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Transparent Conductive Films Based on Polymer-Encapsulated Graphene Oxide Sheets

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ABSTRACT

Transparent conductive films (TCFs) play a key role in number of devices, including solar panels, LCD/OLED displays and touchscreens. Graphene has emerged as a promising material in this area due to its unique mechanical and electrical properties. Despite noteworthy progress in the fabrication of large-area graphene sheet-like nanomaterials, the vapor-based processing still requires sophisticated equipment and a multistage handling of the material. An alternative approach to manufacturing functional graphene-based films includes the employment of graphene oxide (GO) micron-scale sheets as precursors. However, search for a scalable manufacturing technique for the production of high-quality GO nanoscale films with high uniformity and high electrical conductivity is still continuing.

The study presented in this dissertation is dedicated to the fabrication and characterization of electrically conductive films made of reduced graphene oxide sheets (rGO) deposited on both rigid and flexible substrates. Here we show that conventional dip-coating technique can offer fabrication of high quality mono- and bilayered films made of GO sheets. The method is based on our recent discovery that encapsulating individual GO sheets in a nanometer-thick copolymer layer poly(Oligo Ethylene Glycol methyl ether Methacrylate [OEGMA]- Glycidyl Methacrylate [GMA]) allows for the nearly perfect formation of the GO layers on hydrophilic substrates. By thermal reduction at 1000 °C the bilayers (cemented by a carbon-forming polymer linker) are converted into highly conductive and transparent reduced GO films with a high conductivity up to $10^4$ S/cm and optical transparency on the level of 90%. The value is the highest electrical conductivity
reported for thermally reduced nanoscale GO films and is close to the conductivity of indium tin oxide (ITO) currently in use for transparent electronic devices, thus making these layers intriguing candidates for replacement of ITO films.

To facilitate the deposition of GO sheets on rigid and flexible hydrophobic substrates, the amphiphilic copolymer poly(Oligo Ethylene Glycol methyl ether Methacrylate [OEGMA]- Glycidyl Methacrylate [GMA]- Lauryl Methacrylate [LMA]) with additional hydrophobic block was used. The results show that the obtained GO layers had well-defined and uniform structure. Thus, it leads to enhanced hydrophobic-hydrophobic (van der Waals) interaction between the hydrophobic substrate and GO. To this end, the morphology, opto-electrical properties and electro-mechanical stability of chemically reduced GO layers are also investigated. Finally, we demonstrate the excellent stability of rGO on polymeric substrates with no delamination or significant loss in conductivity even after 50000 bending cycle.
DEDICATION

I dedicate this dissertation to my loving, supportive and caring wife, Oksana Savchak, whose unconditional love and kind attitude gave me the strength and belief to follow my dreams. I also dedicate this dissertation to my always encouraging and ever faithful parents, Stefan and Mariya Savchak, and to my brother, Vasyl Savchak.
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CHAPTER ONE
INTRODUCTION

Transparent conductive films (TCFs), materials possessing high electrical conductivity and optical transparency, have received wide attention due to their applications in solar cells, displays, gas/moisture/biosensors, thin film transistors and many others. ITO (indium tin oxide), for example, is often used when conductivity has to be paired with transparency. However, employment of such metal oxide appears to be increasingly problematic because of limited indium source, its susceptibility to ion diffusion into polymer substrate layers, their instability in acid or base, and the brittle nature of metal oxides\textsuperscript{1-7}. Many new materials or structures such as graphene, carbon nanotubes (CNTs)\textsuperscript{8}, metal nanowires\textsuperscript{9}, silver nanoparticles\textsuperscript{10}, conducting polymers\textsuperscript{11} have been tested as possible replacement for ITO\textsuperscript{12,13}. Graphene (GR), for instance, appears to be a strong contender due to its unique physical and electrical properties: high carrier charge mobility (conductivity on the order of $10^5$ S/cm), outstanding mechanical (1 TPa Young’s modulus, high flexibility, high aspect ratio) and optical (90 % transmittance for corresponding sheet resistance of 20 $\Omega$/sq)\textsuperscript{14}. Whereas this substitution is highly feasible, based on our current knowledge of GR properties the major stumbling block is practical and cost-effective fabrication process including synthesis of GR itself and GR functional pattern formation.

An alternative low-cost and up-scalable method is the reduction of graphene oxide (GO) (an oxidized form of graphene) to its conductive form – reduced graphene oxide (rGO). Moreover, due to the presence of oxygen-containing functional groups physical
properties of GO can be easily tuned with an appropriate chemistry applied, which gives it high processability in various polar solvents (water included) unlike pristine graphene \(^{15}\). The literature on graphene-based electronics abounds with the examples of employment of GO sheets in fabrication of large area TCFs \(^{16-18}\). To this end, rGO-based films have not yet approached pristine GR in terms of its conductive properties, although its optical properties showed a great promise \(^{19}\).

When considering the integration of TCFs into flexible electronics the following requirements for TCFs should be met: \(R_s \approx 500 - 2,000 \ \Omega/{\text{sq}}\) and \(T > 90\%\) at 550 nm \(^{14}\). Furthermore, flexible electronics have to incorporate all functional attributes of conventional rigid electronics while surviving significant and often repeatable mechanical deformations.\(^ {20}\) Bendable, foldable, rollable, wearable flexible electronic devices assembled on polymeric substrates have been already transforming the ways in which electronics is used.\(^ {21-23}\) The flexible devices are actively considered or already used for a number of applications including packaging, communications, alternative energy, display technology, sensors, biomedical devices, frequency identification tags \(^{20, 23-33}\). A key concern for flexible electronic engineering is electro-mechanical behavior of devices or ability of the incorporated materials to withstand the applied mechanical stresses while retaining satisfactory electrical performance \(^{23-24, 34-35}\). Thus far, the embedding of GR or GO into bendable electronics has been achieved, but direct and cost-effective deposition of GR/GO on flexible polymeric substrates has proved to be a challenging task \(^{36}\).

To this end, the ultimate goal of this dissertation was to fabricate and characterize (study its opto-electrical and mechanical properties) electrically conductive reduced...
graphene oxide (rGO) films on both rigid and flexible substrates. The work was conducted as follows. First, the methodology for the formation of uniform and well-defined GO mono/bilayers on rigid substrates was developed. Specifically, our approach was based on enveloping GO into especially designed molecular bottlebrush reactive copolymers such as poly(Oligo Ethylene Glycol methyl ether Methacrylate [OEGMA]- Glycidyl Methacrylate [GMA]) (P1) and poly(Oligo Ethylene Glycol methyl ether Methacrylate [OEGMA]- Glycidyl Methacrylate [GMA]- Lauryl Methacrylate [LMA]) (P2), that allows formation of well-defined GO layers via simple dip-coating procedure. Namely, using GO modified with P1 (GO-P1) the uniform films were obtained only on hydrophilic substrates while GO modified with more hydrophobic or amphiphilic copolymer P2 (GO-P2) rendered itself suitable for both hydrophilic and hydrophobic rigid/flexible substrates. Next, chemical or thermal reduction methods were employed to make copolymer-modified GO films electrically conductive. A general schematic of the typical workflow for the fabrication of rGO films on flexible substrate is depicted in Figure 1.1.

![Figure 1.1](image_url)  
**Figure 1.1:** (A-E) Diagram representation of the approach employed by this project: A) and B) functionalization of pristine GO sheets with amphiphilic copolymer. C) Deposition of a monolayer of GO enveloped with a polymer layer by dip-coating. D) Final monolayer of polymer-modified GO film on flexible substrate. E) Reduction step.
Specifically, Figure 1.1A and Figure 1.1B represent the synthesis and modification of GO sheets with copolymer. Figure 1.1C represents the dip-coating procedure to achieve monolayer deposition of copolymer-modified GO sheets on the substrate (Figure 1.1D). Figure 1.1E shows the reduction step at which GO converts to electrically conductive rGO due to removal of GO functionalities and copolymer. The morphology, structure and properties of deposited GO films were characterized using atomic force microscopy (AFM), optical microscopy, Raman spectroscopy, X-ray photon spectroscopy, Fourier transform infrared spectroscopy (FTIR), UV-Vis, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and mechanical testing (tensile and bending tests).

This dissertation is structured as follows:

- **Chapter 2** of this dissertation gives a literature review of methods for the synthesis of graphene/graphene oxide and their structure-property relationship. It also discusses functionalization techniques of GO surface, GO film formation methods and challenges in the fabrication of reduced GO films with high electrical conductivity and optical transparency.

- **Chapter 3** describes the synthesis and characterization of sterically stabilized GO sheets in water, subsequent formation of a monolayer and multilayer (bilayer) films based on polymer modified GO sheets on hydrophilic rigid substrate (SiO₂/Si).

- **Chapter 4** focuses on morphological and opto-electrical properties of thermally reduced GO-P1 monolayers and bi-layers. Furthermore, this chapter discusses the method for electronic band gap determination.
• **Chapter 5** is devoted to the deposition of GO modified with GO-P2 directly on hydrophobic silane-modified SiO$_2$/Si and polymeric substrates via dip-coating from water solution. Additionally, this chapter includes comparative studies of interaction of GO-P1 and GO-P2 with the hydrophobic interface using quartz crystal microbalance with dissipation monitoring (QCM-D).

• **Chapter 6** discusses morphology, structure, opto-electrical and mechanical properties of chemically reduced GO-P2 films prepared on hydrophobic silane-modified SiO$_2$/Si as well as polymeric substrates. Specifically, electro-mechanical response and life-cycle durability of rGO-P2 films on plastics of different thicknesses have been investigated.

• **Chapter 7** concludes and summarizes the findings of this dissertation.
References


CHAPTER TWO

LITERATURE REVIEW

2.1: Graphene

Graphene is atomically thick, two-dimensional sheet composed of sp² carbon atoms arranged in a honeycomb structure, as shown in Figure 2.1.

![Figure 2.1: Schematics of graphene sheet.](image)

In the last decade GR has emerged as an exciting new material, with potential to impact many scientific and technological fields after Geim and co-workers first isolated GR onto SiO₂ substrate and studied its opto-electrical properties\(^1\)-\(^4\). Nowadays, GR has been considered as the most promising candidate for thin flexible electronics due to its high electrical conductivity (up to 1.6×10⁵ S/cm)\(^1\)\(^2\), excellent optical transmittance and chemical stability \(^1\)\(^3\). In addition, some of GR characteristics demonstrated exceptionally high values, nearing theoretically predicted limits: room temperature charge carrier mobility of 2.5×10⁵ cm² V\(^{-1}\) s\(^{-1}\) \(^1\)\(^4\), zero bandgap \(^1\)\(^5\) which can be tuned via lithography \(^1\)\(^6\), a Young modulus of
1TPa and intrinsic strength of 130 GPa, thermal conductivity (3,000-5,300 W/(mK)), gas impermeability, and large surface area (theoretical limit: 2630 m²/g). Furthermore, the surge in GR research also paved the way for search and investigation of other 2D materials. For instance, the discovery of MXenes implies that combining such 2D crystals with GR can produce hybrid 2D superstructures (Figure 2.2) with a wide variety of properties, which can be used for the fabrication of flexible field-effect transistors (FETs).

**Figure 2.2:** Schematic 2D heterostructures based on van der Waals interlayer force. Reprinted by permission of Springer Nature.

### 2.2: Synthesis of Graphene

The process which allows one to fabricate or extract GR of desired size and purity is referred to as synthesis of graphene. There are a number of operative ways for obtaining mono- and multilayered graphene sheets, which eventually can be categorized into two
distinct strategies: bottom-up and top-down \(^2, 6, 24\). An overview of graphene synthesis techniques is shown in the flow chart in **Figure 2.3**.

**Figure 2.3**: A process flow chart of GR synthesis \(^6\). Reprinted by permission of Springer Nature (open access).

**Bottom-up Graphene**

Bottom-up GR growth process is based on atom by atom growth. It includes chemical vapor deposition (CVD) on transition metals \(^25\), epitaxial growth on SiC \(^26\), molecular beam epitaxy \(^27\) and others (electron beam irradiation of electrospun PMMA nanofibers \(^28\), arc discharge of graphite \(^29\), thermal carbonization of polycyclic aromatic hydrocarbons \(^30\)). The predominant technique for obtaining larger-scale graphene film is CVD, which allows good control over synthesis, film thickness, and properties. A general mechanism for CVD-based graphene includes the following steps \(^8\): (1) mass transport of the reactant, (2) reaction of the film precursor, (3) gas molecules diffusion, (4) adsorption of the precursor, (5) precursor diffusion into the substrate, (6) surface reaction, (7) product desorption, and (8) by-product removal (**Figure 2.4**). Typically, a CVD-process requires the presence of transition metal catalyst (Au, Cu, Ni, etc.) to activate chemical reactions of
precursors at the growth substrate surface/interface (or dehydrogenate the precursor species)\(^25\). High roughness of the catalytic metal surface makes it difficult for GR to grow uniformly and to cover 100% of the substrate.

In addition, CVD GR can be contaminated by the residual metallic impurities after etching of the metal substrate. Furthermore, further device integration the film has to be transferred to a targeted substrate via a quite-sophisticated methodology for further device integration. For this reason, there is limited opportunity for scalability, with only two reports describing successful attempts to fabricate larger (10th of centimeter/meter)-scale CVD-obtained graphene films via roll-to-roll transfer with low sheet resistance (150–500 \(\Omega/sq\) without chemical doping) and high conductivity (\(10^4\) S/cm)\(^31-32\). We note that the

**Figure 2.4:** Diagram of the general growth mechanism of CVD-based graphene: transport and reaction processes \(^8\). Reprinted by permission of The Royal Society of Chemistry.
transferred films had a significant density of defects (e.g., cracks, wrinkles, multilayered
islands, non-uniformity, impurities), especially for the monolayer and bi-layered graphene
films.

Recently, significant efforts have been made to fabricate GR on semiconductor and
dielectric substrates (quartz, SiO2) using non-catalytic direct-growth of GR, which offers
low process cost and shorter experimental processes\textsuperscript{33-35}. However, the drawback of this
method is the slow growth rate and poor quality of GR compared with the catalytic direct
growth, which makes it not suitable for large-area high-quality GR manufacturing\textsuperscript{8}. In
addition, high temperatures (>1000 °C) are required for thermal CVD to make up for the
absence of metal catalyst\textsuperscript{36-37}. In 2017 Zheng et al. reported an innovative method for
synthesizing high-quality GR directly on Al2O3 and SiO2 substrates. The method was based
on the use of NH\textsubscript{3}-assisted microwave plasma-enhanced chemical vapor deposition
\textsuperscript{(MPECVD)}\textsuperscript{38}. As a result, metal-catalyst-free polycrystalline GR layers were grown at a
temperature range of 650 °C to 750 °C with sheet resistances in the range of 3.8 – 6.6 kΩ/sq\textsuperscript{1}.

Direct growth of GR on flexible organic substrates is very attractive for the number
of flexible optoelectronics applications \textsuperscript{39}, health-monitoring sensors \textsuperscript{40} and e-skin \textsuperscript{41-42}. However, low thermal stability of organic substrates makes it challenging to directly grow
GR on the flexibles substrates. Because of that, most of the studied growth methods still
rely on the catalytic conversion of organic precursors to graphitic layers.
Kim et al. fabricated graphene-graphitic carbon (G-GC) films on a Cu layer deposited on a polyimide substrate using inductively coupled plasma-enhanced CVD. The Cu layer was then etched and G-GC film was then directly transferred onto an underlying flexible substrate. Raman spectroscopy and transmission electron microscopy (TEM) were used to study the structural quality and crystallinity of G-GC films. The electrical and optical properties of the films were measured by four-probe method and UV-Vis respectively. It was shown that opto-electrical properties can be influenced by growth temperature, plasma power and growth time. Sheet resistances in the range of 3.8 – 6.6 kΩ/sq-1 at 80% transparency at 550 nm were achieved 43.

**Top-down graphene**

In top-down process (Figure 2.5), graphene or modified graphene sheets are produced from graphite source by solvothermal synthesis, mechanical/chemical exfoliation, and unzipping carbon nanotubes 44-46. Exfoliation can be done using such methods as scotch tape, ultrasonication, electric field, transfer printing technique 47.
Chemical exfoliation or synthesis is the most appropriate method for large-scale production of graphene. Graphene obtained by this method is generally referred to as graphene oxide (GO). Chemical synthesis of GR involves the following steps: (i) oxidation of graphite, which causes an increase in interlayer spacing between stacked GR sheets, and (ii) exfoliation through rapid heating or sonication. Literature reports the following most common synthesis methods of GO: Brodie, Staudenmaier and Hummers methods.

**Figure 2.5:** Diagram of the top-down approach for GR synthesis. Reproduced with permission.
2.3: Graphene Oxide

GO sheets are monolayers of sp²-hybridized carbon atoms partially derivatized to sp³ with hydroxy and epoxy groups on both sides and carboxy/carbonyl groups around the edges. GO has a typical carbon/oxygen ratio of 2/1 (Figure 2.6). GO platelets are decorated with carboxylic acid groups at their edges, and epoxy and hydroxyl groups on the basal planes.

Figure 2.6: Schematic representation of graphene oxide sheet.

GO sheets serve as a “precursor” for its electrically conductive derivative, so-called reduced graphene oxide (rGO). GO is a poor electrical conductor, because of the defects such as oxygen containing functional groups that are present in the structure. Reduction of GO (which yields rGO) restores to a substantial degree electrical, mechanical and other properties of the graphene. However, certain oxygen amount still remains in RGR structure (about 10% or C/O ~10/1). The approach based on GO has significant potential...
to rapidly grow to industrial scale. The methods of reduction are discussed more in detail in Section 2.6. In fact, GO possesses several advantages over pristine graphene materials from a manufacturing point of view: it is inexpensive and can be produced at a large scale from readily available graphite. In addition, GO has excellent dispersibility in polar solvents, including water, and its surface can be straightforwardly modified. Therefore, GO has extreme adaptability and compatibility with various liquid media and solid substrates, which are important for the employment of standard methods of layer nanomanufacturing. In fact, significant progress has been reached in this area over the past decade, as described in a number of comprehensive review articles on the topic.

2.4: Functionalization of Graphene Oxide

The multiple functional groups and unique 2D morphology make GO ideal template for the construction of different organic/inorganic composites structures. Polymer grafted GO composites drew lots of attention because of their wide applications in high-strength and conductive materials, catalysts and fire retardants. Specifically, the GO functional groups can be used to covalently and non-covalently attach functional (macro)molecules to optimize physical and chemical properties of the material. Covalent attachments, which typically involve chemical reactions at the hydroxyl, epoxy and carboxylic acid groups are made using “grafting to” and “grafting from” methods. The non-covalent physisorption on GO, which involves sp² regions, can be realized via π-π stacking, electrostatic or van der Waals interactions.
For instance, Lu et al. reported a simple and effective way to enhance the dispersibility of GOs in alkaline cementitious solutions\(^\text{11}\). The method was based on the steric stabilization of GO with polycarboxylate-ether copolymer (PCE) via van der Waals interactions between PMA backbone in PCE and sp\(^2\)– hybridized carbon backbone in GO, as shown in Figure 2.7. The improved dispersion of GO in the aqueous solution resulted from the stronger hydrogen bonding and steric repulsion between GO/PCE sheets provided by PEG side chains in PCE copolymer. As a result, GO-PCE-Cement composite showed improvement in flexural and compressive strengths with corresponding values of 14.6 and 27.14 MPa.

![Figure 2.7: Steric stabilization of GO-PCE suspensions via van der Waals interactions\(^{11}\). Reprinted by permission of Elsevier.](image)

In the “grafting from” approach, the polymerization is initiated right on the surface of GO\(^{67, 70-72}\). For example, Ref.\(^7\) reports “grafting from” technique to fabricate PNIPAM-GO-based thin film, exhibiting temperature- and NIR-controllable wettability via \textit{in situ} free-radical polymerization (Figure 2.8). The material obtained in this way demonstrated
a reversible switching of wettability between hydrophobic and hydrophilic states which can be promising for practical applications in smart coatings, sensors, drug delivery and catalysis.

Cano et al. reported on the modification of GO with poly(vinyl alcohol) (PVA) leading to the mechanical improvement of GO-based composites\(^9\) (Figure 2.9). Specifically, Young’s modulus and strength of GO-PVA paper material increased by approximately 60% for GO-PVA loadings below 0.3 vol.%. 

Figure 2.8: Preparation of GO-PNIPAM hybrids via “grafting from” technique using \textit{in situ} free-radical polymerization\(^7\). Reprinted by permission of The Royal Society of Chemistry.
2.5: GO Film Formation Methods

To produce highly transparent conductive films, GO sheets should be deposited onto a substrate uniformly without folds or gaps between them. The solution-processing approach is of particular interest since it has great potential to be implemented into roll-to-roll technique for continuous large-scale production of flexible transparent conductors. Therefore, significant effort has been made to produce uniform GO films in a controlled and reproducible manner, including methods such as spin-coating, spray-coating, ink-jet printing, dip-coating, Langmuir-Blodgett [L-B] method, layer-by-layer [L-b-L] deposition, vacuum filtration, rod-coating and drop-casting. However, it is still challenging to control the thickness and property of graphene-based conductive films during the process of fabrication. Among the methods used for the formation of rGO layers, dip-coating, spray-coating, and drop-casting have the highest potential to be used for the manufacturing of larger-scale conductive and transparent coatings. However, to the best of our knowledge (beside our recent work, described in detail in this dissertation), there are no reports in the scientific literature describing the formation of highly conductive rGO nanoscale layers with a well-defined morphology and properties by these methods. As of today, the most-used method for obtaining several-nm-thick rGO films is spin-coating, which, indeed, allowed the production of highly conductive nanoscale rGO films. The best results for the rGO films in terms of perfectness of morphology and electrical/optical properties were also obtained using L-B deposition and interfacial self-assembly.
The dip-coating technique is known for its low cost, operating simplicity, coating uniformity and easy scalability. For example, GO material can be deposited on different polymeric substrates via roll-to-roll method (Figure 2.10). In addition, the thickness, morphology and opto-electrical properties of the prepared GO-based films can be controlled via withdrawal speed, GO concentration and the number of coating cycles 76.

![Schematic of fabrication of GO film on flexible substrate via dip-coating method.](image)

**Figure 2.10:** Schematic of fabrication of GO film on flexible substrate via dip-coating method.

### 2.6: Reduction of Graphene Oxide

In general, at the structural/chemical level the aim of the reducing procedures is to remove oxygen containing moieties from the GO structure, restore and expand graphene sp² structural regions. Therefore, an effective deoxygenation process or “reduction” must be performed, which aims to convert practically non-conducting GO material (5*10⁻³ S/cm ⁹⁷, 5*10⁻⁶ S/cm ⁹⁸) to its conductive form, reduced graphene oxide ⁹⁹. The level of reduction success significantly varies depending on the reduction method applied, but at least several orders of magnitude increase in conductivity is always observed.
There are several major techniques allowing the reduction of GO into rGO. Specifically, GO can be reduced to graphene-like structures by chemical, electrochemical, microwave, thermal, hydrothermal, and photothermal reducing techniques\(^{100-103}\). The actual conductivity values can be as low as 2 S/cm for hydrazine hydrate\(^5\)\(^6\) and microwave reduction\(^{104}\) to 10\(^3\) S/cm order of magnitude for high temperature treatment in UHV\(^{105}\), reduction in the presence of H\(_2\)^{106} or by HI\(^{100,104,107}\).

High temperature reduction has demonstrated the most promising results. The mechanism of GO transformation upon the heating involves thermal deoxidation (removal of oxygen containing groups from the sheets)\(^\text{108}\). For example, thermally reduced rGO can be produced by heating GO in inert environment and high temperature (600-1000 °C)\(^{54}\),\(^{109-110,111}\). The additional treatment of the thermally reduced graphene at ~1500 °C can increase C/O ratio to 660/1 practically eliminating oxygen in the rGO structure. It is necessary to highlight that there are reports published on generation of rGO from GO by \textit{in-situ} (inside polymer matrix) thermal reduction at lower temperatures (2-3h, ~200 °C)\(^{112-113}\).

Despite contributing to the increase in conductivity value thermal reduction process often introduces defect into final rGO structure by “pulling out” carbon atoms attached to oxygen from the structure\(^{114-115}\). An interesting approach to heal the defects was proposed by Lopez et al\(^{116}\). The healing process was performed at high temperature in ethylene vapor (the conditions similar to one used for CVD growing of carbon nanotubes) on previously thermally reduced GO. Two orders of magnitude increase in conductivity value (level of 10\(^2\) S/cm) was observed comparing to standard high temperature annealing.
process. Similar effect was demonstrated by Dai et al.\textsuperscript{117}, but in this case the carbon source (methane) was introduced at high temperature during the reduction process. Thus, the reduction and healing occurred at the same time. Yet again, significant increase in conductivity (level of $4 \times 10^2$ S/cm) was achieved. Su et al.\textsuperscript{118} also demonstrated the healing effect at high temperatures, but this time produced by large aromatic molecules associated with GO. Reduced GO conductivity as high as $10^3$ S/cm was demonstrated.

Although, thermal reduction of GO is a very simple and eco-friendly method it is not suitable for applications in flexible devices. Low temperature chemical reduction\textsuperscript{100, 107}, on the other hand, is believed to offer the most promising route towards the large scale and low cost production of GR for transparent flexible conductors\textsuperscript{10, 119-120}. To date, many reduction reagents have been used such as NaBH$_4$, hydroquinone, sulfur compounds, hydrazine, ascorbic acid, and hydrohalic acids\textsuperscript{121}. Among all these processes, the reduction of GO films using hydrohalic acids has been regarded as the fastest way to produce highly conductive graphene in large quantities with preserved integrity\textsuperscript{10, 122-123}.

Cheng et al. have demonstrated the reduction of free-standing GO films at 100 $^\circ$C for 1 h using concentrated HI acid\textsuperscript{10}. The obtained rGO films demonstrated much higher electrical conductivity (298 S/cm and 85% transparency at 550 nm) and C/O atomic ratio ($\sim 12$) than those of films reduced by other chemical methods, for example hydrazine. Furthermore, the authors showed that HI-reduced rGO films had preserved original flexibility, strength and integrity. The pathway of HI reduction mechanism is shown in Figure 2.11: (a) the ring-opening reaction of an epoxy group and (b) the substitution reaction of a hydroxyl group by halogen atom. Finally, graphene can be produced (final
step (b)) by elimination of iodine atoms \(^{124}\). However, one of the drawbacks of using chemical reduction is possible introduction of heteroatomic impurities \(^{49}\), which may play a dual role: (i) iodine can act as a p-type dopant enhancing the conductivity of monolayer Gr \(^{125}\) or (ii) it can compromise the underlying polymeric substrate by lowering its tensile strength, Young’s modulus and making it more brittle (Appendix (Figure A14)).

**Figure 2.11:** Possible reaction mechanism of GO reduction by hydrohalic acids. (a) Ring-opening reaction of an epoxy group. (b) Halogenation substitution reaction of a hydroxyl group. (X = iodine or bromine) \(^{10}\). Reprinted by permission of Elsevier.

### 2.7: Challenges in the Fabrication of rGO Films

During the assembly of GO flakes into larger area films/coatings with a thickness on the order of several nm the electrical characteristics of the films are significantly reduced in comparison to individual graphene sheets. In fact, for these films a conductivity of \(10^2\)-\(10^3\) S/cm and sheet resistance on the level of \(10^3\) \(\Omega/\text{sq}\) and higher is usually reported\(^{44-45}\).
There are at least two major challenges for the layers made of rGO sheets: (i) the properties/morphology of individual rGO sheets and (ii) the properties/morphology of the rGO layers. At the individual rGO sheet level, one has to deal with only a partial reduction of the original GO, the presence of numerous defects, and a mosaic of conductive and non-conductive parts. All these features reduce the material’s ability to conduct electric current. In addition, at the GO layer level, the availability of GO/rGO only in the form of micrometer size sheets causes high inter-sheet contact resistivity. This resistivity originates from untight/imperfect sheet arrangements/contacts in plane (edge-to-edge) and plane-to-plane (stacking) contacts. Therefore, striving for a thinner rGO layer to achieve the largest transparency value dramatically decreases the overall electrical-optical property balance with increase of the contribution of the inter-sheet resistivity. Thus, it is suppressing the facile formation of highly conductive and transparent flexible films for prospective micro/nano-electronic applications. The electrical characteristics of the films are significantly reduced in comparison to individual graphene sheets.

2.8: Transparent Conductive Plastics

Polymeric films are the most common flexible substrates employed in flexible electronic devices. Among key polymer materials are polyimides (such as Kapton), polycarbonate (PC), polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyarylate (PAR), polydimethylsiloxane (PDMS), polyurethanes (PU), and styrene ethylene butadiene styrene (SEBS). When polymeric substrate is selected for a
particular application beside cost the following polymer characteristics have to be taken into account: mechanical properties, mechanical stability, thermal stability, thermal expansion coefficient, solvent resistance, diffusivity, optical clarity, dielectric constant, roughness, surface energy/wettability. However, to the best of our knowledge there are no published reports on the formation of highly conductive rGO nanoscale layers with a well-defined morphology and properties directly from water on flexible polymer hydrophobic substrates/films. One of the major challenges is significant capillary forces affecting “perfectness” of nanoscale structure as water is evaporating. Another challenge is low surface energy of the polymer films. It is shown that even for deposition of less-defined and thicker multilayered coatings it is necessary to overcome low wettability of polymer films by water-based GO suspensions. Therefore, GO material cannot be deposited directly on the polymer surface without preliminary (quite harsh) chemical or physical treatment to achieve appropriate water wettability for the polymer film.

There have been done lots of studies on how to make hydrophobic surfaces more hydrophilic including oxygen plasma, ultraviolet exposure, ion-beam etching, acid/base treatments, laser ablation and chemical functionalization to make it more hydrophilic. It is necessary to point that the treatment at the relatively harsh conditions can compromise structural integrity and properties of polymer films. Also, the treatment may generate by-products (e.g. volatile hydrocarbon products as a result UV/ozone treatment) or wastes (such as strong bases/acids) which are not environmentally friendly, which complicate the scale-up of such process.
2.9: Light Absorption in Graphene

The structure of electronic bandgap plays an important role in light-matter interactions in graphene. The band gap is defined as the energy difference between the top of valence band and the bottom of the conduction band \(^{146}\). In Figure 2.12 (left) the schematic of the band structure of pristine graphene is shown \(^{147}\). As expected, ideal defect-free graphene reveals typical semi-metallic nature where the bottom of the conduction band overlaps with the top of the valence band. Points of overlap, K and K', are called Dirac points \(^{148}\). The electronic states are formed from the additional electron in the \(p_z\) orbitals of carbon atoms. Further away from Dirac points there is a saddle point singularity at the M point (van Hove singularity (VHS), \(\sim 5\) eV gap). At the \(\Gamma\)-point the conduction and valence bands are widely separated \(\sim 20\) eV gap. The absorption of a photon by graphene may give rise to direct or indirect intraband and interband electron transitions (Figure 2.12 (right)).

