my appreciation to Dr. Modi Wetzler, Dr. Brian Dominy, and Dr. Jeffrey N. Anker for lighting road to pursuit knowledge.

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CHAPTER ONE

INTRODUCTION

The Position of Solar Cells in Energy Structure

Fossil fuels (coal, oil, nature gas) powered the rapid economy development and improved peoples’ life in the 20th century. Without considering greenhouse effects and the pollution introduced by fossil fuels, this non-renewable energy will exhaust in this or next century. Renewable energy, such as hydropower, wind power, and solar energy, is been considered and developed to substitute fossil fuels. Solar energy is an important renewable and clean energy source. Application of solar energy has been developed into the following technologies: photothermal conversion, photovoltaic conversion, and photochemical reactions. Photovoltaics have experienced rapid development in the past decade. The highest power conversion efficiency has reached 46.0% for the concentrated multi-junction solar cell. However, in order to achieve broad applications of photovoltaics as significant energy sources, a balance between cost, stability, and efficiency must be reached. The traditional solar cells, such as silicon, GaAs, CdTe, InGaP, InGaAs and CIGS (CuInGaxGa(1-x)Se2), have good efficiency and stability, but the cost is very high. Some new types of photovoltaics, such as dye-sensitized solar cells, organic solar cells, and quantum dots solar cells are lacking stability.

Theory of Solar Cell

When characterizing solar cells, the most common parameters are power conversion efficiency (PCE), fill factor (FF), short-circuit current density (Jsc) and open circuit potential ( Voc). The PCE is determined by the light trapping efficiency, charge
carrier separation efficiency, and carrier collection efficiency. Inefficient light trapping in light absorption materials decreases $J_{sc}$ and PCE. There are three parameters affect the light trapping efficiency: the reflectivity, the absorption coefficient of the material and the contact coverage of the solar cell surface. The reflection losses are more pronounced for high refractive index materials. For example, according to Fresnel equation, over 30% of normally incident light is reflected from a silicon surface. The high absorption material traps more light and the minimization of the top contact further increases the effective absorption area of the solar cell.

Excitons generated upon the abortion of photos in the light absorption semiconductor. An exciton is a bound state of an electron and a hole by the electrostatic interaction. The binding energy of exciton varies with the electronic screening and localization of both conduction and valence band edges: its value varies from a few meV in inorganic semiconductors to several hundred meV in organic semiconductors. A small binding energy in inorganic semiconductors cannot hold electrons and holes tightly for a long time producing free electrons and holes in the light absorbing material. Without extracting free carriers out of the light absorption material, recombination of electrons and holes takes place in three ways: radiative, the recombination on the defect, and Auger recombination. The radiative recombination mainly happens in direct semiconductors such as GaAs but can be neglected in indirect semiconductors. The energy of photons reemitted from direct recombination has similar energy to the band gap. The absorption coefficient at the edge of the band gap is often low. The reemitted photons cannot be efficiently trapped by the light absorption semiconductor thereby decreasing $J_{sc}$ of the solar cell. In addition,
all materials contained unintentionally or deliberately added impurities, which generate low band gap defects and serve as the recombination centers for electron-hole pairs. Auger recombination involves an electron-hole pair and another electron in the conduction band and is important at high carrier concentrations caused by heavy doping or high light intensities.

The lifetime of the carriers is the time from their generation until the recombination or extraction by carrier collection electrodes. The extracted carriers are only the carriers that diffuse to the carrier collecting electrodes. The carrier diffusion length in efficient solar cells must be longer than the absorption depth and wider than the film thickness. Carrier diffusion length is the square root of the product of the diffusion coefficient and the carrier lifetime (equation 1). The diffusion coefficient affected by the carrier mobility and temperature (equation 2).

The carrier mobility is reduced by the low band gap defects, ionized impurity scattering, phonon scattering, piezoelectric scattering, surface disorder scattering, and carrier-carrier scattering. To achieve long diffusion lengths, a semiconductor should have minimal crystal defects, doping, narrow band gap impurities, interfacial disorder, and dangling bonds. The conductivity of a semiconductor is the product of the carrier mobility and the free carrier concentration. The free carrier concentration increases with the intensity of sunlight. Low carrier concentration in light absorption semiconductor does not increase series resistance but increase PCE of the solar cell. The photogenerated electrons and holes arrive at the carrier extracting layers via the diffusion in the light absorbing semiconductor. Ohm contacts should be formed between the light absorption semiconductor and carrier extracting materials to avoid building up the
space charge. The space charge will increase the recombination ratio and decrease FF, $J_{sc}$, and $V_{oc}$. Energy level matching between the carrier extracting materials and the light absorbing semiconductor can be used to estimate the formation of Ohm contacts as well as $V_{oc}$.

$$L_d = \sqrt{D\tau} \quad (1)$$

$$D = \frac{\mu k_B T}{q} \quad (2)$$

Where $L_d$ is the carrier diffusion length, $D$ is the diffusion coefficient, $\tau$ is the lifetime of the carrier, $\mu$ is the carrier mobility, $k_B$ Boltzmann’s constant and $T$ is the absolute temperature.

**Single Junction Solar Cell Structures**

$n^+\text{-}p\text{-}p^+$ or $n^+\text{-}n\text{-}p^+$ Homojunction Solar Cell

![Diagram of n^+\text{-}p\text{-}p^+ or n^+\text{-}n\text{-}p^+ homojunction solar cell.]

**Figure 1.1.** Schematic cross section of n^+\text{-}p\text{-}p^+ or n^+\text{-}n\text{-}p^+ homojunction solar cell.

Single crystal silicon solar cells exhibit the highest efficiency among different silicon cells and often adopt the $n^+\text{-}p\text{-}p^+$ or $n^+\text{-}n\text{-}p^+$ structure as shown in Figure 1.1. The substrate used in the crystalline silicon solar cells is a silicon wafer with a thickness of ~200 $\mu$m and doping concentration of $10^{15} - 10^{16}$ cm$^{-3}$. The fabrication of the solar cell
includes the wafer cleaning, surface texturing for light-trapping, doping, removing SiO₂, the surface passivation, front side antireflection and backside reflection coating, and making metal contact. Pyramidal surface structures and an antireflection coating are used to decrease the reflection and increase trapping of light. Surface passivation of both front and back sides of the solar cell is essential to reduce the surface recombination to achieve high efficiency.⁶ The heavy doped area and the electrode contact area are optimized to enhance light penetration as well as to decrease the series resistance and recombination at the interface between electrodes and the semiconductor. The highest efficiency achieved by using n⁺-p-p⁺ or n⁺-n-p⁺ homojunction structure in single crystal silicon solar cells is 21.4% under terrestrial solar irradiation.⁶ Polycrystalline silicon cells also produced 19.6% efficiency using this structure.⁷ Further modifications of this structure resulted in the record efficiency of 25.6% for the single crystal solar cell. These modifications include the deposition of silicon nitride as a transparent low surface recombination/passivation layer on the front surface of a silicon wafer, the modification of the back surface with a wider bandgap intrinsic amorphous silicon and then with n- or p-doped amorphous silicon, and interdigitated back contacts.⁸

p-i-n Homojunction Solar Cell
Figure 1.2. Schematic cross section of p-i-n homojunction solar cell.

The single crystal silicon solar cell has high efficient but comes with high cost. An alternative approach is a structure of p-i-n homojunction (Figure 1.2). A glass substrate is first coated with a light reflecting metal and a transparent conductive oxide (TCO), such as Ag/ZnO:Ga. Hydrogenated amorphous silicon is then deposited in the following sequence: p/n type, intrinsic, n/p type with a total thickness of ~ 2 µm. The front contact is achieved by the deposition of TCO and screen printing of silver electrode. The efficiency of this thin film silicon solar cell has reached 11.8% but is still much lower than single crystal silicon solar cells. The main reason for the low performance is that the amorphous silicon has many defects such as dangling bonds as well as has low carrier mobility and short diffusion length.

p-n Heterojunction Solar Cell

The heterojunction structure is widely used in crystalline and thin film solar cells with both wide and narrow bandgap semiconductors (Figure 1.3). The narrow bandgap semiconductors server as light absorption materials, whereas wide bandgap semiconductors, such as ZnO and TiO₂, are used to selective extract electrons from the light absorption materials and block the majority holes due to a large valence band offset.
Crystalline InP solar cell with an efficiency of 19.2% is manufactured by using p-n heterojunction structure. P-type InP wafer with a thickness of 350 μm and a carrier density of $2 \times 10^{17}$ cm$^{-3}$ is used as the substrate. 10 nm of amorphous TiO$_2$ is deposited via the atomic layer deposition technique on the wafer to selectively extract electrons. Indium tin oxide (ITO) transparent electrode is sputtered on the top of TiO$_2$ followed by the deposition of a Ag grid electrode to decrease the series resistance. Back contacts are made of Zn and Au. The thin layer of amorphous TiO$_2$ effectively and selectively extracts electrons thereby increasing the solar cell efficiency to 19.2% from 9.9% of the cell without TiO$_2$.

![Diagram](image)

**Figure 1.3.** Schematic cross section of p-n heterojunction solar cell.

Copper indium gallium selenide (CIGS) solar cell has achieved 17.4% efficiency using p-n heterojunction structure. The CIGS cell uses a glass substrate with a direct current magnetron sputtered 400 nm Mo layer as a hole collecting electrode. CIGS layer with a thickness of 2 μm was deposited on the top of Mo layer by the co-evaporation of Cu, In, Ga, and Se. CdS buffer layer (~50 nm) is then deposited by the chemical bath deposition followed by the radio frequency magnetron sputter deposition of intrinsic n-type ZnO (~70 nm) and transparent Al-doped ZnO (~250 nm) electrode. CdS free CIGS
solar cells had also achieved efficiency of 17.2% with the cell structure consisting of glass/Mo/CIGSs/Zn(O, S, OH)x/ZnO:B.\textsuperscript{12} Cu$_2$ZnSnS$_4$ solar cells also use a p-n heterojunction structure and a cell of glass/Mo/Cu$_2$ZnSnS$_4$/Zn$_{1-x}$Cd$_x$S/i-ZnO/ITO configuration has achieved efficiency of 9%. Cu$_2$ZnSnS$_4$ layer was deposited by co-sputtering Cu/ZnS/SnS precursors with a post-sulfurization procedure and Zn$_{1-x}$Cd$_x$S was deposited by successive ionic layer adsorption and reaction method.\textsuperscript{13} Cu$_2$ZnSnS$_x$Se$_{4-x}$ with structure of glass/Mo/Cu$_2$ZnSnS$_x$Se$_{4-x}$/CdS/i-ZnO/ITO has achieved efficiency of 12.6%. The Cu$_2$ZnSnS$_x$Se$_{4-x}$ absorption layer was prepared by spin coating of CuS-S, ZnSe, and SnSe-Se hydrazine solutions and post-annealed at 540 °C under sulfur atmosphere.\textsuperscript{14} It is important to indicate that all CIGS and CZTS solar cells require a post annealing step in selenium or sulfur atmosphere at about 500 °C. This step necessitates an inert substrate such as Mo on glass. The p-n heterojunction structure is also used in perovskite solar cells\textsuperscript{15} and cells with the structure of glass/FTO/TiO$_2$/CH$_3$NH$_3$PbI$_3$/carbon achieved an efficiency of 14%.\textsuperscript{16} CdTe solar cells of Mo/Cu/CdTe/CdS/ZnO/ZnO:Al structure have achieved efficiency of 17.1%.\textsuperscript{17}

**p-i-n Heterojunction Solar Cell**

Planar and mesoporous p-i-n heterojunctions are widely used in perovskite, dye-sensitized and quantum dot solar cells (Figure 1.4). An intrinsic narrow bandgap semiconductor is used for the absorption of light and generation of electrons and holes. Wide bandgap p & n-type semiconductors selectively extract holes and electrons from the narrow bandgap light absorber, respectively. The p-type hole-extracting layer has a high conduction band energy level and effectively blocks the diffusion of electrons to the hole-
extracting layer thereby decreases the recombination loss in this layer. The n-type electron extracting layer has a low valence band energy level that effectively prevents the diffusion of holes into the electron extracting layer thus decreasing the recombination in the n-type semiconductor.\textsuperscript{5} The reduced carriers recombination by the single carrier extracting layers improves \( J_{sc} \), \( V_{oc} \), and FF.\textsuperscript{5,18} A planar p-i-n structure is used when the light absorption layer has a long diffusion length of electrons and holes. The carrier diffusion length should be much longer than the absorption depth and the film thickness, for example, the diffusion lengths of electron and hole in CH\(_3\)NH\(_3\)PbI\(_3\) are both longer than 175 \( \mu \)m under 1 sun\textsuperscript{19} but less than 0.40 \( \mu \)m thick of CH\(_3\)NH\(_3\)PbI\(_3\) film is used due to its high absorption coefficient.\textsuperscript{15} A perovskite solar cell having glass/FTO/TiO\(_2\)/CH(NH\(_2\))\(_2\)PbI\(_3\)/polytriarylamine/Au structure has achieved efficiency of 20.1%\textsuperscript{20}.

Figure 1.4. Schematic cross section of (a) planar and (b) mesoporous p-i-n heterojunction solar cell.

A mesoporous p-i-n heterojunction is used when the light absorption materials have very short carrier diffusion length, such as organic dyes and quantum dots. The mesoporous wide band gap n-type TiO\(_2\) layer is prepared by blade coating of TiO\(_2\) nanoparticles followed by sintering in TiCl\(_4\) solution at high temperature. Dyes or quantum dots are then
adsorbed on the mesoporous frame forming an ultrathin tightly compacted layer. The ultrathin light absorption layer enables the carrier diffusion to the surface and their extraction by electron and hole extracting layers. The light absorption layer also prevents the direct contact between hole and electron extracting layers thus decreasing the carrier recombination in the extracting layers. The thickness of the TiO$_2$ is about 10 µm providing a large surface area to absorb enough light absorption materials. Dye synthetized solar cells (DSSC) with the structure of glass/FTO/TiO$_2$/porphyrin dye SM315/Co(bpy)$_3$(TFSI)$_2$ : Co(bpy)$_3$(TFSI)$_3$/graphene/FTO/glass has achieved efficiency of 13%.$^{21}$ The efficiency of solid state DSSC of glass/FTO/TiO$_2$/N719/CsSnI$_2.95$F$_{0.05}$/Pt:FTO/glass structure has achieved 10.2% efficiency.$^{22}$ CsSnI$_2.95$F$_{0.05}$ is a p-type hole extracting semiconductor with a high hole mobility.$^{22}$ Quantum dot solar cell having structure of glass/FTO/TiO$_2$/Zn–Cu–In–Se quantum dot/NaS:S/C:Ti has achieved efficiency of 11.6%.$^{23}$ The fabrication process of quantum dot solar cells is similar to that for DSSC. Quantum dots are adsorbed on a TiO$_2$ mesoporous frame and are used to capture light.

**p-n Bulk Heterojunction Solar Cell**

![Schematic cross section of p-n bulk heterojunction solar cell.](image)

**Figure 1.5.** Schematic cross section of p-n bulk heterojunction solar cell.
Bulk heterojunction structures are widely used in organic solar cells to separate electrons and holes (Figure 1.5). Organic semiconductors have a small dielectric constant and have overlap between HOMO and LUMO orbits. As a result, organic semiconductors have large exciton binding energies that can be separated only at the interface between p and n semiconductors. The bulk heterojunction structure creates abundant junction interface to separate the excitons but the extensive interface also increases the recombination rate of free carriers. Wide bandgap p and n-type carrier extracting semiconductors selectively extract holes and electrons from the bulk heterojunction and prevent the recombination near the electrodes. The bulk heterojunction is prepared by a solvent co-deposition of p & n semiconductors. Careful section of the solvent and deposition conditions is needed to obtain organized phase separation between p and n semiconductors and to avoid island like domains in the bulk junction. Holes and electrons which are trapped in the island domains cannot be delivered to the extracting layers. As a result, it is very difficult to obtain high internal quantum efficiency in disordered bulk heterojunction solar cells. Fullerene is widely used as the electron extracting material in current organic polymer solar cells. It is important to indicate that the PEC of these organic solar cells is mainly limited by low $V_{oc}$ because of the low LUMO of fullerene. The world record efficiency of organic solar cell is 11.7% with glass/ITO/ZnO/PffBT4T-C$_9$C$_{13}$:PC$_{71}$BM/V$_2$O$_5$/Al structure.$^{24}$

p-i-n Micro Heterojunction Solar Cell

Quantum dot solar cells are assembled by the absorption of quantum dots into a mesoporous wide band gap carrier extracting layer similarly to DSSC. It is well known that
quantum dots have large surface area and many defects capable of quenching the carries. Another factor to consider is that high-quality single crystals have much better electronic performance than polycrystalline and amorphous materials because the interface between crystallites scatters and traps the carriers. For some materials, such as CZTS, it is hard to obtain high-quality crystal thin films as light absorption layers for traditional solar cell structures. However, these materials are relative easily to synthesize in the form of nano or even micro crystals. The p-i-n micro heterojunction (Figure 1.6) is an effective way to combine the advantages of single crystals with the convenience of solution process techniques. Solution methods have been developed for processing of wide bandgap materials such as ZnO, TiO$_2$, MoO$_3$, V$_2$O$_5$, WO$_3$, CuSCN that can selectively extract electron or holes and decrease carrier recombination.

**Figure 1.6.** Schematic cross section of p-i-n micro heterojunction solar cell.

The p-i-n micro heterojunction can be built on glass/ITO substrate by spin coating or electrochemical deposition of wide bandgap semiconductors, such as n-type ZnO and p-type CuSCN, followed by spin-coating or the self-assembly of nanocrystals. The deposition of surface passivation materials and insulators can also be achieved by spin-coating. In addition, spin-coating can be used to deposit the other semiconductor layer.
followed by a wet deposition of the top electrode. All these steps are extensively described in the literature.\textsuperscript{15,25-26}

Summary

Traditional single crystal and polycrystalline silicon solar cells are dominating the current photovoltaic market but they require ultra-high purity silicon, energy-intensive crystal growth techniques, and high-temperature processes that all lead to high cost of silicon solar cells. Alternative high-efficiency solar cells have been developed, such as GaAs (28.8%), InP (22.1%), CIGS (21%), and CdTe (21%). However, these solar cells still have a high cost associated with semi-precious metals (In, Ga, Te). Low-cost alternatives have been developed such as organic solar cells (11.7%)\textsuperscript{24}, DSSC (13%)\textsuperscript{21} and quantum dot solar cell (11.6%)\textsuperscript{23}, but they lack the efficiencies and the stability of other inorganic cells. Perovskite solar cells have achieved efficiency of 20.1\%\textsuperscript{20,27} and have the potential for commercialization after improving the current fabricating techniques. CZTS solar cell is a good candidate for future inexpensive solar cells because of its stability and environmental friendliness. The bottleneck for the cost-efficient production of these cells relates to the lack of effective methods for the preparation of CZTS high-quality crystal thin films. The utilization of the p-i-n micro heterojunction structure has potential to ease the requirement for high-quality CZTS thin films and is expected to result in high efficient, environmentally friendly and solution-processed solar cells.

