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Organic solar cells: electrodes, performance enhancement and degradation mechanisms

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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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Organic solar cells: electrodes, performance enhancement and degradation mechanisms

(Thesis format: Integrated Article)

by

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Graduate Program in The Department of Physics and Astronomy

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

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Abstract

In this thesis I focus on a number of aspects associated with the fabrication and characterization of organic photovoltaics. Specifically, my work focuses on evaluating solution processed graphene electrodes for use in organic photovoltaics, improving the performance of indium tin oxide transparent contacts by coating them with Au nanoparticles, and understanding the degradation pathways of poly(3-hexylthiophene-2,5-diyl): phenyl-C$_{61}$-butyric acid methyl ester (P3HT:PCBM) organic solar cells. In my work on graphene electrodes for organic solar cells I worked out a relationship between the sheet resistance and the film transmittance that is useful to optimize such electrodes. Investigation of organic solar cell degradation in a controlled "70-70-70" test (i.e. keeping a device for 70 hours at 70°C under 70% humidity conditions) showed several possible pathways in which the active layer of these photovoltaics degrade. In addition to the typical morphological degradation, a strong increase in paramagnetic defect density in the active layer contributes to their degradation. Formation of paramagnetic defects in P3HT:PCBM layers was attributed by us to the creation of charge transfer complexes between P3HT and oxygen. Our attempts on improving indium tin oxide electrodes for their use in organic photovoltaics included a study of the effects of nucleation of Au-containing molecular nanoclusters. It was discovered that different types of Au nanoparticles with specific properties can be formed by annealing such clusters at different temperatures and under different conditions. This discovery was utilized to fabricate Au nanoparticle layers on indium tin oxide which were then utilized as plasmonic enhancement layers for organic solar cells.

Keywords

Semiconductor physics, condensed matter physics, organic materials, organic photovoltaics, graphene electrodes, solar cell electrodes, gold nanoparticles, gold molecular clusters, plasmonic enhancement, solar cell degradation.
Co-Authorship Statement

Chapter 2 was a co-authored publication by Reginald J. Bauld, Faranak Sharifi, and Giovanni Fanchini. R. Bauld primarily worked on the first section of the chapter where the various methods of solution-based Graphene exfoliation are reviewed. R. Bauld and G. Fanchini worked together to determine the relation between sheet conductivity and film transmittance that is seen in this chapter. F. Sharifi wrote the section of the chapter that focuses on the uses of graphene in organic solar cells. This chapter is based on the publication: R. Bauld, , F. Sharifi, & G. Fanchini, “Solution processed graphene thin films and their applications in organic solar cells.” International Journal of Modern Physics B 26, 1242004 (2012). Reproduced with author permissions © copyright World Scientific Publishing Company.

Chapter 3 was a co-authored publication by Reginald J. Bauld, L. M. Fleury, M. Van Walsh, and G. Fanchini. R. Bauld was responsible for the data analysis in the paper, in addition to most of the experimental measurements present in the paper. L. Fleury and M. Van Walsh assisted in sample preparation and the performance of some of the AFM measurements. This chapter is based on the publication: R. Bauld, , L. M. Fleury, , M. Van Walsh, & G. Fanchini, “Correlation between density of paramagnetic centers and photovoltaic degradation in polythiophene-fullerene bulk heterojunction solar cells.” APL: Organic Electronics and Photonics 5, 204–204 (2012) reproduced with permission from AIP Publishing LLC.

Chapter 4 and 5 are a co-authored publications by R. Bauld, M. Hesari, M. S. Workentin, & G. Fanchini. M. Hesari and M. S. Workentin synthesized the Au molecular clusters use in this work. R. Bauld synthesized the samples and performed the measurements shown in the chapter in addition to writing the publication. G. Fanchini assisted greatly in aspects of experimental design and writing. These chapters are based on the following publications: Bauld, R., Hesari, M., Workentin, M. S. & Fanchini, G. "Thermal stability of Au_{25} molecular precursors and nucleation of gold nanoparticles in thermosetting polyimide thin films." Applied Physics Letters 101, 243114–243114–4 (2012) reproduced with permission from AIP Publishing LLC and R. Bauld, M. Hesari, M. S. Workentin, and G. Fanchini, “Tessellated gold nanostructures from Au_{144}(SCH_{2}CH_{2}Ph)_{60} molecular precursors and their
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Chapter 1

1 Photovoltaics, degradation and plasmonic nanoparticles

1.1 Introduction

Solar cells are ubiquitous throughout the modern world and are used to provide power to a number of portable applications including calculators, water taps, and traffic lights. In addition solar power is increasingly receiving attention as a sustainable grid power source. Monocrystalline silicon, c-Si, solar cells are one of the most popular and well understood types of photovoltaics. They can reproducibly achieve a relatively high power conversion efficiencies (PCE) around 18% [1]. The materials required for fabrication of these cells are cheap since their main component, silicon, comprises of a large percentage of the earth’s crust. However, these cells are expensive to produce and are not very competitive with conventional power sources such as coal and oil. Most of the costs in constructing these kinds of solar cells is due to fabrication. High purity silicon is required and doping the silicon involves treating the wafer with temperatures up to 1800°C. Furthermore, Si solar cells are not mechanically flexible.

To find a solution to these issues of c-Si researchers have looked for other materials with potentially easier and cheaper processing. Organic materials have shown great promise in this regard. Organic solar cells (OSCs) are composed of carbon-based molecules and can be fabricated from a large variety of different small organic molecules and conducting polymers [2-4]. These materials typically have the advantage that they can be processed directly from solution. Briefly, the organic materials are dissolved in an organic solvent and the solar cell can be fabricated simply by spin coating[5], ink jet printing[6], or spraying[7] to name a few possibilities.

For the long term use of specific solar cell technologies in applications of power generation it is important to gain an understanding of the processes that can lead to low efficiency, degradation, and eventually the failure of photovoltaic devices. To understand their failure processes we must understand the basic physics behind the operation of solar cells. The structure of OSCs differ significantly from their inorganic counterparts and so
the degradation mechanisms involved in these cells are unique. OSCs also degrade significantly faster. OSCs will degrade significantly in as little as 60 hours [8] in air while silicon solar cells can last several years before drops in PCE become problematic [9].

1.2 The fundamentals of photovoltaics

Solar cells all work under the same basic principles. A material that absorbs photons in the visible range is illuminated, thereby creating an excited population of electrons and holes. These charge carriers are then ‘harvested’ by a carefully designed device architecture and then subsequently collected at two opposite electrodes. In this section I review some of the basic physics required to understand solar cell operation.

1.2.1 Optical absorption in semiconductors

Optical absorption in semiconductors is a vast topic with a considerable amount of literature[10-12] available on the subject. Here I explain the fundamentals of interband absorption processes that are required to understand solar cell operation. Semiconductors are best described in terms of a band structure where the electrons of the material are arranged into specific bands of energy. The most relevant of these bands are the highest energy filled band called the valence band and the lowest energy unfilled band called the conduction band. In a molecular system this corresponds to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) respectively. When a photon is incident upon a material it has a probability per unit length of being absorbed. This probability is known as the optical absorption coefficient and is measured in cm$^{-1}$. This process is best described by considering two different situations. In a first case, if $E_g > E_{\text{photon}}$ the photon does not have enough energy to excite an electron into the conduction band and hence the optical absorption coefficient is close to zero. In a second case, if $E_{\text{photon}} \geq E_g$ an electron can be excited by the photon, with a capture probability that is determined by the optical absorption coefficient of the material. In this second case, a portion of the energy is dissipated as interactions with the atomic lattice of the medium thermalize the electron to the bottom of the conduction band. For a solar cell, this means that a portion of the photon energy, $E_{\text{photon}} - E_g$, will be lost for any photons with $E_{\text{photon}} > E_g$. These two effects are primarily responsible for
the theoretical PCE limit of a single junction solar cell. This is known as the Shockley–Queisser limit [13] and it is approximately 33% for a single junction solar cell with a bandgap of 1.3 eV. These inherent physical limitations can only be overcome by the use of multi-junction solar cells where several different materials are utilized to absorb the incoming light or other relatively sophisticated solutions [14].

1.2.2 Excitons

The excitation of an electron into the conduction band of a solid creates a positively charged "hole" in the valence band. In semiconductor systems a hole is a deficiency of a single electron that can be treated as a positive charge. The two oppositely charged quasi-particles are then bound together by coulombic forces that creates a bound state. The bound electron-hole pair is can be modeled as a single quasi-particle in a potential and is called exciton, with energy levels that are modeled after those of the hydrogen atom [15]. Under this approximation, the Rydberg binding energy of an exciton can be calculated as in eq. (1.1).

$$R_y = 13.6 \frac{\mu}{\epsilon^2 m_0} \text{ (eV)}$$

(1.1)

Where $\epsilon$ is the dielectric constant of the material, $m_0$ is the free electron mass and $\mu$ is the reduced mass given by,

$$\mu = \frac{m_e m_h}{m_e + m_h}$$

(1.2)

with $m_e$ and $m_h$ as the effective electron and hole masses respectively. This means that photogenerated excitons can have a total energy less than the band gap of a material. The consequence of this is that a semiconducting material with excitons at low temperatures show a sharp optical absorbance peak just below the bandgap [16]. Solar cells typically operate at higher temperature but even though excitons tend to delocalize at room temperature in many semiconductors used in the solar industry, excitonic effects must be taken into account when modeling the operation of solar devices.
For a solar cell to generate an electrical current, neutral excitons must be dissociated into charge carriers. For inorganic materials, the energy required to separate an exciton is relatively weak, on the order of $k_B T \approx 0.025 \text{ eV}$ so dissociation naturally occurs at room temperature. However, exciton dissociation in solar cells typically utilize internal electric fields that can also provide the energy that is necessary to dissociate an exciton in a solar device. Electric field related dissociation of excitons is dominant in organic solar cells in which the exciton binding energy is higher.

Two types of analytical models, Frenkel and Wannier-Mott, can be used to theoretically describe excitons under specific conditions [11]. In the Wannier-Mott model, excitons are assumed to have a low, $\sim 0.1 \text{ eV}$ or less, binding energy and are typically present in materials with a high dielectric constant. Frenkel excitons have a much higher binding energy, $\sim 0.1$ to $1 \text{ eV}$, and are present in materials with a low dielectric constant. The dielectric constant $\varepsilon$ of a material heavily influences the exciton binding energy, as we can see by examining equation (1.1) the binding energy is inversely proportional to $\varepsilon^2$. As an example, silicon has a dielectric constant of $\varepsilon \approx 12$ [17], this produces a strong electrostatic screening effect between the electron and hole that results in a small binding energy of $\approx 0.01 \text{ eV}$ [10]. Organic materials have smaller dielectric constants with $\varepsilon \approx 2$ [18], hence we expect a difference in binding energy to be around $\sim 10^2$. Indeed measurements on organic materials have shown [19] binding energies ranging between $0.1$-$1 \text{ eV}$. This high binding energy is problematic this binding energy must be broken to produce a net current in a photovoltaic device.

### 1.2.3 p-n junctions and bulk heterojunctions

P-n junctions are interfaces between two semiconducting materials, ‘p-type’ and ‘n-type’ respectively. In ‘p-type’ materials electrical transport occurs via holes. In these materials holes are more plentiful and therefore act as the majority carriers. Vice versa, in ‘n-type’ materials electrons act as majority carriers. A classic example of p-n junction is a diode formed by the two differently doped regions of silicon. Silicon can be hole-doped by adding in a group 13 element, such as boron. Boron has one less valence electron in comparison to Si, so any B atoms introduced into the crystal lattice will introduce a single hole into the system. Similarly group 15 elements can be used to introduce electrons and
produce n-type regions. When such a junction is formed, the excess electrons from the n-type material will flow into the electron deficient p-type material [10, 11], as shown in Figure 1-1. This charge transfer creates two effects, at the interface there is a pairing up of electrons and holes that results in a small region of low carrier density called the depletion region. This is the effect that is essential for the operation of a diode. For a solar cell, however, it is the local electric field created by this charge transfer that assists greatly in separating excitons and moving charges to the appropriate electrode.

In a perfect solar cell all photogenerated excitons would be dissociated and collected at their respective electrodes. The ratio of charge carriers arriving at the electrodes to the number of photogenerated excitons is known as the Internal Quantum efficiency (IQE). The IQE normally depends on the incident light wavelength and is a measure of how well a solar cell separates photogenerated excitons. IQE values of 100%, at specific wavelengths, can be easily approached by crystalline silicon solar cells. In special situations IQE values above unity [20] can be obtained. This is possible when high energy UV light is used to excite the sample. An individual photon can transfer enough energy to an electron that it can undergo impact ionization and transfer its excess energy to another electron. This then results in two excitons generated from one incident photon.

Organic solar cells require careful optimization of the active layer to reach performance comparable to silicon-based devices. In organic materials the strong exciton binding energy and short exciton diffusion length, of 3-9 nm[4], means that a photogenerated exciton needs to find an p-n interface relatively quickly for efficient exciton dissociation to be possible. Although it is possible to achieve an operational solar cell using a bi-layer structure these cells typically have very low efficiencies on the order of ~1%[21]. To avoid these difficulties a different type of solar cell was introduced that uses an active layer structure that consists of a nanoscale, interpenetrating mixture of two organic materials. A "donor" phase that donates electrons to another compound and an "acceptor" phase that accepts the donated elections. This structure, the so called bulk heterojunction (BHJ) shown in Figure 1-1b, produced a dramatic improvement in organic solar cell efficiencies with the first example resulting in solar cells with 2.9% PCE [22].
1.2.4 The fate an exciton in a solar cell

To ultimately create a photocurrent, an exciton needs to be dissociated and the hole and electron need to be collected at the appropriate electrical contacts. The electrical contacts of solar cells are typically chosen in such a way to aid in this charge collection. This is done by selecting a cathode material such that the work function is slightly less than the energy level of the active layer conduction band while conversely choosing an anode material to have a slightly higher energy level than the active layer valence band. This arrangement achieves two things. First, the difference in work function of the electrodes sets up an electric field over the entire device which aids in charge collection and exciton

Figure 1-1 a) Diagram of a p-n junction showing how charges are arranged at the interface to produce a local electric field. b) Morphology of a bulk heterojunction solar cell. The donor and acceptor phases are intermixed on a nanoscale level to ensure generated excitons can reach an interface before they recombine.
separation. Secondly, charge transfer of an electron from the valence band to a metallic electrode of a lower energy level would is a favorable transition and requires no additional energy to be provided.\textsuperscript{[23]}

In addition to using appropriate metals as electrodes, the electronic structure of the active layer is often specifically designed in a way to facilitate exciton separation in an efficient manner. An exciton in an organic system has a limited lifetime and hence a limited diffusion length. If a given exciton cannot reach a p-n junction or donor-acceptor interface in this timeframe it will undergo recombination in one of two ways indicated in Figure 1-2: radiatively or non-radiatively. In radiative recombination, the exciton binding energy is released in the form of secondary photons as the electron-hole pair is annihilated. This phenomenon generates photoluminescence in several solar cell materials if special precautions to prevent radiative recombination are not used. Ideally, photoluminescence should be minimized as it competes dramatically with exciton dissociation processes. Consequently, photoluminescence spectroscopy is a valuable tool in understanding exciton recombination in solar cells because it is helpful in understanding under what specific conditions exciton dissociation does not occur.

In addition to radiative recombination, an exciton in solar cells can undergo non-radiative recombination, in which the excited state energy is transferred to the lattice in the form of heat. These forms of parasitic recombination typically occur in the presence of charge trapping defects that give rise to electronic states in the band gap of semiconductors\textsuperscript{[24]}. There are few direct probes of this effect, but one notable example is photo thermal deflection spectroscopy where the mirage effect is utilized to probe the optical heating effects at the surface of a sample. More detailed information on these types of measurements can be found in the literature\textsuperscript{[25]}. 
To excite an electron into the conduction band an incident photon of energy higher than the band gap energy must be provided. The two recombination mechanisms shown here are radiative recombination, where a photon is released during the transition, and non-radiative recombination, where no photon is released during the transition. In this case the excess energy is released to the lattice in the form of heat.

1.3 Solar cell fabrication and testing

Every step of the fabrication procedure of a solar cell is important for its optimal operation. Below, I will review the essential of the procedures and architectures that are utilized by us in the fabrication of organic solar cells and specifically on the cell architecture used primarily in this thesis.

1.3.1 Organic solar cell fabrication procedures

In this thesis I focus on a common architecture and material for organic solar cells with the objective to discover possible solutions for improving organic photovoltaics in terms of intrinsic performance, charge collection capability of the electrodes and degradation mitigation. The architecture I have extensively used consists of: 1) an anode (normally indium tin-oxide (ITO) or a few-layer graphene-based thin film); 2) a Poly(3,4-
ethylenedioxythiophene) Polystyrene sulfonate (PEDOT:PSS) hole-transport, electron-blocking layer; 3) a regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) bulk heterojunction thin film forming the active layer of the device, and 4) a bilayer calcium/aluminum (Ca/Al) cathode, as shown in Figure 1-3. For reference, the molecular structures of these materials are shown in Figure 1-4.