Figure 2.12: Electronic structure of graphene: (a) electronic dispersion of the \(\pi\)-bands in the graphene Brillouin zone showing K- and K'- points and the saddle point (van Hove singularity) at the M-point \(^{147}\). Reprinted by permission of Elsevier
An indirect transitions involve number of scattering-assisted effects by disorders (impurity or phonons)\textsuperscript{149}. For low photon energies (infrared) the intraband (free-carrier) transitions play dominant role, while for higher photon energies (ultraviolet spectral range) the optical response is primarily due to interband (excitons) transitions\textsuperscript{150} at saddle-point singularity (M).

The structure of electronic band gap is strongly influenced by the defects, degree of oxidation and size of graphene sheets \textsuperscript{151}. In 2016 Roy and coworkers \textsuperscript{152} demonstrated that the distortion of linear dispersion and opening of bandgap at K-point takes place with the addition of different types of oxygen adsorbates and perturbations (Figure 2.13). Furthermore, the results presented in Ref. \textsuperscript{153} demonstrate that $E_g$ is also sensitive to the measurement environment such as humidity and moisture.

Bhanotnagar et. al \textsuperscript{151} experimentally and theoretically investigated the optical band gap in graphene-derived nanomaterials (oxidized graphite, graphene oxide and graphene quantum dots) as a function of oxidation as well as size. They showed that the reduction in size of graphene directly influences its optical band gap and conducting behavior. The optical band gap for GO was found in the range 2.7 – 4.2 eV.
Figure 2.13: Model, calculated band structure and schematic visualization of band dispersions around Dirac K-point of (a) pure graphene (b) graphene with C=O and (c) graphene with C=O and epoxy adsorbed on the surface. Reprinted by permission of Elsevier.
2.10: References


https://tigerprints.clemson.edu/all_dissertations/1015
69. Galabura, Yuriy, "SYNTHESIS AND CHARACTERIZATION OF NANOSCALE POLYMER FILMS GRAFTED TO METAL SURFACES" (2014). All Dissertations. 1300.

https://tigerprints.clemson.edu/all_dissertations/1300

70. Thomas, H. R.; Phillips, D. J.; Wilson, N. R.; Gibson, M. I.; Rourke, J. P., One-step grafting of polymers to graphene oxide. Polymer chemistry 2015, 6 (48), 8270-8274.


CHAPTER THREE
SYNTHESIS AND CHARACTERIZATION OF POLYMER-MODIFIED GO MULTILAYERS

3.1: Introduction

This chapter is devoted to (i) the synthesis and characterization of sterically stabilized GO sheets in water, (ii) subsequent formation of GO monolayer and (iii) then bilayer GO films based on polymer-enveloped GO sheets. A general schematic of the method is depicted in Figure 3.1A-D. We employ water-soluble, surface-active and reactive copolymer poly(GMA-stat-OEGMA) [GMA: glycidyl methacrylate; OEGMA: oligo ethylene glycol methyl ether methacrylate] (P1) to generate a nanoscale coating evenly enveloping the GO sheets. This coating allows the dip-coating of the GO monolayer from water-based dispersion onto the surface of non-conductive substrates. To form the bilayered GO structure, a polymer interlayer/linker made of PAA is deposited on the GO monolayer by adsorption. Specifically, the adsorption deposition process is based on the formation of a complex between the copolymer, covering the GO sheets and the polymer linker. The linker is employed to promote the formation of the second GO monolayer (by dip-coating) and provides carbon atoms for the rGO sheets’ “healing” and “welding” during the GO reduction, which will be discussed later in Chapter 4.
3.2: Experimental

3.2.1: Preparation of Graphene Oxide Sheets

The graphene oxide (GO) aqueous suspension was prepared using the Hummers method in Dr. Tsukruk’s laboratory. Natural 300-mesh graphite powder (Alfa Aesar) was added with 2.5 g of sodium nitrate (NaNO₃) in 107 mL of 98% sulfuric acid (H₂SO₄), which was cooled to 0 °C before mixing. Then 15 g of potassium permanganate (KMnO₄) was slowly added with vigorous stirring to avoid the temperature raising above 20 °C. The mixture was heated to 35 ± 3 °C and maintained for 30 min before adding 214 mL of water; we then waited for the temperature to raise to 98 °C and maintained at this temperature for 15 min. Finally, 850 mL of warm ultrapure water and 1–2 mL of 30% hydrogen peroxide (H₂O₂) was added sequentially to dissolve the side products of the oxidation (black particulates), during which the color of the solution turned from dark brown to bright.

Figure 3.1: (A-D) Schematic representation of the method for nanomanufacturing of rGO-based films. (A): deposition of a monolayer of GO-P1 sheets enveloped with a polymer layer by dip-coating, (B): deposition of a polymer interlayer (“linker”) by adsorption, (C): deposition of the second GO layer by dip-coating, (D): final double layer system composed of GO.
yellow. The as-synthesized graphene oxide suspension was purified via water rinsing and ultracentrifugation (10000 rpm for 1 h) five times to remove the electrolytes.

3.2.2: Synthesis of P1 Copolymer

The procedure of copolymer synthesis was carried out in Dr. Luzinov’s laboratory by Dr. Nikolay Borodinov. Poly(glycidyl methacrylate-co-oligoethylene glycol methyl ether methacrylate) copolymer was synthesized by free-radical polymerization initiated by azoisobutyronitrile using glycidyl methacrylate (GMA) and oligoethylene glycol methacrylate (OEGMA, average molecular weight 950 mol/g) monomers using the general method published elsewhere ². GMA (97%), azoisobutyronitrile (AIBN), OEGMA, and inhibitor removers (beads for removing hydroquinone and monomethyl ether hydroquinone [MEHQ] and tert-butylcatechol [BHT]) were purchased from Sigma-Aldrich. All solvents used in this study were purchased from VWR International and used as received. P1 was synthesized by the solution polymerization. MEHQ inhibitor remover beads were added to the GMA prior to synthesis. MEHQ and BHT inhibitor remover beads were added to the OEGMA dissolved in methyl ethyl ketone (MEK) prior to synthesis, and the suspensions were shaken for 45 min. The monomers were then filtered using 0.2 μm syringe filters and loaded into the reaction flask with AIBN (0.01M in monomer + MEK solution). The charged OEGMA/GMA molar ratio was 80:20, and the overall monomer concentration was 0.5 M. The solution was kept under nitrogen purge for 45 min and then immersed into a water bath preheated to 50 °C. The polymerization reaction was terminated after 1.5 h by opening the flask to the ambient atmosphere and cooling. The product of the
reaction was precipitated in diethyl ether, centrifuged, and dissolved in MEK. This procedure was repeated three times to remove the unreacted monomers and initiator.

*Analysis of the copolymer composition by NMR*

Nuclear magnetic resonance (NMR) analysis with a Bruker AVANCE-300 spectrometer, TopSpin 1.3 PL4, and Delta 5.0.4 software was used to characterize the copolymer (spectra are shown in Appendix A1). The OEGMA:GMA molar ratio was estimated as 68.5:31.5 and corresponds to a 94.0:6.0 mass ratio. The copolymer composition was also investigated with Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (spectra are not shown). A Thermo Nicolet Magna 550 Fourier transform infrared (FTIR) spectrometer with the Thermo-Spectra Tech Endurance Foundation Series Diamond ATR accessory was used, and 16 scans were averaged. An ATR correction and baseline correction were performed using Thermo Scientific OMNIC software version 8.0. Data processing and plotting were completed using Origin MicroCal 6.1. The ratio of the intensities of the peaks located at 1100 cm\(^{-1}\) and 1727 cm\(^{-1}\) corresponding to ether and ester bonds, respectively, was used to estimate the composition of the P1: OEGMA:GMA= 63.8:36.2. Therefore, the OEGMA:GMA molar ratio in the copolymer is approximately 66:34, as evidenced by the comparison of the NMR and FTIR measurements. The dynamic light scattering study was used to estimate the molecular weight of the P1 to be \(M_w \approx 2858\) kg/mol. Specifically, the Malvern Zetasizer ZS Dynamic Light Scattering and Zeta Potential (DLS-Zeta) instrument was used to measure the size of the polymer coil in methyl ethyl ketone to estimate the molecular weight. A set of
monodisperse polystyrene standards with molecular weights ranging from 200 up to 3000 kDa dissolved in methyl ethyl ketone was used for calibration.

3.2.3: Modification of GO Sheets with P1 Copolymer

For the modification (Figure 3.2), an aqueous suspension of GO (~ 0.75-1.5 mg/ml) was mixed with an aqueous solution of P1 (~ 3-4 mg/ml) in a mass ratio of 1:6. During the procedure, the dispersion of P1 was added dropwise to the dispersion of sonicated GOs in 40 ml centrifugation tubes. Such order of mixing ensured that the particles would modify the GOs and prevent nanoparticle bridging between the individual GO sheets. The mixture was vigorously shaken for 15 min and then kept at room temperature on an orbital shaker for at least 4 h up to 24 hours. Next, the suspension of GO-P1 was redistributed into small 2 ml vials and subjected to centrifugation at 15000 rpm (Mini Spin Plus, Eppendorf) for 5-10 minutes. After all solids (GO-P1 sheets) were separated from the rest of the solution, the latter was pipetted out and the remaining GO-P1 particulates were again redispersed into new portion of DI water by rigorous shaking for 10 minutes. Such rinsing procedure was repeated at least 3 times to ensure complete removal of unattached/unreacted P1 chains from aqueous solution of GO-P1.

Then, the content from each 2 ml test-tube was combined into 40 ml centrifugation tubes and centrifuged at 1000 and 500 rpm (Prexision 100 Durafuge) for 15 min to remove any flocculated sheets. Afterwards, the top portion of the suspension was pipetted off until 10 ml of suspension was left. The top portion of the suspension was pipetted off until 2-5 ml of suspension was left. This procedure was repeated two more times.
3.2.4: Chemical analysis of GO and GO-P1

Fourier-transform Infrared Spectroscopy (FTIR)

The composition of GO, P1 and GO-P1 materials were also investigated by FTIR. A Thermo Nicolet 6700 FTIR spectrometer equipped with a transmission base plate and a “Continuum” microscope was used for the FTIR studies of the GO and GO-P1 materials. Si wafer (500 µm in thickness). Highly polished silicon wafers, cut to ~2 × 4 cm size, (University Wafer: P/Boron, <100>, 1–10 Ohm·cm, 500 um) were used as substrates for background and sample collection. All films for FTIR measurements were prepared via...
drop-casting method followed by at least 24-hour drying in ambient conditions. To achieve high signal-to-noise ratio we used 256 scans during background and sample collection steps. To reduce the influence of moisture and CO₂ (located around 2350 cm⁻¹) all samples were kept in nitrogen-purged chamber for 10-15 minutes prior to the beginning of scan. An FTIR correction and baseline correction were performed using Thermo Scientific OMNIC software version 8.0. Data processing and plotting were completed using Origin 2016 (version 9.3.2, Academic version).

**X-ray Photon Spectroscopy**

Further analysis of the chemical composition and the chemical states of the GO, GO-P1, and rGO-P1 films were conducted with a Thermal Scientific K-alpha X-ray Photon Spectroscope (XPS) using an aluminum K-alpha radiation X-ray source (1486.7 eV). The survey scans were done by integrating the two scans between the binding energy of -10 and 1350 eV at a 1.0 eV step size and a 50 ms dwell time for each step. The high-resolution elemental spectra were collected by integrating four scans of the corresponding binding energy ranges at a 0.1 eV step size and a 50 ms dwell time. All XPS data were fit using XPSPeak 4.1 software. The background was considered to be Tougaard type, and each component peak shape was considered to be a mixture of Lorentzian and Gaussian (L/G ~ 0.3). All XPS measurements were taken by Drs. Ruilong Ma and Kesong Hu under the supervision of Prof. V. Tsukruk at Georgia Institute of Technology. Highly polished, single-crystal, undoped non-conductive silicon wafers, cut to ~1.5 × 3 cm size, (University Wafer: <100>, 10000–20000 Ohm·cm, 500 um) were used as substrates.
3.2.5: Analysis of Thermal Properties of GO and GO-P1

Thermal stability of GO-P1

To study the thermal decomposition of P1, PAA and the GO before and after the modification with P1, thermogravimetric analysis (TGA) was performed using a Q-5000 TA Instruments and AutoTGA 2950HR V5.4A under nitrogen gas from room temperature to 700 °C using a ramp rate of 15 °C min⁻¹.

Differential scanning calorimetry (DSC) (Model 2920; TA Instruments) was carried out at a heating/cooling rate of 20 °C/min. The temperature range of the experiment was set from -100 °C to 100 °C. At least 1 mg of substance was used in each DSC and TGA experiment.

Kinetics of copolymer adsorption

To study the adsorption kinetics we mixed a 3 mg ml⁻¹ concentrated water solution of adsorbent (GO) with a 5 mg ml⁻¹ P1 in water in ratio 1:6. Such system was held at constant room temperature. Then we gently evacuated small amount of the suspension after 20 minutes, 1, 2.5, 4.5 hours of adsorption and rinsed it well with DI water at least 3 times. Next, we did TGA for each time point using conditions specified above.

3.2.6: Procedure for the Calculation of Polymer Thickness from TGA Data

TGA data can be used to calculate the thickness/amount of polymer bound to the surface of the particulates. The thickness of polymer bound to the surface of the particulates is directly proportional to the amount of weight loss in the TGA experiment and depends on the surface area of the particulates. It was assumed that the polymer is
uniformly distributed across the surface of the GO particulates. Equation 3.1 was used to calculate the thickness (t) of the polymer attached to the planar GO nanoparticulates. This equation is derived from geometrical considerations:

\[ h_p = h_{GO} \cdot \frac{m_p \rho_{GO}}{m_{GO} \rho_p} \]  

(3.1)

where \( h_{GO} \) is the thickness of the pristine GO (whisker or nanoparticle), \( \rho_{GO} \) and \( \rho_p \) are the densities of the bulk GO and polymer, \( m_p \) and \( m_{GO} \) are the weight fractions for the polymer and nanoparticulates as indicated by TGA, respectively.

3.2.7: Formation of GO-P1 Monolayer

Preparation of SiO₂/Si substrates

Highly polished, single-crystal, undoped non-conductive silicon wafers, cut to \( \sim 2 \times 4 \) cm size, (University Wafer: <100>, 10000–20000 Ohm·cm, 500 µm) were used as substrates. Before deposition of the GO-P1 monolayer the wafers were first cut using diamond cutter and cleaned in an ultrasonic bath for 30 min, placed in a hot “piranha” solution (3:1 concentrated sulfuric acid 30% hydrogen peroxide) for 1 h, and then rinsed several times with high-purity DI water (18MΩ·cm, Nanopure). After being rinsed, the substrates were dried under a stream of ultra-high purity nitrogen (purchased from Airgas).

GO-P deposition via adsorption

In order to study the possibility of GO-P1 monolayer formation via adsorption deposition clean wafer of SiO₂/Si was placed into a 40 ml test-tube with 0.025 wt. % water solution of GO-P1 and left there for 12 and 24 hours (Figure 3.3A). During that time the solution was subject to gentle shaking. Next, the sample was taken out from the test-tube
and placed in DI water for 1 hour. Water in the test-tube was replaced at least three times. After being rinsed, the sample was dried under a stream of ultra-high purity nitrogen and then scanned with AFM. The same procedure was repeated for reference wafer in pristine GO solution. From Figure 3.3 (B and C) we can see that no layers were formed by adsorption for both pristine GO (B) and GO-P1 (C).

**Figure 3.3:** (A): Schematic representation of GO adsorption on bare SiO$_2$/Si. (B): Adsorption of pristine GO. (C): Adsorption of GO-P1.

**GO-1P deposition via dip-coating**

The GO-P1 monolayer was deposited on clean SiO$_2$/Si substrate by dip-coating (Figures 3.1A) from 0.025 wt. % GO-P1 suspension at a 300 mm/min withdrawal speed (Mayer Feintechnik dip coater, model D-3400).

**3.2.8: Formation of GO-P1 Multilayer**

*Adsorption deposition of polymer linker layer on GO-P1 monolayer*
Two SiO$_2$/Si samples (labeled as #1 and #2) with the deposited GO-P1 monolayers were immersed in a 2 wt. % solution of polyacrylic acid (PAA) with a pH of 2.5–2.8 (35 wt. % water solution obtained from Sigma-Aldrich, Mw = 100 kDa) and kept there for 20 min. To remove unattached PAA from the surface, samples were rinsed at least three times each with different solvent for 15 minutes: sample #1 was rinsed with methanol and sample #2 - with DI water. After the rinsing procedure samples were dried in ambient conditions. It was revealed by AFM imaging that methanol is a better candidate for rinsing purposes as water completely removed adsorbed PAA layer from sample #2 (Figure 3.4B). Therefore, in all our next experiments we only used methanol as a solvent to rinse PAA layers.

*Deposition of second GO-P1 monolayer*

A second layer of GO-P1 was deposited over the first one modified with PAA by dip-coating using at least 300 mm/min withdrawal speed (Figure 3.1C and D). To emphasize on the importance of PAA as a linker layer dip-coating was performed on both samples #1 (Figure 3.16) and #2 (Figure 3.4). In contrast to sample #1 sample #2 showed no bilayer presence after second GO-P1 deposition (Figure 3.4).

**Figure 3.4: Sample #2.** AFM images showing (A): dip-coated GO-P1 monolayer with adsorbed PAA and (B): the same spot of GO-P1/PAA monolayer after being rinsed with Methanol and second dip-coating in GO solution (vertical scale: 20 nm for 30x30 μm$^2$).
3.2.9: Surface Morphology of GO-P1 Films

*Morphological studies*

Morphology, microstructure and changes in thickness of individual GO sheet after modification with the polymers were studied with a Dimension 3100 (Veeco Digital Instruments, Inc.) in the tapping mode. Silicon tips with a spring constant of 50 N m⁻¹ were used for all scans at 1 Hz. Analysis of AFM images was carried out using Gwyddion version 2.45 with the assistance of Dr. Ruslan Burtovyy.

*Optical and Scanning Electron Microscopy*

Scanning electron microscope (SEM) (Hitachi S-4800, acceleration voltage of 0.5 - 1 kV) and optical microscope (HUVITZ HRM-300) were used as means to further investigate morphology and microstructure of GO-P1 layers on silicon substrate.
3.3: Results and Discussion

3.3.1: Modification of GO Sheets with P1 Copolymer

The statistical copolymer (P1) used for the GO modification consists of two different methacrylic monomeric units (reactive via epoxy group and hydrophobic glycidyl methacrylate [GMA] and the polar oligoethylene glycol methyl ether methacrylate [OE] responsible for solubility of the P1 in water). We hypothesized, that during the modification of GO with P1, GMA epoxy groups react with (hydroxyl, carboxyl, and epoxy) GO functional groups via non-condensation reactions (Figure 3.5)\(^5\).-\(^6\).

The presence of multiple reactive groups along the polymer chain is needed to ensure that every macromolecule will form multiple connections with GO surface to form the thin polymer coating enveloping the sheets. It is necessary to highlight that the suspension of the GO sheets modified with P1 is stable for a long time. In fact, we used the same suspension for the formation of GO layers for up to 6 months. This observation

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Figure 3.5: Reactions of GMA epoxy groups with functional groups of GO.
indicates that the copolymer chains anchored to the GO surface provide an effective steric stabilization of the colloidal suspension.

Chemical, structural and morphological properties of the GO-P1 particulates were comprehensively investigated by means of various characterization techniques: AFM, FTIR, XPS, DSC, TGA and Raman.

3.3.2: Chemical Analysis of GO-P1

The attachment of P1 on pristine GO surfaces was attested by Fourier transform infrared spectroscopy (FTIR). Figure 3.6 illustrates the FTIR spectra of Pristine GO, P1, and GO-P1 respectively. The results of FTIR spectra were analyzed using readily available spectral databases for organic compounds. The broad peak at 3400 cm\(^{-1}\) is from O-H groups, and two narrow peaks assigned to the carbonyl group (C=O stretching) and the skeletal vibration of unoxidized graphitic domains on GO sheets (aromatic C=C) can be observed at 1740 and 1620 cm\(^{-1}\) (Figure 3.6a). The range of 1000-1280 cm\(^{-1}\) corresponds to ethers and/or epoxide groups. For P1 (Figure 3.6b), the C-H stretching group is represented by the peak at 2870 cm\(^{-1}\).
The absorbance peaks at 1732, 1250, 1111 cm\(^{-1}\) can be attributed to carbonyl (C=O), epoxy (C-O-C) and ether (C-O) stretching vibrations. In the spectrum of GO-P (Figure 3.6c) the absorption bands detected at 2873, 1732 and 1250 cm\(^{-1}\) are the characteristic of the C-H, C=O and C-O-C groups of the grafted P1, respectively.\(^8\) As evidenced from the spectra of P1 the intensities of epoxy at 1138 cm\(^{-1}\) decreased (relatively to CH peak) after modification of GO with P1, which implies possible chemical reaction between two compounds (consumption of epoxy via esterification reactions).

In order to further study the chemical composition of GO films and find C/O ratio of GO before and after modification we used XPS. Curve fitting of C\(_{1s}\) XPS spectra of each sample was performed using the Gaussian-Lorentzian distribution. It is reported elsewhere \(^9\)-\(^{13}\) that the values of chemical shifts are normally assigned at 284.5-285.0 eV for C-C/C=C and the rest of the peaks reveal the following chemical shift from the latter one: +1.3 - +1.7

Figure 3.6: FTIR spectra for: (a) pristine GO, (b) P1, and (c) GO-P1.
eV for C-OH, +2.5 - +3.0 eV for C=O/C-O-C and +4.0 - +4.5 eV for COOH. Since our films are less than 10 nm in thickness, we could not reliably define C/O ratio from the survey spectrum due to the presence of SiO$_2$ layer on silicon wafer which significantly contributes to $O_{1s}$ peak. Therefore, the C/O ratio was estimated by Equation 3.2 based on the deconvoluted C$_{1s}$ peak:

$$\frac{C}{O} = \frac{A_{C_{1s}}}{(0.57 \times A_{C-OH} + 0.5 \times 0.57 \times A_{C=O/C-O-C} + 0.5 \times 0.4 \times A_{C=O/C-O-C} + 0.72 \times A_{COOH})}$$

(3.2)

where $A_{C-OH}$, $A_{C=O/C-O-C}$, and $A_{COOH}$ correspond to the area of each peak in the C$_{1s}$ spectrum and $A_{C_{1s}}$ is total peak area.

![Figure 3.7: High resolution C1s spectra of (A) pristine GO and (B) GO-P1 monolayer.](image)

The atomic % for different O related functional groups is calculated with respect to the total area of the C$_{1s}$ spectrum as a sum of the areas of each component weighted by the corresponding stoichiometric ratio. As seen from the Figure 3.7A C=O/C-OC at 287.5 eV
(epoxy) peak is of comparable intensity to C=C at 284.5 eV. In contrast, P1-modified GO showed significant decrease in epoxy peak relatively to C=C at the expense of C-OH increase at 286 eV as shown in Figure 3.7B. These results align well with the FTIR results, suggesting effective grafting of P1 polymer chains to GO sheets mediated by chemical reactions of epoxy functional groups shown in Figure 3.5.

**3.3.3: Thermal Properties of GO-P1**

Next, thermogravimetric analysis (TGA) and dynamic scanning calorimetry (DSC) were used to further investigate the process of GO modification with P1 copolymers: (i) to study the thermal stability of pristine GO, P1 and GO-P1 (ii) to study the kinetics of copolymer adsorption and (iii) to find out the weight ratio between copolymer and GO material after adsorption process is completed.

*Thermal stability of GO-P1*

To study the thermal stability of pristine GO, P1, GO-P1 and PAA the samples were heated to 700 °C at a rate of 15 °C/min in a nitrogen atmosphere. From Figure 3.10, it can be observed that pristine GO is not thermostable: mass loss of GO started below 100 °C, which is attributed to the volatilization of stored water in its π-stacked structure 14. The main weight loss of GO around 200 °C is caused by the decomposition of labile oxygen-containing functional groups yielding CO, CO₂ and H₂O steam 15. The overall weight loss of pristine GO is 44%. The curve of P1 shows a fast weight reduction at 415 °C. The reduction is caused by the decomposition of P1 polymer, leaving about 6% of carbon. As for GO-P1, about 70% weight fraction loss is observed from 200 to 500 °C, which is due
to the decomposition of P1 and some oxygen functional groups of GO sheets. The peak analysis was done by taking first derivative of the GO-P1 curve with respect to temperature, then subsequent fit deconvolution and was done using Pseudo Voigt I function in Origin 9.0 (2016). From this, the ratio of the GO to polymer can be found. Based on TGA curves we found that P1 constituted about 50% of total mass of GO-P1 being decomposed. Taking the bulk density of GO as 1800 kg/m\textsuperscript{3} \textsuperscript{1617} and assuming the density of P1 to be close to that of PEG 1200 kg/m\textsuperscript{3} \textsuperscript{18}, and knowing that 56% of total mass of P1 corresponds to polymer, total thickness of P1 was estimated – 1.78 nm according to Equation 3.1 (~0.9 nm of polymer on each side of GO). Also, TGA curve for PAA showed that approximately 15 % of carbon is left after PAA decomposition.

**Figure 3.8:** Thermogravimetric analysis of pristine GO, P1, GO-P1 and poly acrylic acid (PAA).
Kinetics of copolymer adsorption

TGA curves for GO-P1 and the resulting kinetic isotherm for P1 adsorption onto GO surface are presented in Figure 3.9. We found that adsorption equilibrium was reached within about 20 minutes and the grafted copolymer weight content was equal to 53%. It suggests that grafting process is very fast at initial stage and is similar to the observed grafting from melt 4.

In order to further analyze the adsorption process we used appropriate kinetic models. According to the literature, two kinetic models, namely the pseudo-first order (PFO) and pseudo-second-order (PSO) equations, are commonly used to describe adsorption process under non-equilibrium conditions 19-20. In this study, the non-linear form of PFO was used to fit the experimental kinetic data for the adsorption of P1 copolymer to the surface of GO in water. The PFO (3.3) and PSO (3.4) kinetic equations for adsorption analysis can be expressed as follows:

\[
A_t = A_\infty \left(1 - e^{-k_1 t}\right) \quad (3.3)
\]

\[
A_t = \frac{k_2 A_\infty^2 t}{1 + k_2 A_\infty t} \quad (3.4)
\]

where \(k_1\) and \(k_2\) are the rate constants of corresponding models, \(A_t\) is the amount of solute (P1) adsorbed on the adsorbent (GO) at time \(t\), and \(A_\infty\) is the amount at equilibrium. In this study, we used the \(R^2\) values to determine the relationship between the experimental data and the kinetic models 19. The kinetic parameters obtained from the non-linear fittings by Equation 3.3 and 3.4 are shown in Figure 3.11A. The value of \((R^2)\) show that the PSO
model was better than the PFO model in the simulation of kinetics of P1 adsorption on pristine GO in water. Therefore, the adsorption process of P1 on GOs was probably controlled by the chemical adsorption process as suggested in ref. 21-22. The above conclusion may prove the hypothesis (see Section 3.3.1) that P1 chains get chemically attached to GO sheets via covalent interactions between GMA epoxy groups and (hydroxyl, carboxyl, and epoxy) GO functional groups. The software, Origin 9.0 (2016), was used to fit the experimental data.

**Figure 3.9:** (A) TGA thermograms of GO grafted with P1 as a function of grafting time; (B) Grafted amount of copolymer to GO from water as a function of time.

**DSC studies of the interaction between the GO and P1**

*Figure 3.10* shows the DSC curves of GOs before and after P1 introduction to the GOs. The obtained results clearly demonstrate the following: (1) the melting point depression of P1 from \( \sim 34.5 \, ^\circ C \) to 29.3 \( ^\circ C \) and (2) a notable suppression in the intensity of endothermic peak associated with melting.
According to previous research results \(23-24\) it is the interaction between the GO surface and stabilizing polymer that decides the shift direction of the melting point. The observed 5 °C decrease in the melting point of primary peak is due to the significant interaction between the GO sheets and P1 chains. By contrast, an increased phase change temperature will occur when the interaction between polymer chains becomes highly attractive which is through hydrogen bonding between side OEGMA units in free P1 chains.

![DSC thermograms for P1 and GO-P1.](image)

**Figure 3.10:** DSC thermograms for P1 and GO-P1.

Next, a notable suppression in endothermic peak indicates that most OEGMA segments are amorphous, which in turn suggests that most of mobility of the OEGMA side segments is restricted by the surface anchoring.

### 3.3.4: Colloidal Stability of GO-P1

*Influence of molecular weight of P1 on colloidal stability of GO*
It is expected that when P1 polymer is adsorbed on GO surface there will be a repulsive steric entropic force generated with a range determined by the radius of gyration of the polymer ($R_g$)\(^{25}\). However, at distances less than $R_g$ attractive dispersion forces start to dominate resulting in GO flocculation and bridging. Thus, it was hypothesized that aggregation/flocculation of GO increases with the decrease in P1/GO ratio (by count) which negatively impacts the quality of a monolayer after deposition. **Figure 3.11** presents AFM images of GO modified with P1 of different molecular weight: $M_w1 = 500$ kDa and $M_w2 = 2000$ kDa. Mixing of P1\(_{500 \text{ kDa}}\) (0.5 wt\%) and GO (0.15 wt\%) at mass ratio of 1:1 resulted in dense and uniform GO-P1 monolayer formed after dipcoating. On the other hand, when P1\(_{2 \text{ MDa}}\) (0.5 wt\%) was mixed with GO (0.15 wt\%) flocculates or aggregates GO-P1 were present on top of GO-P1 layer, as shown in **Figure 3.11C**. This aggregation of GO sheets is ascribed to the bridging effect\(^{26-27}\). Specifically, larger $R_g$ of P1\(_{M_w = 2 \text{ MDa}}\) enhances attractive dispersion forces, causing polymer-bridging induced aggregation of GO sheets (polymer chains are long enough to adsorb onto more than one GO particle\(^{28}\)). Therefore, shorter polymer chains of P1\(_{M_w = 500\text{kDa}}\) are better choice for obtaining uniform and well-defined GO-P1 monolayer.