References

CHAPTER TWO

FABRICATION OF LEAD HALIDE PEROVSKITE FILM BY CONTROLLING REACTIVITY AT ROOM TEMPERATURE IN MIXED SOLVENTS

Introduction

Lead halide perovskite (e.g., PbCH$_3$NH$_3$X$_3$)-based solar cells have brought a new avenue for achieving low-cost photoelectric conversion.\textsuperscript{1-4} Perovskite solar cells went through a rapid evolution, both in cell structure and power conversion efficiency, in the past few years. Organometallic halide perovskite materials were first used as a light absorber in liquid electrolyte-based mesoscopic dye-sensitized solar cells in 2009.\textsuperscript{4} However, this application was abandoned due to the instability of PbCH$_3$NH$_3$X$_3$ in liquid electrolytes. The emergence of solid-state mesoscopic heterojunction perovskite solar cells in 2012 has alleviated the long term instability problem.\textsuperscript{5-6} Mesoscopic perovskite solar cells are made by using n-type metal oxide semiconductor (e.g., ZnO and TiO$_2$) and perovskite,\textsuperscript{7-8} often as a filler in mesoporous structures of insulating material (e.g., Al$_2$O$_3$) or titania.\textsuperscript{6,8} Planar heterojunction perovskite solar cells was also developed in 2013 using a p-i-n structure.\textsuperscript{9-10} Power conversion efficiency of mesoscopic heterojunction and planar heterojunction perovskite solar cells have exceeded 15\%.\textsuperscript{8,9,11} The most recent news report stated the efficiency as high as 19.3\%.\textsuperscript{12}

It is well recognized that the quality of perovskite films plays an important role in achieving high-efficiency solar cells, therefore the development of perovskite preparation methods is an active area of research.\textsuperscript{9,13-14} Methods that are often used to make perovskite films can be divided into solution-based methods and vapor deposition. Solution-based
spin coating of the precursor was used in the first solid state perovskite solar cell. Due to the crystallinity of perovskite materials and the lack of good solvents for the precursors, spin coating often gives films with the island structure, pin holes, and incomplete surface coverage. Lead iodide spin-coated films dipped into CH$_3$NH$_3$I isopropanol solution comprised a two steps solution-based method, in which excess of methylammonium iodide was removed by rinsing with isopropanol. Due to the high reactivity of lead iodide with CH$_3$NH$_3$I the method was quite sensitive to the concentration of the organic halide, temperature and reaction time resulting in difficulty of controlling the quality of the films. Subsequent 2-propanol rinsing can partially dissolve perovskite and convert it back to lead iodide. To better control the reactivity, CH$_3$NH$_3$I vapor was used to convert PbI$_2$ to perovskite and the 2-propanol rinse to remove excess of CH$_3$NH$_3$I. Methylammonium iodide vapor was produced at 150 °C under N$_2$ environment, the conditions that may not be compatible with many polymer substrates. High-quality CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ films were also obtained by thermal vapor codeposition of CH$_3$NH$_3$I and PbCl$_2$. However, this method is more energy costly and requires expensive high vacuum systems.

Here, we presented a simple, reliable method based on mixing different solvents to fabricate uniform, small grain CH$_3$NH$_3$PbI$_3$ thin film at room temperature. The concept is based on the reversible reaction between PbI$_2$ and CH$_3$NH$_3$I (Scheme 1), in which the key step is to control the reaction kinetics by using an appropriate solvent mixture. This approach allows the control of the grain size and surface roughness of CH$_3$NH$_3$PbI$_3$ thin film. The resulted perovskite films were uniform across the large surface area without residual PbI$_2$. The method is robust in that it is fairly insensitive to reaction conditions such
as small changes in temperature, reactant concentration and the reaction time once the reaction is allowed to proceed to completion. The method appears suitable for a large area fabrication of perovskite solar cells including cells on flexible substrates.

Scheme 1. The reversible reaction.

**Experiment Section**

**Materials**

Hydroiodic acid (Sigma-Aldrich, 57 wt % in H₂O, 99.99%), methylamine solution (Aldrich, 33 wt % in absolute ethanol), lead acetate trihydrate (J. T. Baker, A.C.S. reagent), potassium hydroxide (Amresco, reagent grade), zinc acetate dihydrate (J. T. Baker, Baker analyzed reagent), hexane (Burdick & Jackson, HPLC grade), 2-propanol (J. T. Baker, HPLC grade), cyclohexane (Alfa Aesar, HPLC grade) and N,N-dimethylformamide (DMF) (Sigma-Aldrich, 99.8%) were used as received. Float glass microscope slides (VWR micro slides) were used for all substrates. Fluorine-doped tin oxide (FTO) glass (~7 Ω/sq) and indium tin oxide (ITO) glass received from Sigma and Delta Technologies, LTD, respectively.

**Synthesis**

Methylammonium iodide was synthesized by using hydroiodic acid and methylamine following previously reported method.⁶ Lead iodide was synthesized by using hydroiodic acid and lead acetate trihydrate. In a typical reaction,
Pb(CH₃COO)₂·3H₂O (18.97 g, 50.00 mmol) was dissolved in H₂O (200 mL) with stirring. HI (57 wt % in H₂O, 19.79 mL) was dissolved in H₂O (100 mL) at room temperature. HI solution was then added to the Pb(CH₃COO)₂ solution drop by drop with stirring at room temperature over a period of 10 min. The reaction mixture was further stirred at room temperature for additional 2 h. After filtration, the yellow PbI₂ solid was washed with H₂O following by drying in a vacuum oven at 120 °C overnight.

ZnO nanoparticles

ZnO nanoparticles were synthesized following literature method. In short, Zn(CH₃COO)₂·2H₂O (0.979 g, 4.46 mmol) and H₂O (100 µL) was dissolved in CH₃OH (42 mL) with stirring at 60 °C. KOH (0.486 g, 7.22 mmol) was dissolved in CH₃OH (23 mL) with stirring at room temperature. KOH solution was then added to the Zn(CH₃COO)₂ solution drop by drop with stirring at 60 °C over a period of 13 min. The reaction mixture was further stirred at 60 °C for additional 2 h 15 min. After cooling to room temperature during 1 h, the supernatant was decanted and the precipitate was washed twice with CH₃OH following by dispersing in n-butanol (14 mL). ZnO suspension was then filtered through a 0.2 µm PTFE syringe filter before using.

CH₃NH₃PbI₃ film fabrication

CH₃NH₃PbI₃ films were prepared under ambient environment. Glass substrates (1.5 cm × 2.5 cm) were first cleaned with detergent using sonication, rinsed with water followed by sonication in acetone and ethanol for 20 min respectively. Glass substrates were then further cleaned by air plasma for 10 min. The substrates were coated with ZnO
nanoparticles by spin-coating from butanol suspension at 3000 r.p.m. for 30 s. The nanoparticles were spin coated three times to get a uniform film. PbI$_2$ solution (prepared by dissolving PbI$_2$ (500 mg) in DMF (1.0 mL) at 70 °C) was then spin coated on the substrate at 6000 r.p.m. for 45 s. After drying in air, the substrate was dipped into a suspension of CH$_3$NH$_3$I (10 mg) in a mixture of isopropanol and cyclohexane or hexane (total volume 30 mL) for varying the time between 15 min and 12 hours and then dried under ambient environment.

Instrumentation

UV-vis extinction spectra were measured with Shimadzu UV-2501 PC spectrophotometer. Powder X-ray diffraction (PXRD) data was collected using a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 25 °C. Imaging was performed with AIST-NT SmartSPM-1000 atomic force microscope (AFM) operating in AC mode. Root mean squared (RMS) roughness was calculated by using Nanotec Electronica WSxM software based on a 20 μm × 20 μm scan area. Grain size was calculated by using PDXL software (RIGAKU Corporation) from PXRD data. Laurell WS-400B-6NPP-Lite Manual Spinner was used for spin-coating. PXRD pattern simulation was performed on Mercury 3.3 software by using a tetragonal CH$_3$NH$_3$PbI$_3$ single crystal structure (a = 8.849(2) Å, c = 12.642(2) Å and space group I4cm).

Results and Discussions

Zinc oxide is usually an n-type semiconductor often used for the fabrication of heterojunction photovoltaic devices. Zinc oxide compact layers can be easily prepared by spin coating of ZnO nanoparticles at room temperature without the requirement of further
post-treatment steps. In this work, ZnO was selected as an underlayer for CH$_3$NH$_3$PbI$_3$ films to mimic the heterojunction in a real perovskite solar cell. High-quality PbI$_2$ films were made by using a high concentration of PbI$_2$/DMF solution (34.6 wt%) spin coated at 6000 rpm spin rate. As is shown in Figure 2.1a, PbI$_2$ films consisted of small particles uniformly coating the surface. The measured 14 nm RMS roughness of the films together with their uniformity resulted in the low background in UV-vis spectra. The films appeared completely clear with uniform yellow color and exhibited a characteristic band gap absorption spectrum (Figure 2.1b). XRD spectra of PbI$_2$ films matched exactly to a standard spectrum demonstrating the purity of the films without the DMF-PbI$_2$ complex (Figure 2.2a). The 18 nm grain size calculated from XRD was in a good agreement with 14 nm RMS roughness measured by AFM. Lead iodide films were also spin-coated under the same conditions onto clean float glass surface (without ZnO), ITO and FTO-coated substrates. In all cases, the films were uniform, appear alike and exhibited 12 –14 nm RMS roughness (Figure S2.1).

Figure 2.1. PbI$_2$ film on the glass/ZnO substrate: (a) AFM high image; (b) UV-Vis spectrum.

Lead iodide films were converted into perovskite films by dipping the substrates into methylammonium iodide saturated solution in various mixed solvents (Table 2.1). In
order to obtain the uniform conversion of PbI$_2$ to CH$_3$NH$_3$PbI$_3$, it was critical to allow all particulates to precipitate on the bottom in the saturated solution before exposing PbI$_2$ films. Otherwise, the films appeared blotchy and opaque due to large roughness and nonuniformity, most likely because of a high local CH$_3$NH$_3$I concentration around suspended particulates.

**Table 2.1.** RMS roughness and grain size of the films after different reaction conditions.

<table>
<thead>
<tr>
<th>Solution$^a$</th>
<th>Time (h)</th>
<th>RMS (nm)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbI$_2$</td>
<td>0</td>
<td>14</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>7.5% Hex</td>
<td>0.25</td>
<td>17</td>
<td>mix$^b$</td>
</tr>
<tr>
<td>7.5% Hex</td>
<td>0.5</td>
<td>20</td>
<td>29 ± 3</td>
</tr>
<tr>
<td>7.5% Hex</td>
<td>12</td>
<td>25</td>
<td>37 ± 4</td>
</tr>
<tr>
<td>3% Chex</td>
<td>2.5</td>
<td>39</td>
<td>mix$^b$</td>
</tr>
<tr>
<td>3% Chex</td>
<td>12</td>
<td>31</td>
<td>79 ± 13</td>
</tr>
<tr>
<td>5% Chex</td>
<td>0.5</td>
<td>22</td>
<td>mix$^b$</td>
</tr>
<tr>
<td>5% Chex</td>
<td>1.0</td>
<td>22</td>
<td>mix$^b$</td>
</tr>
<tr>
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<td>2.5</td>
<td>24</td>
<td>73 ± 11</td>
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<tr>
<td>5% Chex</td>
<td>12</td>
<td>32</td>
<td>82 ± 13</td>
</tr>
<tr>
<td>7.5% Chex</td>
<td>0.5</td>
<td>21</td>
<td>mix$^b$</td>
</tr>
<tr>
<td>7.5% Chex</td>
<td>1.0</td>
<td>21</td>
<td>80 ± 14</td>
</tr>
<tr>
<td>7.5% Chex</td>
<td>2.5</td>
<td>27</td>
<td>75 ± 10</td>
</tr>
<tr>
<td>7.5% Chex</td>
<td>12</td>
<td>26</td>
<td>71 ± 11</td>
</tr>
<tr>
<td>10% Chex</td>
<td>0.5</td>
<td>19</td>
<td>mix$^b$</td>
</tr>
<tr>
<td>10% Chex</td>
<td>1.0</td>
<td>19</td>
<td>57 ± 9</td>
</tr>
<tr>
<td>10% Chex</td>
<td>2.5</td>
<td>24</td>
<td>71 ± 11</td>
</tr>
</tbody>
</table>

$^a$ CH$_3$NH$_3$I saturated 2-propanol/hexane (Hex) and 2-propanol/cyclohexane (Chex) solution. $^b$ mix $=$ a mixture of PbI$_2$ and CH$_3$NH$_3$PbI$_3$.

The key point of this method is to maintain the optimum concentration of CH$_3$NH$_3$I in the reaction solution in order to control the reaction kinetics and to produce perovskite films with low RMS roughness and, at the same time, have a constant supply of CH$_3$NH$_3$I from the saturated solution to convert all PbI$_2$ into perovskite. It was also hypothesized that
the reversibility of the reaction, i.e. the decomposition of CH₃NH₃PbI₃ into PbI₂ and CH₃NH₃I, facilitates a ripening process resulting in the films consisting of small fairly uniform nanoparticles, the process similar to Ostwald ripening in colloidal suspensions.¹⁴

The implementation of this approach was accomplished by a selection of two miscible solvents. One is a relatively good solvent for methylammonium iodide and can also slightly dissolve both lead iodide and perovskite. The other nonpolar, aprotic solvent does not dissolve or degrade the reactants and the product. By mixing the two solvents, the reaction kinetics and mass transfer process can be controlled.

In order to select appropriate solvent mixtures, the stability of CH₃NH₃PbI₃ film was first tested in several solvents at room temperature by immersing for 30 min. The CH₃NH₃PbI₃ film did not show visible color changes in following nonpolar solvent, anisole, kerosene, ethyl ether, cyclohexane, and hexane. The color of CH₃NH₃PbI₃ has changed from brown to yellow or the films were completely dissolved in following relative polar solvent, acetonitrile, acetone, ethyl acetate and diethylene glycol dimethyl ether. Considering the boiling point and relative toxicity, cyclohexane and hexane were chosen as a second solvent for the method. Cyclohexane and hexane are poor solvents but 2-propanol is a good solvent for CH₃NH₃I and can slightly dissolve both PbI₂ to CH₃NH₃PbI₃. The optimum concentration of CH₃NH₃I can be adjusted by selecting the ratio of 2-propanol to hexane or cyclohexane. The reaction of CH₃NH₃I with PbI₂ film consumes CH₃NH₃I in solution but CH₃NH₃I solid in the precipitate provides a constant supply. Furthermore, excess CH₃NH₃I is beneficial for shifting the equilibrium toward the formation of CH₃NH₃PbI₃.
Suspension of CH$_3$NH$_3$I in 7.5% 2-propanol/hexane was used to investigate the conversion kinetics of PbI$_2$ into CH$_3$NH$_3$PbI$_3$. XRD spectra measured at different reaction time demonstrate the graduate increase of the perovskite and decrease of the lead iodide phases (Figure 2.2a). After 30 min, lead iodide was complete converted into tetragonal crystal structure of CH$_3$NH$_3$PbI$_3$. No lead iodide remained in the film as was evident from the disappearance of its characteristic diffraction peak at 12.69$^\circ$. AFM images revealed smooth and uniform films with the RMS roughness of 17 nm, 20 nm, and 25 nm after 15 min, 30 min and 12 hours reaction time, respectively (Figure 2.2b–2.2d). The grain size calculated from XRD spectra was 29 nm and 37 nm after 30 min and 12 hours, respectively. UV-Vis spectra showed the characteristic bandgap absorption for perovskite and a low background due to the smoothness and uniformity of the films (Figure 2.2e). The thickness of the films was estimated to be 300 nm from the UV-vis data.

When methylammonium iodide was dissolved in 2-propanol/hexane mixture, the appearance of yellow color was noticed after several hours of storing the solution. The subsequent UV-vis analysis revealed the presence of characteristic peaks at 291 and 358 nm due to I$_3^-$ in addition to 217 nm from I$^-$ (Figure S2.3j). Even though HPLC grade hexane was used, it was postulated that unidentified impurities were oxidizing I$^-$ to I$_3^-$. This observation prompted switching to cyclohexane because it was expected that it could have less oxidizing impurities due to a different preparation method. Whereas hexane is a distillation product from crude, cyclohexane is often produced by hydrogenation of benzene. Indeed, storing methylammonium iodide in cyclohexane did not produce any color and only one peak at 219 nm due to I$^-$ was observed in UV-vis spectra (Figure S2.3j).
Figure 2.2. (a) XRD spectra of CH$_3$NH$_3$PbI$_3$ films obtained after various reaction time in CH$_3$NH$_3$I saturated 7.5% 2-propanol/hexane mixture; (b), (c), and (d) AFM images of the films after 15 min, 30 min, and 12 h of the reaction, respectively; (e) UV-Vis spectrum of the film after 12 h of the reaction.

The conversion of PbI$_2$ into CH$_3$NH$_3$PbI$_3$ was studied in 2-propanol/cyclohexane mixture for the alcohol concentrations ranging from 3% to 10%. The conversion rate ranging from incomplete conversion after 2.5 hours for 3% to the full conversion in less
than 1 hour for 10% (Table 2.1) was observed. All perovskite films appeared to have the similar roughness and grain size (Figure S2.2 to S2.4). XRD spectra confirmed the conversion of PbI₂ into CH₃NH₃PbI₃. However, the conversion rate was about half of that in the hexane for the same concentration of 2-propanol. This is most likely due to of higher solubility of CH₃NH₃I in 2-propanol/hexane than in 2-propanol/cyclohexane mixture.

Perovskite films were also fabricated on float glass, ITO and FTO substrates, all without ZnO, using 5% 2-propanol/cyclohexane solution. The films appeared significantly heterogeneous, with poor adhesion (have not passed Scotch tape test) due to insufficient wetting of these substrates by CH₃NH₃PbI₃. Having ZnO underlayer was essential to obtain high-quality perovskite films with this method.

Conclusions

The reaction kinetics of converting lead iodide to perovskite can be effectively controlled by mixing two solvents, one of which is a good solvent for methylammonium iodide such as 2-propanol, also capable of slightly dissolving both lead iodide and perovskite and the other is a poor aprotic solvent such as hexane or cyclohexane that does not dissolve or degrade the reactants and the product. This simple and reliable approach allows reproducible fabrication of smooth and uniform, fully converted perovskite films at room temperature, an important advancement for the large scale manufacture of perovskite-based solar cells.

Acknowledgements
We gratefully acknowledge the support of this work through Department of Energy, Grant DE-FG02-06ER46342, and Clemson University Center for Optical Materials Science and Engineering Technologies.