Figure 1-3 Diagram showing how a P3HT:PCBM solar cell can be constructed. The solar cell is illuminated from the bottom, through the glass and ITO and current is collected from the ITO and Ca/Al electrodes.
Figure 1-4 Molecular structures of organic materials used in this thesis. a) P3HT, b) PCBM, and c) PEDOT:PSS

When ITO is utilized as the anode, ITO-coated glass substrates (Sigma-Aldrich) were utilized directly as purchased, with a sheet resistance of 15-25 Ω/□. These films are prepared by plasma-sputtering deposition [26]. Consequently, due to the effects of plasma in limiting the grain boundaries, the resulting ITO surface is relatively smooth, with a root mean square roughness of the order of 2-3 nm [27]. Anode smoothness is critical in the fabrication of efficient devices. To a certain degree, the roughness of the ITO layer can be beneficial to light collection in a solar cell, as it can act as an anti-reflection layer [28]. However, ITO electrodes that are too rough may come into direct contact with the Ca/Al cathode, shorting through the electron blocking layer and the active layer. Hence it is desirable to have an ITO layer with a roughness not much more than 10-20 nm. This surface roughness can be altered by various means including UV treatment [29], HCl treatment[30], and plasma treatment[27].
In addition to roughness considerations, treating the ITO layer with a UV irradiation can produce other favorable effects. UV light of sufficient intensity will create a large quantity of ozone in the vicinity of the ITO layer, this ozone in turn reacts with the surface and it is thought to create O and OH groups on the surface[31]. This process has several beneficial effects. First, the additional groups on the surface help change the surface affinity from hydrophobic to hydrophilic. This aides in the deposition of the water based PEDOT:PSS electron blocking layer, as an improved hydrophilicity will improve the wetting and adhesion of the PEDOT:PSS solution and ultimately result in a more uniform film. Secondly, ozone will vigorously react with any organic contaminants on the ITO layer and produce gaseous byproducts of water and CO$_2$.[32, 33] These contaminants will almost certainly interfere with charge collection at the electrode. Finally, it has been shown [34] that this ozone treatment increases the work function of the ITO electrode and thereby can increase the open circuit voltage of the solar cell.

After UV treatment of the ITO electrode a PEDOT:PSS electron blocking layer is deposited on top. This layer works to prevent photoexcited electrons from being collected at the ITO electrode. PEDOT:PSS has a high hole mobility in comparison to its electron mobility and so helps prevent the transport of electrons to the ITO electrode.

The deposition of PEDOT:PSS can be done using any solution based processing method, but in my experiments I prefer to spin-coat a water based mixture of PEDOT:PSS. Spin coating is a relatively simple, cheap, and above all reproducible method of depositing thin films. Spin coating is a process in which the material to be deposited is suspended in a solvent and then dispensed directly onto a substrate. The substrate is then spun at high speed (1000 rpm to 8000 rpm) to achieve a desired film thickness. The resulting film thickness depends on many factors, but the easiest to control in an experimental environment is the concentration of polymer in the solution and the spin speed. Higher concentrations of solute naturally give thicker films while increasing the spin speed will give thinner films. It is difficult to tell beforehand what conditions will produce the desired film thickness and so this is left primarily to experimentation to find the optimal spin coating parameters.
Typically PEDOT:PSS hole-transport, electron-blocking layers are annealed at temperatures between 100-200°C in an inert environment. The annealing process removes excess moisture from this layer with the end result being a more conducting PEDOT:PSS layer [35]. However, excessive temperature may bring PEDOT:PSS above the glass transition temperatures of both these polymers, resulting in their degradation. In our case a N\textsubscript{2} loaded glove box with <5 ppm of moisture and oxygen was used (Nexus II, Vacuum Atmospheres Inc.) and a temperature of 140°C was chosen. PEDOT:PSS can be annealed at a wide range of temperatures[36] from 70 °C to 200 °C and still produce solar cells with similar power conversion efficiencies.

### 1.3.1.1 Fabrication of the active layer

The fabrication of the active layer is obtained by mixing equal weight ratios, of P3HT and PCBM in an appropriate solvent. The essential point when making a bulk heterojunction in this way is that both materials must form an interpenetrating network with percolating conduction pathways. If too much of either material is used, then charge carriers can have difficulty reaching an electrode as there may be few such conducting pathways. The optimal ratio of P3HT to PCBM has been determined experimentally with researchers finding it between 1:0.7 to 1:1 P3HT:PCBM by weight. [37] The molecular weight of P3HT is also important. It is kept constant throughout this thesis with the number of monomers $M_n = 15,000$-$45,000$.

For the solvent we use chlorobenzene, however other solvents can be used. Solvents with low boiling points and small vapor pressure are preferred as they result in slower drying that allows more time for crystallization to occur. This change in crystallinity can be seen by comparing the x-ray diffraction patterns of films prepared with different solvents, as shown by Chang et al. [38]. The improved crystallinity helps greatly in improving the charge transport properties of the active layer by dramatically increasing the mobility. This results in a superior charge collection and better overall power conversion efficiency [39, 40].

Due to the reactive nature of P3HT with oxygen [41] these types of solar cells need to be fabricated in an inert environment of N\textsubscript{2} for the best results. After the P3HT and PCBM
are fully dissolved into chlorobenzene the resulting mixture is deposited onto the substrate to form the active layer. The use of spin-coating for depositing the active layer is a cheap and simple method for depositing the active layer. However, many factors come into play that can complicate film deposition. Parameters like spin-speed, solvent drying time and concentration can dramatically change the resulting film morphology [42, 43]. Therefore it is critically important to use a spin-coater that has a very reproducible spin-speed to achieve consistency between subsequent spin-coatings.

This as-spun P3HT:PCBM mixture naturally produces the BHJ structure required for efficient charge collection as discussed in section 1.2.4. During solvent evaporation the two organic components can separate into two distinct phases that are intermixed on the nanoscale. The nature of the phase separation appears to be spinodal, however some researchers dispute this[44]. Organic solar cells of this design produce power conversion efficiencies (PCEs) around 3%[40]. This is a dramatic improvement from their bilayer variants, which only achieved PCEs of ~1% [21] thereby demonstrating the effectiveness of the BHJ. Additional advances in fabrication techniques where realized by Ma et al. [40] by annealing the solar cell after spin-coating the active layer. This annealing is now known to result in the stacking and crystallization of P3HT [45]. This complex process is not fully understood, but the reasons behind the improved cell efficiency are considered to be a higher optical absorption in tandem with increased carrier mobility [45].

1.3.1.2 Fabrication of the cathode

Efficient charge collection of photogenerated electrons requires an electrode with a work function that is well matched to the HOMO of the acceptor component of the active layer, PCBM. PCBM has a HOMO level of 4.0 eV so if we want a good charge transfer to the electrode it is essential we choose an electrode material that has a work function that is slightly higher.

Al is a common electrode for these kinds of solar cells and has a work function around 4.2 eV [46]. This gives a mismatch of 0.2 eV and hence reduces the ultimate open circuit voltage of the solar cell. The solution is to use a bilayer electrode consisting of approximately 20 nm of Ca in contact with the active layer followed by 80 nm of Al[47].
Ca has a work function of 2.9 eV [46] so the thin layer of Ca between the active layer and the Al contact effectively lowers the work function of the electrode so it is better match with the HOMO of PCBM. This effect can be seen by noting that P3HT:PCBM solar cells prepared with Ca/Al electrodes have a higher open circuit voltage in comparison to cells prepared with Al alone[47].

Fabrication of our electrodes is done utilizing a thermal deposition vacuum chamber affixed to the glovebox. This allows for the deposition of Ca/Al electrodes without ever exposing the active layer to oxygen.

1.3.2 Solar cell efficiency characterization

A great deal of information can be gained by looking at current-voltage or IV curves of a solar cell. The potential across the electrodes is scanned, often in the range -1 to -1V, and the resulting current is recorded. Illumination of a solar cell produces electrons that are then collected at the cathode. Using the convention that forward current is from the anode to the cathode a photogenerated current is a reverse current through the cell. The bottom right quadrant of the IV curve is the section that allows power generation. For maximal power generation of the cell, the voltage across the cell must be optimized depending on the cells characteristics. The power output of the cell, given by \( P(V_{bias}) = -IV \). \( P(V_{bias}) \), has a maximum value labeled as \( P_{max} \). Figure 1-5 shows an example IV curve of a monocrystalline solar cell and its corresponding power vs voltage curve. The important characteristics for calculating the solar cell efficiency are labeled. The short circuit current \( (I_{sc}) \) is the current where \( V_{bias} = 0 \). \( I_{sc} \) is closely related to the photogenerated current \( I_L \) and in solar cells with very small series resistance they are approximately the same.

The open circuit voltage \( (V_{oc}) \) is the voltage of the cell when \( I = 0 \). For inorganic solar cells, this parameter is largely dependent on the energy levels of the active layer and the work functions of the counter electrodes. Ultimately a solar cell cannot have an open circuit voltage greater than the difference between the HOMO of the donor and LUMO of the acceptor material. This also requires that the electrodes are perfectly matched to the
energy levels. Organic solar cells tend to have a $V_{oc}$ that is smaller than their bandgap although the reason behind this is not fully understood.

The peak power, $P_{\text{max}}$, is simply the maximum power output of the cell, and can be seen in the P-V curve in Figure 1-5. Voltage and Current at peak power are referred to as $V_{\text{max}}$ and $I_{\text{max}}$ respectively. This is the absolute maximum power the cell can output and for power generation purposes it is advantageous to operate the solar cell at this point.

The fill factor is defined as the ratio between areas enclosed by blue rectangles in Figure 1-5. More precisely it is given by the following equation,

$$FF = \frac{V_{\text{max}} I_{\text{max}}}{V_{oc} I_{sc}}$$

From these parameters, if we know the incoming power, $P_{\text{in}}$, the cell efficiency can be calculated as,

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{|V_{\text{max}} I_{\text{max}}|}{P_{\text{in}}} = \frac{|V_{oc} I_{sc}| * FF}{P_{\text{in}}}$$

1.3.3 Characterization under standard conditions

Solar cells are typically characterized under illumination by an appropriate light source. The standard light source is a solar simulator, a light source that simulates the spectrum of the sun with the provision that this is the vacuum spectrum of the sun. That is, the spectrum that would be measured outside of earth's atmosphere. Solar cells are most often operated within the earth's atmosphere so it is more useful to evaluate their PCE using a light spectra that closely resembles the spectrum of the sun after it has passed through the earth's atmosphere. The light spectrum of the sun at the equator is known as the solar spectrum at air mass one (AM1). Most terrestrial power installations are located, not on the equator, but either in the northern or southern hemisphere. Therefore most characterization is done at AM1.5. This yields the solar spectrum equivalent to that observed at a solar zenith angle of around 48° [48].
Figure 1-5 An example IV and power curve of a single crystal silicon solar cell with \( \mu = 12.2 \% \). The bottom panel shows the region of the IV curve that produces a net power output from the cell. The important characteristics of the cell are the short circuit current (\( I_{sc} \)), open circuit voltage (\( V_{oc} \)), fill factor (FF), and the voltage and current and peak power.

In the lab this setup is realized by using an appropriate AM1.5 filter in between the solar simulator and the solar cell under test. The intensity of the light source is then calibrated by using a standard solar cell with a known solar cell efficiency. Typically we calibrate the light source so we have a 1000 W/m\(^2\) light intensity incident on the solar cell with an
AM1.5 solar spectrum. In this thesis we typically deal with organic solar cells, so most of the testing is done in a controlled N\textsubscript{2} atmosphere with less than 1 ppm of O\textsubscript{2} and H\textsubscript{2}O.

1.4 Known organic solar cell degradation processes

1.4.1 Changes in morphology of the active layer

One of the most important properties of a bulk heterojunction is the morphology of the active layer. The donor and acceptor materials need to be mixed on the nanoscale in a specific way to optimize exciton dissociation and subsequent charge collection. As explained briefly in section 1.2.3, the active layer needs to be structured such that the donor and acceptor phases are segregated into clusters of size on the order of the exciton diffusion length. Additionally, once an exciton has reached a donor/acceptor interface the electron and hole must be collected at their respective electrodes to produce a useable current. This means that the donor/acceptor phases must be large enough to allow continuous pathways throughout the active layer. This will allow for efficient charge collection.

Degradation of the active layer morphology has been shown [49] to be a result of an increases phase separation. That is, the donor and acceptor phases congregate into domains with sizes much larger than the exciton diffusion length. This leads to a coarse bulk heterojunction that results in a poor excitation separation.

1.4.2 Solar cell electrodes: problems at the interface

In P3HT:PCBM solar cells the top electrode often consists of aluminum with an additional interfacial layer to help match the work function of aluminum to that of the PCBM donor level. A common problem with this setup is that aluminum can easily oxidize in the presence of oxygen. Aluminum quickly forms a skin oxide that inhibits the charge transfer between the active layer and the electrode. This manifests as an increased series resistance in the cell.

Work by Seeland et al. [50] has shown the effects that oxygen can have on the electrodes of a solar cell. They perform some electroluminescence measurements on a cell under atmospheric conditions and they find that the electrode degradation appears to
be heterogeneous in nature. This strongly suggests that local pinhole defects in the electrode allows oxygen to diffuse into the active layer of the cell and to the electrode interface.

1.4.3 Diffusion of species in the active layer

The diffusion of foreign species into the active layer of a solar cell represents a severe problem for organic solar cells. Due to the polymeric or small molecule nature of organic cells the diffusion rates of oxygen and water are far higher than their dense, crystalline, inorganic counterparts. Under exposure to atmosphere it has been shown\[^{51}\] that there is a significant diffusion of oxygen into the active layer of these kinds of solar cells. Oxygen can readily form weak bonds with P3HT known as a charge transfer complex \[^{52, 53}\]. This is a molecular arrangement where oxygen will accept a small amount of electric charge from the P3HT chain. This results in a local excess of positive charge in the P3HT network that can act as a charge trap. A charge trap will inhibit the transport of electric charges by locally trapping charge carriers near the defects. This results in a decrease mobility in the active layer\[^{52, 53}\] and possibly an increase in charge carrier recombination\[^{8}\].

In addition to the diffusion of species from the ambient environment, it has been shown that the solar cell electrodes can diffuse into the active layer of the cell. Specifically, the diffusion of Al into the active layer has been shown by time of flight Secondary ion mass spectrometry measurements by Norrman et al\[^{54}\]. This form of cell degradation will also result in charge trap states and in an increased charge recombination.

All of these diffusion mechanisms represent problems for the operation of solar cells, however, in this thesis I will focus specifically on the diffusion of oxygen and moisture into the solar cell active layer.

1.5 Light harvesting in thin film solar cells

Solar cells often do not absorb 100% of the light that is incident on the active layer. Often, special light trapping layers are utilized in solar cells to help increase the effective
absorption. In thick, \(~300 ~\mu\text{m}\), solar cells large structures can be used to help trap light into the active layer [55]. These structures often reflect and scatter light tangentially into the cell [56]. This increased the effective path length of light incident on the solar cell and hence increases the proportion of absorbed light. In organic solar cells, the active layer thickness is often times as thin as 200 nm. This makes it impossible to use standard light trapping techniques. Most light trapping mechanisms used for inorganic solar cells would be much larger than the thickness of the active layer, which would render them useless. This means that light trapping nanostructures must be utilized to be effective.

1.5.1 Plasmonic resonance of metallic nanoparticles

Metallic nanoparticles smaller than the wavelength of visible light exhibit a unique property known as plasmonic resonance. This can most simply be described as a collective excitation of the charge carriers in a metallic nanoparticle under the stimulation of an alternating electric field. In this case the electric field is supplied by a photon with a wavelength larger than the MNP in question. The resulting system is similar to a driven simple harmonic oscillator, with the restoring force resulting from a separation of electrons from their respective ions and the driving force being the electric field provided by the incident photon[57], as shown in Figure 1-6.

![Figure 1-6 A metallic nanoparticle in an electric field provided by a photon with a wavelength larger than the particle diameter. The electric field induces a dipole](image-url)
across the particle. The columbic attraction between the ions of the MNP and the electron could constitutes a restoring force.

Ultimately the position of the resonance peak depends on several factors including the dielectric constant of the metal, the surrounding environment, and the size of the nanoparticle.

Plasmonic resonance is particularly important when using MNPs in a light collection scheme. An incident photon that is close to the plasmonic resonance of the MNP interacts strongly which results in both an increased scattering cross section, $Q_{\text{sca}}$, as well as a strongly enhanced local electric field due to the local surface plasmon resonance (LSPR). The scattering cross section, $Q_{\text{sca}}$, is the effective area by which an incident photon can be scattered by the MNP. Close to the resonance frequency $Q_{\text{sca}}$ can be an order of magnitude larger than the actual size of the nanoparticle. Additionally, for any incident photon there is a possibility of it being adsorbed. This is determined by the absorption cross section $Q_{\text{abs}}$. Ideally we would like to have $Q_{\text{sca}} \gg Q_{\text{abs}}$ so a minimal amount of light is absorbed by the plasmonic enhancement layer while a maximum amount of light is scattered into the active layer of the solar cell. Spherical metallic particles have known cross sections that are given by the following equations:

\begin{align}
Q_{\text{abs}} &= 4\pi x \text{ Im} \left( \frac{\epsilon_i - \epsilon_0}{\epsilon_i + 2\epsilon_0} \right) \\
Q_{\text{sca}} &= \frac{8}{3} x^4 \left| \frac{\epsilon_i - \epsilon_0}{\epsilon_i + 2\epsilon_0} \right|^2
\end{align}

with $x = 2\pi a (\epsilon_0)^{1/2}/\lambda$, $\epsilon_0$ is the dielectric constant of the surrounding medium, $\epsilon_i$ is the dielectric constant of the MNP, $\lambda$ is the wavelength of the incident light, and $a$ is the MNP radius.