![Mixing mass ratio 1:1](A) + 

GO (0.15%) : P1 (0.5%)

![AFM images](B)  
$\text{M}_w = 500 \text{ kDa}$  
$30x30 \mu\text{m}^2$

![AFM images](C)  
$\text{M}_w = 2000 \text{ kDa}$  
$30x30 \mu\text{m}^2$
Colloidal stability of GO as a function of mixing ratio between P1 and GO

To investigate what concentrations of GO and P1 (M_w = 2 MDa) would be the most efficient to form stable GO-P1 suspension, as this is predicted to play a large role in a deposition of good quality monolayer on a targeted substrate, we prepared 4 water solutions of GO and P1 at different mixing mass ratios (m_{GO}/m_{P1}): 1:1, 1:3, 1:6, 1:12.

**Figure 3.11**: (A): Schematic representation of pristine GO and P1 copolymer in water before mixing. (B) and (C): representative AFM images of GO-P1(500 kDa) and GO-P1 (2 MDa).

AFM images, shown in **Figure 3.12**, clearly demonstrate that the quality of a monolayer becomes better with lesser bridging effect as the concentration of P1 increases.

**Figure 3.12**: AFM images of GO sheets modified with P1 (M_w = 2 MDa) at different mixing mass ratios of GO and polymer P1. m_{GO}/m_{P1}: 1:1, 1:3, 1:6, 1:12.

AFM images, shown in **Figure 3.12**, clearly demonstrate that the quality of a monolayer becomes better with lesser bridging effect as the concentration of P1 increases.

In summary, our results confirm literature findings that very long polymer (P1_{M_w} = 2 MDa) chains and their low concentrations contribute to bridging flocculation. Therefore, the mixing ratio used in all our next experiments was at least 1:6.
3.3.5: Formation of GO-P1 Monolayer

Thickness of adsorbed copolymer layer

To determine the thickness of the individual GO sheets modified with P1, we used atomic AFM. As indicated by the cross-sectional analysis (Figure 3.13A), the thickness of the pristine GO sheet was on the level of 1 nm, which is comparable to the value typically reported for the GO sheets obtained via Hummers method $^{30-32}$.

**Figure 3.13:** AFM images and corresponding cross-sectional profiles showing (A): a pristine GO layer obtained by dip-coating (vertical scale: 10 and 5 nm for 30x30 $\mu$m$^2$ and 10x10$\mu$m$^2$ images, respectively) and (B): GO-P1 monolayer obtained by dip-coating (vertical scale: 10 and 5 nm for 30x30 $\mu$m$^2$ and 10x10$\mu$m$^2$ images, respectively).
However, the thickness increased more than twofold to ~2.5 nm (Figure 3.13B) upon the GO modification with copolymer. This implies that the P1 monolayer was indeed anchored to the GO surface. Also, the height profile of GO-P1 sheets (Figure 3.13B) suggested that the P1 chains formed even and dense coating encapsulating the sheets. The above result is in good agreement with TGA-found total thickness of ≈2 nm as reported in Section 3.3.3.

3.3.6: Morphology of GO-P1 Monolayer

In our initial experiments with pristine (unmodified with P1) GO sheets, we found that it was impossible to obtain a GO dense monolayer via dip-coating. We obtained either scarce coverage (40-50%) in the first layer or random multilayered/aggregated deposition with local wrinkles when concentration of the GO suspension was increased (Figure 3.13A). On the contrary, the GO-P1 sheets formed a dense monolayer (surface coverage more than 90%) as a result of the dip-coating at a quite high (300 mm/min) withdrawing speed (Figure 3.13B). The virtual absence of the second layer was observed by AFM as well. It is evident that the P1 coating sterically stabilized the GO sheets and prevented the interaction between the sheets during the deposition. At the same time, the P1 layer offered strong adhesion to the silicon oxide surface and the modified GO due to reaction between epoxy functional groups of GMA and silanol groups present on the surface of silicon wafer.33 In fact, a dried GO-P1 monolayer does not delaminate from the surface in water even after an intensive one-hour ultra-sonication treatment (Figure 3.14).
Since GO reveals size-dependent amphiphilicity we used flakes with large (~1600 µm²), medium (~100 µm²), and small (~9 µm²) average areas to investigate how the quality of monolayer coverage is affected by the lateral sheet size. We concluded that the quality of deposited monolayers on hydrophilic silicon substrate does not depend on the initial size of pristine GO flakes, which was manifested through the AFM measurements shown in Figure 3.15(A, B, C).

**Figure 3.14:** Stability of GO-P1 monolayers. AFM images of GO-P1 monolayer on Si wafer before (A) and after 1hour ultra-sonication in water (B). Vertical scale 10 nm.

**Figure 3.15:** Hydrophilic Si wafer. (A-C) modified GO-P1 of different average sheet sizes (~ 40 µm, ~ 10 µm, ~ 3 µm). Height scale (0-10 nm) for all images.
3.3.7: Formation of GO-P1 Multilayers

We have hypothesized that high level of conductivity will be associated with a decrease in the inter-sheet resistance via the addition of a second GO-P1 monolayer above the first one. We had foreseen that the bi-layered structure, where sheets from the top layer are placed over the sheet-to-sheet contact of the bottom layer, will decrease layer resistivity. In addition, we used a polymer linker between the sheets, PAA, which during thermal reduction can serve as a carbon source for the defect “healing” and “welding” of the sheets. In fact, TGA measurements showed that during heating in an inert atmosphere, PAA material produced a significant amount of carbon, 15% by the polymer weight, which is significantly larger than the 5% produced during P1 decomposition (Figure 3.8). Therefore, external supply of carbon can saturate carbon vacancies forming as a result of CO/CO₂ dissociation during the thermal treatment.

The PAA linker layer was adsorbed on the dip-coated GO-P1 monolayer (Figure 3.1B and Figure 3.16A-B) using the approach previously employed for the L-b-L deposition of hydrogen-bonded multilayers. Namely, we utilized the complex formation between polyethylene glycol side chains of P1 and PAA at pH values below 3. AFM imaging confirmed the successful deposition of the PAA layer, as indicated by changes in morphology as well as increase in the roughness and thickness of the individual GO-P1 sheets (Figure 3.16D-E). The result of the AFM cross-section measurements indicated that a PAA layer of about 2.5–3 nm was anchored to the GO-P1 sheets. The employment of PAA did not require any additional modification of the GO-P1 material, and the same suspension of GO-P1 in water was used for the formation of the
second GO-P1 monolayer. The second GO-P1 layer was readily deposited over the first one modified with PAA by dip-coating using the same experimental parameters as for the

**Figure 3.16**: AFM topography images of a GO-P1 monolayer (A) (vertical scale: 12 nm), GO-P1 with adsorbed PAA layer on top (B) (vertical scale: 12 nm) and GO-P1 bi-layer (C, G) (vertical scale: 20 and 12 nm for 30x30 µm² and 5x5 µm² images, respectively) and corresponding cross-sectional profiles (D-F). SEM (H) and optical (I) images of GO-P1 bi-layer film. All films were deposited on undoped SiO₂/Si substrate. From the image (G) we can clearly see two overlapping layers of GO-P1 (second top layer) and GO-P1/PAA (first bottom layer).
first layer’s deposition (Figure 3.16C, F). The virtually uniform double-layer structure with total thickness of ~10 nm was fabricated this way (Figure 3.13AC, F-I). It should be noted that the second GO-P1 layer “heals” the empty areas not covered by the first layer joining individual GO-P1 sheets and forming a monolithic coherent bi-layer structure. It is very important that the surface was found to be virtually free of the extra third-layer presence. We found that without the PAA layer a complete second GO-P1 layer could not be obtained via dip-coating. We associate this phenomenon with steric repulsion (caused by P1 chains) between the GO-P1 sheets already deposited on the surface and the sheets being deposited later.

### 3.4: Conclusions

The following conclusions can be derived as a result of our study reported in Chapter 3:

- Using XPS, TGA and DSC it was confirmed that P1 copolymer can be readily grafted to GO surface through the non-condensation reactions of epoxy functional groups with (hydroxyl, carboxy, and epoxy) functional groups located on the GO surface.
- Steric stabilization of individual GO sheets was achieved through its surface modification with P1 copolymer.
- High molecular weight polymer P1 (M_w = 2MDa) can be used for steric stabilization of GO only at high enough concentrations to avoid polymer-bridging effect.
• Straightforward and technology-friendly dip-coating method allows obtaining uniform monolayers of different-sized GO on the level of 10 cm².

• The method allowed to control the thickness GO-P1 film with single-layer precision.

• GO-P1 monolayer showed strong adhesion to the SiO₂/Si substrate.

• The presence of PAA was necessary to achieve 2nd complete monolayer to form uniform GO-P1 bilayer.
3.5: References


https://tigerprints.clemson.edu/all_dissertations/1948


9. Yumitori, S., Correlation of Cls chemical state intensities with the O1s intensity in the XPS analysis of anodically oxidized glass-like carbon samples. Journal of Materials Science 2000, 35 (1), 139-146.


graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-


CHAPTER FOUR
CHARACTERIZATION OF THERMALLY REDUCED GO FILMS

4.1: Introduction

As discussed in the previous chapter, the GOs can be encapsulated in a nanometer-thick copolymer layer allowing for the nearly perfect formation of the GO layers via dip coating from water on hydrophilic SiO₂/Si substrate. In this chapter, the results on the study of opto-electrical properties of thermally reduced GO-P1 monolayers and bi-layers are presented. Specifically, this chapter focuses on the relationship between the morphology, chemical composition and electrical conductivity of GO-P1 nanoscale films. Additionally, mechanism of electrical conductivity, charge carrier properties and electronic band gap in rGO-P1 bilayer films were investigated using Hall mobility and thermoelectric methods.

4.2: Experimental

4.2.1: Thermal Reduction

*Thermal reduction*

The reduction of GO films on silicon substrates was done in a quartz tube using Across International STF1200 furnace, as schematically shown in Figure 4.1.

![Figure 4.1: Schematic representation of the thermal reduction process.](image-url)
The heating program used involved blowing the oven chamber with ultra-high purity argon (Ar) or nitrogen (N) gas for 10 minutes, heating from room temperature to 1000 °C within 115 min (10°C/min), maintaining that temperature for 60 min, and then cooling to room temperature within 360 min.

**GO-P films on quartz substrate**

At first, we were not able to obtain stable rGO-P1 films on quartz thus to determine optical transparency of our reduced films due to significant crumpling effect and disintegration of GO-P1 sheets after thermal treatment (Figure 4.2A-B) at 10°C/min heating rate.
According to Ref. 1 the heating/cooling rate plays an important role in the structure of the thermally treated graphene oxide films. Especially when treated at higher heating rate (10°C/min) GO-P1 was decomposed into very light soot containing lots of pores of various sizes 1. Therefore, when we reduced heating/cooling rate down to 3°C/min rGO-P1/PAA/rGO-P1 films maintained their integrity with ≈ 95% transparency at 550 nm (Figure 4.2C). Such behavior of rGO-P1 bilayer films can be due to the opposite thermal deformation of GO-P1 and quartz as quartz is known to have very low positive coefficient of expansion while for graphene and graphene oxide it is reported as highly negative 2-4. Therefore, in all our next thermal reduction experiments we used below 3°C/min heating/cooling rate for films deposited on a quartz substrate.

**4.2.2: Materials Characterization**

Optical microscopy was performed using an Olympus LEXT OLS 4000 confocal laser microscope. Scanning electron microscopy (SEM) was performed using Hitachi S-4800 with accelerating voltages of ~0.5 - 1.0kV.

Raman spectra were recorded directly from the samples (quartz and/or undoped Si were used as substrates) using a spectrograph (SPEX, Triplemate 1377) interfaced to a thermoelectrically cooled CCD detector (Andor Technology, Model DU420A-BV) operating at -60 °C. The spectra were excited with 514.5 nm radiation from an Innova 100 (Coherent) argon ion laser. The diameter of 514.5 nm laser beam in our Raman experiment was ~1 mm. Thus, the area it covers is quite large ~3.1 mm² (for circular cross-section of
laser spot). Such spot size is more than enough to ensure that we probe material as a whole: the average area of single GO sheet is $\sim 3.1 \times 10^{-4}$ mm$^2$. At 80% of coverage the number of sheets that are probed within the laser spot is equivalent to: $N = 0.8 \times \frac{3.1}{3.1 \times 10^{-4}} = 8000$.

The laser power was between 0.1–0.5 W at the sample with a total acquisition time of 100 s for each measurement. The scattered light was collected in a backscattering geometry, and the instrument was calibrated using a cyclohexane/toluene, indene or chloroform/bromoform standard depending on the desired spectral region. Raman data and spectra were processed using Origin 2016 and freeware Spekwin32 version 1.7. Raman spectra acquisition was conducted by Drs. Daniel Willett and Emay Wen under the guidance of Prof. G. Chumanov.

To measure the conductivity of the rGO-P1 films, we placed a mask with rectangular cutouts made from aluminum foil and Kapton tape on the wafers and sputtered 100-nm thick gold contacts through physical vapor deposition (PVD). Current-voltage (I-V) curves were produced using an HP 4156B Precision Semiconductor Parameter Analyzer and The Micromanipulator Co., Inc. (VLSI Reliability LAB) probe station. One probe was set to provide a sweep of voltages from -4V to +4 volts in 0.1V increments and the other probe as an ammeter to monitor the current. The slope of the I-V curves correlated to $R^{-1}$, which was used in the same manner as with the multi-meter measurements through the equation $\rho = R \frac{h d}{L}$ (where $R$ - resistance, $\rho$ - resistivity, $L$ - length between contact points, $h$ - the thickness of the graphene layer(s), and $d$- the average width of the two contact points). The sheet resistance was measured by the two-point probe technique. The average thickness $h$ of the films found from the AFM was used in converting the resistance into
conductivity. We used $\sigma = 1/\rho$ to convert the resistance measurements obtained to the values of conductivity. An optical microscope at low magnification was used to precisely measure the lengths between the contacts and the width of contacts. All current-voltage measurements were carried out by Daniel Cutshall in Dr. W. Harrell laboratory at Clemson University. I-V data were processed and analyzed using Origin 2016.

Carrier mobility was measured using Van der Pauw Ecopia HMS-3000 Hall measurement system. A square shaped masked (~7.5 × 7.5 mm²) was used to form a metal electrodes on top of rGO-P1 film deposited on undoped SiO₂/Si (2 nm oxide layer) substrate to get Van Der Pauw configuration. Ti/Ni (30/150 nm) metal stack were deposited as the electrodes using E-beam evaporator with shadow mask (Figure 4.3). Then, prepared Hall sample was mounted on a PCB holder, four electrodes were connected through gold coated needles to the Hall Effect measurement system. A HMS 3000 (Ecopia) system was used, in which a 0.55 T magnet was utilized to apply magnetic field perpendicular to the sample surface. The Hall effect is the production of a voltage difference, namely, the Hall voltage (VH), across a conductor in a direction transverse to the current flux (I) in the conductor in the presence of a magnetic field (B) that is perpendicular to the current. In the Hall Effect measurement, we get the conductivity ($\sigma$) and Hall coefficient ($R_{H} = V_{H}/I_{x}B_{z}$, where $t$ – is the thickness of the sample) from the measurement then extract Hall mobility ($\mu_{Hall}$) and Hall carrier concentration ($n_{Hall}$) from $\mu_{Hall} = \sigma R_{H}$ and $n_{Hall} = q^{-1}R_{H}^{-1}$. Since our SiO₂ layer is quite thin, we also performed Hall mobility tests on thermally treated bare SiO₂/Si and we didn’t see any detectable response, which means Si substrate should not contribute to the measured values of mobilities. PVD
and Hall mobility measurements have been conducted by Hongmei Li in Dr. G. Koley’s laboratory at Clemson University.

![Image](image.png)

**Figure 4.3:** rGO-P1 bilayer film on deposited on SiO$_2$/Si substrate with 4 Ni/Ti contacts for Hall mobility measurements.

The transparency of the reduced double-layer film was measured using UV/vis spectroscopy (Shimadzu UV3600). We used 1/8-inch-thick quartz polished plates purchased from Quartz Scientific Inc as substrate. We used a diamond cutter to achieve the desired size of the plate: 1 cm by 3 cm slides. All quartz substrates were initially cleaned with the piranha solution according to the same procedure as that for Si wafers. The spectra of original cleaned plate were used as baseline in our measurements. We used the following expression (conductivity ratio) to evaluate opto-electrical performance of rGO-P films

$$\frac{\sigma_{DC}}{\sigma_{OP}} = \frac{Z_0}{2R_s \left( T^{-\frac{1}{2}} - 1 \right)}$$

(4.1)

where $\sigma_{DC}$ is DC conductivity, $\sigma_{OP}$ is optical conductivity, and $Z_0 = 377 \, \Omega$ is the impedance of free space. One can expect high opto-electrical properties (high transmittance and low sheet resistance) of rGO-P1 layers if high $\sigma_{DC}/\sigma_{OP}$ is achieved.

**4.2.3: Electronic Band Gap of rGO-P1 Bilayer Film**
The band gap is most often determined by measuring the resistance of semiconductor as a function of temperature\(^{10}\). The dependency of the resistance \((R)\) upon temperature \((T)\) for semiconductors is defined by the following expression\(^{11}\):

\[
R = R_0 e^{\frac{\Delta E}{2kT}}
\]  

(4.2)

where, \(T\) is the absolute temperature in \(K\), \(\Delta E\) is the energy difference between the valence and conducting bands (band gap), \(k\) is Boltzman’s constant and \(R_0\) is a constant which corresponds to the resistance at \(T \rightarrow \infty\). After applying logarithm to both sides of the equation (4.2) we obtain the following expression:

\[
Ln(R) = Ln(R_0) + \frac{\Delta E}{2kT}
\]

(4.3)

Next, the Equation 4.3 was plotted on a semi-log plot as \(Ln(R)\) versus \((1/2kT)\). Then, the band gap \((\Delta E)\) will correspond to the linear portion of the curve.

GO-P1 bi-layers (see Chapter 3) were prepared onto piranha-cleaned quartz substrate (3 cm \(\times\) 1 cm) by dip-coating and then subject to thermal reduction at 1000-1150 °C in Argon or Nitrogen atmosphere. Next, silver paste was used to prepare two contacts (Figure 4.4A). The experimental setup\(^{12}\) used for measurement is illustrated schematically in Figure 4.4B. One part of the diagram includes an electrical furnace (R4) and thermostat used to heat rGO-P1 sample (R3), an ammeter (AM1) used to measure current which passes through R3 thermistor, voltmeter (VM1) to measure voltage drop across R3 and base-emitter (p-n) junction of transistor (VT1). The other part of the schematics represents current regulator, which consists of Zener diode (VD), transistor (VT) and two resistors
(R2, R3). The purpose of a current regulator is to provide a constant current regardless of changes in the input voltage or load current. Therefore, with the regulated current output \( I \) and measured voltage drop \( V \) on R3 the resistance can be defined from Ohm’s law as follows:

\[
R = \frac{V}{I} \tag{4.4}
\]

Figure 4.4: (A) Schematic representation of rGO-P1 bilayer deposited on quartz with indium contacts on top used for Band Gap measurement. (B) Schematic circuit diagram for Band Gap measurement.

4.3: Results and Discussion

4.3.1: Reduced GO-P1 Monolayer

We examined properties of the reduced GO-P1 (rGO-P1) monolayer obtained with the aid of P1 modification. For this purpose the monolayer was deposited on an undoped (non-conductive) Si wafer. GO-P thermal reduction was conducted at 1000 °C–1150 °C in inert atmosphere. This process is reported to enable removal of oxygen-containing functional groups via dissociation of CO/CO\(_2\) molecules. The dissociation process is accompanied with formation of atomic vacancies in the carbon lattice, which are
rapidly saturated with residual oxygen to form quite temperature stable carbonyl and/or ether groups. In our model experiment with pristine GO sheets (no modification with P1) XPS spectra (Figure 4.5A), indeed, showed significant presence of carbonyl/ether groups in the reduced GO sheets. The result also indicated that thermal reduction process applied is quite effective, since significant amount of oxygen is removed from the sheets. C/O ratio (Equation 3.2) is increased from 3 to 6 (or to about 86% of carbon content), which is comparable to the value typically reported for the thermal reduction of GO sheets at the temperatures used.\textsuperscript{13}

For rGO-P1 monolayer obtained at the same conditions from GO modified with P1 XPS spectra showed an increase of the C/O ratio (Equation 3.2) from 2.7 to only 4.1 (Figure 4.5B). XPS results also indicate that significant amount of other than carbonyl/ether oxygen containing groups are present in the rGO-P1 monolayer. We
associate this phenomenon with the P1 polymer (enveloping GO sheets) that contains a significant concentration of oxygen in its structure (Figure 3.2 and Figure 3.7B) and, therefore, changes chemical pathways of the reduction process. AFM, scanning electron microscopy (SEM) and optical microscopy (Figure 4.6A-B) show that rGO-P monolayers preserved their integrity and structure. AFM cross-sectional measurements indicated that the obtained rGO-P1 sheets are 1.5–1.7 nm in thickness (Figure 4.7).
This thickness is higher than the one typically observed for rGO sheets. We attribute the higher thickness after the thermal treatment to presence of carbon/oxygen containing material incorporated in the rGO sheets, which originated during pyrolysis of P1 copolymer.

Figure 4.6: (A): SEM image and (B): optical image. All samples were thermally reduced at 1000 °C-1100 °C in the presence of Argon gas.

Figure 4.7: AFM images of rGO-P1 monolayer reduced at 1100 °C in the presence of argon gas and corresponding cross-sectional profile measurements.
To assess the rearrangement of the carbon atoms in the basal plane during the thermal annealing, we used Raman spectroscopy\textsuperscript{15-20}.

![Raman spectra of GO-P1 monolayer and pristine GO on undoped Si wafer before (A and C) and after thermal reduction (B and D) at 1100 °C in the presence of argon gas.](image)

**Figure 4.8:** The Raman spectrum of the prepared GO-P1 monolayer and pristine GO on undoped Si wafer before (A and C) and after thermal reduction (B and D) at 1100 °C in the presence of argon gas.

The Raman spectrum of the prepared GO-P1 monolayer displays the typical for GO materials carbon D (breathing modes of sp\textsuperscript{2} rings) and G (the first order scattering of the
$E_{2g}$ mode for sp$^2$ carbon lattice) band peaks at $\sim$1353 and $\sim$1595 cm$^{-1}$, respectively (Figure 4.8A-B). As a result of thermal reduction the peaks become narrower due to sp$^2$ ordering of carbon atoms.$^{19}$ The ratio of the peak intensities, D/G is related to the degree of disorder and dimensions/concentration of sp$^2$ ring clusters. It is frequently observed for GO materials that the ratio is increased in course of the reduction and formation of sp$^2$ structures$^{15,18}$. The increase is suggested to be associated with a decrease in the average size of domains but with a growth in the number of sp$^2$ domains upon reduction$^{16-17}$. Simultaneously the D band redshifted by $\sim$9 cm$^{-1}$, which we associate with bond disorder increase (aromatic clusters become smaller), as suggested by Ferrari et al.$^{16}$. For the pristine GO reduced at the same conditions (Figure 4.8C-D) D/G ratio is increased to a higher degree (from 0.96 to 1.26) and higher redshift was observed.

To assess the electrical properties of the rGO-P1 monolayers, we conducted two-point I-V measurements. The distance between electrodes was between 0.5 and 0.8 cm. We report an average of three parallel samples here. The I-V curves for rGO-P1 monolayers (Figure 4.9) revealed a non-linear and somewhat asymmetric behavior, indicating the Schottky barrier between the contact and the film.$^{21}$ This behavior can be associated with a number of defects/traps in the material previously reported for rGO materials, such as the Poole-Frenkel effect$^{22}$, Fowler-Nordheim tunneling$^{23}$ and a space-charge-limited emission$^{24-25}$. We also note that the samples prepared from pristine GO (no prior P1 modification, Figure 3.13A) and having higher C/O ratio demonstrate much lower value of conductivity (Figure 4.9). From the linear portion of the I-V curve (between -0.5 and +0.5 V) we estimated the sheet resistance values for rGO-P1 monolayers to be 23.8 kΩ/sq,
and then, taking into account the thickness of individual rGO-P1 sheets, we found the average conductivity to be only 580 S/cm (Table 4.1).

![Figure 4.9: I-V curves acquired under ambient conditions for bare silicon and rGO samples. All samples were thermally reduced at 1000 °C-1100 °C in the presence of Argon gas.](image)

**Table 4.1:** Electrical conductivity of rGO monolayer on undoped SiO$_2$/Si wafer obtained from I-V measurements for ± 0.5V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrodes</th>
<th>Distance between electrodes, mm</th>
<th>Conductivity, S/cm</th>
<th>Sheet resistance (Ohm/sq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-2</td>
<td>8.2</td>
<td>632</td>
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</tr>
<tr>
<td>2</td>
<td>1-2</td>
<td>4.5</td>
<td>123</td>
<td>54100</td>
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<tr>
<td>3</td>
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<td>Average</td>
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</tr>
<tr>
<td>Standard Dev.</td>
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</tbody>
</table>
These results are in line with most literature reports for rGO materials\textsuperscript{26-31}. We also carried out van der Pauw Hall effect measurements\textsuperscript{32} to extract charge carrier mobility values for our samples. The value for the rGO-P1 monolayer was estimated to be 65 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. This value is significantly (order of magnitude) lower than the highest mobility values reported for rGO\textsuperscript{33-34}. It is obvious that the presence of the large number of trap states caused by the defects significantly diminishes the carrier mobility. The rGO-P1 monolayer fabricated on quartz plate had a quite high transparency of 93\% in the UV-VIS region (Figure 4.10), which yields an optical conductivity ratio ($\sigma_{\text{DC}}/\sigma_{\text{OP}}$) on the level of 0.2.

![Graph showing transmittance percentage vs. wavelength in nm for rGO-P1 monolayer deposited on quartz plate. The graph indicates high transmittance in the UV-VIS region with a peak around 300 nm and a decrease to about 90\% at 700 nm.](image)

**Figure 4.10:** UV-Vis spectrum of rGO-P1 monolayer deposited on quartz plate.

### 4.3.2: Reduced GO-P1 Bilayer

The reduction of GO bilayer was conducted at the same conditions as for the GO-P1 monolayer. AFM (Figure 4.11A-B and E(insets)) imaging clearly showed that the structure of the bi-layer is preserved after the high temperature reduction. It is necessary to
note that residual carbon originating from the PAA (bright dots on the surface of the rGO-P1 sheets) is located in-between the top and bottom layers, creating a “welded” joint between them (Figure 4.11A, B). The sheets of the second top layer did not contain PAA.
Therefore, their surface looks smooth and uniform for the part of the layer that has no direct plane contact with the first layer. We suggest that the numerous “welding” points play a dual role. First, they cement the entire structure, making it more robust and coherent. Second, they create multiple conduction routes for the electrons allowing the omission of

Figure 4.11: (A-C) AFM topographical (30x30 μm² and 5x5μm²) images of rGO-P1 bi-layers deposited on undoped Si wafer and AFM corresponding cross-sectional profiles. Vertical scale: 20 nm. Optical (D) and SEM (E) images of rGO-P1 bi-layer film deposited on undoped Si wafer. (F) SEM images of reduced pristine GO on undoped Si wafer. Insets: corresponding AFM images. Lines of the optical 700x 475 μm² image are artefact originated from the software stitching of the consecutive optical images.
non-conducting or poorly conducting regions, thus, significantly improving the conductivity. In addition, from AFM images it appears that the border between the neighboring rGO sheets is smoothed out (**Figure 3.16C and Figure 4.11A, B**). We suggest that this is a result of “welding” of the sheets by the carbon originated from PAA linker layer. From AFM cross-sectional profiles we estimated that the thickness of rGO-P1 bi-layer is on the level of 3.5 nm. This value of the thickness was used in our estimation of the conductivity. Lower-magnification SEM and optical images confirmed that a nearly perfect rGO-P1 bi-layer was formed on the surface of the silicon wafer (**Figure 4.11D, E**). In contrast, reduced pristine GO showed highly damaged and disintegrated structure with topological defects/irregularities in form of holes, folds etc. as evidenced from **Figure 4.11F**.

The XPS results (**Figure 4.12A-B**) showed that after the thermal reduction the intensities of all the related oxygen peaks were sharply decreased. The C:O ratio of the bi-layer rGO-P1 film was greatly improved to approximately 17:1 (or to about 94% of carbon content), and the C-C/C=C peak downshifted from 284.9 to 284.3 eV, indicating that the delocalized π conjugation was restored to a significant extent\textsuperscript{35-36}. The C/O ratio is more than two times higher than the one determined for pristine rGO sheets obtained from pristine GO. It is also 3.5 times higher than the ratio found for rGO-P1 monolayer. We associate the significant increase in the C/O ratio with the carbon originating from the PAA linker layer. Raman spectroscopy confirmed efficient reduction of GO-P1 bi-layer as well (**Figure 4.12C-D**). The D and G peaks become sharper and D/G intensity ratio significantly increased from ~1.00 to ~1.46, which indicates increase in number of the
conductive sp² domains⁶⁻¹⁷, 3⁷. Simultaneously, a blue shift of ~10 cm⁻¹ and ~7 cm⁻¹ was observed for the D and G bands, respectively. Moreover, a 2D band of around 2700 cm⁻¹ was readily detectable.

These characteristics are indicative of the change in electron bands⁶, 1⁹⁻²⁰ caused by the transition from amorphous carbon to nanocrystalline graphite or sp² clustering and conjugation recovery (graphitization)⁶, 3⁸.

**Figure 4.12:** High resolution C1s spectra of GO-P1 bi-layer film (A) and rGO-P1 bi-layer film (B). Raman spectra of GO-P1 bi-layer film (C) and rGO-P1 bi-layer film (D).

These characteristics are indicative of the change in electron bands⁶, 1⁹⁻²⁰ caused by the transition from amorphous carbon to nanocrystalline graphite or sp² clustering and conjugation recovery (graphitization)⁶, 3⁸.
To assess the electrical properties of the rGO-P1 bi-layers, we conducted two-point I-V measurements. The distance between electrodes was between 0.5 and 1.5 cm. We report an average of 13 independent measurements on 9 different bi-layer samples.

**Table 4.2**: Electrical conductivity of rGO-P1 bi-layer deposited on undoped Si wafer obtained from I-V measurements for ± 4V.

<table>
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<tr>
<th>Sample</th>
<th>Electrodes</th>
<th>Distance between electrodes, mm</th>
<th>Conductivity, S/cm</th>
<th>Sheet resistance, Ohm/sq</th>
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</tbody>
</table>
We found a virtually metallic property (close-to-linear $I-V$ curve) for the bi-layer film in contrast to the rGO-P1 monolayer (Figure 4.9). The electrical properties for all samples are listed in Table 4.2. The two-point transport measurements indicated an average sheet resistance of $1.170 \pm 0.487 \, \text{k}\Omega/\text{sq}$, which resulted in average conductivities of $3250 \pm 2376 \, \text{S/cm}$. We associate the relatively high standard deviation for our samples with manual handling of each sample (e.g. positioning of the samples in dip-coater grip). We expect that the consistency of the samples can be greatly improved with more precise automatic/robotic sample handling/alignment. In this respect for the three best samples the sheet resistance and conductivity are $0.490\pm0.150 \, \text{k}\Omega/\text{sq}$ and $0.7\pm0.26 \times 10^4 \, \text{S/cm}$, respectively. Our measurements indicated that, to the best of our knowledge, we obtained rGO nanoscale films with the highest conductivity ever reported. It is also necessary to note that the rGO-P bi-layer conductivity is fairly close to the conductivity of indium tin oxide, which is $\sim 10^4 \, \text{S/cm}$.