References

CHAPTER THREE
SOLUTION-PROCESSED PLANAR PEROVSKITE SOLAR CELL WITHOUT A HOLE TRANSPORT LAYER

Introduction

In order to achieve broad application of solar cells as a significant energy source, a balance between cost, stability, and efficiency must be reached. Rapid evolution of lead halide perovskite solar cells, specifically by increasing power conversion efficiency, brought new potentials for their practical applications.\textsuperscript{1-4} Lead halide perovskite materials were first used as dyes in liquid dye-sensitized solar cells in 2009.\textsuperscript{4} A breakthrough in perovskite solar cells was achieved when the first solid-state mesoscopic heterojunction perovskite solar cell was built in 2012.\textsuperscript{5-6} Planar heterojunction perovskite solar cells were further developed in 2013.\textsuperscript{7-8} Power conversion efficiencies of mesoscopic heterojunction and planar heterojunction perovskite solar cells have exceeded 18\%, while the most recent, verified perovskite solar cell efficiency is as high as 20.1\%.\textsuperscript{9-11, 12} An important problem that needs to be addressed is how to decrease the manufacturing cost as well as improve the stability of the solar cells. Current perovskite solar cells often require high temperature processed TiO\textsubscript{2},\textsuperscript{13} expensive fullerene derivatives,\textsuperscript{9} or other unstable organic materials as electron/hole collecting layers,\textsuperscript{11,14} and expensive rare metals (eg, silver or gold) as electrodes.\textsuperscript{9,11} Also, the manufacturing process often requires high vacuum conditions and an oxygen-free atmosphere. These factors add to the high manufacturing cost and thus hinder the widespread application of the solar cells.
Recent developments of carbon-based perovskite solar cells have significantly reduced the manufacturing cost.\textsuperscript{15-17} Carbon black and graphite have suitable work functions (about – 5.0 eV) and can serve as a hole collecting electrode.\textsuperscript{13,18} These solar cells often employ FTO/TiO\textsubscript{2}(dense layer)/TiO\textsubscript{2} or ZrO\textsubscript{2} (mesoporous layer)/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/carbon structures and require high-temperature processing of TiO\textsubscript{2}.\textsuperscript{13,18} In contrast, ZnO compact layers can be easily prepared by spin coating ZnO nanoparticles at room temperature without heat treatment steps. Currently, ZnO-based planar perovskite solar cells have achieved 15.7% efficiency.\textsuperscript{19} The manufacturing cost can be further reduced by using ZnO as n-type material in carbon based perovskite solar cells.

Another way to reduce the manufacturing cost is to optimize the solar cell structure. Perovskite solar cells utilize planar and mesoporous structures. Mesoporous structures are more favored because they prevent the direct contacts between cathodes and anodes. These structures also improve the electron injection, thereby minimizing the hysteresis effect.\textsuperscript{20} In contrast, planar structures are simpler to manufacture because they do not need the additional mesoporous layer. Further simplification can be achieved by eliminating a dedicated hole transport layer. In this case, pinhole free perovskite films are required to avoid short circuits. It is well recognized that the quality of perovskite films plays an important role in achieving high-efficiency solar cells in both planar and mesoscopic structures.\textsuperscript{7,21-23}

In our previous work, a simple, reliable and scalable method for the fabrication of high-quality CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films at room temperature based on the reaction of PbI\textsubscript{2} films with a saturated solution of CH\textsubscript{3}NH\textsubscript{3}I in 2-propanol/cyclohexane was developed.\textsuperscript{24}
Here, this method, together with other solution processing methods were used to fabricate efficient planar perovskite solar cells. A planar ITO/ZnO/CH$_3$NH$_3$PbI$_3$/carbon electrode structure was selected to minimize the fabrication cost. These solar cells were built under ambient conditions at room temperature without vacuum and inert atmosphere. This low-cost method provides opportunities for the development of commercially viable perovskite solar cells.

**Experimental Section**

**Materials**

Fluorine-doped tin oxide (FTO) glass (~7 Ω/sq) and indium tin oxide (ITO) glass (8 – 12 Ω/sq) were received from Sigma and Delta Technologies, LTD, respectively. Cyclohexane (Alfa Aesar, HPLC grade), 2-propanol (J. T. Baker, HPLC grade), N,N-dimethylformamide (DMF) (Sigma-Aldrich, 99.8%), sodium sulfate (Fisher Scientific, certified A.C.S. grade), ammonium sulfate (Sigma-Aldrich, 99.0%), graphite rod (Alfa Aesar, 99%) and acetylene carbon black (50% compressed) (Strem Chemicals) were used as received. Methylammonium iodide, lead iodide, and zinc oxide nanoparticles were synthesized following previously reported methods.$^{24}$

**Instrumentation**

UV-vis extinction spectra were measured using a Shimadzu UV-2501 PC spectrophotometer. Electrochemical exfoliated graphite flakes were further dispersed in a VWR 750D ultrasonic cleaner. Powder X-ray diffraction (PXRD) data was collected using a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 25 °C.
Imaging and thickness measurements were performed using an AIST-NT SmartSPM-1000 atomic force microscope (AFM) operating in AC mode. Electron microscope images were obtained with H-9500 transmission electron and S-4800 field emission scanning electron microscopes (Hitachi). Laurell WS-400B-6NPP-Lite Manual Spinner was used for spin-coating. PXRD pattern simulation was performed on Mercury 3.3 software by using a tetragonal CH₃NH₃PbI₃ single crystal structure (a = 8.849(2) Å, c = 12.642(2) Å and space group I4cm). The current–voltage curves of solar cells were measured by using an electrochemical workstation (CH Instruments, CH440) with linear sweep voltammetry. The solar cells were illuminated by an in-house built solar simulator equipped with a Mega-9 AM1.5G filter at a calibrated intensity of 100 mW cm⁻². The effective area of the solar cell was defined as 0.49 cm² with a non-reflective metal mask. The standard deviation was calculated from the measurements of eight solar cells. The impedance measurements were performed using Solartron analytical 1470E cell test system by applying a 0.015 V sinusoidal signal over the constant applied bias and the frequency range from 0.5 Hz to 100 kHz.

**Electrochemical exfoliation of graphite**

Mixtures of graphite particles and graphene sheets (from here on called graphite suspension) were obtained from electrochemically exfoliated (EE) graphite by a modified literature method.²⁶ Briefly, cathode and anode graphite rods were placed into Na₂SO₄ or (NH₄)₂SO₄ (0.05 mol L⁻¹, 800 mL) electrolyte solution at a distance of 2.0 cm. Electrochemical exfoliation was carried out at 5 °C by applying 10 V between the two graphite rods. After the complete disintegration of the anode, the EE graphite was obtained.
in the form of a fluffy precipitate that was collected via vacuum filtration. The EE graphite was then washed 3 times with deionized water and 2 times with ethanol followed by dispersing in ethanol (30 mL). NaBH₄ (300 mg, 7.93 mmol) was added to the above suspension and the reaction mixture was stirred at room temperature for 2 h. The EE graphite was collected by the vacuum filtration followed by washing 3 times with deionized water and 2 times with ethanol. A mixture of the EE graphite and 4-methyl-2-pentanone was sonicated at room temperature for 40 min. Following the centrifugation at 460 G for 30 min to remove large particles, the supernatant containing ~ 0.8 mg mL⁻¹ of graphite was used to fabricate all solar cells.

Solar cell fabrication

Devices were fabricated under an ambient environment. ITO-coated glass substrates (1.5 cm × 2.5 cm) were masked by scotch tape and etched by a mixture of 2.0 mol L⁻¹ HCl and zinc powder. The substrates were then rinsed with 18 MΩ water followed by sonication in acetone, ethanol and water for 15 min in each solvent. The substrates were further cleaned by air plasma for 10 min. The substrates were coated with ZnO nanoparticles by spin-coating from CHCl₃/n-butanol suspension at 3000 rpm for 30 s. The spin coating was performed three times to obtain uniform films. Perovskite films were made according to the previously described procedure.²⁴ PbI₂ (3.0 g) was dried in a vacuum oven at 120 °C for 20 min and dissolved in anhydrous DMF (6.0 mL) at 70°C without stirring. It was found that stirring degraded the quality of the CH₃NH₃PbI₃ films by introducing pin holes, possibly from microscopic debris produced during the stirring process. After cooling to room temperature overnight, the PbI₂ solution was heated again
at 70 °C for 2 h and then cooled to room temperature. After the second heating and cooling cycle, about 10 mg of insoluble precipitate was formed at the bottom of the container and further removed and discarded. The supernatant solution was used for spin coating. The purification process of PbI₂ solution reduced the formation of pin holes in CH₃NH₃PbI₃ films. 100 µL of the PbI₂ solution was dropped onto glass/ITO/ZnO substrates multiple times until the solution completely covered the surface. After waiting 2 min, the substrates were spun at 3000 rpm for 3 min under the continuous blow of clean air. After drying in air, the substrates were immersed for 5 h into CH₃NH₃I saturated solution in 5/95 (v/v) 2-propanol/cyclohexane. The graphite layer was fabricated by spin coating of the graphite suspension in 4-methyl-2-pentanone. 100 µL of the suspension was delivered drop by drop at the rate of one drop per 15 s onto a substrate spinning at 1000 rpm. To make the direct electrical contact to the ITO substrate, all layers were removed from a small area by wiping with cotton swabs wetted in acetone and, separately, 2M HCl aqueous solution. Acetylene carbon black was used to improve electrical contact between graphite layer and the top electrode that was either FTO-coated glass, copper or any other metal. For convenience purposes, flat FTO-coated glass was mainly used as the top electrode for the devices reported here. The entire structure was mechanically clamped together with two binder clips.

Results and Discussion

Electrochemical exfoliation is an effective method for disintegrating bulk graphite. The resultant EE graphite can be dispersed in appropriate solvents to produce a suspension containing a mixture of graphite particles and graphene sheets. Graphene sheets prepared
by this method were shown to exhibit hole mobility of ~310 cm$^2$ V$^{-1}$ S$^{-1}$. The high hole mobility supports the efficient hole extraction from semiconductors, thereby increasing the power conversion efficiency in solar cells. The electrochemical exfoliation of graphite rods was performed in a two electrode system in Na$_2$SO$_4$ and (NH$_4$)$_2$SO$_4$ electrolytes. It was found that the concentration of Na$_2$SO$_4$ affected the yield of EE graphite. After testing various concentrations (0.10, 0.25, 0.50, 0.75 and 1.0 mol L$^{-1}$), 0.5 mol L$^{-1}$ was found to be optimal and was used throughout the studies. The same concentration of (NH$_4$)$_2$SO$_4$ consistently yielded 4-5 times fewer graphite particles and graphene sheets. The exfoliation at lower temperature produced graphite suspensions with a higher concentration of graphite particles and graphene sheets. Several solvents such as dimethylformamide (DMF), acetone, ethyl acetate, chlorobenzene, 1,2-dichlorobenzene, 2,4-dimethyl-3-pentanone, cyclopentanone, and 4-methyl-2-pentanone were tested to optimize the graphite suspension. The EE graphite was dispersed in each solvent by sonicating for 15 min at room temperature followed by centrifuging at 460 G. Only DMF and 4-methyl-2-pentanone produced stable graphite suspensions after the centrifugation, whereas the other solvents gave a clear supernatant and a black precipitate. Even though the DMF suspensions contained higher concentrations of graphite particles and graphene sheets, 4-methyl-2-pentanone graphite suspensions were used in the device fabrication, since DMF dissolved CH$_3$NH$_3$PbI$_3$.

When this suspension was spin-coated onto CH$_3$NH$_3$PbI$_3$ films and heated at 60 °C for 5 min, the color of the films changed from deep brown to yellow. The graphite was not expected to interact with CH$_3$NH$_3$PbI$_3$, therefore the color change was ascribed to the
oxidation of I\(^{-}\) to I\(_2\) by oxidizing groups that were present on the surface of the graphite and produced during the anodic exfoliation of graphite rods. The oxidization reaction was confirmed in an independent experiment, in which NaI solution exposed to EE graphite in 4-methyl-2-pentanone produced a strong absorption peak at 358 nm due to I\(_3^{-}\).\(^{27}\)

**Figure 3.1.** AFM image of graphite treated with NaBH\(_4\) and drop-casted on a silicon wafer from 4-methyl-2-pentanone suspension. Inset: height profile along the white line.

The stability of CH\(_3\)NH\(_3\)PbI\(_3\) films was significantly improved after the EE graphite was treated with NaBH\(_4\) prior to dispersing in 4-methyl-2-pentanone. The films remained brown after heating for 15 min at 100 °C. SnCl\(_2\) was also tested as a possible reductant for EE graphite, but this treatment rendered graphite indispensable in 4-methyl-2-pentanone. In order to characterize the morphology of the graphite after the treatment with NaBH\(_4\), the suspension was drop-casted on a silicon wafer and imaged with AFM. As can be seen in Figure 3.1, the majority of graphite was in the form of nanoparticles with a small amount of 2-dimensional graphene sheets. The thickness of the majority graphene sheets was
measured to be less than 10 nm with less than 30 atomic layers in the sheet. This morphology was quite different from that previously reported in similar exfoliation experiments, in which the yield of graphene ($\leq 3$ layers) in excess of 85% was observed.\textsuperscript{26} The apparent discrepancy could be from the fact that graphite rods were used in this study instead of graphite sheets used in the referenced work.

\textbf{Figure 3.2.} (a) XRD spectrum of a CH$_3$NH$_3$PbI$_3$ film on glass/ITO/ZnO substrate, XRD spectrum of the glass/ITO/ZnO substrate and simulated XRD spectrum of tetragonal CH$_3$NH$_3$PbI$_3$. Diffraction peaks at 14.02°, 19.97°, 24.55°, 28.52°, 31.68°, 40.51°, and 43.11° were assigned as the (110), (020), (022), (220), (222), (040), and (330) planes of
tetragonal perovskite, respectively. (b) AFM image of a CH$_3$NH$_3$PbI$_3$ film on glass/ITO/ZnO substrate (c) UV-Vis spectra of CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$/graphite films on glass/ITO/ZnO substrates. (d) AFM image of the graphite film on a glass/ITO/ZnO/CH$_3$NH$_3$PbI$_3$ substrate.

The devices were fabricated by the sequential deposition of ZnO, perovskite, graphite and carbon black layers on ITO substrates, as described in Experimental section. The thickness of ZnO and CH$_3$NH$_3$PbI$_3$ layers was previously optimized, and no further optimization was required in this study. The formation of the perovskite films was confirmed by XRD (Figure 3.2a). AFM and SEM images revealed compacted and uniform films with 21 nm RMS roughness (Figure 3.2b & Figure S3.2a). The band-edge absorption for CH$_3$NH$_3$PbI$_3$ was observed at 783 nm (Figure 3.2c). The total absorption of the glass/ITO/ZnO/CH$_3$NH$_3$PbI$_3$/graphite structure increased after spin-coating a graphite layer and reached the instrument saturation level at wavelengths shorter than 475 nm (Figure 3.2c). The graphite layer completely covered the surface of the CH$_3$NH$_3$PbI$_3$, as was confirmed by AFM and SEM (Figure 3.2d & Figure S3.3a).

Both forward and reversed scans of ITO/ZnO/CH$_3$NH$_3$PbI$_3$/carbon black/FTO solar cell (without graphite layer) produced a short circuit current density ($J_{sc}$) more than 15 mA cm$^{-2}$ but a low fill factor (FF) (Figure 3.3). The open circuit potential ($V_{oc}$) in the reverse and forward scans was measured to be 0.91 V and 0.80 V, respectively, indicating a strong hysteresis effect previously also observed for planar perovskite solar cells. Even though the mechanism of the hysteresis effect is not completely understood, it is often ascribed to the deficient extraction of carriers leading to complex charging/discharging
phenomena as well as the residual polarization associated with structural changes in the perovskite material.\textsuperscript{20,28-33} Wojciechowski et al. have minimized the hysteresis effect by improving the electron injection into TiO$_2$ at the interface with CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$.\textsuperscript{29} In our case, the hysteresis could be due to the phenomena at both ZnO/CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_3$/ (graphite) carbon black interfaces, however improving FF and the efficiency is more important for the operation of the cell. Good efficiencies and FF were previously demonstrated in perovskite solar cells with ZnO as an electron extraction layer,\textsuperscript{19} Therefore the low efficiency and FF observed for ITO/ZnO/CH$_3$NH$_3$PbI$_3$/carbon black/FTO solar cell was ascribed to be due to the interface between CH$_3$NH$_3$PbI$_3$ and carbon black.

![Figure 3.3](image)

**Figure 3.3.** J–V curves of a glass/ITO/ZnO/CH$_3$NH$_3$PbI$_3$/carbon black/FTO solar cell measured at 0.01 V s$^{-1}$ scan rate. The forward scan was from 0.0 V to 1.0 V and the reverse scan was from 1.0 V to 0.0 V.

The optimization of the interface was made by inserting a layer of graphite between CH$_3$NH$_3$PbI$_3$ and the carbon black electrode. In method B (Table 3.1), the thickness of the graphite layer was increased relative to that in method A by spin-coating twice the amount...
of the graphite suspension. No significant improvement was observed in the cell characteristics including the power conversion efficiency (PCE), indicating that the charge collection efficiency of the thinner graphite layer was already at its maximum. In method C, the graphite layer was first deposited onto a PbI$_2$ film followed by converting lead iodide into perovskite to give an in situ converted device. It was previously reported that the efficiency of perovskite solar cells significantly increased when candle soot was deposited on PbI$_2$ prior to converting into perovskite.$^{18}$ The characteristics of our in situ converted devices did not change significantly except the apparent decrease of the hysteresis. $V_{oc}$, $J_{sc}$ and FF for the reverse and forward scans were consistently closer to each other. In method D, the graphite suspension prepared by the electrochemical exfoliation in (NH$_4$)$_2$SO$_4$ electrolyte was used. Not only the (NH$_4$)$_2$SO$_4$ electrolyte produced lower yields of the graphite suspension, the performance of the devices was slightly inferior to that of devices made with Na$_2$SO$_4$ graphite suspensions. The stability of the devices made by method A was examined by storing them at the ambient atmosphere and in a desiccator at room temperature for two months. The devices stored at the ambient atmosphere exhibited yellowing and the significant performance degradation. Storing in the desiccator resulted in a slight decrease of the average PCE from 7.3 ± 0.8% to 6.7 ± 0.6% as measured in the reverse scan at 0.01 V s$^{-1}$. These results indicate that the structure is inherently stable providing that moisture is eliminated. Additional packaging and sealing the devices is required when solar applications are considered.

**Table 3.1.** Device characteristics for solar cells prepared with different deposition methods of the graphite layer.$^a$
<table>
<thead>
<tr>
<th>Method</th>
<th>Scan direction</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Reverse</td>
<td>0.94 ± 0.02</td>
<td>12.9 ± 2.0</td>
<td>0.61 ± 0.11</td>
<td>7.3 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>0.86 ± 0.02</td>
<td>20.1 ± 0.7</td>
<td>0.38 ± 0.04</td>
<td>6.7 ± 0.9</td>
</tr>
<tr>
<td>B</td>
<td>Reverse</td>
<td>0.95 ± 0.01</td>
<td>14.1 ± 1.4</td>
<td>0.54 ± 0.06</td>
<td>7.2 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>0.84 ± 0.01</td>
<td>21.4 ± 0.8</td>
<td>0.37 ± 0.01</td>
<td>6.6 ± 0.3</td>
</tr>
<tr>
<td>C</td>
<td>Reverse</td>
<td>0.91 ± 0.04</td>
<td>12.3 ± 2.1</td>
<td>0.58 ± 0.05</td>
<td>6.4 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>0.88 ± 0.02</td>
<td>15.2 ± 2.4</td>
<td>0.45 ± 0.03</td>
<td>6.0 ± 0.9</td>
</tr>
<tr>
<td>D</td>
<td>Reverse</td>
<td>0.92 ± 0.01</td>
<td>11.6 ± 0.7</td>
<td>0.54 ± 0.02</td>
<td>5.8 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>0.88 ± 0.01</td>
<td>17.9 ± 1.1</td>
<td>0.37 ± 0.01</td>
<td>5.8 ± 0.6</td>
</tr>
</tbody>
</table>

$^a$ Solar cell structure ITO/ZnO/CH$_3$NH$_3$PbI$_3$/graphite/carbon black electrode. Na$_2$SO$_4$ was used as electrolyte to exfoliate graphite in methods A, B, and C; (NH$_4$)$_2$SO$_4$ was used as an electrolyte in D. 100 $\mu$L of graphite suspension was spin-coated on the CH$_3$NH$_3$PbI$_3$ film in A and D; 200 $\mu$L of the suspension was used in B. In C, 100 $\mu$L of graphite suspension was spin-coated on a PbI$_2$ film followed by converting to CH$_3$NH$_3$PbI$_3$. Device characteristics were measured at a scan rate of 0.01 V s$^{-1}$. The forward scan was from 0.0 V to 1.0 V, the reverse scan was from 1.0 V to 0.0 V.