These equations can, to an extent, assist us in finding the optimal size of our MNPs for the purpose of optimal scattering. It is clear that for small nanoparticle size $Q_{\text{abs}}$ is dominant due to the linear term in Eqn. (1.5) so we will have $Q_{\text{abs}} > Q_{\text{sca}}$. Since $Q_{\text{sca}}$ grows as $\propto a^4$ it indicates that eventually the scattering cross section will grow larger.
than the absorption cross section. It is however important to note that equations (1.5) and (1.6) are only valid for $a < \lambda$. In the situation that $a > \lambda$ quadrupole terms start to dominate and the resonance effect becomes muted and eventually disappears for particles with $a >> \lambda$. That being the case, for each specific environment giving a different $\epsilon_0$ and each metal with a dielectric constant $\epsilon_i$ there will be an optimal MNP size that maximizes $Q_{sca}$ while minimizing $Q_{abs}$. In practice the optimal diameter tends to be around 50-100 nm size[59].

The second effect that can lead to improved solar cell efficiency, as mention previously, is localized surface plasmon resonance (LSPR). Plasmonic resonance not only yields increased scattering cross sections, but it also results in an enhanced electric field close to the surface of the MNP. Absorption is proportional to the electric field so if the enhanced electric field from the LSPR extends into the active layer of the solar cell this can lead to an increased absorption. The extent of this electric field is short, around 10 nm, so the MNP needs to be situated close to the active layer for LSPR to have an appreciable effect [60]. In plasmonic enhancement layers typically both the scattering of light and LSPR will have a positive effect on absorption.

1.5.2 The use of MNPs to improve light collection efficiency in thin film solar cells

There exist several strategies to incorporating MNPs into solar cells. The MNPs can be placed either in front of the solar cell, between the window electrode and the active layer, in the active layer itself, or above the active layer as shown in Figure 1-7.
Figure 1-7 Possible ways to incorporate MNPs into an organic solar cell. a) The MNPs are imbedded into the hole blocking layer, b) in the active layer, and c) between the active layer and the back electrode.

The two arrangements shown in Figure 1-7b,c have the MNPs in direct contact with the active layer. This gives the greatest LSPR based enhancement and this strategy has been successfully implemented by several researchers [61, 62]. There are some problems that can be introduced by these methods. Having the MNPs directly contact the active layer can be detrimental in the function of the cell. The surface of the MNPs can act as charge traps and thereby increase electron-hole recombination. This will result in a lower fill factor and hence a reduced cell efficiency. In this thesis we focus mostly on the arrangement shown in Figure 1-7a. It has several inherent advantages since the MNPs are
not in direct contact with the active layer. They are imbedded into the electron blocking layer, so the electronic structure of the solar cell should not change significantly.

1.6 Thesis overview

Chapter 2 was published as a review article in the international journal of modern physics B. The purpose of this chapter is to examine the feasibility of using graphene based transparent and conducting electrodes in organic photovoltaics. The first half of the chapter is a review on methods to exfoliate graphene and prepare transparent and conducting thin films. Additionally I also examine a way to model the resulting conductivity and transparency of the resulting films. This model provides a way to compare different methods of exfoliation and thin film preparation. The second half the chapter focuses on the use of graphene in various kinds of solar cells.

Chapter 3 is an article that focuses on the degradation of organic solar cells. Organic solar cells are known to experience significant degradation when exposed to air. This study specifically investigates the degradation that occurs in the active layer itself with focus on oxygen and moisture incorporation into the active layer of the cell under elevated temperature and humidity conditions. This is done to better understand both how such devices degrade, but to understand the physics underlying charge transport in organic devices.

Chapter 4 is the start of my work on plasmonic enhancement layers. In this chapter we begin by investigating the properties of Au molecular clusters under annealing temperatures between 150 °C - 450 °C. The goal of this work was to discover potential uses of Au molecular clusters. Previously these clusters were only of use in studying fundamental chemistry. We find an novel way to fabricate Au nanoparticles from Au molecular clusters precursors in a polymer environment. We examine both the plasmonic effects and the purity of the resulting nanoparticles. This work brings such clusters from the realm of blue sky thinking to potential practical applications in optoelectronic devices.
Chapter 5 features the fabrication of Au NP thin films via a similar method used in chapter 4. The goal of this chapter is to utilize the knowledge obtained in chapter 4 to produce a genuine practical application for organic photovoltaic devices. I use Au<sub>144</sub> molecular clusters to fabricate plasmonic enhancement layers directly on ITO. I study the morphology, particle size, and then test the enhancement layer in an organic solar cell. The enhanced cell shows a small improvement over the standard solar cell construction.

Chapter 6 consists of some concluding remarks and the outline of some future work that should be perused based on what was discovered in this thesis.


Chapter 2

2 Solution processed graphene thin films and their applications in organic solar cells

2.1 Introduction

Graphene is an allotrope of carbon that consists of a sheet of one-atom thick sp² bonded carbon atoms as shown in Figure 2-1a. Since its isolation in 2004[1] graphene has attracted significant attention due to its outstanding electrical and physical properties[2-5]. Single-layer graphene sheets exhibit properties such as high transparency, high electron mobility, excellent mechanical strength, and impressive thermal conductivity. It has been proposed for applications in a variety of different fields and technologies, including solar cells[6-11], energy storage[12], batteries[13], fuel cells[14], and in biotechnology. While many applications of graphene have been suggested, its commercial deployment remains limited due to the inherent difficulties of scalably, reproducibly and cost-effectively preparing graphene samples of high quality.

So far chemical vapor deposition (CVD) has had the greatest success in producing large area graphene thin films and boasts impressive characteristics such as ~97% transparencies at ~200Ω/□ sheet resistances[15]. However, the drawback of this method is in that it tends to be very difficult to implement in practice and requires an extreme control on the deposition conditions in order to prevent the seeding of a second layer. Other methods, including solution processing, end up with lower quality of the films, but with much lower manufacturing costs and at a higher reproducibility. A typical optical image of a solution-processed graphene film is shown in Figure 2-1b.
Figure 2-1 a) Ball-stick model of graphene that shows the sp$^2$ bonding structure responsible for its unique properties. b) A typical optical microscope image of a solution-processed graphene films prepared by vacuum filtration on a SiO$_2$ substrate.

One particular application for solution-processed graphene thin films which has been widely studied is their use as a flexible replacement of indium tin oxide (ITO) as a transparent and conducting electrode in the construction of solar cells and digital displays. ITO films have excellent properties with transmittances of ~99% and sheet resistances ~10-30 $\Omega/\square$, but its widespread use in computer displays and limited supply of indium has resulted in a high price. The abundant supply of graphitic carbon available in nature, combined with the high conductivity and transparency of graphene, makes it an excellent candidate for ITO replacement.

In this review we will focus primarily on the preparation of graphene thin films, by solution processing and then examine how graphene can be utilized in organic solar cells to lower their cost and improve their performance. Specifically, we will examine the feasibility of using solution processed graphene thin films as electrode replacements.

2.2 Solution-based graphene exfoliation

The basic mechanism for exfoliation of graphite and the dispersion of graphene in solution relies on a close matching of the surface energy of graphene and the surface energy of a specific solvent. Ultimately, it will take some energy to create a liquid-surface interface so that the minimization of this energy will provide the most stable
graphene-liquid dispersions. The theory of stabilization of graphene flakes in solution has been described thoroughly[16-18] and heavily relied on the results previously achieved for the dispersion of carbon nanotubes (CNT). Although theoretical knowledge is certainly important in developing new dispersion methods, trial and error approaches have been more successful in practice due to the complicated nature of graphene dispersions.

The dispersion of graphene in the appropriate solvent is a necessary step for preparing graphene thin films from graphite. The four primarily used methods of dispersion include: i) the dispersion in aqueous solutions by the addition of stabilizing surfactants, [19, 20] ii) the use of organic solvents,[21] iii) the treatment of graphite by strong acids,[22-24] iv) the oxidation of graphene with the formation and subsequent reduction of graphene oxide. 24 To date none of such methods proved more advantageous than another.

All of the four methods of dispersion rely on the same principle of surface energy minimization and electrostatic stabilization. Specific advantages and drawbacks arise when they are considered in the context of solar cell fabrication. In addition to the transparency and conductivity of the films, features like surface roughness, voids, and “wettability” become very important in organic solar cells with graphene contacts, as will be discussed later.

2.2.1 Oxidation-reduction methods

The first solution-exfoliation methods that have been developed are based on the dispersion of graphene oxide (GO) in water. GO is most often prepared using Hummer's method.[25] The procedure consists of the oxidation of graphite by refluxing it in the presence of a strong oxidizer, such as potassium permanganate (KMnO4), in concentrated sulfuric acid (H2SO4) for a period up to three days.[25-31] The resulting graphite oxide slurry can be easily dispersed in water by mild ultrasonication34. The process ends with a clear yellow solution of GO flakes in water, which can be used to prepare thin films.
GO films are insulating, so they must be reduced to improve their electrical conductivity. Reduction of GO films can be done by exposure to strong reducing agents such as hydrazine monohydrate or by heating up to high temperature, \( T \sim 500-1000^\circ C \), under inert atmosphere.[32, 33] Such treatments result in a partially restored conductivity of reduced graphene oxide (RGO) films. The reduction removes \( \text{sp}^3 \) bonded O and OH functional groups thereby restoring the delocalized \( \pi \)-electron network typical of pristine graphene, which yields a dramatic increase in electrical conductivity. However, the resultant RGO sheets are not infrequently damaged by this process.

The harsh nature of the oxidation/reduction scheme introduces a variety of defects into the hexagonal lattice.[34] The presence of defects in the hexagonal structure tends to reduce the mobility of the charge carriers by acting as scattering centers that reduce the mean free path and moves the transport away from the ideal ballistic transport seen in pristine graphene sheets produced by mechanical exfoliation. In addition RGO tends to lose the unique electronic properties of graphene[26, 35] and the sheet resistance of the resulting films is too poor to produce efficient solar cells.

Even with the destructive nature of this method it is still appealing due to the high concentration dispersions achievable, as high as \( 7 \text{ mg/ml} \).[36] Oxidation-reduction techniques, in combination with a method to repair the defects could result in practical production method. Chemical vapor deposition on reduced graphene oxide has shown some promise to this end.[37] Deposition on top of RGO films have resulted in an order of magnitude improvement in conductivity over reduced graphene oxide. Although, CVD has a limited throughput and having to resort to CVD for the purposes of improving conductivity essentially eliminates the benefits of solution processed graphene films.

Less destructive oxidation methods exist that do not require an aggressive oxidation scheme as utilized in Hummer's method. One such method that shows some promise involves the partial oxidation of graphene and sonication in DMF. [38] Exfoliation does not happen spontaneously as in strong oxidation of Graphite, so sonication is required to complete the dispersion. This however tends to reduce the mean flake size by fracturing the graphene sheets which then has implications to the resulting film conductivities.
Smaller flakes sizes mean more flakes are required to cover a given area so this leads to the presence of more grain boundaries and hence a higher resultant sheet resistance. An ideal solution based method would require no sonication or oxidation so as to produce pristine graphene.

Research into oxidation processes other than the Hummer's method is one avenue that yielded to some interesting results. Recently oxidation by dichromate[16] has resulted in an alternate route to GO. The production of GO paper as a protective coating and is still an application of interest, hence future research into advanced oxidation methods is certainly to be expected.

Dispersion of GO in solvents other than water have also been investigated by Paredes et al [29]. GO was dispersed in a wide variety of organic solvents by sonication, resulting in GO concentrations far less than what is seen in water. Concentrations are on the order of \(~0.1\text{mg/ml}\), but the ability to disperse GO in different solvents opens up a range of processing possibilities and reactions that are simply not possible in aqueous solution. With new high-yield methods of pristine graphene exfoliation emerging and a limited capability to repair RGO films, we suspect this route to graphene films may fall out of favor with regards to the production of high-quality devices.

### 2.2.2 Organic solvent exfoliation

With the inherent limitations of GO exfoliation and reduction, searches have moved to simple solvent-based exfoliation. It has been discovered that graphene can be exfoliated in a number of organic solvents[38-42]. This method shows promise due to its inherent simplicity and the fact that it results in pristine mono-layer sheets of graphene with respectable electronic properties. The yield and solution concentrations were once less than those achievable by oxidative methods, but with further development extremely high concentrations have been achieved. Graphene dispersion concentrations as high as 63 mg/ml have been achieved by dispersion and reprocessing using N-methyl-2-pyrrolidinone.[42] This specific dispersion has yet to be examined to determine if it can produce high quality conducting films, but the general trend appears to be promising.
Unfortunately, sonication is required to assist in the dispersion which will result in smaller mean flake sizes, and hence reduced film conductivities.[39, 41] Graphene films created from these solutions tend to contain many multi-layer graphene sheets with only a minority of the flakes, ~1%, being mono-layer.

2.2.3 Surfactant assisted exfoliation

Surfactants have proven useful dispersing nanotubes in solutions[43-47], so it is only natural to try a similar method for the dispersion of graphite. Work by Lotya et al [16] using water solutions of sulfonates has demonstrated the viability of this method. More recent work[48-50] has resulted in significant improvements in the concentration of flakes in the solution, in the yield of mono-layer graphene flakes in the solution and in the overall conductivity of the films. Recent work by Sharifi et al. focused on biologically inspired surfactants, including ribonucleic acids (RNA) which not only led to improved transport properties, but also opened an avenue towards biocompatible devices[48-50]. A drawback of surfactant-assisted techniques may be in the amount of surfactant that is left behind in the films, which may be detrimental to some specific applications.

2.2.4 Superacid exfoliation

Chlorosulphonic acid has been proven effective to disperse nanotubes[51] and graphite[52]. Concentrations of graphene flakes up to 20 mg/ml and the formation of a liquid crystal have been reported. Film conductivities of 110,000 S/m have been measured, comparable to that of micromechanical cleavage[53]. This is likely due to fact this method leaves the graphene without functional groups as well the exfoliation occurs without sonication resulting in larger mean flake sizes.

The exfoliation is thought to be the result of protonation of carbon[51, 52]. The protonated sheets become positively charged resulting in electrostatic repulsion. Due to the high concentrations, sheet quality, and large flake size obtained by this method, it appears that protonation is the way to go for solution based exfoliation. However, the resulting graphene is suspended in very corrosive acid, which presents difficulties in creating a film directly from solution. Vacuum filtration can only be done on very
resilient filters making it difficult to transfer the film to another substrate via the vacuum filtration/etching method.

2.3 Thin film preparation methods from graphene dispersions

2.3.1 Vacuum filtration

The most commonly used solution-based method to fabricate graphene thin films is vacuum filtration. This is in large part due to the ease of the method, the consistency of film thickness attainable, and the obvious utility in preparing films from a water-based solution, or dispersion. Typically, with this method, a solution of exfoliated graphite or graphite oxide in water or organic solvents is prepared as described in section 2. The suspension is left to sediment overnight and is subsequently centrifuged at several thousand rpm. The resulting supernatant is then used to prepare films using a vacuum-filtration apparatus originally proposed by Wu et al [54] for carbon nanotube networks and adapted by Eda et al [26] for graphene films. Graphene suspensions are vacuum filtrated through filter membranes with nanometric pore sizes. The filter membrane is chosen specifically to be etchable, typically a nitrocellulose or ester-based membrane is utilized. After filtration the membrane is transferred film side down to any desired substrate and then dried under load in an oven or vacuum desiccator. Once dry, samples are washed in sequential baths of acetone and methanol to etch the filter membrane leaving behind a graphene film on its substrate. A schematic of the vacuum-filtration method is shown in Figure 2-2.

This method is particularly useful since the film thickness is uniform and the total thickness of the film can be controlled by altering the concentration and the filtrated volume of the dispersion. The graphene flakes tend to block the solution; hence, the procedure is self regulating as regions of the filter that are high in flake density will have lower flow rates and so this mechanism results in a uniform film[26, 27, 55]. In the case of fabrication of GO “bucky paper”, the films may even be thick and flexible enough so they can simply be peeled off without the need for filter etching.
Monolayer films can also be created using this method[26] and the use of a nitrocellulose filter allows the film to be placed on any desired substrate by placing the filter film side down on the substrate with pressure and then etching with acetone. However, this method is not without its limitations. Clearly any graphene solution that would dissolve or destroy the nitrocellulose filter could not be filtrated in this manner, as is the case with some organic solvents or superacid exfoliation[52]. Using a filter that is more resilient typically means it will be more difficult to etch. In the case of exfoliation with chlorosulfonic acid the films are generally examined directly on a nanotube filter without the ability to transfer to another substrate.