We conducted van der Pauw Hall effect measurements to extract charge carrier mobility values for our samples. We obtained an average value of $\sim 500 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ for the rGO-P1 bi-layer, which is in good agreement with the highest mobility values reported for rGO\textsuperscript{34,41}. Increased value of Hall mobility could be explained by nearest neighbor hopping (NNH) transport mechanism which is dominated at room and higher temperatures\textsuperscript{42-43}. According to this theory several factors may be responsible for improved mobility: (1) lower hopping energy, (2) longer localization length, (3) smaller hopping distance, and (4) minimal defect density. For example, the reported by Feng et al.\textsuperscript{41} in $(123 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1})$ mobility was measured on and individual rGO sheet which is in direct contact with the
substrate. In our case we have at least two layers and charge carriers have better pathways for tunneling. Similarly, for the graphene samples in direct contact with substrates, the carrier mobilities are typically in the \( \sim 10^3 \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) range\(^{44}\).

We prepared the rGO-P1 bi-layers on the surface of a quartz plate to determine their optical properties. AFM imaging confirmed the formation of the rGO-P1 bi-layer film on the quartz slide with the similar structure as that for the one fabricated on the silicon wafer (Figure 4.13A-B).

![AFM images of rGO-P1 bi-layer film fabricated on quartz plate.](image)

**Figure 4.13:** (A-B): AFM images of rGO-P1 bilayer film fabricated on quartz plate. Vertical scale: 60 and 10 nm for 15x15 \( \mu \text{m}^2 \) and 5x5 \( \mu \text{m}^2 \) images, respectively. Inset: optical image of quartz plate covered with rGO-P1 (left) and original quartz plate (right). (C): UV-Vis transmittance spectra of GO-P1 bi-layer film (I) and rGO-P1 bi-layer film (II). (D): FTIR spectrum of rGO-P1 bi-layer film.
The sheet resistance and conductivity of the film were also comparable to the parameters of the rGO-P1 film deposited on the silicon wafer (Table 4.3).

Table 4.3. Electrical conductivity of rGO-P1 bi-layer deposited on quartz plate obtained from multimeter measurements at 1V.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Distance between electrodes, mm</th>
<th>Conductivity, S/cm</th>
<th>Sheet resistance, Ohm/sq</th>
<th>Conductivity ratio, $\sigma_{DC}/\sigma_{OP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>6.0</td>
<td>2100</td>
<td>1362</td>
<td>2.31</td>
</tr>
<tr>
<td>3-4</td>
<td>6.0</td>
<td>3650</td>
<td>783</td>
<td>4.45</td>
</tr>
<tr>
<td>1-4</td>
<td>8.6</td>
<td>1764</td>
<td>1619</td>
<td>1.94</td>
</tr>
<tr>
<td>1-3</td>
<td>10.4</td>
<td>1680</td>
<td>1700</td>
<td>1.85</td>
</tr>
<tr>
<td>Average</td>
<td>7.8</td>
<td>2300</td>
<td>1366</td>
<td>2.6</td>
</tr>
<tr>
<td>Standard Dev.</td>
<td></td>
<td>796</td>
<td>414</td>
<td>1.2</td>
</tr>
</tbody>
</table>

The UV-VIS spectra for the film is presented in Figure 4.13C. It is shown that the rGO-P1 bi-layer has an average transparency of $\sim 89\%$ at 550 nm in comparison with bare quartz. It is reported $^{45}$ that unreduced GO-P1 exhibits a maximum of adsorption at 231 nm (which corresponds to the $\pi \rightarrow \pi^*$ transitions of aromatic C=C bonds) and a shoulder at $\sim 300$ nm (ascribed to the $n \rightarrow \pi^*$ transitions of C=O bonds). After reduction, the maximum redshifts to about 272 nm (as observed in our case), which is indicative of the restored electronic conjugation within the carbon framework $^{46}$. The calculated $\sigma_{DC}/\sigma_{OP}$ value for the rGO-P1 bi-layers deposited on the quartz plate was between 2 and 4.5 (Table 4.3). A comparison with the data in the literature clearly indicates that our $\sigma_{DC}/\sigma_{OP}$ ratio is one of the highest reported for rGO-P1 films $^{29, 47-48}$. We also carried out Fourier Transform Infrared measurements (Figure 4.13D) for the rGO-P1 bi-layer film deposited on silicon wafer and observed that the rGO-P1 bi-layer is $> 94\%$ transparent over the range of 6667–
2500 nm (4000–1500 cm\(^{-1}\)). For the significant IR spectra regions the transparency is on the level of 99%. This level of IR transparency for the rGO-P1 bi-layer is similar to the transparency of graphene sheets\(^{49-50}\). It is also important to point that conductive ITO films have very low transparency in IR spectral region\(^{51}\). Therefore, rGO-P1 bi-layer films reported here have definite advantage in the applications requiring IR transparency of conductive coatings.

### 4.3.3: Electronic Band Gap of rGO-P1 Bilayer Film

*Mechanism of electrical conductivity in rGO-P1 bilayer films*

One of the parameters that determines the potential usefulness of any new semiconductor material is its energy gap. It is a major factor determining the electrical conductivity and optical properties of a solid. Thus, the precise determination of electronic band gap is important for device design and performance projections. The basic theory of direct and indirect transitions in semiconductors was formulated by Bardeen et al.\(^ {52}\).

Here, we used thermoelectric method described in experimental Section 4.2.3 to determine electronic band gap of rGO-P1 bilayer film. Before exploring the temperature dependence of electrical conductivity, it is important to define the predominant type of primary charge carriers (electrons or holes) as it influences the band gap structure\(^ {53}\). Another important parameter to consider is the level and type of impurities or defects in rGO-P1 film. It has been shown in literature\(^ {54}\) that the type of conductivity of rGO (p-type or n-type) can be tuned by changing the type and the amount of functional groups present on it via thermal reduction\(^ {55}\). Namely, an electron-donating groups (sp\(^2\)-bonded hydroxyl,
ether, and epoxide groups) will give rGO n-type conductivity whereas an electron-withdrawing groups (carboxyl, carbonyl, and sp<sup>3</sup>-bonded hydroxyl, ether and epoxide groups) will make it a p-type<sup>54</sup>

Therefore, it is possible to qualitatively predict the type of conductivity in rGO-P1 using XPS results. **Table A1** in **Appendix** shows the ratio of the area of corresponding oxygen-containing functional group and the total carbons. From these data we concluded that our rGO-P1 bilayer film must have n-type conductivity as the sp<sup>2</sup>-hydroxyl (C-OH% ≈ 7%) and sp<sup>2</sup> ether groups (C-O-C% ≈ 5%) became predominant after almost complete removal of carboxyl groups (COOH% < 1%). This finding is in good agreement with the reported results in Ref. <sup>54</sup>.

For more quantitative verification of the above conclusion we relied on the Hall effect measurements to determine the carrier concentrations and mobilities in the rGO-P1 bilayer films (**Sections 4.2.1**). The sign of the Hall coefficient (R<sub>H</sub>) indicates whether the primary charge carriers are holes or electrons<sup>54</sup>. Based on the results shown in (**Appendix, Table A2** (reduced GO-P1 bilayer)) we confirmed that both rGO-P1 monolayer and bilayer possess n-type characteristics.

Next, we determined the band gap of rGO-P1 bilayer film using the procedure described in **Section 4.2.3**. All measurements were carried out by Dr. Borys Turko in Dr. Kapustianyk’s laboratory at Ivan Franko National University of Lviv, Ukraine. The results shown in **Figure 4.14A** demonstrate three regions of temperature dependence of the current. These regions are denoted as extrinsic range (256 K to ~ 333 K), exhaustion range
(333 K to ~ 378 K) and intrinsic range (378 K to ~ 450 K) \(^{56}\). In the extrinsic region (blue curve) the conductivity depends on the dopants, electrons of which populate the donor level \((E_d)\). As the temperature increases more and more of these donor electrons get excited into the conduction band until a temperature is reached such that donor level becomes emptied. This is referred to as exhaustion region (black curve). Conductivity in this region is constant. As the temperature proceeds into the intrinsic region the lattice scattering mechanisms due to thermal agitation start to play dominant role, which is why we observe a slight decrease in current flow around 378 K.

![Graph showing the temperature vs. current for rGO-P1 bilayer](image)
Figure 4.14: (A): Temperature dependence of the current in rGO-P1 bilayer film. (B): Energy band gap diagram for rGO-P1 film. (C): Plot of $R(T)$ data in the form of Equation 4.3. $E_g = 42$ meV and $E_c - E_d = 6$ meV correspond to an activation energy needed to promote electron from valence and donor energy level to a conduction band respectively. Inset: schematic of rGO-P1/quartz sample with two indium contacts.
After that, as temperature increases above 378 K, there is enough thermal energy to induce the transition of electrons from the valence band into the conduction band (intrinsic range). As this continues, the concentration of valence electrons in the conduction band rapidly increases while mobility decreases due to significant lattice thermal vibrations and scattering effects. Nevertheless, the current linearly increases as there are now so many more electrons in the conduction band. Based on the above results and discussion presented in Section 2.9 we suggest that obtained value of band gap \( (E_g = 42 \text{ meV}) \), which is rather small, corresponds to K-point in the electronic band gap shown in Figure 2.11. For comparison, the value of \( E_g = 29 \text{ meV} \) was reported in Ref. 57 for CVD deposited graphene films. The non-zero band gap, \( E_g \), between the conduction and valence band is an indicative of the possible break up of lattice symmetry at the Dirac points (K) of the rGO film due to the presence of defects and/or moisture, as discussed in the Section 2.9.

### 4.4: Conclusions

The following conclusions can be drawn as a result of the study reported in Chapter 4:

- Highly conductive (up to \( 10^4 \) S/cm) and transparent (\( \sim 90\% \)) rGO-P1 monolayers and bi-layers on non-conductive substrates were produced.

- In contrast to pristine rGO, rGO-P1 double layer film revealed nearly defect-free morphology with high coherency and preserved integrity.

- GO-P1 flakes showed higher level of reduction and carbonization/graphitization in the presence of PAA carbon residue as evidenced from XPS and AFM.
• Low heating and cooling rate plays a crucial role for preventing GO-P1 sheets from buckling and decomposing on rough surfaces like quartz.

• Electronic energy band gap of rGO-P1 bilayer was calculated to be \( \sim 29 \) meV at K-point on electronic band diagram of graphene.
4.5: References


CHAPTER FIVE

GO LAYERS ON HYDROPHOBIC SUBSTRATES

5.1: Introduction

As mentioned in Section 2.8 polymeric films are widely employed in flexible electronics as flexible substrates. However, these films are often hydrophobic by nature and have poor adhesive properties, which inhibit the deposition quality of GO layers from water-based solutions. Therefore, it raises the need for surface modification to these substrates to reduce their inherent surface hydrophobicity. As an alternative, the surface of GO can be made more hydrophobic to enable stronger interaction with the hydrophobic substrate. In both cases, it is important to understand the influence of the hydrophobic substrate on morphology of deposited GO layers.

In general, the results of this chapter demonstrated that it is difficult to obtain a stable and uniform monolayer of GO modified with P1 on hydrophobic surfaces. Specifically, heavy wrinkling, crumpling and scrolling of GO-P1 sheets was observed after dipcoating/deposition from water solution. We suggest, these events are directly related to the lack of hydrophobic interaction between the surface of the substrate and GO-P1 individual flake. Additionally, as discussed in Chapter 3 the presence of polymer linker layer (PLL) was necessary to fabricate a bi-layer of GO-P1, which makes it inconvenient from the manufacturing point of view.

To this end, this chapter reports on the development of fundamental and practical approach to the deposition of sub-nanometer GO films directly on hydrophobic polymeric
substrates via scalable water-based dip-coating. Our final successful approach relies on the enveloping GOs into especially designed (1-2 nm thick) amphiphilic copolymer shell poly(Oligo Ethylene Glycol methyl ether Methacrylate [OEGMA]- Glycidyl Methacrylate [GMA]- Lauryl Methacrylate [LMA]) (P2) that allows controlled formation of monolayer and/or multilayer upon single dipcoating procedure/step, thus eliminating the need of PLL.

Spectroscopic and thermal methods, such as XPS, FTIR, TGA and DSC were used to confirm covalent attachment/grafting of copolymer to GO and to study any compositional changes in GO during modification. Like in Chapter 3, the kinetics of copolymer grafting to GO sheets was investigated using thermogravimetric analysis (TGA), which also helped us to evaluate the level of grafting of copolymer to the GOs after copolymer adsorption saturation.

In addition, the surface properties, such as the morphology and the surface energy of GO-modified layers, were investigated using atomic force microscopy (AFM), Quartz crystal microbalance with dissipation monitoring (QCM-D) and contact angle measurements. The thickness of copolymer bound to the surface of the GO particulates was also defined from AFM images of GO-copolymer monolayers on SiO2/Si.

5.2: Experimental

5.2.1. Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

In QCM-D experiments, a quartz crystal is driven by applying and alternating electric field at one of its resonance frequencies: 5, 15, 25, ..., 65 MHz. QCM-D measures changes in resonance frequency, $\Delta F$, and dissipation, $\Delta D$, of a sensor crystal upon
interaction of (soft) matter with its surface (Figure 5.1). The QCM-D response is sensitive to the mass (including hydrodynamically coupled water) and the mechanical properties of the surface-bound layer [1]. As a first approximation, a decrease in $\Delta F$ indicates a mass increase, while high (low) values of $\Delta D$ indicate a soft (rigid) film. All QCM-D measurements were performed with a Q-Sense E1 system (Biolin Scientific AB).

5.2.2. Surface Functionalization of QCM-D Sensor with P1 Copolymer Layer

Substrate Preparation

The surface of the SiO$_2$-coated AT-cut quartz crystals (4.95 MHz, QSX 303, Q-Sense AB) was functionalized with P1 copolymer following the procedure described in the next section. The quartz crystal was cleaned by plasma treatment using O$_2$-plasma etcher (the generator power switch was set at 12 W at 0.2-torr atmospheric pressure) for 15 min followed by immersion in 2 vol % sodium dodecyl sulfate (SDS) solution in high purity MilliQ water (18 MΩ·cm) for 30 min, rinsing with Milli-Q water, drying with ultra-high-purity nitrogen, and a final O$_2$-plasma treatment for 15 min.

Deposition of P1 film

The P1 layer was then deposited by dipcoating at 5 mm/sec from 2% solution of P1 in 2-butanone (MEK). The resulting film was allowed to dry under ambient conditions for 24 hours. Then, unattached copolymer chains were removed by rinsing the sample in water and MEK three times for 30 min each.

The thickness of P1 film before and after the rinsing was monitored using single-wavelength ellipsometry (COMPEL automatic ellipsometer, InOmTech, Inc.) at 70° angle.
of incidence. Based on the five measurements the thickness of the as-deposited film and after rinsing was (40 ± 8 nm) and (38 ± 8 nm) respectively.

Swelling Experiments

The temperature for QCM-D experiments was held at 25 °C. The flow rate for all water-ethanol solutions (0%, 10%, 50%, 70% and 100% of ethanol content) was kept at 100 µL/min using a peristaltic pump (ISIMATEC, IPC-N). A baseline for each measurement was established by flowing all solutions over bare quartz crystal in sequential manner until stable signal was achieved. Then, after the crystal was removed from the measuring chamber, thoroughly cleaned with O2-plasma and dried with nitrogen, P1 layer was grafted to the activated surface of SiO2 followed by drying under ambient conditions overnight. Next, the swelling experiments were run on grafted copolymer layer with the same water-ethanol solutions as for bare crystal. The collected raw data on P1 swelling was corrected using the $\Delta F/n$ and $\Delta D$ values from bare quartz crystal. This allowed us to accurately determine viscoelastic properties of hydrated copolymer layer and to account for any changes in the viscoelastic properties of the surrounding fluid.

5.2.3. Modeling of the QCM-D Response for Swelling of Nanoscale P1 film in Water-Ethanol Mixtures

QCM-D data for P1 swelling in water ethanol mixtures was collected using Q-Sense E1 instrument. Adsorbed mass of thin and nondissipative layers can be calculated using Sauerbrey model 2:

$$\Delta m = - C \Delta F/n$$  \hspace{1cm} (5.1)
where \( n = 1, 3, \ldots \) is the overtone number, \( \Delta F \) is the frequency change, and \( C = 17.7 \) ng/(cm\(^2\)Hz) at 5 MHz - sensitivity constant of quartz crystal. However, the Sauerbrey equation is not applicable for highly hydrated and highly viscous polymer films which result in high dissipation shifts \( (\Delta D_n/(-\Delta F_n/n) > 0.4 \times 10^{-6} \text{ Hz}^{-1}) \).

The Voigt viscoelastic model, in turn, has been successfully used previously \(^3\) to calculate the adsorbed mass and viscoelastic properties of highly dissipative polymer brushes \(^4-5\) and adsorbed proteins layers \(^6-7\). In summary, the adsorbed/swollen layer can be described by four parameters: effective density \( (\rho) \), shear viscosity \( (\eta) \), shear elastic modulus \( (\mu) \), and thickness \( (h) \). Since each harmonic acoustic frequency has different penetration depth at least three overtones need to be simultaneously fitted using the Voigt model to obtain values of \( \rho, \eta, \mu \) and \( h \) of viscous layers \(^8\).

We used Voigt viscoelastic model embedded in Smartfit algorithm of QSense Dfind and QTools software packages \(^9\) to fit our experimental QCM-D response in form of frequency \( (\Delta F) \) and dissipation shifts \( (\Delta D) \). Three overtones (third, fifth, seventh) were

![Figure 5.1: (A, B) QCM-D sensing mechanism.](image)

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used to fit the following parameters: layer viscosity, layer shear (elasticity) and layer thickness, while the value of layer density ($\rho_{\text{wet}}$), fluid density ($\rho_{\text{fluid}}$), and fluid viscosity ($\eta_{\text{fluid}}$) was fixed. The density of solvated P1 layer was estimated from the relative weighting of the densities of the dry polymer film ($\rho_{\text{dry}}$) and the solvent ($\rho_{\text{fluid}}$) using the ellipsometry and QCM-D mass measurements

$$\rho_{\text{wet}} = \rho_{\text{dry}} \left( \frac{m_{\text{dry}}}{m_{\text{wet}}} \right) + \rho_{\text{fluid}} \left( \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{wet}}} \right)$$ (5.2)

The effective solvated film thickness ($h_{\text{wet}}$), can be determined from the mechanical coupling of the ‘wet’ mass of the solvated polymer with the quartz crystal resonator in QCM-D using the following relationship,

$$h_{\text{wet}} \left[ \text{nm} \right] = \frac{m_{\text{wet}} \left[ \text{ng/cm}^2 \right]}{\rho_{\text{wet}} \left[ \text{g/cm}^3 \right]} \times 10^{-2}$$ (5.3)

The mass per unit area for wet/solvated film ($m_{\text{wet}}$) is the mass of polymer plus the mass of adsorbed solvent molecules and it was found directly from the QCM-D data using Voigt model. Effective density of the swollen polymer film ($\rho_{\text{wet}}$) was estimated from the Equation 5.2. Unlike $h_{\text{wet}}$, $m_{\text{wet}}$ does not depend on the choice of the input parameter $\rho_{\text{wet}}$. The mass per unit area for dry film ($m_{\text{d}} = \rho_{\text{dry}} \cdot h_{\text{d}}$) was calculated by multiplying the thickness of dry polymer film which was measured using ellipsometry with the assumed density of the dry P1 film ($1150 \pm 100 \text{ kg/m}^3$). The values of $\rho_{\text{fluid}}$ and $\eta_{\text{fluid}}$ were taken from the reference for 0%, 10%, 50% and 100% of ethanol content.

5.2.4: Formation of Hydrophobic Test Surface with Self-Assembled Monolayers (SAMs) on SiO$_2$/Si substrates
To prepare hydrophobic model-surface on silicon, chlorosilane-based self-assembled monolayers (SAMs) were obtained on SiO$_2$/Si substrate via a vapor-phase coating process $^{15}$, as shown in Figure 5.2. A silicon wafer (step 1) was cleaned using “piranha” solution and washed with DI water. Then, the cleaned silicon wafer was placed in tightly closed vial with 3-4 droplets of chlorosilane compound (step 2). Over-night vapor deposition of chlorosilane took place through the condensation reaction with the hydroxyl groups of activated silicon substrate $^{16-17}$. After the deposition was complete, the modified substrate (step 3) was removed from vial and rinsed with MEK three times for 10 minutes to remove unbound deposited materials. The thickness and surface morphology of the silane films were determined using ellipsometry and AFM, respectively.

![Figure 5.2: Schematic representation of the method for self-assembly of hydrophobic monolayers on silicon substrate. Water contact angle on silane-modified silicon was 100°.](image)

**Figure 5.2:** Schematic representation of the method for self-assembly of hydrophobic monolayers on silicon substrate. Water contact angle on silane-modified silicon was 100°.

### 5.2.5: Modification of GO Sheets with P2

Copolymer P2 was synthesized by solution free-radical polymerization $^{18}$. For the modification (Figure 5.12), an aqueous suspension of GO ($\sim$ 0.75-1.5 mg/ml) was mixed
with an aqueous solution of P2 (~ 3-4 mg/ml) in a mass ratio of 1:6 according to the procedure described in Section 3.2.3.

5.2.6. QCM-D Investigation of Viscoelastic Properties of Adsorbed GO-P1 and GO-P2 layers on Hydrophobic Surfaces

![Diagram]

**Figure 5.3**: Schematic of adsorption of GO-P1/2 onto silane-modified quartz crystal.

Pristine GO, GO-P1 and GO-P2 adsorption to silane-coated crystals was performed using QCM-D at 25 °C under 200 μL/min flow rate (**Figure 5.3**). Three aqueous suspensions were used at the same concentration of 0.016 wt.%.

All adsorbed materials were modeled as homogeneous single viscoelastic layers with acoustic thickness $d$, density $\rho$, storage modulus $G'(f)$, and loss modulus $G''(f)$. The storage modulus is a measure for the elasticity of the film. The loss modulus is related to the film’s viscosity $\eta(f)$ by $G''(f) = 2\pi f \eta(f)$. Both $G'$ and $G''$ (and $\eta$) are frequency-dependent. If $G' \gg G''$ - material is predominantly elastic, and if $G' \ll G''$ - material is predominantly viscous, and in case of $G' \approx G''$ it is viscoelastic. The viscoelastic properties are represented by the loss and storage modulus as the frequency dependent complex shear moduli, $G_f$ of the layer.

$$G_f = \mu_f + i2\pi f \eta_f = G'_f + iG''_f \quad (5.4)$$
where \( f \) is frequency of oscillation and \( \mu_f \) is shear elastic modulus.

The relationship between \( G''/G' \) gives a measure of the stiffness of the film and is called the loss tangent or loss angle, \( \tan(\delta_L) \). For soft and dissipative films loss angle is higher than for rigid non-dissipative ones\(^{19}\).

\[
\tan(\delta_L) = \frac{G''}{G'} = \frac{j''}{j'}
\]

(5.5)

5.2.7. Deposition of GO-P2 multilayers on polymeric substrate

In this particular work we selected to focus on manufacturing of the GO layers on four polymer films possessing different surface energy, mechanical properties, thermal transitions, and internal structure. Specifically, in our research we will employ Kapton (polyimide, 25 µm, DuPont), PP (6 µm, Chemplex), PC (125 µm, MacMaster) and UHWPE (125 µm, MacMaster). Characteristics of those polymers are well known\(^{20-21}\) and films of different thicknesses are commercially available. The following water contact angles were measured: Kapton – (80 ± 6)°, PP - (94 ± 3)°, PC - (76 ± 1)° and UHWPE - (92 ± 3)°. Sharp razor-blade was used to cut films into stripes of 1x4 cm\(^2\). Kapton, PP, UHWPE samples were thoroughly rinsed with acetone, chloroform and

![Image](Image)

**Figure 5.4:** Deposition of a monolayer of GO-P2 on flexible polymeric substrate.
methanol for 10 min each to remove contaminants. Hexane was used for PC. Then, each sample was sandwiched between 2 magnetic frames with cut-out windows. Finally, dip-coating was performed (Figure 5.4). After the deposition, polymer films were allowed to dry under ambient conditions.

### 5.2.8. Estimation of surface energy for GO-P1 and GO-P2

We obtain the contact angles of two different liquids on solid surface by drop shape analysis Kruss, Germany at room temperature, and use the results to calculate the surface energy of the solid substrate by the Owens-Wendt method (Equation 5.6) \(^{22}\).

\[
\gamma_{11}(1 + \cos \theta_1) = 2\sqrt{(\gamma_s^d \gamma_{11}^d) + 2(\gamma_s^p \gamma_{11}^p)}
\]

\[
\gamma_{12}(1 + \cos \theta_2) = 2\sqrt{(\gamma_s^d \gamma_{12}^d) + 2(\gamma_s^p \gamma_{12}^p)}
\]

\[
\gamma_s = \gamma_s^d + \gamma_s^p \tag{5.6}
\]

where \(\gamma_s\) and \(\gamma_l\) are the surface tensions of the solid and liquid, respectively. The subscripts \(d\) and \(p\) correspond to dispersion and polar components of the surface tension, respectively. Surface free energy (\(\gamma_s\)) and its polar (\(\gamma_s^p\)) and dispersion (\(\gamma_s^d\)) components of the GO surfaces were determined using two sets of contact angle measurements of water and hexadecane. The \(\gamma_l^p\) and \(\gamma_l^d\) components of liquids shown in Table 5.1 were used in the calculations.
Table 5.1. Water and hexadecane contact angles for P1, P2, GO-P1 and GO-P2. $\gamma_f^P$ and $\gamma_f^d$ components of liquids are taken from reference 23.

<table>
<thead>
<tr>
<th>Liquefied</th>
<th>$\gamma_f^d$ (mJ m$^{-2}$)</th>
<th>$\gamma_f^P$ (mJ m$^{-2}$)</th>
<th>$\gamma_f$ (mJ m$^{-2}$)</th>
<th>P1</th>
<th>P2</th>
<th>GO-P1</th>
<th>GO-P2</th>
<th>GO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecane (1)</td>
<td>26.35</td>
<td>0</td>
<td>26.35</td>
<td>(15 ± 6)$^\circ$</td>
<td>0$^\circ$</td>
<td>0$^\circ$</td>
<td>0$^\circ$</td>
<td>0$^\circ$</td>
</tr>
<tr>
<td>Water (2)</td>
<td>21.8</td>
<td>51</td>
<td>72.8</td>
<td>(38 ± 4)$^\circ$</td>
<td>(94 ± 3)$^\circ$</td>
<td>0$^\circ$</td>
<td>(51 ± 2)$^\circ$</td>
<td>0$^\circ$</td>
</tr>
<tr>
<td>Surface Energy (mJ m$^{-2}$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>59.3</td>
<td>28.3</td>
<td>73.1</td>
<td>50.8</td>
<td>73.1</td>
</tr>
</tbody>
</table>

Thus, using WCA and HCA values derived from the experiment and Equation 5.6 the surface energy of the GO-P1 and GO-P2 films were found to be $\sim 73$ mJ m$^{-2}$ and $\sim 51$ mJ m$^{-2}$ respectively (Table 5.1). Analysis of water and hexadecane contact angles (HCAs) was done in Dr. Kornev’s laboratory using a KRUSS DSA10 drop shape analyzer at 20 s after droplet deposition on the grafted copolymer surface.

5.3: Results and Discussion

5.3.1: GO-P1 Layers on Hydrophobic Substrates Deposited from Aqueous Solution by Dipcoating

In this section of the dissertation we investigate whether the pristine GO (unmodified with the copolymer) and GO-P1 can uniformly coat the hydrophobic Silane-SiO$_2$/Si substrates. Specifically, we investigated the effect of GO sheet sizes on the quality of monolayer formation on hydrophobic substrates.

In our initial experiments with pristine (unmodified with the copolymers) GO sheets we found that it was impossible to obtain a GO monolayer via dip-coating on hydrophobic surfaces (Figure 5.5A). Image presented in Figure 5.5B reveals that
deposition of GO-P1 on hydrophobic surface resulted in non-uniform coverage and crumpling of GO-P1 flakes. Furthermore, the data shown in Figure 5.6 shows that the quality of deposited GO-P1 layers on hydrophobic surface is strongly size-dependent. For example, GO-P1 < 5 µm could not be deposited on hydrophobic surface by the dipcoating (Figure 5.6A) while the largest GO-P1 flakes (~80 µm, Figure 5.6G) resulted in highly non-uniform and crumpled/scrolled particulates and a monolayer with only slightly wrinkled ~5 µm GO-P1 sheets (Figure 5.6B). Similar scrolling and wrinkling phenomenon has been already reported in literature 24–28, although it is still not well understood. We associate this observation with poor adhesion of hydrophilic/polar OEGMA units to the hydrophobic surface and capillary forces originated from solvent evaporation 29–30. The development of sharp wrinkles/atomic scale corrugations and folds in GO is the direct result of significant local stresses as suggested elsewhere 31 and extreme flexibility of individual GO flake (low bending modulus) 32. The formation of such features is also energy-favorable because it can reduce the number of interaction contacts between two unlike surfaces - hydrophilic OEGMA units and hydrophobic Si substrate. The thickness of the wrinkled and scrolled GO-P1 sheets ranged from 3 to 500 nm as determined from AFM profiles (Figure 5.6(C, F, H)).
Therefore, an extra efforts were made to obtain GO-P1 with well defined morphology on hydrophobic surfaces (see Section 5.3.3).

**Figure 5.5:** Atomic force microscopy of pristine graphene oxide (A) and GO-P1 (B) deposited on hydrophobic substrate. The size of the scans is 30x30 μm², vertical scale is: 2 nm (A), 70 nm (B, inset). GO was deposited by dip-coating.

**Figure 5.6:** AFM images showing GO-P1 with different average flake sizes deposited on hydrophobic substrates: ~3 μm (A); ~5 μm (B); ~7 μm (D); ~30 μm (E); ~95 μm (G); (vertical scale: 2 nm (A), 10 nm (B), 25 nm (D), 150 nm (E), 600 nm (G)). Corresponding cross-sectional profiles (C, F, H).

