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Kelvin Probe Force Microscopy on Graphene Thin Films for Solar Cell and Biosensing Applications

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Graduate Program in Physics

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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KELVIN PROBE FORCE MICROSCOPY ON GRAPHENE THIN FILMS FOR SOLAR CELL AND BIOSENSING APPLICATIONS

(Thesis format: Integrated Article)

by

Faranak Sharifi

Graduate Program in Physics

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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The University of Western Ontario
London, Ontario, Canada

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Abstract

Graphene, a one atom thick planar sheet of carbon atoms, has attracted much attention in scientific and technological communities due to its remarkable electronic and physical properties. Graphene has been widely studied as an alternative to transparent conducting indium tin oxide (ITO) electrodes in organic photovoltaics fabrication. Graphene platforms have also attracted interest in biological applications. However, large area graphene films are not yet widely commercialized because the fabrication techniques needed to prepare high quality graphene are expensive and non-scalable. More importantly, most of the low-cost fabrication techniques require using toxic materials, which are not biocompatible for using graphene in bio-applications.

In this work, we have proposed ribonucleic acid (RNA), a nonionic surfactant, for exfoliation of graphite into single and few layered graphene flakes in water solution and the subsequent preparation of transparent and conducting graphene-RNA thin films. A number of pre- and post-deposition treatments were performed to improve the electrical and optical performance of graphene-RNA thin films. We further assembled organic photovoltaics on such graphene electrodes using poly(3-hexyl-thiophene):phenyl-C$_{61}$-butyric acid methyl ester blended photoactive layers. Such photovoltaic devices exhibited high open circuit voltages compared with the reference ITO-based devices. The origin of open circuit voltage was investigated using Kelvin probe force microscopy (KPFM) in the dark and under light irradiation.

In our study, we have also demonstrated the fabrication of photovoltaic devices from cost-effective, water-soluble, and bio-sensitive acridine orange molecules. We investigated the morphology and work function of acridine orange using atomic force microscopy and KPFM. Acridine orange’s ability to generate sufficient amounts of photo carriers was also demonstrated using KPFM under laser irradiation.

To this end, the adhesion of eight proteinogenic amino acids, including arginine (Arg), tryptophan (Trp), histidine (His), lysine (Lys), phenylalanine (Phe), alanine (Ala), asparagine (Asn), and aspartic acid (Asp), on the graphene samples was studied using
KPFM. The adhesion energy was increased in the order of Ala < Asp < Asn < Lys < Phe < His < Trp < Arg. The results were in good agreement with previous theoretical calculations of the van der Waals contributions to the adsorption energies of different amino acids with the graphene surface.

**Key words:**

Co-Authorship Statement

This thesis contains previously published papers. The list of co-authors includes Mr. Reginald Bauld, Mr. Muhammad Shafiq Ahmed, and Dr. Giovanni Fanchini. Faranak Sharifi was supervised by Dr. Giovanni Fanchini over the course of this thesis work. She was the principal investigator and primary author and was responsible for the final revisions of the papers included in Chapters 3 (published in Small 2012) and 5 (published in J. Appl. Phys., 2013). Scientific content and editing of all papers was provided by Dr. Giovanni Fanchini.

Faranak Sharifi was co-author for the publication of the review paper (published in IJMP B, 2012), which was partly used in Chapter 1. Her contribution was the same as that of the first author, who was Mr. Reginal Bauld. The first part of the paper was written by the first author, while the second part, including graphene in organic photovoltaics, was written by her.

In Chapter 3, the Raman spectra of the graphene samples were taken by Dr. Giovanni Fanchini. Mr. Muhammad Shafiq Ahmed and Mr. Reginal Bauld helped Faranak Sharifi to get familiarize with electrical conductivity measurements and atomic force microscopy, respectively. Series and shunt resistances of the acridine orange-based solar cells, presented in Chapter 5, were calculated by an undergraduate student, William Choi, who developed a computer program for such measurements. In Chapter 6, the UV-visible measurements of graphene-amino acids composite samples were performed mainly by an undergraduate student, Edith Yeung.
Acknowledgments

I would like to express my sincere gratitude to my supervisor Dr. Giovanni Fanchini for his continuous support, meticulous suggestions, and astute criticism during my PhD. Dr. Fanchini was always willing to give guidance and his office was always open to anytime discussion about research. Without his help, it was not possible to resolve issues, which always arise in research.

It gives me immense pleasure to thank my advisory committee members, Dr. John R. de Bruyn and Dr. Jeffrey L. Hutter, for their time, precious suggestions and guidance. Many special thanks goes to Dr. John R. de Bruyn for allowing me to use his laboratory equipment, editing the abstract for my presentation in a conference, and writing support letters.

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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>Ala</td>
<td>Alanine</td>
</tr>
<tr>
<td>AM</td>
<td>Air Mass</td>
</tr>
<tr>
<td>AM</td>
<td>Amplitude Modulation</td>
</tr>
<tr>
<td>AO</td>
<td>Acridine Orange</td>
</tr>
<tr>
<td>AO-HH</td>
<td>Acridine Orange Hydrochloride Hydrate</td>
</tr>
<tr>
<td>AO-HZC</td>
<td>Acridine Orange Hemi Zinc Chloride</td>
</tr>
<tr>
<td>Arg</td>
<td>Arginine</td>
</tr>
<tr>
<td>Asn</td>
<td>Asparagine</td>
</tr>
<tr>
<td>Asp</td>
<td>Aspartic acid</td>
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<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>BCP</td>
<td>Bathocuproine</td>
</tr>
<tr>
<td>BEO</td>
<td>Band Energy Offset</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DMF</td>
<td>Dymethylformamid</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic Acid</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-Sensitized Solar Cells</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>d-GIM</td>
<td>dynamic Graphene-Insulator-Metal</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
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<tr>
<td>FTO</td>
<td>Fluorinated Tin Oxide</td>
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<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>FM</td>
<td>Frequency Modulation</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>His</td>
<td>Histidine</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
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<td>KPFM</td>
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<td>LPGE</td>
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<td>LUMO</td>
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<td>Metal-Insulator-Metal</td>
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<td>Molecular Dynamics</td>
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<tr>
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<td>Microcrystalline graphite</td>
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<td>N-methyl-2-pyrrolidone</td>
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<td>n-G</td>
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</tr>
<tr>
<td>OPV</td>
<td>Organic Photovoltaics</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PCBM</td>
<td>Phenyl-C61-butyric acid methyl ester</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly-(ethylene glycol)</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly-3,4-Ethlenedioxythiophene:Polystyrene sulfonate</td>
</tr>
<tr>
<td>Phe</td>
<td>Phenylalanine</td>
</tr>
<tr>
<td>RNA</td>
<td>Ribonucleic Acid</td>
</tr>
<tr>
<td>RGO</td>
<td>Reduced Graphene Oxide</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium dodecylbenzenesulfonate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-Walled Carbon Nanotubes</td>
</tr>
<tr>
<td>SOMO</td>
<td>Singly-Occupied Molecular Orbital</td>
</tr>
<tr>
<td>Trp</td>
<td>Tryptophan</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-Visible Absorption Spectroscopy</td>
</tr>
<tr>
<td>vdW</td>
<td>van der Waals</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction and literature review

Graphene is a two dimensional allotrope of carbon consisting of sp² hybridized carbon atoms arranged in a honeycomb lattice forming a one atom thick planar sheet. It is a building block of graphite, a three-dimensional allotrope of carbon, which consists of stacked layers of graphene weakly coupled by van der Waals forces. The schematic structures of graphene and graphite are shown in Figure 1.1.

![Figure 1.1: The schematic structure of (a) graphene and (b) graphite. Graphite consists of stacked layers of graphene weakly bonded by van der Waals forces, which is represented by solid lines in panel (b) schematically. The Figure was taken from reference [13].](image)

It was thought that two-dimensional crystals are unstable at room temperature [1,2] until Geim and co-workers at Manchester University recognized that they had isolated a single layer graphene in 2004 [3]. Graphene has attracted much attention in scientific and technological communities due to its remarkable electronic and physical properties [4-6]. It has high transparency across the light spectrum from visible to the IR range [7], excellent electron mobility, high mechanical flexibility, and remarkable thermal conductivity. These properties make graphene a unique and suitable option for a variety of applications, including solar cells [8, 9], field-effect transistors [10], energy storage
[11] and biotechnology [12]. In this chapter, various fabrication methods and fundamental properties of graphene thin films, the application of graphene in organic photovoltaics, and graphene-biomolecule composites will be reviewed.

### 1.1-Fabrication of Graphene Thin Films

Graphene is not yet widely commercialized because the fabrication techniques needed to prepare high quality graphene are expensive, non-scalable, and are not highly reproducible [14]. The Manchester group successfully isolated single layer graphene by mechanical exfoliation of highly oriented pyrolytic graphite (HOPG) using common cellophane tape to remove layers of graphite flakes from the bulk of the HOPG as shown in Figure 1.2 [15-17]. The tape is then pressed onto a target substrate and subsequently peeled off of that substrate. The van der Waals interaction between the graphitic flakes and the target substrate helps to adhere single and layered graphene flakes to the substrate when the tape is removed.

**Figure 1.2:** (a) Fabrication of graphene flakes by mechanical exfoliation using regular cellophane tape. (b) and (c) show the atomic force microscopy and the transmission electron microscopy of the isolated graphene flakes. (Figures 1.2a and 1.2c are reprinted by permission from Macmillan Publishers Ltd: *Nature* [17, 18], copyright (2012) and (2007). Figure 1.2b is reprinted from *PNAS*, “Two-dimensional atomic crystals” [16], Copyright (2005) *National Academy of Sciences, U.S.A.*
Although the method is simple to apply to prepare high quality graphene flakes, it needs a great deal of patience, luck, and experience to deposit a single layer graphene. Moreover, this method does not lead to high-throughput preparation of large-scale graphene films covered continuously by graphene flakes. A number of more sophisticated approaches, including chemical vapor deposition (CVD) and chemical efforts for liquid phase graphene exfoliation (LPGE), have been proposed to fabricate large-area graphene films. These approaches, along with their pros and cons, will be discussed in the following sections.

### 1.1.1- Chemical Vapor Deposition

CVD grown graphene, on Ni and Cu substrates, was first reported in 2008 [19, 20]. In the CVD process, a metal substrate is heated to around 1000 °C in a vacuum and exposed to a mixture of CH$_4$/H$_2$ hydrocarbon gases. The hydrocarbon gases decompose into carbon radicals at the surface of the metal substrate. Depending on the carbon solubility of the metal substrate, the carbon radicals can either deposit onto the surface of the substrates through chemical adsorption, or diffuse into the metal substrate. Subsequently, the substrate cools down, leading to a reduction in the solubility of carbon in the substrate, and carbon atoms from the metal substrate diffuse and precipitate onto the metal surface. The cooling process then causes the crystallization of the carbon atoms at the surface, which leads to the formation of single layer and few-layers graphene [21]. It is worth mentioning that only metal substrates for which carbon radicals can create chemical bonding can be used to grow graphene. Figure 1.3a shows the schematic of the CVD process.

As shown schematically in Figure 1.3b, graphene grown by CVD can be transferred to any desired substrate by removing the catalytic metal substrate. Once graphene grows on a substrate, different types of polymers, such as polymethyl methacrylate, can be spin coated on the graphene surface to support it and the metal substrate is then etched away. This leaves a graphene layer coated by the polymer layer that can be transferred to any targeting substrate. Once it is positioned on the substrate, the polymer layer is etched by solvents, such as acetone, leaving behind a graphene layer [21]. A 1×1 cm$^2$ graphene
region, grown on Cu foil, has been reported by Ruff et al., and showed more than 95% monolayer graphene flakes with a small fraction of bilayer (~ 3 to 4%) and few layer (<1%) graphene regions [20].

So far, CVD has the greatest success in preparing large area high quality graphene films, and the size of the grown graphene is limited only by the sizes of the substrate and vacuum chamber. The quality and thickness of the grown graphene flakes are extremely dependent on the experimental parameters, including temperature, cooling rate, concentration of hydrocarbon gas, and growth time [19, 21]. Experimental parameters require fine adjustments to control the growth without seeding an additional second layer. Moreover, the microstructure and crystallinity of the substrate affect the quality and formation of graphene morphology [21]. These experimental difficulties in the fabrication method make the CVD technique difficult to implement. In addition, the necessity of a vacuum chamber limits the CVD method as a scalable and cost effective technique for mass production and commercialization of graphene thin films.
1.1.2- Liquid Phase Graphene Exfoliation

Liquid phase graphene exfoliation is based on the exfoliation of graphite and stabilization of the exfoliated graphene flakes in a solution environment. The theory of the stabilization of graphene in a solution has taken advantage of similar models previously used for describing the dispersion of carbon nanotubes in liquids [22, 23]. The stabilization of the dispersed graphene flakes in liquid is based on two different mechanisms, electrostatic stabilization and steric stabilization. In the electrostatic stabilization mechanism, low surface energy at the graphene-liquid interface is essential to compensate the van der Waals interaction between graphene flakes and thus prevent graphene flakes from re-aggregation, which leads to the creation of a stable graphene-liquid dispersion. In the case of steric stabilization, the presence of the steric barrier between the dispersed graphene flakes is responsible for the stability of the dispersed graphene. It is worth noting that, depending on the type of the liquid phase exfoliation and the material used, either one or both of the stabilization mechanisms can occur.

Several approaches to prepare dispersed graphene flakes in a liquid phase have been reported, including oxidation-reduction of the graphene oxide, surfactant free liquid phase exfoliation using organic solvents, and surfactant assisted liquid phase exfoliation, all of which are explained below.

1.1.2.1- Oxidation-Reduction of Graphene Oxide

Ruoff’s group established the solution-based exfoliation process for the first time to produce single layer graphene flakes in 2007 [24]. The method is based on a chemical modification of graphite to produce graphite oxide and a further exfoliation of the graphite oxide to graphene oxide (GO) layers, which are soluble and dispersible in water. The schematic of the oxidation-reduction process is shown in Figure 1.4. GO is prepared most often by the Hummer method [25]. In this method, graphite is oxidized using potassium permanganate (KMnO₄) and sulfuric acid (H₂SO₄). The resulting graphite oxide is then dispersed in water by mild ultrasonication and finally the yellow solution of GO flakes appears and can be used for the preparation of GO thin films. GO contains different oxygen functional groups, including hydroxyl and epoxy functional groups in
the basal plane and carbonyl and carboxyl groups at the sheet edge due to the oxidation process [26]. These functional groups reduce the interlayer interaction of GO layers by increasing their distance to 0.7 nm in oxidized graphite from 0.35 nm in graphite, which improves the exfoliation process [26]. In addition, oxygen functional groups make GO extremely hydrophilic, which leads to the efficient dispersion of GO in water and prevents re-aggregation of GO flakes [26].

**Figure 1.4**: Schematic diagram of the oxidation-reduction process. The blue and red parts determine the various oxygen functional groups introduced to the graphite during the oxidation process. These functional groups will remove partially through the reduction process as shown schematically. (Figure is reprinted from *Advanced Materials*: “Functional Composite Materials Based on Chemically Converted Graphene” [28], Copyright (2011), WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)
The C-O bonds due to the additional functional groups in GO are covalent and disrupt the sp² conjugation of the hexagonal graphene lattice. This affects the electronic properties of graphene and makes GO an insulator. Therefore, GO needs to be reduced to improve its electrical conductivity for various applications. The reduction of GO can be done with various methods, including exposure of GO to chemical reducing agents, such as hydrazine hydrate or dimethylhydrazine, and thermal treatment under inert atmosphere [27]. The reduction process partially removes the covalent sp³ bonded of O and OH functional groups and restores the delocalized sp² carbons, which leads to improved electrical conductivity in the Reduced Graphene Oxide (RGO) films. Mattevi et al. reported that sp² carbons can be recovered up to 80% in RGO films after exposure to hydrazine vapor and thermal treatment up to 1000 °C [26]. Although these reduction treatments improve the electrical conductivity of RGO films by recovering the delocalized sp² carbons, their electrical transport properties are not yet the same as pristine graphene [26]. The reduction process cannot recover all the defects introduced into the RGO through the oxidation process [24]. These defects disrupt the electronic properties of graphene and reduce the mobility of charge carriers by acting as scattering centers, which results in changes in the ideal ballistic transport of pristine graphene [5].

Although the oxidation-reduction process is destructive due to the defects introduced into the graphene lattice during the oxidation process, it is still an attractive method due to its high concentration dispersion yield, as high as 7 mg/ml [29], possibility for mass production, low expense, and easy process. It is worth mentioning that a less destructive oxidation method has also been reported by Li et al. [30], which involves a weaker oxidation process compared with the Hummer method. In this method, graphite is partially oxidized and ultrasonicated in dymethylformamid (DMF). While the milder oxidation process reduces the defect density in GO flakes, the use of DMF as a solvent, which is known as a toxic material, is not beneficial in comparison to water.

1.1.2.2- Surfactant Free LPGE Using Organic Solvents

The limitations of the GO exfoliation and reduction method led to the introduction of simpler and less destructive routes to prepare dispersed graphene in solutions, including
the exfoliation of graphite in organic solvents by the assistance of ultrasounds [31]. In this process, graphite powder is first dispersed in an organic solvent. Shear forces and cavitation due to pressure fluctuations in the solvent during the ultrasonication process induce exfoliation and create graphene flakes [31]. The schematic process of this is shown in Figure 1.5a. The process is followed by centrifugation to separate single and few layer graphene flakes from thicker and heavier graphitic layers.

**Figure 1.5:** Schematic of liquid phase graphene exfoliation (a) in the absence and (b) in the presence of surfactants. (Figure is reproduced from reference [31] with permission of *The Royal Society of Chemistry*.)

Such exfoliation requires a close match between the surface tension of graphene and the solvent to minimize the surface tension of the graphene-liquid interface and overcome the
interlayer interaction of graphene layers [31, 32]. Hernandez et al. investigated the surface tension of the ideal solvents for the exfoliation of graphite by considering the concentration of dispersed graphene flakes as a function of solvent surface tension in a variety of different solvents. They found that the highest concentration of dispersed graphene can be achieved when the surface tension of the solvents is in the range of approximately 40-50 mJ/m$^2$ [32], which is sufficiently close to the literature values of the graphite surface tension with the same range of 40-50 mJ/m$^2$ [33, 34]. Therefore, it has been suggested by Hernandez et al. that the ideal solvents for the efficient exfoliation of graphite may have a surface tension of $\approx$ 40-50 mJ/m$^2$ [31]. For instance, it has been reported that $N$-methyl-2-pyrrolidone (NMP – with a surface tension of $\gamma \approx$ 40 mJ/m$^2$) and $N,N$-dimethylformamide (DMF – $\gamma \approx$ 37.1 mJ/m$^2$) can successfully exfoliate graphite to prepare dispersed graphene flakes [31, 32]; however, these solvents are known as toxic materials. Therefore, several alternative solvents have been used by different research groups; for instance, Bourlinos et al. used a range of perfluorinated aromatic molecules. Their highest achievements for concentration yield of graphene flakes was reported to be 0.1 mg/mL [35]. The average flake thickness was estimated by atomic force microscopy (AFM) to be between 0.6 and 2 nm, which verified the presence of few layer graphene flakes.

Increasing the sonication time has been shown to improve the concentration of graphene dispersion [31]; however, the concentration is still lower than the GO oxidation-reduction method. More importantly the longer sonication time reduces the size of the graphene flakes, which then has implications on the conductivity of graphene films prepared by these smaller graphene flakes. Smaller flake sizes mean more flakes are required to cover a given area, which leads to the presence of more grain boundaries and hence a higher resultant sheet resistance. This is not favorable for many applications of graphene, specifically in organic electronics.

The most suitable solvents with the closest surface tension to the optimized values of $\gamma \approx$ 40-50 mJ/m$^2$ have a high boiling point. For instance, the boiling points for NMP and DMF are 203 °C and 154 °C, respectively [31]. The high boiling point results in retaining the solvent in the graphene films prepared by the graphene flakes dispersed in such
solvents. The remnant solvent on the graphene films is detrimental for applications of graphene thin films since it may alter the transport and morphological properties of the graphene films. It is preferable to exfoliate graphite and disperse graphene in a water solution, but the surface tension of water (72.8 mJ/m²) is unsuitable considering the above-mentioned optimized surface tension. This limits the direct exfoliation and dispersion processes, and thus additional materials, such as surfactants, need to assist the process. It is also worth mentioning that surfactants have advantages in the dispersion process by covering the dispersed graphene flakes and preventing them from re-aggregation. The surfactant assisted liquid phase graphene exfoliation is explained in the next section.

1.1.2.3- Surfactant Assisted LPGE

The procedure of surfactant assisted LPGE is similar to the surfactant free LPGE as it also includes three steps: exfoliation, ultrasonication, and centrifugation. Surfactants promote the exfoliation process specifically when their adsorption energies to graphene are higher than those of the solvent molecules to the graphene surface [31]. They also enhance the stabilization of exfoliated graphene flakes in the solution by covering the surface of the graphene flakes, which prevents their aggregation, as can be seen in Figure 1.5b. There are different types of surfactants, including ionic and non-ionic surfactants with different stabilization mechanisms. Ionic surfactants can provide both electrostatic and steric repulsion, between covered graphene flakes by surfactants, and prevent them from aggregation. In the case of non-ionic surfactants, the presence of nonelectrical steric barriers between the graphene flakes covered by surfactants stabilizes the graphene flakes in the solution.

Exfoliation and dispersion of graphene in water is challenging because the surface tension of water is unsuitable, as mentioned in Section 1.1.2.2. Using surfactants appears to be the only possible way to exfoliate and disperse pristine graphene in water. Lotya et al. used sodium dodecylbenzenesulfonate (SDBS) as an ionic surfactant for efficient graphene exfoliation and dispersion [22]. Using transmission electron microscopy observations, they reported that ~ 43% of the flakes were < 5 layers with 3% of single
layer graphene flakes. The population of few layer graphene was further increased by recycling the sedimentation remaining from centrifugation. This decreased the flake thicknesses with 67% of flakes having <5 layers along with large quantities of bilayers and trilayers. Varieties of ionic and non-ionic surfactants have also been investigated by Guardia et al. for exfoliation and stabilization of graphene in water [36]. They reported a high concentration of dispersed graphene flakes in water, as high as 0.9 mg/mL, using the Pluronic P-123 nonionic surfactant. This is superior to the concentration of dispersed graphene flakes, < 0.1 mg/mL, using SDBS as the ionic surfactant with similar experimental preparation conditions as Pluronic P-123 [36]. The AFM characterization reported by Guardia et al. revealed that ~10-15% of the flakes are single layer graphene, while the rest of them are few layer graphene flakes with up to 5 layers. In their investigations using varieties of ionic and non-ionic surfactants, they found that the non-ionic surfactants generally perform better than the ionic ones in preparation of graphene dispersion in water. This is attributed by the authors to the higher suspending ability of non-ionic surfactants compared with the ionic ones for graphene flakes, which suggests that steric repulsion is more efficient than electrostatic repulsion in the stabilization of graphene sheets in water [36]. It is worth mentioning that, although steric repulsion can also occur in the presence of ionic surfactants, their effect on the stabilization mechanism compared with the non-ionic surfactants is strongly related to their chemical structure. For instance, longer hydrophilic chains in Pluronic P-123 consisting of polyethylene oxide compared with SDBS enhance the steric stabilization [36].

The ability to prepare graphene suspended in water using non-ionic surfactants led us to utilize ribonucleic acid (RNA) as a non-ionic and biological surfactant to exfoliate and disperse graphene in water. This work will be discussed in detail in Chapter 3 [37].

The greatest disadvantage of the surfactant assisted LPGE method is the residual surfactant on the graphene flakes, which is detrimental for some applications, and cannot be removed easily by even prolonged washing and needs further treatment for complete removal. However, the simple preparation method, the possibility of preparation of graphene flakes in water, low cost and possibility to scale up overcome the disadvantages of this method and make it appealing for many purposes.
1.1.3- Preparation of Graphene Thin Film from Liquid Phase Exfoliation

In the liquid phase graphene exfoliation method, graphene flakes are suspended in a solution and need to be transferred to the substrate for many applications, such as utilizing graphene thin films in optoelectronic devices. Several methods have been proposed to fabricate graphene thin films from the liquid phase, including the widely used spin coating and spray coating methods [5]. In the spin coating method, a few drops of the graphene suspension are centered on a substrate, which is then spun at a specified rotational speed. The suspension is spread on the substrate and covers it to form a thin film by centrifugal force. The thickness of the graphene films is controlled by the rotational speed and the concentration of graphene dispersion. This deposition method is appealing for many applications due to its fast processing time and ease of implementation. The spray coating deposition method involves spraying a dispersion of graphene onto a substrate. The major advantage of this method is its ability to form large area graphene films. This technique can be used to make thicker films; however the thickness control is more difficult compared with the spin coating method. Drop casting, which places a droplet of graphene suspension on a substrate and lets it dry either in a controlled environment or ambient conditions, has also been used to fabricate graphene thin films [5]. Moreover, graphene thin films can be prepared from graphene dispersion using a more reproducible and controlled vacuum filtration technique. This method is first proposed by Wu et al. [38] for fabrication of thin films from carbon nanotube dispersion and further developed by Eda et al. [39] for graphene thin films.

In the vacuum filtration method, suspensions of either graphene or graphene oxide in water or organic solvents are vacuum filtered on a filter membrane. The filter membranes are typically nitrocellulose or ester-based with micrometric pore size and are etchable in acetone and methanol. The graphene covered filter membranes are then transferred to any desired substrates, such as plastic or glass by putting the membrane side down such that the graphene layer is on top of the substrate. The substrates are next dried under load in an oven or vacuum desiccator. At the final step, samples are washed by sequential acetone and methanol baths to remove the filter membrane and leave behind a graphene
film on its substrate [5]. A schematic of the procedure is shown in Figure 1.6. The thickness of graphene films can be controlled by the amount of filtrated volume and the concentration of graphene suspension.

**Figure 1.6:** Schematic diagram of the vacuum filtration technique to prepare graphene-based thin films. (Figure is reprinted from “Solution Processed Graphene Thin Films And Their Applications In Organic Solar Cells”, R. Bauld, F. Sharifi, G. Fanchini, *IJMP B*, 26, 21, Copyright (2012), World Scientific Publishing Company [5]).

The vacuum filtration method is simple to implement and can be employed on any desired substrate. However, similar to other above mentioned deposition techniques, the graphene thin films always contain stacks of multi-layer graphitic flakes in addition to single and few-layer graphene flakes. In addition, not all of the graphene flakes on the filter membrane may transfer to the substrate resulting in non-continuous graphene films which requires controlling the filtration volume to prepare continuous graphene films.
1.2-Fundamental physical properties of graphene thin films

Among different properties of graphene thin films, two essential properties are required for their use as transparent conductors either in solar cells or in flexible electronic displays: the film transmittance ($T$) and the sheet conductivity ($S$). It is critical to understand how these two properties are correlated as a means for evaluating and comparing the efficiency of different methods of exfoliation, dispersion and deposition of graphene flakes. In this section a phenomenological model is presented that explains the relation between the electrical conductivity and transmittance of graphene films, which appears to be followed by virtually all of the vacuum-filtrated few-layer graphene thin films that have been reported in the literature and is shown in Figure 1.7 [22, 30, 32, 37, 40-41].

Figure 1.7: Various sheet conductivities plotted vs. transmittance for a large set of films available from the literature. Solid lines are fits to the data according to Equation (1.6). (Figure is reprinted from “Solution Processed Graphene Thin Films And Their Applications In Organic Solar Cells”, R. Bauld, F. Sharifi, G. Fanchini, *IJMP B*, 26, 21, Copyright (2012), World Scientific Publishing Company [5].)

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1 This section was taken from the paper published in International Journal of Modern Physics, which I am the coauthor [5].
First, let consider the relationship between the film conductivity and the fraction of the substrate that is covered by flakes, $f$. Such a relationship was previously described in carbon nanotube thin films in terms of percolation theory [42], and can be written as follows:

\[ S = S_0 \cdot (f - f_0)^x, \]  

where $S_0$ is a parameter that depends only on the average conductivity of the individual flakes in the film [42] (and, consequently, on the quality of graphitic material that has been exfoliated and pre-deposition and post-deposition treatments of the flakes [37]). In Equation (1.1), $f_0$ is the percolation threshold for disks which has a universal value $f_0 \approx 0.3$. Basically, if the surface fraction of the substrate covered by flakes is below the percolation threshold, there will be no continuous electrical pathway within the films and $S(f \leq f_0) = 0$ [43, 44]. For $f > f_0$, the number of continuous electrical pathways per surface unit that can be drawn within the sample increases as a power law, \( \sim (f - f_0)^x \), where the exponent $x$ depends on the dimensionality of the system, ranging between 1 and 3 and, typically, increasing from two-dimensional to three-dimensional percolating systems [43,44]. It is important to note that Equation (1.1) is valid only for values of $f$ sufficiently close to $f_0$. This expression also ignores the contact resistance between the flakes.