![Figure 2-2 Schematic of the vacuum filtration method used for depositing solution-processed graphene thin films.][26] This process includes dispersion of graphene or graphene oxide in water or organic solvents, filtration on sacrificial filter membranes, transfer of the film on the requisite substrate and etching the membrane, leaving behind the graphene thin film on its substrate.

2.3.2 Other preparation methods

Spin coating from graphene-containing solutions has been widely used as a simple, proof-of-concept method to deposit graphene films onto flat surfaces. Film thickness can be controlled by selecting different rotation speeds and solution concentrations. Although relatively uniform thin GO films have been fabricated using this method[32], reproducibility tends to be lower than by vacuum filtration.
Other methods include drop casting (i.e. placing a drop of the solution on a substrate, then drying it either in a controlled environment or in ambient conditions) and dip coating. These are quick method than can be used to examine the quality and size of individual graphene flakes. Spray coating is also a popular method, and can be used to make thicker films. A solution is loaded into an air brush and sprayed onto a substrate[27].

2.4 Transmittance and sheet conductivity of graphene thin films

Two essential properties of graphene thin films are required for using them as transparent electrodes 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 given method of exfoliation, dispersion and deposition of graphene flakes. In this section we present a phenomenological model 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 has been reported in the literature and is shown in Figure 2-3.

First, let us 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 CNT thin films in terms of percolation theory[56], and can be written as follows:

$$S = S_0 \cdot (f - f_0)^x$$  \hspace{1cm} (2.1)

where $S_0$ is a parameter that depends only on the average conductivity of the individual flakes in the film[56] (and, subsequently, by the quality of graphitic material that has been exfoliated and by pre-deposition and post-deposition treatments of the flakes[50]). In eq. (2.1), $f_0$ is the percolation threshold for disks which has a universal value $f_0 \approx 0.3$. 

Figure 2-3 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 2-5.

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 \( S(f \leq f_0) = 0 \).\cite{58-60} 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.\cite{58-60} It is also important to note that eq. (2.1) is valid only for values of \( f \) sufficiently close to \( f_0 \) and ignores the contact resistance between the flakes. Which, based on what is observed in CNTs, is generally negligible at room temperature, but may be relevant at cryogenic temperatures.\cite{61}

An additional characteristic of the vacuum filtration method (and, possibly, of several other solution-processing methods used to prepare graphene thin films) 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.[26] This means that the number of layers being deposited, \( N \), is inversely proportional to the fraction of voids being left on the filter membrane, \( 1-f \), which implies the existence of a quasi-linear relationship between \( N \) and \( f \):

\[
N \propto 1/(1-f) \approx A \cdot f
\]  

(2.2)

where 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 eq. (2.2) for a number of different conditions of vacuum filtration, as demonstrated in Figure 2-4a for graphene and graphitic films deposited under the same conditions used by Lotya et al [16] by determining the average layer thickness \( N \) from atomic force microscopy (AFM) profiles and the area of substrate covered by flakes from multiple AFM images. For the specific case shown in Figure 2-4, a value of \( A \) can be inferred from the linear fit of \( N \) vs. \( f \), as demonstrated by the blue solid line in Figure 2-4. Substituting eq. (2.2) into eq. (2.1), we obtain:

\[
S = S_0' \cdot (N - N_0)^x
\]  

(2.3)

where \( S_0' = S_0/A^x \) and \( N_0 = A \cdot f_0 \). Therefore, we have demonstrated that equation 1, which is typical of electrically percolating systems, holds for both the fraction of covered area, \( f \), or the average number of layers in a given film.

Let us now consider the optical properties of graphene films. The normal-incidence transmittance of such films, shown in Figure 2-4b, demonstrates that in a set 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 2-4c, 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:

$$T = 100\% \cdot \exp\left(-\frac{N}{M}\right) \quad (2.4)$$

where $\exp(-1/M) \approx 0.98$ is the transmittance of a single-layer sheet of graphene[62], which gives $M \approx 50$.

It is worth noting that the values of $N$ appearing in equation 4 refer to an average “optical thickness” of the films while, in equations 1 and 3, $N$ determines the average thickness for which the electrical conductance is defined. Nevertheless, Figure 2-4 demonstrated that little discrepancy exists between such values when $N$ is directly measured by AFM, which ultimately substantiates the validity of our model. Combining equations (2.2), (2.3) and (2.4), we obtain the following relationship between the sheet resistance and the film transmittance, which is valid for $\ln(1/T) \geq f_0 \cdot A/M \approx 0.006 \cdot A$:

$$S = S_0 \cdot (M/A) \cdot \ln(1/T) - f_0 \approx S_0 \cdot \left[(50/A) \cdot \ln(1/T) - 0.3\right] \quad (2.5)$$

Fitting of the data in Figure 2-3 to equation (2.5) 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) 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 are reported in Table 2-1. From these values, it can be observed that the lower $A$ the higher $S_0$. This is a direct consequence of the fact that better dispersion of graphitic flakes in water and organic solvents occurs when flakes are more defective and richer in impurities, which is, for instance, the case for strongly oxidized GO.[16]
Table 2-1 Summary of fit parameters from Figure 2-3

<table>
<thead>
<tr>
<th>Reference</th>
<th>$S_0$ ($\Omega^{-1} \text{ cm}^{-1}$)</th>
<th>A</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>[[32]] 1100°C Annealing</td>
<td>2.41$\cdot$10$^{-4}$</td>
<td>4.0</td>
<td>1.1</td>
</tr>
<tr>
<td>[[32]] 400°C Annealing</td>
<td>2.40$\cdot$10$^{-6}$</td>
<td>4.0</td>
<td>1.9</td>
</tr>
<tr>
<td>[[57]] RGO</td>
<td>4.18$\cdot$10$^{-6}$</td>
<td>7.1</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Figure 2-4 a) Average flake thickness as determined by AFM as a function of $f$ for a set of films prepared as in ref. 16 - b) UV-Vis spectroscopic measurements on graphene films at different fraction of area coverage $f$. c) Transmittance vs average flake thickness of a graphene thin film prepared by vacuum filtration. There is a clear exponential relation between flake thickness and transmittance that establishes the validity of equation 4.
2.5 Graphene in organic solar cells

While the potential associated to using transparent and conducting graphene platelets in solar cells has been recognized quite early[2-5], the most optimal architecture for exploiting the outstanding properties of graphene in these devices is still unclear. Several 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. [2-5] The vastest 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, which requires it to be sandwiched between two collection electrodes with much higher conductivity: a transparent “window” electrode and a “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, for allowing the cell to work in a tandem configuration, or simply, for allowing a more efficient process of collection of photoexcited charge carriers. 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 demonstrated in Figure 2-5. In inorganic materials, excitonic diffusion lengths are relatively large (typically ~100-500 nm) and the excitons may cover relatively long distances before being dissociated at the p-n interface and generate a hole current drifting towards the ITO window electrode and an electron current drifting towards the backing electrode, as in Figure 2-5a. Conversely, excitonic diffusion lengths are very short in organic materials (typically ~5-10 nm) as Figure 2-5b. 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 for being 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

![Diagram of Inorganic and Organic Solar Cells](image)

Figure 2-5 Various types of thin film solar cells: a) Inorganic solar cells in which the excitons 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 organic photovoltaics (OPVs) and dye sensitized solar cells (DSSC)

components of the photoactive layer for the excitons to encounter a p-n interface as soon as possible and dissociate. Therefore, 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 2-5b.

In OPVs, the active layer is formed by a p-type organic material (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 indium-tin oxide (ITO) thin film. The typical material of choice for organic hole-transport layers is a water soluble blend of Poly-3,4-Ethlenedioxythiophene: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 little 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. Eq. 5 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 Sect. 2.5.1, functionalized graphene thin films are suitable of matching the work function of both ITO and FTO, the two current materials of choice for window electrodes.
For what concerns 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, as demonstrated in Sect. 2.4, several attempts of using these materials as counter electrodes have been made and will be discussed in Sect. 2.5.2. 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, DSSC 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. Reports also exist on the use graphene films as counter electrodes in thin film solar cells.

In addition, there is some evidence that solution-based graphene materials may also play a role in the active layer of these devices. These applications include the use of functionalized graphene or graphene oxide as an organic acceptor or as an interfacial layer in DSSC as will be discussed in Sect 2.5.3.

All the aforementioned solar 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 is 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[42, 48, 63]. 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 [48]. Nonetheless, the inherent roughness of graphene thin films compared to other electrode materials may also be turned into an opportunity to increase the charge collection area, with obvious improvements in term of the efficiency of this process.

Even with the above mentioned collateral issues, graphene is an extremely promising candidate for the improvement of photovoltaic devices. Here we present some uses that have proven successful and parameters such as the power conversion efficiency, $\eta$, fill factors (FF), short-circuit currents ($I_{sc}$) and open circuit voltages ($V_{oc}$) of a variety of graphene-based solar cells will also be considered. The summary of these parameters for a number of recent studies are summarized in Table 2-2.
Table 2-2 Summary of studies of graphene incorporation into various parts of a solar cell, with the relevant parameters describing the solar cell performance under AM1.5 sunlight illumination

<table>
<thead>
<tr>
<th>Type of solar cell</th>
<th>Location of graphene sheet</th>
<th>$I_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye-sensitized</td>
<td>Electrode</td>
<td>1.01</td>
<td>0.7</td>
<td>0.36</td>
<td>0.26</td>
<td>[7]</td>
</tr>
<tr>
<td></td>
<td>FTO as a comparison</td>
<td>3.02</td>
<td>0.76</td>
<td>0.36</td>
<td>0.84</td>
<td>[7]</td>
</tr>
<tr>
<td>Organic</td>
<td>Electrode</td>
<td>0.36</td>
<td>0.38</td>
<td>0.25</td>
<td>0.29</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>ITO as comparison</td>
<td>1.0</td>
<td>0.41</td>
<td>0.48</td>
<td>1.17</td>
<td>[6]</td>
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<tr>
<td>Organic</td>
<td>Electrode</td>
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<td>0.34</td>
<td>0.4</td>
<td>[32, 64]</td>
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<tr>
<td></td>
<td>ITO as comparison</td>
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<td>0.47</td>
<td>0.54</td>
<td>0.84</td>
<td>[32, 64]</td>
</tr>
<tr>
<td>Dye-sensitized</td>
<td>Graphene/PEDOT-PSS electrode</td>
<td>12.96</td>
<td>0.72</td>
<td>0.48</td>
<td>4.5</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td>PEDOT-PSS electrode as comparison</td>
<td>10.99</td>
<td>0.72</td>
<td>0.28</td>
<td>2.3</td>
<td>[65]</td>
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<tr>
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<td>Electron acceptor</td>
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<td>4.2</td>
<td>0.37</td>
<td>1.4</td>
<td>[66]</td>
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<tr>
<td>Dye-sensitized</td>
<td>Graphene-TiO$_2$ as interfacial layer</td>
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<td>0.741</td>
<td>0.42</td>
<td>5.26</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$-FTO comparison</td>
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<td>0.687</td>
<td>0.4</td>
<td>4.89</td>
<td>[67]</td>
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<tr>
<td>Organic</td>
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<td>2.39</td>
<td>0.32</td>
<td>0.27</td>
<td>0.21</td>
<td>[57]</td>
</tr>
<tr>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Graphene treated by UV radiation</td>
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<td>0.74</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>Graphene modified by PBASE</td>
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<td>0.55</td>
<td>0.51</td>
<td>1.71</td>
<td>[57]</td>
</tr>
<tr>
<td></td>
<td>ITO as comparison</td>
<td>9.03</td>
<td>0.56</td>
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<td>3.1</td>
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<td>0.48</td>
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<td>0.48</td>
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<td>0.44</td>
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2.5.1 Graphene as a window electrode

In this section, we will be focusing on the use of graphene as a transparent conductor in OPVs and DSSCs as a replacement for ITO and FTO, respectively.

Mullen et al.[7] 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. The backing electrode was a gold cathode, as demonstrated in Figure 2-6a. Proper matching of the energy levels of the electrode and the active materials is essential for efficient power conversion. Figure 2-6b shows the energy level diagram of the graphene/TiO$_2$/spiro-OMeTAD/Au device. Since 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)[7]. 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 a percolation mechanism inside the porous TiO$_2$ structure. The current-voltage (I-V) characteristics of the device under illumination showed a short-circuit photocurrent density $I_{sc} = 1.01$ mA/cm$^2$, with an open-circuit voltage $V_{oc} = 0.7$ V a
Figure 2-6 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 TiO2, and graphene film. (B) The energy level diagram of graphene/ TiO2/dye/spiroOMeTAD/Au device.[7] (Reprinted from Nano Letters, 8 / 1 , Xuan Wang, Linjie Zhi, and Klaus Müllen , “Transparent, Conductive Graphene Electrodes for Dye-Sensitized Solar Cells”, p323-327., Copyright (2008), with permission from American Chemical Society)

fill factor FF = 0.36 and an overall efficiency η = 0.26%. A control FTO-based solar cell was also fabricated and evaluated for comparison. The FTO based cell gave $I_{sc} = 3.02$ mA/cm$^2$, $V_{oc} = 0.76$ V and the same fill factor of the graphene solar cell, even though at a much superior efficiency ($\eta = 0.84\%$). The somewhat lower values of $I_{sc}$ and $\eta$ 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 electron bands at the interfaces.[7]
Transparent graphene anodes synthesized by chemical vapor deposition (CVD) have been reported by Wang et al.[11] and polymeric solar cells were assembled on them. The utilized active layers were the “standard” bulk heterojunctions of regioregular poly(3-hexylthiophene) and phenyl-C61-butyric acid methyl ester (P3HT:PCBM). These graphene-based devices demonstrated 0.21% efficiency when assembled on a pristine graphene electrode, but the efficiency could be risen up to 1.71% when the graphene film was modified by pyrene butanoic acid succinimidyl ester (PBASE). This was only 55.2% of the efficiency obtained from the ITO control device, which may lead to conclude that P3HT:PCBM 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.

An interesting alternative to polymer-fullerene blends are OPVs assembled from small polyaromatic molecules. This is a very promising approach, since several systems of small polyaromatic molecules are uniquely positioned to self-assemble on graphene and create the most optimal interfaces for efficient charge collection. The PEDOT 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[10] (also known as Bathocuproine, or BCP), the electron transport material of choice for organic light-emitting devices. For instance, Gomez de Arco et al. [10] compared solar cells constructed from graphene and ITO electrodes fabricated on flexible polyethylene terephthalate (PET) substrates and utilizing copper phtalocyanine-fullerene (CuPc-C60) active bilayers and they obtained efficiency values of 1.18% and 1.27% respectively, a figure that 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 cells architectures are required in order to optimize solar cells assembled on graphene electrodes and the optimization process cannot simply rely on the results obtained from the optimization of organic solar cells on ITO.
P3HT:PCBM solar cells has also been fabricated\cite{10} by using graphene thin films directly synthesized from organic reagents, which hold a normal-incidence transmittance $\sim 85\%$ 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 highest external quantum efficiency (EQE) of this type of cells was observed at 520 nm monochromatic light\cite{10} and, at the same conditions, the efficiency of a control ITO device was found to be 47\%. Under 510 nm monochromatic light, the efficiency of this graphene-based cell was 1.53\%, similar to the ITO-based cell. However, under AM1.5 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 cell and the control 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 of were attributed by the authors to the high resistance of the prepared graphene films.\cite{6}

Graphene films prepared by spin coating a suspension of reduced graphite oxide (or by reducing a thin layer of spin-coated graphene oxide) have been widely used as window electrodes in organic photovoltaics \cite{32, 64}. AFM characterization revealed that the thickness of these RGO layers is 10 nm or less, with a surface roughness lower than 3 nm. Additional analysis demonstrated that the transparency of the film was better than 80\% at less than 20 nm film thickness, but the resistance of the films ranged from 1 to 5 M$\Omega$\cite{64}, which does not favorably compare with ITO. In fact, the organic solar cells fabricated using these electrodes held efficiencies $\sim 0.4\%$, 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.

In order to consider the application of graphene as substitute for ITO anodes in organic solar cells, an OPV was built from a stack of layers of graphene and PEDOT:PSS/CuPc/$C_{60}$/BCP/Ag, as in Figure 2-7.\cite{9} This 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]. A challenge that has been identified was 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] and graphene layers at different thicknesses were optimized. In one set of solar cells reported in ref. 9, the wettability of the graphene surface by PEDOT:PSS was improved by dissolving PEDOT in an organic solvent (dimethyl sulfoxide, DMSO) and by replacing PSS with poly-(ethylene glycol) (PEG). 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 to take 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 AuCl₃, which was preceded by an oxygen plasma treatment of the films. Spin coating of PEDOT:PSS on graphene films functionalized by AuCl₃ was found to be much easier than on pristine graphene films, which significantly improved the device performance. In these 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].
2.5.2 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 (Pt) electrodes in dye-sensitized solar cells. 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, without any heat treatment. The transmittance of the as prepared nanocomposite thin films were higher than 80% at 390-780 nm wavelength. Figure 2-8a shows the photocurrent-voltage curves of the cells with PEDOT:PSS, PEDOT:PSS:graphene and Pt counter electrodes, respectively.
Recently, a new counter electrode for DSSC, in which graphene functionalized with 1-pyrenebutyrate was incorporated in FTO, has also been reported. The efficiency of the cell with graphene-modified FTO as a counter electrode approaches $\eta = 2.2\%$ and is significantly higher than the efficiency of a control DSSC assembled on FTO ($\eta = 0.048\%$). However, the efficiency of the graphene-based solar cell was lower than that of a control cell with platinum as counter electrode ($\eta = 3.98\%$) [70].