Therefore, an extra efforts were made to obtain GO-P1 with well defined morphology on hydrophobic surfaces (see Section 5.3.3).
5.3.2: Theoretical Aspect of Crumpling/Scrolling: Folding Criteria of GO-P1 Sheets

The present section discusses the possible formation mechanism of GO-P1 curled-up structures and nanoscrolls. Previously, capillary interaction between water and GO is reported to be liable for the formation of folded GO nanostructures on hydrophobic substrates during “molecular combing” ²⁸, ³³.

Similarly, in this dissertation, there are several actions which may lead to the formation of GO nanoscrolls. Firstly, hydrophobic interaction ³⁴ between GO sheets and hydrophobic substrates contributed to the pinning of some GO sheets to the surface. Secondly, substrate-enhanced dewetting of liquid film allowed the capillary force to induce the folding or scrolling of GO sheet ³¹.

In the next step of our discussion, the theoretical assessment of folding criteria of GO-P1 sheet is carried out. According to the scientific literature, the folding/bending in unconstrained submicron solid films (few hundred nanometers) or carbon nanotubes could be modeled using the classical Bernoulli-Euler beam theory ³⁵-³⁷. However, it was proven to fail for nanometer scale monolayer of graphene/graphene oxide sheets since the physical thickness becomes close to the size of constituent particles (carbon atoms, bonds) and particle-scale features need to be accounted for ³⁸-³⁹. In contrast to bi- and multilayered systems the bending rigidity of atomic monolayers involves much different mechanisms. The bending behavior of such sheets is expected to be affected by strain and torsional gradients accompanied by changes of atomic bond and dihedral angles ⁴⁰-⁴¹. In conventional theory, the resistance of a thin sheet to elastic deformation is defined by the
Young’s modulus $E$ and the out-of-plane bending modulus (bending spring constant), $D_0$, respectively. These two parameters are related by the following Euler equation \(^\text{36}\):

$$D_0 = \frac{EH^3}{12(1-v^2)} \quad (5.6)$$

where $H$ is the GO thickness, $v \approx 0.07$ – Poisson ratio \(^\text{42}\) (for 0.18 degree of oxidation), $E \approx 200$ GPa - elastic modulus of GO \(^\text{43}\). To account for the size-dependent bending rigidity due to non-local effects in GO-P1 flake, we used a correction to the bending modulus given by \(^\text{40}\):

$$D = D_0 \left[ 1 + 6(1 - v) \left( \frac{l}{H} \right)^2 \right] \quad (5.7)$$

where $l$ is the length scale at which classical elasticity breaks down for the specific material. Parameter $l$ becomes important for materials possessing a nonhomogeneous structure like amorphous solids or polymers \(^\text{38, 44}\). Thus, following the ref \(^\text{38}\) we assumed $l \approx 60$ nm for GO-P1 system.

Next, using the minimization of total free energy (the sum of surface energy and elastic energy) with respect to in-plane and out-of-plane strains the instability criteria for buckling is obtained as follows \(^\text{36}\):

$$\gamma \geq f_{cr}^B = \frac{\pi^2D}{2L^2} \quad (5.8)$$

where $\gamma \approx 73$ mJ m\(^{-2}\) corresponds to the surface energy of GO-P1 layer, calculated in Section 5.2.8.

In this work we assumed the contribution of the interaction energy term (interaction between GO-P1 flake and hydrophobic surface) to be negligible. Equation 5.8 shows that the crumpling of GO is governed by surface free energy and the elastic energy \(^\text{27}\). The
evaluation of the critical surface stress required to induce buckling lead to the conclusion that only GO-P1 sheets with a spring constant higher than $f_{cr}^B \sim 73 \text{ mJ m}^{-2}$ could resist complete scrolling/folding, corresponding to $L_{cr} = 6 - 8 \mu m$ and $H = 2 – 3 \text{ nm}$ (Figure 5.7). Thus, GO-P1 scrolling will take place only if the surface tension force $\gamma$ acting at the junction of receding water meniscus - 2D material – air dominates over strain/elastic forces arising from GO-P1 bending $^{31, 45}$.

![Figure 5.7](image)

**Figure 5.7:** Elastic force as function of GO-P1 sheet size based on Equation 5.8. AFM images showing GO-P1 with different average flake sizes deposited on hydrophobic substrates. The size of the scans is 10x10 $\mu$m² (A, B), 100x100 $\mu$m² (C); Vertical scale: 10 nm (A), 70 nm (B), 600 nm (C). GO-P1 was deposited by dip-coating from water-ethanol mixtures. Red spot corresponds to critical conditions at which crumpling/folding takes place.

Also, the stability of these crumpled formations was tested in the same manner as for the hydrophilic case, and no detachment was observed after intensive ultrasonic
treatment (sample were left in water on a shaker for an hour then sonicated 3 times for 10 minutes, and no changes were observed in the AFM results). The above results suggest that the nanoscrolls were well fixed in the strained state \(^{34,46}\) on the substrate.

Hence, the above results suggest that the scrolling is driven mainly by the capillary forces which depend on the evaporation rate of the solvent \(^{47-49}\). The latter one in turn is associated with the rate of dewetting and ambient temperature \(^{50}\).

**5.3.3: GO-P1 Layers on Hydrophobic Substrates from Water-Ethanol Mixtures**

*Influence of dewetting rate on GO-P1 morphology*

The results presented in Section 5.3.1 suggest that it is challenging to obtain well-defined GO-P1 layers directly on hydrophobic substrate. Specifically, GO-P1 sheets tend to assume crumpled and scrolled conformation when in contact with hydrophobic substrate. As it was shown in previous section, the interplay between surface energies of solvent, GO-P1 sheets and substrate plays a crucial role in crumpling effect. Therefore, another variable to be considered in the formation of GO-monolayers is the solvent in which GO-P1 flakes were dissolved in. In this part of dissertation we investigated the influence of solvent’s conditions (surface tension and temperature) on the ability of GO-P1 sheets to form a monolayer on hydrophobic substrates.

Based on the Equation 5.8 we hypothesized that the addition to water of organic solvents with lower surface tension and much less self-hydrogen-bonding ability (ethanol, methanol or acetone \(^{51}\)) would promote the interaction between the hydrophobic surface and GO-P1 by diminishing water’s free energy of cohesion \(^{52}\). Therefore, ethanol was
introduced into GO-P1 in water solution at: 0%, 10%, 50%, 70% and 100%. Then we performed a deposition of GO-P1 layers on hydrophobic and hydrophilic Si substrates via dip-coating at 300-500 mm/min withdrawal speed and the surface of each sample was scanned using AFM as shown in Figure 5.8.

The results show that instead of increased coverage, there is a pronounced crumpling/scrolling effect already at 10 weight percent of ethanol added (Figure 5.8D), resulting in loosely folded GO-P1 structures on hydrophobic Si (Figure 4 - 5C, D). Next, we found that even the smallest sized sheets scrolled up such that GO-P1 flake could not maintain its planar structure after a contact with hydrophobic silane-SiO$_2$/Si substrates. Next, as the ethanol amount was further increased up to 30% and 70%, no further influence was revealed on the scrolling/folding behavior of GO-P1 sheets (Figure 5.8(D-I)).

![Hydrophilic wafer](image)

![Hydrophobic wafer](image)
In contrast, the use of hydrophilic Si substrates prevented GO-P1 from folding (Figure 5.8(A-C)). Previously, it has been reported that the hydrophobic substrate is indeed favorable for the formation of crumpled and folded graphene 28, 53.

Swelling of P1 layer in water-ethanol by QCM-D

In order to better understand the mechanism of scrolling of GO-P1 sheets we investigated the responsive behavior of P1 grafted layers in the external environment (water-ethanol mixtures). For this, P1 layer was deposited on SiO$_2$/Si substrate (Section 5.2.2) and QCM-D was employed as a tool to monitor real-time changes in film thickness, mass, and viscoelastic properties of solvated P1 layer. Initial thickness of the dry copolymer layer was $h_{\text{dry}} \approx 40$ nm as measured by ellipsometry. The raw data from a typical QCM-D measurement (changes in frequency ($\Delta F$) and dissipation ($\Delta D$)) for the P1-solvent system is displayed in Figure 5.9. As can be seen from the graph, overtone-normalized frequency shows overtone-dependent behavior for all harmonics, which together with the fact that $\Delta D > 0$ indicates a viscoelastic nature of the swollen film 54. Therefore, the above
result imply that the Sauerbrey equation (Equation 5.1) would be invalid for such highly hydrated and viscous surface-grafted polymer layers that result in high dissipation shifts.

Therefore, using the viscoelastic Voigt model and Equation 5.9, thickness and viscosity of swollen P1 layer as a function of ethanol content were found. The solvent content in P1 film for different ethanol-water mixing ratios was estimated by Equation 5.9.

\[
\text{% Solvent Content} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{wet}}} \cdot 100\% 
\]

(5.9)

Figure 5.9: GO-P1 swelling in water-ethanol. QCM-D results showing changes in the 3rd, 5th and 7th harmonic frequencies (blue) and dissipations (red).

Table 5.2 summarizes the values of solvation of different solvent/P1 systems. One can see from Figure 5.10 (A) that the thickness of grafted P1 layer undergoes its minimum of \(~228\) nm at 50\% ethanol content and then reaches maximum value of 254 nm at 100\% ethanol. In contrast, Figure 5.10 (B) demonstrates only gradual deswelling of P1 with the
addition of ethanol. We suggest that the following events take place when ethanol is introduced into the system: (i) initial dehydration is caused by water being expelled out of outermost layers of P1 leading to thickness decrease; (ii) hydrated ethanol associates/clusters get hydrodynamically coupled to the polymer layer, thus increasing its shear viscosity (at 50%); (iii) substitution of water molecules with larger ethanol molecules introduces free volume into P1 layer which increases thickness of the layer at the expense of density ($\rho_{\text{wet}}$) decrease.

**Table 5.2:** QCM-D parameters of solvent/P1 systems.

<table>
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<tr>
<th>Amount of ethanol in water</th>
<th>$m_{\text{dry}}$ [ng/cm$^2$]</th>
<th>$\rho_{\text{dry}}$ [g/cm$^3$]</th>
<th>$h_{\text{dry}}$ [nm]</th>
<th>$\rho_{\text{fluid}}^*$ [g/cm$^3$]</th>
<th>$\eta_{\text{fluid}}^*$ [mPa·s]</th>
<th>$m_{\text{wet}}$ [ng/cm$^2$]</th>
<th>$\rho_{\text{wet}}$ [g/cm$^3$]</th>
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<td>-</td>
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</tr>
<tr>
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<td>-</td>
<td>-</td>
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<td>0.9</td>
<td>23859</td>
<td>1.026</td>
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<tr>
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<td>-</td>
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<td>0.868</td>
<td>2.25</td>
<td>22380</td>
<td>0.926</td>
</tr>
</tbody>
</table>

![Graph A](image1.png) ![Graph B](image2.png)

**Figure 5.10:** QCM-D measurement in **Figure 5.9** modeled using Voigt-based model (A and inset); B: solvent content in P1 film as a function of ethanol concentration.
Another result also shows that shear viscosity (Figure 5.10, inset), obtained by fitting experimental data from Figure 5.9 to Voigt model (see Section 5.2.3), reaches its maximum at 50% of ethanol concentration, implying highly dissipative nature of copolymer layer. This may result from a strong interaction between molecules of water and ethanol leading to the formation of clusters of the hydrated ethanol micelles \(^{55}\) coupled with OEGMA units via hydrogen bonding. It is necessary to point out that viscosity measurements using QCM-D captures only local viscosity in the vicinity of the quartz SiO\(_2\)/Si crystal being coated with copolymer. Therefore, these events may explain why we observed more pronounced scrolling/folding of GO-P1 sheets in the presence of ethanol-water mixtures. Specifically, as more volume is introduced by ethanol molecules P2 chains assume more “loose” conformation due to ethanol being poorer solvent than water (Figure 5.10B). It may lead to higher evaporation rate causing faster dewetting during dipcoating procedure, which in turn creates larger surface stress on GO-P1 sheets, promoting even small size GO-P1 sheets to fold.

To conclude, the addition to water of organic liquids like ethanol creates unfavorable conditions for obtaining a uniform and well-defined GO-P1 monolayer on hydrophobic substrate.

Influence of temperature on GO-P1 morphology

Literature has reported that wrinkles and ripples can be enhanced via thermal manipulation due to the negative thermal expansion coefficient of graphene \(^{56}\). To verify this effect of temperature, we performed dipcoating from 80 °C hot GO-P1 water solution.
The AFM image shown in Figure 5.11 demonstrates heavily shrunk and compressed/warped GO-P1 sheets suggesting that larger temperature-induced capillary compression has been exerted on GO sheets. Surprisingly, crumpled GO sheets self-assembled into short fiber-like structures similar to porous graphene fibers observed by Li et al., which can be associated with intermolecular hydrogen bonds in OEGMA segments as water becomes poor solvent nearing the LCST point of OEGMA.

It is expected that folded graphene oxide structures could constitute a new class of stimuli-responsive materials well suited for drug delivery systems or nanostorage.

5.3.4: Modification of GO Sheets with P2 Copolymer

We showed in the sections above that due to the minor interaction with hydrophobic substrate, flat GO-P1 becomes unstable with increasing lateral dimensions leading to self-fold or scroll. As mechanical structures enter the nanoscale regime, the influence of hydrophobic and van der Waals forces increases. Therefore, there was a need in a new polymer which would improve interaction of GO sheets with hydrophobic surfaces.

In view of this, the statistical copolymer P2 was synthesized in Dr. Luzinov’s laboratory by Dr. Nikolay Borodinov. The copolymer consists of
three different methacrylic monomeric units (reactive via epoxy group and hydrophobic glycidyl methacrylate [GMA], polar oligoethylene glycol methyl ether methacrylate [OEGMA]

responsible for solubility of the P1 in water and hydrophobic lauryl methacrylate [LMA] responsible for hydrophobic interaction between the polymer and low-energy polymeric substrates \(^ {46, 62}\) (Figure 5.12). It is hypothesized that the hydrophobic (Van der Waals) force, enabled by LMA segment, clamps graphene flakes to substrates, and holds together the individual graphene sheets in multilayer fashion. The ability of P2 copolymer (containing hydrophobic LMA) to dissolve in water is essential to the process of surface modification as it opens venues to reduce the use of potentially environmentally hazardous solvents.

We suggest that during the modification of GO with P2, GMA epoxy groups react with (hydroxyl, carboxyl, and epoxy) GO functional groups \(^ {63-64}\). The presence of multiple reactive groups along the polymer chain is needed to ensure that every macromolecule will
form multiple connections with GO surface to form the thin polymer coating enveloping the sheets. Similarly to GO-P1 (as discussed in Chapter 3) the suspension of the GO sheets modified with P2 is stable for a long time (6-8 months). Following the experimental approach described in Chapter 3, structural and morphological properties of the GO-P2 particulates were also thoroughly investigated using AFM, FTIR, XPS, DSC, TGA and Raman.

**5.3.5: Chemical Properties of GO-P2**

The successful attachment of P2 on pristine GO surfaces was confirmed by Fourier transform infrared spectroscopy (FTIR).

![FTIR spectra](image)

**Figure 5.13:** FTIR spectra for: (a) pristine GO, (b) P2 and (c) GO-P2.

As shown in Figure 5.13a, the broad peak at 3320 cm\(^{-1}\) is from O-H groups and two narrow peaks assigned to the carbonyl group (C=O stretching) and the skeletal vibration of unoxidized graphitic domains on GO sheets (aromatic C=C) can be observed at 1720 and 1610 cm\(^{-1}\). The range of 1000-1280 cm\(^{-1}\) corresponds to ethers and/or epoxides groups. For P2 (Figure 5.13b), the C-H stretching group is shown by the peak at 2868 cm\(^{-1}\). The
absorbance peaks at 1725, 1250, 1111 cm\(^{-1}\) can be attributed to carbonyl (C=O), epoxy (C-O-C) and ether (C-O) stretching vibrations. In the spectrum of GO-P2 hybrid (Figure 5.14c) the absorption bands detected at 2873, 1732 and 1250 are the characteristic of the C-H, C=O and C-O-C groups of the grafted P2, respectively 65.

We further confirmed the attachment of the copolymer to the GO surface with XPS (Figure 5.14). As seen from the Figure 5.14B system of GO-P2 showed similar energy peaks to those of GO and GO-P1 (Figure 5.14A) and the amount of oxygen-containing groups (OH) significantly increased as the epoxy decreased, suggesting effective grafting of P2 polymer chains to GO sheets. The C/O ratio was estimated by Equation 3.2 based on the deconvoluted C\textsubscript{1}s peak.

![Graph](image1.png)

**Figure 5.14**: High resolution C\textsubscript{1}s spectra of pristine GO (A) and GO-P2 (B).

### 5.3.6: Thermal Properties of GO-P2

The process of GO modification using water solution of P2 copolymer has been investigated with thermogravimetric analysis, TGA and dynamic scanning calorimetry (DSC). In this section we show that, like P1 copolymer, the P2 copolymer can be readily
grafted to GO surface through the non-condensation reactions of epoxy functional groups with (hydroxyl, carboxy, and epoxy) functional groups located on the GO surface.

**Thermal properties of GO-P2**

The samples were heated to 700 °C at a rate of 15 °C/min in a nitrogen atmosphere. From Figure 5.15, it can be observed that pristine GO is not thermostable: mass loss of GO started below 100 °C, which is attributed to the volatilization of stored water in its π-stacked structure.66

![Figure 5.15: TGA analysis of pristine GO, P2 and GO-P2.](image)

The main weight loss of GO around 200 °C is caused by the decomposition of labile oxygen-containing functional groups yielding CO, CO₂ and H₂O steam 67. The overall weight loss of pristine GO is 44%. The curve of P2 shows a fast weight reduction at 415
°C. The reduction is caused by the decomposition of P2 polymer, leaving about <1% of carbon. As for GO-P2, about 80% weight fraction loss is observed from 200 to 500 °C, which is due to the decomposition of P2 and some oxygen functional groups of GO sheets. From the ratio the GO to P2 and using Equation 3.1 total thickness of P2 layer was estimated to be around 1.8 – 2.0 nm (0.9 – 1 nm on one side of GO sheet).

Kinetics of copolymer adsorption

The kinetic isotherm for P2 attachment to GO is presented in Figure 5.16 (right). Based on TGA curves we found that the adsorption mechanism of P2 copolymer is fast and similar to what was observed earlier for P1 case. Following the equations (3.3) and (3.4) the kinetic parameters were calculated from the non-linear fittings using PFO and PSO models. Since the PSO model provided better fit to experimental data we concluded that the adsorption of P2 on GOs is also governed mostly by chemisorption (Figure 5.16 (right)).
DSC studies of the interaction between the GO and P2

The results from DSC (Figure 5.17) showed that melting peak is largely suppressed, which indicates that the mobility of OEGMA segments in P2 copolymer are restricted, preventing crystallization. Similarly to GO-P1 (see Section 3.3.3) the observed ~9 °C decrease in the melting point of primary peak is due to the significant interaction between the GO sheets and P1 chains. By contrast, an increased phase change temperature will occur when the interaction between polymer chains becomes highly attractive because of hydrogen bonding between side PEG units in free P1 chains.

Figure 5.16: (A) TGA thermograms of GO grafted with P2 as a function of grafting time; (B) Grafted amount of P2 copolymer to GO from water as a function of time.
5.3.7: Morphology of GO-P2 films on Hydrophilic and Hydrophobic Surfaces

Next, we found that the grafting of the copolymers to GO surface, indeed, allows formation of GO monolayers on surfaces of various polarity via the conventional dip-coating from water. As a hydrophilic surface we used chemically cleaned SiO$_2$/Si wafer with 0° water contact angle. In order to mimic the hydrophobic nature of polymeric films and facilitate characterization of GO-P coatings on such surfaces we used Si/SiO$_2$ substrates covered with ~1 nm layer of chlorodimethyl-n-octylsilane (water contact angle ~ 100°). It allowed us to determine true thickness of GO-P2 layers and reveal the morphology of GO-P2 sheets on substrates. Thus, in experiments with pristine (unmodified with the copolymers) GO sheets, we found that it was impossible to obtain a uniform GO monolayer via dip-coating on hydrophilic and hydrophobic surfaces (Figure 5.18A, B). In contrast, individual GO-P2 sheets were uniformly distributed on the surface of both hydrophilic and hydrophobic SiO$_2$ (Figure 5.18C, D). Furthermore, we found that

![Figure 5.17: DSC thermograms for P2 and GO-P2.](image-url)
thickness/structure of GO-P2 layers deposited can be carefully regulated via concentration of the GO sheets in water suspension (Figure 5.18E).

**Figure 5.18**: Atomic force microscopy of pristine graphene oxide deposited on hydrophilic (A) and hydrophobic (B) surface, and GO-P2 on hydrophilic (C) and hydrophobic (D) surface. (E): Hydrophobic silicon wafer dip-coated with GO-P2 using suspension of different concentrations. The size of the scans is 30x30 μm², vertical scale is: 30 nm (A), 2 nm (B), 70 nm (C, D, E). GO was deposited by dip-coating.
Atomic force microscopy has been also used to determine the thickness of individual GO sheet modified with P2.

\[
h = (1.1 \pm 0.1) \text{ nm}
\]

\[
h = (3.3 \pm 0.3) \text{ nm}
\]

\[
h = (2.9 \pm 0.4) \text{ nm}
\]

**Figure 5.19:** AFM images and corresponding cross-sectional profiles showing (A): a pristine GO layer, (B): GO-P2 monolayer on hydrophilic Si substrate and (C): GO-P2 on hydrophobic Si (silane-modified). The size of the scans is 5x5 μm², vertical scale is: 5 nm (A), 10 nm (B, C). GO was deposited by dip-coating.
As indicated by the cross-sectional analysis (Figure 5.19A), the thickness of the pristine GO sheet was on the level of 1 nm, which is comparable to the value typically reported for the GO sheets obtained via Hummer’s method \(^{70-72}\). However, cross-sectional analysis revealed that thickness of pristine GO sheet increased roughly by 1.5 nm (Figure 5.19B). It confirmed that the copolymer layer was indeed anchored to graphene oxide sheets. Also, the height profile of GO-P2 sheets suggested that the P2 polymer chains formed even and dense coating encapsulating the sheets. Figure 5.19C shows GO-P2 sheets on a hydrophobic silane-SiO\(_2\)/Si substrate with its corresponding height profile. Further analysis of AFM images revealed that GO-P2 on hydrophobic substrate tends to be slightly wrinkled in contrast to GO-P1 on hydrophilic substrate. This is why, the same amount of GO-P1 layers may result in higher average thicknesses on hydrophobic substrate. As shown in Figure 5.18E, we can easily control the number of such layers by varying concentration of GO-P2 in water.
5.3.8: Comparative Studies of Interaction of GO-P1 and GO-P2 with the Hydrophobic Interface Using QCM-D

In previous sections we showed that it is possible to obtain a uniform monolayer on hydrophobic substrates using GO modified with P2 copolymer. In contrast, using both pristine GO and GO-P1 we were unable to achieve a well-defined monolayer. Thus, it is important to understand key differences between these materials. The interaction and the subsequent binding of the GO, GO-P1 and GO-P2 flakes to hydrophobic silane-SiO₂/Si surface was analyzed both qualitatively and quantitatively in real time using QCM-D. Figure 5.20 reports typical change in frequency (ΔF) and dissipation (ΔD) data associated with the adsorption of the above-mentioned substances onto the hydrophobic surface. Specifically, pristine GOs revealed no adsorption to the hydrophobic surface as it is evidenced by the very small shift in ΔF value of less than 5 Hz. In contrast, large ΔF shift of about 20-27 Hz for both GO-P1 and GO-P2 is an indicative of a significant adsorption on the surface of the crystal.

Figure 5.20: Real time QCM-D data of the normalized third overtone. Frequency shifts (A) and dissipation shifts (B) for pristine GO, GO-P1 and GO-P2 adsorption to hydrophobic silane-modified SiO₂/Si substrate.
However, the large dissipation shift seen for the adsorption of GO-P1 is in striking contrast to the lack of dissipation shift for GO-P2. This suggests the intrinsically different structure of the adsorbed layers on the hydrophobic surface.

As stated in Section 5.2.5, a reduction in frequency (negative $\Delta F$ value) provides only rough estimate of the mass of adsorbed material. Therefore, qualitative analysis has been carried out by analyzing time-independent dissipation ($\Delta D$) versus frequency ($\Delta F$) curves (Figure 5.21), known as $\Delta D/\Delta F$ or $DF$ plots $^{73-74}$.

![DF plot](image)

Figure 5.21: Typical $\Delta D/\Delta F$ plots of adsorbed GO-P1 and GO-P2 layers on a hydrophobic (silane-modified) SiO$_2$/Si substrate

Changes in $\Delta D/\Delta F$ ratio provided an unambiguous identification of structural differences in surface-adsorbed layers, giving a unique fingerprint of how the conformational state (rigid/nonrigid) of the adsorbed layer evolves with coverage $^6, ^{75}$. Consequently, all the above results imply that the GO-P1 forms less compact structure (larger slope in $DF$ curve), which via internal friction will cause an increase in the energy dissipation $^{76}$. If to consider the hydrophobic interaction as the primary driving force, such behavior is expected to be
energetically favorable for the adsorption of an amphiphilic molecule/particle onto a hydrophobic surface in an aqueous solution (“hydrophobic effect”) \textsuperscript{52}.

**Quantitative analysis of the adsorption**

In our next step, we performed a quantitative analysis by applying viscoelastic model to fit $\Delta D$ and $\Delta F$ values for three overtones ($3$, $5$, $7$) using SmartFit algorithm in QSense Dfind software (license provided by Biolin Scientific AB \textsuperscript{77}). Modeled values of the thickness, shear viscosity and shear elastic modulus for adsorbed GO-P1 and GO-P2 layers were plotted as a function of time and are displayed in Figure 5.22.

![Graph showing modeled QCM-D results for GO-P1 (A) and GO-P2 (B) adsorbed layers. Red dashed line indicates the time when water was introduced.](image)

**Figure 5.22:** Modeled QCM-D results for GO-P1 (A) and GO-P2 (B) adsorbed layers. Red dashed line indicates the time when water was introduced.
We can see from the graphs, QCM-D thickness of adsorbed GO-P1 layer is around 35 nm which is much larger than 3.7 nm of GO-P2 layer. Also, it can be observed that the GO-P2 sheets adsorb in a multilayer fashion which is evident from the step at around 60 minutes. GO-P1 thickness, in contrast, was constant over time of adsorption process.

Equations 5.6, 5.7, and 5.8 were combined and used to estimate the loss angles, \( \tan(\delta_L) \), of adsorbed GO-P1 and GO-P2 films at \( f_0 = 4.95 \) MHz frequency (Figure 5.23). Since \( \tan(\delta_{GO-P1}) = 4.53 \gg \tan(\delta_{GO-P2}) = 0.13 \), we can conclude that GO-P1 is loosely attached to the hydrophobic surface and thus reveals predominantly dissipative and viscous mechanical properties while GO-P2 is rigid and stiff.

To complement the QCM-D measurements, AFM was used to investigate and compare the morphology of GO-P1 and GO-P2 sheets after adsorption on hydrophobic QCM-D quartz crystal surface. Obtained images show that GO-P1 is heavily crumpled and scrolled while GO-P2 is just slightly wrinkled. In addition, we can observe multilayer formations of the latter one.

Figure 5.23: GO-P1 (A) and GO-P2 (B) on silane-modified quartz QCM-D crystal.

5.3.9: Morphology of GO-P2 on Polymeric Surfaces
Besides the positive outcome with GO layers deposition on hydrophobic SiO$_2$/Si substrates we still needed to show that we can achieve the same result on flexible polymeric substrates. As we have hypothesized earlier the formation of GO monolayers on surfaces of various polarity via dip-coating from water will be associated with enhanced hydrophobicity of individual GO flakes through the grafting of amphiphilic P2 copolymer to their surface.

We conducted dip-coating of GO-P2 on pristine Kapton, ultra-high molecular weight polyethylene (UHWPE) and polypropylene films. For instance, it is worth noting that the surface of UHWPE polymer was completely dry after dip-coating step using pristine GO suspension (Figure 5.24 (left)). In contrast, after using GO-P2 suspension the entire surface of UHWPE substrate has been uniformly covered (“wetted”) with GO-P2-water layer, as shown in Figure 5.24 (right). Herein, it was virtually impossible to obtain a GO film via dip-coating on various polymeric surfaces with pristine GO sheets (unmodified with the copolymer). The AFM images revealed the formation of well-defined GO monolayers on the flexible hydrophobic substrates (Figure 5.25 (right)).
The following conclusions can be made as a result of the study reported in Chapter 5:

- The weaker van-der Waals attraction between GO-P1 and hydrophobic substrates allowed GO-P1 to fold and scroll due to molecular interactions with water.

- Crumple formations depend on the original size of the sheet and the compression/capillary forces acting on the GO sheet.

**Figure 5.24:** Photograph UHWPE (125 µm) film dipcoated in pristine GO solution (left) and GO-P2 solution (right).

**Figure 5.25:** AFM images of plain polymeric substrates (left) and polymeric substrates covered with GO-P2 layer (right).

**5.4: Conclusions**

The following conclusions can be made as a result of the study reported in Chapter 5:

- The weaker van-der Waals attraction between GO-P1 and hydrophobic substrates allowed GO-P1 to fold and scroll due to molecular interactions with water.

- Crumple formations depend on the original size of the sheet and the compression/capillary forces acting on the GO sheet.
• Enhanced hydrophobic-hydrophobic interaction allowed to achieve formation of uniform layers on both hydrophilic and hydrophobic surfaces by using more hydrophobic P2 copolymer.

• It was confirmed experimentally that P2 copolymer can be readily grafted to GO surface through the non-condensation reactions of epoxy functional groups with functional groups located on the GO surface.

• On contrary to GO-P1, GO-P2 formed a dense and well-defined monolayer on the hydrophobic surfaces of various polarity (surface coverage > 85 %) as a result of the dip-coating.

• The attraction of GO-P2 and hydrophobic substrate is too strong which prevented GO-P2 sheets from folding.
5.5: References


9. [https://www.biolinscientific.com/qsense/software/](https://www.biolinscientific.com/qsense/software/)


[https://tigerprints.clemson.edu/all_dissertations/1300](https://tigerprints.clemson.edu/all_dissertations/1300)


1/16/2018).


69. Min, X.; Fang, M.; Huang, Z.; Liu, Y. g.; Huang, Y.; Wen, R.; Qian, T.; Wu, X., Enhanced thermal properties of novel shape-stabilized PEG composite phase change
materials with radial mesoporous silica sphere for thermal energy storage. Scientific Reports 2015, 5, 12964.