An additional characteristic of the vacuum filtration method is that, for any particular dispersion condition, precipitation of the flakes from the suspension onto the sacrificial filter membrane occurs via a layer-by-layer process [39]. This means that the number of layers being deposited, $N$, is inversely proportional to the fraction of voids being left on the filter membrane, $1 - f$, and also depends on the quality of exfoliation and dispersion processes. Therefore, the relationship between $N$ and $f$, can be written as:

\[ N \propto \frac{1}{1-f} \approx A(1+f), \]  

where $A$ is the proportionality factor and the last term is the first order Taylor expansion of $\frac{1}{1-f}$. The first term in the Taylor series can be attributed to the minimum value of the number of layers that occur always for the conditions below the percolation threshold.
Since we are interested in the number of layers above the percolation threshold, which provides conductivity for the graphene thin films, we neglected and simplified the Equation (1.2) by only considering the second term in the Taylor series. Thus Equation (1.2) can be written as:

\[ N \approx Af. \]  

(1.3)

The low values of the proportionality coefficient \( A \) indicate that a relatively high concentration of single-layer or few-layer graphene flakes are being deposited on the filter membrane, even at a relatively high degree of coverage of the filter pores, which may also indicate a good yield of monolayer flakes of graphene in the starting solution. Therefore, \( A \) is a measure of the quality of the specific solution processing conditions used. We specifically verified Equation (1.3) for a number of different conditions of vacuum filtration, as demonstrated in Figure 1.8a for graphene and graphitic films deposited under the same conditions used by Lotya et al. [22] by determining the average layer thickness \( N \) from atomic force microscopy profiles and the area of substrate covered by flakes from multiple AFM images. For the specific case shown in Figure 1.8, a value of \( A \) can be inferred from the linear fit of \( N \) vs. \( f \), as demonstrated by the blue solid line in Figure 1.8a. Substituting Equation (1.3) into Equation (1.1), we obtain:

\[ S = S'_0(N - N_0)^x, \]  

(1.4)

where \( S'_0 = \frac{S_0}{A^x} \) and \( N_0 = Af_0 \). Therefore, we have demonstrated that Equation (1.1), which is typical of electrically percolating systems, can be written for both the fraction of covered area, \( f \), or the average number of layers in a given film.

Let now consider the optical properties of graphene films. The normal-incidence transmittance of such films, shown in Figure 1.8b, demonstrates that in a set of films prepared under the same conditions, the normal transmittance in the visible photon energy range is generally weakly dependent on the wavelength. Furthermore, from Figure 1.8c, reporting the transmittance of a set of films at 2.25 eV photon energy (550 nm wavelength), we can observe that \( T \) is related to the film thickness by a simple exponential relationship:
\[ T = 100\% \cdot \exp(-N/M), \]  

(1.5)

where \(\exp(-1/M) \approx 0.98\) is the transmittance of a single-layer sheet of graphene [45], which gives \(M \approx 50\).

Figure 1.8: (a) Average flake thickness as determined by AFM as a function of \(f\) for a set of films prepared as in reference [22] (b) UV-Vis spectroscopic measurements on graphene films at different fractions of area coverage \(f\). (c) Transmittance vs. average flake thickness of graphene thin films prepared by vacuum filtration. There is a clear exponential relation betweeen flake thickness and transmittance that establishes the validity of Equation (1.5). (Figure is reprinted from “Solution Processed Graphene Thin Films And Their Applications In Organic Solar Cells”, R. Bauld, F. Sharifi, G. Fanchini, IJMP B, 26, 21, Copyright (2012), World Scientific Publishing Company [5].)
Combining Equations (1.3), (1.4) and (1.5), we obtain the following relationship between the sheet conductivity and the film transmittance, which is valid for $\ln\left(\frac{1}{T}\right) \geq f_0 A/M \approx 0.006A$:

$$S = S_0[(M/A) \ln(1/T) - f_0]^x \approx S_0[(50/A) \ln(1/T) - 0.3]^x,$$

(1.6)

Fitting of the data in Figure 1.7 to Equation (1.6) demonstrates the validity of our model and allows us to extract the parameters $S_0$ (which contains all of the information on the transport properties of the individual flakes) $x$ and $A$, which contains the relevant information on the quality of the dispersion of the flakes in solution. $M$ and $f_0$ can be kept constant during the fits, as they are intrinsic to the specific material and geometry that is being considered. The obtained fitting parameters for a few works shown in Figure 1.7 are reported in Table 1.1.

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<th>$x$</th>
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<td>[41] 1100°C Annealing</td>
<td>(2.41± 0.24)$\times 10^3$</td>
<td>4.0 ± 0.2</td>
<td>1.1</td>
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<tr>
<td>[41] 400°C Annealing</td>
<td>(2.40± 0.24)$\times 10^6$</td>
<td>4.0 ± 0.2</td>
<td>1.9</td>
</tr>
<tr>
<td>[40] RGO</td>
<td>(4.18± 0.42)$\times 10^6$</td>
<td>7.1 ± 0.2</td>
<td>0.95</td>
</tr>
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</table>

1.3- Graphene in organic photovoltaics

While the potential associated with using transparent and conducting graphene platelets in solar cells has been recognized quite early [4], the most optimal architecture for exploiting the outstanding properties of graphene in these devices is still unclear. Several

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2 Table 1.1 is reprinted from “Solution Processed Graphene Thin Films And Their Applications In Organic Solar Cells”, R. Bauld, F. Sharifi, G. Fanchini, _IJMP B_, 26, 21, Copyright (2012), World Scientific Publishing Company [5].

3 This section was mainly taken from a paper published in the IJMP B, for which I am a coauthor [5].
reports exist in the literature about the use of graphene-based materials in photovoltaics and offer a variety of different and unrelated approaches about the most appropriate utilization of such materials [8, 9, 40, 46-54]. The vast majority of these reports refer to the use of graphene in solar cells adopting thin film architectures.

In photovoltaics, the thin film architecture is preferable over a planar architecture only when the solar cell active layers display excessively poor carrier transport properties. In these photovoltaics the active layers are sandwiched between two collection electrodes with high conductivity: a transparent window electrode and “backing” electrode. Additionally, thin film solar cells may also benefit from the insertion of additional conducting materials buried within the active layer in order to improve their transport properties, allowing the cell to work in a tandem configuration. Examples of thin film solar cells are amorphous photovoltaic devices, organic photovoltaics (OPV) and dye-sensitized solar cells (DSSC).

A major difference between inorganic and organic thin film photovoltaics rests in the nature of the excitons generated by light absorbed in the active layer of the cell, as illustrated in Figure 1.9. In inorganic materials, excitonic diffusion lengths are relatively large (typically ~100–500 nm) [55] and the excitons may cover relatively long distances before being dissociated at the p-n interface and generate a hole current drifting towards the indium tin oxide (ITO) window electrode and an electron current drifting towards the backing electrode, as in Figure 1.9a. Conversely, excitonic diffusion lengths are very short in organic materials (typically 5–10 nm) [56] as in Figure 1.9b. Since excitons in such materials may only cover relatively short distances, they need to encounter a p-n interface at distances within their diffusion length to be dissociated into an electron and hole, instead of recombining radiatively with the emission of a photon. This means that, in organic solar cells, an extremely high surface area is required between the p-type and n-type components of the photoactive layer for the excitons to encounter a p-n interface as soon as possible and dissociate. A suitable architecture for thin film organic solar cells is formed either by an ultrathin planar p-n junction or a nanostructured approach must be adopted in order to maximize the density of p-n interfaces. Subsequently, the p-type and n-type constituents of the active layer are frequently mixed at the nanoscale. Typical
examples of nanostructured organic photovoltaics are represented by bulk heterojunction OPVs and dye-sensitized solar cells, as depicted in Figure 1.9b.

**Figure 1.9:** Various types of thin film solar cells: (a) Inorganic solar cells in which the exciton diffusion length is relatively large and a p-n junction architecture is suitable for efficient excitonic dissociation processes, (b) nanostructured organic solar cell architectures with high density of interfaces, for materials with short excitons diffusion lengths: bulk heterojunction OPVs and dye sensitized solar cells (DSSCs). See text for details. (Figure is reprinted from “Solution Processed Graphene Thin Films And Their Applications In Organic Solar Cells”, R. Bauld, F. Sharifi, G. Fanchini, IJMP B, 26, 21, Copyright (2012), World Scientific Publishing Company [5]).

In bulk heterojunction OPVs, the active layer is formed by a p-type organic material (typically: conducting polymers or molecular nanocrystals) blended by an acceptor material, typically fullerene derivatives. In order to prevent the recombination of the electron at the window electrode, a thin electron-blocking, hole-transport layer is
generally inserted at the interface between the active layer and such electrode, generally formed by a transparent conducting ITO thin film. The typical material of choice for organic hole-transport layers is a water soluble blend of poly-3,4-ethylenedioxythiophene:polystyrene sulfonate (PEDOT:PSS). In a typical DSSC, the excitons photogenerated inside specific organic dye molecules recombine with the oxidation of an iodine-based liquid electrolyte and the subsequent formation of an electronic current within a nanostructured porous layer of conducting titania (TiO$_2$) that collects the electrons towards a window electrode of fluorinated tin oxide (FTO).

Several research efforts are undergoing for finding suitable replacement materials for ITO and FTO, due to their high costs and low flexibility. Graphene research for optoelectronic applications has been largely motivated by these efforts. Even though the present transport properties of graphene films are not yet sufficient for transforming them into strong competitors of ITO and FTO, the cost effectiveness of solution-processed graphene platelets makes them extremely attractive for use in low cost OPVs and DSSCs.

For a transparent electrode (“window”) material, the most basic requirement is a good tradeoff between the optical transparency and the sheet resistance. Equation (1.6) offers the necessary tool for designing graphene window electrodes with the optimal compromise between transmittance and conductivity. In addition, a work function of the transparent conductor matching the energy level of one of the two species of photoexcited carriers, (either electrons or holes) is also essential for the use of a specific thin film as a window electrode material. As will be discussed in Section 1.3.1, graphene thin films are suitable of matching the work function of both ITO and FTO, the two current materials of choice for window electrodes. A number of studies using graphene as window electrode will be reviewed in Section 1.3.1.

Concerning the “backing” electrode of thin film solar cells, the most relevant requirements are good reflectance and the possibility to match the energy level of the other species of photoexcited carriers (either holes or electrons). Although the reflectance of graphene thin films is minimal for visible light, several attempts of using these materials as counter electrodes have been made and will be discussed in Section 1.3.2.
There are two fundamental reasons beyond these attempts. First, although graphitic materials are weakly reflecting for visible light, their reflectance dramatically increases at their plasmon resonance frequency, located in the infrared, which may help recovering the infrared portion of the solar spectrum. Secondly, DSSCs require backing electrodes that must retain their conductivity even in the presence of extreme oxidation conditions and graphene seems to possess this requirement and has been proposed as a candidate for the replacement of platinum counter electrodes in dye-sensitized solar cells.

In addition to the use of graphene-based thin films as window or counter electrodes, several groups have reported the use of graphene and graphene oxide at different parts of solar cell architecture such as the active layer and hole transporting layer in OPVs as well as the interfacial layer in DSSCs that will be discussed in Section 1.3.3.

All the aforementioned solar cell applications of graphene thin films have a number of common issues. One general issue for assembling organic materials at the top of a graphene thin film rests in the poor wettability of graphene. The most popular organic layers used in optoelectronics tend not to adhere well to the graphene surface, resulting in poor coatings and reduced efficiencies, or even outright device failure. Some remedies to these problems have been found [9] and will be discussed below. This, of course, comes with the drawback of another treatment step that will ultimately increase the net cost of the resulting cell.

Another issue is that, to date, no solution processing method has been able to produce films primarily consisting of single layer graphene. Typically, distributions of single, double, and multi-layer sheets are found [5]. This introduces an inherent surface roughness in the films that is a source for electrical shorts between the electrodes, which in turn reduces the efficiency. A great deal of care must be taken to reduce the occurrence of thick flakes, and this typically requires a “reprocessing” of a dispersed solution. This is normally done by collecting the sediment after a solution dispersion process and re-dispersing in a solution. This tends result in better quality films with lower mean flake thickness [22].
Even with the above mentioned collateral issues, graphene is an extremely promising candidate for the improvement of photovoltaic devices. Here we present some uses of graphene along with the efforts to overcome the above mentioned issues that have been proven successful. The related photovoltaic parameters, such as the power conversion efficiency ($\eta$), fill factor (FF), short-circuit current density ($J_{sc}$) and open circuit voltage ($V_{oc}$) of a variety of graphene-based solar cells will also be considered. The summary of these parameters for a number of recent studies are reported in Table 1.2.

Table 1.2: Summary of studies of graphene incorporation into various parts of a solar cell, with the relevant parameters describing the solar cell performance under air mass (AM) 1.5 sunlight illumination

<table>
<thead>
<tr>
<th>Type of solar cell</th>
<th>Location of graphene sheet</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPV-Bulk heterojunction</td>
<td>Electrode</td>
<td>0.36</td>
<td>0.38</td>
<td>0.25</td>
<td>0.29</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>ITO as comparison</td>
<td>1.00</td>
<td>0.41</td>
<td>0.48</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>OPV-Thin planar</td>
<td>Electrode</td>
<td>2.82</td>
<td>0.46</td>
<td>0.44</td>
<td>0.57</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>I-Pristine graphene/PEDPT:PSS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>I-Pristine graphene/PEDPT:PSS-DMSO</td>
<td>5.31</td>
<td>0.22</td>
<td>0.28</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>I-Pristine graphene/PEDPT:PEG</td>
<td>4.00</td>
<td>0.28</td>
<td>0.32</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>I-ITO/PEDOT:PSS as comparison</td>
<td>3.10</td>
<td>0.48</td>
<td>0.43</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II-Pristine graphene/PEDPT:PSS</td>
<td>3.46</td>
<td>0.48</td>
<td>0.45</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II-Doped graphene/PEDPT:PSS</td>
<td>6.44</td>
<td>0.46</td>
<td>0.52</td>
<td>1.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II-ITO/PEDOT:PSS as comparison</td>
<td>6.48</td>
<td>0.45</td>
<td>0.46</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III-Pristine graphene/PEDPT:PSS (treated with O₂)</td>
<td>6.32</td>
<td>0.49</td>
<td>0.44</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III-Doped graphene/PEDPT:PSS (treated with O₂)</td>
<td>9.15</td>
<td>0.43</td>
<td>0.42</td>
<td>1.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III-ITO/PEDOT:PSS as comparison</td>
<td>6.88</td>
<td>0.46</td>
<td>0.56</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>OPV-Thin planar</td>
<td>Electrode on PET</td>
<td>4.73</td>
<td>0.48</td>
<td>0.52</td>
<td>1.18</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>ITO as comparison</td>
<td>4.69</td>
<td>0.48</td>
<td>0.57</td>
<td>1.27</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2 is reprinted from Ref. [5].
In this section, we will review the use of graphene as a transparent conductor in different organic photovoltaics and dye sensitized solar cells as a replacement for ITO and FTO.

Mullen and collaborators [50] fabricated the first dye-sensitized solid solar cell utilizing spiro-OMeTAD and porous TiO$_2$ as the hole and the electron collector, respectively. The graphene film was the window electrode and replaced FTO, and the backing electrode
was a gold cathode, as demonstrated in Figure 1.10a. Proper matching of the energy levels of the electrode and the active materials is essential for efficient power conversion. Figure 1.10b shows the energy level diagram of the graphene/TiO$_2$/spiro-OMeTAD/Au device. Because the calculated work function of graphene is 4.2 eV and the mostly reported work function of HOPG is 4.5 eV, it was reasonable to presume that the work function of as prepared graphene film was close to FTO electrode (4.4 eV) [50]. The electrons are first injected from the excited state of the dye into conduction band of TiO$_2$ and then reach the graphene electrode via the porous TiO$_2$ structure.

![Figure 1.10: Schematic of a solar cell based on graphene electrodes. (a) Illustration of DSSC using graphene film as electrode, the four layers from bottom to top are Au, dye-sensitized heterojunction, compact TiO$_2$, and graphene film. (b) The energy level diagram of graphene/TiO$_2$/dye/spiroOMeTAD/Au device. (Figure is reprinted with permission from Nano Letters, “Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells”, X. Wang, L. Zhi, K. Mullen 8, 1[50]. Copyright (2008) American Chemical Society.)](image)

The current-voltage (I-V) characteristics of the device under illumination showed an overall efficiency $\eta = 0.26\%$, while the efficiency of the FTO-based control solar cell was $\eta = 0.84\%$. The lower value of $\eta$ of the graphene-based cell might be due to the series resistance of the device, the lower transmittance of the electrode, as well as changes in the electronic bands at the interfaces [50].

In another work, Wang et al. [8] reported transparent graphene anodes that were synthesized directly from organic reagents, which held a normal-incidence transmittance
~85% at 4 nm thickness. The advantage of this approach should be in the more accurate control of the roughness of the electrode and in smoother platforms. The polymeric solar cells were then assembled on these anodes by utilizing active layers based of “standard” bulk heterojunctions consisting of regioregular poly(3-hexylthiophene) and phenyl-C61-butyric acid methyl ester (P3HT:PCBM). The highest external quantum efficiency (EQE) of this type of cells was observed to be 43% at 520 nm monochromatic light and, at the same conditions, the EQE of a control ITO device was 47% [8]. Under 510 nm monochromatic light, the efficiency of this graphene-based cell was 1.53%, similar to the ITO-based cell. However, under AM 1.5 sunlight illumination, the graphene-based solar cell showed efficiency $\eta = 0.29\%$, which is, again, much lower than the value reported for the control cell ($\eta = 1.17\%$). The performance in terms of open circuit voltage of the graphene-based and the control cells were comparable, which may indicate a limited $\pi-\pi$ electron conjugation between the graphene electrode and the active layer. The relatively low values of short-circuit current, fill factor and EQE were attributed by the authors to the high resistance of the prepared graphene films [8].

P3HT:PCBM solar cells have also been fabricated by using CVD grown graphene electrodes [57]. These graphene-based devices demonstrated 0.21% efficiency when assembled on a pristine graphene electrode, but the efficiency could be raised to 1.71% when the graphene film was modified by pyrene butanoic acid succinimidyl ester (PBASE). The modification of graphene by PBASE increases the hydrophilic properties of the graphene surface, which leads to better wettability of graphene by an aqueous solution of PEDOT:PSS, and the work function of graphene to be better match with the PEDOT:PSS layer. However, the device performance was only 55.2% of the efficiency obtained from the ITO control device. This may lead to the conclusion that either the P3HT:PCBM graphene-based OPVs are not optimized, due to the limited knowledge of their physical mechanisms and the unclear effect of graphene in the charge collection process in graphene-based OPVs, or the P3HT:PCBM layer is not the best platform for graphene solar cells, even when the quality of the graphene films is supposedly high, as in the case of CVD-grown graphene. The effect of graphene electrode on the physical mechanism and subsequently the performance of the solar devices has not been widely
studied and reported in the literature that led us to investigate, the results of which is reported in detail in Chapter 4. In addition, several alternatives to the P3HT:PCBM layer have been introduced to explore the best platform for graphene-based OPVs.

Attractive alternatives to polymer-fullerene blends are OPVs assembled from small polyaromatic molecules. This is a very promising approach, since several systems of such molecules are uniquely positioned to self-assemble on graphene and create optimal interfaces for efficient charge collection. The PEDOT:PSS blocking layer between graphene and the active layer of the cells is sometimes avoided in these cases and can be replaced by the insertion of a hole-blocking, electron-transport layer between the active layer and the backing electrode. A possible choice for the hole-blocking layer is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline [46] (also known as Bathocuproine, or BCP). For instance, Gomez de Arco et al. [46] compared solar cells constructed from graphene and ITO electrodes fabricated on flexible polyethylene terephthalate (PET) substrates and utilizing copper phthalocyanine-fullerene (CuPc-C_60) active bilayers, for which they obtained efficiency values of 1.18% and 1.27%, respectively. This indicates that the graphene solar cell possesses an efficiency comparable to the ITO control device, within the fabrication uncertainties. The message that can be extracted from this work is that a specific design and specific solar cell architectures are required in order to optimize solar cells assembled on graphene electrodes.

In work done by Wu et al., [47] graphene films, prepared by reducing a thin layer of spin-coated graphene oxide, have been used as window electrodes in organic photovoltaics [47]. The structure of photovoltaics assembled on reduced graphene oxide electrodes was CuPC-C60 as the active layer with PCB and Ag for the hole-blocking layer and backing electrode, respectively, without inserting the conventional PEDOT:PSS hole transporting layer. AFM characterization revealed that the thickness of the reduced graphene oxide electrodes was between 4 nm and 7 nm, with a surface roughness lower than 3 nm. Additional analysis demonstrated that the transparency of the films was 85% – 95%, but the resistance of the films ranged from 100 to 500 kΩ/sq, which does not favorably compare with the ITO used (~20 Ω/sq) [47]. In fact, the organic solar cells fabricated using these electrodes held efficiencies ~0.4%, much inferior than those attained with
ITO as an electrode (0.84%). This was most likely due to the very large sheet resistance of the reduced graphene oxide films as well as absence of the hole transporting layer which leads to high contact resistance and possible recombination of carriers.

In other research conducted by Park et al., graphene-based OPVs were fabricated from the same stack layers reported by Wu et al, with an additional PEDOT:PSS hole transporting layer [9]. This work helped to elucidate the complementary roles of graphene and PEDOT:PSS in graphene-based OPVs and understand the influence of factors such as the work function and the surface wettability. Graphene sheets with controlled number of layers were used as transparent electrodes in this case, and different preparation conditions have been explored in order to optimize the solar cell photoconversion efficiency [9]. As mentioned previously, the challenge in using graphene is the limited surface wettability of graphene electrodes by the aqueous suspensions used to spin coat PEDOT:PSS, the hole transporting layer. Uniform coverage of the graphene surface by PEDOT:PSS plays a crucial role in the performance of graphene photovoltaic devices. However, the hydrophobic surface of pristine graphene makes it difficult to uniformly dispense aqueous suspensions of PEDOT:PSS on graphene.

In order to investigate such an issue, different sets of solar cells were built [9]. In one set of solar cells reported in ref. [9], the wettability of the graphene surface by PEDOT:PSS was improved by dissolving PEDOT:PSS in an organic solvent (dimethyl sulfoxide, DMSO) or by replacing PSS with poly-(ethylene glycol) (PEG). Dissolving PEDOT:PSS in an organic solvent makes the PEDOT:PSS solution more hydrophobic, and replacing PSS with PEG helps to dissolve PEDOT in hydrophobic solvents. Therefore, the hydrophobic PEDOT solution can better cover the hydrophobic surface of the graphene. As a result, the PEDOT/graphene interface improved and the sandwich conductivity increased, which also resulted in an improvement of the short circuit current. However, an overall decrease in open circuit voltage and fill factor prevented them from taking advantage of the benefits related to the increase in short circuit current. This effect was attributed to possible mismatches between the work functions of the electrode and the active layer [9].
Additional attempts to improve the graphene-polythiophene interface were also reported by Park et al. [9]. They reported the functionalization of graphene thin films by AuCl$_3$, which was preceded by an oxygen plasma treatment of the films. Spin coating of PEDOT:PSS on graphene films functionalized by AuCl$_3$ was found to be much easier than on the pristine graphene films because AuCl$_3$ doping makes the surface of graphene more hydrophilic. Furthermore, functionalizing graphene with AuCl$_3$ improved the conductivity of the graphene electrode and shifted its work function such that the work function of the graphene-doped electrode matched better with the other cell constituent resulting in significant improvements in the device performance. In this set of devices, the AM1.5 efficiencies of graphene-based and ITO-based solar cells were found to be comparable, with $\eta = 1.63\%$ and $\eta = 1.77\%$, respectively [9].

**1.3.2- Graphene as a counter electrode**

Graphene thin films can also be used as a counter electrode. This has mainly been done by preparing nanocomposites between graphene and a conducting polymer. Mixing graphene flakes with PEDOT:PSS has been suggested to make an effective, all-in-one, counter electrode that may potentially become a replacement to more expensive platinum electrodes in dye-sensitized solar cells [52]. Considering that PEDOT:PSS is very transparent, but at very poor levels of sheet conductivity, graphene doping of PEDOT:PSS was investigated as an electrode in DSSCs. Hong et al. prepared transparent thin films of graphene/PEDOT:PSS by spin coating an aqueous mixture of graphene and PEDOT:PSS on ITO [52]. The transmittances of the nanocomposite thin films were higher than 80% at 390–780 nm wavelengths. The graphene/PEDOT:PSS thin films were used in fabrication of DSSCs and compared with those using pure PEDOT:PSS and the conventional Pt counter electrodes. The photocurrent-voltage curves of the corresponding solar cells, reported in reference [52], showed that the performance of DSSC using graphene/PEDOT:PSS electrode is superior than that of pure a PEDOT:PSS -based DSSC and is comparable with the cell using a Pt counter electrode.

The efficiency of a DSSC using a counter electrode made by a PEDOT:PSS thin film at 1 wt% content in graphene was measured to be 4.5% [52]. The short circuit current and
open circuit voltage of this device were also found to be close to those of DSSCs with a Pt counter electrode. Compared to a pure PEDOT:PSS thin film, the addition of a small amount of graphene platelets effectively increased the short-circuit current and the fill factor of the cells. This was mainly attributed to the fact that the high specific surface area and the multiple chemical defects present in ultrathin graphene sheets offer a high catalyzation activity towards reduction of iodine. To investigate the effect of graphene content on the performance of DSSCs, a series of counter electrodes with different graphene contents were prepared from graphene/PEDOT:PSS mixtures. As the graphene contents in the mixture increased from 0 to 1 wt%, the energy conversion efficiency of the DSSC increased from 2.3% to 4.5%. However, further increasing the graphene content showed little effect on the energy conversion efficiency of the cell. These results indicate that a small amount of graphene is sufficient for electrochemical catalyzation and can improve the DSSC performance [52].

1.3.3- Other uses of graphene in organic solar cells

In addition to its applications as an electrode material, graphene has also been investigated as an active acceptor material in organic solar cells [48]. Using functionalized reduced graphene oxide as an electron acceptor and poly(3-octylthiophene) (P3OT) or P3HT as electron donors, solar cells with efficiency up to 1.4% were optimized [48].

Moreover, the utilization of solution processed graphene oxide as the hole transporting and electron blocking layer in the standard P3HT:PCBM organic photovoltaics has been demonstrated by Li et al. [58]. They used a thin layer of graphene oxide spin coated on the ITO substrate as the replacement of PEDOT:PSS for the hole transport layer. Devices using graphene oxide at optimized thickness demonstrated the same performance as the conventional PEDT:PSS based devices. This result along with the successful use of graphene as electrode and acceptor material provide a basis for fabrication of organic solar cells all based on carbon material.

In another work, graphene is being considered as an interfacial layer in DSSCs [53]. A mixture of graphene oxide (GO) and nanostructured TiO₂ was applied as an interfacial
layer between the FTO electrode and a nanocrystalline TiO$_2$ thin film. During the fabrication of DSSC, TiO$_2$ nanoparticles are typically deposited as a porous layer on the window electrode. When such a TiO$_2$ layer is formed, the surface of FTO, which is generally rough, is not uniformly covered by the nanoparticles, which leads to the formation of voids at the interface [53]. In addition, TiO$_2$ nanoparticles have the tendency to form large colloids in suspension. Therefore, a fraction of the surface of FTO will not be covered by the TiO$_2$ porous layer, can get in contact with the iodine-based electrolyte and short the cells. Kim et al. [53] have shown that the introduction of a graphene interfacial thin film between FTO and TiO$_2$ resulted in a 0.37% increase in the photoconversion efficiency of their DSSC, due to the retardation of the back transport reaction at the FTO/TiO$_2$ interface [53].