Figure 2-8 a) Photocurrent-voltage characteristics of the DSSCs with different counter-electrodes under irradiation of 100 mWcm$^{-2}$ AM 1.5 white light; (b) plot of graphene content of graphene/PEDOT–PSS electrode versus the conversion efficiency of DSSCs under irradiation of 100mW cm$^{-2}$ AM 1.5 white light.[65](Reprinted from Electrochemistry Communications, 10 /10 , W. Hong, Y. Xu, G. Lu, C. Li, and G. Shi, “Transparent graphene/PEDOT–PSS composite films as counter electrodes of dye-sensitized solar cells”, p 1555-1558., Copyright (2008), with permission from Elsevier)

The efficiency of a DSSC using a counter electrode made by a PEDOT:PSS thin film at 1 wt % content in graphene was measured by Hong et al. and found to be 4.5% $^{66}$. 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 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% as seen in Figure 2-8b. 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. [65]

2.5.3 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.[66] Using functionalized reduced graphene oxide as electron acceptor and poly3-octylthiophene (P3OT) or P3HT as electron donors, solar cells with efficiency up to 1.4% were optimized. The functionalization of reduced graphene oxide was conducted by chemically treating in it phenyl isocyanate [66].

Another use of graphene that is being considered is as an interfacial layer in DSSCs.[67] A mixture of graphene oxide (GO) and nanostructured TiO$_2$ was photocatalytically reduced by UV irradiation and applied as interfacial layer between the FTO electrode and a nanocrystalline TiO$_2$ thin film, as in Figure 2-9. During the fabrication of DSSC, TiO$_2$ nanoparticles with 15-20 nm diameter are typically deposited as a porous layer on the window electrode, with a thickness of 10-12µm. When such a TiO$_2$ layer is formed, the surface of FTO, which is generally very rough, is not uniformly covered by the nanoparticles, which leads to the formation of voids at the interface.[71] 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. Engineering the interface between the FTO electrode and the TiO$_2$ porous layer is essential for the formation of efficient DSSCs. Liu et al[67] have shown that the introduction of a graphene interfacial thin film between FTO and TiO$_2$ resulted in a 54 mV increase in the open circuit voltage of their DSSC, due to the retardation of the back transport reaction at the FTO/TiO$_2$
interface. The photoconversion efficiency subsequently increased from 4.89% to 5.26%\(^\text{67}\).

Another study\(^\text{8}\) investigated the enhancement of the performance of dye-sensitized solar cells (DSSCs) by directly incorporating graphene into porous TiO\(_2\) photoanodes. The graphene-TiO\(_2\) nanocomposites were prepared by heterogeneous coagulation between Nafion-functionalized graphene and commercial TiO\(_2\) nanoparticles (P25 type). Typically, 0.5 wt % graphene has been used.

![Graphene-TiO\(_2\) interfacial layer](image)

Figure 2-9 Model of graphene-TiO\(_2\) interfacial layer used to prevent back-transport reaction of electron carriers.\(^\text{67}\) (Reprinted from Chemical Physics Letters, 483, S.R. Kim, M. Khaled Parvez, and M. Chhowalla, “UV-reduction of graphene oxide and its application as an interfacial layer to reduce the back-transport reactions in dye-sensitized solar cells”, p124-127., Copyright (2009), with permission from Elsevier)

It was observed that graphene causes a significant improvement of DSSCs by two main effects. First, by making a high porosity of P25-graphene film which led to higher surface area of P25-graphene film and introduces more sites for the absorption of dye molecules,
which harvest more light and leads to more photoinduced electrons injected from excited state of the dye into conduction band of P25. Secondly, according to electrochemical impedance spectra (EIS), as shown in Figure 2-10, the P25-graphene electrodes have a lower semicircle size in the middle frequency region rather than P25. This indicates an acceleration of electron transfer process to the film photoanode. In addition, the shift of characteristic frequency peak towards lower frequency for P25-graphene film reveals a more rapid electron transport process and higher electron life time, \( \tau_e = \frac{2\pi f_{md}}{f_{mid}} \), so graphene plays a beneficial role as conductive network and electrons in this network get very long mean free paths, escape charge recombination, and extend the electron lifetime.

![Graph of Electrochemical impedance spectra](image)

**Figure 2-10** Electrochemical impedance spectra of DSSCs with P25 and P25-graphene electrodes. The inset displays Bode-phase of two films.[8] (Reprinted from Applied Physics Letters, 96 / 8 , S. Sun, L. Gao, Y. Liu, “Enhanced dye-sensitized solar cell using graphene-TiO2 photoanode prepared by heterogeneous coagulation”, 083113, Copyright (2010), with permission from AIP)

Another important feature is that the work function of graphene is in the range of 4.42-4.5 eV, which allows an efficient transfer of electrons from the conduction band of P25 to graphene. The electrons transferred through the graphene sheets were then collected by the fluorine-doped SnO\(_2\) (FTO) substrate. In a traditional TiO\(_2\) photoanode, photoinduced
electrons have to transfer through the film which is several micrometers thick before reaching the FTO substrate, and hence have higher chances to recombine with a hole carrier. Since graphene has a similar work function to FTO a TiO$_2$-graphene photoanode acts like many extended current collectors penetrating into the TiO$_2$ matrix, thus electrons will be efficiently collected before exciton recombination. As a result, the short-circuit photocurrent density and overall energy conversion efficiency with P25-graphene electrode increased to 8.38 mA/m$^2$ and 4.28% in comparison to the pristine P25 electrode with 5.04 mA/m$^2$ and 2.70%.

2.6 Conclusions

In summary we have reviewed some of the methods used for preparing dispersions of graphene in water and organic solvents and examined their success for the fabrication of transparent and conducting films that are more cost-effective than CVD-grown graphene. Device-grade transparent and conducting films have been demonstrated, but the quality of the devices tends to be worse than devices fabricated by CVD graphene, albeit with the benefit of cheaper production costs. We have outlined a relation between film conductivity and transparency which appears to be adequate for graphene films prepared by vacuum filtration or spin coating and reasonably reproduces most of the data available from the literature.

We have also examined the use of graphene in solar cell devices, and have shown how graphene can be utilized in many different components of organic solar cells. Graphene can be used effectively as a window electrode and doped graphene can also be used as an electron acceptor and a counter electrode. Even though graphene is yet not yet able to effectively compete with ITO or FTO, we suspect that further development in solution-processing techniques will result in the more widespread adoption of graphene in several areas of optoelectronics and can potentially reduce the fabrication costs of organic solar cells, in competition with more conventional technologies.


Chapter 3

3 Photovoltaic efficiency degradation and formation of paramagnetic centers in polythiophene-fullerene bulk heterojunctions.

3.1 Introduction

Recent improvements have given as much as 10.7% photoconversion efficiency in organic photovoltaics (OPVs)[1], which makes them competitive with their inorganic counterparts including thin film amorphous silicon, CdSe/CdTe, and CuInGaSe (CIGS) photovoltaics. However, degradation of OPVs over time is significant, poorly understood and limits their commercialization. Methods for encapsulating OPVs against degradation have been proposed[2]. These feature methods such as encasing the solar cells in vacuum sealed glass or by a less costly method of vacuum sealing in plastic. Their development is costly and mostly relies on a trial-and-error approach, since knowledge on the physical processes that lead to the formation of defects and degradation of the solar cell active layer is insufficient at the microscopic level.

Two main degradation pathways of the active layer of OPVs that have been suggested are[3] i) morphological degradation of the bulk heterojunction architecture and ii) chemical degradation of the organic materials, which is expected to be related to oxygen and moisture incorporation. For poly(3-hexyl-thiophene) (P3HT), a standard choice as a donor material in OPVs, reasons for chemical degradation which have been suggested are the formation of charge coupled complexes with oxygen[4] and oxidation of the polymer backbone[5]. Quantification of the oxygen and moisture content in OPVs remains a challenge with only qualitative results available. [6, 7] While oxygen and moisture incorporation is universally blamed as the major source for degradation in OPVs,[5, 8-10] little information is available on the specific oxygen-related chemical groups that cause a decrease in efficiency.
In this chapter we examine the physics of degradation of bulk heterojunction solar cells, prepared from P3HT and using Phenyl-C_{61}-butyric acid methyl ester (PCBM) as an acceptor material, during a “70-70-70 test” involving the exposure of non-encapsulated P3HT:PCBM active layers to 70% humidity at 70°C for times up to 70 hours. Quantification of oxygen content during the exposure process was obtained from Rutherford backscattering spectroscopy (RBS). Specific characterization of paramagnetic defects was done by electron spin resonance (ESR) to gain insight into how paramagnetic centers induced by degradation influence the efficiency of our solar cell active layers (P3HT:PCBM) and isolated P3HT or PCBM films. ESR studies on amorphous silicon photovoltaics demonstrated that a strong relationship exists between the presence of paramagnetic defects and the resulting charge collection efficiency in such material.[11]

### 3.2 Experiment and discussion

The OPV fabrication was carried out as follows; substrates of indium tin oxide (ITO) coated glass (sheet resistance ∼90Ω/□) were cleaned in successive baths of water, acetone, and methanol for 15 min. The substrates are then treated in a PSD-UV3 Novascan ozone treatment system for an exposure time of 15 min. This system uses a UV lamp to convert atmospheric O\textsubscript{2} into highly reactive O\textsubscript{3}. Ozone is a powerful oxidant and will rapidly oxidize any organic contaminants on the substrate as well as functionalize the surface to make it more hydrophobic. This process helps the following hole blocking layer to adhere to the surface of ITO. To prepare the hole blocking layer, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, Sigma-Aldrich Cat no. 483095) was deposited on the substrate by spin coating at 4000 rpm immediately after ozone treatment of the substrate. The resulting film was annealed at 130°C for 15 min. in a VAC Nexus glove box filled with N\textsubscript{2}, with oxygen and moisture levels below 5 ppm. To prepare the active layer, a solution of 15:15 mg of P3HT:PCBM was added to 1 mL chlorobenzene and stirred for 1 hr in the glove box. The solution was spin coated at 1500 rpm on top of the PEDOT:PSS film resulting in a film thickness of 200 nm. The sample was then annealed at 130°C for 15 min. The top contact of the solar cell was constructed by thermally evaporated Ca-Al electrodes. Identical samples were prepared for RBS and ESR measurements. Three sets of thin films were produced: one set with only P3HT,
another with only PCBM, and a set of PCBM:P3HT films prepared identically as described previously on low-defect glass substrates, but without the underlying PEDOT:PSS hole transport layer to prevent a spurious ESR signal from free carriers. All of the resulting samples were exposed to the 70-70-70 test in a custom built chamber, with controlled humidity and temperature. Samples were kept in a glovebox loaded with N₂ until they were measured, immediately at the end of the 70-hr test.

RBS spectra were recorded using a 2-MeV \(^{4}\text{He}^+\) ion beam at the Tandetron facility at Western University. RBS utilizes a beam of high energy ions to determine the elemental content in a sample. A portion of the \(^{4}\text{He}^+\) ions that impact the sample are scattered back out of the sample where their energy is measured, as shown in Figure 3-1. The impact of the ions with the sample atoms is modeled using simple kinematic equations to determine the mass, and hence the element, of the collided atoms.

![Figure 3-1](image_url)

Figure 3-1 Diagrams showing how RBS measurements are taken. Panel a) shows the state of the system before the collision. The sample atom is stationary and the incoming \(^{4}\text{He}^+\) atom from the He beam is shown. b) After the collision the \(^{4}\text{He}^+\) atom is backscattered and then its energy is measured in a detector. This measured energy is then used to determine the mass of the sample atom.
A region of the solar cell active layer not covered by ITO was used to record the spectra. The layout of our solar cell architecture is shown in Figure 3-2d and our RBS data are reported in Figure 3-2a. They show several peaks with contributions from both the thin films and the substrate. The carbon, oxygen and sulphur peaks from P3HT:PCBM can be identified at energies ≈500 keV, 720 keV, and 1200 keV respectively. Preliminary spectra simulations revealed that the contributions to the RBS spectra of the PEDOT:PSS hole-blocking layer (30 nm thickness) are negligible. The O and Si peaks of the substrate at energies ≈600 keV and 1050 keV respectively are significant, but due to the energy losses of the \(^4\)He\(^+\) ions through the organic layers, the peaks from oxygen in the film are displaced in energy from the corresponding peak of the substrate. Additionally there are small features in the spectra that are due to alkali impurities in P3HT and they also show trace amounts of indium from ITO.

Quantitative data on the film composition were obtained by analysis of the RBS data using the SIMNRA simulation package[12], which takes into account the roughness of the films.[12] This is achieved by breaking up the active layer into multiple layers of different film densities, as shown in Figure 3-2e. These simulations show that throughout the experiment oxygen content remains measurably unchanged at an atomic concentration of ~10% or at a density of \((4.5\pm1)\cdot10^{20}\) O atoms/cm\(^3\), as demonstrated in Figure 3-2b. Compositional measurements performed by other groups utilizing time of flight secondary ion mass spectrometry[13] had qualitatively shown a relatively small increase in oxygen and water content to organic films exposed to isotope enriched water and oxygen environments. Therefore, we must conclude that any increase of oxygen content is below the experimental detection limits. The only evolution clearly visible throughout the spectra is an increasing surface roughness that results in the peak edges becoming broader and shifted in energy. The RBS spectra of the samples at low time of exposure to moisture \((t < 10\) hrs\) are almost identical with each other. Only at \(t > 10\) hrs
we observed a strong change in surface roughness, which was measurable by RBS. The surface roughness obtained by RBS simulations is shown in Figure 3-2c and is corroborated by atomic force microscopy (AFM) measurements as discussed below.

Figure 3-2 a) Selected RBS spectra on P3HT:PCBM solar cells without top electrode, including simulated spectra. b) Oxygen content vs time as determined by RBS simulations. There is a small increase in oxygen content, but much smaller than our estimated uncertainty. c) Roughness as determined by RBS simulation show increases in surface roughness under increasing exposure time. The roughness is represented as a standard deviation of the areal density of the film. d) Solar cell layout used in this experiment, showing the area utilized for RBS measurements. e) Diagram showing how film roughness is modeled in RBS simulation. The rough layer is broken up into sub layers with varying densities.
Tapping mode AFM images (Witec Alpha300S) were recorded on each complete cell as shown in Figure 3-3. The images show an ongoing degradation in morphology of the P3HT:PCBM active layer at increasing time of exposure to moisture. From 0 to 10 hr exposure, non-uniformity and “grain border corrosion” of the P3HT:PCBM phase proceeds from the boundaries of the nanocrystals. A limited change in nanocrystal size occurs at this stage, even though we can anticipate that a substantial degradation of AM 1.5 solar cell photoconversion efficiency also occurs (from $\eta = 3.2\%$ down to $\eta = 0.25\%$ after 10 hrs of treatment). In agreement with RBS measurements, extensive changes in morphology of the solar cell active layers are noticed only at $t > 10$ hrs of treatment and results in the coalescence of several P3HT and PCBM nanocrystals in larger, smoother and presumably amorphous domains. This justifies the increase in overall roughness indicated by RBS, with an extensive degradation of the AM 1.5 cell efficiency, that drops to less than $\eta = 0.001\%$ after 70 hrs of treatment.

Electron spin resonance spectroscopy (ESR) measurements were recorded on PCBM, P3HT and P3HT:PCBM bulk heterojunction thin films immediately after removing the samples from 70-70-70 test chamber. ESR can directly measure the presence of unpaired electrons in a solid which can give information about the quantity of defects in a material. This is done by first placing the sample in a magnetic field, provided by a powerful electromagnet. The magnetic field results in a Zeeman splitting of unpaired electrons in the sample. A microwave source is used to excite electrons from the lower Zeeman energy level to the higher energy level. This is detected as an increase in absorption in the sample at a specific microwave frequency that is equal to the difference in energy between the Zeeman levels. Zeeman energy splitting is given as[14],

$$E = h\nu = g\mu_B B$$  \hspace{1cm} (3.1)

with $g$ as the effective gyromagnetic ratio or g-factor, $\mu_B$ is the Bohr magnetron, and B is the magnetic field strength. In practice it is difficult to change the photon energy $h\nu$, so in most ESR systems $h\nu$ is kept constant while the magnetic field $B$ is scanned. The measured absorption peak can then be used to determine the spin-density by calibration using a sample of known spin density. In this case we use a solution of (2,2,6,6-
Tetramethylpiperidin-1-yl)oxy (TEMPO) in toluene. Each TEMPO molecule has a single ESR active spin center, so by preparing a solution with a known quantity of TEMPO we obtain a sample with a known number of spins. The intensity of the TEMPO EPR signal is then compared against a Mn$^{3+}$ marker installed in the EPR cavity and that ratio is used to calculate the total number of spins in the measured sample. The calculation is done by using the following relation,

$$S_{\text{sample}} = \frac{A_{\text{sample}}}{Mn_{\text{sample}}} \cdot \frac{Mn_{\text{TEMPO}}}{A_{\text{TEMPO}}} \cdot S_{\text{TEMPO}}$$ (3.1)

where $S_{\text{TEMPO}}$ is the total number of spins of the TEMPO sample, $A_{\text{sample}}$ is the integrated intensity of the sample signal, $A_{\text{TEMPO}}$ is the integrated intensity of the TEMPO signal, and $Mn_{\text{TEMPO}}$ and $Mn_{\text{sample}}$ are the integrated intensities of the Mn marker with the TEMPO or sample installed respectively.