77. https://www.biolinscientific.com/qsense/software/
CHAPTER SIX

FABRICATION AND CHARACTERIZATION OF ELECTRICALLY CONDUCTIVE rGO FILMS ON FLEXIBLE POLYMERIC SUBSTRATES

6.1: Introduction

It was demonstrated (Chapter 5) that GO-P2 layers can be directly deposited on hydrophobic Si (modified with silane) and polymeric substrates (UHWPE, PP, Kapton). The next question arises: Is it possible to make such GO-covered polymer films electrically conductive? In this part of the work, the results on the study of opto-electrical and mechanical properties of chemically reduced GO-P2 nanoscale multilayers deposited on polymer films are presented. Specifically, we have used the acidic agent, hydroiodic (HI) acid, to efficiently reduce GO-P2 films following the procedure described in Ref. 1. This chapter mainly consists of the two parts: (1) chemically reduced rGO-P2 layers on model hydrophobic Si substrate and (2) rGO-P2 layers on various polymeric substrates.

First, the morphology, structure and composition of rGO-P2 films on model hydrophobic Si substrates were investigated by Raman spectroscopy, XPS, X-ray diffraction (XRD), optical microscopy, SEM and AFM. Second, the morphological properties of rGO-P2 films on flexible substrates were studied by means of optical microscopy, SEM and AFM. In brief, optical microscopy and scanning electron microscopy confirmed that rGO-P2 layers had preserved their integrity and structure on a larger scale upon chemical treatment. In addition, we studied the influence of GO-P2 solution concentration (final layer thickness) on electrical conductivity. We have shown that obtained rGO-P2 films can achieve relatively high electrical conductivity of ~60 S/cm.
after chemical reduction by hydrogen iodine acid \(^1\) on both model hydrophobic Si and polymeric substrates.

In our next step, we investigated the electro-mechanical response and life-cycle durability of rGO-P2 films deposited on various polymeric substrates. To better understand the electro-mechanical behavior of rGO-P2 layers on polymer films we performed bending stress analysis with different radii of curvature based on the Finite Element Analysis (FEA) approach. Finally, we demonstrated the operation of a light emitting diode (LED) in a circuit with a bent and suspended transparent UHWPE film coated with rGO-P2 (rGO/UHWPE) as part of the conductive circuit wiring \(^2\).

6.2: Experimental

6.2.1. Chemical Reduction of GO-P2 layers

The reduction of GO-P2 layers deposited on Si wafer and polymeric substrates was performed by immersion GO films into a 57% HI acid solution for 1 hour in a beaker that

**Figure 6.1.** Schematic representation of the proposed workflow for fabrication of conductive GO-based flexible films. **A)**: deposition of a monolayer of GO sheets enveloped with P2 polymer layer by dip-coating. **B)**: final GO layer on polymeric substrate. **C)**: chemical reduction process. **D)**: rGO-P2 film after chemical reduction.
was placed in a thermostatted oil bath (Figure 6.1).

The temperature of HI acid was maintained at 100 °C. Next, the samples were placed in saturated water solution of sodium bicarbonate to neutralize the residue of acid followed by thorough rinsing with DI water. Finally, stream of ultra-high purity nitrogen has been used to dry samples. It is worth pointing out that HI treated rGO-P2 films partially delaminated from the hydrophobic silicon while their integrity was intact when deposited on polymeric substrates.

6.2.2: Materials Characterization

Raman and XPS (see Sections 3.2.4 and 4.2.2 for more details) were used to study the change in microstructure and chemical composition of rGO-P2 layers after HI reduction. An undoped Si with 2 nm SiO₂ was used as a substrate.

The crystal structure of HI-reduced rGO-P2 film was determined using an Ultima IV, Rigaku Corp. XRD. The diffraction pattern was collected from 10° to 70° at 40 kV beam intensity and scan speed of 1 deg./min. The measurement was conducted by Colin McMillen from Department of Chemistry at Clemson University.

AFM, UV/Vis spectrometer (see Sections 3.2.9 and 4.2.2 for more details), variable pressure scanning electron microscope (SEM) (Hitachi SU-6600, acceleration voltage of 10 kV) and optical microscope (HUVITZ HRM-300) were used as means to investigate morphology, microstructure and measure transparency of rGO-P2 layers. To characterize rGO-P2 layers on polymeric substrates with AFM we used silicon substrate with a thin
adhesive layer as a support to which the specimen was attached. The roughness and thickness of rGO-P2 layers on plastics were analyzed using Gwyddion 2.37 software.

To measure conductivity of the rGO-P2 films on plastics, we used silver paste to form two contacts. Then, the sample with silver paste on top was subject to temperature treatment at 80 °C in ambient for at least 1 hour. For 6 µm thin polypropylene substrate both ends needed to be fixated in order to prevent buckling of the film when silver paste was drying. Current-voltage (I-V) curves were produced using two-point probe configuration described in Section 4.2.1.

6.2.3. Electro-Mechanical Response under Compression/Bending

The electro-mechanical responses and life-cycle durability of all fabricated samples were measured by a home-made testing platform (Figure 6.2). Computer-1 was connected to single-axis microstep motion controller (SMC-series Pollux 3) to program movements of the motion platform. The electrical signals of film under compressive bending were recorded using a digital source meter (BK Precision 5492) and saved into Excel on computer-2. Digital camera has been used to record profile images of bent film.
All measurements were conducted in Dr. Kornev’s laboratory with the help of Dr. Chengzi Zhang and Mark Anayee.

The radius of the film profile at a particular point of bending was defined as the radius of the approximating circle using “Three-Point-Circular ROI” plugin in ImageJ software, as shown in Figure 6.3 (right). In addition, film profile calculations based on Euler-Bernoulli model for beams were conducted by Dr. Arthur Salamatin under the guidance of Prof. K. Kornev. The results of the calculations are described in detail in the Appendix (Figure A13 and Table A4).

Figure 6.2. Home-made testing platform (left) and schematic of the compressive/bending setup (right).

Figure 6.3. Photograph of rGO/Kapton film in flat (left) and bent (right) state.
6.2.4. Electro-Mechanical Response under Tensile Strain

The setup for electromechanical tensile testing is shown in Figure 6.4. The two-point probe measurement configuration was used. Many previous studies emphasized that the geometry of the resistance measurement setup may contribute to the measured resistance\(^{5-6}\).

![Figure 6.4. Schematic of the tensile strain measurement system.](image)

Specifically, contacts should be introduced into the clamps or grips that hold the sample during straining\(^5\). Tensiometer (Instron 1125) with 5000 N load cell has been used.

![Figure 6.5. Photograph of a transparent double-sided rGO/UHWPE film.](image)
In addition, hydraulic grips (15000 psi) with rubberized inner faces were used to prevent slippage of the sample. UHWPE sample with rGO-P2 (~6 nm) film on top and sheet resistance of 2.3 MΩ/sq was selected. Razor-blade was used to cut a rectangular sample with a length of 33 mm and a width of 10 mm (Figure 6.5). Two nickel-plated copper wires were directly attached to the film with the help of Kapton tape at 15 mm separation distance. The initial distance between two Instron’s jaws was 10 mm (gage length), as illustrated in Figure 6.4. The experiment was performed at strain rate of 0.05 (mm/mm)min⁻¹.

It is important to note that all conductive films were coated with rGO on both sides, therefore each specimen has been trimmed from all four sides to make sure that electrical signal is acquired on one side only.

6.2.5. Simulation of Mechanical Stresses using Finite Element Analysis (FEA)

To provide additional insight into the mechanical properties of rGO-P2 layers on polymeric substrates, we performed a finite element analysis of the film/substrate system. The purpose of this study was twofold: (1) to investigate the effect of curvature and substrate thickness on the bending stresses generated in uniform films of rGO-P2 films deposited on PP/Kapton/UHWPE substrates and (2) to find the correlation between the resistance change and bending stresses.

Since our bent films assume very complex meander-like/sine-generated shape upon deformation it becomes increasingly difficult to find the reliable analytical formulae to describe such mechanical behavior. Thus, the finite element analysis (FEA) was used
for mapping field variables such stresses and strains that originate when simulated forces or deformations (compression, bending, stretching, etc.) are applied to modeled system. For this we used commercially available ANSYS APDL 15.0⁹. Each FEA model is discretized into many small pieces – “elements”. Each element has several nodes with finite degree of freedom and analysis is performed for every node. In every case FEA analysis procedure involves several steps: (1) defining the type of problem and choosing appropriate type of element, (2) meshing the analysis model, (3) applying the boundary conditions and loads, (5) solving the problem, and (6) results postprocessing and interpretation.

The element used in the bending stress analysis is Shell 181, which is well suitable for thin-wall structure materials (2D materials)¹⁰¹¹. In our virtual model we used one shell with two layers: polymeric substrate as layer one and rGO as layer two. The polymeric substrate was modeled as isotropic material, whereas rGO film was considered as orthotropic. As the rGO film conforms with the substrate the Poisson’s ratio of the substrate was taken for stress simulations in rGO films. All sample dimensions were the same as in experiment. We used the following parameters for the Kapton film: Young’s modulus of 

\[(2.9 \pm 0.2) \text{ GPa}, \text{ Poisson ratio of 0.34 and thickness of 25 \( \mu \text{m} \)}¹²; \text{ UHWPE: Young’s modulus – (0.6 \pm 0.1) GPa, Poisson ratio - 0.46 and thickness - 125 \( \mu \text{m} \)}¹³. For rGO layer the following parameters were used: \( E_x = E_y = 600 \text{ GPa}, E_z = 80 \text{ GPa}, \) where \( E_x, E_y \) and \( E_z \) – is in-plane and out-of-plane Young’s moduli. Young’s moduli values for substrates were found from slopes of linear portion of stress-strain curves following the AATCC D-882 procedure, as shown in the Appendix (Figure A14). The rGO moduli were estimated basing on Ref.¹⁴ from (using XRD diffractometer) interlayer distance in our rGO films.
(0.41 nm) (Section 6.3.1, Figure 6.11). Poisson ratio was considered to be the same as for graphene (~0.21<sup>15</sup>).

**Figure 6.6** shows the example of FEA simulations for rGO-P2/Kapton (rGO/Kapton) film. According to the simulations, the highest stresses developed in the

![Figure 6.6. The example of FEA simulation. The von Mises stress distribution in rGO-P2/Kapton (rGO/Kapton) film versus curvature.](image)

Kapton film are on the level of 100 MPa which is significantly lower than its tensile strength, 231 MPa<sup>12</sup>. For rGO-P2 on Kapton stresses are in the range of 0.4-20GPa.

**6.2.6. Estimation of Young’s Modulus of rGO-P2 Film**

In order to analyze the stresses in rGO films we need to estimate its elastic modulus. As demonstrated elsewhere<sup>16</sup>, the ideal graphene sheet has its Young’s modulus around 1 TPa. However, this value drastically decreases as graphene gets converted to GO.
Numerous research has been done to determine the elastic properties of GO and rGO layered films. For example, Rioboo et al.\textsuperscript{14} quantified the anisotropic behavior of the elastic modulus of thermally reduced GO few-layer films and confirmed that both out-of-plane/transverse and in-plane/longitudinal elastic moduli are strongly dependent on interlayer GO-GO distances, orientation of GO stacks, film thickness as well as the amount of sp\textsuperscript{3}/oxygen content. As shown in \textsuperscript{14}, an in-plane component of Young’s modulus increases from \(\sim 268\) GPa to \(\sim 620\) GPa as the amount of interlayer spacing decreases from 0.8 to 0.5 nm. Based on our XRD results (Section 6.3.1) and using the approach from Ref.\textsuperscript{14} the Young’s modulus was evaluated to be \(\sim 600\) GPa.

6.3: Results and Discussion

6.3.1: Characterization of Chemically Reduced GO-P2 Films on Hydrophobic Si Substrates

First, we prepared GO-P2 films of different thicknesses on hydrophobic Si wafers with \(\approx 300\) nm SiO\textsubscript{2} using dip-coating deposition method. For this we used solutions with various concentrations of GO-P2 sheets. In our next step, we treated all samples (covered with GO-P2 sheets) with 57% concentrated HI acid for 1 hour to make them electrically conductive (Section 6.2.1). Treatment of GO with HI causes an enormous structural change with the recovery of the conjugated system, through the removal of oxygen containing groups (Section 2.6).

Optical Properties

Optical microscopy offers the potential for rapid, non-destructive characterization of large-area samples. Since Gr is much more conductive than GO it is expected their
optical properties will differ markedly from each other at a certain frequency of light \(^\text{17}\). As a general statement, electrical conductors transmit visible light poorly, while an optically transparent substance cannot be a good conductor of electricity \(^\text{18}\). Typically, graphene and other 2D materials are optically detected and inspected by exploiting the interferometrically enhanced optical contrast obtained on Si substrates containing a submicron layer of silicon dioxide (SiO\(_2\)) \(^{17,19-20}\). The total amplitude of the reflected light is affected by the thicknesses and the optical constants of the GO layer, the dielectric layer and the silicon layer.

Here GO monolayers and multilayers, formed on hydrophobic (silane-modified) Si wafer with an intermediate 300 nm thick SiO\(_2\) layer, were qualitatively identified under white light illumination. We could resolve individual GO flakes much easier when they are deposited on such thick SiO\(_2\) as compare to 2 nm thin SiO\(_2\). \textbf{Figure 6.7} shows rGO-P2 layers, prepared from different concentrations of GO-P2 solutions, after chemical reduction with HI. It is evident that rGO-P2 layers are formed by well-overlapped and uniform network of rGO-P2 sheets, with slightly wrinkled morphology. Additionally, the density and thus the thickness of rGO-P2 network could be controlled by solution concentration.
From AFM cross-sectional profiles, measured across the film edges (Figure 6.5, dashed line), we estimated that the thicknesses of rGO-P2 films on Si are on the level of

**Figure 6.7.** Optical images of rGO-P2 films deposited on 300 nm SiO$_2$/Si wafer. Red scale bar corresponds to 100 µm (left side) and 20 µm (right side)

**Thickness of rGO-P2 films**

From AFM cross-sectional profiles, measured across the film edges (Figure 6.5, dashed line), we estimated that the thicknesses of rGO-P2 films on Si are on the level of
6.5 nm, 5.5 nm, 3.5 and 2 nm for corresponding concentrations of GO-P2 solutions: 0.65, 0.32, 0.16, 0.08 mg/ml, (Figure 6.8). These values were used for electrical conductivity calculations.
It is worth mentioning that we could not reliably measure thickness of rGO-P2 layers by forming a scratch on the surface as it produced significant amount of debris on the borders, as shown in Figure 6.9A.

**Figure 6.9.** A: Optical image of the scratch made on rGO-P2 film deposited on 300 nm SiO₂/Si wafer. Red scale bar corresponds to 50 µm. B: High resolution C1s spectrum of HI reduced rGO-P2 film deposited on silicon.

*Microstructural and compositional analysis of rGO-P2 films by XPS and Raman spectroscopy*

In order to study the chemical composition of GO films and to assess the extent of deoxygenation for films after chemical reduction we carried out the XPS analysis. The XPS C1s detailed spectra and calculated C:O ratios for reduced sample (rGO-P2) is presented in Figure 6.9B. It shows that after the chemical reduction the intensities of all the related oxygen peaks were sharply decreased. The C:O ratio of rGO-P2 film was greatly improved
to approximately 4.8, indicating that the delocalized π conjugation was restored to a significant extent \(^{21-22}\).

Raman spectroscopy is a powerful technique for detecting defects \(^{23-24}\) and the amount of dopants in graphene \(^{25}\). In Chapter 4 we demonstrated that Raman can provide insights into the quality of graphene material. In particular, the \(I_{D}/I_{G}\) ratio along with the positions of D and G bands were used as a measure of aromaticity or crystallite size in rGO-P1 films. However, some studies have shown that traditional methods, which rely upon an apparent G and D peaks, are unreliable for a highly defected Gr and rGO \(^{26}\). Consequently, a new Raman metric for the characterization of graphene oxide and its derivatives has been proposed \(^{26-27}\). Herein we interpreted the Raman by fitting spectra of rGO-P2 layers to four functions ascribed to D, D’, D'' and G bands \(^{23}\). Nonlinear Fit was done in Origin 9.3 (2016) using Lorentzian functions. Figure 6.10 shows the Raman spectra of pristine GO (A), GO-P2 (B), chemically reduced rGO-P2 (C) and thermally reduced rGO-P1 bilayer (D). The D’ peak at \(\sim1620\) cm\(^{-1}\) has been reported for defective graphene (with Csp\(^3\) and structural defects) and its intensity is proportional to the amount of defects and crystallite size. D’’ peak at \(\sim1500\) cm\(^{-1}\) - \(\sim1550\) cm\(^{-1}\) indicates the presence of amorphous phase and its intensity decreases when the crystallinity increases. The blueshift of the maximum position of the D’’ to 1537 cm\(^{-1}\) for GO-P2 after HI reduction is an indicative of oxygen decrease in the system.

To analyze the types of defects (vacancies or sp\(^3\) defects) in rGO-P2 layers the ratio of integrated areas, \(A_{D’}/A_{D}\), has been used \(^{23-24}\). The relative area values are collected in Table 6.1. Calculations showed the \(A_{D’}/A_{D}\) value of 0.14 and \(A_{D’}/A_{D} = 0.4\) for HI-reduced
rGO-P2 and thermally reduced rGO-P1 layers respectively. Consequently, our results seem to indicate that sp³ defects predominate in rGO-P2 while vacancies are favored in rGO-P1.

**Figure 6.10.** Examples of deconvoluted Raman spectra of pristine GO film (A), GO-P2 film (B), HI-reduced rGO-P2 film (C) and thermally reduced rGO-P1 bi-layer film (D). All films were made on undoped Si wafer using drop-casting technique.
The crystallographic structure of the rGO-P2 films was studied by X-ray diffraction (XRD) (Section 6.2.2). The XRD pattern of the sample (Figure 6.11) shows a single broad peak at $2\theta = 21.5^\circ$, corresponding to the (002) diffraction plane\(^{28-29}\). Using Bragg’s law we determined an interlayer distance $d_{002} = 0.41$ nm, while for Gr layers it is $0.34$ nm \(^{30}\).

<table>
<thead>
<tr>
<th></th>
<th>$D$ (cm$^{-1}$)</th>
<th>$D''$ (cm$^{-1}$)</th>
<th>$G$ (cm$^{-1}$)</th>
<th>$D'$ (cm$^{-1}$)</th>
<th>$A_{D'}/A_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine GO</td>
<td>1360</td>
<td>1489</td>
<td>1575</td>
<td>1609</td>
<td>0.22</td>
</tr>
<tr>
<td>GO-P2</td>
<td>1349</td>
<td>1482</td>
<td>1576</td>
<td>1610</td>
<td>0.20</td>
</tr>
<tr>
<td>rGO-P2</td>
<td>1350</td>
<td>1537</td>
<td>1593</td>
<td>1622</td>
<td>0.14</td>
</tr>
<tr>
<td>rGO-P1 bilayer</td>
<td>1361</td>
<td>N/A</td>
<td>1589</td>
<td>1616</td>
<td>0.40</td>
</tr>
</tbody>
</table>

**Table 6.1.** Spectral features from a four-peak fit of the Raman spectra from Figure 6.10.

Crystallographic properties of rGO-P2 layers

The crystallographic structure of the rGO-P2 films was studied by X-ray diffraction (XRD) (Section 6.2.2). The XRD pattern of the sample (Figure 6.11) shows a single broad peak at $2\theta = 21.5^\circ$, corresponding to the (002) diffraction plane\(^{28-29}\). Using Bragg’s law we determined an interlayer distance $d_{002} = 0.41$ nm, while for Gr layers it is $0.34$ nm \(^{30}\).

![XRD diffractogram of HI-reduced rGO-P2 film.](image)

**Figure 6.11.** XRD diffractogram of HI-reduced rGO-P2 film.
6.3.2: Characterization of Chemically Reduced GO-P2 Films on Polymeric Substrates

Film surface structure and morphology: AFM and SEM studies

The results of chemical reduction of GO-P2 layers deposited on UHWPE, PP and Kapton are shown in Figure 6.12 and Figure 6.15 respectively. It is important to investigate the morphology and surface structure of HI reduced GO polymer samples since the morphology of GO sheets/layers on a nanoscale strongly influences its electronic characteristics. The equilibrium morphology of the rGO film is governed mainly by two competing factors which contribute to the minimization of total free energy: (1) graphene-substrate interaction energy (characterized by van der Waals forces) and (2) graphene strain energy. If GO is fully conformal to the substrate (tight binding with the surface of the substrate or high adhesion energy) those two parameters significantly increase as the surface of the substrate becomes more corrugated (high roughness) since the GO sheet will also corrugate to closely follow the substrate surface morphology. On the other hand, when the graphene film is non-conformal the adhesive interaction with the substrate will be very low (low adhesion energy), which is usually the case for multilayer graphene membranes. Therefore, the equilibrium rGO morphology can be determined at the minimum of the total free energy of the system (sum of the rGO strain energy and the rGO-substrate interaction energy).
Thus, we measured RMS roughness for polymer substrates with and without rGO-P2 from AFM images of 15x15 mkm size. \textbf{Figure 6.13} presents AFM images of plain (left) and rGO-P2--covered polymer substrates (right).

\textbf{Figure 6.12.} Photograph of HI-reduced rGO-P2 film deposited on both sides of UHWPE (left), PP (middle) and Kapton (right) substrates.
Plain UHWPE, rms = (79 ± 21) nm

rGO/UHWPE, rms = (71 ± 18) nm

Plain PEEK, rms = (25 ± 4) nm

rGO/PEEK, rms = (26 ± 4) nm

Plain Kapton, rms = (8 ± 2) nm

rGO/Kapton, rms = (6 ± 1) nm

Plain PC, rms = (1.3 ± 0.2)

rGO/PC, rms = (4 ± 1) nm
As seen from AFM images the rGO morphology revealed two distinct states: closely conforming to the substrate surface and remaining nearly flat on the substrate surface as the substrate surface roughness decreases. The above results indicate that our GO-P2 films still retain extreme flexibility allowing it to follow the morphology of the substrates to a large degree, as seen from Figure 6.13(D) (RMS $r_{\text{GO}/\text{PEEK}} \approx 26$ nm). However, we observed from Figure 6.13(B) that rGO film partially conformed to the surface of UHWPE with initial RMS of $(79 \pm 21)$ nm, assuming a corrugated morphology similar to the substrate surface grooves but with a slightly smaller amplitude with RMS = $(71 \pm 18)$ nm. Our experimental results are in good correlation with theoretical calculations presented in Ref. 35. There, authors showed that, if the surface roughness is too large the graphene bending energy increases, leading to an increase in total free energy of the system. In contrast, by partially conforming to the substrate the graphene-substrate interaction energy decreases.

We also used SEM and optical microscopy to characterize the physical properties of rGO-P2 layers at the large scale $> (50 \times 50) \ \mu m^2$. Figure 6.14 (A – L) shows SEM and optical images of rGO-P2 (~ 6 nm) on various polymeric substrates. It can be seen, that rGO-P2 films exhibit good film-forming ability and homogeneous smooth surface on polymer substrates with low surface roughness (PC, Kapton, PP). In addition, rGO-P2 layers are well conformed to the underlying substrate with high roughness (PEEK, UHWPE), which is consistent with the results obtained from AFM studies.

Figure 6.13. AFM images of plain polymeric substrates (all on the left) and polymeric substrates covered with HI-reduced rGO-P2 layer (all on the right). The size of the scans is 15x15 \( \mu \text{m}^2 \), and for Kapton – 10x10 \( \mu \text{m}^2 \). Approximate rGO-P2 layer thickness is $\approx 6$ nm (0.65 mg/ml GO-P2 solution was used for dip-coating).
Plain UHWPE (125 µm)

A

Optical

B

SEM

rGO/UHWPE

Plain Kapton (25 µm)

C

Optical

D

SEM

F

rGO/Kapton

E

G

H
To assess the electrical properties of the chemically reduced rGO-P2 films, we fabricated rGO-P2 films of varying thickness on Kapton polymeric substrate (Figure 6.15). Silver electrodes were made for electrical contact according to the procedure described in Section 6.2.2. Figure 6.16(A) shows the representative I-V characteristics at room temperature for HI-reduced rGO/Kapton samples prepared from different GO-P2 concentrations. At least two different samples have been used to acquire I-V curves. The linear I-V characteristics suggest a good electrical contact between adjacent interconnects.

**Electrical properties of rGO-P2 layers on polymeric substrate**
37, since, otherwise the I-V curve would have an exponential shape. This result clearly indicates that the sheet resistance/conductivity of rGO-P2 films is easily controlled by varying the film thickness which in turn is defined by GO-P2 concentration in water. As shown in Figure 6.16(B), the surface resistance/electrical conductivity decreases/increases rapidly with rGO-P2 layer thickness.

**Figure 6.15.** Photograph of HI-reduced rGO-P2 films deposited on both sides of Kapton substrate.

![Photograph of HI-reduced rGO-P2 films deposited on both sides of Kapton substrate.](image)

**Figure 6.16:** (A): I-V curves acquired under ambient conditions for rGO/Kapton samples. (B): Surface electrical conductivity of rGO-P2 layers on Kapton as a function of thickness. I-V curves represent the average of at least two measurements.
Next, we carried out I-V measurements of rGO-P2 deposited on various polymeric substrates from 0.65 mg/ml GO-P2 solution as shown in Figure 6.17. The distance between electrodes was between 1 and 3 cm. Using thickness values found by means of AFM (Section 6.3.1, Figure 6.8) and sheet resistances calculated from I-V slopes we could estimate the electrical conductivities of rGO-P2 layers (= 6 nm) on plastics. The electrical properties for all samples are listed in Table 6.1.

![Graph of 6nm rGO-P2 on different substrates](image)

**Figure 6.17:** I-V curves acquired under ambient conditions for rGO-P2 layers on different polymeric films

For all the different substrates investigated here, the values of sheet resistance measured in air are typically lower than 135 kΩ/sq, with the best values reaching as low as 28.9 kΩ/sq. Various macroscopic and microscopic defects such as wrinkles, folds, tears, cracks, missing carbon atoms can adversely influence the electric conductivity. However, we
observe that even if the polymer films have a rough surface morphology (Figure 6.12 and 6.13 (UHWPE)) the electrical conductance of rGO-P2 layer remains relatively large and the current vs. voltage characteristics reveal linear behavior as expected for Ohmic conduction or metallic property of rGO-P2 sheets²,⁴⁰.

Table 6.2. Electrical conductivity of rGO-P2 layers deposited on various polymeric films obtained from I-V measurements for ± 4V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distance between electrodes, mm</th>
<th>Normalized Slope, Ohm⁻¹</th>
<th>Sheet resistance, Ohm/sq</th>
<th>Conductivity, S/cm</th>
</tr>
</thead>
<tbody>
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Optical Properties of rGO-P2 layers on polymeric substrates: UV-Vis measurements

To investigate optical properties of rGO-coated polymer films we used UV-Vis spectrometry. The transmittance data T(%) as a function of wavelength for three films are presented in Figure 6.18.

![Figure 6.18](image)

**Figure 6.18**: UV-Vis spectra of double-sided rGO/Kapton (A), rGO/UHWPE (B), rGO/PP (C) and spectrum of single rGO-P2 (6 nm) found as a difference between plain PP and rGO/PP.

It is shown that the produced films were also optically transparent in the visible range. PP, UHWPE and Kapton films with rGO-P2 coatings on both sides demonstrated transmittance of 63 %, 27 % and 50 % respectively (measured at 550 nm), whereas the corresponding
transmittance values for bare films are 89 %, 30 % and 65 %. After subtraction of plain PP absorption spectrum from rGO/PP one, the transmittance of single rGO-PP2 layer (≈ 6 nm) was measured at 84 % at 550 nm. Additionally, we could detect the presence of iodine anions ($I^-_3$) (with adsorption at 291 nm and 369 nm$^4$ besides usual $\pi \rightarrow \pi^*$ transitions of aromatic C=C bonds at 266 nm. In order to quantitatively describe the amount of the residual iodine within the rGO-P2 film we measured XPS I3d$_{5/2}$ spectra (Figure A15 in the Appendix). The results show that the atomic ratio of iodine to carbon (I/C) is less than 0.0022.

6.3.3. Electro-Mechanical Response under Compression/Tensile Bending

Besides electrical conductivity and optical transparency, flexible electrode should possess two important properties – durability and reliability in order to be suitable for practical applications. The devices made of flexible electrodes often work under mechanical stresses caused by tension, bending and twisting. Two parameters should be taken into account when subjecting thin films to mechanical deformations: (i) the maximum strain that thin film can withstand with single loading before failure and (ii) the maximum strain that it can withstand with cyclic loading before failure $^2$, $^{42}$. Thus, the effect of bending on the electrical resistance of the rGO-coated polymer films was studied.

*Electrical properties under bending stress*

Flexural stability of the rGO-P2 (≈ 6 nm) deposited on a commercially available Kapton, UHWPE and PP was tested by measuring the dynamic response of normalized electrical resistance variation ((R – R$_0$)/R$_0$) under both extension (tensile strain) and
compression (compressive strain) conditions of bending (Figure 6.19). The latter ones could be controlled by both the radii of curvature and the thickness of polymeric substrate. FEA simulations were used to determine the value of strain and stress (see Sections 6.2.5 and Figure 6.21 for more details). For both rGO/Kapton and rGO/UHWPE the relative resistance ($\Delta R/R_0$) is found to increase with increasing radius of curvature under tensile strain (Figure 6.19(A, B), black curve), while it decreased under compression (Figure 6.19(A), red curve). Similar behavior was previously reported on graphene-coated PET films and CVD grown graphene layers. The maximum bending strain of rGO-P2 film on Kapton was 3% at radius of curvature $R = 0.36$ mm while on UHWPE the bending strain reached 10% at slightly larger $R = 0.56$ mm. It is worth noting that $((R – R_0)/R_0$ for rGO-P2 film on UHWPE did not return to its original value at the end of experiment. For rGO-P2 film deposited on PP we could not achieve any significant signal response due to low PP thickness ($\approx 6$ µm) which produced strains much lower than 1%.
Two factors may lead to the increase/decrease in the resistance: (a) dimensional change in thickness (decrease/increase) on stretching/compression and (b) non-geometrical effects such as sliding between adjacent flakes which disrupt the overlap areas of GO sheets as discussed in.

Figure 6.19: Relative resistance change as a function of time for rGO-P2 film deposited on Kapton (25 µm) (A) and UHWPE (125 µm) (B). “Time steps” correspond to different bending radii.