1.4- Graphene-biomolecule nanocomposites

Combination of graphene-biomolecules has recently attracted great interest [59]. In this section, a few studies done recently on graphene-biomolecule composites will be reviewed briefly. Deoxyribonucleic acid (DNA) and RNA have been reported as dispersing agents for carbon nanotubes, before being used for dispersing graphene. Zheng et al. [60] and Nakashima et.al [61] demonstrated that single-walled carbon nanotubes (SWNT) can be dispersed in water by the use of DNA. DNA, a chiral molecule, has also been proven effective to sort SWNTs according to their chirality [62]. The possibility to disperse SWNTs using RNA has also been investigated to form water-soluble nanocomposites in which RNA wraps the SWNTs and assists them to be dispersed in water [63]. These studies led to further utilization of biomolecules and biopolymers to prepare stable graphene dispersions. The use of DNA for preparation of stable aqueous suspensions of graphene sheets was firstly reported by Patil et al. [64]. They demonstrated that adding single stranded DNA (ssDNA) during the reduction process of graphene oxide by hydrazine leads to formation of a graphene-ssDNA hybrid that is suspended in water and is stable for several months. ssDNA consists of hydrophobic nucleobases bases, which are attached to the hydrophilic sugar backbone. The hydrophobic nucleobases of ssDNA bond with the hydrophobic graphene surface resulting in covering the surface of the graphene sheets. This provides sufficient steric
barriers for covered graphene flakes by ssDNA and prevents them from aggregating. In addition, the hydrophilic sugar backbone in ssDNA assists the graphene flakes to be suspended in water and provide stable graphene dispersion.

Additional studies to determine the binding energies of nucleobases of DNA and RNA with graphene have been carried out by several research groups to understand the interaction mechanism of DNA/RNA with graphene [65, 66]. Both experimental and theoretical studies, determining the binding energies of nucleobases of DNA/RNA with graphene, suggest that their interaction is dominated by van der Waals forces via the \( \pi-\pi \) stacking between the \( \pi \)-electrons of graphene and \( \pi \)-electrons of nucleobases. The success of ssDNA in the preparation of stable graphene dispersions, as reported by Patil et al. [64], and the relatively similar structure of ssDNA to RNA led us to investigate RNA as potential surfactants to exfoliate and disperse graphene in water [37]. It is also worth noting that RNA is less expensive compared with ssDNA, providing an additional advantage in preparation of graphene dispersion using the cost effective liquid phase fabrication technique. We demonstrated that a graphene dispersion can be prepared using RNA without the need for additional toxic materials, such as hydrazine, as utilized by Patil et al. Using toxic materials in the preparation of stable graphene dispersion limits the biocompatibility of such graphene flakes for their potential bio-applications [37].

In addition to nucleic acids, graphene has also been exfoliated and dispersed by other biomolecules such as proteins and peptides [67, 68]. Exfoliation and dispersion of graphene by hydrophobin, a microbial adhesion protein, has been reported by Laaksonen et al. [67]. In the case of using peptides, some biocompatible polymeric dispersants, such as lignin and cellulose derivatives, have been used to prepare high concentration (0.6–2 mg/mL) and stable graphene suspension in water [68]. Moreover, different types of amino acids have been used as stabilizers for graphene dispersion [69]. The adhesion of different proteinogenic amino acids was also previously investigated theoretically [70] and further studied experimentally by us, as will be discussed in Chapter 6.

The resulting graphene flakes fabricated via biocompatible molecules can be used for varieties of bio-applications including platforms for enzymes or biomarkers in biosensors...
or for drug delivery purposes [59].

1.5- References


http://www.sciencedaily.com/releases/2010/10/101005085507.htm


Chapter 2. Experimental characterization techniques

Several different techniques have been proposed to characterize graphene thin films, graphene-based devices and composites, and other organic materials at the nanoscale size with high resolution. Among them, we have utilized atomic force microscopy (AFM), kelvin probe force microscopy (KPFM), Raman spectroscopy, and ultraviolet-visible absorption spectroscopy (UV-vis) in this thesis work. The working principles and the instrumental characteristics of these techniques will be discussed in the following sections.

2.1- Atomic Force Microscopy

Atomic force microscopy is a method used to investigate the sample surface in three dimensions at the nanometer scale [1]. AFM can probe all types of samples ranging from conducting to insulating materials regardless of their transparency and stiffness. AFM is generally used to image samples under atmospheric conditions, but it is also possible to probe samples in liquid environments or under vacuum conditions. It can image the morphology of a sample for topographical studies, such as determining the lateral size or surface roughness of the sample [1].

In AFM, the sample is probed by a tip (a few microns long and less than 100 Å in diameter) attached to the free end of a cantilever (100–200 μm long). The sample is generally scanned under the tip by using a piezoelectric scanner. The piezoelectric scanner can move the sample precisely in x, y, and z directions because it is made of piezoelectric materials, which can change their dimensions in response to an applied voltage. The sample and the tip exert forces on each other, which results in deflecting the cantilever. The cantilever deflection is then measured by a detector and processed by a computer to create the surface morphology of the sample. Typically, the deflection of the cantilever is detected by measuring the displacement of a laser beam reflected from the back side of the cantilever using a position sensitive photodetector. As the cantilever
deflects, the position of laser beam shifts and can be detected by photodetectors. Another method is to use cantilevers prepared by piezoresistive materials. In such cantilevers, the deflection can be detected electrically due to the change in the resistivity of the piezoresistive material caused by mechanical strain.

The force associated with the cantilever deflection is an interatomic force that may contain different contributions, including: i) short range repulsive forces and ii) long range attractive forces between the tip and sample. The long range attractive force is the van der Waals force between the ions of the tip and electrons of the sample and vice versa. The short range repulsive force between the tip and the sample is due to the electrostatic repulsion between the electron clouds of the tip and the sample when they are brought into very close proximity with each other. The interatomic force between the tip and sample as a function of their distance is shown in Figure 2.1.

![Figure 2.1: The interatomic force between AFM tip and sample as a function of their distance. Depending to the tip-sample distance, different operating modes of AFM are shown.](image)

Depending on the distance between the tip and sample, different operating modes for AFM have been established, including contact, non-contact, and intermittent contact modes as indicated in Figure 2.1. In contact mode, the distance between the tip and
sample is typically less than a few angstroms and the interatomic force is repulsive. In non-contact mode, the tip is held above the sample by an order of tens to hundreds of angstroms and the force between the tip and sample is attractive due to the long-range van der Waals interaction. In intermittent contact mode, the tip is held above the sample most of the time with some purely vertical touches on the sample by the tip.

2.1.1- Contact mode AFM

In contact mode AFM, the tip is brought into proximity of the sample, in the order of a few angstroms, to create soft physical contact. At this distance, the electronic clouds of the tip and the sample’s atoms strongly repel each other, which results in a strong repulsive force between them and this force corresponds to the very steep slope of the graph in Figure 2.1 in the contact mode region. In addition to the interatomic repulsive force, other forces affect the contact mode measurements. These forces include: i) capillary forces, which are due to the presence of thin layers of water on the tip and ii) forces exerted on the tip by the cantilever. Capillary forces are attractive such that the magnitude of the force, typically of an order of $10^{-8}$ N [2], depends on the distance between the tip and the sample. The type and magnitude of the force exerted by the cantilever on the tip depends on the deflection of the cantilever and its spring constant.

The deflection of the cantilever due to the exerted forces is measured and is proportional to the height of a protrusion from the sample surface, which allows for the imaging of the morphology of the sample. The topographical image of the sample can be created either by constant-height or constant-force methods. In the constant-height method, the scanner height is fixed at a position and the spatial displacement of the cantilever is used directly. Conversely, in the constant-force method, the motion of the scanner is used to produce topographical data. In this method, the cantilever deflection is the input for a feedback circuit that controls the movement of the scanner by keeping the deflection constant. In the constant-force method, the speed of scan is limited by the response time from the feedback circuit. Of the two, the constant-height method is preferable for atomic-scale imaging of flat surfaces and real-time scanning.
A significant drawback with contact mode AFM is that the shear force between the tip and the sample may cause tearing, abrasion, or deformation of the sample, or it may degrade the tip. These phenomena become more important when the samples are soft, such as in the case of biomaterials or materials that cannot adhere well to the substrate.

2.1.2- Non-contact mode AFM

In non-contact AFM, a vibrating cantilever is placed above the sample at a distance of tens to hundreds of angstroms. The interatomic force between the tip and the sample at this distance is attractive as shown in Figure 2.1. The stiff cantilever vibrates at its resonant frequency with an amplitude of tens to hundreds of angstroms. The change in the resonant frequency or the amplitude of the vibrating cantilever is then measured when the tip is close to the sample. In order to produce the topographical data, either the resonant frequency or the amplitude of the cantilever is kept constant by controlling the motion of the scanner using the feedback circuit. The topographical data is then generated at each position considering the motion of the scanner or, in other words, the sample-tip distance.

In non-contact AFM, the force between the tip and sample is very low, of the order of $10^{-12}$ N, which provides benefits for imaging soft materials with no penetration to the sample. In addition, the non-contact regime prevents the degradation of the tip and deformation of the sample due to no or very little contact between the tip and sample. However, it is worth noting that since the force between the tip and sample is very low, it is more difficult to measure forces in non-contact mode than in contact regime. Moreover, in non-contact mode, the stiffness of the cantilever must be higher than in contact regime because the interatomic force is attractive and it may cause the cantilever to pull down and contact the sample if too soft cantilevers, designed for contact regime, are used. Small force and more rigid cantilevers tend to decrease the signal at the detector and are, therefore, more prone to low signal-to-noise ratios. Intermittent contact mode AFM partially mitigates these difficulties and will be presented in some detail in the next section.
2.1.3- Intermittent contact mode AFM

Intermittent contact mode, also called AC or tapping mode, is similar to non-contact mode except that the tip is brought closer to the sample. The tip barely touches or taps the sample surface at the end of its vibration without any sliding towards the sample surface. The interatomic force between the tip and sample is repulsive when the tip touches the sample surface, while the force is attractive for the rest of the tip oscillation. In intermittent contact mode, as the tip gets closer to the sample, the amplitude of the vibrating cantilever decreases and can be controlled by applying another voltage to prevent contacting and dragging the tip to the sample surface. Similar to the non-contact regime, the change in the cantilever amplitude due to the tip-sample spacing is used to extract the topographical data.

Intermittent contact mode has proved to be beneficial for many applications. In comparison to contact mode, the intermittent contact mode is less sample-damaging because it eliminates lateral forces, including friction, between the tip and sample. This prevents surface deformation and tip degradation, which may occur in contact mode scans. Detecting both repulsive short range and attractive long range forces in the intermittent contact mode increases the signal-to-noise ratio of the detected forces between the tip and sample in comparison to the non-contact mode, which only detects the attractive long range forces. This is beneficial for easier measurements of the force and, in turn, morphological investigations.

In this thesis work, we have used intermittent contact mode AFM for topographical imaging using a Witec Alpha300S microscope. In AFM imaging, tips (NSC 15, Mikromasch) with a frequency of 325 kHz and force constant of 46 N/m were used.
2.2- Kelvin Probe Force Microscopy

Kelvin probe force microscopy is an AFM based technique that measures the local contact potential difference between a conducting AFM tip operating in intermittent contact mode and the sample surface [3]. This tool can map the local contact potential difference and thereby the work function of a sample with high spatial resolution. KPFM was first introduced by Nonnenmacher et al. in 1991 [4]. This technique has been widely used to study the electronic properties of different materials, including metals and semiconductors, as well as semiconductor based devices. Several research groups have employed KPFM to investigate the electronic properties of organic materials, organic based devices, and biological materials [5, 6, 7]. In this thesis work, we have utilized KPFM to determine the work function of graphene based thin films, image the operation of graphene based organic photovoltaics, study the properties of biosensitive photoactive acridine orange, and investigate the amino acids-graphene nanocomposites that will be explained in detail in Chapters 4 to 6.

2.2.1- Principles of KPFM

KPFM implements, on an AFM platform, the macroscopic Kelvin probe method originally proposed by Lord Kelvin in 1898 [8] to determine the contact potential difference ($V_{CPD}$) between a metallic plate and a sample by creating a parallel plate capacitor between these two media. In the macroscopic Kelvin Probe method, a metallic plate oscillates on top of the sample. By applying a periodic change in the sample-plate distance, the subsequent periodic changes of capacitance result in an alternating current passing through a circuit connecting the two plates of the capacitor. This AC current can be nullified by applying a DC voltage that corresponds to the contact potential difference between the two plates, irrespective of the properties of the dielectric medium sandwiched between them. Consequently, if the work function of the metallic plate is known, the work function of the sample can also be determined using this “reference” work function and the $V_{CPD}$. KPFM methods determine $V_{CPD}$ by following the same physical principle. A conducting AFM tip, coated with a material of known work function, performs as the “reference” electrode. A DC voltage is also applied to the
sample. However, in KPFM methods, the electrostatic force between the tip and the sample is the parameter being measured and nullified at each point during the AFM scan, instead of the AC current. Force measurements at the atomic level are easier to perform than atomic-scale measurements of very small currents, which are typically of the order of a few pA or less. In addition, while macroscopic Kelvin probe methods average the contact potential difference over the entire sample, KPFM techniques are able to map $V_{CPD}$ and calculate the work function locally, down to the nanoscale size.

In KPFM, the contact potential difference between the AFM tip and the sample can be determined as [3]

$$V_{CPD} = V_{dc} = \frac{|\varphi_{tip} - \varphi_{sample}|}{e},$$

(2.1)

where $e$ is the electronic charge and $V_{dc}$ is the external DC voltage that nullifies the tip-sample force. In Equation (2.1), $\varphi_{tip}$ and $\varphi_{sample}$ are the work functions of the tip and sample, respectively. When the AFM tip is in the proximity of the sample, the electrostatic force between them is very strong and is proportional to the difference between their Fermi levels and work functions. If the work functions of the sample and the tip are different, electrons flow from the lower work function material to the higher work function material to line up their Fermi energies and reach a charge equilibrium condition. Consequently, when a metallic tip sits in the proximity of a sample, the vacuum levels of the tip and sample are not the same and the surfaces of both the sample and the tip are charged. Thus the $V_{CPD}$ is formed between the tip and sample resulting in an electrostatic force applied between them. Figure 2.2a schematically shows the electronic energy levels of the tip and sample and the contact potential difference generated between them when they are brought close to contact. By applying a DC voltage, the contact potential difference can be compensated and subsequently the force between the tip and the sample will be nullified. The electronic energy levels of the tip and sample after applying the DC voltage are shown in Figure 2.2b. The magnitude of the DC voltage that nullifies the contact potential difference and the resulting force are recorded at each point of a KPFM measurement and are used to determine the work
function of the sample from Equation (2.1) if the work function of the tip is known from scanning a reference sample.

\[ F_{el} = -\frac{1}{2} \Delta V^2 \frac{dC(z)}{dz}, \] (2.2)

where \( \Delta V = V_{dc} - V_{CPD} + V_{ac} \sin(\omega_{ac} t) \) is the total, time-dependent, potential difference between the tip and the sample because the DC and AC voltages are applied to the capacitor, consisting of the tip and sample, in addition to the present contact potential difference between the tip and sample. \( \frac{dC(z)}{dz} \) is the gradient of the capacitance along \( z \),

**Figure 2.2:** (a) Schematic diagram of the electronic energy levels of the tip and sample and the contact potential difference generated between them. (b) Contact potential difference between the tip and the sample can be compensated by applying a DC voltage. The force between the tip and the sample is then nullified. \( E_r \) is the vacuum level and \( E_{ft} \) and \( E_{fs} \) are the Fermi levels of the tip and sample, respectively.

In addition to the DC voltage nullifying the tip-sample force, the application of an AC voltage of amplitude \( V_{ac} \) and frequency \( \omega_{ac} \), both decided by the user, is also a necessary ingredient of the KPFM imaging. In our setup, this voltage is applied to the oscillating AFM cantilever through a custom-made conducting arm, which results in cantilever oscillations at \( \omega_{ac} \). The electrostatic force between tip and sample is subsequently determined by [3]
the normal direction to the sample surface. Consequently, the electrostatic force can be expressed as:

\[ F_{el} = -\frac{1}{2} \frac{dC(z)}{dz} [V_{dc} - V_{CPD} + V_{ac} \sin(\omega_{ac}t)]^2. \]  

Equation (2.3) can be written in a trinomial form, \( F_{el} = F_{dc} + F_{\omega_{ac}} + F_{2\omega_{ac}} \), in which each term represents a specific force component, where the three components are:

\[ F_{dc} = -\frac{1}{2} \frac{dC(z)}{dz} (V_{dc} - V_{CPD})^2, \]  

\[ F_{\omega_{ac}} = -\frac{dC(z)}{dz} (V_{dc} - V_{CPD})V_{ac} \sin(\omega_{ac}t), \]  

\[ F_{2\omega_{ac}} = \frac{1}{4} \frac{dC(z)}{dz} V_{ac}^2 (\cos(2\omega_{ac}t) - 1). \]  

Of the forces in Equations (2.4)-(2.6), \( F_{dc} \) is used for intermittent contact mode AFM measurements that reproduce the topography of the samples, while nullifying \( F_{\omega_{ac}} \) by externally applying a constant voltage \( V_{dc} = V_{CPD} \) at any point of a scan can be used to extract information of the work function via KPFM measurements, as will be done by us in this work. The third component, \( F_{2\omega_{ac}} \), can be used for capacitance microscopy measurements, which are not the subject of this thesis [3]. Consequently, when \( F_{\omega_{ac}} \) is minimized by applying \( V_{dc} = V_{CPD} \), the work function of the sample can be determined using Equation (2.1), while the work function of the tip is calibrated by a known material. Since the AFM tip scans samples at the nanoscale size, the work function of each point on the sample can be determined by KPFM or, in other words, KPFM can map the work function of a sample at a spatial scale that is comparable to the resolution of the AFM instrument on which it is implemented.

### 2.2.2- Operation modes of KPFM: Amplitude Modulation and Frequency Modulation

In KPFM, the electrostatic force \( F_{\omega_{ac}} \) can be detected by either amplitude modulation (AM) or frequency modulation (FM) modes. In the AM mode, \( F_{\omega_{ac}} \) is directly measured
from the amplitude of the cantilever using a lock-in amplifier referenced to the AC potential signal, which is typically produced by a function generator. An interval of voltages $V_{dc}$ is subsequently applied at each point and the specific value $V_{dc,min}$ that minimizes the amplitude of $F_{\omega_{ac}}$ is determined and indicates the actual value of the contact potential difference \([6, 9]\). By comparison, in the FM mode, the gradient of the force, $dF_{\omega_{ac}}/dz$, is measured by detecting the frequency shift of the oscillating cantilever referred to the AC potential signal produced by the function generator. The DC potential is applied to minimize the frequency shift and determine the contact potential difference \([6, 9]\).

In both AM and FM modes, AFM topography data are recorded simultaneously with the KPFM data. Therefore, experimental methods to separate the topographical signal from the KPFM signal for $V_{CPD}$ measurements are required. In AM mode, this separation can be done in two different ways \([3]\). In the simplest possible way, the AFM tip, mechanically excited at its fundamental resonance frequency, scans one line to record the topographical data and then is lifted up by several tens of nanometers and the AC voltage is applied at the same fundamental resonance frequency of the tip for the KPFM detection of $V_{CPD}$. Although this method can separate the topographical data from the $V_{CPD}$ measurements, the sensitivity for the KPFM measurements decreases at large distances between the tip and the sample. This method is also time consuming because of its two processes, first the scan to measure topography and second the scan for the KPFM measurements. A more sophisticated way to separate the topographical AFM data from the $V_{CPD}$ measurements in AM mode is to tune the AC voltage at the second resonance frequency of the cantilever. In this way, the first resonance frequency of the cantilever is responsible for taking topography, as in Equation (2.4), while the amplitude of the cantilever oscillating at its second resonance frequency is used to determine the KPFM data and $V_{CPD}$. Typically, in commercial AFM cantilevers, the second-order resonance is six times greater than the fundamental resonance frequency \([6]\). In FM mode, the cantilever is excited at the first resonance frequency and the AC voltage induces a force modulation at frequency $f_{ac}$. Consequently, the cantilever oscillates at superimposed frequencies $f_0 \pm f_{ac}$, where $f_0$ is the first resonance frequency. The KPFM signal is then
nullified at $f_0 \pm f_{ac}$ by applying a DC voltage [9]. In this method, a demodulation process is then required to separate the topography data, due to the oscillating cantilever at $f_0$, from the $V_{CPD}$ measurements because of the $f_{ac}$.

The AM KPFM mode is superior to the FM mode in terms of energy resolution because the use of resonance conditions allows for relatively high forces to be used in order to minimize the forces and determine $V_{CPD}$ and provides a significant enhancement in the signal-to-noise ratio [6]. The need of a demodulation scheme for $V_{CPD}$ detection in FM mode generates additional noise, which reduces the signal-to-noise ratio and, in turn, the energy resolution. The typical energy resolution for AM mode is 5 meV, while it is 10–20 meV for FM mode [6]. On the other hand, the spatial resolution is better in FM mode than in AM mode. In FM mode, the force gradient, corresponding to the first derivative of the curve in Figure 2.1, is detected and is larger at smaller distances between the tip and the sample and decreases as $z$ increases. Therefore, force gradient detection occurs only at relatively small values of $z$, with the tip apex very close to the sample surface [6]. Consequently, high lateral resolution can be obtained by using very sharp and soft tips that can be brought into close proximity to the sample surface. Although the spatial resolution of AM mode is lower than that of FM mode, AM mode is also capable of providing atomic-scale resolution [6].

In our work, we have utilized KPFM operated in AM mode and its schematic diagram is shown in Figure 2.3. The Witec Alpha300S Atomic Force Microscopy system specifically modified for KPFM applications was used in this thesis work. The AFM system was attached to a Stanford 30 MHz Synthesized Function Generator DS 345 to apply the AC voltage as discussed above. The function generator was locked-in at the second-order resonance frequency of the AFM cantilever using a Stanford Instruments SR844 RF lock-in amplifier. Doped silicon tips with a typical frequency of 75 KHz (Nano Sensores Inc. 76626F2L979) were used for AFM/KPFM imaging. The work functions of the tips were calibrated by using highly doped p and n type silicon and ITO films as references. The tip calibration was carried out at environmental conditions similar to those at which any target samples were imaged. The typical humidity and
temperature at which the KPFM experiments were carried out were better than 24% and below 25 °C, respectively.

**Figure 2.3:** Simplified schematic diagram of Kelvin Probe Force Microscopy. A lock in amplifier is used at the second resonance frequency of the cantilever in AM mode as described in the text.

### 2.3- Raman spectroscopy

Raman spectroscopy is based on inelastic scattering of monochromatic light by the vibrations in molecules or lattice vibrational modes in crystals. This technique provides information about the vibrational, rotational, or electronic energies of molecules and crystals [10]. Raman spectroscopy can be used to study solid, liquid, and gaseous samples. Since the discovery of Raman spectroscopy by Krishna and Raman in 1928 [11], many studies have been published on the theory [12], instrumentation [13], and application [14] of Raman Spectroscopy.

In Raman spectroscopy, an incoming photon of energy \( \omega \) and wavevector \( \vec{k} \) scatters with the vibrating lattice producing an outgoing photon of energy \( \omega' \) and wavevector \( \vec{k}' \). The conservation of energy and momentum can then be written as
$$\omega = \omega' \pm \Omega \text{ and } \vec{k} = \vec{k}' \pm K,$$

(2.7)

where $\Omega$ and $\vec{K}$ are the energy and momentum given to or absorbed from the lattice for
the plus and minus sign, respectively. In crystals, energy and momentum transfers occur
by quanta of lattice vibrations known as optical phonons, and for molecules such energy
and momentum transfers create localized vibrational excitations.

Raman scattering can be described in a simple classical aspect with a polarization
induced in a molecule by the oscillating electric field of the incident photons [10, 15].
The induced dipole subsequently radiates scattered light with or without exchanging
energy with vibrations in the molecule. The strength of the induced polarization is

$$P = \alpha E,$$

(2.8)

where $\alpha$ is the polarizability and $E$ is the electric field component of the incident
monochromatic electromagnetic wave. The time-dependent electric field of the incident
light is

$$E = E_0 \cos(2\pi \nu_0 t),$$

(2.9)

where $E_0$ is the vibrational amplitude and $\nu_0$ is the frequency of the incident
monochromatic light. The molecular vibrations affect the polarizability, $\alpha$, in Equation
(2.8). If a molecule vibrates at frequency $\nu_j$, the time-dependent nuclear displacement, $Q$, in a molecule is

$$Q = Q_0 \cos(2\pi \nu_j t),$$

(2.10)

where $Q_0$ is the vibrational amplitude of the molecule. For a small amplitude of vibration,
polarizability, $\alpha$, can be expanded in a Taylor series in terms of nuclear displacement as

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial Q}\right) Q + \cdots.$$  

(2.11)

In Equation (2.11), $\alpha_0$ is the inherent polarizability of the molecule and $\left(\frac{\partial \alpha}{\partial Q}\right)$ is the rate
of change in $\alpha$ with respect to change in $Q$. 


Combining Equations (2.8), (2.9), (2.10), and (2.11), we obtain

\[ P = \alpha_0 \cos(2\pi\nu_0 t) + \frac{1}{2} \left( \frac{\partial \alpha}{\partial Q} \right) Q_0 E_0 \left[ \cos\{2\pi(\nu_0 + \nu_j) t\} + \cos\{2\pi(\nu_0 - \nu_j) t\} \right]. \] (2.12)

Equation (2.12) contain three terms, which requires that the induced dipoles radiate at three distinct frequencies according to classical theory. The first term in Equation (2.12) represents an oscillating dipole that radiates light at frequency \( \nu_0 \), equivalent to the frequency of the incident photons. Therefore, this term indicates the elastic scattering of light and is called Rayleigh scattering. The two additional terms in Equation (2.12) demonstrate the inelastic (Raman) scattering of light with frequencies below, \( \nu_0 - \nu_j \), and above, \( \nu_0 + \nu_j \), the frequency of the incident light. The former and the latter are known as Stokes and anti-Stokes Raman scattering. According to Equation (2.12), Raman scattering occurs only when the rate of change in polarizability is not equal to zero, \( \frac{\partial \alpha}{\partial Q} \neq 0 \). This condition is usually referred to as the selection rule for the Raman active excitations.

In quantum mechanical aspects, the scattering process is an excitation of a molecule to a virtual state, which is positioned at lower energy than the real electronic transition, with approximately coincident de-excitation leading to changes in vibrational energy levels. The virtual states are not actual quantum states, but can be considered short lived energy levels due to perturbations in the electron cloud of the molecule originating from the oscillating electric field of the incident light and /or molecular vibration. A molecule can be excited either from its ground or excited states. If the molecule is in the ground state, it scatters photons at a lower frequency than the incident photon. In this case, the shift in frequency of photons is a Stokes shift and it is usually observed in Raman Spectroscopy. A small fraction of molecules is also at excited energy levels at room temperature and can scatter photons and de-excite to their ground state energy levels. The scattered photons appear at a higher frequency than the incident photons and the shift in their frequency is an anti-Stokes Raman shift. The intensity of the anti-Stokes shift is always weaker than that of the stoke shift; however both contain the same frequency information.
and they are symmetric with respect to the Rayleigh scattering frequency. The Rayleigh and Raman scattering are shown schematically in Figure 2.4.

**Figure 2.4**: Schematic of Raman and Rayleigh scattering. $\nu_0$ is the frequency of the incident photons. The scattered photons have the same frequency as the incident photons for Rayleigh scattering. In Raman scattering, the frequencies of the scattered photons are below (Stokes Raman) or above (anti-Stokes Raman) the frequency of the incident light.

Raman spectroscopy has been used extensively as a non-destructive technique to study carbon based materials. This technique has been utilized to characterize disordered and amorphous carbons, fullerene, carbon nanotubes, and diamonds [16]. The Raman spectrum of graphite was first taken in 1970 [17] and years after that the Raman spectrum of graphene was obtained in 2006 [18]. Since then, Raman spectroscopy has become an inevitable part of graphene study [14]. This technique has been greatly used to determine the number and orientation of graphene layers as well as quality, doping and disorder in
graphene flakes [14]. In our work, we have used Raman spectroscopy to characterize graphene samples to verify the existence of graphene flakes and determine their qualities, as will be discussed in detail in Chapter 3. A Renishaw InVia spectrometer equipped with a 532 nm laser at 100 mW power was used to record Raman spectra of the graphene films. Power was normally kept low to limit the damage of the sample surface.