EPR Measurements were taken using a JEOL FA-200 X-band ESR spectrometer equipped with a double-compartment TE$_{110}$ cavity that contains a built-in Mn marker in one of the two compartments for accurate estimates of the spin densities. 100 kHz modulation was applied to detect the microwave signal at 0.06 mT amplitude. Measurements were taken under dark conditions to avoid photo-oxidation of the samples during measurement and the creation of excitons which will also give an ESR signal. Measurements were taken at varying microwave powers in order to determine the spin relaxation times of the signal. There are two relaxation times, the spin-lattice relaxation time ($T_1$) and the spin-spin relaxation time ($T_2$). The spin-lattice relaxation time is a measurement of how well the spin system is coupled to the surrounding medium, the 'lattice'. A small spin-lattice relaxation time indicates that the spins interact strongly with the lattice via various mechanisms such as phonon scattering. The spin-spin relaxation time is a measurement of energy transfer within the spin system and is typically around $10^{-7}$ seconds.

The spin-spin relaxation time is often calculated by measuring the width of the EPR spectrum and then utilizing the following relation[15],
with $\gamma = g\mu_B/\hbar$ where $g$ is the g-factor of the signal, $\mu_B$ is the Bohr magneton and $\hbar$ is the reduced planks constant. $\Delta H^0_{pp}$ is the peak to peak difference in magnetic field (typically in mT) of the measured EPR signal.

The measurement of the spin-lattice relaxation time, $T_1$, is slightly more involved. In this case the so called saturation method was used to determine $T_1$. The EPR signal is recorded at several microwave powers such that the spectrum is taken to saturation. $T_1$ can then be estimated using the following relation[15],

$$T_1 = \left( \frac{(1/s) - 1}{KP_w/4} \right) \left( \frac{1}{\gamma^2 T_2} \right)$$

where $s$ is the saturation factor defined as

$$\frac{1}{s} = \left[ \lim_{P_w \to 0} \frac{\Delta H_{pp}}{\Delta H_{pp}} \right]^2$$

and $P_w$ is the microwave power, $K$ is a constant that depends on the Q value of the EPR cavity in use. It should be noted that $\Delta H_{pp}$ is a function of $P_w$. So for every $P_w$ there is a corresponding saturation factor. These equations are derived directly from the Bloch equations, a set of equations that model the dynamics of magnetization in a solid.

From Figure 3-4a, we can observe a rapid increase in spin density of all three sets of samples under short exposure times to moisture. The ESR signal in P3HT films has been assigned to many different kinds of paramagnetic defects including: oxygen doping of the polymer chains by the creation of charge coupled complexes,[4, 7] oxidization[5] and localized defects introduced by ultraviolet light exposure[16]. A previous study on thick
Figure 3-3 Atomic force microscopy measurements taken of the P3HT:PCBM active layer after exposure to the 70-70-70 test. The gray scale bar represents 1 µm. There are significant increases in surface roughness with exposure time that contributes to the incorporation of oxygen into the cell.

P3HT films suggested that a portion of the signal was due to oxygen doping that increased the number of hole carriers[7]. On the other hand, increase in the spin density was also attributed to an increase in the moisture content of the film, since it was shown[17] that moisture provides a similar rise in ESR signal as that of oxygen.
The nature of our 70-70-70 test confirms that the spin density of our P3HT and P3HT:PCBM thin films must be at least partially assigned to the increase of adsorbed water or hydroxyl (OH) groups that are incorporated during our treatment. Fullerenes has also shown similar responses in the presence of oxygen[4], hence the observed increases in the spin density of PCBM can also be assigned to oxygen exposure. All these findings are consistent with RBS measurements since the spin densities measured (<10^{18} \text{ cm}^{-3}) indicate that paramagnetic centers are incorporated in proportions that are well below the O detection limit of RBS (i.e. ~2%).

Surprisingly, we find that, at a constant film thicknesses, the spin densities in P3HT:PCBM bulk heterojunctions are consistently lower than in films composed only of P3HT or PCBM, as can be observed in Figure 3-4a. This happens in spite of the fact that all our films were prepared, treated and measured simultaneously. This effect can be explained by the creation of a depletion region between the two phases. In other words, hole and electron carriers, or moisture-related paramagnetic defects in P3HT and PCBM pair up at the interface between the two phases in a P3HT:PCBM bulk heterojunction. This may decrease the local carrier density as well as the total number of unpaired spins, which result in a smaller total spin concentration. We therefore conclude that oxygen and moisture-related paramagnetic defects existing separately in P3HT and PCBM are also responsible for the increase in spin density in the P3HT:PCBM bulk heterojunctions during the 70-70-70 test, but pairing between P3HT-related and PCBM-related unpaired spins must occur at the P3HT/PCBM interfaces.

ESR Spectra of selected P3HT and PCBM films are shown in Figure 3-4b and c. At the initial stages of the 70-70-70 test, a broad signal with \( g_1 \approx 2.0022 \) is observed in both materials, P3HT and PCBM, which is consistent with a signal that can be assigned to delocalized \( \pi \)-electrons as a consequence of oxygen doping [7]. The PCBM films exhibit an increase in intensity as discussed before, which is consistent with adsorption of relatively small amounts of oxygen below the RBS detection limit, but the peak shape remains largely unchanged throughout the experiment. The P3HT spectra show the appearance of a second ESR signal at \( g_2 = 2.0039 \). We propose that such additional ESR feature arises from the progressive incorporation of \( \text{H}_2\text{O} \), initially in crystalline regions
and, successively, at $t > 10$ hrs, in regions that become more disorderly as the degradation proceeds and the P3HT and PCBM nanocrystals mix in an amorphous phase. Finally, the shape of the ESR signal in P3HT:PCBM bulk heterojunctions can be understood as the superposition of signals from the individual constituents, P3HT and PCBM.

The measurement of the spin-lattice and spin-spin relaxation time give some qualitative information about how defect centers are evolving in the P3HT:PCBM matrix. Figure 3-5 shows the measured relaxation times of the P3HT:PCBM films. While the spin-spin relaxation times remain relatively constant over the length of the experiment, we find that the spin-lattice relaxation time tends to decrease with increasing exposure. This indicates that the electrons associated with the defect centers in the active layer are interacting more strongly with the lattice. This combined with the information from the spin density measurements we find that not only are the number of defects increasing with exposure, but they are becoming more strongly coupled to the lattice.

While Figure 3-6b suggests that the evolution of the spin density, $N_D$, as a function of time in our samples follows a multi-stage process ($N_D \sim t^{1/4}$ for $t \leq 10$ hrs, corresponding to the “grain border corrosion” phase previously observed by AFM, and $N_D \sim t^3$ for $t \geq 10$ hrs, corresponding to AFM-detected “extensive degradation” of the samples) the decrease of the AM 1.5 efficiency of our cells at increasing spin density follows a simpler, single-stage exponential decay, as in Figure 3-6a. We are therefore inclined to assign the decline in efficiency of our solar cells to the limited amount of oxygen and moisture that is incorporated as paramagnetic centers, and not to the overall oxygen or moisture adsorption.
Figure 3-4 a) Spin density vs. time for P3HT, PCBM and P3HT:PCBM thin films. The drop in spin density in the P3HT:PCBM mix is attributed to the formation of a depletion region between the two phases. b) EPR spectra of P3HT films. There is a peculiar evolution of the line shape that remains to be explained. c) EPR spectra of PCBM films at different exposure times show increases in spin density.
Figure 3-5 Spin lattice relaxation times of the PCBM:P3HT film. The spin-spin relaxation times ($T_2$) are essentially constant while the spin-lattice relaxation time ($T_1$) shows an overall decline.
Figure 3-6 a) Spin density measurements of the PCBM:P3HT active layer as a function of solar cell efficiency. There is a strong exponential relationship between paramagnetic defect density that appears to say the reduction in efficiencies depends largely on defect density. b) Efficiency vs time that shows two unique stages of degradation, grain border corrosion and extensive degradation.

Paramagnetic centers form singly-occupied electronic orbitals that act as traps for the recombination of electron-hole pairs.[11] With this in mind, we compared our organic photovoltaics to hydrogenated amorphous silicon (a-Si:H) solar cells in which an increase in non-radiative recombination is known to be associated to the increase in paramagnetic defect density.[11] In a-Si:H the collection efficiency as a function of $N_D$ is given by[11]
\[ \eta = \frac{\mu_c}{\pi \cdot d^2 \cdot r_c^2 v_c N_D} \left[ 1 - \exp \left( \frac{-\pi \cdot d^2 \cdot r_c^2 v_c N_D}{\mu_c V} \right) \right] \]  

(3.4)

where \( V \) is the applied voltage, \( d \) is the film thickness, \( \mu_c \) is the carrier mobility and \( v_c \) is the thermal velocity of carriers. Eq. (3.4) cannot account for the decrease in efficiency in our cells since it decreases as \( \eta \propto N_D^{-1} \) for large \( N_D \) while our data in Figure 3-6a can be well fitted to a simple exponential relation

\[ \eta = \eta_0 \cdot \exp \left( -\frac{N_D}{N_{Cr}} \right) \]  

(3.5)

where \( \eta_0 \) is the exponential prefactor and \( N_{Cr} \) is a critical spin density for which \( \eta \) decreases by a factor of \( e \). From our best fit in Figure 3-6a we obtain \( N_{Cr} = 3.2 \cdot 10^{16} \text{ cm}^{-3} \).

Although understanding the simple trend provided by Eq. (3.5) will require additional theoretical investigations, it is insightful to examine the relationship between \( d_{DD} \), the average distance between defects, and the Onsager capture radius, defined as the critical distance \( r_c \) at which the columbic force between photoexcited electrons or holes and a charge trapping defect equals the thermal energy \( k_B T \):

\[ r_c = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r k_B T} \]  

(3.6)

In Eq. (3.6), \( e \) is the elementary charge, \( \varepsilon_0 \) is the vacuum permeability, and \( \varepsilon_r \) is the dielectric constant of the surrounding material. A value of \( \varepsilon_r \approx 3.5 \) is common for organic polymers and leads to \( r_c \approx 16 \text{ nm}[18] \) at \( T = 300 \text{ K} \). While the difference in \( r_c \) between inorganic and organic materials is significant but not dramatic (\( \varepsilon_r \approx 13 \) gives \( r_c \approx 3.5 \text{ nm} \) in a-Si:H[18]) inorganic materials have exciton diffusion lengths up to 40 \( \mu \text{m}[19] \), which are several orders of magnitude larger than in organics where, typically, \( L_D \approx 5-10 \text{ nm}[20] \). Therefore, inorganic solar materials are in a regime for which \( L_D \gg r_c \) while \( L_D \sim r_c \) for organics, as shown in Figure 3-7.
Figure 3-7  a) Exciton diffusion for inorganic materials with LD >> r_c. b) Exciton diffusion for organic materials with LD ~ r_c. Excitons created near defects recombine within the vicinity of the defect, while excitons created outside this region are able to separate at a polymer-fullerene interface. c) At a critical paramagnetic defect density, NC_r, the defects are separated by a distance equal to the Onsager capture radius. This results in percolating regions of defects. Each red dot represents a spin center and the surrounding red area is the corresponding capture radius.

The assumptions used to derive Eq. (3.4) are no longer valid when LD ~ r_c, such as in organic materials.[11] In these cases excitons are highly localized and diffuse poorly throughout the sample. When they are created in the proximity of a trapping defect their probability to diffuse away and escape non-radiative recombination is minimal, because of the short diffusion length that prevents virtually any excitons created at r < r_c from a defect to dissociate and contribute to the photocurrent. Conversely, excitons photogenerated at r > r_c have the ability to be dissociated at a polymer-fullerene interface without being captured.

The volume fraction of material for which the condition r > r_c holds, is determined by the average distance between defects and, subsequently, the defect density. When N_D < N_{C_r}
defects are extremely sparse and only a minimal fraction of excitons are generated within the capture radius of a defect. At the opposite, the probability of capture and nonradiative recombination of an exciton at a charge trapping defect largely increases for $N_D > N_{Cr}$, when the volume fraction of material for which $r < r_c$ forms a system of percolating spheres. Interestingly, the percolation threshold, for which $d_{DD} \approx 2r_c$, is reached exactly at $N_D = N_{Cr}$, where $d_{DD} \approx N_{Cr}^{-1/3} \approx 32$ nm. This strongly suggests that paramagnetic defects are primarily responsible for the decrease in cell efficiency, and that the capture of excitons by these defects might lead to an exponential decrease in cell efficiency.

### 3.3 Conclusions

In summary, we have shown that, at the critical defect density $N_{Cr}$ for which P3HT:PCBM solar cells undergo the most significant degradation, the Onsager capture radius of excitons equals the average distance between paramagnetic defects. This observation corroborates the inverse-exponential correlation between paramagnetic defect density and cell efficiency, which we find to hold irrespectively of the complex changes in morphologies undergone by the cells during our 70-70-70 test, and irrespectively from the fact that the total O content (as measured by RBS) does not significantly change during our experiments. Our results strongly support the hypothesis that oxygen degrades organic solar cells only when incorporated in the form of paramagnetic defects. This is consistent with recent findings by Sperlich et al[5] who found oxidation is responsible for the irreversible degradation of P3HT. These findings may have important applications for designing encapsulation systems for organic solar cells of improved performance.


Chapter 4

4 Nucleation of gold nanoparticles from Au$_{25}^-$ molecular precursors in a thermosetting polyimide

4.1 Introduction

Nanoplasmonics has been the driving force for recent studies[1, 2] into the fabrication and dispersion of metallic nanoparticles with controlled diameter distributions in thin film architectures. Plasmon resonance produces a local electric field enhancement for specific wavelengths of light in the proximity of optically resonant nanoparticles and greatly increases the photon scattering cross section. These two effects combined are known[1, 2] to improve harvesting of light in thin film solar cells.

For plasmonic applications, it is advantageous to disperse the metallic nanoparticles into polymeric thin films by facile solution processing methods. Plasmonic thin films can be fabricated either by ex situ synthesis of nanoparticles, and their subsequent dispersion inside the requisite polymer, or by in situ growth and nucleation in a given polymeric thin film.[3] While the first type of processes tends to result in random aggregation of nanoparticles, which is undesirable for plasmonic applications, in situ growth has shown a good degree of dispersion of gold nanoparticles (Au-NP).[3, 4] Au-NP are extremely promising for nanoplasmonics because they combine strong resistance to oxidation with the appropriate plasmon resonance frequencies for harvesting light in the visible range.[1, 5] However, the most common precursors for nucleation of Au-NP are primarily water soluble, which strongly restricts the classes of compatible polymers that can be used [6]. An alternative technique that has been recently proposed for in-situ nucleation of Au-NP is the thermal evaporation and subsequent annealing of multilayer films of gold and polymers [7], but also this method has limited practical applications due to the large amount of Au dissipated during the evaporation process and the need for high vacuum systems.

In addition to plasmonic applications structures of metallic nanoparticles embedded in a polymer matrix have been shown to be useful in the production of
resistive memory devices. Work by Ouyang et al.[8] has pioneered work in this field by dispersing Au-NPs in a polystyrene matrix with 8-hydroxyquinoline acceptors. The authors are able to induce a charge transfer between the Au-NP and the 8-hydroxyquinoline acceptors by applying an electric field. The result is a decrease in the resistance across the device that is persistent. The material that we present in this chapter represents a possible memory device with a durability that is inherently higher than a polystyrene film.

In this chapter, we demonstrate the homogeneous and heterogeneous nucleation of spherical Au-NP, with tunable size and narrow diameter distributions, in polyimide (PI), a very popular and widely used electronic grade polymer.[9] With this technique, previously unobserved spherical microclusters of gold (Au-μC) can also be obtained. Au-NP and Au-μC are demonstrated to spontaneously nucleate when a gold molecular cluster, TOA\(^{+}[(\text{Au}_{25} (\text{SC}_{2} \text{H}_{4} \text{Ph})_{18})]^{-}\), is dispersed in PI and rapidly cured at temperatures from 150°C to 450°C. In addition to temperature, the oxygen content in the curing atmosphere (from room conditions down to a few ppm) is demonstrated to be a strong factor of influence in determining the size of the resulting nanostructures.