$J$–$V$ curves of solar cells are commonly measured by applying a compensating potential that is scanned from zero to a potential slightly larger than $V_{oc}$. The scan direction of the compensating potential has a noticeable effect on the performance of the devices reported here, but the effect was smaller from that previously reported for the similar structures.$^{20,28-33}$ The hysteresis was studied as a function of the scan rate and scan direction, revealing different hysteresis for different structures (Figure 3.4 and Table 3.2). The apparent performance of a device improved and the hysteresis decreased as the scan rate
increased. The short circuit current, $J_{sc}$, also increased with the scan rate, especially in the reverse scan. The best device fabricated in this work showed increased $V_{oc}$ to 0.960 V in the reverse scan from 0.915 V in the forward scan. Also, reverse scans always yielded higher fill factors. Based on these results, it seems more appropriate to report device characteristics as measured in the reverse scan with a slow scan rate starting from a potential close to $V_{oc}$ because the system is expected to be more in equilibrium.

Table 3.2. Best device performance under different scan conditions.$^a$

<table>
<thead>
<tr>
<th>Scan rate (V s$^{-1}$)</th>
<th>Scan direction</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>Reverse</td>
<td>0.945</td>
<td>13.6</td>
<td>0.67</td>
<td>8.6</td>
</tr>
<tr>
<td>0.10</td>
<td>Reverse</td>
<td>0.960</td>
<td>21.3</td>
<td>0.50</td>
<td>10.2</td>
</tr>
<tr>
<td>0.01</td>
<td>Forward</td>
<td>0.875</td>
<td>20.4</td>
<td>0.45</td>
<td>8.1</td>
</tr>
<tr>
<td>0.10</td>
<td>Forward</td>
<td>0.915</td>
<td>20.5</td>
<td>0.50</td>
<td>9.4</td>
</tr>
</tbody>
</table>

$^a$ Forward scan was from 0.0 to 1.0 V, the reverse scan was from 1.0 to 0.0 V.

Figure 3.4. J–V curves of the planar perovskite solar cell, ITO/ZnO/CH$_3$NH$_3$PbI$_3$/graphite/carbon black electrode, measured at scan rates 0.01 V s$^{-1}$ and 0.10 V s$^{-1}$. The forward scan was from 0.0 to 1.0 V, the reverse scan was from 1.0 to 0.0 V.
Electrochemical impedance spectroscopy (EIS) can potentially provide insights into charge transfer processes across interfaces in solar cells. EIS data is often fit into an equivalent electrical circuit, and great effort is made to assign each element in the circuit to a specific charge transfer process in the device. Here, we took a different approach, in which EIS spectra from two different structures, specifically devices with and without graphite layer are compared to each other using Nyquist plots (Figure 3.5). Such relative comparison allowed us to focus only on perovskite/graphite electrical contact that was determined to have the largest effect on the overall performance of the studied devices.

The spectra were acquired at 0 V and 0.550 V forward potential bias from 0.5 Hz to 100 kHz with 0.015 V potential modulation. The latter bias was selected because it was in the same region where all tested devices produced the maximum power. The devices without the graphite layer (carbon black was directly deposited onto the perovskite layer) exhibited...
two characteristic semicircle-like features. The radius of the first, high-frequency circle corresponded to the electron transfer resistance through ITO/ZnO/perovskite and carbon black/back electrode (Figure 3.5). This assignment was made based on largely unaltered Nyquist plots for all devices in this frequency region as well as the fact that these layers were the same for all devices. The electron transfer exhibited both capacitive and resistive characters due to the polarization of the corresponding interfaces and the finite electron transfer rates through the interfaces and materials. The similar assignments were previously made for other solar cells.\textsuperscript{34-35} As expected, the overall electron transfer resistance dropped at 0.550 V bias relative to that at zero bias for devices without the graphite layer (Figure 3.5).

When the graphite layer was incorporated into devices, dramatic changes in the Nyquist plots were observed in the low-frequency region. The overall electron transfer resistance increased by more than an order of magnitude at zero bias but dropped back to the previous values when 0.550 V bias was applied. The increase of the resistance was likely due to the initial formation of a poor electrical contact between the perovskite and graphite layers. This contact was substantially improved when the bias was applied. It is well known that electrical contacts could exhibit large resistance at low applied potential differences but became highly conductive when the potential difference is increased. Besides, the resistance at zero bias is not important for the device operation because these devices are intended to operate under internal bias around 0.550 V.

A region of the negative capacitance can also be seen in the Nyquist plot at 0.550 V bias in the frequency range between 3 Hz and 225 Hz (Figure 3.5). The region of the
negative capacitance implies the inductive-like behavior characterized by the current lagging the applied potential. There is no firm consensus among explanations of the negative capacitance observed in solar cells. The ionic conductivity is often involved for the explanation, it is also known that Schottky and PN-junctions can exhibit inductive-like behavior. A common factor in these cases is the presence of nonohmic (nonlinear) conductivity. The incorporation of graphite between the perovskite and carbon black layers created two interfaces: graphite/carbon black and perovskite/graphite. Both interfaces acted as resistors and when a bias was applied, the current produced a potential drop and polarization across each interface. Whereas the first interface is expected to behave as a linear resistor, the second one could exhibit a nonlinear resistance: the resistance becomes a function of the passing current. This nonlinear resistance could result from ions in perovskite moving in and out the interfacial region when the polarization changed. It is expected that, when AC potential is applied to such system, the current will lag the applied potential leading to the inductive-like response and the negative capacitance. It was previously shown that ions can move in the perovskite under applied bias. The fact that the negative capacitance was seen at low frequencies indicated a slow process that could be associated with the ionic conductivity in the perovskite.

**Conclusion**

A simple, potentially low-cost method based on bench top wet chemistry for fabricating efficient perovskite solar cells with a structure of ITO/ZnO/CH$_3$NH$_3$PbI$_3$/graphite/carbon black electrode is described. All films were deposited by spin coating under ambient conditions without heat treatment. The structures
did not have a designated hole-transport layer; instead, an electrochemically exfoliated graphite layer increased the power conversion efficiency by improving the electrical contact between perovskite and the hole collecting electrode. The best device demonstrated PCE of 10.2%, $V_{oc}$ of 0.960 V, and $J_{sc}$ of 21.3 mA cm$^{-2}$ as measured at 0.10 V s$^{-1}$ scan rate. The reported method presents more opportunities for achieving a low cost perovskite solar cell.

Acknowledgment

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References

CHAPTER FOUR

SOLUTION-PROCESSED PLANAR LEAD IODIDE PHOTOVOLTAIC DEVICE

Introduction

A photovoltaic industry that is rapidly developing with the annual growth rate more than 40% during the past 10 years is largely driven by monocrystalline and polycrystalline silicon solar cells. However, the manufacturing cost of commercial solar cells is still the high hindering broader application of this technology as a significant energy source. Costs analysis indicates that a standard 180-µm wafer accounts for 58% of the total cost of a monocrystalline silicon solar cell. A significant cost reduction is possible by replacing silicon with other low-cost light absorption semiconductors. A solution processed lead halide perovskite could be an alternative material.

Perovskite solar cells are currently rapidly evolving since the first report of the cell based on solid-state mesoscopic TiO$_2$ heterojunction structure in 2012. The power conversion efficiency (PCE) has increased from 9.7% to 20.1% during the last 4 years and cells were simplified to planar structures without a delicate mesoscopic layer. High temperature processed TiO$_2$ was replaced by room temperature ZnO and the manufacturing cost was further reduced by using carbon electrodes instead of silver or gold electrodes and a solution only process under ambient conditions. Perovskite films that can be produced using one- or two-step solution-based methods largely determine the cell efficiency. A precursor containing a mixture of lead halide and CH$_3$NH$_3$I is spin-coated and annealed to form a light absorbing perovskite layer in one-step methods. In contrast, PbI$_2$ films are first deposited by various methods on substrates followed by converting to
perovskite with CH$_3$NH$_3$I in a two-steps method. Residual PbI$_2$ was often observed in both methods by powder X-ray diffraction (PXRD) showing a characteristic diffraction peak at 12.67°. The assumption that the residual PbI$_2$ imparts a negative effect on the cell performance stimulated efforts to completely convert PbI$_2$ to perovskite. At the same time, some researchers reported highly efficient perovskite solar cells containing PbI$_2$ in perovskite layer and indicated that annealing generated PbI$_2$ can passivate the surface of the perovskite and increase PCE.

Lead iodide that is a direct band gap semiconductor with a band gap of 2.38 eV at room temperature is crystallized in the hexagonal system with lattice parameters a = b = 4.56 Å, c = 6.98 Å, α = β = 90°, γ = 120°. It has high electron (4600 cm$^2$ v$^{-1}$ s$^{-1}$) and hole (3000 cm$^2$ v$^{-1}$ s$^{-1}$) mobility, and exhibits high light absorption coefficient of 3.16 × 10$^4$ cm$^{-1}$ near the band gap edge at 495 nm. The high absorption coefficient and high mobility benefit the carriers generation and collection in solar cells. The maximum theoretical power conversion efficiency (PCE) of a single junction solar cell fabricated using PbI$_2$ as an active layer is 18%. The band gap of PbI$_2$, 2.38 eV, is also close to the optimum band gap of the upper cell (2.55 eV) in four-junction solar cells. Therefore, it is important to investigate the photovoltaic performance of cells containing the only PbI$_2$ without perovskite. The first PbI$_2$ based solar cell was reported in 2014 having FTO/TiO$_2$ (compact)/TiO$_2$ (mesoporous)/PbI$_2$/spiro-MeOTAD/Ag structure and exhibiting PCE of 1.74%. It was also concluded that, when present in perovskite solar cells, the residual PbI$_2$ plays a negative role and should be avoided.
In our previous work, tightly packed smooth and uniform PbI$_2$ films were prepared by spin-coating of PbI$_2$ solution in DMF under air flow and further converted to CH$_3$NH$_3$PbI$_3$ perovskite.$^{22}$ Planar ITO/ZnO/CH$_3$NH$_3$PbI$_3$/graphite/carbon black structure solar cells with 10.2% power conversion efficiency were built at ambient conditions without vacuum, high temperature and inert atmosphere.$^8$ We found that the perovskite devices show high efficiency even in the presence of residual PbI$_2$. In this work, photovoltaic devices containing the only PbI$_2$ were fabricated and studied. The reported here ITO/ZnO/PbI$_2$/graphite/carbon black devices demonstrated power conversion efficiency of 0.32% under the AM 1.5G solar radiation. To our best knowledge, this is the first report of fully room temperature solution-processed photovoltaic devices based on pure PbI$_2$.

**Experimental Section**

**Materials**

Fluorine-doped tin oxide (FTO) glass (~7 Ω/sq) and indium tin oxide (ITO) glass (8 – 12 Ω/sq) were received from Sigma and Delta Technologies, LTD, respectively. N,N-dimethylformamide (DMF) (Sigma-Aldrich, 99.8%), 12 micron tungsten powder (Aldrich Chem. Co. 99.9%), hydrogen peroxide, 30% (J.T. Baker, electronic grade), 2-methoxyethanol (Sigma-Aldrich, 99.8%), and acetylene carbon black (50% compressed) (Stream Chemicals) were used as received. Lead iodide, zinc oxide nanoparticles and graphite suspension in 4-methyl-2-pentanone were synthesized following previously reported methods.$^8,22$
**WO₃ dispersion**

WO₃ dispersion was synthesized by modifying previously reported methods.²⁶-²⁸ A suspension of tungsten powder (0.919 g, 5.00 mmol) in H₂O (6.0 mL) was cooled to 0 °C in an ice bath. H₂O₂ 30% (w/w) in H₂O (6.0 mL, 60 mmol) was added to the above suspension drop by drop at 0 °C over 5.0 min while continuously stirring followed by the addition of 1.0 mL 17.5 mmol acetic acid. The reaction mixture was further stirred at room temperature for 48 h before removing the solvents at 30 °C in a vacuum oven. White powder was obtained and was dispersed in ethanol to give a 10 mg mL⁻¹ WO₃ dispersion. The WO₃ dispersion was then filtered through a 0.45 µm PTFE syringe filter before using.

**Instrumentation**

UV-vis extinction spectra were measured using a Shimadzu UV-2501 PC spectrophotometer. PXRD data was collected using a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 25 °C. Imaging and thickness measurements were performed using an AIST-NT SmartSPM-1000 atomic force microscope (AFM) operating in AC mode. Laurell WS-400B-6NPP-Lite Manual Spinner was used for spin-coating. The current–voltage curves of devices were measured by using an electrochemical workstation (CH Instruments, CHI440) with linear sweep voltammetry. The devices were illuminated by an in-house built solar simulator equipped with a Mega-9 AM1.5G filter at a calibrated intensity of 100 mW cm⁻². The effective area of the device was defined as 0.35 cm² with a non-reflective metal mask. The standard deviation was calculated from the measurements of five devices.
Solar cell fabrication

Devices were fabricated under ambient conditions. ITO-coated glass substrates (1.5 cm × 2.5 cm) were masked by scotch tape and etched by a mixture of 2.0 mol L\(^{-1}\) HCl and zinc powder. The substrates were then rinsed with 18 MΩ water followed by sonication in acetone, ethanol and water for 15 min in each solvent. The substrates were further cleaned by air plasma for 10 min. The substrates were spin-coated with ZnO nanoparticles from CHCl\(_3\)/n-butanol suspension at 3000 rpm for 30 s. The spin coating was performed four times to obtain uniform films. WO\(_3\) films were spin-coated from the above-prepared dispersion in ethanol at 3000 rpm for 30 s following by annealing in air at 180 °C for 30 min. PbI\(_2\) films were made according to the previously described procedure, in which the substrates were first exposed to the solution for 2.0 minutes before spinning at 3000 rpm, 4500 rpm, and 6000 rpm under a continuous flow of clean air.\(^8\) The air flow and 2.0 min loading time were essential to obtain a tightly packed uniform film. The graphite layer was fabricated on PbI\(_2\) films by spin-coating of the graphite suspension in 4-methyl-2-pentanone. 300 µL of the suspension was delivered dropwise at the rate of one drop per 15 s onto a substrate spinning at 1000 rpm over 6.0 min. The graphite layer was further coated with carbon black to provide electrical contact to the second electrode, for which FTO glass was selected in all reported devices. The back electrode was made by pressing FTO slides to the carbon black layer. The electrical contact to the ITO substrates was made by removing all deposited layers from a small area with cotton swabs wetted in acetone and 1 mol L\(^{-1}\) HCl solution. The entire structure was mechanically clamped together with two binder clips.
Results and Discussion

The devices were fabricated by the sequential deposition of ZnO, PbI$_2$, graphite and carbon black layers on ITO substrates, as described in Experimental section. The thickness of PbI$_2$ was controlled by using three different spin rate: 3000 rpm, 4500 rpm, and 6000 rpm. The individual crystals in the polycrystalline PbI$_2$ films were preferentially oriented with (001) plane parallel to the substrate, as was evident from PXRD (Figure S4.1). This preferred orientation was not affected by the spin rate and the thickness of PbI$_2$ films. All PbI$_2$ films on glass/ITO/ZnO substrates showed a similar surface structure with the RMS roughness slightly increased from 7.8 nm to 9.8 nm, and 12.9 nm as the spin rate decreased from 6000 rpm to 4500 rpm, and 3000 rpm (Figure S4.2). Optical absorption of PbI$_2$ films increased when the thicknesses increased as is shown in UV-vis spectra (Figure 4.1). The band-edge absorption for the PbI$_2$ film was determined to be at 521 nm corresponding to 2.38 eV band gap.

![UV-Vis absorption spectra of PbI$_2$ films on glass/ITO/ZnO and glass/ITO/WO$_3$ substrates with different thicknesses.](image)

**Figure 4.1.** UV-Vis absorption spectra of PbI$_2$ films on glass/ITO/ZnO and glass/ITO/WO$_3$ substrates with different thicknesses.
Table 4.1. Device characteristics for solar cells with different cell structures.\(^a\)

<table>
<thead>
<tr>
<th>Device</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.63 (\pm) 0.02</td>
<td>1.4 (\pm) 0.2</td>
<td>0.32 (\pm) 0.00</td>
<td>0.27 (\pm) 0.03</td>
</tr>
<tr>
<td>B</td>
<td>0.62 (\pm) 0.04</td>
<td>0.89 (\pm) 0.05</td>
<td>0.31 (\pm) 0.01</td>
<td>0.17 (\pm) 0.01</td>
</tr>
<tr>
<td>C</td>
<td>0.66 (\pm) 0.02</td>
<td>0.55 (\pm) 0.07</td>
<td>0.32 (\pm) 0.01</td>
<td>0.12 (\pm) 0.01</td>
</tr>
<tr>
<td>D</td>
<td>0.19 (\pm) 0.09</td>
<td>1.3 (\pm) 0.4</td>
<td>0.27 (\pm) 0.02</td>
<td>0.06 (\pm) 0.03</td>
</tr>
</tbody>
</table>

\(^a\) Devices A, B, and C had ITO/ZnO/PbI\(_2\)/graphite/carbon black structures with thicknesses of PbI\(_2\) films 138 nm, 161 nm, and 198 nm respectively. Device D had ITO/WO\(_3\)/PbI\(_2\)/graphite/carbon black structure with 142 nm thicknesses of PbI\(_2\) film. Device characteristics were measured by the reverse potential scanning method from 0.80 V to 0.00 V at 0.10 V s\(^{-1}\) scan rate.

Table 4.2. Performance of a typical ITO/ZnO/PbI\(_2\) (138 nm)/graphite/carbon black device under different scan conditions.\(^a\)

<table>
<thead>
<tr>
<th>Scan rate (V s(^{-1}))</th>
<th>Scan direction</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>Reverse</td>
<td>0.63</td>
<td>1.8</td>
<td>0.26</td>
<td>0.29</td>
</tr>
<tr>
<td>0.10</td>
<td>Reverse</td>
<td>0.65</td>
<td>1.5</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>0.01</td>
<td>Forward</td>
<td>0.68</td>
<td>1.4</td>
<td>0.32</td>
<td>0.30</td>
</tr>
<tr>
<td>0.10</td>
<td>Forward</td>
<td>0.64</td>
<td>1.4</td>
<td>0.28</td>
<td>0.24</td>
</tr>
</tbody>
</table>

\(^a\) Forward scan was from 0.00 to 0.80 V and the reverse scan was from 0.80 to 0.00 V.

The effect of PbI\(_2\) thickness on the performance of ITO/ZnO/PbI\(_2\)/graphite/carbon black was studied by changing the spin rate during the deposition process. As shown in Table 4.1, no significant improvement of the open circuit voltage \(V_{oc}\) and fill factor (FF) was observed when the thickness was increased from 138 to 198 nm. In contrast, the short-circuit current density \(J_{sc}\) decreased from 1.4 to 0.55 mA cm\(^{-2}\) when the thickness
increased. As a result, the PCE was also decreased from 0.27% to 0.12%, indicating that thinner layer of PbI$_2$ benefited the carrier collection in the PbI$_2$ solar cells.