2.4- Ultraviolet-Visible absorption spectroscopy

Ultraviolet-visible absorption spectroscopy has been extensively used for characterization of materials due to the versatility, simplicity, speed, and inexpensive nature of this technique. It is based on the Bohr-Einstein relationship

\[ \Delta E = E_2 - E_1 = h\nu = \frac{hc}{\lambda}, \]  

(2.13)

that connects the discrete atomic or molecular energy states, \( E \), to the frequency, \( \nu \), or wavelength, \( \lambda \), of the electromagnetic radiation [19]. In Equation (2.13), \( h \) is the Plank’s constant and \( c \) is the speed of light. Upon the absorption of the electromagnetic radiation, a specific electronic transition occurs between the electronic energy states. Among the overall range of the electromagnetic spectrum, the ultraviolet and visible radiations are of extreme importance because the electronic transitions for many atoms and molecules lie in this region and thus UV-vis can provide information about their electronic structure.

When light strikes a sample, different processes can happen, including absorption, transmission, reflection, and scattering of photons. If the wavelength of the incident light does not match with any electronic transitions in the media as described in Equation (2.13), the incident photon can either be transmitted through the sample, reflected from the sample at specific directions, or scattered by the sample in different directions. When light is absorbed by a sample, it promotes electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) energy states. Since the electronic energy states are discrete, according to the quantum theory, discrete sharp lines at different wavelengths in the absorption spectra are expected. Each of line occurs at a specific wavelength, which corresponds to the required energy that matches specific electronic transition. However, in practice most of the absorption spectra contain some
broad peaks rather than discrete sharp lines, which means that the molecule absorbs light over a band of wavelengths. One reason for this observation is that molecules have vibrational energy states in addition to their electronic energy levels. Thus the electronic transition upon the absorption of light is more likely to be accompanied by the transition between vibrational states so that their energy levels are a little below or above the electronic energy levels. In addition, the interaction of molecules with each other can broaden the absorption lines.

The absorption and transmission processes in UV-vis absorption spectroscopy are well described by the Bouguer-Lambert-Beer law. The law states that there is a logarithmic relation between the transmittance and absorbance that are defined in Equations (2.14) and (2.15), respectively, as:

\[ T = \frac{I}{I_0} \times 100 \%, \quad (2.14) \]

\[ A = -\log\left(\frac{T}{100}\right), \quad (2.15) \]

where \( I \) and \( I_0 \) are the intensity of the transmitted and incident light, respectively. The law also states that the absorbance is proportional to the concentration of a substance as:

\[ A = \varepsilon \cdot c \cdot l, \quad (2.16) \]

where \( \varepsilon \) is the molar extinction coefficient, which is dependent to the nature of the substance and wavelength. It is also independent of the concentration of the material provided that the solution of substance under examination is diluted. In Equation (2.16), \( c \) is the concentration of substance and \( l \) is the pathlength of the sample.

According to the Equations (2.14), (2.15), and (2.16) transmittance and concentration of a specific substance can be determined. Moreover, the optical absorption spectrum provides a finger print for elemental analysis due to specific transitions that may occur in different materials. The HOMO-LUMO gap for different materials can also be determined from their absorption spectra.
In this thesis work, a Varian DMS-80 UV-visible spectrophotometer was utilized to record the absorption spectra of different samples, investigated in this work, at normal incident in the 200–800 nm wavelength range.

### 2.5- References


Chapter 3. Transparent and conducting Graphene-RNA-based nanocomposites

3.1- Introduction

Transparent and conducting thin films from graphene-based materials have attracted strong interest during the last few years [1, 2]. Applications that are being considered for these thin films include replacement of indium tin oxide (ITO) in optoelectronic devices [3], thermal conductors [4-6], ultrafast laser optics [7], and battery electrodes [8]. Biological applications of graphene thin films have also been proposed [9], as they are expected to combine excellent optical and transport properties with the biocompatibility typical of graphite-based materials. However, the current methods for preparing large-area graphene films by solution processing are not expected to be well suited for biological and other applications [10-12]. Techniques for solubilizing graphene in aqueous solutions for the preparation of graphene-based thin films have been extensively discussed in Chapter 1, Section 1.1.2. They can be divided into two classes: chemical exfoliation of graphite, with the formation and subsequent reduction of graphene oxide [10], and mechanical exfoliation of graphite in liquids with the assistance of specific surfactants [11, 12]. Typically, the first class of techniques involves the use of non-biocompatible chemical agents, including strong oxidizers and toxic reducing agents (e.g., hydrazines). Traces of these materials may remain in the films even after prolonged washing. Surfactant-assisted exfoliation also presents some drawbacks for biocompatibility, since several ionic surfactants that have been shown to be promising to exfoliate graphite are classified as corrosive [11].

In this Chapter, we report on our study proposing ribonucleic acid (RNA) as a surfactant for exfoliating graphite and producing a new class of biologically inspired RNA-graphene based nanocomposites that may be used for applications in areas in which the

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biocompatibility of graphene is essential. It is well known that RNA can be used as a template for the incorporation of proteins and a large class of biological agents [13, 14]. RNA was also previously proposed as a dispersing agent for carbon nanotubes [15, 16]. It is worth mentioning that although RNA is an ionic biopolymer, because each phosphodiester group presents in RNA fiber is negatively charged, it behaves like a non-ionic surfactant. In fact, ionic surfactants typically contain only a single charged group at the very end of an entirely non-charged lipophilic chain, while each nucleotide in RNA fiber contains both a hydrophobic base and a hydrophilic (phosphodiester group) site as will be shown in the following sections. Our graphene-RNA-based thin films, prepared using RNA as a surfactant, possess optical and electrical transport properties that are comparable, if not superior, to those of other classes of graphene films prepared from ionic surfactants, such as sulfonates [11]. A qualitative model for understanding the specific mechanisms of graphene exfoliation in RNA-water solutions and the formation of our transparent conducting graphene-RNA-based nanocomposites will also be presented.

3.2- Experimental section

In our experiments, two different types of ribonucleic acid extracted from *Torula utilis*, RNA VI (SigmaAldrich Inc., R6625) and RNA IX (SigmaAldrich Inc., R3629), were dissolved at room temperature in deionized water at a concentration of 0.6 mg mL\(^{-1}\). The length of RNA was not known and the statistical distribution of length was very broad. Solutions of RNA IX are yellow in appearance since they contain fractions of diethyl-aminoethanol salt for keeping the RNA nanofibers monodispersed and free from aggregates [17], thereby ensuring a higher solubility for this type of RNA. The maximum solubility level for RNA IX was 12 mg mL\(^{-1}\), while it was 3 mg mL\(^{-1}\) for RNA VI.

Two different types of graphite powder, microcrystalline (mic-G with average particle size of \(d_{av} \approx 30 \, \mu m\)) and nanocrystalline (n-G, \(d_{av} \approx 700 \, nm\) with a significant tail of the distribution up to 3-5 \(\mu m\)) were ultrasonicated for four hours in RNA VI-water or RNA IX-water solutions. Suspensions were left to sediment overnight at 2 °C and the top three-quarters of the suspension was subsequently centrifuged at 6000 rpm for 1 hr. The
supernatant was then used to prepare graphene-RNA films using the vacuum-filtration technique, discussed in Chapter 1, Section 1.1.3, originally proposed by Wu et al. for carbon nanotube networks [18] and adapted by Eda et al. [19] for graphene films. Briefly, graphene suspensions in water-RNA solutions were filtered through a nitrocellulose filter membrane (220 nm pore size, Millipore). The membrane was then transferred onto silicon wafers coated with 300 nm-thick thermally-grown SiO$_2$, glass, fused silica, plastics or other substrates, and dried under load. Silicon wafers coated with SiO$_2$ are commonly used to visualize graphene using optical microscopes, because the internal reflections between graphene and SiO$_2$ assist the reflected light to have different contrast from the light reflected without the presence of graphene. It has been reported that the white light contrast is optimized when the thickness of the SiO$_2$ is $\approx$ 300 nm [20]. Acetone and methanol baths were used to etch the filter membrane, leaving behind a graphene film on its substrate. The differences between the various films discussed in this work are only in the amount of suspension filtered, type of RNA used, and the type of graphite.

Post annealing treatment on the graphene-RNA nanocomposite films was performed at 300–510 °C on a hot plate for 30 minutes inside a VAC Nexus glove box loaded with nitrogen, at oxygen and moisture levels less than 2 ppm in volume. Additional annealing experiments were performed in a quartz tube under continuous Argon flow at temperatures similar to those used for annealing in glove box, with no detectable differences in properties between the two sets of samples.

The graphene-RNA nanocomposite thin films were also functionalized at room temperature in sequential HNO$_3$ and SOCl$_2$ baths for 3 hrs, as described by Parekh et al. [21]. For the preparation of selected samples, we also pretreated our graphite starting materials by ultrasonicating them in a 3:1 concentrated mixture of H$_2$SO$_4$:HNO$_3$ for 24 hrs. The resulting graphite materials were filtered on polycarbonate filter membranes and further dispersed in Piranha reagent, a 4:1 combination of H$_2$SO$_4$:H$_2$O$_2$ as described by Liu et al. [22]. Pretreated graphite flakes were subsequently recovered on 100 nm pore size polycarbonate filter membranes, washed with copious deionized water, dispersed in aqueous solutions of RNA, and used to prepare films, as described previously.
Electrical data were obtained at room temperature from current-voltage two-point measurements in the ±5 V range. These measurements were performed using a Keithley 2400 Digital sourcemeter automated using a computer routine written using the Matlab™ Data Acquisition Toolbox [23]. Transmittance data were recorded at normal incidence using a Varian DMS80 UV-visible spectrometer in the 250–800 nm wavelength range. Raman spectra were recorded using a Resishaw InVia spectrometer with 532 nm laser excitation. Low incident powers were used and special care was taken to prevent sample damage. Tapping mode atomic force microscopy (AFM) images were recorded using a Witec Alpha300S microscope as described in Chapter 2, Section 2.1.3.

3.3- Results

3.3.1- Solution characterization and differences between RNA VI and RNA IX

The UV-visible transmission spectra of our RNA solutions in water are shown in Figure 3.1 before addition of graphite. Figure 3.1a shows that the transmittance of aqueous solutions of RNA IX is about 100% above 700 nm wavelength, irrespective of the RNA concentration. This is consistent with the complete monodispersion of RNA IX in water.

In contrast, Figure 3.1b shows that the transmittance of RNA VI in water at long wavelengths, \( \lambda = 700 \) nm and higher, decreases with increasing concentration. Even higher concentrations of RNA VI give rise to suspensions that are milky in appearance, with large aggregates forming a supernatant. Since RNA is completely non-absorbing in the long-wavelength spectral region, we assign the non-complete transparency of RNA VI in water in such region to diffuse reflectance and the presence of micro- or nano-aggregates of RNA VI.

Two different types of graphite, microcrystalline and nanocrystalline, were subsequently dispersed in the above mentioned RNA solutions and used to prepare our films by solution processing using the vacuum filtration method [18, 19].
Figure 3.1: Optical transmittance as a function of wavelength for an aqueous suspension of (a) RNA IX and (b) RNA VI for different concentrations in the range of 250–750 nm. The inset illustrates transparency as a function of concentration for RNA VI and RNA IX at 700 nm wavelength. The decrease in transmittance of RNA VI aggregates as a consequence of diffused reflectance is evident.

With this method, films are prepared by filtering variable amounts of suspension from a few milliliters up to a few tens milliliters on a sacrificial porous filter membrane placed at the top of a flat funnel of fritted glass. The funnel is attached to a vacuum flask. When flakes deposit at a specific location on top of the filter membrane during the filtration process, they occlude the pores of the membrane and prevents any additional suction from occurring at that location. Thus, the suction continues in regions of the membrane that are still free from flakes. This may tend to prevent flakes from depositing one on the top of another until the entire membrane is covered by a first layer [19]. However, it is worth mentioning that suction also occurs in between the edges of the flakes that have already been deposited, which leads to partial overlaps of different flakes. An advantage of this method is in the fact that sizes of funnels and membranes are scalable from a fraction of an inch up to several feet in diameter [18]. Such membranes can be subsequently applied on the desired substrate and etched, thereby leaving behind the films on the requisite substrate, as described by Wu et al. [18] and Eda et al. [19] and in
Section 3.2.

### 3.3.2- Thin film characterization

Figure 3.2a shows the Raman spectra for two of our samples, obtained by filtering very small (5 mL) and very large (80 mL) amounts of suspension of RNA VI and n-G. The zone-boundary, second-order Raman D-mode (2D), which is considered an important signature of single- and few-layer graphene [24], is dramatically different for the two samples.

![Figure 3.2:](image)

**Figure 3.2:** (a) Raman spectra for sparse (red line) and dense (blue line) films at 532 nm excitation. The downshifted 2D peak reveals that the sparse film is dominated by single-layer graphene flakes, while the up shifted 2D peak for dense film indicates the thickness of the flakes increases in this sample. The inset shows that the 2D peak of a sparse film can be simulated with a single Lorentzian component (centre frequency: 2635 cm$^{-1}$, half-width at half maximum: 53 cm$^{-1}$). (b) and (c) Optical images of the dense and sparse films, respectively, on silicon coated with 300-nm SiO$_2$.

The sample from the 5 mL filtered suspension exhibits a 2D mode that is formed only by one individual peak, located at $\approx$ 2650 cm$^{-1}$. Ferrari et al. [24] demonstrated that such a feature is the signature of Raman spectra dominated by single-layer graphene and,
therefore, such a film contains a relatively large proportion of monolayer flakes, although, certainly, some amounts of multilayer graphene are also present. The 2D Raman mode is composed of multiple peaks and is more upshifted for the film prepared at the highest filtered volume (80 mL). It has been shown that, at green light Raman excitation, a composite 2D mode with peak frequency above $\approx 2700 \text{ cm}^{-1}$ has to be assigned to multiple $\pi-\pi^*$ sub-bands at the boundary of the Brillouin zone, which is the signature of few- or multi-layer graphene [24].

Figures 3.2b and 3.2c show optical images of the film regions where we recorded our spectra and they confirm our spectroscopic indications. Films prepared by filtering amounts of solutions between 5 mL and 80 mL exhibit Raman spectra with characteristics that are intermediate between these two extreme conditions.

In addition, Figure 3.2a shows that, in thinner films, the I(2D)/I(G) intensity ratio between the 2D mode and the zone-center, first-order Raman G-mode ($\approx 1590 \text{ cm}^{-1}$) is significantly higher than that of thicker films. This is also consistent with thinner flakes in our more sparse samples. Although Ferrari et al. [24] reported I(2D)/I(G) >1 for a single-layer of relatively “ideal” graphene, which is higher than in our thinner films, several other authors reported low I(2D)/I(G) for solution processed, single-layer graphene flakes [25]. Such a difference can easily be reconciled by noticing that graphene flakes in our samples are likely to strongly interact with large concentrations of impurities, including RNA. This may lead to quantitative changes in the cross sections of the various Raman peaks. Maultzsch et al. [26] suggested that the absolute intensity of the 2D-peaks in carbon materials may dramatically change by quantum interference between the various components of the Raman transition matrix element, including coupling between the incoming photon and a $\pi$-electron, electron-phonon coupling and coupling between the $\pi$-electron and the outgoing photon [27]. Recently, it has been shown for graphene that changes of intensity related to quantum interference may affect the I(2D) and I(G) ratio in opposite ways in the case of impurities [25], as these peaks come from different zones of the phonon dispersion relation. Even very low concentrations of dopants substantially decrease the I(2D)/I(G) intensity ratio [25]. This effect may be particularly strong in the presence of strong charge transfer that may affect the
occupation of the $\pi$ and $\pi^*$ electronic bands, as is indeed the case in the presence of RNA. Therefore, the I(2D)/I(G) ratios in our films are not inconsistent with the fact that our Raman spectra are dominated by single-layer graphene.

\[ \text{Figure 3.3:} \] (a) AFM phase image and cartoon demonstrating the arrangement of RNA VI aggregates on specific surface regions of small graphene flakes exfoliated from n-G, and (b) the uniform coverage of larger flakes exfoliated from mic-G-RNA IX by a uniform layer of RNA IX. (c) Adhesion mechanism of RNA, with $\pi$-bonded hydrophobic bases (blue) adhering to the graphene lattice via van der Waals forces and hydrophilic phosphodiester groups (red) responsible for keeping graphene-RNA complexes suspended in water.
As demonstrated in Figure 3.3, we used AFM phase images for our morphological characterization because they enhance the contrast between RNA and graphite/graphene phases in our material, which possess different adhesion coefficients. Figure 3.3a shows a typical phase image for a film obtained from the suspension of n-G and RNA VI. This image demonstrates that our film contains single- and few-layer graphene flakes with RNA VI adhering on some regions on top of each flake. Figure 3.3b indicates graphitic flakes prepared from mic-G–RNA IX suspension that are covered completely by RNA IX.

We suspect that the adhesion of RNA to the graphene surface is possible because RNA fibers are formed by nucleotides, each one containing a hydrophobic base, including adenine, guanine, cytosine, and uracil, with \( \pi \)-bonded electrons that are affine to delocalized \( \pi \)-electrons in graphene. Therefore, such bases may adhere to graphene sheets via van der Waals forces. As discussed in Chapter 1, Section 1.4, several theoretical and experimental studies determined the binding energies of the RNA bases to the graphene surface and stated that the interaction between RNA and graphene is dominated by van der Waals interactions [28]. Each nucleotide of RNA also contains a hydrophilic phosphodiester group, which leads to the solubility of RNA in water. This hydrophilic group may also help to prepare suspension of graphene flakes attached to RNA in water solution and provide a stabilized dispersion of graphene flakes. The interaction mechanism of RNA with the graphene surface is shown schematically in Figure 3.3c.

3.4- Discussion

3.4.1- Thin film deposition model and differences between mic-G and n-G

Interestingly, we obtained transparent and conducting graphene-RNA films from both n-G–RNA VI (Figure 3.3a) and mic-G–RNA IX suspensions (Figure 3.3b), but not from n-G–RNA IX or mic-G–RNA VI suspensions. Even though films can also be formed from n-G–RNA IX or mic-G–RNA VI suspensions, they are extremely insulating with more
than 100 MΩ/sheet resistance. Comparison of Figures 3.3a and 3.3b reveals that n-G–RNA VI and mic-G–RNA IX composites exhibit dramatically different morphologies. While the first is formed by relatively small flakes of graphene with a few overlapping aggregates of RNA VI, the second is composed of larger and generally thicker flakes, uniformly coated by a thin layer of fibers of RNA IX, which do not form aggregates.

Such differences led us to suspect that a simple model based on the Derjaguin-Landau-Verwey-Overbeek theory, demonstrated by Lotya et al. [11] for the electrostatic stabilization of graphene in Sodium DodecylBenzeneSulfonate (SDBS) and other ionic surfactants, is not appropriate for graphene-RNA-based nanocomposites. Such a model cannot account for the very different behavior we observed for n-G and mic-G in both types of RNA, since these two types of graphite possess the same surface energy [29].

While sulfonate-based surfactants are ionic [30], with only one negatively charged, hydrophilic, sulfonate group terminating an entirely hydrophobic chain, RNA fibers act as non-ionic surfactant, because each nucleotide along the fiber contains both a hydrophobic base and a hydrophilic site (phosphodiester group) as shown in Figure 3.3c. Thus, each RNA fiber contains a very large number of hydrophilic groups, which prevents – or limits – the aggregation of graphene-RNA nanocomposites in water and creates ideal conditions for steric stabilization of graphene sheets [31], by preventing them from reapproaching once they have been intercalated by RNA fibers or aggregates. Therefore, while electrostatic stabilization is responsible for the dispersion of graphene flakes using ionic surfactants, we believe that the steric stabilization is the mechanism occurs in the presence of RNA biopolymers. Due to the relatively low solubility of RNA in water with respect to ionic surfactants, the critical step for obtaining RNA-based graphene films lies in attaining selective precipitation of thicker graphitic flakes, while retaining thinner graphene flakes in suspension.

Figure 3.3a shows that RNA VI tends to form aggregates adhering to the graphene surface. These aggregates are less dense than water, as demonstrated by the formation of supernatant when this type of RNA is dispersed in excess to its saturation limit. Thus, the buoyant forces of RNA VI aggregates adhering to small and light graphene flakes
exfoliated from n-G are sufficient to keep them suspended in water. Conversely, RNA VI aggregates cannot offer sufficient buoyant forces to thicker and heavier graphite flakes, which lead to their precipitation during sedimentation or centrifugation of our suspensions. Selective precipitation of thick graphite flakes accounts for the observed formation of transparent films composed of thin flakes of n-G and RNA VI.

For the same reason, aggregates of RNA VI are not capable of suspending larger and heavier graphene flakes exfoliated from microcrystalline graphite, which can easily explain why we could not obtain transparent and conducting films from mic-G using such a type of RNA. Relayering of microcrystalline graphene flakes due to relatively large surface zones that remain free from RNA VI aggregates may also play an important role in the insufficient dispersion of mic-G by RNA VI.

On the other hand, RNA IX possesses a higher solubility in water than RNA VI and does not form aggregates. It covers graphitic surfaces more uniformly than RNA VI, as shown in Figure 3.3b. While such uniform coverage is beneficial for steric stabilization, and for ensuring a better dispersion of graphene flakes, it involves a higher fraction of RNA in the films and leads to the presence of insulating RNA fibers at the junctions between nearest-neighbor graphene flakes. This may be detrimental to the film transport properties, especially in films prepared from n-G, where electric transport is expected to be affected by the flake-to-flake electrical contact resistance of a large number of junctions of relatively small flakes. This observation may explain why we can prepare conducting composites from RNA IX and mic-G, but not from RNA IX and n-G.

A strong indication towards steric stabilization in our films is that the adhesion of RNA on graphene is strong enough to resist removal, which was not possible by extensive washing of the filter membranes in the filtration apparatus. Conversely, SDBS and other ionic surfactants could be removed by repeatedly washing the carbon films in deionized water [18]. Thus, RNA-assisted dispersion of graphene leads to the formation of a new class of RNA-graphene nanocomposites, with properties and morphologies that are relatively stable at low or moderate temperatures.
3.4.2- Electrical properties

Figure 3.4 demonstrates the electrical properties as well as the effects of thermal annealing on our samples. The decrease in sheet resistance as a function of the annealing temperature for some of our films is shown in Figure 3.4a, which indicates that annealing is effective in improving the conductivity up to 12 times at a constant transparency. Since RNA tends to decompose above room temperature, the amount of RNA aggregates intercalating the graphene flakes decreases dramatically upon annealing. Figures 3.4b and 3.4c compare the AFM images of the same sample before and after annealing at 510 °C. Since RNA is an insulator, we suggest that the insulation resistance between graphene flakes decreases upon removal of RNA, thus leading to better electrical connections between the flakes. Therefore, we attribute the improvement in conductivity following annealing to an improvement of interflake conductivity. The interflake conductivity which is due to the contact resistance between partially overlapped graphene flakes affects the overall conductivity of the films. Interflake contact resistance is not considered in Equation (1.1), which describes the conductivity of thin films according to the percolation theory.

While increasing the interflake conductivity in our films is beneficial for improving their transport properties, increasing the inherent intraflake conductivity may also be profitable to the overall film conductivity that, according to Equation (1.1), is proportional to the conductivity of the individual graphene flakes. We explored covalent functionalization as a way to improve the individual conductivity of our flakes, by using the chemical process that was developed by Parekh et al. to improve the conductivity of individual carbon nanotubes (CNTs) in transparent CNT thin films [21]. The results showing the effect of functionalization are presented in Figure 3.4a, with the sheet resistance decreasing after initial exposure to a nitric acid (HNO₃) bath, followed by a further decrease after soaking in thionyl chloride (SOCl₂). Typically, this process leads to an overall improvement of our conductivities up to 25 times at a constant transparency. We suggest that the mechanism leading to such an improvement may be the same in graphene and CNT thin films, and may be assigned to shifts of the Fermi level and doping in delocalized systems of π-bonded electrons [21, 32].
Figure 3.4: (a) Sheet resistance as a function of annealing temperature for n-G-RNA VI films at different filtration volumes. Red dots indicate the decrease in sheet resistance upon HNO$_3$ and SOCl$_2$ treatments at room temperature for the 20 mL sample. The y-axis error bar is ±5%. (b) AFM image for the 20 mL sample before annealing. (c) AFM image of the same sample after annealing, showing the increased connectivity between graphene flakes. (d) Histogram of flake thickness distribution for sparse (5 mL) and dense (20 mL) films, without and with stacking of graphene flakes during vacuum filtration, respectively. Histograms were obtained by tracing random cross sections on five AFM images and removing those that intersected RNA aggregates. (e) Our flake thickness distribution for sparse films favorably compares with those obtained by other authors from dispersions in ionic surfactants (Lotya et al. [11] and Khan et al. [35]).
In summary, our electrical experiments are consistent with the preparation conditions of our films if we assume that their electrical properties are controlled by three different factors: 1) interflake insulation resistance determined by RNA, which can be decreased by annealing the films, as shown in Figure 3.4a; 2) inherent intraflake resistance of individual graphene flakes, which can be improved by functionalization [32]; and 3) the fraction of the film surface covered by graphene flakes. Films are not conducting if such a fraction falls below a critical value, which can be estimated to be \( \approx 30\% \) from our AFM images and agrees very well with the percolation threshold of graphene flakes that can be predicted using a two-dimensional percolation theory for disks [33].

Finally, Figure 3.4d and 3.4e compare the thickness of RNA-exfoliated graphene flakes in our films with other solution-based methods. It can be seen that, consistently with Raman spectra, exfoliation of graphite by RNA produces films with relatively large amounts of individual graphene layers in sparse films (5 mL filtered volume). Filtration of larger amount of graphene-RNA-based suspension (e.g. 20 mL) involves the relayering of graphene flakes on the filter paper and the formation of thin films with thicker flakes, as shown in Figure 3.4d.

3.4.3- Relationship between electrical and optical properties

Figure 3.5 shows the transmittance at a wavelength of 550 nm as a function of the sheet resistance for a large set of our samples. It is reasonable to assume that RNA is non-absorbing to visible light and that the flake-to-flake insulation resistance and the inherent resistance of individual graphene flakes form an electrical series. Under such hypotheses, the resistance of our films will be independent of the film transmittance and the fraction of surface covered by graphene flakes if the film resistivity is dominated by flake-to-flake resistance and, therefore, by the amount of RNA that separates the graphene flakes. Figure 3.5a shows that this is indeed the case for films prepared from mic-G, for which AFM images show that the graphene flakes are completely covered by a layer of RNA IX of constant thickness, as shown in Figure 3.3b.

Conversely, if the electrical transport is significantly controlled by the formation of percolation pathways between graphene islands (and, therefore, by the inherent resistance
and the amount of individual graphene flakes), the fraction of the film surface covered by graphene affects both the transparency and the resistivity in our materials. Increasing the amount of graphene-RNA suspension filtered leads to a higher fraction of substrate area that is covered by graphene, which corresponds both to lower transmittances and sheet resistances. This is the case for films prepared from n-G, as shown in Figure 3.5a, where trends are relatively similar to those previously obtained for transparent and conducting thin films prepared from CNT networks [34]. It is worth noting that, for such films, RNA VI was shown to cover only limited regions of the graphene surface (Figure 3.3a), which may account for the availability of RNA-free graphene surfaces and a smaller flake-to-flake resistance than in mic-G–RNA IX films.

![Figure 3.5:](image)

**Figure 3.5:** (a) Transmittance at 550 nm wavelength as a function of sheet resistance for a set of thin films prepared from as-received mic-G-RNA IX and as-received and oxidized-nG-RNA VI. (b) Evolution of the transmittance and sheet resistance for oxidized nG-RNA VI after annealing at 540 °C and functionalization in HNO₃/SOCl₂. The x-axis error bars for both panel (a) and (b) are ±5%.

At a constant fraction of the surface of the film covered, the transmittance of the films is also controlled by the thickness of the flakes. Single-layer graphene transmits $\approx 98\%$ of incident light, while multilayer graphitic flakes with thicknesses of a few tens of
nanometers are almost completely absorbing [33]. Although diffuse reflectance from RNA fibers may also limit the transmittance of our films, an important step in improving the film transparency is in optimizing the ability of RNA VI to disperse graphene and obtain thin conducting flakes.