Two factors may lead to the increase/decrease in the resistance: (a) dimensional change in thickness (decrease/increase) on stretching/compression and (b) non-geometrical effects such as sliding between adjacent flakes which disrupt the overlap areas of GO sheets as discussed in.
Thus, the results of this section demonstrated that the electrical response (relative resistance change) of rGO-P2 can be precisely modulated by varying the radius of bending and/or underlying substrate’s properties (modulus, thickness). Furthermore, the ability to distinguish between different types of deformations (tensile or compressive) is attractive and promising for practical applications in wearable electronics 44.

rGO/Kapton as a strain sensor

The above results imply that rGO/Kapton film can be used as a strain sensor to reflect both tensile and compressive deformations. Strain sensors are attractive and promising for practical applications in wearable electronics such as the detection of acoustic vibration, electronic skins, wearable monitoring systems 45.

Herein, we investigated the responses in the resistance of rGO/Kapton as a strain sensor at different tensile bending frequencies (0.017 Hz and 0.2 Hz), as shown in Figure 6.20A. The measurements were repeated on the same rGO/Kapton sample under compression over the same strain range and the results are also illustrated in Figure 6.20B.
Figure 6.20: Dynamic response curves of rGO/Kapton film under tensile strain (A) and compressive strain (B).
Similarly to \textsuperscript{43,46}, gauge factor was used to evaluate the sensing performance of the rGO/Kapton sensor and it is defined as $GF = \frac{\delta(\Delta R/R_0)}{\delta \varepsilon}$, where $\varepsilon$ is the strain. The GF was found from the slope of the relative resistance-strain curve shown in Figure 6.21B. Thus, the GF of rGO/Kapton sensor was calculated to be $\sim 3.6$ within 1\% - 3 \% strain, which is in accord with recently reported data in \textsuperscript{44}. As a result, this strain sensor can be used to detect both stretching and compressing deformations with high sensitivity and excellent repeatability.

*Simulation of mechanical stresses and strains using finite element analysis (FEA)*

The stress distributions and strain values in rGO-P2 films deposited on UHWPE and Kapton were estimated with the help of FEA (Figure 6.6). Finally, we obtained a “master-curve” of $R/R_0$ plotted against the strains and von Mises stresses generated in rGO-P2 upon bending (Figure 6.21(B)). The critical/minimal stress in rGO of at least 15 GPa is required to cause 3\% signal change. More details about FEA can be found in Section 6.2.5. Mathematically, the dependence of the relative resistance ($R/R_0$) of the applied strain ($\varepsilon$) can be approximated with the following expression:

$$\frac{R}{R_0} = e^{4\varepsilon + 42.5\varepsilon^2}$$  \hspace{1cm} (6.1)
Thus, using the Equation 6.1 one can predictively estimate the expected signal response of rGO-P2-based sensor provided the information about strain or stress is given.

6.3.4. Electro-mechanical response under tensile strain

It is important for flexible electronic device to not only withstand repetitive flexing/bending but also demonstrate high stability during one-time mechanical stretching. In this section, the maximum strain that chemically reduced rGO-P2 on UHWPE (rGO/UHWPE) can withstand under tensile load has been investigated in situ (in a two-point probe geometry). The schematic and details of the two-point probe resistance measurement setup are presented in Section 6.2.4.
In the elastic regime the growth of the resistance is directly proportional to the strain. When a film starts to deform plastically the ideal curve for the relative electrical resistance satisfies the following equation 5-6:

\[
\frac{R}{R_0} = \left(\frac{L}{L_0}\right)^2 \equiv (1 + \epsilon)^2
\]  

(6.2)

Here \( R \) is the electrical resistance of rGO-P2 film stretched to length \( L \). \( R_0 \) and \( L_0 \) are respectively the initial resistance and distance between the contacts, and \( \epsilon \) is the applied strain. However, the Equation 6.2 becomes invalid when film exhibits substantial structural modifications (cracks, tears) which lead to resistivity or volume changes during the experiment. The failure strain is generally defined as the strain at which the experimental curve deviates from the theoretical curve (Equation 6.2) by more than 5% 6, 47.

Figure 6.22 displays the change of stress (bottom) and resistance (top) of rGO/UHWPE film as a function of uniaxial tensile strain. From Figure 6.22(top) two stages of resistance-

![Figure 6.22: Relative resistance versus relative elongation (top) and stress versus relative elongation (bottom).](image-url)
strain dependency can be identified. In the stage I, the resistance at strains lower than 15% hardly showed any change with respect to applied tensile stress. This could be due to the flattening of wrinkles within rGO/UHWPE film and sliding between adjacent flakes. However, further stretching of the sample over 10-15% (stage II) shows dramatic increase of resistance, which may originate from significant separation distances between individual rGO sheets. A maximum failure strain of 23% was obtained.

The fact that the resistance starts to deviate from theoretical curve at 10-15% tensile strain suggests the initiation of plastic deformation of rGO-P2 film due to loss of its integrity. Therefore, the strains of rGO-P2 larger than ~10% should be avoided in any wearable sensing applications where durable stability is of primary importance.

6.3.5. Life-Cycle Testing

In this section of the dissertation we tested the durability of ~6 nm rGO-P2 layers deposited on three different substrates: UHWPE (thickness of 120 µm), Kapton (25 µm) and PP (6 µm). The samples were subjected to at least 40000 bending cycles with frequencies ranging from 0.5 Hz to 2 Hz and radii of curvature ~0.3-0.5 mm. Using FEA in Section 6 the following tensile strain/strength values ($\Delta L/L_0$) for films bent to the above-mentioned radii of curvature were estimated: 0.6%, 3% and 10% for PP, Kapton and UHWPE respectively.

Figure 6.23 presents the dynamic response curves for three samples during cyclic deformations. We observed very unstable signal with less than 5% change during first 30000 bending cycles for 6 nm rGO-P2 deposited on 6 µm PP (Figure 6.23A). For
rGO/Kapton sample (Figure 6.23C) bent up to 30000 times the relative resistance increased only by 8% with almost complete recovery in about 20 minutes (with 4 % loss in conductivity) (Figure 6.23D). Recent studies have revealed similar trend where the resistance of rGO-P2 recovers to the original value after cyclic deformations due to the reconnection of rGO-P2 sheets upon stress relaxation in polymer substrate.43, 49 Meanwhile, the resistance of rGO-P2 deposited on 120 µm UHWPE changed by more than 200 % (Figure 6.23E) with only 20 % recovery, as shown in Figure 6.23F. Such low recovery may be due to the fact that our rGO/UHWPE film was underwent permanent plastic deformation upon 100000 repetitive bending (Figure 6.23F, inset).
Figure 6.23: Dynamic response curves for three different samples under cyclic bending. rGO/PP (A, B), rGO/Kapton (C, D) and rGO/UHWPE (E, F).
It is obvious that as the applied strain increases up to 10% due to substrate being thicker the contact area of graphene sheets gets significantly reduced leading to a decreased number of conductive pathways and thus an increase in resistance is observed. It is necessary to highlight that these testing conditions are quite severe, since the typical radius into which a circuit can be bent is several millimeters.

Our results indicated that at more practical lower bending frequency and radius of curvature even better performance could be expected for such materials. Nevertheless, in terms of durability our electrically conductive rGO-P2 films are still in the range acceptable for highly flexed devices, as they were able to withstand 100000 bending cycles at 10% tensile load without complete loss of its integrity.

6.3.6. The Overview of Other Potential Applications of Transparent Conductive Films

Flexible and transparent conductive films (TCFs) have broad range of potential applications such as biomedical sensors, electronic paper, displays, photovoltaic cells, electronic textiles, electrochemical devices, super capacitors, wiring. Flexible electronic devices built on such films are more comfortable and cost effective due to being bendable, lighter and smaller. Many of the above applications require electrical conductivities higher than 1000 S/cm, which means our rGO films on polymeric substrates with conductivities in the range of 1 – 100 S/cm do not meet that requirement. However, such types of films may become very effective in lightweight transparent electromagnetic interference (EMI) shields for the radio frequency range in defense and aerospace
applications. For EMI shielding the conductivity should be at least $10^{-3} - 10^{-1}$ S/cm. The EMI shielding is particularly important and very difficult to attain in the areas of visual observation - observation windows, electronic displays. Various transparent materials have been investigated for this role, but the promising and low cost are carbon-based materials, especially in applications where mass should be as low as possible. The fabrication method of EMI shields is based on two approaches the introduction of the conductive material into the polymer matrix or the deposition of conductive coatings to the surface of polymeric substrate. For example, Kim et. al demonstrated that 20 nm thick and 73% transparent (in visible range) rGO film with conductivity of only 12 S/cm exhibited ~ 50% shielding of incident waves. Thus, we expect that our rGO films can be practically used in the above-mentioned applications.

### 6.3.7. rGO/UHWPE as Flexible Transparent Conductor

To further demonstrate the potential usage of rGO-coated polymer substrate as flexible conductor we integrated it in a circuit with light emitting diode (LED) (Figure 6.24). The LED operates well at the same voltage when rGO/UHWPE is in bent or unbent state. The radius of bending was ≈ 5-7 mm.
Therefore, our rGO-P2-covered polymer films could be used as lightweight electrode materials where good mechanical stability and transparency are important.

6.3.8. Towards Conductive Textiles: Coating PP Mesh with rGO-P2

Surface structure and morphology of rGO-PP mesh

In this section of the dissertation we demonstrate that our rGO-P2 nanoscale layers can be integrated into textiles to make porous conductors. For this, we used melt-blown polypropylene mesh (PP-mesh) fabric with 160 kg/m$^3$ density or ~83% porosity. Conductive rGO-PP-mesh material was prepared by dip-coating from 0.65 mg/ml GO-P2 solution and subsequent HI reduction. For practicality, the PP-mesh was not subject to any pretreatment or preliminary rinse with solvents.

The SEM and optical images of PP mesh covered with rGO-P2 sheets (rGO-PP-mesh) are shown in Figure 6.25(A-F). In Figure 6.25(A, B) shows the control PP-mesh with clearly visible interlace fibers whose surface is clean and smooth. After the dip-coating and chemical reduction process, rGO-P2 sheets could be detected, as shown in Figure 6.25(C, F). They appear to be well-deposited on the surface of PP mesh with no visible aggregation. Enlarging to the higher magnification the spiderweb-like structure of rGO-P2 nanosheets attached to the PP fibers can be observed from Figure 6(E, F). These results suggest, that the network of well-overlapped rGO-P2 sheets could result in...

Figure 6.24: Photograph of an electric circuit with LED light, closed with rGO/UHWPE. At least 4V was necessary to light up the LED.
electrically conductive PP textile fabric. In the next section we studied the electrical conductivity of rGO-PP-mesh using two-point probe method.

**Figure 6.25:** Optical (A) and SEM (B) images of plain PP-mesh. Optical (C) and SEM (D – F) images of PP-mesh coated with rGO-P2 on the mesh fiber surface.
Electrical conductivity of rGO-PP mesh

Figure 6.26A shows a conductive fabric rGO-PP-mesh with two contacts made of silver paste. Current vs. voltage (I-V curve) of the rGO-PP-mesh fabric is shown in Figure 6.26B. The I-V curve was measured within the bias voltage range -4 to 4 V at 0.1 V intervals. The electrical conduction conforms to Ohm’s law, as the I-V curve reveals linear behavior. The sheet resistance $R_s$ of $\approx 1.27 \, \text{M}\Omega/\text{sq.}$ was found as an inverse slope (slope = 1/$R_s$) of I-V curve normalized by (W/L) ratio, where W and L are termed as width and length of conductive channel.

Figure 6.26: Plain PP mesh next to conductive rGO-PP-mesh with two silver contacts (A) and I-V curve acquired under ambient conditions (B).

The obtained results indicated that rGO-PP-mesh could be used in applications of electromagnetic interference (EMI) shielding, as shown in Ref. 70. Furthermore, it was
revealed in the next section that rGO-PP-mesh fabric possesses efficient electro-mechanical properties suitable for truly wearable electronics, where repetitive bending/wrinkling often takes place.

Life-cycle testing

To test the electro-mechanical stability of rGO-PP-mesh we performed bending test (Figure 6.27). According to the bending results shown in Figure 6.27 (inset) the relative resistance of rGO-PP-mesh started to decrease rapidly during first ~2000 bending cycles, which can result from tighter overlap/compression between rGO-covered fibers due to tensile strain. However, more research is needed to be done to further understand the linear decrease in signal during 100000 bending cycles.
6.4: Conclusions

The following conclusions can be determined as a result of our study reported in Chapter 6:

- Owing to the van der Waals forces and strong interactions between the films and the plastic substrates, the GO-P2 films were not damaged or detached from the polymeric substrates during the chemical reduction process.
- When rGO-P2 is on the “rough” polymer surface it does not lie flat on top of the target surface, instead it conforms to the morphological features on the surface.

Figure 6.27: Electrical resistance change of the rGO-PP-mesh with repeated cycles of bending.
• Reduced GO-P2 films on thin Kapton and PP substrates exhibited ohmic behavior and high tolerance to flexural deformations.

• The electrical and optical properties of rGO-P2 films can be modulated by varying the concentration of GO-P2 solution during dip-coating step.

• The results demonstrated that our fabricated rGO/Kapton and rGO/PP films had long cycling stability even if bent to extreme radii of curvature.

• New approach for Raman spectra analysis showed a great promise for differentiating the nature of defects in graphene oxide material.
6.5: References


CHAPTER SEVEN

CONCLUSIONS

This chapter is devoted to concluding body of work presented in this dissertation. The study of transparent conductive films based on polymer-encapsulated GO resulted in a number of observations about transparent conductive films. The following major conclusions can be drawn:

- Steric stabilization of individual GO sheets was achieved through its surface modification with P1 copolymer.
- GO-P1 monolayer showed strong adhesion to the SiO₂/Si substrate.
- Highly conductive (up to 10⁴ S/cm) and transparent (~ 90%) rGO-P1 monolayers and bi-layers on non-conductive substrates were produced.
- GO-P1 flakes showed higher level of reduction and carbonization/graphitization in the presence of PAA carbon residue as evidenced from XPS and AFM.
- Enhanced hydrophobic-hydrophobic interaction allowed to achieve formation of uniform layers on both hydrophilic and hydrophobic surfaces by using more hydrophobic P2 copolymer.
- The electrical and optical properties of rGO-P2 films can be modulated by varying the concentration of GO-P2 solution during dip-coating step.
- Reduced GO-P2 films on thin Kapton and PP substrates exhibited ohmic behavior and high tolerance to flexural deformations.
Appendix A

Figure A1. $^1$HNMR spectra of P1 copolymer as received.

NMR has been done by Dr. Nikolay Borodinov.
Surface morphology of GO-P1 and GO-P2 by high resolution AFM studies

To further investigate surface morphology of polymer modified GO flakes we performed a high-resolution AFM of a single GO-P1 and GO-P2 deposited on hydrophilic SiO$_2$ wafer from water and water-methanol mixture in 1:1 ratio using dip-coating and spin-coating. Figure A2 (C, D)) shows that polymer extension or corona of spindles was only observed for films spun from solutions with at least 1:1 water-methanol ratio, while it has not been so for GO-P1/P2 flakes dispersed in water (Figure A2 (E, F)). We could clearly distinguish the individual strands of copolymer protruding out of edges of GO-P1/P2 sheets (Figure A2(C, D)) after spin-coating but not dip-coating. It was demonstrated in Section 5.3.3 that POEGMA copolymer tends to extend in water-alcohol mixtures containing more than 50% alcohol, leading to an increase in apparent thickness.

High resolution AFM imaging has been done by Anise Grant under the guidance of Dr. Tsukruk from Georgia Institute of Technology. The images were captured using a Dimension Icon (Veeco Digital Instruments, Inc.) atomic force microscope in the tapping mode. Silicon tips with a spring constant of 45 N m$^{-1}$, a tip radius of approximately 8 nm, and resonance frequency of 350 kHz that was operated at scanning speed of 1 Hz. The analysis of AFM images was carried out using Nanoscope 1.40r1.
Figure A2. High resolution AFM: height (A, B) and phase images (C, D) of GO-P1 and GO-P2 on hydrophilic SiO$_2$ surface after deposition from water-methanol solution and water solution (E, F). Layers were deposited by spin-coating.
Figure A3. (A): Total free boundary as a function of average sheet size at given percentage of surface coverage for GO-P1 monolayer. (B): Monolayers of different sized GO-P1 sheets on hydrophilic Si substrate.
GO-P1/PAA/GO-P1 on hydrophilic SO₂/Si

Figure A4. Samples after thermal reduction at 1150 °C in Argon. The results illustrate the healing/welding process of rGO-P1/PAA/GO-P1 double layers.
rGO-P1 (Argon)

rGO-P1/PAA (Argon)

rGO-P1/PAA/GO-P1 (Nitrogen)
rGO-P1/PAA/GO-P1 (Argon)

Figure A5. Samples after thermal reduction at 1150 °C in Argon and Nitrogen. The results illustrate the healing/welding process of rGO-P1/PAA/GO-P1 double layers.
Figure A6. Optical image of rGO-P1/PAA/GO-P1 double layer on hydrophilic Si after thermal reduction at 1150°C in Argon.
Figure A7: AFM images and corresponding cross-sectional profiles showing (A): rGO-P1 monolayer and (B): GO-P1/PAA. Samples were thermally annealed/reduced at 1150 °C in Argon atmosphere.
Table A1. XPS data for peak area ratio of each functional group of each sample evaluated by the curve fitting technique with Gaussian-Lorentzian distribution.

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<tr>
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<td>3.7</td>
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<td>(2) C-OH</td>
<td>286</td>
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<tr>
<td>(3) C-C/C=C</td>
<td>285</td>
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<td>(3) C-C/C=C</td>
<td>284.5</td>
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<th>C/O cal.</th>
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<th>Peak Position (eV)</th>
<th>Area</th>
<th>Peak area ratio (%)</th>
<th>C/O cal.</th>
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Figure A8. Characteristic XPS data. (A) High resolution C1s spectra of as-prepared GO-P1/PAA before thermal treatment. (B) High-resolution C1s spectra of rGO-P1/PAA and (C) PAA after thermal reduction at 1150 °C in Argon.
Table A2. Hall mobility measurements for reduced GO monolayer, rGO-P1/PAA and rGO-P1 bilayer films. All samples were thermally reduced at 1150°C in Argon.

### Reduced GO-P1-bilayer

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<th>T(K)</th>
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Rs: 1.291E+03
### Reduced GO-P1/PAA

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<th>RHA</th>
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<th>Vmac</th>
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<tr>
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<td>-103.286</td>
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<td>358.840</td>
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<tr>
<td>364.837</td>
<td>-147.825</td>
<td>-677.652</td>
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| -I:  |      |      |      |       |     |
| 393.927 | 173.974 | 270.206 | 275.872 | 262.646 |
| 215.604 | -122.544 | 118.039 | 115.596 | 121.186 |

| Rs | 8.991E+03 |

**Note:**

The table above represents the experimental data collected for the Reduced GO-P1/PAA study. The columns denote different parameters related to the measurements, including current, resistance, and various coefficients measured under different conditions.
## Reduced GO-P1 monolayer

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<th>D_δ</th>
<th>M_δ</th>
<th>N_δ</th>
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</thead>
<tbody>
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<td>0.100</td>
<td>1000</td>
<td>300</td>
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</table>

<table>
<thead>
<tr>
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<th>rho</th>
<th>RH</th>
<th>RHA</th>
</tr>
</thead>
<tbody>
<tr>
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<table>
<thead>
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<th>V_c</th>
<th>V_m</th>
<th>V_m_δ</th>
<th>V_m_c</th>
<th>V_m_c</th>
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</table>
A  Reduced GO-P1 monolayer

B  Reduced GO-P1/PAA
Figure A9. I-V curves for (A) rGO-P1, (B)rGO-P1/PAA, and (C)rGO-P1/PAA/GO-P1 samples. Films were deposited on hydrophilic Si substrates and subjected to thermal reduction at 1150 °C in Argon.
rGO-P1 monolayer

Current [A] vs Voltage [V]

-4.0 -3.0 -2.0 -1.0 0.0 1.0 2.0 3.0 4.0

RT1 100C 165C 225C 255C RT2

- RT1
- 100C
- 165C
- 225C
- 255C
- RT2

Graph shows the relationship between current and voltage under varying temperatures.
Figure A10. I-V curves for different samples using varying temperatures: Room Temperature (RT), 100, 165, 225, 255 °C.
I-V sweeping cycles were performed to see whether non-linearity would disappear. From Figure A11 it is seen that there is still linear behavior after 10 sweep cycles.

**Figure A11.** I-V sweeping cycles measured at room temperature for rGO-P1/PAA. Sample was reduced at 1150 °C in Argon.
Analysis of Raman Spectra

Also, the most used and most debated approach to quantify the Raman spectrum is the one exploiting the Tuinstra-Koenig (TK) equation $^1$-$^3$, which allows to estimate the average size $L_a$ of the sp$^2$-hybridized C domains in graphene oxide by measuring the ratio $I_D/I_G$ between the D and G peak intensities:

$$L_a (\text{nm}) = (2.4 \times 10^{-10}) \lambda_L^4 (\frac{I_D}{I_G})^{-1}$$

where $\lambda_L$ (nm) is the laser excitation wavelength. The results for all corresponding spectra were tabulated in Table 1. It can be concluded that sheets in rGO/PAA/GO film are comprised of ordered graphitic regions with a size of $\sim$11 nm surrounded by areas of oxidized carbon atoms or point defects $^4$.

Therefore, the Raman results confirm the conclusion derived from the XPS data that the reduction efficiency is lower for GO-P sheets covered with POEGMA.
**Table A3.** Raman characteristics for seven selected samples reduced at 1150 °C in Argon.

<table>
<thead>
<tr>
<th></th>
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<th>GO-P1 monolayer</th>
<th>GO-P1 bilayer</th>
<th>rGO</th>
<th>rGO-P1 monolayer</th>
<th>rGO-P1 bilayer (436 S/cm)</th>
<th>rGO-P1 bilayer (3653 S/cm)</th>
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<td>1359</td>
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<tr>
<td>G (cm⁻¹)</td>
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<td>1594.8</td>
<td>1597.5</td>
<td>1599.1</td>
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<td>1599.2</td>
<td>1603.2</td>
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<tr>
<td>t₀/tₜ</td>
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<td>1.00</td>
<td>1.26</td>
<td>1.14</td>
<td>1.22</td>
<td>1.88</td>
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<tr>
<td>Lₜ (nm)</td>
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<td>16.3</td>
<td>16.7</td>
<td>13.3</td>
<td>14.7</td>
<td>13.8</td>
<td>8.9</td>
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<tr>
<td>2D/(D+G)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Reduced Films (Ar, 1150 °C)</strong></td>
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<td></td>
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<td></td>
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<tr>
<td>D (cm⁻¹)</td>
<td>1359.6</td>
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<td>1343.8</td>
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<td>1603.2</td>
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<tr>
<td>t₀/tₜ</td>
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<td>Lₜ (nm)</td>
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<tr>
<td>2D/(D+G)</td>
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<td>-</td>
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</table>
Figure A12. (b) Raman spectra of selected samples after thermal reduction at 1150 °C in Argon: (1) rGO, (2) rGO-P1 monolayer, (3) rGO-P1/PAA, (4) rGO-P1/PAA/GO-P1 bilayer with low conductivity - 436 S/cm and (5) rGO-P1/PAA/GO-P1 double layer with high conductivity - 3653 S/cm.
Beam Profile Calculations

The composite, originally flat plate, is subject to two-dimensional bending under axial load $P$ and bending couples $M_0$ at its distant ends. The process is two-dimensional, and the Cartesian system of coordinates is introduced with $Z$-axis parallel to the compression force $P$. It goes through the centers of mass of every cross-section, and $X$ and $Y$-axis coincide with the principal axes of inertia of the plate cross-section: they are parallel to the sides of rectangle.

The strained state is described in terms of the Euler-Bernoulli model for beams. In this model the plate is considered as a thin and wide beam of length $L$ with rectangular cross-section of thickness $h$ and width $a$ in the non-deformed state, and the material plane $X = 0$ is called the neutral surface within the two-dimensional bending of Euler-Bernoulli beam. The main model assumption is that every cross-section $Z$ (that is orthogonal to the $Z$-axis) remains orthogonal to the neutral line after deformation. So, every cross-section only rotates around the $Y$-axis on the angle $\theta$ remaining flat, shear deformations are neglected.

The beam strains could be decomposed into the sum of homogeneous strain $u^{(P)}$, caused by axial loading $P$, and inhomogeneous part due to bending of the $u^{(M)}$. Due to inextensibility constraint which defines the position of the neutral line, the total strain component in the $Z$ direction is given as:

$$u = u^{(P)} + u^{(M)} = \frac{P}{ahE_{\text{eff}}} + \kappa(s) x, \quad \kappa = \frac{d\theta}{ds},$$  \hspace{1cm} (1)
where $\kappa$ is the curvature of the neutral line, and $s$ is the arc length along the line. It is attributed to the $z$ coordinate of the undeformed beam. The apparent Young’s modulus $E_{\text{eff}}$ accounts for the inhomogeneity of the two-layered composite beam, and defined as

$$E_{\text{eff}} = \frac{h_1}{h} E_1 + \frac{h_2}{h} E_2, \quad h = h_1 + h_2,$$

where $h_1$ and $h_2$ are thicknesses of plate layers – graphene and lower polymer substrate, and $E_1$ and $E_2$ are their Young’s moduli respectively.

The axial stress $\sigma$ is linear in every layer, but due to isostrain condition implicitly assumed in (1) there is a jump at $X = h_1$ surface, i.e.

$$\sigma = E(x)u = \frac{P}{ah} \frac{E(x)}{E_{\text{eff}}} + \kappa x E(x), \quad E(x) = \begin{cases} E_1, & -h/2 < x < h_1 - h/2; \\ E_2, & h_1 - h/2 < x < h/2. \end{cases}$$

(2)

So, the bending moment around the $Y$-axis in the $s$ cross-section of deformed beam is given as

$$M \equiv a \int_{-h/2}^{h/2} \sigma x dx = \frac{P}{ah E_{\text{eff}}} \int_{-h/2}^{h/2} E(x) x dx + \kappa(s) D, \quad D = \int_{-h/2}^{h/2} E(x) x^2 dx.$$

The first term on the right-hand side of equation is zero for homogeneous material, however in the case of composite beam – it is not. Nevertheless, this term does not depend on cross-section position $s$. The quantity $D$ is the bending stiffness of the beam:

$$D = \int_{-h/2}^{h/2} E(x) x^2 dx = \frac{E_1}{3} \left( (h_1 - h/2)^3 + (h/2)^3 \right) + \frac{E_2}{3} \left( (h/2)^3 - (h_1 - h/2)^3 \right).$$

(*)
For a homogeneous material $D$ is equal to the product of Young’s modulus and moment of inertia with respect to $Y$-axis.

From the free body diagram

$$M(s) = -Pv(s),$$

(3)

where $v(s)$ is the vertical displacement of the neutral surface, and $v'(s) = \sin \theta$. Upon differentiation of Eq. (3) with respect to $s$ the following two-point boundary value problem can be written to determine the neutral line curve of the buckled beam under axial load $P$

$$\frac{d\theta}{ds} = \kappa,$$

(4)

$$D\frac{d\kappa}{ds} = -P\sin \theta,$$

(5)

$$\theta|_{s=0,L} = 0, \quad \kappa|_{s=0} = \kappa_0 > 0,$$

(6)

$$\frac{dX}{ds} = \cos \theta, \quad \frac{dY}{ds} = \sin \theta,$$

(7)

$$X|_{s=0} = X_0, \quad Y|_{s=0} = Y_0,$$

(8)

$$X|_{s=L} = X_0 + \Delta X, \quad Y|_{s=L} = Y_0.$$

(9)

Here the curvature $\kappa_0$ proportional to bending couple at the beam end-points has to be found from the condition that both beam ends are clenched, and $X_0$ and $Y_0$ are the coordinates of the left beam end-point, where $s = 0$. Boundary conditions (9) determine the location of the right, movable, clenched end of the beam. It is assumed that $\Delta X < L$, so the beam end-points come closer.
The problem (4)–(9) is solved numerically, using shooting method. The unknowns parameters \( P(\Delta X, L, D) \) and \( \kappa_0(\Delta X, L, D) \) are determined at the iteration process. Starting with the initial guess for \( P \) and \( \kappa_0 \) for given values of \( X_0, Y_0, \Delta X, L, \) and \( D, \) the right-hand side boundary conditions (6) and (9) are satisfied minimizing the difference between \( \theta(s = L), \) and \( X(s = L) \) and their imposed values \( \theta|_{s=L} = 0, \) and \( \theta|_{s=L} = \Delta X + X_0. \) When two parameters of the beam, \( P \) and \( \kappa_0, \) are determined the parameters \( X_0, Y_0, \Delta X, \) and \( L \) are matched in to order to match the theoretical curve and experimentally observed beam profile. So, every dataset is correlated with respective values of \( P \) and \( \kappa_0 \) which allow to calculate curvature \( \kappa(s) \) at every point, particularly at the symmetry point, \( \kappa_{0.5} = \kappa(s = L/2). \)

Therefore, the distributions of axial components of strain and stress at the central cross-section are given by the following expressions

\[
\begin{align*}
\sigma &= \left( \frac{P}{ahE_{\text{eff}}} + \kappa_{0.5}x \right) E(x), \\
E(x) &= \begin{cases} 
E_1, & -h/2 < x < h_1 - h/2; \\
E_2, & h_1 - h/2 < x < h/2.
\end{cases}
\end{align*}
\]

\( (10) \)

\( \kappa_{0.5} = \kappa(s = L/2) \) – these values can be found in Table A4.

The force \( P \) is calculated as follows:

\[ P = \pi_2 D / L^2, \]

where total length \( L \) and dimensionless complex \( \pi_2 \) are given in Table A4.
Figure A13. Bending of rGO/Kapton film. Results of fitting using Equation 10 derived based on Euler-Bernoulli beam theory. 10 curve profiles at different radii of bending have been modelled.
### Table A4. The results of beam profile calculations.

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<th>Curvature (1/mm)</th>
<th>PI2 (-)</th>
<th>L (mm)</th>
<th>X (mm)</th>
<th>Y (mm)</th>
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<td>6.846</td>
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<td>54.128</td>
<td>6.984</td>
<td>1.215</td>
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The above tensile results presented in Figure A14 suggest that HI-treated Kapton becomes more brittle after chemical reduction with HI acid while mechanical properties of polyethylene do not change.