### 4.2 Experimental procedure

TOA\(^{+}[(\text{Au}_{25} (\text{SC}_{2} \text{H}_{4} \text{Ph})_{18})]^{-}\) molecules (here referred as \text{Au}_{25}^{-} for the sake of simplicity), were synthesized, purified and characterized using the method developed by Murray et al.[10] and dispersed in commercial grade PI [Poly(3,3′,4,4′-benzophenonetetracarboxylic dianhydride-co-4,4′-oxydianiline 1,3-phenylenediamine, Sigma-Aldrich, cat. no. 431206]. The molecular structures of these materials are shown in Figure 4-1. 10 mg of crystallized \text{Au}_{25}^{-} was mixed with 600 mg of PI by ultrasonication in an ice bath for 1 hr. The resulting solution was spun at 8000 rpm and subsequently cured from 150°C to 450°C in an N\(_2\) atmosphere with 1000 ppm of O\(_2\) for 5 minutes. An additional sample was prepared in atmosphere and annealed at 200°C to determine if O\(_2\) has an effect on the nucleation process. A set of pure PI thin films (i.e. without \text{Au}_{25}^{-}) were also prepared and used as a reference.
Figure 4-1  a) Molecular structure of the polyimide used in this chapter. b) Molecular structure of TOA$^+$[(Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$)]. Purple balls are Au, Yellow is sulfur, and grey are the stabilizing ligands.

The films were characterized by several methods. UV-Visible transmission spectra were recorded at normal incidence on a Varian DMS80 spectrophotometer. Data were measured on each sample before and after curing to assess the changes induced by heating. UV-Vis measurements are essential as they can easily detect the formation of Au-NPs by the presence or absence of a plasmonic resonance peak.

Morphological characterization of our films was performed by two methods. Scanning near field optical micrographs (SNOM) were recorded on a WiTec Alpha300 system utilizing a 532 nm laser source (Spectra Physics, 50 mW), a diagram of which is shown in Figure 4-2. SNOM is a method to measure the optical properties of materials with nanoscale resolution. In a particular implementation of SNOM we are using an aperture type near field optical system that consists of an atomic force microscope (AFM) cantilever with an aperture drilled at the end of the tip and a microscope objective to focus the light through the aperture. The transmitted light is then collected in
transmission by an inverted microscope. This technique allows for optical resolutions of around 100nm with lateral topography resolution around 120 nm.

Scanning electron microscope (SEM) measurements were performed on the low oxygen samples using a LEO (Zeiss) 1530 field emission SEM operating with beam energy of 5 keV. These measurements provide complementary information to the morphology provided by the SNOM measurements. Specifically it can provide higher resolution images of the resulting Au nanoparticles and allow accurate particle size distributions to be calculated. In addition, Energy dispersive X-ray spectroscopy (EDX) was utilized for elemental characterization of the some of the samples. This was done to determine the purity of the resulting Au-NPs. The initial Au$_{25}^-$ molecules have a relatively high sulfur content. For device and plasmonic applications it would be advantageous to have sulfur free Au-NPs as they tend to have higher electrical conductivity.

4.3 Results and discussion

The UV-Vis measurements recorded before curing the samples, show three optical absorption peaks, at 680 nm, 450 nm and 420nm, respectively, which are a typical signature of interband molecular-like transitions in Au$_{25}$. [11] Such peaks indicate that Au$_{25}^-$ molecules are intact before curing and compatible with PI. Figure 4-3 also shows that such peaks are no longer detectable after curing, consistently with what was observed when heating similar Au$_{25}^-$ molecules dissolved in D$_2$O.[12]
Figure 4-2 Diagram showing our SNOM setup used to take measurements. An AFM cantilever with an aperture at the end of the probe tip is used to perform optical scans of the sample with resolutions better than 100 nm. Light transmitting through the sample is then collected by the use of an inverted microscope and a photomultiplier tube.

In contrast to what was observed in the liquid state,[12] other features emerge in our solid state transmission spectra of Au-containing films as shown in Figure 4-3. The most noticeable difference is the appearance of a strong peak in absorbance at 530 nm, which increases in magnitude at higher curing temperatures. Peaks of this nature are often associated with the presence of metallic nanoparticles as a result of plasmon resonance [13]. With this in mind, the change in position and width of such peak is in good qualitative agreement with the model of Haiss et al.[14]. They show that any increase in size of Au-NP results in a narrower plasmon resonance, accompanied by a red shift of the resonance peak. A similar behavior is observed by us as the curing temperature increases, which corroborates the fact that the optical properties of our films are enhanced by plasmonic effects in Au-NP. Curing under atmospheric conditions also results in a
plasmonic scattering peak, but at much lower annealing temperature. This demonstrates that the nucleation process is dependent on the presence of oxygen in the film.

SNOM and corresponding AFM topography images of our samples are shown in Figure 4-4. Comparison of AFM and SNOM images from the same location offers a qualitative indication of the in-depth position of the particles (on the surface or below the surface) because SNOM in transparent samples is bulk-sensitive while AFM is not.[15] AFM shows large (up to 2 μm) metallic microclusters emerging in the proximity of the surface of the samples, while smaller (<500 nm) nanoparticles are generally observable much deeper in the films, only by SNOM.

In addition of the x-y SNOM images shown in Figure 4-4a-d, we also performed SNOM scans along the x-z plane above the sample. These scans image the scattered waves and electric field enhancement at a distance z above the surface, by exploiting the ability of the piezo-scanner of the Witec microscope to control the distance between the cantilever and the sample surface, as sketched in Figure 4-4e. These data are demonstrated in Figure 4-4f and show an enhanced light scattering intensity close to the surface of the films, which is essential for their use as plasmonic enhancement layers.
Figure 4-3 UV-VIS spectrophotometer measurements on Au$_{25}$-PI films prepared at different annealing temperatures. Included is a single spectra obtained before annealing that shows the Au$_{25}$ core is still intact. The spectra have been shifted vertically for clarity. A strong plasmon resonance peak appears at $\lambda=530$ nm with increasing temperature. The strong absorbance in the ultraviolet region is due to the polymer.

Quantitative particle size analysis carried out on the SNOM images is displayed in Figure 4-5. It is apparent that the particle size distributions are bimodal, and two different populations of gold particles are present in all of our films: a population of bulk-related Au-NPs and a population of surface-related clusters of micrometric size. These findings can be easily explained by noticing that nucleation of metallic particles in the bulk of solid media is generally an homogeneous process,[15] while growth at the surface can be controlled by heterogeneous nucleation.[15] With this in mind, we can explain the formation of a population of larger particles in the proximity of the surface because the growth rate can be much larger in the case of heterogeneous nucleation.[15] Additional
information an be inferred on the width of the distribution of the particles. In the sample cured at 150 °C (Figure 4-5a), we find a very broad distribution of sizes while the distribution is significantly narrower for higher curing temperatures. This effect is in conjunction with a marked decrease in size. Both effects point to a higher nucleation rate.

[15] SNOM image of the film cured in atmosphere is shown in Figure 4-4d. We find much smaller cluster sizes of ≈250 nm in this film. This indicates that the presence of oxygen in the film influences the nucleation process, although at this point the exact mechanism remains unclear.

SEM images of our samples are displayed in Figure 4-6. They reveal that the Au-µCs observed in Figure 4-4 are composed of much smaller nanoparticles, with larger Au-NP and smaller Au-µCs forming with increasing annealing temperature. This effect is characteristic of Ostwald ripening in which larger particles grow in size at the expense of smaller particles by a process of diffusion.[16] In the 250°C and 450°C annealed samples, Figure 4-5d and e respectively, we observe a sea of Au-NPs of sizes ≈10-20 nm that are uniformly distributed throughout the film. Since the Au-µCs detected in such samples are too large to produce the observed plasmon resonance, we conclude that it is these widely dispersed nanoparticles that are responsible for the plasmon resonance peaks observed in Figure 4-3.

EDX measurements of our samples are displayed in Figure 4-7. The measurements for the samples cured in low-oxygen environment are displayed in Figure 4-7. Elemental maps, shown in Figure 4-7b and c, confirm that these particle clusters are composed primarily of gold with small amounts of sulphur. These elements are not present in PI and, therefore, we conclude that Au-µCs are composed primarily of remnants of Au$_{25}$. Figure 4-7d shows the summed EDX spectra for the 150 °C annealed sample. Several peaks are identifiable, including C and O from the polymer at 0.37 keV and 0.52 keV, respectively. Au and S peaks are clearly visible at 2.14 keV and 2.32 keV, respectively.
Figure 4-4 (a) AFM (left side of the image) and SNOM (right side of the image) of the same region of the sample annealed at 150 °C in low oxygen environment (1000 ppm). Similar data are reported for the corresponding samples cured at (b) 250 °C, and (c) 450 °C. (d) The corresponding sample annealed at 250 °C and 20% O$_2$ (atmospheric conditions) shows notably different morphology with only small ≈250 nm particles being observed. (e) Set up for x-z SNOM scans. The film is illuminated from below and evanescent light is collected at the tip that is lifted at a distance z from the surface. (f) SNOM x-z scan recorded above the 250 °C annealed sample.
Figure 4-5 (a) Particle size analysis for samples cured at 150 °C in low O₂ environment (1000 ppm in N₂ atmosphere) with histograms of bimodal distribution of particle sizes from SNOM measurements. Dotted lines are visual aids indicating particles near the surface (green) and nanoparticles localized in the bulk of the films (blue). The sample cured at 150 °C shows a very broad distribution that narrows dramatically upon increased annealing temperature, but the particle size distribution dramatically decrease for curing at (b) 250 °C, and (c) 450 °C. (d) In high O₂ environment (20% O₂, atmospheric conditions), particles with smaller diameter are observed likely as a result of higher nucleation rate during curing.
Examining the evolution of the elemental content, we find that the C and O content of the film to remain relatively constant with annealing temperature. S content, however, is observed to decrease. Specifically, the S/Au ratio decreases significantly from 0.48 to 0.02, as shown in Figure 4-7e. Considering that the sulfur to gold ratio is S/Au=0.72 in pure Au$_{25}^-$, it is clear that a large fraction of Au$_{25}^-$ has reacted and nucleated even at relatively low annealing temperatures. Since S atoms in Au$_{25}^-$ play a critical role in the stabilization of the molecule,[12] we conclude that their expulsion effects the removal of the stabilizing ligands surrounding the Au$_{25}^-$ molecules which then results in their subsequent nucleation into the larger Au-NPs as observed by SEM. Additionally, considering that the sulphur appears to vanish from the polymer film and that such S is known to oxidize readily[12] we suspect that the presence of oxygen can play a major role in the nucleation of these Au-NPs. This is corroborated by our SNOM measurements on our sample cured in air, as seen from Figure 4-4d.

Figure 4-6 Morphological characterization by SEM is displayed (Zeiss LEO 1530 FE microscope). The images show successive evolution stages of the particle clusters as demonstrated in Figure 4-4a-f. (a) At 150 °C annealing temperature, the clusters consist of a complex arrangement of gold nanoparticles of sizes ≈20 nm. (b) At 250 °C, the clusters start to coalesce into larger particles of sizes ≈100 nm. (c) At 450 °C large, 1 μm globules are formed. More uniform distribution of smaller gold nanoparticles is observed in the samples cured at (e) 250 °C and (f) 450 °C.
Figure 4-7 Elemental maps performed by EDX measurements are shown. Panel (a) shows an electron microscope image, (b) Au elemental map, and (c) S elemental map for the 150°C annealed sample. The white scale bar represents 1µm. (d) Cumulative EDX spectra for the entire image that shows the presence of Au, S, C, O, and trace metals. (e) Displayed is a plot is the ratio of S at. % to Au at. %. The decrease in S to Au ratio indicates the degradation of Au$_{25}^-$ particles and expulsion of S from the film.

Considering the rapid oxidation of sulfur-containing ligands above room temperature in the presence of oxygen[12] and the fact that Au-NP’s have a melting point that is strongly size dependant, [17] our observations seem to suggest a four-stage model for the decomposition of Au$_{25}^-$: (i) oxidization of S-containing ligands; (ii) nucleation of Au$_{25}^-$ molecules into Au-NP’s in the molten state; (iii) condensation of molten Au-NPs into large droplets, with the formation of Au-µC’s; and (iv) solidification of super-cooled
Au-μCs with the formation of globules. Basically, when the S-containing ligands that keep Au$_{25}^-$ monodispersed become oxidized, nearby Au$_{25}^-$ molecules start to nucleate into very small Au-NPs. Considering that each Au$_{25}^-$ core is less than 0.5 nm in diameter, nucleated AuNP’s are initially $\approx$1 nm in size, a diameter that, according to Dick et al., [18] indicates that these particles are in the molten state even at 150 °C, the lowest temperature at which we observe nucleation. The subsequent stage of condensation of liquid Au-NPs in larger droplets (stage (iii)) is controlled by a number of factors, including: the presence of residual S-containing ligands (that prevent the particles to aggregate completely and lead to spherical Au-μCs composed by a high number of Au-NPs) and the cross-linking of the PI matrix at increasing curing temperature, which implies that the diffusion of Au-NPs in the polymer is slower at higher temperatures and explains the smaller diameters observed at higher temperatures. Eventually, at the highest temperatures (stage (iv), 400 °C-450 °C), Au-μCs are almost completely depleted in S-containing ligands and coalesce into larger globules up to 1 μm in size. At this size, melting temperature is above 1000 μC and globules tend to solidify and contract, even before the end of the curing process, leaving behind a gold depleted region that is clearly visible in Figure 4-5c,e. Therefore, due to the peculiarity of phase transitions in nanostructures, our Au-NP’s show an unique behavior for which they transition from liquid into solid as the temperature increases.

4.4 Conclusions

In summary, we demonstrated in situ nucleation of Au-NPs and Au-μCs in thermosetting polyimide thin films using Au$_{25}^-$ molecules as precursors. PI thin films incorporating Au-NPs show a strong plasmon resonance peak at 530 nm, indicating that these films could be useful as a chemically and thermally stable plasmonic enhancement layer. Oxygen was found to play an important role in the nucleation process by the oxidation of the Au$_{25}^-$ stabilizing ligands. This allows the density of resulting Au-μCs to be tuned by controlling the oxygen in the environment during the curing process. Our method opens up a broad range of possible nucleation schemes since Au$_{25}^-$ molecules can be synthesized with a variety of different ligands. This will allow them to be incorporated into any number of different polymers by the appropriate choice of the ligand.


Chapter 5

5 Tessellated gold nanostructures from \( \text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60} \) molecular precursors and their use in plasmonic organic solar cell enhancement

5.1 Introduction

Metallic nanoparticles (MNPs) have been utilized successfully to improve the performance of thin film solar cells.[1-4] Incorporation of MNPs into different components of photovoltaic devices can improve their light collection efficiency as well as their overall performance. In MNPs charge carriers collectively interact with incident photons at specific wavelengths corresponding to the plasmon resonance of the particles, [4] which results in a strong interaction with light at specific frequencies. This interaction is highly dependent on the size and shape of the specific system of nanoparticles being considered. [4, 5] The resulting enhancement of the local electric field in the proximity of the nanoparticles may lead to a higher absorption of incident light in a solar cell active layer located in the vicinity of MNPs. In addition, the increased optical cross section offered by MNPs of specific sizes may lead to an increased amount of light that can be scattered and trapped into the solar cell active layer. [6-8] Additional enhancements in solar cell performance are possible when MNPs are deposited directly onto the transparent conducting oxide thin film electrode of a solar cell. Transparent electrodes decorated with MNPs have resulted in an improved sheet conductivity[9] and, thereby, improved solar cell photoconversion efficiency. [4, 10]

Several methods to incorporate metallic nanoparticles in thin film solar cells have been developed to date, which loosely fit in two categories. A first category, “top down” fabrication methods, relies on costly and time-consuming fabrication techniques, including optical and electron-beam lithography to pattern nanoscale metallic enhancement layers. [4] These methods provide the best control of the nanoparticle size and spacing. They lead to relatively high performance enhancements. Conversely, a second category of techniques, “bottom up” methods, involves random growth of MNPs onto the requisite substrate by solution processing, [3, 11] thermal evaporation of metallic
thin films followed by thermal annealing, or other similar methods. [5] These approaches are more cost effective than “top down” methods, but distributions of particle shape, size, and spacing need to be carefully optimized in order to produce beneficial effects on the solar cell performance. Solution-processing techniques are promising methods for the incorporation of metallic nanoparticles into organic photovoltaics,[12] but their effectiveness is still a matter of debate due to the difficulty in obtaining narrow distributions in particle size and a controlled patterning of MNPs.