To this end, we find that a preliminary oxidation treatment [22] of n-G in acid mixture and Piranha solution prior to dispersion in water-RNA is strongly beneficial in decreasing the resulting thickness of our films. As can be seen from Figure 3.5a, the treatment improves the transparency of the films. Such improvements are very consistent with the exfoliation and sedimentation mechanism we proposed for n-G in RNA VI. The treatment is the same as that previously used to cut single-walled CNTs, while introducing only a moderate number of defects on the tube sidewalls [22]. This treatment may lead to cutting of some of the graphitic flakes during the sonication process in the pretreatment procedure mentioned in the Section 3.2, and makes the flakes smaller and more easily suspended by the buoyant forces from RNA VI aggregates. Moreover, the smaller regions of the smaller graphene flakes that are not covered by RNA VI aggregates, prevents the graphene flakes from reaggregation, and thereby, improves the transparency of the graphene films. Furthermore, the peroxidation process increases the interlayer distance between graphene layers in bulk graphite, which leads to easier intercalation by RNA and, in turn, more efficient exfoliation process. The preoxidizing treatment may also increase the defect density in n-G and the number of preferential sites where RNA VI can adhere on the exfoliated graphene flakes.

In addition, recycling the sediments and re-processing them in the preparation of graphene suspension in the surfactant-water solution was found to be beneficial to improve the transparency of the graphene flakes as reported by Lotya et al. [11]. It was suggested that reprocessing the sedimentation provides better exfoliation yield in comparison to using the original graphite powder. The second sonication in the preparation process can break the already partially exfoliated graphite into smaller pieces for which surfactant can intercalate easier and thus exfoliation occurs more easily [11]. In our experiment, it was found that the transparency of the graphene-RNA-based thin films can improve by 10% by reprocessing the sedimentation. The transparency versus sheet
resistance results for the pretreated n-G, shown in Figure 3.5a, were obtained after recycling the sedimentation in the preparation process.

Finally, Figure 3.5b shows how the various treatments described above can be combined for improvement of both transparency and conductivity of our graphene-RNA thin films. Optimizing the thickness and transparency of the individual flakes via preoxidation of the starting material and reprocessing the sedimentation, followed by thermal annealing of the films and their subsequent functionalization in HNO$_3$ and SOCl$_2$ lead to thin films with $R \approx 200 \ \Omega/\square$ at 50% transmittance, or $R \approx 2.3 \ \text{M}\Omega/\square$ at 85% transmittance. Although this performance is inferior to that in graphene materials epitaxially grown on copper, they are comparable, if not superior, to those of other classes of graphene-based thin films; for instance, SDBS-based graphene dispersions led to 22 k$\Omega/\square$ sheet resistance at 62% transmittance [11].

3.5- Conclusions

In conclusion, this chapter explains how we prepared transparent conducting graphene-RNA nanocomposite thin films by surfactant-assisted exfoliation of graphite in the presence of RNA, a biocompatible surfactant. Our work forms an ideal link between the fundamental building blocks for nanobiology and carbon nanotechnology, RNA and graphene, and may open an avenue towards a large number of biological applications of graphene materials.

Our results show that the exfoliation process and the subsequent performance of our films are strongly dependent on the type of RNA and graphite used, with the best performance obtained when nanocrystalline graphite was exfoliated in the presence of types of RNA that form aggregates. Our experiments suggest that, depending on the specific morphologies obtained, the electrical transport properties of these films can be determined either by interflake resistance or by the fraction of surface covered by, and the resistance of, individual graphene flakes. The electrical performance of our samples still needs to be improved to be comparable with ITO transparent conductors, enabling the application of these films in flat panel displays. However, it is worth mentioning that
the performance of our samples is comparable to that of other graphene samples that are already used as electrodes in the fabrication of organic solar cells at the laboratory scale. The sufficient transport properties of our graphene-RNA thin films enabled us to fabricate graphene-based organic solar cells for further investigation of the physical mechanism and the origin of the open circuit voltage in such organic solar cells, which will be explained in detail in Chapter 4. Moreover, the properties of our samples are already sufficient for a number of other applications, including biosensors and other electronic devices were the biocompatibility of graphene films is essential. We used the graphene thin film samples, prepared by the method explained in this Chapter, as a template to functionalize them with different proteinogenic amino acids and further study the adhesion of such amino acids to the graphene samples for potential biosensors application, the results of which will be explained in Chapter 6.

In addition, we have shown that the optical and electrical properties of our films can be improved by a number of post-deposition treatments, including annealing and functionalization, and can be brought to levels that compare to those of solution-processed graphene-based thin films obtained from ionic surfactants.

3.6- References


Chapter 4. Photo-induced open circuit voltage in graphene-based organic solar cells and its origin

4.1- Introduction

Graphene exhibits remarkable electronic properties, which indicates that a variety of solution-processed graphene-based thin films may become promising materials for cost-effective applications in organic and inorganic solar cells [1-4]. The utilization of graphene as a transparent electrode in bulk heterojunction organic photovoltaics (OPVs) has been extensively reported [5-9], but graphene-based OPVs generally have poorer performance than their counterparts utilizing indium tin oxide (ITO) thin films as transparent electrodes. The reasons for these lower performances, as well as the most suitable architecture for incorporating graphene in OPVs, are still a matter of intense debate [4, 10-13]. The physical mechanisms leading to efficient injection of photo-induced carriers from organic photoactive materials into graphene thin film electrodes are still poorly understood and consequently the role of graphene-based electrodes in affecting the open circuit voltage ($V_{oc}$) of organic solar cells is unclear.

So far, two different models have been proposed to explain the magnitude of the open circuit voltage of OPV thin film devices: the metal-insulator-metal (MIM) model [14, 15] and the band energy offset (BEO) model [16-18]. In the MIM model, $V_{oc}$ is proportional to the difference in work function between the two contact electrodes:

$$V_{oc} \approx \left( \varphi_{bottom-electrode} - \varphi_{top-electrode} \right)/e = \Delta \varphi/e, \quad (4.1)$$

Where $\varphi_i$ represents the work function of the specific type of electrode $i$. With this model, $V_{oc}$ is not significantly affected by small changes in the band structure of the organic materials forming the photoactive layer. Conversely, in the BEO model, $V_{oc}$ is determined by the band energy offset between the lowest unoccupied molecular orbital (LUMO) of the photoactive acceptor material and the highest occupied molecular orbital
(HOMO) or the singly-occupied molecular orbital (SOMO) \[19\] of the photoactive donor material, diminished by the electron-hole pair binding energy \(E_b\):

\[ V_{oc} \approx |E_{HOMO} - E_{LUMO} - E_b|/e. \]  

(4.2)

Consequently, in the BEO model, \(V_{oc}\) is independent of sufficiently small changes in the work function of the electrodes [16-18].

In this chapter we show that, under air mass (AM) 1.5 illumination at 1 Sun irradiation, thin graphene-based OPVs utilizing poly(3-hexyl-thiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) blends as photoactive layers exhibit relatively high open circuit voltages \(V_{oc} \approx 0.79 \pm 0.01 \text{ eV}\) in comparison to ITO-based control OPVs of the same thickness and architecture, which never exhibit values of \(V_{oc}\) larger than 0.60 eV [6, 8, 20]. To the best of our knowledge, ours are among the highest open circuit voltages that have ever been observed for P3HT:PCBM solar cells [6, 8, 20]. As the efficiency of solar cells tends to increase as \(V_{oc}\) increases, the discovery of specific conditions under which the open circuit voltage of P3HT:PCBM photovoltaics can be significantly improved may have important practical outcomes, in addition to remarkable fundamental interest.

To gain insight into the physical processes determining the high open circuit voltage in graphene solar cells, we carried out Kelvin probe force microscopy (KPFM) experiments, in dark and under laser illumination, on graphene-based and ITO-based OPVs. Under illumination, we found that the work function of graphene thin film electrodes strongly increased with increasing intensity of illumination and the amounts of photoexcited holes injected into graphene. However, from KPFM measurements in the dark, we inferred that the work function of our graphene-based transparent electrodes \((\phi_G = 4.46 \pm 0.02 \text{ eV})\) is significantly lower than that of ITO transparent electrodes \((\phi_{ITO} = 4.80 \pm 0.02 \text{ eV}, \text{ measured by us and reported by other groups})\) [21] and closer to the work function of aluminum counter electrodes \((\phi_{Al} = 4.20 \pm 0.02 \text{ eV}, \text{ measured by us and reported by other groups})\) [22]. Consequently, the larger \(V_{oc}\) observed in graphene-based solar cells appears to be in contradiction with the predictions of the static MIM model, which would suggest a smaller \(V_{oc}\) since \(|\phi_G - \phi_{Al}| < |\phi_{ITO} - \phi_{Al}|\). Furthermore, the BEO model fails to
reproduce our experimental results since it predicts that $V_{oc}$ should not change by replacing ITO with graphene. We subsequently propose a dynamic graphene-insulator-metal (d-GIM) model, based on the specific zero-band gap semiconducting properties of graphene [23] and the strong changes in the work function of this material under hole injection [24] which offers an explanation on the origin of high open circuit voltage in graphene-based OPVs.

4.2- Experimental section

Transparent and conducting graphene films were prepared using the process discussed in Chapter 3 [25]. In brief, this method consists in four steps: i) ribonucleic acid (RNA)-assisted exfoliation of graphite in water with the subsequent production of graphene flakes in suspension; ii) vacuum filtration of graphene-containing suspensions, which results in the deposition of the graphene flakes on the filtration membrane; iii) transferring of the membrane loaded with graphene on the target substrate, and iv) etching of the membrane leaving behind a graphene film on the substrate. As described in Chapter 3, Section 3.2, nanocrystalline graphite (Sigma Aldrich Inc., 332461) was ultrasonicated for 24 hrs in a 3:1 $\text{H}_2\text{SO}_4:\text{HNO}_3$ mixture, dried on a filter paper and, subsequently, mildly oxidized in Piranha reagent ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 4:1$) [26]. 6 mg of the resulting graphitic material were ultrasonicated for 4 h in a 0.6 g/L water solution of RNA VI (Sigma Aldrich Inc., R6625). The resulting slurry was left to sediment overnight at 2 °C in a beaker. The supernatant was then centrifugated and used to prepare graphene thin films by the vacuum filtration method using nitrocellulose filter membrane, which subsequently transferred to glass and ITO substrates. The graphene thin films were then annealed on a hot plate at 540 °C for 30 min inside a VAC Nexus glovebox purged with nitrogen, at oxygen and moisture levels less than 2 ppm.

The solar cells were fabricated by spin coating poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) at 1000 rpm on top of graphene and pre-patterned ITO substrates (sheet resistance 70-100 $\Omega/\square$, Aldrich 576352), which were previously cleaned by ultrasonication in sequential detergent, water, acetone and methanol baths. The PEDOT:PSS/(Graphene or ITO) films were annealed at
135 °C for 30 min in a nitrogen-purged Vacuum Nexus II glove box, at oxygen and moisture levels less than 2 ppm. Photoactive layers consisting of a 1:1 weight ratio blend of P3HT:PCBM dissolved in chlorobenzene were then spun on top of PEDOT:PSS/(Graphene or ITO) films at 700 rpm and subsequently the resulting films were annealed at 140 °C for 30 minutes. Aluminum cathodes (100 nm) were grown on the blend layer by thermal evaporation in a vacuum chamber at a pressure of $4.8 \times 10^{-6}$ mTorr. The performance of the photovoltaic devices was determined in the glove box by using a two-point probe station attached to a computer-programmed HP2400 source meter and positioned under a Newport 9600 solar simulator operating at 1 Sun irradiation intensity and equipped with an AM 1.5 filter. The solar simulator was calibrated using a crystalline silicon reference solar cell (sciencetech SC-LT) certified by the National Institute of Standards and Technology (ISO-17025) and traceable both to the US National Renewable Energy Laboratory and the International System of Units. The solar cell photovonversion efficiency was directly determined from the current-voltage (I-V) curves using the relationship

$$\eta = \frac{V_{\text{max}}I_{\text{max}}}{E A_c},$$

(4.3)

where $V_{\text{max}}$ and $I_{\text{max}}$ are the output voltage and current of the cell generated under maximum power generation conditions, $A_c$ is the area of the device and $E$ is the emissivity of the solar simulator. $E$ is 140 mW/cm² at 1 sun irradiation in our case that are applied to reproduce, during each measurement session, the known short circuit current and photoconversion efficiency of the reference solar cell and account for fluctuations in the lamp operation conditions.

KPFM and atomic force microscopy (AFM) imaging were performed simultaneously and used to determine the work function and morphology of the graphene films as well as to investigate the graphene- and ITO-based solar cells. In the present study, a Witec Alpha 300S AFM system specifically modified for KPFM applications, as described in Chapter 2, Section 2.2.2, was used for KPFM/AFM imaging. For KPFM measurements under illumination, a 532 nm laser (Spectra-Physics90398) at various intensities ranges from...
zero to 0.8 mW/mm² illuminated samples during the scan via inverted microscope, while the KPFM signals were simultaneously collected from the top of the sample.

4.3- Results

4.3.1- Solar cell characteristics and open circuit voltages at 1 Sun

The efficiency of our P3HT:PCBM bulk heterojunction graphene-based devices, fabricated as described in Section 4.2, is one of the highest achieved to date for P3HT photovoltaics on solution-processed graphene thin films. It favorably compares with the performance of solar cells based on much less cost-effective CVD-grown graphene [7-9]. The architecture and the corresponding current-voltage (I-V) curves of typical ITO and graphene-based P3HT:PCBM solar cells are shown in Figure 4.1a and 4.1b, respectively.

Figure 4.1: (a) Architecture of the graphene/ITO-based P3HT:PCBM bulk heterojunction solar cells consist of four layers: graphene/ITO (the transparent electrodes), PEDOT:PSS (hole transporting layer), P3HT:PCBM (photoactive layer), and aluminum (top contacts). (b) The corresponding I-V curves of the solar cells showing high $V_{oc}$ in graphene-based solar cell compared with its ITO-based counterpart.
These I-V curves show that our graphene-based solar cells exhibit open circuit voltages of $V_{oc} = 0.79 \pm 0.01$ V, which are about 0.20 V larger than in the corresponding ITO control cell ($V_{oc} = 0.59 \pm 0.01$ V). This is remarkable because, as for the band energy offset model is concerned, it is expected to predict similar values of $V_{oc}$ for both graphene- and ITO-based solar cells. In order to determine if the metal-insulator-metal model is applicable in our case, it is necessary to measure the work functions of the aluminum top contact as well as the graphene-based or ITO-based bottom contact, because their difference determines $V_{oc}$ according to this model. We determined the work functions of graphene-based thin films, ITO, and Al using KPFM. AFM and KPFM images of one of our graphene-based thin film electrodes are shown in Figure 4.2a and 4.2b, respectively.

**Figure 4.2:** (a) AFM image and (b) the corresponding KPFM image of a typical graphene film. The film consists of graphene flakes with different thicknesses. The KPFM image represents the work function profile of the graphene flakes relative to the tip. (c) Work function of individual graphene flakes as a function of thickness. The work function increases with increasing thickness.
This electrode consists of a collection of few-layer graphene flakes with different thicknesses and a distribution of slightly different work functions. Figure 4.2c reports the work function of individual graphene flakes as a function of their thicknesses measured in the portion of thin film shown in Figure 4.2a. It can be observed that the work function increases with increasing flake thickness with an average value of 4.46 ± 0.02 eV, which is in agreement with the literature. Hibino et al. measured work functions ranging from 4.32 eV to 4.60 eV in single to multi-layer epitaxial graphene [27]. Using the same KPFM set up, we also measured the work functions of ITO and aluminum obtaining values that are very consistent with the results usually reported in the literature [21, 22].

By assuming the work functions of graphene-based thin films, ITO, and aluminum to be $\phi_G = 4.46$ eV, $\phi_{ITO} = 4.80$ eV, and $\phi_{Al} = 4.20$ eV, as measured by us using KPFM, the MIM model would predict an open circuit voltage $V_{oc} = |\phi_{ITO} - \phi_{Al}| = 0.60$ V for ITO-based solar cells and a significantly lower value, $V_{oc} = |\phi_G - \phi_{Al}| = 0.26$ V, for graphene-based solar cells. Although $V_{oc} = 0.60$ V for ITO-based solar cells is in excellent agreement with the experimental value, 0.59 ± 0.01 V, the expected value of 0.26 V for graphene-based solar cells is strikingly lower than our measured value of 0.79 V. This is also in contradiction with the fact that, experimentally, our graphene-based solar cells have been found to have significantly higher open circuit voltages than the control, ITO-based, solar cell. These results suggest that both the MIM and BEO models fail to explain the origin of the open circuit voltage in our graphene-based solar cells. Consequently, we utilized KPFM at different levels of illumination to understand the physical mechanisms determining the high open circuit voltage at 1 Sun in our graphene-based solar cells and to develop a model for $V_{oc}$ that is general enough to be applied to any sufficiently thin organic photovoltaic.

4.3.2- Kelvin probe force microscopy under illumination

In order to gain insight into the origin of high $V_{oc}$ of graphene-based OPVs, as opposed to lower values in ITO-based OPVs, we performed KPFM measurements in the dark and under different levels of green (532 nm) laser illumination intensities, for both graphene-based and ITO-based solar cells. Figures 4.3a and 4.3b show the AFM and KPFM images...
of the ITO-based solar cells obtained when the illumination intensity increases from 0.0 to 0.8 mW/mm$^2$ for each of the 64 lines of the sample during the scan. The corresponding histograms of the KPFM image at different illumination intensities are shown in Figure 4.3c. These histograms have been best-fitted with Gaussian curves and the Gaussian peak positions are shown in Figure 4.3d as a function of the illumination intensity.

**Figure 4.3:** (a) AFM and (b) corresponding KPFM image of the ITO-based solar cell. The KPFM image represents the KPFM signals of the sample relative to the tip. These images were obtained when the illumination intensity of the laser was increased during the scan from 0.0 to 0.8 mW/mm$^2$. (c) The corresponding histograms of the KPFM image, calibrated with the work function of the tip, at different illumination intensities along with their fits by Gaussian functions. (d) The peak positions of the fitted Gaussian functions as a function of illumination intensity. The error bar in panel (d) is 4.7x10$^{-4}$ eV.
The Gaussian functions used for the fits cannot resolve the KPFM signals of P3HT and PCBM independently. We suspect that the existence of \( \pi \)-electron systems in both P3HT and PCBM leads to conjugation between \( \pi \)-electron clouds in P3HT and PCBM and, in turn, this leads to important charge transfer between P3HT and PCBM, which prevents KPFM to measure two distinguishable values for regions of the samples formed by P3HT and PCBM, respectively.

As can be observed from Figures 4.3c and 4.3d, the KPFM signal under illumination is lower than the KPFM signal in the dark; and it decreases as the illumination intensity increases. The KPFM signal in the dark is indicative of the position of the HOMO level, which is fully populated, while the LUMO level is completely empty. When KPFM is measured under increasing levels of illumination, the LUMO level is increasingly populated by electrons that are photoexcited from the HOMO level. Consequently, the KPFM signal under illumination is no longer indicative of the position of the HOMO energy level, but it represents the average between the HOMO and LUMO energy levels weighted by the population of the two levels reached under equilibrium conditions at that specific illumination intensity [28]. Since the LUMO level has a lower energy relative to vacuum, it may be expected that the KPFM signal decreases under illumination, as we have experimentally observed for the ITO electrodes in our P3HT:PCBM solar cells.

Using the same procedure, we also obtained the corresponding AFM and KPFM images of graphene-based solar cells at increasing illumination intensities, as illustrated in Figure 4.4a and 4.4b respectively. Although the underlying graphene flakes are not visible in the AFM image (Figure 4.4a) due to thick layers of PEDOT:PSS and P3HT:PCBM, they can be easily noticed in the corresponding KPFM image (Figure 4.4b). Since graphene and P3HT:PCBM both contain delocalized \( \pi \)-electronic orbitals, the \( \pi \)-electrons of graphene may conjugate with the \( \pi \)-electrons of the P3HT:PCBM layer, which may lead to charge transfer between them and, thus, allow graphene flakes to be detected by KPFM, even though this technique is normally only surface sensitive. Figure 4.4c and 4.4d show the histograms of the KPFM image in Figure 4.4b taken from portions in which graphene flakes are and are not visible (Figure 4.4c and 4.4d, respectively).
Figure 4.4: (a) AFM and (b) corresponding KPFM images of the graphene-based solar cell. The KPFM image represents the KPFM signals of the sample relative to the tip. (c) and (d) are the corresponding histograms of the KPFM image, calibrated with the work function of the tip, at different illumination intensities taken from portions with and without evidence of graphene, respectively, along with their fits to Gaussian functions. (e) and (f) are the corresponding peak positions of the fitted Gaussian functions shown in panel (c) and (d) with error bars of $1.3 \times 10^{-3}$ and $6.8 \times 10^{-4}$ eV, respectively.
By adopting the same approach that was previously used for the ITO-based solar cells, these histograms were fitted with Gaussian functions. The Gaussian peak positions as a function of illumination intensity are shown in Figure 4.4e and 4.4f, for Figures 4.4c and 4.4d, respectively. As can be observed from Figure 4.4c and 4.4e, the KPFM signal for the graphene-based solar cells is higher under illumination than that in the dark and increases as the illumination intensity increases. This trend is at contrary to what was observed in our control ITO-based solar cell. A slight increase in the KPFM signal by illumination also occurs for areas with no evidence of graphene layers (Figure 4.4d and 4.4f); however, it is less important than in the areas with underlying graphene flakes (Figure 4.4c and 4.4e).

Since the active layer of the solar cells for which these histograms are obtained is the same as in the ITO-based control solar cells, one would expect the KPFM signal to decrease at increasing illumination intensity, similar to what we previously observed in Figures 4.3c and 4.3d. Consequently, the different trend observed in the KPFM signal under illumination in graphene-based solar cells, as opposed to ITO-based solar cells, can be assigned to the effects of graphene on the P3HT:PCBM active layer, which also extend to regions of the device in which there is no underlying graphene flake and the P3HT:PCBM thin film is directly sitting on glass. In fact, even from these regions, charge collection occurs through the nearby graphene domains. In order to explain our KPFM observations, we will propose in the next section a model that takes into account the electronic structure of graphene, a zero band gap semiconductor with negligible amount of free charge carriers, as opposed to ITO and other conventional transparent conducting materials, that are metallic in nature, with large reservoirs of free charge carriers, of the order of $10^{21}$ cm$^{-3}$ or more [29]. This model, that will correctly predict the open circuit voltage of graphene-based solar cells at different intensities of illumination, assumes a semiconductor-insulator-metal architecture of our devices, as opposed to the metal-insulator-metal architecture assumed by the MIM model for ITO-based solar cells. In fact, our model will be a dynamic graphene-insulator-metal theory taking into account the injection of a significant concentration of photogenerated holes from the solar cell active layer, which substantially affect the free carrier concentration in graphene.
4.4- Discussion

4.4.1- The dynamic Graphene- Insulator-Metal (d-GIM) model

The increase in the KPFM signal at increasing illumination intensity in graphene-based solar cells suggests that the changes in the work function of graphene upon hole injection from P3HT need to be considered in order to explain our Kelvin probe experiments, as well as the high open circuit voltage observed by us in these devices. Specifically, we will assume that the work function of the graphene thin film is not constant, but rises dynamically, penetrating into the $\pi$ valence band, as the amount of holes collected by such an electrode increases upon increasing photogeneration rate of holes in P3HT. Lin et al. recently reported that the work function of graphene increases upon irradiation with near ultraviolet light [24]. In their work, electrons are directly photogenerated in the $\pi^*$ conduction band of graphene, with the subsequent formation of holes in the $\pi$ valence band. In our case, the amount of holes present in the valence band is significantly higher than in the study of Lin et al. [24] because they are indirectly injected in graphene by P3HT, a photoactive material, capable of generating large amounts of photocarriers in the visible range, as it possesses very high internal photoconversion efficiency [30]. This amount of holes, which is significant over the very limited amount of preexisting holes in graphene, leads to a substantial change in the position of the Fermi level. Since the work function of graphene in the dark (4.46 eV) is lower than the HOMO level of P3HT (5.20 eV), hole transfer to graphene from the HOMO level of P3HT may easily occur without any need of activation energy. This phenomenon is shown schematically in Figure 4.5a. Figure 4.5b shows the schematic diagram of the ITO-based control solar cell, in which the position of Fermi level is fixed.
Figure 4.5: (a) Schematic of hole generation and Fermi level shift in graphene-based solar cells under illumination. Electrons are excited to the LUMO level in P3HT, with the formation of holes in the HOMO level (i.e., in the π valence band), which leads to p-type doping of graphene. (b) The energy diagram schematic of the ITO-based control cell, in which the position of Fermi level is constant. (c) The schematic of the interlayer π-electron conjugation between π-electron wave functions of graphene (green) and the π-electron wave functions of P3HT:PCBM (yellow).

Recall that in our experiments, KPFM measurements could not resolve the exact work function of individual P3HT and PCBM phases. As mentioned earlier, the possibility of π-electron conjugation between π-electrons of P3HT and PCBM leads to charge transfer between these two materials, preventing the KPFM to measure their individual work
functions. However, PCBM clusters are visible in our KPFM image and can be seen in Figure 4.4b although their work functions are only slightly different from the work function of the surrounding P3HT region. The KPFM signal of the top layer of the ITO-based solar cell in the dark is measured to be $W_{d-P3HT:PCBM} \approx 5.77$ eV, which is neither the work function of P3HT ($\phi_{P3HT} \approx 5.2$ eV) nor the work function of PCBM ($\phi_{PCBM} \approx 6.1$ eV). We modeled $W_{d-P3HT:PCBM}$ as the mean value of the work functions of P3HT and PCBM, shown by Equation (4.4), since the two phases present in a 1:1 ratio. The mean obtained is equal to $W_{d-P3HT:PCBM} \approx 5.77$ eV within 2.1% uncertainty.

$$W_{d-P3HT:PCBM} \approx (\phi_{P3HT} + \phi_{PCBM})/2$$ (4.4)

The effective work function of a 1:1 P3HT:PCBM blend in a graphene-based solar cell is $W_{d-G} \approx 4.94$ eV in the dark, as can be inferred from Figure 4.4c. This is different from the corresponding effective work function of this material blend in an ITO-based solar cell ($W_{d-P3HT:PCBM} \approx 5.77$ eV). $\pi$-electron conjugation between graphene and P3HT:PCBM may occur, which may lead to such differences. Figure 4.5c schematically shows the $\pi$-electron conjugation between $\pi$-electrons of graphene and P3HT:PCBM layer. In our model, we assume that the effective work function of graphene:P3HT:PCBM in our solar cells in the dark is determined by a linear combination of the partial contributions of two distinct phases, graphene and P3HT:PCBM. Consequently we write it as

$$W_{d-G} = (1 - x)W_{d-P3HT:PCBM} + x\phi_{G}$$ (4.5)

where $\phi_{G} = 4.46$ eV is the work function of graphene measured by KPFM on a bare graphene thin film electrode prior to the deposition of P3HT:PCBM, and $x$ is a measure of the interlayer $\pi$-electron conjugation strength. If the $\pi$-electron wave functions of graphene and P3HT:PCBM are completely separated, we have $x = 0$, there is no spatial overlap between $\pi$ electrons in graphene and P3HT:PCBM and $W_{d-G}$ is the same as measured for P3HT:PCBM in a control ITO-based solar cell ($W_{d-P3HT:PCBM} = 5.77$ eV). It is worth noting that, in our model, we neglect the effect of $\pi$-electrons of PEDOT and possible $\pi$-electron conjugation between graphene, PEDOT:PSS, P3HT, and PCBM. This assumption represents a remarkable simplification in our calculations, but we anticipate
that our model would still lead to the same results, at least qualitatively, if PEDOT:PSS was included in it.

In both ITO-based and graphene-based solar cells, the effective work function of P3HT:PCBM under illumination can be modeled by assuming that it is the average of the HOMO and LUMO of P3HT:PCBM weighted by their respective populations. Specifically, for ITO-based solar cells, we will have an effective work function under illumination that can be calculated as

\[
W_{\text{ill}} - \text{P3HT:PCBM} = [1 - y(p)]W_{\text{d}} - \text{P3HT:PCBM} + y(p)W_{\text{L}} - \text{P3HT},
\]

where \(y(p)\) is the population of the LUMO level of P3HT relative to the HOMO level, which varies with the illumination intensity, \(p\), and \(W_{\text{L}} - \text{P3HT}\) is the LUMO level of P3HT. \(y(p)\) is considered to be the same for both ITO and graphene-based solar cells. This assumption is justified since the concentration of P3HT and the structure of the solar cells are the same for both cases. It is worth noting that equation (4.6) predicts that \(W_{\text{ill}} - \text{P3HT:PCBM}\) is always lower than the corresponding value in the dark, \(W_{\text{d}} - \text{P3HT:PCBM}\), because LUMO levels always sit at a lower energy relative to vacuum than the corresponding HOMO levels. When the illumination intensity is \(p = 0\), the LUMO level of the P3HT is empty and does not influence the KPFM signal. When the solar cell is illuminated, electrons are excited from the HOMO level of P3HT to its LUMO level and thus the LUMO level also contributes to the KPFM measurements according to its population as considered in Equation (4.6).