Figure A14. Instron tensile tests performed on various polymeric films before and after HI-treatment.
Table A5. The results of tensile measurements for polymer films before and after chemical reduction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elongation at Maximum Load (mm/mm)</th>
<th>Tensile stress at Maximum Load (MPa)</th>
<th>Area (cm^2)</th>
<th>Modulus (MPa)</th>
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</thead>
<tbody>
<tr>
<td>Plain Kapton</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#1</td>
<td>0.167</td>
<td>160</td>
<td>0.00250</td>
<td>3055</td>
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<tr>
<td>#2</td>
<td>0.171</td>
<td>166</td>
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<tr>
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<td>119</td>
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<td>3096</td>
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<td>0.00250</td>
<td>2914</td>
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<tr>
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<td>189</td>
<td>0.00263</td>
<td>2798</td>
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<tr>
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<td>0.00011</td>
<td>127</td>
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<td></td>
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<tr>
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<td>576</td>
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<tr>
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<tr>
<td>Mean</td>
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<td>0.01245</td>
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<tr>
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<td>5</td>
<td>0.00026</td>
<td>144</td>
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<tr>
<td>HI-UHWPE</td>
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<td></td>
<td></td>
<td></td>
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<tr>
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Figure A15. XPS survey scan of chemically reduced rGO on silicon substrate.
/NOPR ! Suppress printing of UNDO process
/PMACRO ! Echo following commands to log
FINISH ! Make sure we are at BEGIN level
/CLEAR,NOSTART ! Clear model since no SAVE found
! WE SUGGEST YOU REMOVE THIS LINE AND THE FOLLOWING STARTUP LINES
! WE SUGGEST YOU REMOVE THIS LINE AND THE FOLLOWING STARTUP LINES
! WE SUGGEST YOU REMOVE THIS LINE AND THE FOLLOWING STARTUP LINES
/input,start150,ans,'C:\Program Files\ANSYS Inc\v150\ANSYS\apdl\'
/REPLOT,RESIZE
!*
/NOPR
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KEYW,PR_ELMAG,0
KEYW,MAGNOD,0
KEYW,MAGEDG,0
KEYW,MAGHFE,0
KEYW,MAGELC,0
KEYW,PR_MULTI,0
/GO
!*
!*
/PREP7
!* ET,1,SHELL181
!* KEYOPT,1,1,0
KEYOPT,1,3,0
KEYOPT,1,8,2
KEYOPT,1,9,0
!*
!*
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MPTEMP,1,0
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MPTEMP,1,0
MPDE,EX,1
MPDE,PRXY,1
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MPDATA,PRXY,2,,0.21
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secdata,6e-9,2,0.0,3
secoffset,MID
seccontrol,,,,,,
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K,3,0,01,0.005,0,
K,4,0,0.005,0,
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K,6,0,01,0.00065,0,
K,7,0,01,0.00435,0,
K,8,0,0.00435,0,
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FINISH
/PREP7
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FITEM,2,7
FITEM,2,3
FITEM,2,4
FITEM,2,8
FITEM,2,5
A,PS1X
FINISH
/SOL
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FITEM,2,4
FITEM,2,-6
!*
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FLST,2,3,4,ORDE,3
FITEM,2,1
FITEM,2,-2
FITEM,2,8
!*
/GO
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FITEM,2,-2
FITEM,2,8
!*
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!*
/GO
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!*
/GO
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!*  
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ASEL,,,1
CM,.Y1,AREA
CHKMSH,'AREA'
CMSEL,S,.Y
!*  
AMESH,.Y1
!*  
CMDELE,.Y  
CMDELE,.Y1
CMDELE,.Y2
!*  
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ESEL,,,P51X
CM,.Y1,ELEM
CMSEL,S,.Y  
CMDELE,.Y
!*  
!*  
EREF,.Y1,,,1,0,1,1  
CMDELE,.Y1
!*
APPLICATIONS OF REDUCED GO FILMS: rGO/KAPTON BOLOMETER

Introduction

Due to the increased attention towards the usage of reduced graphene oxide (rGO) in light-sensitive applications we utilize rGO/Kapton to show the possibility for the application for an IR detector. One of the key properties of rGO is to have tunable optical absorption and detection window by controlling the level of its oxidation. One can alter the optical band-gap of rGO between ultraviolet and mid infrared spectral range. Furthermore, large specific surface area of GO offers an effective absorption of the incident photons. Thus, much work has been shifted towards using GO as detector of light, especially in near IR/mid IR range.

There are two main types of detectors: thermal (bolometer) and photonic (photodetector). Bolometers rely on temperature-dependent resistance change and efficient light absorption. Thermal detectors are favored at longer wavelengths and high operating temperatures. Such devices are increasingly important for applications in healthcare, astronomy, smart energy systems, security, automotive, motion tracking. Moreover, bolometers require no cooling to operate at room temperature (RT). Partially reduced graphene oxide has been known to reveal strong bolometric effect, since its residual functional groups actively absorb in near and mid IR. In this chapter we demonstrate the use of rGO/Kapton as bolometer-sensitive material in near-IR range.
Experimental

The schematic diagram of bolometric measurements setup and rGO/Kapton sensor configuration is shown in Figure 7.1. Silver paste was used to attach two nickel-plated copper wires to the sample. As source of irradiation we used green, red and near-IR lasers with power of 0.3 mW, 3.7 mW and 280 mW respectively, placed at a distance of 50 mm above the sample. We used power and energy meter (Scientech 365, provided by Dr. Chumanov) to determine output power of the lasers. The laser beam was aligned perpendicular to the center of rGO/Kapton sensor with the laser spot covering the rGO film and electrode area. Distance between electrodes was $\approx 1.6$ mm and channel width $\approx 5.1$ mm. Initial resistance $R_0 = 70.9 \, \text{k}\Omega$ and room temperature $T_{\text{room}} = 21.3 \, ^\circ\text{C}$. The sample was irradiated with ON/OFF alternative pulses with duration of 2 minutes.

Figure A16: Schematic of the photoresponse measurement setup.
The experiment to determine the temperature dependence of resistance of rGO/Kapton sensor was conducted by keeping the rGO/Kapton sample on a regulated hot plate. The surface of the plate was in full contact with the back side of the Kapton substrate to ensure proper thermal equilibrium between the plate and the sample. Temperature was monitored with thermocouple attached to the plate.

**Results and Discussion**

**Flexible bolometric sensor**

The performance of a bolometer is dependent on various parameters such as IR absorption, temperature coefficient of resistance (TCR), thermal isolation, and noise properties. One of the most important performance indicators for a bolometer is TCR (in units %K$^{-1}$) and it is defined as:

$$TCR(R_0) = \frac{1}{R_0} \frac{dR}{dT} \times 100\%,$$  

(Equation 7.1)

The TCR corresponds to the normalized resistance change per Kelvin around the operating point $R_0$ (Equation 7.1). For instance, typical values of TCR in metallic and semiconducting bolometers are $\sim 0.4 \%K^{-1}$, and $\sim -2 - -4 \%K^{-1}$ respectively, whereas the largest reported value for carbon nanomaterials corresponds to vertically aligned graphene nanosheets with TCR of $\sim 11 \%K^{-1}$. The largest TCR, to date, for reduced GO films has values of approximately $-2$ to $-4 \%K^{-1}$.
In order to evaluate the TCR the temperature dependence of the resistance of this typical device was measured (Figure A17). It was found that the resistance decreased almost linearly with increase in temperature over the temperature range 295 - 483 K, which indicates semiconducting behavior of rGO-P2 films. A similar trend has been reported for PECVD-grown nanographene on quartz 27, reduced graphene oxide on silicon 17 and Kapton 13 substrates. Thus, TCR is found to be -0.42% K^{-1} at 295 K. According to Ref. 28, the negative TCR coefficient originates from the thermal generation of charge carriers, while the slope and shape of the R-T curve are determined by electron and hole scattering and acoustic phonons.

![Figure A17: Resistance as a function of temperature for rGO-P2 on Kapton.](image)
We have analyzed the photoresponse of as prepared rGO-Kapton film to a different white light power densities, since bolometers are often required to measure power of incident light. For this we used halogen fiber optic illuminator (Fiber-Lite Model 190) that emits a broad spectrum, ranging from \( \sim 400 \) to \( \sim 2000 \) nm as reported by the manufacturer.

Similar configuration was used as with lasers, except the sensing surface of the sample was placed at a distance of 10 mm from the light source (the radius of light spot was \( \approx 12 \) mm). The rGO/Kapton bolometer showed a change in resistance up to -2\%, -3\% and -4.5 \% for power density of 0.057 mW/mm\(^2\), 0.094 mW/mm\(^2\) and 0.14 mW/mm\(^2\), respectively (Figure A18A). Based on power-dependent studies we established linear relation between integral power and sensitivity (relative resistance change), which is shown in Figure A18B. To the best of our knowledge such rGO/Kapton bolometric sensor has not been reported yet. Despite not having the greatest TCR and sensitivity, the advantage of our bolometric device lies in the fact that it is transparent, lightweight and it can be easily

**Figure A18:** A: Temporal response of rGO/Kapton at different white light illumination powers. B: Relation between the incident integral power of LED lamp and relative change of resistance.
produced on flexible substrate by dip-coating in large quantities which is viable for practical applications in the mass market. In addition, it can be simultaneously used as a robust strain sensor which we demonstrated before. Rather moderate bolometric response reported here shows the potential of rGO-Kapton films to function as a sensitive element of infrared radiation where excellent mechanical stability is required. If needed, the TCR can be further increased by varying the degree of rGO reduction and rGO film thickness.

Conclusions

The following conclusions can be made as a result of the study presented in Chapter 7:

- Transparent and lightweight bolometric device has been made using rGO/Kapton material.
- Negative TCR coefficient has been found to be -0.42% K⁻¹ at 295 K.
- Linear relation between integral power of irradiation and sensitivity has been established.

Thermally Reduced GO-P2 layers on polymeric substrate

Figure A19: GO-P2 water dispersions at different concentrations and corresponding AFM images
Figure A20: (A) Schematic of reduction (thermal conversion) procedure of GO-P2 on Kapton (termed as GO/Kapton) and (B) GO/Kapton (left) and thermally reduced (@ 370 °C) rGO/Kapton (right).
Figure A21: (A) Thermally reduced (@ 370 °C) rGO/Kapton prepared from different concentrations of GO-P2 solution using dip-coating method. (B) Thermally reduced rGO/Kapton films prepared from Xin = 0.647 mg/ml using multiple dipcoating cycles (number of dipcoating cycles specified by marker).
Morphology of thermally reduced rGO (6nm) on Kapton

Figure A22: SEM images of (A) pristine Kapton film and (B) thermally reduced (@ 370 °C) rGO/Kapton film.
The results from Figure A24 showed that minimum reduction temperature of 370 °C is needed to remove/decompose P2 polymer from GO-P2 structure. Such temperature is low enough not to cause the decomposition of Kapton substrate.

Figure A23: (A) AFM images of thermally reduced (@ 370 °C, Argon) rGO-P2 on hydrophobic Si substrate and (B) thickness of GO-P2 layer as a function of reduction temperature.
Figure A24: GO-P2 films on model hydrophobic Si substrate before (left) and after (right) thermal reduction at 370 °C.
Figure A25: Raman spectrum of GO-P2 film after thermal reduction at 370 °C.
Figure A26: XPS spectrum of GO-P2 film after thermal reduction at 370 °C.
Figure A27: Optical images of GO-P2 film after thermal reduction at different temperatures. GO-P2 film was deposited on hydrophobic (silane-modified) Si substrate with thick SiO$_2$ layer (approx. 300nm) using 0.64 mg/ml GO-P2 solution.
C = 0.32 mg/ml

C = 0.16 mg/ml
Figure A28: SEM images of thermally reduced rGO-P2 films with different concentration of GO sheets.
Electrical conductivity

To assess the electrical properties of the rGO-P2 films on hydrophobic silane-modified substrates, we conducted two-point I-V measurements. We used 2-point probe method, since the channel resistance is sufficiently large therefore the contact resistance to be neglected. Figure X shows the representative I-V characteristics at room temperature for thermally reduced Kapton samples with different rGO film thicknesses. The distance between electrodes was between 1 and 3 cm. An average of 3 independent measurements on 3 different samples has been carried out. Using thickness found by means of AFM we can estimate electrical conductivity.

Figure A29: I-V curves acquired under ambient conditions for rGO-P2 on model hydrophobic Si substrate. All samples were thermally reduced at 370 °C in Argon atmosphere.
Figure A30: (A) I-V curves acquired under ambient conditions for rGO-P2 on Kapton substrates. All samples were thermally reduced at 370 °C in Argon atmosphere. (B) Comparison between electrical conductivities of thermally reduced and chemically reduced GO-P2 films deposited Kapton substrate.
GO-based composites

Electrically conductive composites may become very effective in lightweight transparent electromagnetic interference (EMI) shields for the radio frequency range in defense and aerospace applications. For EMI shielding the conductivity should be at least $10^{-3} - 10^{-1}$ S/cm. The EMI shielding is particularly important and very difficult to attain in the areas of visual observation - observation windows, electronic displays, etc. Various transparent materials have been investigated for this role, but the promising and low cost are carbon-based materials, especially in applications where mass should be as low as possible. The fabrication method of EMI shields is based on two approaches the introduction of the conductive material into the polymer matrix or the deposition of conductive coatings to the surface of polymeric substrate. For example, Kim et al. demonstrated that 20 nm thick and 73% transparent (in visible range) rGO film with conductivity of only 12 S/cm exhibited ~ 50% shielding of incident waves. Thus, we believe that our rGO films can be practically used in the above mentioned applications.

The procedure of the introduction of the conductive material (reduced GO) into the polymer (polypropylene (PP)) matrix is shown in Figure A32(A, B). The approach involves the following steps: (1) GO-P2 layer is deposited on PP film via conventional dipcoating to obtain GO-PP film; (2) GO-PP film is sandwiched inbetween two plain PP films (Figure A32A) to obtain PP/GO-PP/PP triple layer. Finally, PP/GO-PP/PP is placed into home-built steal mold and pressed with weight of at least 10 kg. Then, the mold with samples was placed into preheated oven at 220 °C for at least 2 hours. Slight vacuum was
maintained inside the oven. After annealing, the mold was taken out of the oven and was slowly cooled down to room temperature under ambient conditions.

Figure A31: Preparation of rGO-PP composite material. (A) rGO-covered polypropylene sandwiched between two plain PP films PP/GO-PP/PP. (B) Schematic of the procedure for rGO-PP fabrication. 12 µm-thick PP films were used for composite preparation.
Figure A32: Optical images of (C-G) PP/GO-PP/PP composite films and (H) plain PP film.
Figure A33: DMA testing of 4 layer rGO-PP composites.
Figure A34: MoS$_2$ (left) and MoS$_2$-P2 (right) on model hydrophobic substrate.
Synthesis and Properties of Composite Material for Photocatalysis

Based on Zinc Oxide Nanostructures and Reduced Graphene Oxide Bilayers (Data obtained in collaboration with Dr. Kapustianyk and Dr. Turko)

A promising method of water purification from the organic dyes is photocatalysis based on employment of semiconductor materials. In this respect the most studied and used are the photoactive materials based on TiO₂, WO₃, Zn₂SnO₄ and ZnO. Among them zinc oxide-based catalysts are low cost, stable, non-toxic materials that do not require reactivation. ZnO is a wide-band semiconductor (Eg 3.37 eV) in which electron-hole pairs are generated by ultraviolet illumination. To this end we prepared composite materials from zinc oxide nanorods and reduced graphene oxide (rGO) sheets. Nano- and microstructures of zinc oxide were obtained by hydrothermal methods on the surface of rGO layers.

The photocatalytic properties of ZnO/rGO-based nanocomposites (Figure A36) were tested using photocatalytic degradation of the aqueous solution of methyl orange (MO) dye as a model. ZnO nanostructures were grown on the silicon (001) substrates by two different methods. rGO monolayers were formed by the thermal reduction techniques. The samples and aqueous dye solutions were irradiated using UV light. The source of UV radiation was a DRT-125 Hg-quartz lamp with a radiation power not higher than 26 W in the wavelength range of 315-400 nm. The lamp was warmed up for 10 min before the experiments in order to stabilize its light intensity. Test samples were placed into a standard 3.5 mL quartz cuvette at a distance of 10 cm from the radiation source. The dye photodegradation kinetics was studied by its concentration change, determined with
Specord M-40 spectrophotometer measuring the optical density at the dye absorption maximum (465 nm). The degradation efficiency of MO was calculated using the formula:

\[ C_r = \frac{(C_0 - C_t)}{C_0} \cdot 100\% = \frac{(A_0^{465} - A_t^{465})}{A_0^{465}} \cdot 100\% , \]  

(1)

where \( C_0 \) – is the starting dye concentration; \( C_t \) - the dye concentration after UV irradiation during time \( t \); \( A_t^{465} \) and \( A_0^{465} \) – the dye solution optical densities at 465 nm before and after irradiation during time \( t \).

After one hour of UV irradiation the samples grown by the hydrothermal method on a rGO-P1 monolayer had \( C_r = 85\% \) (Figure A37).
Figure A35: ZnO nanorods grown by hydrothermal method on rGO-P1 mono- and bilayer films.
Thermoresponsive mixed polymer brushes

Introduction

The reported study focuses on the synthesis and characterization of mixed polymer brush platform that can respond to temperature variations. The brush is based on the tethered chains of polyethylene glycol [PEG] and poly(N-isopropylacrylamide) [PNIPAAM]. Specifically, the responsive surface was obtained by sequential grafting of carboxy-terminated PEG and PNIPAAM to a silicon wafer using poly(glycidyl methacrylate) anchoring layer. Quartz microbalance (QCM-D) was used as a primary tool to test the switchability of the brush and its affinity towards protein (fibrinogen) adsorption. Also kinetics of the protein adsorption process and viscoelastic properties of the polymer brush layer was studied by that technique. It is expected that the switchable polymer brush

![Figure A36: The dye photodegradation kinetics](image-url)
platform will have a broad applications in bioengineering, medicine as a tool for the guided
differentiation of stem cells or as a targeted drug delivery system.

**Experimental and materials**

**Grafting**

Firstly, using “grafting to” method we investigated grafting of polymer brushes to the reference surface. Silicon wafers used as model surfaces in our experiments. Highly polished single crystal silicone wafers (Semiconductor Processing Co.) were cleaned in an ultrasonic bath for 30 minutes, placed in a hot “piranha solution” (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for 1 hour and then rinsed several times with high purity water. Next, the surface of the wafers was covered with ultrathin polyglycidyl methacrylate (PGMA) film \((M_n=176000, M_w=640409, \rho=1.08\text{g/cm}^3)\) from 0.05% chloroform solution and subsequently annealed in a vacuum at 120°C for 10 minutes. Unbounded polymer was removed from the surface by multiple washing with chloroform. Then, monocarboxy terminated poly(\(N\)-isopropylacrylamide) (PNIPAM_1x) \((M_n=23000, M_w=26500, PDI=1.15, \rho=1.05\text{g/cm}^3)\) from 1% methylethyl ketone (MEK) solution was grafted to the surface covered with the primary PGMA anchoring layer and also annealed in a vacuum at 150°C for 1 hour. The same procedure was held for the dicarboxy terminated poly(\(N\)-isopropylacrylamide) (PNIPAM_2x) \((M_n=35500, PDI=1.55, \rho=1.05\text{g/cm}^3)\) from 1% methylethyl ketone (MEK) solution. Unbounded polymers were extracted by multiple washing with MEK. Polyethylene glycol (PEG) \((M_n=5000)\) grafting to PGMA anchoring layer was performed from the melt in a vacuum at 110°C. Unbounded PEG was removed from the surface by multiple washing with methanol. The polymer brushes attached to the
surface of PGMA-modified Si-wafers were examined by scanning probe microscopy
(Dimension 3100, Digital Instruments, Inc.) and ellipsometry. The static contact angle
measurements were carried out by goniometer (Kruss, model DSA 10). Secondly, the same
grafting procedure was applied to the SiO₂-coated AT-cut quartz crystals (QSX 303 - 14
mm in diameter with ≈60 nm thick SiO₂ layer on the top of the gold electrode) from Q-
Sense AB. Before grafting, all sensors were treated by UV/ozone for 10 minutes. Next,
sensors were immersed in the 2% Sodium Dodecyl Sulfate (SDS) solution in milliQ water
for 30 min. Then careful rinsing with milliQ water, followed by drying with nitrogen gas
took place. Finally, UV/ozone treatment for 10 minutes was repeated.

Interfacial processes (protein adsorption/desorption) were monitored in situ with
subsecond time resolution. QCM-D measurements were performed with a Q-Sense E1
system (Biolin Scientific AB). The system was operated in flow mode with a flow rate of
100 μL/min (PBS buffer) using a peristaltic pump (ISMATEC, IPC-N). Time-resolved Δf
and ΔD were measured at the fundamental (n = 1) and six overtones (n = 3, 5, ...,13),
corresponding to resonance frequencies of fn ≈ 5, 15, 25, ..., 65 MHz.
Figure A37: Synthesis of mixed polymer brushes.
**QCM-D modelling**

Rigid film

\[ \Delta F = \frac{\eta_L}{2 \pi \delta_L m_q} - F_0 \frac{m_f}{m_q}, \]
\[ \Delta D = \frac{\eta_L}{n \pi \delta_L m_q}, \]
\[ m_f = \rho_f h_f. \]

Viscoelastic film

\[ \Delta D_n / (\Delta F_n / n) < 0.4 \times 10^{-6} \text{ Hz}^{-1} \]

\[ \Delta D_n / (\Delta F_n / n) > 0.4 \times 10^{-6} \text{ Hz}^{-1} \]

\[ \text{DF ratio provides rough estimation of film's intrinsic viscosity} \]

Sauerbrey model

Small load approximation (SLA), Voigt model

\[ \Delta F = - \frac{\eta_L}{2 \pi \delta_L m_q} - F_0 \frac{m_f}{m_q} \left[ 1 - \frac{2}{\rho_f} \left( \frac{\eta_L}{\delta_L} \right)^2 \frac{G''}{G'' + G'''^2} \right], \]
\[ \Delta D = \frac{\eta_L}{n \pi \delta_L m_q} + \frac{m_f}{m_q} \left[ \frac{4}{\rho_f} \left( \frac{\eta_L}{\delta_L} \right)^2 \frac{G'}{G'' + G'''^2} \right], \]
\[ G = G' + iG'', \quad \mu = \mu_L + i \eta_L \]

\( G' \) - shear storage modulus,
\( G'' \) - shear loss modulus
\( m_f \) - mass of deposited film

**Figure A38**: QCM-D modelling principles.
Below viscoelastic modeling of QCM-D data by QTM (SLA model) are presented for the following brushes: PEG+monocarboxy terminated PNIPAM (PEG_PNIPAM_1x, Figure 2), monocarboxy (PNIPAM_1x, Figure 3) and dicarboxy (PNIPAM_2x, Figure 4.) terminated PNIPAM and PEG (Figure 5).

Figure A39: Thickness of thin films grafted to SiO₂/Si substrate as measured by single wavelength ellipsometer.
Table A6: The results of modelling based on small load approximation (SLA) approach.

| Polymer brush       | $G'_0$ (MPa) | $G''_0$ (MPa) | $|G^{-}|$ (MPa) |
|---------------------|--------------|---------------|-----------------|
| PNIPAAM_1x          | 25°C         | 0.51 ± 0.21   | 0.48 ± 0.11     | 0.71 ± 0.23     |
|                     | 37°C         | 0.75 ± 0.18   | 0.73 ± 0.13     | 1.07 ± 0.03     |
| PNIPAAM_2x          | 25°C         | 0.35 ± 0.14   | 0.38 ± 0.07     | 0.53 ± 0.08     |
|                     | 37°C         | 0.76 ± 0.12   | 1.06 ± 0.05     | 1.3 ± 0.07      |
| PEG                 | 25°C         | 0.22          | 0.49            | 0.53            |
|                     | 37°C         | 0.18          | 0.36            | 0.40            |
| PNIPAAM_1x/PEG      | 25°C         | 0.33 ± 0.01   | 0.98 ± 0.45     | 1.04 ± 0.43     |
|                     | 37°C         | 0.29 ± 0.21   | 0.88 ± 0.35     | 0.97 ± 0.23     |
| PNIPAAM_2x/PEG      | 25°C         | 0.52 ± 0.25   | 0.54 ± 0.14     | 0.75 ± 0.26     |
|                     | 37°C         | 0.48 ± 0.23   | 0.45 ± 0.09     | 0.66 ± 0.23     |

Figure A40: The dependency of normalized frequency upon overtone number (n) indicating a viscoelastic nature of grafted polymer brushes.
Figure A41: (A) Thickness change upon brush swelling in water and (B) swelling ratio of homo and mixed polymer brushes during temperature change. “Dry thickness” was found from ellipsometry. The results (A) show good correlation between viscoelastic Voigt and SLA models while Sauerbrey model underestimated thickness of polymer brushes.
Figure A42: PNIPAM homobrush. Adsorption studies of Fibrinogen protein to mixed
**Figure A43:** Relaxation time of Fibrinogen adsorbed onto carboxy-terminated PNIPAM homobrush above LCST (37 °C) and below LCST (25 °C). Higher relaxation time indicates more compact structure/morphology (less dissipative) of the protein or tighter binding with the surface.
Figure A44: PNIPAM/PEG mixed polymer brushes. Adsorption studies of Fibrinogen protein to mixed polymer brushes.
Fabric Modification with Nanocellulosic Fibers as Functional Carriers

Grinded from inexpensive pulp sheets, cellulose powders are processed via high-pressure homogenization, which produces a stable nanocrystalline (NC) hydrogel containing NC fibers. The prepared nanocellulose fibers exhibit a gel-like appearance, which remains stable and shows no signs of phase separation or precipitation after several months.

- **Homogenization Process:**

Grinded from inexpensive pulp sheets, cellulose powders are processed via high-pressure homogenization, which produces a stable NC hydrogel containing NC fibers. The prepared nanocellulose fibers exhibit a gel-like appearance, which remains stable and shows no signs of phase separation or precipitation after several months.

![Figure A45: Manufacturing of NC fiber gel. (a) cellulose pulp sheet, (b) knife mill, (c) homogenizer, and (d) stable hydrogel containing nanocellulose fibers.](image-url)
Nanofibril cellulose (NFC) vs crystalline nanocellulose (CNC):

Main focus of a project: innovative approach to fabric dyeing using nano-cellulose

- Hydroxyl functionalities that can covalently bond with the conventional reactive dye moieties
- CNC does not have adhesive properties due to the absence of hemicellulosic amorphous part

Data provided by Dr. Yucheng Peng
NFC and CNC structure and morphology (AFM studies):

- The surfaces of dried CNC were much smoother than those of NFC, indicating a denser packing for CNC. This is attributed to the much smaller size of cellulose nanocrystals in the suspensions compared with that of NFC.

- **Pad dying process**

NC gel is mixed with reactive dyes and dye auxiliaries, and subsequently applied to cotton fabric by pad dyeing or printing method. Thermal curing at 120°C completes the coloration of cotton fabrics.
NFC test results:

The performance of dyeing is assessed by dye exhaustion and dye fixation:

1) Commercially available reactive red 120 (chemical structure shown in Figure 2a) is selected because of high reactivity with cellulosic fibers.

2) Dye exhaustion is a measure of how many dye molecules are consumed and absorbed to textile fibers during dyeing process, which is determined by the ratio between the absorbance of dyeing solution associated with dye molecule employed before and after dyeing process.

3) Dye fixation is a measure of how many dye molecules are permanently fixed on fabric surfaces during dyeing process, which is determined by the ratio between the color strength of colored fabrics associated with dye molecule employed before and after soaping process.
The performance of dyeing is assessed by dye exhaustion and dye fixation:

- Concentration of dye in effluent during dyeing and rinsing processes is greatly decreased.
- The dye exhaustion and dye fixation for NC-dye-based dyeing surpasses traditional technology due to the high specific area and high chemical reactivity of NC to dyes.

Surface modification of NFC by POEGMA copolymer (type I):
Can we further improve dye fixation and decrease stiffness of the fabric?

- Types of bonding between NFC and POEGMA:
  1) non-condensation reaction btw epoxy and –OH
  2) H-bonding
The disappearing band (11595 cm\textsuperscript{-1}) is related to the absorbed water. After modification with POEGMA those sites become unavailable, thus less water can be bound to NFC.
NFC on cotton fabric

NFC-POEGMA on cotton fabric
NFC-POEGMA test results:

- **Dye Exhaustion**
  - Conventional dyeing
  - NFC-dye
  - NFC-dye-POEGMA

- **Dye Fixation**
  - Conventional dyeing
  - NFC-dye
  - NFC-dye-POEGMA

- **Stiffness**
  - Conventional dyeing
  - NFC-dye
  - NFC-dye-POEGMA

- **Air permeability**
  - Conventional dyeing
  - NFC-dye
  - NFC-dye-POEGMA
### Colofastness to laundering

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### CROCKING test

**NFC**

Before washing

Dry | Wet
---|---
Cotton | Cotton | Cotton | Cotton
Nylon | Nylon | Nylon | Nylon
Polyester | Polyester | Polyester | Polyester

After washing

50 cycles
CROCKING test results

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washing

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Abrasian test

Determination of the abrasion resistance of textile fabrics
Using the rotary platform, double-head tester (RPDH)

Type of wheel used: Calibrase CS-10
Conclusions

- Using NC-dye the performance of dyeing is substantially improved: about 70% of the dye was bound while only 30% was lost.

- All fabrics modified with NFC_POEGMA retain more color even after washing as compare to NFC.

- The experiments demonstrate 100 fold lower rate of waste water as compared with a traditional dyeing technology (1:2 ratio)

- Relatively high stiffness of fabric with NFC-dye-POEGMA is another issue which needs more thorough investigation

Methodology and Experiments

- Modification of NFC with POEGMA (poly oligo ethylene glycol methyl ether methacrylate):
  - Gel of dyed fibril nanocellulose (NFC_red) was diluted 10 times in water and then mixed with 0.5 % PGMA-POEGMA (for polyester - PGMA-POEGMA with slightly less Mw) in DI water in ratio 1:1. After that it was kept at room temperature on orbital shaker at least for 4 hrs to let polymer adsorb to the surface of NFC.
  - All NFC solutions have been centrifuged 3 times before modification and thoroughly rinsed with water to remove all free dye.
  - Each piece of fabric has been soaked in NFC/NFC_P solution for two hours, then roller squeegee at 30 psi of hydraulic pressure were used for pushing excess
solution off the fabric. Afterwards, samples were dried in the oven at 60 °C for 15 min and at 120 °C for 1 hour subsequently.

- **Colorfastness to laundering:** AATCC test method 61, test No. 1A
- **Stiffness test:** Cantilever method (Shirley stiffness tester)
- **Air permeability:** ASTM D737-96
- **Colorfastness to crocking:** AATCC test method 8 (dry and wet crock testing)
- **Abrasion test:** rotary platform, double-head method; ASTM test method D 3884
References


6. Abid; Sehrawat, P.; Islam, S. S.; Mishra, P.; Ahmad, S., Reduced graphene oxide (rGO) based wideband optical sensor and the role of Temperature, Defect States and Quantum Efficiency. Scientific Reports 2018, 8 (1), 3537.