![Figure 4.2. J–V curves of a typical ITO/ZnO/PbI$_2$ (138 nm)/graphite/carbon black device measured at different scan rates and scan directions. The forward scan was from 0.0 to 0.8 V and the reverse scan was from 0.8 to 0.0 V.](image)

It was previously reported that the performance of the perovskite solar cells is often affected by the scan direction and the scan rate, at which the compensating potential is changed.$^{29-35}$ Hysteresis in $J$–$V$ curves is observed when the scan direction is changed. Small hysteresis in ITO/ZnO/PbI$_2$/graphite/carbon black device was observed for the slow and fast scan (Figure 4.2). This hysteresis was similar to that previously observed in perovskite cells of the same structure. The perovskite cells exhibited better apparent PCE during the fast scan relative to that of the slow scan. The difference between the fast and slow scans was notably smaller for PbI$_2$-based devices. At the same time, the fill factor for PbI$_2$-based devices was also significantly smaller than that of the perovskite. The low fill factor is indicative of low shunt resistance and high series resistance. The high series
resistance was at ZnO/PbI₂ or/and PbI₂/graphite interfaces due to the inefficient carrier extraction. The other two interfaces, specifically ITO/ZnO and graphite/carbon black can be ruled out because the same interfaces were used previously in perovskite cells exhibiting large FF.⁸ Significantly lower FF was observed in perovskite cells without the hole extracting graphite layer. The best PbI₂-based devices without the graphite layer with ITO/ZnO/PbI₂ (138 nm)/carbon black structure exhibited \( V_{oc} = 0.66 \) V, \( J_{sc} = 0.15 \) mA cm⁻², \( FF = 0.26 \) and \( PCE = 0.03\% \). The low \( J_{sc} \) and poor reproducibility of the devices without the graphite layer further confirming that a graphite layer next to an active layer is a simple way of improving the hole extraction and the performance of solar cells.

Lead iodide based devices containing WO₃ instead of ZnO were also fabricated and exhibited similar \( J_{sc} \) but lower \( V_{oc} \), FF, and PCE as compared to devices with ZnO. The WO₃ layer was acting as an electron collector in ITO/WO₃/PbI₂/graphite/carbon black structure contrary to the previous reports, in which it was used as a high work function hole transporting material in heterojunction devices.³⁶ Whereas PXRD of WO₃ powders annealed at 180 °C in air for 30 min revealed about 2 nm crystals (Figure S4.3) ²⁶⁻²⁷ thin WO₃ layers on glass/ITO substrates did not exhibit discerned diffraction peaks that can be related to tungsten oxide (Figure S4.4). AFM images of ITO substrates with and without tungsten oxide also appeared similar except a smaller reduction of RMS roughness from 4.8 nm to 2.3 nm for the substrates with WO₃ (Figure S4.5). The UV-vis spectroscopy, however, indicated the presence of a thin tungsten oxide layer on the ITO substrate as was evident from a small increase of the extinction in 360 – 500 nm spectral range (Figure S4.6). A discussion of the spectral changes associated with WO₃ and ZnO layers can be
found in the legend of Figure S4.6. The other evidence of the WO$_3$ layer on ITO substrates was obtained from UV-vis spectra of quartz slides, on which a WO$_3$ layer was deposited by the same spin-coating method as that used in the fabrication the devices. The band gap absorption at 352 nm indicative of WO$_3$ was observed (Figure S4.7).

**Conclusion**

Photovoltaic devices with a structure of ITO/ZnO (or WO$_3$)/PbI$_2$/graphite (or without graphite)/carbon black were fabricated by spin coating at ambient conditions. The PCE of the ITO/ZnO/PbI$_2$/graphite/carbon black devices increased when the thickness of the PbI$_2$ decreased and 138 nm PbI$_2$ films resulted in the best PCE. The inclusion of graphite layer improved $J_{sc}$, PCE, and reproducibility without changing $V_{oc}$ compared to the devices of ITO/ZnO/PbI$_2$/carbon black structure. The substitution of ZnO by WO$_3$ in ITO/WO$_3$/PbI$_2$/graphite/carbon black devices decreased $V_{oc}$ but did not change $J_{sc}$. $V_{oc}$ of the best device was 0.68 V which was smaller than the theoretically possible maximum considering 2.38 eV band gap of PbI$_2$. Future work should focus on selecting appropriate n-type and hole transporting materials and processed method to improve $V_{oc}$, $J_{sc}$, and FF of PbI$_2$ based photovoltaic devices.

**Acknowledgment**

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**References**
CHAPTER FIVE

SOLUTION SYNTHESIS OF PURE 2H CuFeO₂ AT LOW TEMPERATURES

Introduction

Solution processed thin film solar cells is a promising approach for broad utilization of solar energy. Successful thin film solar cells should balance power conversion efficiency (PCE), manufacturing cost, stability, and environmental friendliness. The absorbing layer in an efficient thin film mono-junction solar cell should satisfy several requirements. (a) The band gap of the material should be close to 0.9–1.6 eV, optimum for mono-junction cell operating at AM 1.5G.¹ (b) The absorption coefficient should be larger than $10^4 \text{ cm}^{-1}$ to provide at least 80% of light absorption within a film thickness of about 1 μm. The thickness of the absorption layer in most thin film solar cells, such as CuInₓGa(1–ₓ)Se₂, Cu₂ZnSnS₄(Se), organic solar cells, and perovskite solar cells, are less than 2 μm.² Higher absorption coefficients permit smaller absorption depths thereby favoring the carrier extraction relative to the carrier recombination. (c) The carrier diffusion distance should be longer than the absorption depth. (d) The exciton binding energy should be low to produce free carries rather than bound states. The exciton binding energy in inorganic materials is often lower due to the higher dielectric constant that effectively screens the electrostatic attraction between the carriers. (e) In structures where the absorbing layer is an intrinsic semiconductor sandwiched between p- and n-type semiconductor layers, the p-i-n solar cell, the valence band maximum of the absorber should be slightly below and the conduction band minimum slightly above the corresponding bands of p- and n- layers, respectively. (f) The light absorbing material should be cheap, stable, easily processed, and
environmentally friendly. A solution processed CuFeO$_2$ could be an effective light absorption material since it meets most of the requirements mentioned above, including a suitable band gap, high absorption coefficient, low cost, high stability, and environmental friendliness.

CuFeO$_2$ crystallizes in a rhombohedral (3R)-type$^3$ structure with lattice parameters $a = b = 3.034$ Å, $c = 17.163$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ and a hexagonal (2H)-type$^4$ structure with lattice parameters $a = b = 3.035$ Å, $c = 11.449$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. 3R CuFeO$_2$ is a p-type semiconductor with 1.47 eV$^5$ band gap and its conductivity is due to ionized Cu vacancies and interstitial oxygen.$^6$ It has high light absorption coefficient of $7.5 \times 10^4$ cm$^{-1}$ near the band gap edge at 700 nm$^5$ and sufficiently high hole mobility of $34$ cm$^2$ v$^{-1}$ s$^{-1}$ even at doping levels as high as $1.8 \times 10^{19}$ cm$^{-3}$. The high absorption coefficient and high mobility benefit the carrier generation and extraction. CuFeO$_2$ is made of earth-abundant elements and has good stability in aqueous environments$^8$, and as such was investigated as photocathodes for photoelectrochemical reduction of CO$_2$,$^9$-10 solar water reduction,$^5,11$ and as a cathode material in Li batteries.$^{12}$ Whereas 3R phase was somewhat characterized, only X-ray diffraction$^4$ and theoretical calculation$^{13}$ of $e_g$ and $t_{2g}$ occupancies of the Fe$^{3+}$ are available for 2H CuFeO$_2$.

CuFeO$_2$ is often synthesized by solid state reactions at a temperature higher than 850 °C under oxygen free atmosphere for more than 24 h resulting in 3R phase.$^9,12$ Sol-gel methods decreased the required reaction temperature and time to about 700 °C and 12 h, respectively.$^5,11$ The electrodeposition of CuFeO$_2$ precursor decreased the calcination temperature to 650 °C and the reaction time to 3 h.$^{10}$ Hydrothermal synthesis further
decreased the reaction temperature to below 200 °C but the resulting material was a mixture of 3R and 2H phases in a highly aggregated state of individual crystals hindering the formation of high-quality thin films.\textsuperscript{14-16} Pure 2H CuFeO\textsubscript{2} and other 2H delafossite-type oxides are difficult to synthesize.\textsuperscript{17} To the best of our knowledge, the only pure 2H CuFeO\textsubscript{2} crystals were isolated from a mixture as a byproduct of the synthesis of iron-copper-arsenates.\textsuperscript{4}

Here, we present a simple and reliable method to synthesize pure 2H CuFeO\textsubscript{2} nanocrystals at 100 °C. We systematically studied the effect of the concentration of reactants, reaction temperature and reaction time on the formation and purity of 2H CuFeO\textsubscript{2} and characterized the material using powder X-ray diffraction (PXRD), electron microscopy and spectroscopic techniques. The work was motivated by the need to study fundamental properties of this material and its potential suitability for solar applications. In preliminary studies reported here, we demonstrated that 2H CuFeO\textsubscript{2} can be used as an efficient light absorbing material, capable of exhibiting the photovoltaic effect.

**Experimental Section**

**Materials**

Fluorine-doped tin oxide (FTO) glass (~7 Ω/sq) and indium tin oxide (ITO) glass (8 – 12 Ω/sq) were received from Sigma and Delta Technologies, LTD, respectively. Polyethylene glycol 6000 (PEG 6000) (EMD Millipore), sodium hydroxide (BDH, ACS grade), potassium hydroxide (Ameresco, reagent grade), copper iodide (Acros Organics, 98%), Iron(III) chloride hexahydrate (Macron, AR) and acetylene carbon black (50% compressed) (Stream Chemicals) were used as received. Zinc oxide nanoparticles and
graphite suspension in 4-methyl-2-pentanone were synthesized following previously reported methods.\textsuperscript{18-19}

**Instrumentation**

UV-Vis-Near infrared extinction spectra and diffuse reflectance spectra were measured using a Shimadzu UV-3600 spectrophotometer. Powder X-ray diffraction data was collected using a Rigaku Ultima IV X-ray diffractometer with Cu K\textalpha\ radiation (\(\lambda = 1.5418\) Å) at 25 °C. Diffraction peaks were assigned by referring PDF card using card number 01-79-1546 for $2\text{H-CuFeO}_2$, 00-39-0246 for $3\text{R-CuFeO}_2$, 00-001-1053 for $\alpha$-$\text{Fe}_2\text{O}_3$, 00-005-0667 for Cu$_2$O and 00-040-0129 for Fe(OH, I)$_{2.55}$. Crystallite sizes and phase ratios were calculated from PXRD using Scherrer equation and Rietveld quantitative analysis, respectively and Rigaku PDXL 1.8.1.0 software. Thickness measurements were performed using an AIST-NT SmartSPM-1000 atomic force microscope (AFM) operating in AC mode. Electron microscope images were obtained with Hitachi S-4800 field emission scanning electron microscopes. Raman spectra were collected using 514.5 nm light from an Ar$^+$ ion laser (Innova 200, Coherent, 500 mW). Scattered light was collected by a f/1.2 camera lens in a backscattering geometry and analyzed by a triple spectrometer (Triplemate 1877, Spex) equipped with a CCD detector (iDUS 420, Andor). Raman spectra of indene and a mixture of chloroform and bromoform were used for spectral calibration. Laurell WS-400B-6NPP-Lite Manual Spinner was used for spin-coating. The current–voltage curves of solar cells were measured by using an electrochemical workstation (CH Instruments, CHI440) with linear sweep voltammetry. The solar cells were illuminated by an in-house built solar simulator equipped with a Mega-9 AM1.5G filter at a calibrated
intensity of 100 mW cm\(^{-2}\). The effective area of the solar cell was defined as 0.35 cm\(^2\) with a non-reflective metal mask.

**CuFeO\(_2\) Synthesis**

In a typical process, H\(_2\)O (18 MΩ) (3.5 mL) was bubbled with high purity N\(_2\) over 30 min, in which a certain amount of CuI and FeCl\(_3\)-6H\(_2\)O was dispersed by stirring under N\(_2\) atmosphere over 15 min. NaOH or KOH solid was further dispersed in the mixture by strong stirring for 15 min following by dissolving additives with strong stirring for an additional 15 min. The reaction mixture was then heated in an oven at a set temperature between at 80 °C and 190 °C for a set time.

**Photovoltaic device fabrication**

Devices were fabricated under an ambient environment. Glass/ITO/ZnO substrates prepared by following previously reported methods\(^{18-19}\) were coated with CuFeO\(_2\) particles by drop-casting from H\(_2\)O suspension. The graphite layer, direct electrical contact to the ITO substrate, acetylene carbon black layer, and the top electrode were fabricated by following previously reported methods.\(^{18-19}\) The entire structure was mechanically clamped together with two binder clips.

**Results and Discussion**

Highly aggregated CuFeO\(_2\) crystals were previously synthesized by using water-soluble Cu(II), Fe(III) salts and propionaldehyde as a reductant.\(^{20}\) When attempting to repeat this method, a sticky yellow polymer was formed as a byproduct due to the aldol reaction of propionaldehyde under high basic condition. The contamination by this
insoluble polymer as well as the high aggregation state of the CuFeO$_2$ crystals deemed this product unsuitable for application in thin film electronic devices. In addition, the final product was a mixture of 3R and unknown amorphous green compound(s) that did not produce PXRD peaks. In another reported method, Cu(II) and Fe(II) salts were used and, upon increasing pH of the reaction by the addition of NaOH, the newly formed Fe(OH)$_2$ reduced Cu(II) to Cu(I) while simultaneously being converted to Fe(III). This reaction requires the exact stoichiometric ratio of Cu(II) and Fe(II) because an excess of Cu(II) will result in highly doped CuFeO$_2$ with decreased carrier mobility and an excess of Fe(II) will result in $\alpha$-Fe$_2$O$_3$ byproduct that is difficult to remove. Pure Fe(II) salts without Fe(III) are also difficult to obtain. In addition, the method produced a mixture of 3R and 2H phases.

The method for synthesizing the pure 2H phase of CuFeO$_2$ described here is based on using Cu(I) and Fe(III) as a more stable iron salt as compared to Fe(II). NaI, which was formed when CuI reacted with FeCl$_3$·6H$_2$O and NaOH, reduced Cu(II) that could be present in the reaction to Cu(I). The addition of an excess amount of CuI can produce Cu$_2$O as a byproduct; however, it can be easily removed by washing with ammonium hydroxide. This method enabled the synthesis of pure 2H CuFeO$_2$ phase.

The effect of the reaction time and temperature on the formation of CuFeO$_2$ was studied at 80 °C, 90 °C, 120 °C, 150 °C and 190 °C in the reaction mixture comprised of 0.75 mmol CuI, 0.75 mmol FeCl$_3$·6H$_2$O, 5.5 mmol NaOH and 3.5 mL H$_2$O (Table S5.1). As can be seen from PXRD spectra (Figure S5.1), a mixture of 3R and 2H phases was always formed even after the reaction time of 48 h at 150 °C. The ratio of the two phases also remained roughly the same independent of the reaction temperature and time. When
the reaction was carried at 80 °C for 24 h, α-Fe₂O₃, Fe(OH, I)x, and Cu₂O were also detected as products in addition to 3R and 2H CuFeO₂.

The effect of the reaction basicity was studied at 190 °C (Table S5.2). PXRD indicated that only α-Fe₂O₃ and Cu₂O were formed when using stoichiometric amount NaOH (3.00 mmol) (Figure S5.2). A small increase of NaOH amount to 3.35 mmol resulted in pure, primarily 3R CuFeO₂ with a small contribution from 2H CuFeO₂ (Figure S5.2). The addition of 13.5 mmol NaOH substantially increased the amount of 2H CuFeO₂ in the mixture. In an attempt to further shift the formation equilibrium towards 2H phase, additives such as polyethylene glycol (PEG) 6000, propanoic acid and 5-phenylpentanoic acid were considered (Table S5.3). However, as can be seen from PXRD spectra (Figure S5.3), these additives did not change the phase composition of CuFeO₂.
**Figure 5.1.** PXRD spectra of CuFeO\(_2\) synthesized by using CuI (0.75 mmol), FeCl\(_3\)-6H\(_2\)O (0.75 mmol), H\(_2\)O (3.5 mL) at 120 °C for 24 h with various amount of NaOH.

![PXRD spectra](image)

**Figure 5.2.** PXRD spectra of CuFeO\(_2\) synthesized by using CuI (0.75 mmol), FeCl\(_3\)-6H\(_2\)O (0.75 mmol), H\(_2\)O (3.5 mL), NaOH (55.5 mmol) at various reaction temperatures.

It was assumed based on the initial experiments that the reaction at high basic conditions could yield pure 2H CuFeO\(_2\) phase. Indeed, as the amount of NaOH was increased the purity of 2H CuFeO\(_2\) phase also increased until the pure 2H phase, as was determined from PXRD, was obtained at 55.5 mmol NaOH, at 120 °C for 24 h (Figure 5.1 and Table S5.4). The reaction intermediates were captured by changing the reaction time (Table S5.5). A mixture of a brown suspension, most likely amorphous Fe(OH)\(_3\)\(\cdot\)xH\(_2\)O that cannot be detected by PXRD, and a blackish orange precipitate composed of 2H CuFeO\(_2\) and Cu\(_2\)O mixture was obtained after 1.5 h reaction (Figure S5.4). Slightly longer reaction
time, 2 h, resulted in pure 2H CuFeO$_2$ phase. Contrary to the expectation, further increasing the reaction time to 48 h under the same conditions did not result in a significantly larger crystallite size from 42 nm initially observed after 6 h. However, increasing the reaction temperature had a profound effect on the crystallite size as was evident from PXRD (Figure 5.2). The crystallite size grew from 42 nm at 100 °C to 58 nm at 160 °C and to 73 nm at 200 °C (Table S5.6). Relative diffraction intensities of PXRD did not change when the amount of reactants (CuI and FeCl$_3$·6H$_2$O) decreased from 0.75 to 0.25 mmol. Further decreasing the amount to 0.07 mmol resulted in Cu$_2$O presence in the product as well as poor reproducibility of the reaction indicating that the formation of 2H CuFeO$_2$ is a concentration-dependent process (Table S5.6 and Figure S5.5). When KOH was used as base in the reaction, pure 2H CuFeO$_2$ was only formed at relative high concentrations of CuI and FeCl$_3$·6H$_2$O; decreasing the concentration resulted in the inclusion of a small percent of 3R CuFeO$_2$, the amount of which did not change when the reaction time was increased from 18 h to 48 h (Table S5.7, Figure S5.6, and Figure S5.7). It was also observed that 2H CuFeO$_2$ synthesized from KOH had better dispersibility in H$_2$O leading to more uniform films when drop casting compared to that synthesized from NaOH.

\[
2\text{FeCl}_3 + 2\text{CuI} \rightarrow \text{I}_2 + 2\text{FeCl}_2 + 2\text{CuCl} \quad (1)
\]

\[
\text{I}_2 + 2\text{FeCl}_2 + 2\text{CuCl} + 8\text{NaOH} + x\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_3 \cdot x\text{H}_2\text{O} + 2\text{CuOH} + 6\text{NaCl} + 2\text{NaI} \quad (2)
\]

\[
2\text{CuOH} \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (3)
\]

\[
\text{Cu}_2\text{O} + 2\text{NaOH} + \text{H}_2\text{O} \rightleftharpoons 2\text{Na[Cu(OH)]}_2 \quad (4)
\]

\[
\text{Fe(OH)}_3 \cdot x\text{H}_2\text{O} + \text{Na[Cu(OH)]}_2 \rightarrow \text{CuFeO}_2 + \text{NaOH} + (2+x)\text{H}_2\text{O} \quad (5)
\]
The proposed mechanism for the formation of CuFeO$_2$ at high basic condition is based on the reactions (1) – (5). Fe$^{3+}$ is reduced to Fe$^{2+}$ by CuI at low pH (eq. 1) and then reverted back as Fe(OH)$_3$·xH$_2$O because I$_2$ is an efficient oxidant for Fe$^{2+}$ at high basic condition (eq. 2). At the same basic condition, CuOH is formed (eq. 2) that is not stable at room temperature and is dehydrated to Cu$_2$O (eq. 3). The formation of Cu$_2$O was confirmed by its orange color and PXRD (Figure S5.4). The complexation of Cu$_2$O with OH$^-$ at high basic condition produces [Cu(OH)$_2$]$^-$ (eq. 4) thus increasing the solubility of Cu$_2$O that is further increased with the increasing of the reaction temperature. [Cu(OH)$_2$]$^-$ reacts with amorphous Fe(OH)$_3$·xH$_2$O and crystallizes into CuFeO$_2$ (eq. 5).