For graphene solar cells, the determination of the effective work function under illumination is more complicated, not only because more energy levels, from graphene and from the HOMO and LUMO of P3HT:PCBM, are involved, but also because the work function of graphene changes depending on the amount of holes injected into it from P3HT and, consequently, on the illumination intensity due to the few-electron nature of graphene, which is a consequence of the fact that this material is a zero band-gap semiconductor. Assuming that the interlayer electron conjugation strength is the same for both the \(\pi\) (HOMO) and \(\pi^*\) (LUMO) orbitals, we can write
\[ W_{\text{ill-}G} = W_{\text{ill-}P3HT:PCBM}(1 - x) + x \varphi_{G-\text{ill}}(p), \]  

(4.7)

where \( \varphi_{G-\text{ill}} \) is the work function of graphene when the overlaying solar cell is illuminated at an intensity \( p \), \( W_{\text{ill-}P3HT:PCBM} \) is the same as in equation (4.6) and both \( W_{\text{ill-}P3HT:PCBM} \) and \( W_{\text{ill-G}} \) can be determined from KPFM measurements under illumination on ITO-based and graphene-based solar cells, respectively.

The work function of graphene at different illumination intensities can subsequently be determined using Equation (4.7), while \( x \) can be determined from Equation (4.5). Therefore, we can determine the shift in the work function of graphene electrodes in graphene-based solar cells under illumination with respect to graphene electrodes in the dark.

4.4.2- Explanation of different values of \( V_{oc} \) in ITO-based and graphene-based solar cells

First of all, we determined \( \varphi_{G-\text{ill}} \) using the experimental data from KPFM measurements in the dark and under illumination at various illumination intensities for both ITO-based and graphene-based solar cells and replacing them into Equations (4.5) and (4.7). In Equation (4.5), \( x \) was calculated to be 0.63 by substituting the experimental results. The resulting values of \( \varphi_{G-\text{ill}} \) are shown in Figure 4.6a. It can be observed that the work function of graphene increases with the illumination intensity as expected, which verifies p-type doping of graphene by illumination as stated in the proposed model. We can subsequently determine the shift in the work function of the graphene electrode \( (\Delta \varphi_G) \) in the graphene-based solar cell with respect to the work function of pristine graphene (4.46 eV).

The shift in the work function of graphene is correlated to its hole density according to the well-established expression for the Fermi energy of Dirac fermions in graphene [23, 24, 31], which is given by:
\[ \varphi_{G-ill} - \varphi_G = \hbar v_f \sqrt{\pi N_{hole-G}}. \] (4.8)

In this expression, that is a direct consequence of the electronic band structure and density of states of single-layer and few-layer graphene, \( \hbar \) is the Planck’s constant, \( v_f \) is the Fermi velocity, and \( N_{hole-G} \) is the hole concentration in graphene. By substituting the experimentally measured shifts in the work function of graphene at various illumination intensities in Equation (4.8), we were able to calculate the corresponding hole density in the electrode. In our calculations we used \( v_f = 1.1 \times 10^6 \) m/s, the most commonly reported value of the Fermi velocity in single layer graphene [32]. Figure 4.6b shows the hole density as a function of illumination intensity.

**Figure 4.6:** (a) The work function of graphene layer and (b) the corresponding hole concentration in graphene layer as a function of illumination intensity in the graphene-based solar cell.

Using Figure 4.6b we could determine the hole density in the graphene electrode at 1 Sun AM 1.5 illumination by extrapolating the illumination power at these conditions, which was found to be \( N_{hole-G} = 35.2 \times 10^{14} \) 1/m². According to Equation (4.8), the work function of graphene at 1 Sun down-shifts as much as 0.48 eV below the canonical point, at which is situated in the dark. Consequently, the work function of the graphene-based
thin film electrode increases from 4.46 eV, the value in the dark, to 4.94 eV at 1 Sun illumination. Such a significantly larger value of the work function at the practical conditions at which solar cells are operated offers a convincing explanation for the high open circuit voltage in graphene-based solar cells.

According to the MIM model, $V_{oc}$ represents the difference between the work functions of the bottom and top electrodes. Consequently, the increase in the work function of graphene by illumination leads to an increase in the open circuit voltage. Therefore, differently from the MIM model in which the work functions of the electrodes are considered as constant values, we are considering a “dynamic” work function for the graphene electrode, which varies with the illumination intensity, in order to explain the large values of $V_{oc}$ of graphene-based solar cells. The work function of ITO and the dynamic work function of graphene at 1 Sun irradiation are 4.80 eV and 4.94 eV, respectively, while the work function of the top aluminum electrode is 4.20 eV. Therefore, according to our d-GIM model, we can expect values of $V_{oc} = 0.60$ V and $V_{oc} = 0.74$ V, for ITO-based and graphene-based organic solar cells, respectively. These predictions are in a good agreement with our measured data (see Figure 4.1b). Although our model still underestimates the open circuit voltage, it provides better agreement than the MIM model with the experimental values and points out the reliability of our model, as can be observed from Table 4.1.

<table>
<thead>
<tr>
<th></th>
<th><em>ITO-based OPV</em></th>
<th><em>Graphene-based OPV</em></th>
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<tbody>
<tr>
<td><strong>BEO [16-18]</strong></td>
<td>&lt;1.5 V</td>
<td>&lt;1.5 V equal in ITO and Graphene OPVs</td>
</tr>
<tr>
<td><strong>MIM [14,15]</strong></td>
<td>0.60 V</td>
<td>0.26 V</td>
</tr>
<tr>
<td><strong>d-GIM (1 Sun)</strong></td>
<td>0.60 V</td>
<td>0.74 V</td>
</tr>
<tr>
<td><strong>Experiment (1 Sun)</strong></td>
<td>$0.59\pm0.01$ V</td>
<td>$0.79\pm0.01$ V</td>
</tr>
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Table 4.1: Comparison of the open circuit voltages predicted from the various models
Conversely, the work function of ITO does not appreciably change upon the injection of charge concentrations of \( \sim 10^{14} \, \text{m}^{-2} \), the order of magnitude actually predicted by Figure 4.6b, because the surface density of free electrons in ITO, a three dimensional metallic material, is \( \sim 10^{21} \, \text{m}^{-2} \) [29] which is several orders of magnitude larger than in graphene and, therefore, the MIM model is fairly accurate for ITO devices. The predictions of the MIM model substantially coincide with those of the d-GIM model for ITO solar cells.

### 4.5- Conclusions

In conclusion, we investigated the origin of the open circuit voltage in graphene-based solar cells, from I-V measurements at 1 Sun irradiation and using KPFM under green laser illumination at different intensities. We have observed that thin P3HT:PCBM bulk hetrojunction OPVs assembled on transparent graphene electrodes exhibit higher open circuit voltages than identical ITO-based OPVs. Our experiments demanded the development of a dynamic graphene-insulator-metal model to be satisfactorily reproduced because the use of the “static” value for the work function of graphene (\( \phi_G = 4.46 \, \text{eV} \), as measured in the dark) would lead to very inaccurate underestimation of the 1 Sun open circuit voltage of graphene-based solar cells, \( V_{oc} = 0.26 \, \text{V} \), much lower than the open circuit voltage of ITO-based solar cells in striking contradiction with the experiment. We estimated the increase in the work function of graphene thin film electrodes as a function of the hole concentration. The consequent dynamic increase in the work function of graphene when overlaying P3HT:PCBM layers are illuminated and inject holes into it is able to quantitatively explain the relatively high open circuit voltage of graphene-based solar cells. From the work function of aluminum (\( \phi_{Al} = 4.20 \, \text{eV} \)) and the dynamic work function of graphene (\( \phi_{G-ill} = 4.94 \, \text{eV} \)) at 1 Sun irradiation, our d-GIM model predicts an open circuit voltage of \( V_{oc} = 0.74 \, \text{V} \) for thin graphene-based solar cells. This value compares well with the value of \( V_{oc} = 0.79 \pm 0.01 \, \text{V} \) that could be directly measured from I-V curves at 1 Sun. The work function of ITO does not appreciably change upon hole injection from P3HT because ITO is a three-dimensional metallic material, which forms a large reservoir of free carriers. Therefore, the MIM model, predicting \( V_{oc} = 0.60 \, \text{eV} \) irrespectively of the illumination intensity, is fairly accurate for
thin ITO-based OPVs and reproduces very well our directly measured value of $V_{oc} = 0.59 \pm 0.01$ V at 1 Sun in these devices.

Conversely, both the BEO and the MIM models that were previously reported in the literature failed to explain the high open circuit voltage in graphene-based OPVs. Our measurements led us to conclude that the work function of graphene transparent electrodes strongly increases upon increasing illumination intensity due to hole transfer from the HOMO level of P3HT and such an increase has critical implications for the operation of graphene-based organic solar cells. Since the efficiency of a solar cell is proportional to the open circuit voltage, our understanding and improving the high open circuit voltage of graphene-based P3HT:PCBM solar cells has been a critical step towards improving the performance of organic photovoltaics. Furthermore, our d-GIM model, which is necessary to understand the origin of unusually high values of $V_{oc}$ in graphene-based P3HT:PCBM photovoltaics, sheds light on the factors that influence controlling the open circuit voltage in virtually any ultrathin organic solar cell.

4.6- References


Chapter 5. Acridine orange as a biosensitive photovoltaic material

5.1- Introduction

Organic photovoltaics are receiving significant attention due to their promise as low-cost sources of solar energy [1, 2] that are adaptable to multiple contexts, including printable and flexible solar cells on plastics and lightweight photovoltaic modules for powering mobile devices. The need for cost effective organic photovoltaics and photo-sensors is a driving force behind the search for abundant and easily processable organic materials. Organic photoactive materials that are most widely investigated in solar cell research are conjugated polymers and, specifically, different types of polythiophene derivatives. Regioregular poly(3-hexyl-thiophene) (P3HT) is a very popular choice in organic photovoltaic research, which has been utilized in Chapter 4 of this thesis. Interest in small organic molecules as alternatives to conjugated polymers in photovoltaic device fabrication has increased in the past few years because of several advantages, such as ease of synthesis, chemical modification and purification [3] as well as thin film morphological control [4]. Among small polyaromatic molecules, acenes have shown to be promising photoactive materials in organic photovoltaics [5-9]. However, photoactive conducting polymers and small molecules that have been developed to date for solar applications, including polythiophenes and small molecules of acenes, cannot be used in selectively sensing light when they are, or are not, attached to nucleic acids. This is due to their intrinsic lack of biosensitivity, which can be defined as a different absorption of light experienced by a specific molecule when attached to biological matter. Additionally, many organic photoactive materials require to be dissolved in organic solvents to be used in solution-processable photovoltaic fabrication methods, while water-soluble molecules are more desirable in general [10-12] and for bio-sensing in

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particular. The search for water-soluble photoactive materials with biosensing capabilities is critical for the fabrication of photo-biosensors.

In this Chapter, we investigated Acridine Orange (AO), a biosensitive molecule that is customarily used for labeling nucleic acids including DNA and RNA, as a cost effective and water soluble photoactive material. We have studied the optical and morphological properties of AO thin films for their use as a donor material in organic photovoltaics. We have also determined the electronic energy levels of AO using Kelvin probe force microscopy (KPFM) and UV-visible spectroscopy (UV-vis). The effect of anticrystallization agents, as well as low-temperature annealing, on the work function of AO was also investigated. In addition, the electron-hole pair photogeneration process in AO films was studied in our work from the changes of work function under illumination, detected by KPFM. We have constructed bilayer solar cells from AO and phenyl-C61-butyric acid methyl ester (PCBM) and evaluated their performance. We have also studied the effects of the morphology of different types of AO thin films spun from different solvents on the performance of bilayer photovoltaic. AO is a bio-sensitive material that changes its properties when it interacts with nucleic acids [13, 14]. Since the intensity of the UV-visible absorption peaks of AO differ in the presence of different concentrations of RNA, the photocurrent generated from AO photovoltaic devices may also change in the presence of RNA. Consequently, our study indicates that photocells using AO as a photoactive material may be promising for photo-bio-sensing applications, although additional work is still required to demonstrate the practical applicability of our devices for this specific use.

5.2- Experimental details

Our thin films were prepared from solutions of two different types of AO. Acridine Orange Hydrochloride Hydrate (AO-HH) (SigmaAldrich, 318337) and Acridine Orange Hemi Zinc Chloride (AO-HZC) (SigmaAldrich, A6014) were dissolved in either methanol or water at concentrations of 125 mg/mL. AO thin films were subsequently fabricated from these solutions spun at 2000 rpm onto silicon and indium tin oxide (ITO) substrates using a commercial spin-coater (Laurell, WS-400 BZ-6NPP). Selected samples
were annealed at 100°C, either in open atmosphere or inside a glove box (Vacuum Atmospheres Co. Nexus II) filled with high purity nitrogen, with O₂ and moisture levels below 5 ppm.

The work function and morphology of the samples were simultaneously determined by KPFM and atomic force microscopy (AFM) using a Witec Alpha 300S atomic force microscope specifically modified for KPFM experiments, which is described in Chapter 2, Section 2.2.2. For each point of an AC-mode AFM scan of the sample, bias voltages in the \( V_b = 0–5 \) V range were applied to the tip-sample and the voltage \( V_b' \) resulting in the minimum force between the tip and the sample was determined using a proportional-integral feedback control system. If expressed in eV, the value of \( V_b' \) recorded during KPFM scans represents the work function of the sample relative to the tip [15]. In order to use KPFM to investigate the photo-induced charge generation process that lead to a non-equilibrium population of electrons and holes in the conduction and valence bands of the material, KPFM images were also performed under illumination of the samples using a Spectra Physics Excelsior 90398 laser (532 nm wavelength) at 25 mW power. Similar experiments were described by Hoppe et al. [16] and Palermo et al. [17] for other organic photovoltaic materials. Laser illumination of the samples has been performed through an inverted optical microscope attached to the Witec Alpha 300S AFM/KPFM system. The optical absorption spectra of the AO thin films investigated in this work were measured using a Varian DMS 80 UV-visible spectrophotometer in the 300–800 nm wavelength range and the optical band gaps were extracted from such measurements by using the Tauc method under the assumption of non-direct optical transitions [18]. This procedure assumes that the function \( [\alpha(E)].E]^{1/2} \), where \( \alpha(E) \) is the absorption coefficient and \( E \) is the photon energy, is linear in the proximity of the band gap and estimates the band gap as the intercept between the linearized \( [\alpha(E)].E]^{1/2} \) function and the energy axis. The so-called Tauc gap determined in this way is indicative of the first visible offset of an optical absorption peak. To demonstrate the bio-sensitivity of acridine orange, the UV-vis absorption spectra of AO-HZC water-based solutions in the presence of different concentrations of RNA VI (SigmaAldrich Inc., R6625), ranging from 0.019 mg/mL to
0.077 mg/mL were measured as well, while the concentration of AO-HZC was kept constant at 0.005 mg/mL.

Fabrication of bilayer photovoltaic devices was carried out from AO thin films on either pre-patterned ITO substrates with sheet resistance of 70 Ω/□, that were cleaned by ultrasonication in sequential detergent, water, acetone and methanol baths, or graphene thin films, which were prepared by the same procedure discussed in Chapter 3, Section 3.2 using nanocrystalline graphite and RNA VI. The AO thin films were subsequently introduced into the aforementioned Vacuum Atmosphere Co. Nexus II glove box, in which the deposition of the acceptor layer, consisting of a PCBM thin film, took place. For each type of AO, PCBM films were spun at 500-3000 rpm on top of the AO films from anhydrous chlorobenzene (30 mg/ml). AO-PCBM bilayers were subsequently transferred into an ultra-high vacuum chamber that is directly accessible from the glove box without exposure of the samples to air. Backing cathode electrodes, consisting in 100 nm thick aluminum layers, were grown on the AO-PCBM bilayers by thermal evaporation using Al pellets (99.999% purity) as precursors, after the vacuum chamber had been evacuated at a base pressure better than 10^{-6} mTorr. The pellets were placed in alumina crucibles supported by tungsten basket heaters (Kurt J. Lesker Inc.). Thickness of the electrodes was controlled using a computer-programmed monitoring system based on a quartz microbalance (STM-2, Sycon Instruments).

I-V characteristics of the photovoltaic devices were measured directly in the glove box, by using a two-point probe station attached to a computer-programmed HP 2400 source meter and positioned under a Newport 9600 solar simulator operating at 1 Sun irradiation and equipped with an Air Mass 1.5 filter. The solar simulator was calibrated using a crystalline silicon reference solar cell (Sciencetech SC-LT) with certification accredited by the National Institute of Standards and Technology (ISO-17025) and traceable both to the US National Renewable Energy Laboratory and the International System of Units. The solar cell photovonversion efficiency was directly extracted from the I-V curves with the same procedure explained in Section 4.2 of Chapter 4 using the relationship

\[ \eta = \frac{V_{max}I_{max}}{EA_c} \]  

(5.1)
where $V_{max}$ and $I_{max}$ are the output voltage and current of the cell generated under maximum power generation conditions, $A_c$ is the area of the device and $E$ is the emissivity of the solar simulator.

5.3- Results and discussion

5.3.1- Morphological characterization and work functions of acridine orange thin films

We investigated the morphology of AO-HH and AO-HZC thin films spun from water- and methanol-based solutions using optical microscopy and AFM. Figures 5.1a and 5.1b are optical images of AO-HH thin films, in which AO is used without any presence of anticrystallization agents. Therefore, the structure of the films is presumed to be crystalline under these growth conditions.

Figure 5.1: Optical microscope images of (a) and (b) AO-HH films using methanol and water as a solvent, respectively, and (c) and (d) AO-HZC films spun from methanol and water based solutions, respectively.
Figure 5.1a shows an AO-HH thin film spun using methanol as a solvent, in which the film appears to be smooth and continuous at a microscopic level, in comparison to the AO-HH film illustrated in Figure 5.1b, spun from a water solution, for which isolated crystals of 2-5 μm in size with well-defined grain boundaries can be observed. This may lead one to conclude that AO-HH films spun from methanol-based solutions that uniformly cover the underlying ITO layer at the microscale could have, at least in principle, better interface contacts with the bottom electrode and the top layer in a typical photovoltaic devices. This is expected to decrease the contact resistance and, subsequently, increase the charge collection efficiency at the interface [19].

The optical images of the thin films prepared from AO-HZC are shown in Figures 5.1c and 5.1d. AO-HZC contains ZnCl₂ as an anticrystallization agent [20, 21] and, therefore, the structure of these films is presumed to be non-crystalline and disordered. In addition, in AO-HZC thin films, the microstructure appears to be significantly different when films are spun from methanol (panel c) and water (panel d) solutions. AO-HZC films spun from methanol are formed by a collection of smooth and round domains of AO, approximately 1-2 μm in diameter intercalated by voids of 0.5-2 μm in width, while AO-HZC films prepared using water solutions exhibit layers that are relatively smooth and continuous at the microscale, except for the presence of “Swiss-cheese” voids of 8–15 μm in diameter. The larger voids in the films spun from water-based solutions are a consequence of the lower evaporation rate of this solvent when compared to methanol. The better continuity of the water-based film may be a consequence of the better wettability of the ITO substrate for this solvent. Pretreatment of the ITO surfaces with an ozone cleaner, as previously successfully attempted for several organic polymers [4] did not modify the adhesion of AO-HZC thin films on the ITO substrates. The typical optical images of the AO-HZC films spun from water-based solutions on the ITO substrates when the substrates were pretreated by an ozone cleaner at different times are shown in Appendix A. The presence of voids in these acridine orange layers may cause microscopic short-circuits between the device layers at the top and at the bottom of the AO-HZC films if these are used to fabricate multilayer organic photovoltaic devices. On the other hand, the excellent smoothness of AO domains in AO-HZC suggests that these
films, especially the water-based ones, have the optimal morphological characteristics for forming good interfaces that will allow the most efficient electron-hole pair dissociation processes when these films are used as photoactive layers in bilayer solar cells.

Figure 5.2: Optical images of AO-HH films (a) annealed at 100 °C in air, and (b) nitrogen. Darker spots may indicate the crystallization of acridine orange by annealing, which is less pronounced in the sample annealed in air. AO-HZC films annealed at 100 °C (a) in air and (b) nitrogen. Neither annealing in air nor in nitrogen changed the morphology of AO-HZC.

In order to gain insight into the role of ZnCl₂ additive on the morphology of the resulting acridine orange thin films, we performed annealing experiments on both AO-HH and AO-HZC thin films at 100 °C either in nitrogen or in air atmosphere. Figure 5.2a and 5.2b show optical images of AO-HH films spun from methanol and annealed in air and nitrogen, respectively, which can be compared with Figure 5.1a that shows the corresponding sample prior to annealing. The dark spots in both Figures 5.2a and 5.2b that can be attributed to the increase in crystallization of AO-HH and crystal grains, possibly created from the coalescence of smaller micro- and nano-crystals, can be clearly
observed in these images. Such attribution is also confirmed by AFM analysis, as will be discussed below. It can also be seen, from the comparison of Figures 5.2a and 5.2b, that crystallization is less pronounced in air than in nitrogen. This may indicate that the presence of oxygen at the grain boundaries limits the growth rate of crystal grains. While annealed AO-HH thin films suffer from the formation of crystals that affect the film uniformity, annealing neither in air nor in nitrogen changed the morphology of AO-HZC as can be seen from Figures 5.2c and 5.2d, respectively. These Figures show microstructures that are identical to the one of the non-annealed sample, shown in Figure 5.1d. Therefore, it is apparent that ZnCl$_2$ prevents acridine orange from crystallizing and leads to more thermally stable microstructures of this material.

![AFM topography of AO-HH films](image1)

**Figure 5.3:** AFM topography of AO-HH films spun from (a) methanol and (b) water solutions. KPFM images of films spun from (c) methanol and (d) water solutions.

The use of acridine orange thin films in photovoltaic applications requires knowledge of the work function of the films. We determined the work function of our AO-HH and AO-
HZC films using KPFM. Figure 5.3 shows the morphology (panels a and b) and the corresponding KPFM images, (panels c and d) of AO-HH films spun from methanol and water solutions, respectively. From both Figures 5.3c and 5.3d, the work function of AO-HH is $3.60 \pm 0.02$ eV, irrespectively of the type of solvent used to spin coat the films and on their structure, microcrystalline or nanocrystalline. We also measured the work function of AO-HZC films as shown in Figure 5.4, where the morphology of films spun from methanol and water solutions are shown in panels a and b, respectively, with the corresponding KPFM images being shown in panels c and d. Interestingly, the work function of disordered AO-HZC is $4.70 \pm 0.02$ eV, a much higher value than in micro/nano-crystalline AO-HH, but, again, independent of the solvent used and the size of the disordered domains of AO. Consistent values of work functions were obtained for films prepared at different thicknesses and from different batches of starting material.

**Figure 5.4:** AFM topography of AO-HZC films spun from (a) methanol and (b) water solutions. KPFM images of films spun from (c) methanol and (d) water solutions representing the work function profile of the sample relative to the tip.
The strong difference between the work functions of AO-HH and AO-HZC requires an explanation. AO-HH films show faceted crystals and, therefore, the work function measured by KPFM may be assigned to the crystal facets that preferentially orient parallel to the surface of the substrate. Conversely, the presence of ZnCl₂ as the anticrystallization agent ensures that AO-HZC films have a continuous and grainless surface and are disordered at the molecular-scale level. This leads us to assume that their work function is averaged over all of the possible crystallographic orientations. We also determined the work function of AO-HH samples annealed at 100 °C in air and nitrogen. Figure 5.5 shows the morphology (panels a and b) and the KPFM images (panels c and d) of the samples annealed in air and nitrogen, respectively. Our results indicate that their work function increased from 3.60 ± 0.02 eV, before annealing, to 3.80 ± 0.02 eV and 3.90 ± 0.02 eV for samples annealed in air and N₂, respectively. These values are intermediate between those of the as grown AO-HH and AO-HZC samples.

Figure 5.5: Morphology of AO-HH annealed film at 100 °C in (a) air and (b) nitrogen; KPFM image of AO-HH annealed film at 100 °C in (c) air and (d) nitrogen representing the work function profile of the sample relative to the tip.
Any change in the superficial characteristics of our thin films, including adsorption of oxygen or partial crystallization, can induce substantial variations in the work function measured by KPFM. Acridine orange films annealed in air have been exposed to oxygen and moisture from the atmosphere, and the dipole moment of any absorbed species can directly induce a difference in contact potential and, subsequently, a shift in their work function [22]. This mechanism is less important for acridine orange films annealed in N₂. On the other hand, the morphology of the acridine orange films annealed in air is different from those annealed in N₂ due to crystallization, as discussed earlier. Crystallization changes the electronic structure of the surface and thus may affect the work function [23]. Since the change in morphology of AO-HH film is more substantial in the samples annealed in N₂, as revealed by the comparison of Figures 5.5a and 5.5b, this may have a stronger impact on the work function, as witnessed by its slightly larger increase.

5.3.2- Investigation of photo-induced charge generation in acridine orange thin films

In order to gain insight into the performance of acridine orange as a photoactive material, we conducted KPFM measurements under 532 nm laser light illumination and investigated photo-induced charge generation in this material. Figures 5.6a and 5.6b show KPFM images of an AO-HZC film, spun from water-based solution, under laser illumination and the subsequent changes in the KPFM signal, respectively. The contact potential and, consequently, the work function, shifts by $\Delta \varphi_f \approx 160 \text{ meV}$ when the sample is illuminated by the laser, as it is evident in Figure 5.6b. This shift is due to the photogenerated population of charge carriers excited into the conduction bands, as previously reported by other authors in well-established organic photoactive donor materials. KPFM measurements under illumination were reported by Palermo et al. for regioregular P3HT, with $\Delta \varphi_f \approx 65 \text{ meV}$, [17] and Hoppe et al. for poly-[2-(3,7-dimethyloctyloxy)-5-methyloxy]-para-phenylene-vinylene, with $\Delta \varphi_f \approx 150 \text{ meV}$ [16]. Similar experiments were conducted by us on bare regions of the ITO substrate and did not reveal any measurable difference in the KPFM signal with and without illumination.
This experiment was done to ensure that the shift in the KPFM signal is not an artifact because of the change in the work function of the tip due to changes in temperature associated with laser illumination.

**Figure 5.6:** (a) KPFM image of AO-HZC spun from water solution under illumination cycles and (b) contact potential profile of the film relative to the tip represented by the blue line in panel a.

We developed a physical model to quantify photo-induced charge generation processes by considering KPFM experiments with and without illumination. During the measurements in the dark, the force \( F' \) between the tip and the sample is proportional to the difference between the valence band energy level \( E_V \) of the sample and the work function of the tip \( \varphi_{tip} \) expressed in Volts, augmented by the positive bias voltage applied to it:

\[
F' \propto |E_V - (\varphi_{tip} - V_b)|.
\]  

Minimization of the force between the tip and the sample at each point of a KPFM scan occurs at \( V'_b \approx \varphi_{tip} - E_V \) so that \( eV'_b \), the KPFM signal expressed in eV, offers a measurement of the work function of the sample relative to the tip. Under illumination, a fraction of the electrons in the photoactive material are excited into the conduction band.
and thermodynamic equilibrium is established between photogeneration and de-excitation of photogenerated carriers due to their finite lifetime. Consequently, a significant fraction of the electronic states with which the tip interacts are conduction band states and Equation (5.2) does not provide an adequate description of KPFM experiments under illumination, since it does not consider the conduction band energy states. The force between the tip and the sample during KPFM scans under illumination ($F^*$) depends on both the energy levels of the valence and conduction electronic states, weighted by the relative populations, as

$$F^* \propto (1 - n)|E_V - (\varphi_{tip} - V_b)| + n|E_C - (\varphi_{tip} - V_b)|,$$  \hspace{1cm} (5.3)

where $E_C$ is the conduction band energy level relative to vacuum and $n$ is the fraction of electrons sitting in the conduction band at the specific intensity of illumination that is being used. Inspection of Equation (5.3) indicates that minimization of $F^*$ during KPFM scans under illumination occurs at a voltage

$$V_b^* \approx V_b' + nE_g,$$  \hspace{1cm} (5.4)

where $E_g = E_V - E_C$ is the optical band gap energy of the sample. Since $V_b'$ and $V_b^*$ can be determined from KPFM measurements under dark and illumination conditions, respectively, Equation (5.4) will provide information on $n$ if the optical band gap of the material is known. In addition, the density of photogenerated carriers in specific photoactive materials can be calculated from $n$ if the optical absorption coefficient of the material at the illumination wavelength is known.