The reaction between the dissolved [Cu(OH)$_2$]$^-$ and insoluble Fe(OH)$_3$·xH$_2$O is limited by the diffusion of the iron species. Amorphous Fe(OH)$_3$·xH$_2$O is highly hydrated and forms a gel-like matrix that is more stable against precipitation when high concentrations are used. At low concentrations, the hydrated network is not as developed resulting in faster precipitation. The formation of the gel-like matrix requires vigorous stirring during the addition of NaOH in order to provide sufficient mixing for the homogeneous reaction. Good mixing and high concentrations favor the reaction of [Cu(OH)$_2$]$^-$ and Fe(OH)$_3$·xH$_2$O into CuFeO$_2$, whereas low concentrations and insufficient mixing results in the fast precipitation of Fe(OH)$_3$·xH$_2$O. When heated, the precipitated Fe(OH)$_3$·xH$_2$O undergoes dehydration resulting in α-Fe$_2$O$_3$ with reduced reactivity towards [Cu(OH)$_2$]$^-$ due to low solubility of α-Fe$_2$O$_3$. The formation of CuFeO$_2$ from [Cu(OH)$_2$]$^-$ and Fe(OH)$_3$·xH$_2$O and the formation of α-Fe$_2$O$_3$ by the dehydration of
Fe(OH)$_3$·xH$_2$O are two competing paths. When α-Fe$_2$O$_3$ is formed, it remains as a byproduct without being converted into CuFeO$_2$ even after heat treatment for 7 days at 220 °C.

Figure 5.3. SEM images of 2H CuFeO$_2$ synthesized by using CuI (0.75 mmol), FeCl$_3$·6H$_2$O (0.75 mmol), H$_2$O (3.5 mL), NaOH (55.5 mmol) at (a) 100 °C, (b) 120 °C, (c) 160 °C and (d) 200 °C, respectively.

Scanning electron microscopy revealed that 2H CuFeO$_2$ crystallized into irregular plates at 100 °C but more hexagonal plates were formed at 200 °C when using NaOH (Figure 5.3 and Figure S5.8). The thickness of the plates was determined from the SEM images to be about 100 nm and did not significantly change with increasing the reaction
temperature from 160 to 200 °C. SEM images, combining with PXRD, indicated that the crystallinity was improved at high temperature. Although PXRD showed a small amount of 3R CuFeO$_2$, predominantly 2H CuFeO$_2$ was synthesized with low concentrations of reactants in KOH, no significant difference was noticeable in SEM images when compared to pure 2H CuFeO$_2$ synthesized with high concentrations of the reactants. 2H CuFeO$_2$ synthesized from KOH was crystallized into an irregular disk with the thickness about 90 nm. (Figure S5.9 and Figure S5.10)

![Raman spectra of CuFeO$_2$ synthesized with NaOH as a base.](image)

**Figure 5.4.** Raman spectra of CuFeO$_2$ synthesized with NaOH as a base. (a) NaOH 6.5 mmol, 120 °C. (b) NaOH 24.0 mmol, 120 °C. (c) NaOH 55.5 mmol, 120 °C. (d) NaOH 55.5 mmol, 200 °C.

Raman spectra were collected to monitor the formation of CuFeO$_2$ at different basicities and reaction temperatures (Figure 5.4). Whereas the Raman spectrum of 3R CuFeO$_2$ phase was previously described, to the best of our knowledge this is the first report
of Raman spectra of 2H CuFeO$_2$. The 2H phase exhibits three distinguishable bands: a doublet at 351, 365 cm$^{-1}$ and a single band at 690 cm$^{-1}$. As the reaction temperature was increased from 120 °C to 200 °C the doublet became more pronounced, most likely due to the improved crystallinity. For a mixture of 2H and 3R phases synthesized at 24 mmol of NaOH that showed similar intensities of the corresponding diffraction peaks in PXRD spectra (Figure 5.1) only a broad band at 346 cm$^{-1}$ was observed in Raman spectra. The decrease of NaOH to 6.5 mmol resulted in the predominant 3R phase based on PXRD and two characteristic bands in Raman spectra at 348 and 688 cm$^{-1}$ previously assigned in the literature.$^{25}$ The Raman spectra of both 2H and 3R phases did not change after exposing the samples to high intensity (~100 W cm$^{-2}$) of laser light (514.5 nm) under ambient conditions for 2 h thereby indicating that both 3R and 2H phases of CuFeO$_2$ are expected to have good photostability.

**Figure 5.5.** The UV-Vis-Near infrared absorption spectrum of 2H CuFeO$_2$ film drop-casted on a glass substrate. The average thickness of the film was 450 nm.
Figure 5.6. Diffuse reflectance spectra of 2H and 3R CuFeO$_2$ powder on BaSO$_4$ standard white board. As calculated from PXRD by using Rietveld quantitative analysis, 3R CuFeO$_2$ powder contained 6.1 ± 0.5% 2H CuFeO$_2$ phase.

2H CuFeO$_2$ thin films can be easily fabricated by drop-casting aqueous suspensions on various substrates. As can be seen in Figure S5.11, a glass/ITO/ZnO substrate was fully covered by CuFeO$_2$ plates. The band-edge absorption for 2H CuFeO$_2$ film was determined to be at 935 nm corresponding to 1.33 eV band gap (Figure 5.5). The absorption coefficient near the band gap edge at 700 nm was calculated to be $3.8 \times 10^4$ cm$^{-1}$. In order to compare optical properties of 3R and 2H CuFeO$_2$, diffuse reflectance spectra of the corresponding powders were measured against BaSO$_4$ standard. The diffuse reflectance spectra were quite similar for both compounds, as can be seen in Figure 5.6.

In order to establish the potential applicability of 2H CuFeO$_2$ for photovoltaic applications, a simple thin film device was fabricated by the sequential deposition of ZnO, 2H CuFeO$_2$, graphite and carbon black layers on ITO substrates, as described in Experimental section. The device exhibited 0.29 V open circuit potential, 8.8 $\mu$A cm$^{-2}$ short
circuit currents, 0.17 fill factor and 0.0005% power conversion efficiency (Figure 5.7). The low fill factor is indicative of a low shunt and high series resistance of the structure. High series resistance was most likely at ZnO/CuFeO$_2$ or/and CuFeO$_2$/graphite interfaces leading to an inefficient carrier extraction. The other two interfaces, specifically ITO/ZnO and graphite/carbon black can be ruled out because the same interfaces were used previously in high efficient perovskite cells.$^{19}$ Even though the described simple structure showed only the low power conversion efficiency, the fact that 2H CuFeO$_2$ exhibited photovoltaic effect, has a high light absorption coefficient and suitable band gap as well as good photostability warrants its further studies for solar applications.

![Figure 5.7. J–V curves of a typical ITO/ZnO/CuFeO$_2$/graphite/carbon black structure under AM 1.5G illumination.](image)

**Conclusion**

CuFeO$_2$ was synthesized at a temperature as low as 90 °C from CuI and FeCl$_3$·6H$_2$O. At low basic conditions, a mixture of 3R and 2H phases of CuFeO$_2$ was formed. At high basic conditions, pure 2H CuFeO$_2$ was formed as nanoplates with a thickness of about 100
nm. The crystallinity of 2H CuFeO$_2$ phase increased with the increase of reaction temperature. The material has 1.33 eV band gap and high absorption coefficient of $3.8 \times 10^4$ cm$^{-1}$ near the band gap edge at 700 nm. It demonstrated a photovoltaic effect when placed into thin film structures composed of ITO/ZnO/2H CuFeO$_2$/graphite/carbon black. To the best of our knowledge, this is the first example of solution synthesis of pure 2H CuFeO$_2$ at low temperature. The synthesized material has the potential for applications in solar cells and for solar catalysis.

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We gratefully acknowledge the support of this work through Department of Energy, Grant DE-FG02-06ER46342, and Clemson University Center for Optical Materials Science and Engineering Technologies. Reproduced from Ref. Jin, Y.; Chumanov, G., Solution Synthesis of Pure 2H CuFeO$_2$ at Low Temperatures. *RSC Advances*, 2016, 6, 26392-26397 with permission from the Royal Society of Chemistry.

**References**

CHAPTER SIX

SYNTHESIS OF Cu$_x$Zn$_{y}$Sn$_{2-0.25x-0.5y}$S$_4$ BY CATION EXCHANGE REACTION FROM ZnS

Introduction

Cu$_2$ZnSnS$_4$ (CZTS) is a p-type semiconductor with a band gap of 1.4–1.6 eV and a high light absorption coefficient of over $10^4$ cm$^{-1}$. It is made of earth-abundant and nontoxic elements and has good stability in the ambient environment. CZTS was investigated as a light absorption material in solar cells, photocatalyst for rhodamine B degradation, and photocathode for water splitting. A broad array of techniques have been used to synthesize CZTS, such as organic solvent assistant direct synthesis, hydro/solvent thermal synthesis, chemical vapor deposition, pulse laser deposition, sputtering, evaporation, electrochemical deposition, sol-gel coating, spray pyrolysis, and successive ionic layer absorption and reaction. Sulfurization by H$_2$S or S at about 500 °C is essential to obtain highly crystallized CZTS in all these methods. In addition, the high-temperature sulfurization process is able to sulfurize metal oxide semiconductors such as ZnO, TiO$_2$, thereby limiting the development of new highly efficient solar cells. The synthesized CZTS is often contaminated by impurities such as high conductive or narrow bandgap Cu$_x$S, Sn$_x$S, and Cu-Sn-S. These impurities trap carriers act as recombination centers. As a result, electrons and holes cannot reach the surface of the semiconductor, and this leads to the low conversion efficiency of photocatalysts and low open circuit voltage, current density and fill factor in solar cells.
Polycrystalline and amorphous materials have much more crystal defects and dangling bonds than single crystal materials and these disorder states increase the carriers scattering and decrease their lifetime, mobility, and diffusion length. The semiconductor in the single crystal state shows much better carrier mobility and diffusion length than in the polycrystalline and amorphous states. However, there is no effective method currently available to synthesize pure large crystals of CZTS at low temperature. Furthermore, many studies have shown that Zn-rich CZTS exhibits much better photovoltaic effect than Cu-rich CZTS. It is essential to develop an effective method to synthesize highly crystalline CZTS by controlling the concentration of Zn in the product. Cation exchange reactions is an effective method to synthesize complex compounds with certain morphologies. The first cation exchange synthesis of CZTS was the reaction of Cu$_2$SnS$_3$ with zinc diethyldithiocarbamate in a mixture of 1-dodecanethiol and trioctylamine at 250 °C to result in ~15 nm CZTS nanoparticles. CZTS thin plates with a thickness of about 12 nm were also prepared from a cation exchange of CuS with zinc 2,4-pentanedionato monohydrate and tin(IV)chloride bis(2,4-pentanedionate) in a mixture of oleylamine, sulfur and 1-dodecanethiol at 260 °C. A slight modification of this method by reacting CuS with Zn(CH$_3$COO)$_2$·2H$_2$O and SnCl$_2$·2H$_2$O in triethylene glycol at 205 °C generated CZTS nanoplates with thickness of about 35 nm. All these reported methods started from relatively thermodynamically stable narrow band gap Cu$_2$SnS$_3$ (1.2 eV) and CuS (1.6 eV) so that residuals of these narrow band gap phases in the final product will provide trapping sites for the carriers resulting in low performance of the devices.
Here, we present the synthesis of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ by a cation exchange reaction of wide bandgap (3.5 eV) and low conductive cubic ZnS with CuCl$_2$ and SnCl$_4$ in triethylene glycol. The composition of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ was controlled by the feeding ratio of the reactants resulting in the zinc rich products. This new method is expected to promote the development of highly efficient CZTS devices.

**Experimental Section**

**Materials**

Anhydrous tin(II) chloride, , (Alfa Aesar, 99%), zinc acetate dihydrate (J. T. Baker, Baker analyzed reagent), anhydrous copper (II) chloride, (Acros Organics, 99%), tin (IV) chloride pentahydrate (Fisher Science Education, lab grade), triethylene glycol (TCI, 99.0%) and thiourea (Alfa Aesar, 99%) were used as received.

**Instrumentation**

Powder X-ray diffraction data was collected using a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 25 °C. PXRD pattern simulation was performed with Mercury 3.5.1 software by using cubic ZnS (a = 5.40 Å),$^{13}$ hexagonal CuS (a = b = 3.729 Å c = 16.11 Å),$^{14}$ and tetragonal Cu$_2$ZnSnS$_4$ (a = 5.4335(3) Å, b = 5.4335(3) Å, c = 10.8429(10) Å)$^{15}$ single crystal structures. Crystallite sizes were calculated from PXRD using Scherrer equation and Rigaku PDXL 1.8.1.0 software. Electron microscope images were obtained with Hitachi S-4800 field emission scanning electron microscopes and HD2000 field emission scanning transmission electron microscope equipped with the capability of energy-dispersive X-ray spectroscopy.
spectra were collected using 514.5 nm excitation light from an Ar+ ion laser (Innova 200, Coherent, 500 mW). Scattered light was collected by a f/1.2 camera lens in a backscattering geometry and analyzed by a triple spectrometer (Triplemate 1877, Spex) equipped with a CCD detector (iDUS 420, Andor). Raman spectra of indene and a mixture of chloroform and bromoform were used for the spectral calibration.

Synthesis of CuS

CuCl$_2$ (0.538 g, 4.00 mmol) was dissolved in hydrochloric acid (4.0 mL, 1.0 mol L$^{-1}$). Thiourea (0.335 g, 4.4 mmol) was dissolved in H$_2$O (4.0 mL). The thiourea solution was then added to the CuCl$_2$ solution drop by drop with stirring at room temperature over a period of 10 min. The reaction mixture was further stirred at room temperature for additional 10 min and then sealed in 23 mL PTFE lined digestion vessel. The reaction mixture was then heated in an oven to a set temperature of 220 ºC and kept for 24 h. After cooling to room temperature, the colorless supernatant was discarded and the black precipitate was washed with H$_2$O three time and then dried in a vacuum oven at 60 ºC for 15 h.

Synthesis of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ from CuS

Zn(CH$_3$COO)$_2$ · 2H$_2$O (28 mg, 0.13 mmol) and SnCl$_2$ (25 mg, 0.13 mmol) were dissolved in triethylene glycol (5 mL). CuS (50 mg, 0.52 mmol) was then added to the solution followed by stirring at room temperature for 10 min. The reaction mixture was transferred to 23 mL PTFE lined digestion vessel and kept in an oven at a set temperature of 220 ºC for 96 h, Alternatively, the reaction mixture was transferred to a 25 mL round
bottom flask and refluxed with stirring for 22 h. After cooling to room temperature, the reaction mixture was centrifuged and the black precipitate was washed twice with ethanol and twice with water.

Synthesis of ZnS

Zn(CH$_3$COO)$_2$·2H$_2$O (2.63 g, 12.0 mmol) and thiourea (0.913 g, 12.0 mmol) were dissolved in H$_2$O (8 mL). The solution was then transferred to a 23 mL PTFE lined digestion vessel and kept in a 220 °C oven for 24 h. After cooling to room temperature, the colorless supernatant was discarded and the white precipitate was washed with H$_2$O three time and then dried in a vacuum oven at 60 °C for 15 h.

Synthesis of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ from ZnS

CuCl$_2$ (54 mg, 0.40 mmol) and SnCl$_4$·5H$_2$O (70 mg, 0.20 mmol) were dissolved in triethylene glycol (5 mL). ZnS (78 mg, 0.80 mmol) was then added to the solution followed by refluxing for 3 h. After cooling to room temperature, the reaction mixture was centrifuged and separated into a slightly yellow-brown supernatant and a black precipitate. The black precipitate was washed twice with ethanol and twice with water.

Results and discussion
Figure 6.1. PXRD spectra of CuS synthesized by the reaction of CuCl$_2$ with thiourea at 220 °C for 24 h and the simulated pattern of hexagonal CuS. Diffraction peaks at 27.5°, 28.0°, 29.6°, 32.1°, 33.1°, 39.1°, 43.4°, 44.6°, and 48.2° were assigned as the (100), (101), (102), (103), (006), (105), (106), (008), and (107) planes, respectively. Crystallite size of CuS is 65 nm.

Figure 6.2. Raman spectrum of CuS synthesized by the reaction of CuCl$_2$ with thiourea at 220 °C for 24 h.
Figure 6.3. PXRD spectra of Cu$_x$Zn$_y$Sn$_{2.05-0.5y}$S$_4$ synthesized from CuS at the reaction conditions (a) SnCl$_2$ as a tin source, 220 °C, 96 h; (b) SnCl$_4$·5H$_2$O as a tin source, refluxed 3 h; (C) SnCl$_2$ as a tin source and CuS which is synthesized from 5 equivalent thiourea as a copper source, refluxed 22 h. PXRD pattern of Cu$_2$ZnSnS$_4$ was simulated from tetragonal phase and the PDF card number for the standard X-ray diffraction powder pattern of Cu$_2$S is 00-053-0522.

Figure 6.4. Raman spectra of Cu$_x$Zn$_y$Sn$_{2.05-0.5y}$S$_4$ synthesized from CuS at the reaction conditions (a) SnCl$_2$ as a tin source, 220 °C, 96 h; (b) SnCl$_4$·5H$_2$O as a tin source, refluxed
3 h; (c) SnCl$_2$ as a tin source and CuS which was synthesized from 5 equivalent thiourea as a copper source, refluxed 22 h.

A cation exchange reaction was previously used to prepare Cu$_2$ZnSnS$_4$ nanosheet from CuS.$^{10}$ Here, CuS was synthesized through hydrothermal reaction by using CuCl$_2$ and thiourea as reactants. As shown in Figure 6.1, hexagonal CuS was obtained with a crystallite size of 65 nm. CuS also exhibited a characteristic band at 474 cm$^{-1}$ in Raman spectra (Figure 6.2). The cation exchange reaction was then carried out at 220 °C for 96 h in a PTFE reactor as described in the literature.$^{10}$ As shown in Figure 6.3, the product contained Cu$_2$S and Cu$_2$ZnSnS$_4$ or possibly other phases with a similar diffraction pattern as that of Cu$_2$ZnSnS$_4$. However, its Raman spectrum showed high fluorescent background and only a weak peak at 338 cm$^{-1}$, which is often assigned to Cu$_2$ZnSnS$_4$ (Figure 6.4). For simplicity, Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ was used to represent the compounds exhibited PXRD and Raman spectra similar to Cu$_2$ZnSnS$_4$ according to the following discussion. We modified the reaction condition by increasing the reaction temperature from 220 °C to the boiling point of triethylene glycol (285 °C) and refluxed the mixture for 22 h. Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ was obtained with the crystallite size of 47 nm but also revealed two additional unassignable impurity peaks at 46.6° and 48.8° (Figure 6.5). The product was further soaked in 2.0 M HCl or 1.0 M NH$_3$ solution at room temperature for 30 min followed by 3 times washing with water. As was shown by PXRD, HCl treatment did not change the diffraction pattern of the product and the peaks from the impurities were not removed (Figure 6.5). In contrast, the impurity peak at 48.8° disappeared after treating with NH$_3$. 

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Raman spectra of the as-synthesized product showed two peaks at 337 and 288 cm$^{-1}$ which are often assigned to non-polar A-symmetry modes of Cu$_2$ZnSnS$_4$.$^{16}$ No observable peak can be found around 476 cm$^{-1}$ indicating no detectable Cu$_3$S in the product (Figure 6.6). After 30 min treatment with HCl or NH$_3$, Raman spectra of the product did not change, but the longer reaction time with HCl or NH$_3$ resulted in a new peak at 476 cm$^{-1}$, which is from Cu$_3$S. A similar product was obtained when using SnCl$_4$ · 5H$_2$O instead of SnCl$_2$ (Figure 6.3 & 6.4). Further studies showed that these reactions cannot be repeated very well and were strongly affected by the synthetic history of the CuS. CuS synthesized from 5.0 equivalent thiourea exhibited lower reactivity to Zn$^{2+}$ and Sn$^{2+}$ than that synthesized from 1.0 equivalent thiourea. As a result, the unreacted Cu$_2$S in the product exhibited characteristic diffraction peaks at 28.0° (111), 32.4° (200), 46.3° (220), 54.8° (311) in PXRD spectra and a Raman peak at 472 cm$^{-1}$ (Figure 6.3 & 6.4). In addition, as shown in the reaction (1), the copper-rich environment promotes the formation the copper-rich product. The copper-rich product is often contained with narrow bandgap defects trapping electrons and holes, which is harmful for the application in photovoltaics.$^{2-3}$ The reaction is actually very complicated. As shown in reaction (2) and (3), CuS is reduced to Cu$_2$S by triethylene glycol and CuCl$_2$ is reduced to CuCl at high temperature, therefore CuS was not used as a reactant in the cation exchange reaction.

$$4\text{CuS} + \text{Zn(CH}_3\text{COO)}_2 + \text{SnCl}_2 \rightarrow \text{Cu}_2\text{ZnSnS}_4 + \text{CuCl}_2 + \text{Cu(CH}_3\text{COO)}_2$$ (1)  

$$2\text{CuS} + \text{Triethylene glycol} \rightarrow \text{Cu}_2\text{S} \quad (2)$$  

$$\text{CuCl}_2 + \text{Triethylene glycol} \rightarrow \text{CuCl} \quad (3)$$
Figure 6.5. PXRD spectra of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ synthesized from CuS as a reactant under refluxing for 22 h. The simulated pattern of tetragonal Cu$_2$ZnSnS$_4$, in which diffraction peaks at 28.4°, 32.9°, 47.3° and 56.1° were assigned to (112), (200), (220) and (312) planes, respectively. The crystallite size of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ was 47 nm.

Figure 6.6. Raman spectra of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ synthesized from CuS as a reactant under refluxing for 22 h.

$$4\text{ZnS} + 2\text{CuCl}_2 + \text{SnCl}_4 + \text{Triethylene glycol} \rightarrow \text{Cu}_2\text{ZnSnS}_4 + 3\text{ZnCl}_2$$  \hspace{1cm} (4)

$$\text{ZnS} + \text{CuCl}_2 \rightarrow \text{CuS} + \text{ZnCl}_2$$ \hspace{1cm} (5)
4CuS + 2ZnCl$_2$ + SnCl$_4$ + Triethylene glycol → Cu$_2$ZnSnS$_4$ + 2CuCl$_2$  \hspace{1cm} (6)

The cation exchange reaction of ZnS with CuCl$_2$ and SnCl$_4$ is more thermodynamically favorable than the reaction of CuS with Zn(CH$_3$COO)$_2$ and SnCl$_2$ (reaction (4)). The formation of CuS from ZnS is thermodynamically feasible and kinetically favorable than the formation of Cu$_2$ZnSnS$_4$. As discussed previously, the reaction (6) is also thermodynamically feasible. According to our results, the reaction (5) proceeded fast when using ZnS as a reactant with the crystallite size of 5 nm. After adding CuCl$_2$ into the suspension of 5 nm ZnS in triethylene glycol, the white suspension was changed to the black CuS in 30 seconds. In contrast, ZnS with a crystallite size of 95 nm slowly reacted with CuCl$_2$ at room temperature. The reaction mixture of 95 nm ZnS and CuCl$_2$ in triethylene glycol still showed white color after stirring at room temperature for 5 h, indicating that there was no CuS formed. The low reactivity of large ZnS crystallite with CuCl$_2$ makes it feasible to run the cation exchange reaction at high temperature to achieve thermodynamically stable Cu$_2$ZnSnS$_4$ and limit the formation of the kinetic products such as CuS.
Figure 6.7. PXRD spectra of ZnS synthesized by the reaction of Zn(CH$_3$COO)$_2$ with thiourea at 220 °C. The simulated pattern of cubic ZnS. Diffraction peaks at 28.6°, 33.1°, 47.6°, and 56.5° were assigned to (111), (200), (220), and (311) planes, respectively. Crystallite size of ZnS is 96 nm.

Figure 6.8. Raman spectrum of ZnS synthesized by the reaction of Zn(CH$_3$COO)$_2$ with thiourea at 220 °C.
Figure 6.9. PXRD spectra of Cu$_x$Zn$_y$Sn$_{2.25x-0.5y}$S$_4$ synthesized at the reaction conditions (a) SnCl$_2$ as a tin source, refluxed for 16 h; (b) SnCl$_4$ · 5H$_2$O as a tin source, 200 °C, 2 h. Simulated PXRD patterns of tetragonal Cu$_2$ZnSnS$_4$ and hexagonal CuS.

Figure 6.10. Raman spectra of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ synthesized at the reaction conditions (a) SnCl$_2$ as a tin source, refluxed for 16 h; (b) SnCl$_4$ · 5H$_2$O as a tin source, 200 °C, 2 h.

Figure 6.11. PXRD spectra of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ synthesized from ZnS, CuCl$_2$, and SnCl$_4$ · 5H$_2$O at the reflux conditions for different reaction times. The simulated PXRD pattern of tetragonal Cu$_2$ZnSnS$_4$. Diffraction peak at 46.4° was assigned to (220) plane of...
cubic Cu$_2$S (PDF card #: 00-053-0522). Crystallite sizes of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ were 83, 79, 85, 82, and 84 nm for the reaction time of 0.5, 1, 2, 3, and 24 h, respectively.

Figure 6.12. Raman spectra of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ synthesized from ZnS, CuCl$_2$, and SnCl$_4$ · 5H$_2$O at the reflux conditions for different reaction times. Raman peaks at 288 and 335 cm$^{-1}$ were assigned to Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$; peak at 349 cm$^{-1}$ was assigned to ZnS; and peak at 472 cm$^{-1}$ was assigned to Cu$_2$S.

Highly crystallized ZnS was obtained from the hydrothermal reaction of Zn(CH$_3$COO)$_2$ with thiourea. As shown in Figure 6.7, pure cubic ZnS was obtained with a crystallite size of 96 nm. The synthesized ZnS also showed a characteristic Raman peak at 351 cm$^{-1}$ (Figure 6.8). The cation exchange reaction of ZnS with SnCl$_2$ and CuCl$_2$ was tried and the product contained Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ and unassignable impurities as shown in the PXRD (Figure 6.9). In contrast to the PXRD, only one peak at 337 cm$^{-1}$ was detected in the Raman spectrum (Figure 6.10). The cation exchange reaction was further attempted using SnCl$_4$ · 5H$_2$O reacted at 200 ºC for 2 h. As shown in the PXRD, the product contained a mixture of hexagonal CuS and Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ (Figure 6.9). The Raman spectrum
of the product also showed two peaks. One peak was at 334 cm\(^{-1}\) from Cu\(_x\)Zn\(_y\)Sn\(_{2-0.25x-0.5y}\)S\(_4\) and another peak was at 471 cm\(^{-1}\) from CuS (Figure 6.10). The reaction temperature was further increased to the boiling point of triethylene glycol (285 °C). The product contained only Cu\(_x\)Zn\(_y\)Sn\(_{2-0.25x-0.5y}\)S\(_4\) as shown in the PXRD and Raman spectra (Figure 6.11 & 6.12). The effect of the reaction time on the formation of Cu\(_x\)Zn\(_y\)Sn\(_{2-0.25x-0.5y}\)S\(_4\) was further studied at 0.5 h, 1.0 h, 2.0 h, 3.0 h, and 24 h in the reaction mixture of ZnS, CuCl\(_2\), and SnCl\(_4\) \(\cdot\) 5H\(_2\)O at reflux reaction condition. As can be seen from the PXRD and Raman spectra (Figure 6.11 & 6.12), Cu\(_2\)S was formed as a by-product with short reaction time 0.5 h and 1.0 h. Residual ZnS was also detected after 0.5 h reaction as indicated by Raman spectrum exhibiting a characteristic peak at 349 cm\(^{-1}\). The much longer reaction time, 24 h, generated detectable impurities in the PXRD although the impurities cannot be detected by Raman spectroscopy. The crystallite size of Cu\(_x\)Zn\(_y\)Sn\(_{2-0.25x-0.5y}\)S\(_4\) did not change when increasing reaction time from 0.5 h to 24 h.

**Figure 6.13.** PXRD spectra of Cu\(_x\)Zn\(_y\)Sn\(_{2-0.25x-0.5y}\)S\(_4\) synthesized from ZnS, CuCl\(_2\), and SnCl\(_4\) \(\cdot\) 5H\(_2\)O with different molar feed ratios at the reflux condition. The simulated PXRD
pattern of tetragonal $\text{Cu}_2\text{ZnSnS}_4$. Crystallite sizes of $\text{Cu}_x\text{Zn}_y\text{Sn}_{2-0.25x-0.5y}\text{S}_4$ were 43, 67, 82, and 73 nm for the molar feed ratio of 1 : 0.5 : 4, 1.6 : 0.8 : 4, 1.9 : 0.95 : 4, and 1.6 : 0.91 : 4, respectively.

The effect of the reactant feeding ratios was studied at the reflux condition for 2 h. PXRD and Raman spectra indicated that only $\text{Cu}_x\text{Zn}_y\text{Sn}_{2-0.25x-0.5y}\text{S}_4$ formed (Figure 6.13 & 6.14). The extra amount of ZnS cannot be differentiated from $\text{Cu}_x\text{Zn}_y\text{Sn}_{2-0.25x-0.5y}\text{S}_4$ by the PXRD due to the highly similar diffraction patterns between tetragonal $\text{Cu}_2\text{ZnSnS}_4$ and cubic ZnS. The crystallite size of the $\text{Cu}_x\text{Zn}_y\text{Sn}_{2-0.25x-0.5y}\text{S}_4$ increased from 43 nm to 82 nm with increasing the molar feed ratio of $\text{CuCl}_2 : \text{SnCl}_4 : \text{ZnS}$ from 1 : 0.5 : 4 to 1.9 : 0.95 : 4. According to literature, the zinc-rich $\text{Cu}_2\text{ZnSnS}_4$ with an atom ratio of $\text{Cu} : \text{Sn} : \text{Zn} = 1.6 : 0.91 : 1$ exhibited high performance in the solar cells. Here, the molar feeding ratio of $\text{CuCl}_2 : \text{SnCl}_4 : \text{ZnS} = 1.6 : 0.91 : 4$ was also used to synthesize $\text{Cu}_x\text{Zn}_y\text{Sn}_{2-0.25x-0.5y}\text{S}_4$ with a crystallite size of 73 nm and the strongest peak of the $\text{Cu}_x\text{Zn}_y\text{Sn}_{2-0.25x-0.5y}\text{S}_4$ was shifted from 335 cm$^{-1}$ to 330 cm$^{-1}$ in the Raman spectrum when compared to the other $\text{Cu}_x\text{Zn}_y\text{Sn}_{2-0.25x-0.5y}\text{S}_4$ synthesized from ZnS.
Figure 6.14. Raman spectra of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ synthesized from ZnS, CuCl$_2$, and SnCl$_4$·5H$_2$O with different molar feed ratios at the reflux conditions. Raman peaks at 288, 335 and 370 cm$^{-1}$ were assigned to Cu$_2$ZnSnS$_4$.

Scanning electron microscopy revealed that ZnS crystallized into the shape of irregular plates when the reaction was carried out at 220 °C (Figure 6.15). After the cation exchange reaction with CuCl$_2$ and SnCl$_4$·5H$_2$O at the reflux conditions for 2 h, the shape did not change but plates exhibited rough edges. This means that the original shape of the ZnS was conserved in the Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ product. Therefore it is expected that a desired shape of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ can be obtained from the same shape of ZnS. The one-step synthesis of a predefined shape of ZnS is much easier than that of Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$. The cation exchange reaction simplifies the preparation of the required Cu$_2$ZnSnS$_4$ nanocrystals. The synthesized Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ also exhibited a uniform distribution of all elements in the EDX elemental maps (Figure 6.16). This further confirmed that the cation exchange reaction is a powerful method to synthesize high-quality Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ nano- and microcrystals.
Figure 6.15. SEM images of (a) ZnS synthesized by the reaction of Zn(CH$_3$COO)$_2$ with thiourea at 220 °C (b) Cu$_x$Zn$_y$Sn$_{2-0.25x-0.5y}$S$_4$ synthesized from ZnS, CuCl$_2$, and SnCl$_4$ · 5H$_2$O at reflux condition for 2 h.
Figure 6.16. STEM images and EDX elemental maps of Cu$_{x}$Zn$_{y}$Sn$_{2-0.25x-0.5y}$S$_{4}$ synthesize from ZnS, CuCl$_{2}$, and SnCl$_{4}$·5H$_{2}$O at reflux condition for 2 h.

Conclusion

A new method based on the cation exchange reaction for the synthesis of Cu$_{x}$Zn$_{y}$Sn$_{2-0.25x-0.5y}$S$_{4}$ with the crystallite size more than 85 nm was developed. The material was characterized by powder X-ray diffraction, electron microscopy, Raman spectroscopy and energy dispersive X-ray elemental mapping. This method appears promising for facilitating the development of Cu$_{2}$ZnSnS$_{4}$ based devices.

References


CHAPTER SEVEN

SUMMARY AND FUTURE WORK

Uniform, fully converted CH$_3$NH$_3$PbI$_3$ films were synthesized at room temperature by converting PbI$_2$ in a saturated solution of CH$_3$NH$_3$I in 2-propanol/hexane (cyclohexane). This simple and robust method yields films with 20 nm RMS roughness and provides a new opportunity for a low-cost fabrication of large area perovskite solar cells. (This was published in Chemistry Letters 43(11): 1722) Solar cells with a structure of ITO/ZnO/CH$_3$NH$_3$PbI$_3$/graphite/carbon black electrode were fabricated by spin coating at ambient conditions. The incorporation of electrochemically exfoliated graphite improved the fill factor, open circuit potential, and short circuit current density. The best device yielded 10.2% power conversion efficiency. (This was published in ACS Appl. Mater. Interfaces 7(22): 12015) PbI$_2$-based photovoltaic devices having ITO/ZnO (or WO$_3$) /PbI$_2$/graphite (or without graphite) /carbon black structure were also fabricated by spin coating at ambient conditions. The structures were characterized using AFM, PXRD, and UV-vis spectroscopy. The best devices yielded 0.32% power conversion efficiency. The short circuit current decreased with increasing the thickness of the PbI$_2$ film and without the graphite layer. The open circuit voltage decreased when replacing ZnO by WO$_3$. Selecting better n-type and hole transporting materials as well as improving manufacturing methods will increase PCE of PbI$_2$ based devices.

Pure 2H CuFeO$_2$ nanoplates with a thickness of about 100 nm were synthesized at temperatures as low as 100 °C from CuI and FeCl$_3$·6H$_2$O. Systematic studies revealed that the formation of 2H CuFeO$_2$ was affected by reactant concentrations, basicity, temperature
and the reaction time. The material was characterized by powder X-ray diffraction, electron microscopy, Raman, and absorption spectroscopy. 2H CuFeO$_2$ has a band gap of 1.33 eV, high absorption coefficient of $3.8 \times 10^4$ cm$^{-1}$ at 700 nm and is highly photostable. When incorporated into an indium tin oxide/ZnO/2H CuFeO$_2$/graphite/carbon black structure an open circuit photovoltage of 0.29 V was observed. The material appears promising for solar applications. (The work was published in RSC Advances 6(31): 26392)

$\text{Cu}_x\text{Zn}_y\text{Sn}_{2-0.25x-0.5y}\text{S}_4$ with crystallite size more than 85 nm was synthesized by cation exchange reaction from ZnS, CuCl$_2$ and SnCl$_4$ in triethylene glycol. The material was characterized by powder X-ray diffraction, electron microscopy, Raman and energy dispersive X-ray elemental mapping. This method appears promising for promoting the development of Cu$_2$ZnSnS$_4$ based devices.

Future work will focus on following areas: (a) the fabrication of a highly efficient perovskite solar cell submodule and the development of sealing techniques to meet the stability requirement for the successful commercialization; (b) the synthesis of CuFeO$_2$ single crystals in the reductive solvent environment and measuring the carrier mobility, lifetime, and the diffusion length; (c) the optimization of the reaction conditions to synthesize about 400 nm thick monodispersed hexagonal CuFeO$_2$ crystals; (d) the assembly of a p-i-n micro heterojunction solar cell with CuFeO$_2$ as a light absorbing material; (e) the optimization of the reaction conditions to achieve about 2 $\mu$m thick hexagonal ZnS microplates followed by converting them to Cu$_2$ZnSnS$_4$; (f) the assembly of a p-i-n micro heterojunction solar cell using 2 $\mu$m thick hexagonal Cu$_2$ZnSnS$_4$ microplates as light absorption material.
We have already prepared 400 nm thick hexagonal CuFeO$_2$ plates but they were highly aggregated and therefore hard to disperse. It is reasonable to assume that it is possible to synthesize monodispersed CuFeO$_2$ by minimizing the aggregation. In preliminary experiments, the assembly of CuFeO$_2$ on ZnO and CuSCN thin films and filling the gaps between CuFeO$_2$ w ZnO and CuSCN has been already demonstrated using electrochemical deposition methods. Polymer filling between nanoparticles has been also demonstrated in our lab. As a result, the fabrication of p-i-n micro heterojunction CuFeO$_2$ solar cell is feasible.