In this way, we could estimate the carrier density in a typical AO-HZC film at the illumination power of 0.8 mW/mm$^2$ when we determined the optical band gap of AO to be $E_g = 2.2$ eV from its UV-visible measurement. By replacing in Equation (5.4) the average values of $V_b' \approx 0.79$ V and $V_b^* \approx 0.95$ V measured by KPFM in the dark and under illumination, respectively, shown in Figure 5.6b, we obtain $n = 0.07$ and, by considering an incident photon flux $\Phi = 2.8 \times 10^{21}$ m$^{-2}$ s$^{-1}$ at the illumination intensity of 0.8 mW/mm$^2$, the photogenerated carrier density in an AO-HZC thin film can be
estimated as
\[ C = n \Phi A(\lambda), \]  
(5.5)

where \( A(\lambda) = 0.46 \) is the optical absorbance of the AO film at \( \lambda = 532 \) nm determined from UV-visible measurements. By replacing the measured values of \( n, \Phi \) and \( A(\lambda) \), in Equation (5.5), we obtain \( C = (9.0 \pm 1.2) \times 10^{19} \text{ m}^{-2} \text{s}^{-1} \), which leads to an internal quantum yield of \( Y = C / \Phi = 3.2\% \) in AO. This value compares well with \( C = 1.0 \times 10^{20} \text{ m}^{-2} \text{s}^{-1} \) and \( Y = 3.4\% \) in P3HT [17], which indicates that AO is capable of generating sufficient amounts of carriers in photovoltaic devices.

5.3.3- Bilayer photovoltaic devices using acridine orange as the photoactive material

We fabricated bilayer photovoltaic devices using both AO-HH and AO-HZC as donor materials, and PCBM as the acceptor material. Complete devices have a structure consisting of ITO/AO/PCBM/Al multilayers, as shown in Figure 5.7a and 5.7b for AO-HZC and AO-HH, respectively. The energy levels of all these materials are also shown in Figures 5.7a and 5.7b. In these Figures, the conduction band energy level of AO was determined from its energy band gap and the work function obtained from KPFM measurements. Specifically, we found that \( E_C = 2.5 \text{ eV} \) for AO-HZC and \( E_C = 1.4 \text{ eV} \) for AO-HH. Since the work function of AO-HH can be increased by annealing, this means that \( E_C \) in AO-HH can be 1.6-1.7 eV if samples are annealed. Only solar devices fabricated from AO-HZC photoactive layers spun from water-based solutions have shown measurable photovoltaic effects. In order to optimize the efficiency of these devices, we optimized the thickness of the PCBM acceptor layer. We found that increasing the spin-coating speed for the PCBM layer deposition increases the short circuit current density (\( J_{SC} \)) but decreases the fill factor of the cells. This leads to an increase in the overall efficiency up to 0.20 % when the thickness of the PCBM layer is approximately 85 nm corresponding to a deposition spin speed of 3000 rpm. The current-voltage (I-V) curve of such device is shown in Figure 5.7c. Table 5.1 summarizes the relevant parameters for photovoltaic devices prepared at different thicknesses of the
PCBM layers. The detailed information for the calculation of the series and shunt resistance for the above mentioned devices can be found in Appendix A.

Figure 5.7: (a) ITO/acridine orange/PCBM/aluminum photovoltaic device structure and energy band diagrams determined by KPFM for AO-HZC layers and (b) AO-HH layers (in which lower values, 3.6 eV and 1.4 eV, refer to as-grown samples and the higher values, 3.9 eV and 1.7 eV, refer to annealed samples). (c) The current-voltage characteristics of the resulting photovoltaic devices.
As can be seen from Table 5.1, AO-based photovoltaics have a high series resistance relative to state-of-the art P3HT:PCBM devices [1], which offers an explanation for their relatively low efficiency. Such a high series resistance might be ascribed to high intrinsic resistance of the AO thin films, since the work function of AO-HZC matches the work function of ITO, 4.8 eV, with very slight difference. While the uniform structure of the AO-HZC layers spun from water solution may facilitate the formation of a large interface for electron-hole pair dissociation, the presence of large microscopic voids may also lead to microscopic short-circuits in some parts of the devices, in which the PCBM acceptor layer is directly in contact with the ITO cathode, therefore limiting the devices efficiency.

Table 5.1: Parameters of photovoltaic devices with various thicknesses of the PCBM layer.

<table>
<thead>
<tr>
<th>PCBM thickness (nm)</th>
<th>Open-circuit voltage $V_{oc}$ (V)</th>
<th>Short-circuit Current density $J_{sc}$ (A/cm$^2$)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
<th>Series resistance ($10^4$ Ω)</th>
<th>Shunt resistance ($10^5$ Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.35</td>
<td>0.02</td>
<td>34.8</td>
<td>0.004</td>
<td>0.34</td>
<td>8.1</td>
</tr>
<tr>
<td>220</td>
<td>0.30</td>
<td>0.02</td>
<td>36.1</td>
<td>0.006</td>
<td>0.25</td>
<td>3.8</td>
</tr>
<tr>
<td>150</td>
<td>0.52</td>
<td>0.03</td>
<td>29.9</td>
<td>0.012</td>
<td>2.2</td>
<td>1.4</td>
</tr>
<tr>
<td>110</td>
<td>0.57</td>
<td>0.03</td>
<td>27.2</td>
<td>0.018</td>
<td>0.60</td>
<td>1.3</td>
</tr>
<tr>
<td>85</td>
<td>0.62</td>
<td>0.06</td>
<td>27.5</td>
<td>0.20</td>
<td>2.0</td>
<td>0.47</td>
</tr>
</tbody>
</table>

A typical I-V curve for an AO-HH/PCBM bilayer solar device is also shown in Figure 5.7c. Unlike devices fabricated from AO-HZC films, AO-HH based devices did not show any measurable photovoltaic characteristics. This is understandable because the mismatch in the energy levels between AO-HH and ITO is significant with $\varphi_{AO-HH} = 3.6$ eV and $\varphi_{ITO} = 4.8$ eV. This mismatch in energy levels remains significant even after annealing the AO-HH films, in which case $\varphi_{AO-HH} = 3.9$ eV. The work function of AO-HH is also very close to the conduction band energy level of the PCBM, at 3.7 eV. The small difference between the valence band energy level of AO-HH and the conduction band
energy level of PCBM may also lead to a strong reverse current that prevents the device from functioning as a solar cell, which explains its short-circuit characteristics. In addition, the granular morphology of AO-HH, which is different from the grainless morphology of AO-HZC, as shown in the cartoons representing the solar cell architectures in Figures 5.7a and 5.7b, may also have played a role in the different performance of the devices.

We also fabricated bilayer devices consisting of AO/PCBM/Al layers assembled on the bottom graphene electrodes, which were prepared following the same procedure discussed in Chapter 3 and Section 5.2. Neither AO-HH based nor AO-HZC devices using graphene electrodes showed photovoltaic current-voltage characteristics. Graphene electrodes have a work function of 4.46 eV (see Chapter 4, page 85), which reasonably matches the valence band electronic energy level of AO-HZC, with its work function of 4.7 eV. This facilitates the collection of the holes photo-generated in the AO-HZC layer; however, the presence of large microscopic voids in the AO-HZC layer on top of graphene, similar to what we observed for the ITO substrate (see Appendix A), can cause a direct electrical contact between the graphene film and the top electrode, which ultimately leads the device to short-circuit. In addition, the relatively large surface roughness of graphene thin films, in which a certain number of multi-layer graphitic protrusions present, compared with the ITO substrate provides a larger possibility for the bottom graphene electrode to penetrate to the top layers of the device and come to direct contact with the top electrode. The sheet resistance of graphene electrodes is also higher than in ITO electrodes, which leads to an increase in the series resistance of the device fabricated using graphene. Combining all these limitations with the high intrinsic resistivity of AO-HZC may cause the AO-HZC based devices on graphene electrodes to fail, in spite of the similar ITO-based devices, which demonstrated the photovoltaic characteristics. Further developments in the preparation of graphene electrodes in terms of conductivity and surface roughness will be required to fabricate AO-HZC based photovoltaic devices using graphene. In the case of the devices using AO-HH photoactive material and the graphene electrodes, similar reasons as mentioned for the device failure using ITO electrodes along with the aforementioned limitations of the graphene electrodes are more likely responsible for the absence of the photovoltaic characteristics.
It is worth mentioning that the photovoltaic results we obtained in ITO/AO-HZC/PCBM/Al bilayer devices are promising in respect to the use of acridine orange as a suitable photoactive material in photo-sensor applications in which high photoconversion efficiency is not required, but bio-sensitivity is essential. Although the efficiency of photovoltaic devices could be in principle improved by mixing AO with water-soluble pyrrolidinium-type fullerene derivatives [24] with the formation of bulk heterojunction device structures, the crystallographic restructure of AO in these systems would be difficult to predict and the biosensitivity of these blends is questionable as well.

5.3.4- Assessment of the biosensitivity of acridine orange

We investigated the biosensitivity of acridine orange by measuring the UV-visible optical absorption spectra of AO water-based solutions in the presence of RNA VI. Figure 5.8 shows the absorption coefficient of AO-HZC in water, also containing different concentrations of RNA VI. The concentration of AO-HZC was kept constant in this set of experiments.

Figure 5.8: Absorption coefficient spectra of AO-HZC water-based solutions in the presence of various concentrations of RNA. The peak positions of the spectra are upshifted in the presence of RNA and the intensities of the peaks are strongly related to the concentration of RNA.
As can be observed from Figure 5.8, the optical absorption spectrum of pure AO-HZC exhibits a distinct peak at \( \approx 452 \pm 1 \) nm with a shoulder at \( \approx 428 \pm 1 \) nm. The peak positions for the absorption spectra of AO-HZC solutions are somewhat upshifted in the presence of RNA and the two peaks can be observed at 435±1 nm and 460±1 nm in this case, with little dependence on the RNA concentration. The peaks that are present in the absorption spectra shown in Figure 5.8 can be assigned to the vibronic transitions [18], which occur between different vibrational-electronic energy levels of a molecule, AO-HZC in our case. The attachment of RNA to AO-HZC may lead to a change in the electron-phonon coupling within the molecule, which results in different relative intensity of different vibronic peaks referred to pure AO-HZC. The peak at 435±1 nm is more intense in the presence of RNA, while only a weak shoulder was present in the absorption spectrum of pure AO-HZC. From Figure 5.8, it can also be observed that the intensities of both peaks are strongly dependent on the concentration of RNA. For instance, at 0.019 mg/mL RNA concentration, the 435 nm peak is more intense than the 460 nm peak, while the relative intensity of the two peaks is reversed at a higher RNA concentration, 0.077 mg/mL. These observations support the fact that the optical absorption spectrum of acridine orange is sensitive to the presence of nucleic acids. Since the amount of photons absorbed in the photoactive layer is proportional to the short-circuit photocurrent generated by a photovoltaic device, acridine orange is a promising candidate for the fabrication of photodetectors that are sensitive to the concentration of RNA at their surface.

5.4- Conclusions

We have demonstrated the fabrication of photovoltaic devices from cost-effective, water-soluble, and bio-sensitive acridine orange molecules that are used for labeling nucleic acids, including DNA and RNA [13, 14]. Our experiments indicate that the presence of ZnCl₂ as an anti-crystallization agent is beneficial for the use of acridine orange as a photovoltaic material. Acridine orange containing ZnCl₂ can be used to prepare more uniform and grainless thin films that are suited for device fabrication. Thin films of acridine orange containing ZnCl₂ are amorphous, but they offer better photovoltaic device performance than micro- and nano-crystalline acridine orange thin films because of their
higher work function that matches the energy level of ITO ($\phi_{AO-HZC} = 4.7$ eV). Instead, AO crystals orient in a way that may only specific crystallographic directions with relatively low work function ($\phi_{AO-HH} = 3.6$–$3.9$ eV) interface with ITO. KPFM measurements under laser illumination have confirmed that acridine orange is capable of generating a significant amount of photocarriers. Bilayer devices consisting of ITO/AO-HZC/PCBM/Al layers show photovoltaic characteristics. The biosensitivity of acridine orange was also assessed by considering the absorption coefficient of AO in the presence of RNA, which shows the strong dependence of AO absorption coefficient to the concentration of RNA. This indicates that the optical properties of AO can be tuned using various concentrations of RNA. Although the efficiency of the AO-HZC-based solar cells is low in comparison to other organic photovoltaic materials, it may open an avenue towards the fabrication of biosensitive and nucleic acid sensitive photovoltaic devices, in which the bio-sensitivity of acridine orange is essential.

5.5- References


Chapter 6. On the adsorption of proteinogenic amino acids on graphene thin films

6.1- Introduction

Adsorption of biomolecules on graphene has recently attracted strong interest for biological applications [1]. Specific studies motivated by biological applications of graphene include its noncovalent functionalization with peptides, proteins, and small biomolecules [2, 3]. Development of these bio-functionalized graphene systems have been prompted by their use in biosensing [4-12], drug delivery in living cells [13, 14], and bio imaging [14-16], which require detailed knowledge of the interaction of peptides and proteins with the graphene surface. The fundamental constituents of peptides and proteins are a variety of different proteinogenic amino acids. Understanding the adhesion of individual amino acids on graphene is vital for the use of functionalized graphene materials for biological applications.

Several experimental and theoretical efforts [17-20] have been undertaken for studying the interaction of different amino acids with graphene and graphene oxide and the associated adsorption energies. Zhang et al. experimentally estimated the adsorption energies of a few proteinogenic amino acids with the surface of graphene oxide [17]. In their experiments, a mixture of different proteinogenic amino acids, consisting of arginine, histidine, lysine, tyrosine, tryptophan, and phenylalanine, was incubated with graphene oxide in a buffer solution and centrifuged. The decrease in concentration of each amino acid in the supernatant extracted from the centrifugation process was assumed to be a measure of the adsorption energy of that specific amino acid on the graphene oxide surface. Although these authors assumed that the entire decrease of amino acid concentration in the supernatant was due to amino acid-graphene oxide interaction, amino acid-amino acid interaction may also occur, which leads to heavier amino acid complexes that could also be removed from the supernatant during
centrifugation. In this case, the decrease in amino acids concentrations in the supernatant cannot be only attributed to their adhesion on graphene oxide. More accurate measurements are required to determine the adsorption energy of a specific type of amino acid on graphene, as opposed to considering a combination of different amino acids simultaneously. The results of Zhang et al. were used for the fabrication of peptide biosensors utilizing the graphene oxide platform, based on the consideration that peptides consist of a combinations of different amino acids. However, in the absence of more detailed information on the adsorption energy of each specific proteinogenic amino acid, these types of sensors may not be sufficiently accurate when information on a particular type of amino acid is desired.

Theoretical studies using density functional theory (DFT) and molecular dynamics (MD) simulations to calculate the adsorption energies of amino acids on the surface of graphene have also been reported [18-20]. Rajesh et al. [19] and Vovusha et al. [20] determined the adsorption energies of specific aromatic amino acids without taking into account the possible role of solvents in affecting their interaction with graphene. In order to complement these studies with more information on the solvation effects, Dragneva et al. [18] calculated the adsorption energies of the complete set of 20 proteinogenic amino acids on graphene using a force field method. Since this method is less computationally heavy than MD and DFT, the effects of a specific solvent, water, on the adsorption energy could also be taken into account. These authors found that the adsorption processes are dominated by the van der Waals (vdW) interactions between graphene and the amino acids, which were shown to be proportional to their molecular mass. However, in the simulations carried out by Dragneva et al [18], force field methods required strong assumptions on the interactions between delocalized $\pi$-electron clouds of graphene and specific amino acids. Moreover, in these theoretical studies, a single amino acid molecule was assumed to be placed on top of a perfectly flat graphene sheet. In fact, amino acid molecules are expected to distort the graphene lattice, due to distortions in the sp$^2$ hybridization of carbon atoms with possible additional contributions from the solvent. In principle, this may lead to adsorption energies between the amino acid and the distorted graphene surface, which could be different from those determined in the absence of
distortions. In addition, the surfaces of graphene prepared by laboratory techniques of practical interest, presented in Chapter 1 Section 1.1 of this thesis, are significantly different from ideal graphene, as it was considered in these theoretical simulations. For all of these reasons, experiments that are capable of estimating the adsorption energy of proteinogenic amino acids on graphene under realistic conditions are necessary to validate these theoretical estimations.

In this chapter, we have used Kelvin probe force microscopy (KPFM) and UV-visible (UV-vis) spectrophotometry to develop a methodology to investigate the adhesion of eight proteinogenic amino acids, arginine, histidine, lysine, aspartic acid, asparagine, alanine, phenylalanine, and tryptophan, to the surface of graphene thin films prepared using RNA as a surfactant, which was subsequently removed from the films. The method for preparation of graphene thin films is the same as what was discussed in detail in Chapter 3, Section 3.2 of this thesis. The proteinogenic amino acids selected for our tests were chosen to represent different categories of these molecules with different side chain properties and specifically: i) proteinogenic amino acids with hydrophilic-polar and basic side chain (arginine, histidine, and lysine); ii) proteinogenic amino acids with hydrophilic-polar and acidic side chain (aspartic acid); iii) proteinogenic amino acids with hydrophilic-polar and neutral side chain (asparagine); and iv) proteinogenic amino acids with hydrophobic-nonpolar side chain (alanine, phenylalanine, and tryptophan). Comparison of histidine, phenylalanine, and tryptophan is particularly useful since they all contain aromatic rings with delocalized \( \pi \)-electrons that may interact with the \( \pi \)-electrons of graphene via vDW forces, but the magnitude and type of the interaction may significantly vary depending on the polarity or non-polarity of the side chain (i.e., in histidine vs. phenylalanine) or, for non-polar chains, depending on the degree of aromaticity (i.e., in phenylalanine vs. tryptophan). The selected group of proteinogenic amino acids also offers a wide range of different molecular weights, which, according to Dragneva et al. [18], should provide a quite different intensity of van der Waals interactions with the surface of graphene. The complete list of proteinogenic amino acids, along with their abbreviations and chemical formulas, is reported in Table 6.1, in which the specific ones that were considered in our study are highlighted.
In our experiments, the concentration of proteinogenic amino acids on graphene has been detected from the intensity of the UV-vis signal obtained from the samples upon reaction of the specific amino acid with ninhydrin, an amino acid marker. For each proteinogenic amino acid included in our study, the adsorption energy on graphene was estimated qualitatively from the shift of its work function, in the presence and in the absence of graphene, with a larger shift indicating a stronger interaction. Our model implicitly assumes a negligible binding energy of each amino acid on the reference substrate, indium tin oxide (ITO) in our case. We found a good correlation between our experimentally measured shifts of the work function and the van der Waals contributions of the adsorption energies calculated by Dragneva et al. [18], which seems to indicate that, in spite of the strong assumptions associated with their force field methods, the interaction between proteinogenic amino acids and graphene thin films could be successfully described by their theoretical model. From their theoretical results as well as our experiments, it can be concluded that the presence of amine groups and aromatic rings in the side chains plays a critical role in the adsorption energy of proteinogenic amino acids on graphene.

**Table 6.1.** Proteinogenic amino acids along with their molecular weights and chemical structures. Those considered in our work are highlighted.

<table>
<thead>
<tr>
<th>Name of amino acid</th>
<th>Abrev.</th>
<th>Mol. weight (g/mol)</th>
<th>Chemical formula</th>
<th>Side chain property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arginine</td>
<td>Arg</td>
<td>174.20</td>
<td><img src="image" alt="Chemical structure of Arginine" /></td>
<td>Hydrophilic Basic</td>
</tr>
<tr>
<td>Histidine</td>
<td>His</td>
<td>155.15</td>
<td><img src="image" alt="Chemical structure of Histidine" /></td>
<td></td>
</tr>
<tr>
<td>Lysine</td>
<td>Lys</td>
<td>146.19</td>
<td><img src="image" alt="Chemical structure of Lysine" /></td>
<td></td>
</tr>
<tr>
<td><strong>Amino Acid</strong></td>
<td><strong>IUPAC</strong></td>
<td><strong>CAS</strong></td>
<td><strong>Properties</strong></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-----------</td>
<td>---------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td><em>Aspartic Acid</em></td>
<td>Asp</td>
<td>133.10</td>
<td>Hydrophilic, Acidic</td>
<td></td>
</tr>
<tr>
<td>Glutamic Acid</td>
<td>Glu</td>
<td>147.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Serine</td>
<td>Ser</td>
<td>105.09</td>
<td>Hydrophilic, Neutral</td>
<td></td>
</tr>
<tr>
<td>Threonine</td>
<td>Thr</td>
<td>119.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Asparagine</em></td>
<td>Asn</td>
<td>132.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glutamine</td>
<td>Gln</td>
<td>146.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Alanine</em></td>
<td>Ala</td>
<td>89.09</td>
<td>Hydrophobic, Neutral</td>
<td></td>
</tr>
<tr>
<td>Isoleucine</td>
<td>Ile</td>
<td>131.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leucine</td>
<td>Leu</td>
<td>131.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methionine</td>
<td>Met</td>
<td>149.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Phenylalanine</em></td>
<td>Phe</td>
<td>165.19</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### 6.2- Experimental details

Graphene samples were prepared using the same procedure described more in detail in Chapter 3, Section 3.2 [21]. In brief, nanocrystalline graphite (Sigma Aldrich Inc., 332461) was ultrasonicated for 24 h in a 3:1 H₂SO₄:HNO₃ mixture, dried on filter paper and, subsequently, mildly oxidized in Piranha reagent (H₂SO₄:H₂O₂ = 4:1) [21]. 6 mg of the resulting, mildly oxidized, graphitic material were ultrasonicated for 4 h in a 0.6 g/L water solution of RNA VI (Sigma Aldrich Inc., R6625). The resulting suspension was left to sediment overnight at 2 °C in a beaker. The top three-quarters of the suspension were centrifuged at 6000 rpm for 1 hr to remove heavier and thicker layers of graphitic flakes from the suspension. The supernatant was filtrated through a nitrocellulose filter membrane (220 nm pore size, Millipore), which was then transferred to quartz or ITO substrates and dried under load. Consecutive acetone and methanol baths were used to
etch the membrane leaving behind thin graphene flakes on the substrate in the form of thin films. Finally, the graphene films were annealed on a hot plate at 540 °C for 30 min inside a VAC Nexus glovebox purged with nitrogen at oxygen and moisture levels less than 2 ppm to remove RNA from the films. In this work, the graphene thin films were not treated by HNO$_3$/SOCl$_2$, because the main goal here was not to improve the conductivity of graphene and also preparing graphene with the highest quality and lowest amounts of impurities was desired.

A set of different proteinogenic amino acids were used in our study, including l-arginine (Sigma Aldrich Inc., A8094), l-tryptophan (Sigma Aldrich Inc., T8941), l-histidine (Sigma Aldrich Inc., H6034), l-lysine (Sigma Aldrich Inc., L5501), l-phenylalanine (Sigma Aldrich Inc., P5482), l-alanine (Sigma Aldrich Inc., A7627), l-asparagine (Sigma Aldrich Inc., A0884), and l-aspartic acid (Sigma Aldrich Inc., A9256). Each of these amino acids was dissolved in water prior to our test. Since different amino acids have different water solubility, a fixed concentration at 56 mg/mL was used. For those amino acids in which the solubility was below such threshold, the following concentrations close to saturation were used: 35 mg/mL for Asn, 4.5 mg/mL for Asp, 19.6 mg/mL for Trp and Phe, and 41.6 mg/mL for His. Drop casting was chosen to leave a considerable amount of amino acids on the substrate and enable their detection by UV-vis spectrophotometry. In order to prepare graphene-amino acid composites, 0.25 mL of solution of each amino acid was drop cast on a graphene thin film deposited on quartz and a bare quartz substrate, as a control sample. For the amino acids for which the concentration was different from 56 mg/mL (see above) the amount of drop-casted solution was adjusted accordingly. Samples were left to dry in ambient atmosphere and they were subsequently dipped in a solution of ninhydrin (Sigma Aldrich Inc., N4876), at 178 mg/mL concentration in ethanol, for two minutes. The samples were next annealed at 85 °C for 20 minutes on a hot plate in air. Ninhydrin was discovered in 1910 by Siegfried Ruhemann and since then it has become an important analytical tool for chemistry and biochemistry studies [22]. It is well known that when an amino acid heats up in the presence of ninhydrin, it reacts with it and forms a compound with a deep blue or purple color [22-24]. The following reaction scheme, shown in Figure 6.1, is expected to occur [22]:
The product of this reaction, known as Ruhemann’s purple, has a pigmentation that will lead to a characteristic UV-vis optical absorption spectrum of the sample if amino acids are present [22]. At each step of our preparation process, a UV-vis spectrum was recorded at normal incidence using a Varian DMS-80 UV-visible spectrophotometer in the 200-800 nm wavelength range. The schematic procedure of sample preparation for UV-vis measurements is shown in Figure 6.2a.

Graphene thin films for KPFM measurements were prepared on ITO substrates (sheet resistance 70–100 Ω/sq., Sigma Aldrich Inc., 576352) because high conductivity of the substrate is required for these measurements. In order to add amino acids to graphene samples for KPFM measurements, we dipped them into 19.6 mg/mL solutions of amino acids in water for 3 h. In the case of aspartic acid, for which the solubility level was relatively low, 4.5 mg/mL, the dipping time was increased to 13 h, in order to compensate for this low solubility level. The schematic of the preparation process of these samples is shown in Figure 6.2b.
Figure 6.2: Schematic procedure of the sample preparation (a) for UV-visible spectroscopy and (b) for Kelvin Probe Force Microscopy measurements.

Atomic force microscopy (AFM) topography and KPFM images of the resulting samples were recorded on a Witec Alpha 300S AFM system specifically modified for KPFM measurements as described in Chapter 2, Section 2.2.2. Doped silicon probes (characteristic frequency ~75 KHz, Nano Sensors Inc.) were used for AFM/KPFM imaging. The work function of the probes was calibrated using bare ITO thin films as references. The work function of ITO was assumed to be 4.8 eV [25]. Shifts in the work function in the correspondence of aggregates of amino acids on graphene and ITO were determined from the KPFM signal at different areas, coated and uncoated with graphene platelets, of the image. Sufficiently large areas were scanned to average statistical fluctuations of the work function, which was calculated from histograms extracted from KPFM images, best-fitted with Gaussian functions using a least-square method.
6.3- Results and discussion

6.3.1- Detection of amino acids on graphene thin films

The reaction process of amino acids with ninhydrin, shown in Figure 6.1, leads to the production of an intensely blue-purple pigment [26]. The actual color of the pigment may slightly vary depending on the type of amino acid being detected, as well as with different experimental conditions [27]. The UV-vis spectrum of Ruhemann’s purple includes an absorption peak generally found at about 400 nm and a higher wavelength absorption peak, typically sitting between 470 nm and 600 nm [28]. In most cases, this absorption peak is found at 570 nm, but different factors (including hydrolysis, oxidation, and photolysis of the sample) may also affect the interaction of a specific amino acid with ninhydrin and change the position of such peak [28]. It has also been reported that temperature and ninhydrin concentration can either affect the intensity of the peak or shift the peak position [29, 30].

![Absorption spectra for graphene and bare quartz substrates functionalized with different amino acids and marked with ninhydrin.](image)

**Figure 6.3:** Absorption spectra for (a) graphene and (b) bare quartz substrates functionalized with different amino acids and marked with ninhydrin. The absorption peak between 470-600 nm is the signature of the presence of amino acids on the substrate. The intensities of the absorption peaks on graphene are normally larger than those on the quartz substrates, and indicate that greater amounts of amino acids are absorbed on top of graphene surfaces. The absorption peak was not observed for a few amino acids and this may be due to small amounts of amino acids present on the surface or non-reacted amino acids with ninhydrin.
We recorded the UV-vis spectra of the graphene thin films functionalized with different amino acids and marked with ninhydrin, shown in Figure 6.3a, to detect the presence of amino acids on the graphene surface. The amino acids used in these experiments are highlighted in green in Table 6.1. The UV-vis spectra of the amino acids on the bare quartz substrates, also marked by ninhydrin, were also taken in parallel to use them as control samples. These spectra are shown in Figure 6.3b.