The synthesis of 2 $\mu$m thick hexagonal ZnS is expected to be much easier than the direct syntheses of pure Cu$_2$ZnSnS$_4$ crystals. The groundwork that was laid down here provides a foundation for the development of a complete new p-i-n micro heterojunction Cu$_2$ZnSnS$_4$ solar cell. This development will be the focus of future work.
APPENDICES
Appendix A

Supporting Information for Chapter Two

Figure S2.1. (a), (b) and (c) AFM high images of PbI$_2$ on float glass, ITO and FTO substrates respectively.

Figure S2.2. (a) XRD spectra of CH$_3$NH$_3$PbI$_3$ films obtained after various reaction time in CH$_3$NH$_3$I saturated 3% 2-propanol/cyclohexane mixture and PXRD simulation pattern of
tetragonal CH$_3$NH$_3$PbI$_3$, diffraction peaks at 14.02°, 19.97°, 24.55°, 28.52°, 31.68°, 40.51°, and 43.11° were assigned as the (110), (020), (022), (220), (222), (040), and (330) planes, respectively; (b) and (c) AFM high images after 2.5 h and 12 h of the reaction respectively.

**Figure S2.3.** (a) and (b) XRD spectra of CH$_3$NH$_3$PbI$_3$ films obtained after various reaction time in CH$_3$NH$_3$I saturated 5% and 7.5% 2-propanol/cyclohexane mixture respectively; (c), (d), and (e) AFM high images after 30 min, 2.5 h, and 12 h of the reaction in 5% mixture respectively; (f) UV-Vis spectrum after 12 h of the reaction; (g), (h), and (i) AFM high images after 30 min, 2.5 h, and 12 h of the reaction in 7.5% mixture respectively; (j) UV-
Vis spectrum of CH$_3$NH$_3$I saturated in 7.5% 2-propanol/hexane and 7.5% 2-propanol/cyclohexane solution.

**Figure S2.4.** (a) XRD spectra of CH$_3$NH$_3$PbI$_3$ films obtained after various reaction time in CH$_3$NH$_3$I saturated 10% 2-propanol/cyclohexane mixture; (b), (c), and (d) AFM high images after 30 min, 1.0 h, and 2.5 h of the reaction respectively.
Figure S2.5. UV-Vis spectra of the CH$_3$NH$_3$PbI$_3$ film, obtained after 2.5 h reaction in CH$_3$NH$_3$I saturated 5% 2-propanol/cyclohexane mixture, were taken from 4 different positions on the film. The insertion is the photo of the film on the strong white light background.
Appendix B

Supporting Information for Chapter Three

Figure S3.1. (a) TEM image of ZnO nanoparticles. (b) & (c) SEM and AFM images of ZnO film on a glass/ITO substrate, respectively. (d) UV-Vis spectrum of ZnO film on a quartz substrate. The thickness of the ZnO film was 40 nm.
Figure S3.2. (a), (b) & (c) SEM, AFM images and UV-vis spectrum of CH$_3$NH$_3$PbI$_3$ on a glass/ITO/ZnO substrate, respectively. The thickness of the CH$_3$NH$_3$PbI$_3$ film was 390 nm.
Figure S3.3. (a) & (b) SEM and AFM images of graphite film on a glass/ITO/ZnO/CH$_3$NH$_3$PbI$_3$ substrate, respectively. (c) & (d) UV-vis spectrum of graphite films on quartz and glass/ITO/ZnO/CH$_3$NH$_3$PbI$_3$ substrates, respectively. The thickness of the graphite film was 75 nm.
Figure S3.4. PCE distribution of devices made by method A.
Figure S4.1. PXRD spectra of PbI$_2$ films on glass/ITO/ZnO and glass/ITO/WO$_3$ substrates, respectively, PDF card of hexagonal PbI$_2$, and PXRD spectrum of the glass/ITO/ZnO substrate. Diffraction peaks at 12.89°, 25.65°, 38.89°, and 52.54° were assigned as the (001), (002), (003), and (004) planes of hexagonal PbI$_2$, respectively.
**Figure S4.2.** AFM image of the PbI$_2$ film on glass/ITO/ZnO substrates with the different spin-coating rate of 6000 rpm (a), 4500 rpm (b), and 3000 rpm (c), respectively. AFM image of the PbI$_2$ film on glass/ITO/WO$_3$ substrate with the spin-coating rate of 6000 rpm (d). The thickness of PbI$_2$ films was 138 nm, 161 nm, 198 nm and 142 nm, respectively. RMS were 7.8 nm, 9.8 nm, 12.9 nm and 16.4 nm, respectively.
Figure S4.3. PXRD spectrum of bulk ZnO nanoparticles and PDF card of hexagonal ZnO. Diffraction peaks at 31.73°, 34.49°, 36.18°, 47.39°, 56.46°, and 62.75° were assigned as the (100), (002), (101), (102), (110), and (103) planes of hexagonal ZnO, respectively.

PXRD spectrum of bulk WO₃ powder which was annealed under air at 180 °C for 30 min and PDF card of monoclinic WO₃.

Figure S4.4. PXRD spectrum of WO₃ on the glass/ITO substrate. Diffraction peaks indicated by stars were from glass/WO₃ substrate.
**Figure S4.5.** AFM image of glass/ITO (a) and WO$_3$ on glass/ITO substrate (b), RMS of the surfaces were 4.8 nm and 2.3 nm, respectively.

**Figure S4.6.** UV-Vis spectra of glass/ITO substrates with different oxide layers. Commercial ITO coated float glass substrates have 120-160 nm ITO layer (8-12 Ohms/sq.) and 20-30 nm passivating SiO$_2$ layer between the ITO and the glass. The extinction spectrum reflects glass/ITO absorption below 350 nm and weak features above 350 nm due to the interference from different layers. The deposition of a thin WO$_3$ layer onto ITO
surface increased the extinction between 350 and 500 nm but had no significant effect above 500 nm. This additional increase was ascribed to increased reflection in this spectral range due to the larger refractive index dispersion of WO$_3$ compared to that of ITO.$^{1-2}$ A contribution from the direct light absorption by WO$_3$ is also possible. Evidence for the direct absorption can be seen in Figure S4.7. When 40 nm of ZnO was deposited on the ITO surface, the spectrum exhibited a bump at 350 nm due to the band gap absorption in ZnO as well as a significant decrease of the extinction in the 370-450 spectral range. The later is due to the antireflecting coating effect.

Figure S4.7. UV-Vis spectra of ZnO and WO$_3$ on quartz substrates, respectively.

References

Appendix D

Supporting Information for Chapter Five

Table S5.1. Reaction details for synthesizing CuFeO$_2$ crystals at different reaction time and temperature by using NaOH as a base.

<table>
<thead>
<tr>
<th>No.</th>
<th>CuI mmol</th>
<th>FeCl$_3$·6H$_2$O mmol</th>
<th>NaOH mmol</th>
<th>Temp. °C</th>
<th>Time h</th>
<th>Phase composition</th>
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<td>0.75</td>
<td>0.75</td>
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<td>0.75</td>
<td>5.5</td>
<td>150</td>
<td>48</td>
<td>CuFeO$_2$ (3R$^a$, 2H$^b$), CuFeO$_2$ (3R$^a$, 2H$^b$), CuFeO$_2$ (3R$^a$, 2H$^b$), CuFeO$_2$ (3R$^a$, 2H$^b$), CuFeO$_2$ (3R$^a$, 2H$^b$)</td>
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<td>0.75</td>
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<td>80</td>
<td>24</td>
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<td>190</td>
<td>24</td>
<td>CuFeO$_2$ (3R$^a$, 2H$^b$)</td>
</tr>
</tbody>
</table>

$^a$ majority phase, $^b$ minor phase
**Figure S5.1.** PXRD spectra of CuFeO\(_2\) synthesized by using CuI (0.75 mmol), FeCl\(_3\)-6H\(_2\)O (0.75 mmol), H\(_2\)O (3.5 mL), NaOH (5.5 mmol) with different reaction time and temperature.

**Table S5.2.** Reaction details for synthesizing CuFeO\(_2\) crystals with different amount of NaOH at 190 °C for 2 h.

<table>
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<th>No.</th>
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<th>FeCl(_3)-6H(_2)O mmol</th>
<th>NaOH mmol</th>
<th>Temp. °C</th>
<th>Time h</th>
<th>Phase composition</th>
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<td>2</td>
<td>CuFeO(_2) (3R(^a), 2H(^b))</td>
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</table>

\(^a\) majority phase, \(^b\) minor phase

**Figure S5.2.** PXRD spectra of CuFeO\(_2\) synthesized by using CuI (0.75 mmol), FeCl\(_3\)-6H\(_2\)O (0.75 mmol), H\(_2\)O (3.5 mL) at 190 °C for 2 h with different amount of NaOH.
**Table S3.** Reaction details for synthesizing CuFeO$_2$ crystals with different additives.

<table>
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<th>FeCl$_3$·6H$_2$O mmol</th>
<th>NaOH mmol</th>
<th>T $^\circ$C</th>
<th>t h</th>
<th>Phase composition</th>
<th>additives</th>
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</thead>
<tbody>
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<td>4.75</td>
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<td>24</td>
<td>CuFeO$_2$ (3R$^a$, 2H$^b$)</td>
<td>PEG 6000 (0.75 mmol)$^c$</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>0.75</td>
<td>4.75</td>
<td>120</td>
<td>24</td>
<td>CuFeO$_2$ (3R$^a$, 2H$^b$)</td>
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<tr>
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<td>6.50$^d$</td>
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<td>Propanoic acid (1.75 mmol)</td>
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<td>0.75</td>
<td>6.50$^d$</td>
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<td>CuFeO$_2$ (3R$^a$, 2H$^b$)</td>
<td>5-phenylpentanoic acid (1.75 mmol)</td>
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</table>

$^a$ majority phase, $^b$ minor phase, $^c$ the molar amount was calculated based on repeat unit of PEG 6000, $^d$ the effective NaOH was 4.75 mmol after reacting with carboxylic acid.

**Figure S5.3.** PXRD spectra of CuFeO$_2$ synthesized by using CuI (0.75 mmol), FeCl$_3$·6H$_2$O (0.75 mmol), H$_2$O (3.5 mL), NaOH (effective amount 4.75 mmol), at 120 $^\circ$C for 24 h with different additives.
Table S5.4. Reaction details for synthesizing CuFeO₂ crystals with different amount of NaOH at 120 °C for 24 h.

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<tr>
<th>No.</th>
<th>CuI mmol</th>
<th>FeCl₃·6H₂O mmol</th>
<th>NaOH mmol</th>
<th>Temp. °C</th>
<th>Time h</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.75</td>
<td>6.5</td>
<td>120</td>
<td>24</td>
<td>CuFeO₂ (3R&lt;sup&gt;a&lt;/sup&gt;, 2H&lt;sup&gt;b&lt;/sup&gt;)</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>0.75</td>
<td>13.5</td>
<td>120</td>
<td>24</td>
<td>CuFeO₂ (3R&lt;sup&gt;a&lt;/sup&gt;, 2H&lt;sup&gt;b&lt;/sup&gt;)</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>0.75</td>
<td>24.0</td>
<td>120</td>
<td>24</td>
<td>CuFeO₂ (3R&lt;sup&gt;b&lt;/sup&gt;, 2H&lt;sup&gt;a&lt;/sup&gt;)</td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>0.75</td>
<td>38.0</td>
<td>120</td>
<td>24</td>
<td>CuFeO₂ (3R&lt;sup&gt;b&lt;/sup&gt;, 2H&lt;sup&gt;a&lt;/sup&gt;)</td>
</tr>
<tr>
<td>5</td>
<td>0.75</td>
<td>0.75</td>
<td>46.8</td>
<td>120</td>
<td>24</td>
<td>CuFeO₂ (3R&lt;sup&gt;b&lt;/sup&gt;, 2H&lt;sup&gt;a&lt;/sup&gt;)</td>
</tr>
<tr>
<td>6</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>120</td>
<td>24</td>
<td>CuFeO₂ (2H)</td>
</tr>
</tbody>
</table>

<sup>a</sup> majority phase, <sup>b</sup> minor phase

Table S5.5. Reaction details for synthesizing CuFeO₂ crystals with a high concentration of NaOH at 120 °C for different reaction time.

<table>
<thead>
<tr>
<th>No.</th>
<th>CuI mmol</th>
<th>FeCl₃·6H₂O mmol</th>
<th>NaOH mmol</th>
<th>Temp. °C</th>
<th>Time h</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>120</td>
<td>1.5</td>
<td>CuFeO₂ (2H), Cu₂O</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>120</td>
<td>2</td>
<td>CuFeO₂ (2H)</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>120</td>
<td>6</td>
<td>CuFeO₂ (2H)</td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>120</td>
<td>12</td>
<td>CuFeO₂ (2H)</td>
</tr>
<tr>
<td>5</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>120</td>
<td>24</td>
<td>CuFeO₂ (2H)</td>
</tr>
<tr>
<td>6</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>120</td>
<td>48</td>
<td>CuFeO₂ (2H)</td>
</tr>
</tbody>
</table>
Figure S5.4. PXRD spectra of CuFeO$_2$ synthesized by using CuI (0.75 mmol), FeCl$_3$·6H$_2$O (0.75 mmol), H$_2$O (3.5 mL), NaOH (55.5 mmol) with different reaction time at 120 °C.

Table S5.6. Reaction details for synthesizing CuFeO$_2$ crystals at different concentration of reactants and reaction temperature.

<table>
<thead>
<tr>
<th>No.</th>
<th>CuI mmol</th>
<th>FeCl$_3$·6H$_2$O mmol</th>
<th>NaOH mmol</th>
<th>T °C</th>
<th>t h</th>
<th>Phase composition</th>
<th>crystallite size nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>100</td>
<td>17</td>
<td>CuFeO$_2$ (2H)</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>160</td>
<td>2</td>
<td>CuFeO$_2$ (2H)</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>200</td>
<td>2</td>
<td>CuFeO$_2$ (2H)</td>
<td>73</td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>0.75</td>
<td>55.5</td>
<td>120</td>
<td>3</td>
<td>CuFeO$_2$ (2H)</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>0.35</td>
<td>0.35</td>
<td>55.5</td>
<td>120</td>
<td>3</td>
<td>CuFeO$_2$ (2H)</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>0.25</td>
<td>55.5</td>
<td>120</td>
<td>3</td>
<td>CuFeO$_2$ (2H)</td>
<td>36</td>
</tr>
<tr>
<td>7</td>
<td>0.07</td>
<td>0.07</td>
<td>55.5</td>
<td>120</td>
<td>3</td>
<td>CuFeO$_2$ (2H), Cu$_2$O</td>
<td>–</td>
</tr>
</tbody>
</table>
Figure S5.5. PXRD spectra of CuFeO\textsubscript{2} synthesized by using H\textsubscript{2}O (3.5 mL), NaOH (55.5 mmol) at 120 h for 3 h with different amount of CuI and FeCl\textsubscript{3}-6H\textsubscript{2}O.

Table S5.7. Reaction details for synthesizing CuFeO\textsubscript{2} crystals at different concentration of reactants and reaction time with a high concentration of KOH at 100 °C.

<table>
<thead>
<tr>
<th>No.</th>
<th>CuI mmol</th>
<th>FeCl\textsubscript{3}-6H\textsubscript{2}O mmol</th>
<th>KOH mmol</th>
<th>Temp. °C</th>
<th>Time h</th>
<th>Phase composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.35</td>
<td>0.35</td>
<td>55.5</td>
<td>100</td>
<td>24</td>
<td>CuFeO\textsubscript{2} (2H\textsuperscript{a}, 3R\textsuperscript{b})</td>
</tr>
<tr>
<td>2</td>
<td>0.525</td>
<td>0.525</td>
<td>55.5</td>
<td>100</td>
<td>24</td>
<td>CuFeO\textsubscript{2} (2H\textsuperscript{a}, 3R\textsuperscript{b})</td>
</tr>
<tr>
<td>3</td>
<td>0.700</td>
<td>0.700</td>
<td>55.5</td>
<td>100</td>
<td>24</td>
<td>CuFeO\textsubscript{2} (2H)</td>
</tr>
<tr>
<td>4</td>
<td>1.05</td>
<td>1.05</td>
<td>55.5</td>
<td>100</td>
<td>24</td>
<td>CuFeO\textsubscript{2} (2H)</td>
</tr>
<tr>
<td>5</td>
<td>0.35</td>
<td>0.35</td>
<td>55.5</td>
<td>100</td>
<td>6</td>
<td>CuFeO\textsubscript{2} (2H), Cu\textsubscript{2}O</td>
</tr>
<tr>
<td>6</td>
<td>0.35</td>
<td>0.35</td>
<td>55.5</td>
<td>100</td>
<td>12</td>
<td>CuFeO\textsubscript{2} (2H\textsuperscript{a}, 3R\textsuperscript{b})</td>
</tr>
<tr>
<td>7</td>
<td>0.35</td>
<td>0.35</td>
<td>55.5</td>
<td>100</td>
<td>18</td>
<td>CuFeO\textsubscript{2} (2H\textsuperscript{a}, 3R\textsuperscript{b})</td>
</tr>
<tr>
<td>8</td>
<td>0.35</td>
<td>0.35</td>
<td>55.5</td>
<td>100</td>
<td>36</td>
<td>CuFeO\textsubscript{2} (2H\textsuperscript{a}, 3R\textsuperscript{b})</td>
</tr>
<tr>
<td>9</td>
<td>0.35</td>
<td>0.35</td>
<td>55.5</td>
<td>100</td>
<td>48</td>
<td>CuFeO\textsubscript{2} (2H\textsuperscript{a}, 3R\textsuperscript{b})</td>
</tr>
</tbody>
</table>

\textsuperscript{a}majority phase, \textsuperscript{b}minor phase
Figure S5.6. PXRD spectra of CuFeO$_2$ synthesized by using H$_2$O (3.5 mL), KOH (55.5 mmol) at 100 °C for 24 h with different amount of CuI and FeCl$_3$·6H$_2$O.
**Figure S5.7.** PXRD spectra of CuFeO$_2$ synthesized by using CuI (0.35 mmol), FeCl$_3$-$6$H$_2$O (0.35 mmol), H$_2$O (3.5 mL), KOH (55.5 mmol) with different reaction time at 100 °C.

**Figure S5.8.** SEM images of CuFeO$_2$ synthesized by using CuI (0.75 mmol), FeCl$_3$-$6$H$_2$O (0.75 mmol), H$_2$O (3.5 mL), NaOH (55.5 mmol) at (a) 100 °C, (b) 120 °C, (c) 160 °C and (d) 200 °C, respectively.
Figure S5.9. SEM images (20K times magnification) of CuFeO$_2$ synthesized by using H$_2$O (3.5 mL), KOH (55.5 mmol) at 100 h for 24 h with different amount of CuI and FeCl$_3$·6H$_2$O, (a) 0.35 mmol, (b) 0.525 mmol, (c) 0.700 mmol, and (d) 1.05 mmol, respectively.
Figure S5.10. SEM images (5K times magnification) of CuFeO$_2$ synthesized by using H$_2$O (3.5 mL), KOH (55.5 mmol) at 100 h for 24 h with different amount of CuI and FeCl$_3$·6H$_2$O, (a) 0.35 mmol, (b) 0.525 mmol, (c) 0.700 mmol, and (d) 1.05 mmol, respectively.
Figure S5.11. SEM image of 2H-CuFeO$_2$ film on glass/ITO/ZnO substrate.
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Clemson University, SC 29631
USA
Phone: +1-864-656-8980
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E-mail: yj@clemson.edu

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Title of Selection: Fabrication of Lead Halide Perovskite Film by Controlling Reactivity at Room Temperature in Mixed Solvents

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