Table 6.2: Summary of the absorption peak positions and intensities for both graphene and bare quartz substrates functionalized with amino acids and marked by ninhydrin.

<table>
<thead>
<tr>
<th>Amino acids</th>
<th>Peak position for graphene/amino acids-ninhydrin (nm)</th>
<th>Peak position for quartz/amino acids-ninhydrin (nm)</th>
<th>Intensity of the peak for graphene/amino acids-ninhydrin</th>
<th>Intensity of the peak for quartz/amino acids-ninhydrin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ala</td>
<td>Broad peak 500-600</td>
<td>Broad peak 470-600</td>
<td>0.097</td>
<td>0.053</td>
</tr>
<tr>
<td>Asp</td>
<td>No peak</td>
<td>No peak</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Asn</td>
<td>No peak</td>
<td>Broad peak 500-600</td>
<td>0</td>
<td>0.035</td>
</tr>
<tr>
<td>Lys</td>
<td>587</td>
<td>587</td>
<td>0.456</td>
<td>0.073</td>
</tr>
<tr>
<td>Phe</td>
<td>569</td>
<td>Broad peak around 577</td>
<td>1.388</td>
<td>0.054</td>
</tr>
<tr>
<td>His</td>
<td>Broad peak around 580</td>
<td>No peak</td>
<td>0.088</td>
<td>0</td>
</tr>
<tr>
<td>Trp</td>
<td>500</td>
<td>500</td>
<td>0.147</td>
<td>0.033</td>
</tr>
<tr>
<td>Arg</td>
<td>598</td>
<td>598</td>
<td>0.852</td>
<td>0.171</td>
</tr>
</tbody>
</table>

The absorption peak positions and their corresponding intensities for both graphene and quartz substrates functionalized with different amino acids were extracted from Figure 6.3a and 6.3b and summarized in Table 6.2. It needs to be mentioned that the UV-vis spectra of the samples were taken at each step, including bare graphene/quartz samples, graphene/quartz functionalized with amino acids without labeling by ninhydrin, and a
pure ninhydrin sample. This was done to ensure that there would be no peak in the UV-vis spectra in the range of 470–600 nm from our samples without labeling with ninhydrin and the resulting absorption peaks in that range are due to the interaction of the amino acids with ninhydrin. Notably, no peaks were observed in the samples at the above mentioned steps without labeling with ninhydrin.

As discussed in Chapter 3, Sections 3.3.2 and 3.4, our graphene thin films are made by collections of graphene flakes with some parts of the substrate that are left uncovered. When the samples are drop casted from solutions of amino acids in water, amino acids are deposited on both the graphene flakes and the bare substrate. The measured absorption spectra subsequently is the integrated absorption from both the areas covered by graphene flakes and bare substrate containing amino acids labelled with ninhydrin. This absorption can be formulated by considering the fraction of areas covered by graphene flakes and can be written as:

$$A_G = fA_{G0} + (1-f)A_Q,$$

where $A_G$ and $A_Q$ are the absorbance resulting from an amino acid on a graphene thin film and from the same amino acid on a bare quartz substrate, respectively. Both these absorbances refer to samples treated by ninhydrin immediately prior to the UV-vis spectroscopy measurement. In equation (6.1), $f$ indicates the fraction of substrate area actually covered by graphene in the graphene thin film, and $A_{G0}$ indicates the contribution to the absorption spectrum that comes from the area of the substrate that is actually covered by graphene flakes. The fraction of covered area was determined from various AFM images of the graphene thin films [31] and was found to be $0.36 \pm 0.06$. The absorption spectra shown in Figure 6.3a indicate the contribution to the absorption that comes only from the areas covered by graphene, $A_{G0}$, and calculated from Equation (6.1).

As can be observed from Figure 6.3 and Table 6.2, both the UV-vis spectra of amino acids-on-graphene and amino acids-on-quartz samples labeled by ninhydrin exhibit the presence of optical absorption peaks in the 470-600 nm wavelength range for most of the samples we investigated, which is a clear signature of the presence of amino acids on
these samples. No peaks were observed for Asp, neither on graphene nor quartz substrates, as well as for Asn on graphene and His on quartz. Possible reasons can be either a too small amount of amino acids in these samples, well below the detection limit of UV-vis spectroscopy, or a too small amount of ninhydrin that was trapped on their surface, or the lack of reaction of these specific amino acids with ninhydrin, which would lead to the absence of Ruhemann’s purple and related optical absorption peaks. Nevertheless, our complementary AFM study (discussed in section 6.3.2) shows that small amounts of Asn and Asp are present on the surface of graphene thin films, even though no optical absorption peak associated to Ruhemann’s purple could be detected in their UV-vis spectra. The absence of purple pigment in the UV-vis spectra could be associated to fact that our marking experiments were not optimized for each specific amino acid and, rather, they were aimed at loosely quantifying the relative amount of each amino acid that was actually absorbed on graphene.

The relative intensity of the absorption peaks shown in Figure 6.3 is indicative of the relative amount of amino acid present on each sample that interacts with ninhydrin. As can be noticed from Table 6.2, the intensities of the absorption peaks on graphene are higher than those of the corresponding peaks on quartz for all of the proteinogenic amino acids we considered in our study, except for Asn. The peak intensities are particularly high for Arg, Trp, Phe, and Lys, which means there are more amounts of these materials present on the graphene surface compared with other amino acids. From an absolute point of view, our peaks intensities are generally lower than those sometimes reported in the literature [29, 30], because, in our case, the test has been made on thin solid films as opposed to solutions in a liquid cell, in which much larger amounts of ninhydrin and amino acids are present. On the other hand, a liquid phase UV-vis study would not have been appropriate in our case due to the fact that we are interested in the physisorption of amino acids on a dry surface.

Although, at a first sight, the entire amount of amino acids that are detected by UV-vis in the proximity of a graphene thin film may be naively associated with their adsorption on graphene, we can anticipate that no clear relationship between the amount of amino acids semi-quantitatively detected from UV-vis absorption peaks of Ruhemann’s purple and
their adsorption energy, measured by KPFM or theoretically predicted by other groups [18], could be found by us. In fact, some of the amino acids existing on our samples may not be actually interacting with quartz or graphene, even though their presence results in the presence of an optical absorption peak due to Ruhemann’s purple. In the opposite direction, strong interaction with the surface could also mean that amino acid molecules are less prone to react with ninhydrin. Furthermore, since ammonia and partially reduced ninhydrin are required for the production of Ruhemann’s purple, it has also been proposed that different amine groups existing within different amino acids may cause different reaction rates with ninhydrin and possibly lead to negative results for the ninhydrin test [27]. Overall, although UV-vis spectroscopy is capable of providing semi-quantitative information on the amount of each amino acid in a sample, it is not at all indicative of the adhesion of that specific amino acid to a surface and, therefore, it is not possible to use it to study the adsorption of amino acids on graphene or other surfaces. In order to more rigorously investigate the adhesion of amino acids to the surface of graphene thin films, we carried out Kelvin probe force microscopy experiments, as will be discussed more in detail in Section 6.3.2.

6.3.2- Assessment of the adsorption energies of amino acids on graphene

We investigated the adsorption energies on graphene of the eight amino acids highlighted in Table 6.1 by considering the shift in the KPFM signal when amino acids are situated on top of graphene relative to the work function of the same amino acids on ITO, to which they are expected to negligibly bind. ITO does not contain π-electrons while graphene and many proteinogenic amino acids contain them. Consequently, when amino acids are situated on top of graphene, the π-electronic clouds are affected by the possible interaction between these two species. This will lead to a change in the work function of the amino acid aggregates, which is proportional to their interaction with graphene. The stronger the adsorption energies, the larger are the changes in the work function of the aggregates and, consequently, the larger are the shifts in the KPFM signal. Consequently, the shifts in the KPFM signals can be considered a measure of the adsorption energies of amino acids to the graphene surface. However, it is not immediate that the magnitude of
the measured energy shift is exactly the same as the magnitude of the adsorption energy of that amino acid to the graphene surface. On the other hand, the shift in the KPFM signal is expected to provide, at least qualitatively, some valuable information of the adsorption energy, in order to make it possible to compare the relative adhesion strength of different amino acids to the graphene surface.

KPFM imaging was performed for samples of all of the eight of the amino acids highlighted in Table 6.1. The AFM topography, AFM phase, and KPFM signal amplitude are shown in Figure 6.4a, 6.4b, and 6.4c, respectively, by using Asn as an example. All the remaining images for the remaining seven proteinogenic amino acids studied in this work are reported in Appendix B.

Figure 6.4: (a) AFM and (b) phase images of Asn on the graphene sample, prepared on the ITO substrate. (c) The KPFM image representing the KPFM signal profile relative to the tip. (d) The histograms corresponding to the KPFM image, calibrated with the work function of the tip when Asn presents on top of the ITO (red line) and graphene (black line) substrates. The histograms were fitted with Gaussian functions, indicated by the blue lines.
Figure 6.4d demonstrates the work function histograms for Asn, corresponding to the KPFM image shown in panel c. Red and black histograms were taken from the areas of the image where amino acid is situated on bare ITO substrate and on the surface of graphene, respectively. Best-fits of the two histograms with Gaussian functions are also shown in Figure 6.4d and all of the corresponding figures in Appendix B. A clear shift in the KPFM signal where the amino acid is situated on top of the graphene surface is clearly noticeable in Figure 6.4d. Considering all of these amino acids, the shift in the KPFM signal, indicated with $\Delta \varphi$, was found to increase in the order of

$$
\Delta \varphi_{\text{Ala}} < \Delta \varphi_{\text{Asp}} < \Delta \varphi_{\text{Asn}} < \Delta \varphi_{\text{Lys}} < \Delta \varphi_{\text{Phe}} < \Delta \varphi_{\text{His}} < \Delta \varphi_{\text{Trp}} < \Delta \varphi_{\text{Arg}}, \quad (6.2)
$$

which corresponds to the order of the increasing adsorption energies to the graphene surface of the corresponding amino acids.

**Figure 6.5:** The shift in the KPFM signal, $\Delta \varphi$, versus the van der Waals contributions of the adsorption energies of different amino acids to the graphene surface that were calculated theoretically. The shift in the KPFM signal, $\Delta \varphi$, can be fitted with a linear function, as the simplest and first order approximation, with the van der Waals contributions of the adsorption energies.
This analysis indicates that our experimental results are consistent with the theoretical calculations of the adsorption energies of aromatic amino acids to the graphene surface reported in the literature [20]. Our results also compare very well with the previously calculated van der Waals contributions of the adsorption energies of different amino acids to the graphene surface in water, calculated by Dragneva et al. using the force field method [18]. As shown in Figure 6.5, there is a close linear correlation between our measured values of $\Delta \varphi$, the shift in work function of the amino acids when they overlap to graphene, and the intensity of vdW interactions calculated by these authors. This observation strongly suggests that the shift in KPFM signal is an excellent measure of the adsorption energy of amino acids on graphene and that stronger values of $\Delta \varphi$ correspond to stronger vdW interactions between amino acids and graphene.

The adsorption energies of the different amino acids, studied in this work, on graphene can be compared qualitatively with each other regarding the properties of their side chains. Among the hydrophobic amino acids studied in this work (Ala, Phe, and Trp), the adsorption energy increases in the order of Trp > Phe > Ala due to stronger van der Waals interactions, in agreement with the theoretical results of Dragneva et al. [18]. Trp and Phe contain aromatic rings with delocalized $\pi$-electrons that are expected to strongly contribute to the $\pi-\pi$ interaction with the $\pi$-electrons of graphene. Trp contains more $\pi$-electrons than Phe, which may indicate that this amino acid interacts more strongly with the $\pi$-electrons of graphene, which should also lead to a stronger adsorption energy between Trp and graphene. Therefore, it is expected that the adsorption energies of Trp, Phe, and Ala on graphene increase in the order of Ala < Phe < Trp. This is consistent with our observed shifts in the KPFM signals. In the case of the hydrophilic amino acids, our experimental results suggest that the presence of amine groups and $\pi$-electrons in the chemical structure of the amino acids both promote their adsorption on graphene thin films. Worth mentioning, Arg with a guanidine group shows the largest shift in its KPFM signal. His, which contains $\pi$-electrons in addition to one amine group, exhibits a larger shift in its KPFM signal, while Lys, that does not possess any $\pi$-electrons, exhibits the lowest shift in this set of amino acids. Both Lys and Asn contain one amine group, but
the shift in the KPFM signal was larger for Lys than for Asn. This can be attributed to the longer side chain in Lys, which may provide stronger vdW interactions compared to Asn.

It is worth noting that the ultimate goal of our study was to investigate the adhesion of different amino acids to the graphene samples by qualitatively comparing their adsorption energies as opposed to determining the exact types of interactions occurring between them and graphene. Although Kelvin probe force microscopy is useful technique for our goal, it cannot determine the exact nature of the chemical interactions between different surfaces. Furthermore, KPFM cannot determine the exact value of the adsorption energies of different amino acids to the graphene surface and it can only provide the qualitative measurements of the adsorption energy by providing a basis to compare the adhesion of different amino acids to the graphene surface. Moreover, KPFM is not capable of determining the adhesion of a single molecule of amino acid to the graphene surface, because the work function, which is the measured value by KPFM, is not well-defined for a single molecule. KPFM can measure the work function of the molecular crystals, with well-defined work functions, of amino acid aggregates and provide information about the shift in the work function due to the effect of bonding to the substrates. Therefore, the measured value of the KPFM signal may also be affected by the amino acid-amino acid interaction in which KPFM is not capable to distinguish between this interaction and the interaction between the amino acids and graphene surface. On the other hand, the agreement between our KPFM experiments and multiple theoretical predictions [18-20] has been extremely remarkable and more physically grounded than previous considerations based on the amount of each specific amino acid remaining in the supernatant of amino acids-graphene oxide mixture [17].

6.4- Conclusion

In conclusion, we investigated the adhesion of eight proteinogenic amino acids on graphene thin films. The choice was made to include different categories of amino acids, with a wide range of molecular weights and van der Waals interactions with graphene. The presence of proteinogenic amino acids on graphene was tentatively detected using ninhydrin as a marker in order to identify the relative amounts of each amino acid in our
samples. The chemical reaction between the amino acids and the ninhydrin marker is expected to produce an amount of Ruhemann’s purple that is proportional to its absorption peak in the UV-vis spectra. The UV-vis spectra of graphene samples functionalized with most of proteinogenic amino acids investigated in our work exhibit an absorption peak in the 470-600 nm wavelength range, which is the signature of the presence of Ruhemann’s purple. The presence of the amino acids on the graphene samples was also corroborated from AFM images. The adsorption energies of the amino acids were then qualitatively studied from the shifts in the Kelvin probe force microscopy signals, measured when amino acids were present on the graphene sample, relative to the same amino acid when sitting on a bare ITO substrate. It was found that the shift in the KPFM signal for the amino acids studied in this work increases in the order of Ala < Asp < Asn < Lys < Phe < His < Trp < Arg. These experimental results show a close linear correlation with the van der Waals contributions of the adsorption energies of different amino acids with graphene, as previously calculated by theorists. Moreover, from our experimental results, it may be inferred that the presence of amine group and aromatic rings containing \( \pi \)-electrons in the side chain of the amino acids play a key role in the adhesion of the amino acids on graphene. Our study provides valuable information towards the use of graphene thin films as a platform in biological applications, for instance for the fabrication of graphene-based biosensors and bioactive implants.

6.5- References


Chapter 7. Conclusions and future work

7.1- Conclusions

In this thesis, we have discussed the fabrication of transparent and conducting graphene-RNA nanocomposite thin films by surfactant-assisted exfoliation of graphite in water using RNA, a biocompatible nonionic surfactant. Thin solid films were subsequently obtained by vacuum filtration of these graphene-based water suspensions. We have observed that the exfoliation process and the properties of graphene-RNA nanocomposite thin films obtained in this way are strongly dependent on the type of RNA and graphite used. The best tradeoff between transparency and electrical conductivity of the films was obtained when nanocrystalline graphite was exfoliated in the presence of types of RNA extracted from Torula utilis which form aggregates. We also have demonstrated that the optical and electrical properties of our graphene-RNA nanocomposite thin films can be improved by a number of pre- and post-deposition treatments. Mild oxidation of nanocrystalline graphite prior to dispersion in water and recycling and re-processing of the sediment were shown to be strongly beneficial in decreasing the thickness of the suspended graphene flakes and, consequently, in improving the transparency of graphene-RNA thin films. The electrical properties of graphene-RNA thin films could also be improved by post-deposition treatments, including annealing up to 510°C and functionalization in HNO₃ and SOCl₂. These treatments significantly improved the performance of our graphene-RNA thin films and they favorably compare with graphene-based thin films obtained from other ionic surfactants.

The optical transparency and electrical conductivity of our graphene-RNA thin films allowed us to use them as transparent electrodes for poly(3-hexyl-thiophene):phenyl-C₆₁-butyric acid methyl ester bulk heterojunction organic solar cells. Under AM 1.5 illumination at 1 sun, these graphene-based organic solar cells exhibit higher open circuit voltage than identical solar cells assembled on ITO electrodes. Two different models available in the literature were considered by us for explaining the origin of the open
circuit voltage in our organic solar cells: the Band Energy Offset model and Metal-Insulator-Metal model. For different reasons, both models failed to explain the high open circuit voltage in graphene-based organic solar cells. In order to develop our own model for explaining these effects, we investigated the origin of the open circuit voltage in graphene-based and ITO-based organic solar cells using KPFM in the dark and under green laser irradiation. These measurements demonstrated that the work function of graphene electrodes increases at increasing laser irradiation intensity, while the work function of ITO electrodes is not significantly affected by illumination. Consequently, the outcome of our KPFM measurements allowed us to develop a quantitative Graphene-Insulator-Metal model for the open circuit voltage of graphene-based solar cells which is successful in predicting the changes in the work function of the graphene electrodes at different levels of laser irradiation.

Alternatives to conjugated polymers in organic photovoltaic device fabrication are small polyaromatic molecules. We have demonstrated that cost-effective, water-soluble, and bio-sensitive acridine orange molecules can be used as electron donors in photovoltaic devices. We investigated the morphology and work function of acridine orange thin films using AFM and KPFM. Our experiments showed that the presence of ZnCl₂, an anti-crystallization agent for acridine orange, is beneficial for preparing more uniform and grainless acridine orange thin films that are better suited for photovoltaic device fabrication. In addition, thin films of acridine orange containing ZnCl₂ (AO-HZC) showed higher work functions than the micro- and nano-crystalline acridine orange thin films and their highest occupied energy level are better aligned with the electronic energy levels of ITO and graphene thin film electrodes. Using KPFM under laser irradiation, we also have demonstrated that acridine orange compares well with semiconducting polymers in generating concentrations of photo carriers. Bilayer devices consisting of AO-HZC/PCBM/Al were fabricated on both ITO and graphene electrodes. The ITO-based devices showed photoconversion efficiencies up to 0.2%, while graphene-based devices were short-circuiting due to the excessive roughness of these electrodes. Although ideal graphene is perfectly flat and atomically thin, our “real” graphene thin films possess relatively high wrinkles and ridges, which are responsible for their roughness, and they also contain a small residual amount of thick graphitic particles. The
optical absorption coefficient of acridine orange in the visible range was also studied as a function of the RNA concentration of the acridine orange-water solution. This study indicated that the visible optical absorption coefficient spectra of acridine orange strongly depend on the concentration of RNA. This dependence suggests that the current-voltage characteristics of acridine orange-based photovoltaics and photodetectors change in the presence of RNA, which may enable their use for biosensing applications.

We also have investigated the adhesion of eight proteinogenic amino acid molecules (arginine, tryptophan, histidine, lysine, phenylalanine, alanine, asparagine, and aspartic acid) on the surface of graphene thin films, prepared using the procedure described in Chapter 3, Section 3.2. These amino acids were detected using ninhydrin as a marker. The optical absorption peaks that have been found in the 470–600 nm wavelength range indicated that Ruhemann’s purple was present at the surface of these samples as a consequence of amino acid decomposition in the presence of ninhydrin. We qualitatively determined the adhesion energies of proteinogenic amino acids on graphene samples by measuring the difference in KPFM signals when amino acids are placed on top of graphene flakes and ITO. The difference in the KPFM signal, and thus the adhesion energies, increased for the amino acids, considered in our work, in the order of Ala < Asp < Asn < Lys < Phe < His < Trp < Arg. These results corroborated previous theoretical calculations, in which the adsorption of different proteinogenic amino acids on graphene was attributed to van der Waals interactions. Our experimental results indicate that the presence of amine groups and aromatic rings in the side chains of the amino acids promote relatively strong van der Waals forces with carbon atoms in graphene and favor their adhesion on the graphene surface.

7.2- Future work

In continuation of our work on the investigation of the origin of the open circuit voltage in graphene-based P3HT:PCBM solar cells using KPFM under laser irradiation, we propose to map the efficiency of graphene-based solar cells using conducting AFM tips while simultaneously performing KPFM. In this proposed experiment, graphene-based solar cells will be irradiated by a laser at different wavelengths by means of an inverted
optical microscope. The KPFM and current-voltage images can be measured at the same time. Their open circuit voltage can be locally determined from the proposed GIM model in Chapter 4, Section 4.4 and can be compared with the open circuit voltage extracted at each point of a cell from a current-voltage image recorded using this scanning probe technique.

In another follow-up of our work, we are proposing to fabricate RNA-sensitive photovoltaic devices using acridine orange in the photoactive layer. As reported in Chapter 5, Section 5.3.3, we could successfully fabricate acridine orange-based photovoltaic devices using ITO electrodes. Our study also indicates that the absorption coefficient of acridine orange and, thus, its optical properties change in the presence of RNA. Consequently, one can sense RNA from the performance of photovoltaic devices containing acridine orange. To this end, a parametric study in which different concentrations of different types of RNA are dispensed on the top of a photovoltaic cell with a freely accessible acridine orange surface is required. The acceptor layer, PCBM, and the top contact can be deposited in a procedure similar to that explained in Chapter 5, Section 5.2, but an inverted solar cell architecture may be required. The performance of these devices then needs to be compared with the performance of control devices with no RNA on the top of them. These devices may have important applications in diagnostics of RNA and in forensic applications.
Appendices

Appendix A. Supplementary information for Chapter 5

This Appendix contains three sections, including the AO-HZC optical images on the ozone cleaner pretreated ITO substrate, the optical images of AO-HZC on the graphene surface, and the detailed calculations of the series and shunt resistances in the acridine orange-based photovoltaic devices discussed in Chapter 5.

A.1- Optical images of AO-HZC on the pretreated ITO substrates and graphene surface

The typical optical images of the AO-HZC films spun from water-based solutions on the ITO substrates are shown in Figure A.1. The substrates were treated with an ozone cleaner at different time lengths prior to the spin coating of the AO-HZC layer. As can be seen from Figure A.1, the pretreatment of the ITO substrates did not improve the adhesion of AO-HZC thin films on the ITO substrates such that the microscopic voids are still present even after pretreating the ITO substrate for 45 minutes.

Figure A.2 shows the optical images of AO-HZC on both graphene and ITO surfaces. It demonstrates the presence of large microscopic voids in the AO-HZC layer on the graphene surface similar to what is observed on the ITO substrate. As discussed in Chapter 5, the presence of such big voids is detrimental for the performance of the photovoltaic devices fabricated by AO-HZC photoactive layers due to the possible direct contacts between the top and bottom electrodes, which may short-circuit the device.
Figure A.1: The optical images of AO-HZC films spun from water-based solutions on (a) non-treated ITO surface and (b), (c), and (d) pretreated ITO substrates with an ozone cleaner for 15, 30, and 45 minutes, respectively.

Figure A.2: (a) Optical images of AO-HZC on the graphene and ITO substrates. (b) and (c) are the magnified optical images on the graphene and ITO surfaces, respectively.
A.2- Calculation of the series and shunt resistances in the acridine orange-based photovoltaics

The most common model for photovoltaic device performance employs a single diode model to characterize the I-V curve of the photovoltaic devices and further determine the relevant photovoltaic parameters [A1-A3]. In such a model, a photovoltaic device is interpreted by an equivalent circuit consisting of a current source, a diode, a resistor in series ($R_s$), and a resistor in parallel called a shunt resistor ($R_{sh}$), as shown in Figure A.3.

![Figure A.3: Single diode equivalent circuit model of a photovoltaic.]

The behavior of such a photovoltaic device modeled by a single diode is mathematically defined by Equation (A.1) [A1-A3]

$$I = I_{ph} - \frac{V + IR_s}{R_{sh}} - I_0 \left[ \exp\left(\frac{V + IR_s}{nV_{th}}\right) - 1 \right],$$  \hspace{1cm} (A.1)

where $I$ and $V$ are the current and voltage of the photovoltaic device, $I_{ph}$ is the photogenerated current, and $I_0$ is the reverse saturation current for the equivalent diode. $n$ is the diode ideality factor, $R_s$ and $R_{sh}$ are the series and shunt resistances, respectively, and $V_{th}$ is the thermal voltage of the photovoltaic device and is equal to $k_B T/q$. Here, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $q$ is the electron charge. In Equation (A.1), current can be expressed as a function of voltage using Lambert’s W function as shown in Equation (A.2) [A4-A7]. Lambert’s W function is the solution $W(x)$ of the equation $x = W(x) \exp[W(x)]$. 

Equation (A.2) can be used to determine the solar cell parameters accurately, including $R_s$ and $R_{sh}$, by fitting the I-V characteristics of the photovoltaic devices extracted experimentally with Equation (A.2). This procedure was developed and programmed by an undergraduate student, William Choi, in our group, and was used to determine the series and shunt resistances of the AO-HZC-based photovoltaic devices mentioned in Table 5.1 in Chapter 5. The algorithm of the program is shown in Figure A.4.

**Figure A.4**: Algorithm of the proposed method to determine values of series and shunt resistance.
A.3- References


Appendix B. Supplementary information for Chapter 6

In this section, the topography, phase, and Kelvin Probe Force Microscopy (KPFM) images of each amino acid, including Arginine, Histidine, Lysine, Aspartic Acid, Alanine, Phenylalanine, and Tryptophan, on the graphene sample are shown. The KPFM image for each amino acid on the graphene sample represents the KPFM signal profile of the sample relative to the tip. In addition, the corresponding histograms of the KPFM image when amino acids present on the ITO and the graphene substrate are shown in each Figure. The KPFM data for histograms are calibrated with the work functions of the tips, which are used in the experiments. These histograms are also fitted with the Gaussian functions and the fitting parameters are summarized in Table B.1.

Figure B.1: (a) Topography, (b) phase, (c) KPFM image, and (d) the corresponding histograms for Arg on the graphene samples prepared on the ITO substrate.
Figure B.2: (a) Topography, (b) phase, (c) KPFM image, and (d) the corresponding histograms for His on the graphene samples prepared on the ITO substrate.

Figure B.3: (a) Topography, (b) phase, (c) KPFM image, and (d) the corresponding histograms for Lys on the graphene samples prepared on the ITO substrate.
Figure B.4: (a) Topography, (b) phase, (c) KPFM image, and (d) the corresponding histograms for Asp on the graphene samples prepared on the ITO substrate.

Figure B.5: (a) Topography, (b) phase, (c) KPFM image, and (d) the corresponding histograms for Ala on the graphene samples prepared on the ITO substrate.
Figure B.6: (a) Topography, (b) phase, (c) KPFM image, and (d) the corresponding histograms for Phe on the graphene samples prepared on the ITO substrate.

Figure B.7: (a) Topography, (b) phase, (c) KPFM image, and (d) the corresponding histograms for Trp on the graphene samples prepared on the ITO substrate.
Table B. 1: The fitting parameters of the Gaussian fits for the histograms corresponding to the KPFM images of the graphene samples functionalized with different amino acids. The fitting parameters are shown for both histograms when amino acids present on the ITO and graphene substrates. The R-Square parameter in the table determines the goodness of the fit. FHWM is the full width at half maximum of the fits.

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The Gaussian function that was used to fit the corresponding histograms of the KPFM images of the graphene samples functionalized with different amino acids is:

$$y = A \exp\left(-\frac{2(x-x_c)^2}{w^2}\right).$$

(B.1)

where $A$ is the amplitude, $x_c$ is the mean of the distribution that was used for determining the shift in the KPFM signal, and $w/2$ is the standard deviation.
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