In this chapter, a novel, simple, and cost-effective solution-processing method to form systems of interconnected gold nanoparticles for plasmonic enhancement applications via Voronoi tessellation is presented. Tessellation is demonstrated at relatively low temperatures directly on indium tin oxide (ITO) thin films. \(\text{Au}_{144}(\text{SCH}_2\text{CH}_2\text{Ph})_{60}\), henceforth referred to simply as \(\text{Au}_{144}\), is here utilized as the molecular gold precursor by first dissolving it in chlorobenzene and by subsequently spin-coating the resulting \(\text{Au}_{144}\) solution onto ITO-coated glass substrates. The sample is then annealed leading to the nucleation of \(\text{Au}_{144}\) molecules into tessellated systems of Au nanoparticles. These nanoparticles are of 5–40 nm in diameter, similar to what we previously observed for the nucleation of \(\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}\) molecular precursors in polyimide. [13] In addition, we are here presenting a method to control both the size and distribution of the resulting nanoparticles by independently changing two parameters: the annealing time and \(\text{Au}_{144}\) concentration in the starting solution. Voronoi tessellation patterns of polystyrene nanoparticles on silicon are known to be attainable by exploiting spin-coating dynamics under specific conditions. [14] Here we demonstrate that the same method can be used to control the nanoscale morphology of systems of MNPs and, specifically, gold nanoparticles, in ways that are not possible with conventional solution processing methods. Work by Yoon et al. [15] focused on depositing MNPs directly from solution. Although their method is relatively simple, it has far less control than ours over the specific MNP morphology. A significant benefit of using \(\text{Au}_{144}\) as a precursor for MNPs is in the large number of organic solvents that can be used for deposition. Consequently, a large variety of morphologies can be fabricated depending on the specific spin-coating dynamics involved. Specifically, using \(\text{Au}_{144}\) and chlorobenzene as
a solvent we have been able to obtain for the first time Voronoi tessellation patterns from gold.

As a proof of concept we demonstrate that our patterned gold layers can provide an improved device power conversion efficiency when they are incorporated into the hole-transport layer of a poly(3-hexyl-thiophene-2,5-diyl):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) bulk heterojunction solar cell. We also demonstrate that under certain conditions they are superior to uniformly distributed gold nanoparticles (AuNPs). Consequently, our work indicates for the first time an avenue towards transferring molecular gold nanoclusters from the realm of fundamental chemistry and physics into practical applications in nanoplasmonics.

5.2 Experimental

Au$_{144}$ molecules were synthesized by a modified Brust–Schiffrin method as reported elsewhere. [16] With this method, HAuCl$_4$·3H$_2$O was dissolved in 50 mL water. Subsequently, 100 mL toluene containing 4.68 mmol of tetra-n-octylammonium bromide (TOABr) was added to the solution. The resulting salt was transferred to the organic phase, which was then separated and cooled to 0 °C. Phenylethanethiol (19.4 mmol) was then added to the product and then the mixture was stirred for 3 hours until its color turned to an opaque white. At that point, 50 mmol (1.89 g) of sodium borohydride, dissolved in 30 mL of ice-cold water was added under vigorous stirring for 24 h. The resulting mixture was then repeatedly purified by solvent extraction using methanol and the purity of the product was checked using UV-visible spectrophotometry, proton nuclear magnetic resonance spectroscopy, as well as electrochemistry methods. [16] [17]

A set of AuNP decorated ITO thin films were prepared using the following methods. ITO-coated glass substrates (Aldrich cat no. 636916, 15–25 Ω/□ sheet resistance) were pre-cleaned in a bath sonicator using sequential detergent, acetone and methanol baths. Solutions of Au$_{144}$ in chlorobenzene (PhCl) were subsequently spin-coated at 8000 rpm onto the ITO substrates. A set of samples was spin-coated by varying the concentration of Au$_{144}$ in PhCl from 0.63 mg mL$^{-1}$ to 5.00 mg mL$^{-1}$. This was done to study the effect concentration has on the resulting AuNP diameter and film
morphology. These ITO thin films, with an Au$_{144}$ layer spun on it, were all annealed for 9 min at 400 °C in air on a hot plate in order to nucleate the AuNPs. A second set of samples was prepared to study the effects of annealing time on the nucleation of AuNPs. This set of films was fabricated by annealing Au$_{144}$ in air at times ranging from 9 min to 132 min at 400 °C while the concentration of the Au$_{144}$ spin-coating solution in PhCl (5 mg mL$^{-1}$) was kept constant. All other spin-coating conditions were kept the same. A LEO (Zeiss) 1540XB scanning electron microscope (SEM) operating at 10 keV was used to record electron microscope images of the samples. Energy-dispersive X-ray (EDX) spectra were recorded with the same SEM instrument in order to verify that the nanoparticles were actually pure gold.

Two sets of solar cells utilizing a P3HT:PCBM bulk heterojunction architecture were prepared in order to demonstrate that our AuNP decorated ITO thin films can lead to an enhancement in solar cell photoconversion efficiency. Thermal annealing of ITO at 400 °C and more is well known to induce structural, optical, and electrical changes in indium-tin oxides.[18][19] Consequently, the reference cell was treated by annealing the ITO layer to match the structural and optical changes undergone while forming the AuNP layer. The first cell architecture (henceforth called Tess-AuNP) featured an Au$_{144}$ layer produced by spin-coating a 5.0 mg mL$^{-1}$ solution of Au$_{144}$ in PhCl directly onto ITO and then annealing in atmosphere at 400 °C for 132 min. A second type of cells (labeled as AuNP) were constructed by using a much thicker and continuous AuNP layer deposited by spin-coating at 1000 rpm from toluene at 10 mg mL$^{-1}$ concentration and then annealing at 400 °C for 10 min.

Each of the solar cells was prepared using the fabrication procedure described in detail in ref. [20] and in Chapter 1 of this thesis. Briefly, an electron-blocking, hole-transport layer consisting of a 30 nm Poly(3,4-Ethylene Di-Oxy-Thiophene):Poly-Styrene sulfonate thin film (PEDOT:PSS, Aldrich cat. no. 483095) was spun at 3000 rpm from aqueous solution. The ITO films, with the PEDOT:PSS layer on the top of them, were introduced in a Nexus II dual glove box (Vacuum Atmospheres Co.) dedicated to organic solar cell fabrication and loaded with high-purity nitrogen, with oxygen and moisture levels less than 5 ppm. In this glove box, the ITO films coated with PEDOT:PSS were
baked on a hot plate at 140 °C for 30 min. The subsequent solar cell fabrication steps also occurred in the same glove box. The photovoltaic active layers were assembled by spinning on the top of PEDOT:PSS a 15:15 mg P3HT:PCBM solution in PhCl (Aldrich, cat no. 698989 and 684430, respectively). A spin-coating speed of 650 rpm, resulting in an active layer thickness of 220 nm, was used. The resulting solar cells were then annealed at 120 °C for 15 min in the glove box and transferred, without direct exposure to air, into a contiguous high vacuum chamber with thermal evaporation facilities. The chamber was pumped down to $10^{-7}$ torr base vacuum. Ca/Al bilayer backing electrodes (20 nm Ca thickness and 80 nm Al thickness, measured by a Sycom STM-2 thickness monitor) were evaporated on each solar cell using a patterned shadow mask. [21] Each solar cell had the resulting device area of 0.245 cm$^2$. The resulting solar cell architectures are presented in Figure 5-5. Solar cell photoconversion efficiencies were determined from I–V curves measured directly in the glove box, using a Newport 9600 1.5 AM solar simulator at 1 sun. The solar simulator was calibrated using a Sciencetech SC-LT standard cell with certification accredited by the National Institute of Standards and Technology (ISO-17025). External quantum efficiency (EQE) measurements were performed outside the glove box using a custom built apparatus[22] consisting of a 1000 W halogen lamp, a monochromator, and a calibrated photodiode.

5.3 Results and discussion

SEM characterization of samples spun from solutions of Au$_{144}$ at variable concentrations are shown in Figure 5-1a-d. We observe that both the size and distribution of the nanoparticles can be readily tuned by altering the concentration of Au$_{144}$ in chlorobenzene. Varying the concentration, from 0.625 mg mL$^{-1}$ to 5.00 mg mL$^{-1}$, gold nanoparticles with mean sizes between 5 nm and 30 nm were obtained in different samples. Resulting particle size distributions obtained at different concentrations of Au$_{144}$ in PhCl are shown in Figure 5-1e. Notably, samples prepared from PhCl solutions at higher concentrations of Au$_{144}$ also exhibit more remarkable aggregation of the resulting gold nanoparticles.

Figure 5-1a-d show that the networks of AuNPs on ITO obtained on these samples form web-like patterns that bear a good morphological resemblance to the
structures described by Stange et al. [14] They found that under specific spin-coating conditions they can deposit interconnected networks of polystyrene. Stange et al. show that such structures are a general result from rupturing of the solvent layer and the subsequent expansion of voids. This leads the polystyrene to form a connected network of polygons known as a Voronoi tessellation (compare Figure 5-1a with Fig. 1d in ref. [14]). Due to the strong similarity between our AuNP films and the polystyrene films of Stange et al. and the similarity between the deposition methods we assert that the same physical processes underlie both of films. More recent work has been done to study these types of films in more detail.[23, 24] The authors find that the interface between the solvent and the substrate strongly influences the resulting film morphologies and that the pattern formation process is driven by de-wetting and evaporation of the solvent. With this in mind we can understand how the different morphologies in Figure 5-1 arise. We have outlined the process undergone during the deposition of these films in Figure 5-2. Initially small voids form in the film due to spontaneous de-wetting, Figure 5-2a. These voids then expand as shown in Figure 5-2b until the voids collide as in Figure 5-2c. During this entire process the concentration of Au_{144} in solution will be continuously rising due to the rapid evaporation of the solvent during spin-coating. Eventually the concentration of the Au_{144} reaches the saturation concentration of the solvent and will start precipitate out of the solution. The key to understanding how the different morphologies in Figure 5-1 arise is to consider that the concentrations of the initial starting solutions is quite different. Therefore for different starting concentrations the saturation concentration will be reached at different times during the spin-coating process. The morphology in Figure 5-1a will result if the solvent reaches saturation concentration during the stage shown in Figure 5-2c as Au_{144} will start to precipitate while the “arms” shown in Figure 5-2c are still present. Continued de-wetting and solvent evaporation transforms the solvent into isolated droplets that result in the films seen in Figure 5-1b and c. The main difference between these films is that the droplets are allowed to reach smaller size before Au_{144} starts to precipitate. This then results in the smaller globules of AuNPs that are observed and even the isolated nanoparticles that are observed in Figure 5-1d.
In order to understand the processes occurring during the nucleation of the AuNPs, the Au$_{144}$ films were examined by SEM before and after thermal annealing at 400 °C. Figure 5-3a shows the films spun from 5 mg L$^{-1}$ solution of Au$_{144}$ in its pre-annealed state. The Au$_{144}$ film (Figure 5-3a) deposits in much the same way as the resulting nanoparticles obtained after annealing (Figure 5-3b). This indicates that the micron scale morphology is due to spin-coating dynamic effects, as discussed above. It is therefore apparent that annealing times as short as 9 min are sufficient to induce a complete transformation from an assembly of Au$_{144}$ molecules on ITO to a corresponding assembly of AuNPs. Longer annealing times permit an increase in the size of the nanoparticles by allowing more time for surface diffusion of Au atoms. This may be explained in terms of a statistical Ostwald ripening process,[25] for which larger particles grow at the expense of the smaller, because they are more thermodynamically stable due to lower surface energies. Small AuNPs will tend to coalesce into larger NPs given a sufficiently long annealing time. This process is observed in Figure 5-3c where we have highlighted a pair of small nanoparticles combining into a larger nanoparticle.

Compositional analysis of AuNP decorated ITO films was performed using EDX in order to estimate the purity of the AuNPs. Au$_{144}$ molecular nanoclusters consist of 60 sulphur atoms per 144 Au atoms.[26] This gives an S/Au atomic ratio of 0.41. EDX measurements on our films show that S/Au = 0.36 ± 0.01 indicating a slight sulphur deficiency in our films. This indicates that not every Au$_{144}$ cluster is completely covered in thiol groups. After annealing EDX spectra of our samples show faint sulphur related peaks, with a nearly undetectable S content in most samples, as demonstrated in Figure 5-4. The reduction in sulphur content upon annealing can be explained by noting that the sulphur to gold bond is not stable at temperatures higher than 160 °C in an oxidizing environment. [27] Hence we expect that at temperatures of 400 °C in air the S bond and ligand will burn resulting in products of H$_2$O, SO$_2$, and CO$_2$. As we have shown[ref] this reaction can also take place in an oxygen free environment. In this case we expect the oxidation of Au$^{1+}$ to result in the formation of disulphide's.
Figure 5-1 Inset images have a scale bar of 200 nm and large images have a 1 μm scale bar. SEM images of AuNP films nucleated from various concentrations of Au$_{144}$ in solution. (a) 5 mg mL$^{-1}$ (b) 2.5 mg mL$^{-1}$ (c) 1.25 mg mL$^{-1}$ and (d) 0.625 mg mL$^{-1}$. All samples were annealed at 400 °C for 9 min. (e) Particle size analysis on different samples. Higher concentration yield to Tess-AuNP structures, as in panel a, while lower concentrations yield small clusters of nanoparticles. Very low concentrations appear to give an even distribution.
Figure 5-2 Diagram to show the process by which these films are deposited. (a) Initial nucleation stage. Voids are created in the solvent film due to de-wetting. (b) Voids continue to expand. (c) Voids collide and can no longer expand. (d) De-wetting continues and results in droplets. The remaining solvent is highly concentrated.

Figure 5-3 SEM images of AuNP films spin-coated at concentration of 5 mg mL$^{-1}$ and then annealed at 400 °C for times up to 132 min. (a) Pre-annealed state (b) 9 min. annealing (c) 72 min annealing, (d) 132 min annealing. Highlighted is a cluster
of NPs coalescing into a larger particle. Longer annealing times lead to Tess-AuNPs.

(e) Particle size distributions were measured from the SEM images.

![Graph showing the ratio of sulfur-to-gold atomic percent ratio as measured by EDX. Initially there is a high S content. Annealing, even at short times removes most of the S from the NPs with the quantity being barely detectable under longer annealing times. Blue line is a stretched exponential fit of the data.]

Figure 5-4 Ratio of sulfur-to-gold atomic percent ratio as measured by EDX. Initially there is a high S content. Annealing, even at short times removes most of the S from the NPs with the quantity being barely detectable under longer annealing times. Blue line is a stretched exponential fit of the data.

Different sets of bulk heterojunction organic solar cells were fabricated to determine if these AuNP films can be used as an plasmonic enhancement layer. Figure 5-5 a and b show the solar cell architecture and the SEM images of the gold–PEDOT:PSS nanocomposite hole-transport layers utilized in the two solar cells incorporating gold nanostructures assembled from Au$_{144}$. The first solar cell (panel a) utilizes a network of Tess-AuNPs at 5 mg mL$^{-1}$ concentration in PhCl annealed for 132 min at 400 °C. The second solar cell (panel b) utilizes uniform layers of AuNPs fabricated by spin-coating 10 mg mL$^{-1}$ of Au$_{144}$ in toluene and annealing for 10 min at 400 °C.
Figure 5-5 Diagram showing the solar cell architectures used in this work (a) using Tess-AuNPs in PEDOT:PSS fabricated by spin-coating 5 mg mL$^{-1}$ of Au$_{144}$ in ClPh and annealing for 132 min. (b) Individual AuNPs in PEDOT:PSS fabricated by spin-coating 10 mg mL$^{-1}$ of Au$_{144}$ in toluene and annealing for 10 min. Scale bars in the SEM images on the right are 200 nm.

Current–voltage curves of the solar cells under AM 1.5 illumination are displayed in Figure 5-6 with additional information shown in table Table 5-1. The Tess-AuNP cell yields $J_{sc} = 6.98 \pm 0.07$ in comparison the reference cell has $J_{sc} = 6.82 \pm 0.07$ for an overall increase in $J_{sc}$ of 2.3%. In contrast in the AuNP/PEDOT cell there is a reduction in $I_{sc}$ of 51%. There are two competing factors that must be considered to understand the differences in these cells. First, that the local surface plasmonic resonance (LSPR) is concentrated strongly around the particle. The extension of the field enhancement is typically only a few nanometers.[28] Therefore the nanoparticle needs to be in close contact with the active layer to produce an enhanced absorption effect. When the AuNPs are placed below the PEDOT:PSS layer the LSPR field can decay significantly before reaching the active layer. It is therefore important to optimize the thickness of the PEDOT:PSS layer to achieve the best field enhancement. In our solar cells PEDOT:PSS
films of approximately 30 nm were utilized. In this cell the AuNPs used are 10 nm in
diameter as seen in Figure 5-5b. Therefore the LSPR has likely decayed before reaching
the active layer and we expect the AuNP cell will yield a small or negligible LSPR
enhancement. Indeed Yoon et al.[15] have constructed similar devices using 5 nm silver
nanoparticles. They report an negligible change in $J_{sc}$ when a MNP layer is deposited
below the PEDOT:PSS layer. When the same MNPs are deposited on top of the active
layer they then report an increase in $J_{sc}$. This effect can also cause an increased optical
absorption in the PEDOT:PSS layer which can further reduce the amount of available
light collected in the active layer. The second factor involved is exciton quenching at the
donor/acceptor interface. Work by Fung et al. [28] has shown that large concentrations of
AuNPs have a detrimental effect on $J_{sc}$ by way of exciton quenching. The interface
between PEDOT:PSS and P3HT:PCBM gets increasingly rough and then results in a
reduced $J_{sc}$ by way of exciton quenching at the donor/acceptor interface.

In contrast, our Tess-AuNP cell shows an improvement in $J_{sc}$. In Figure 5-3d and
e, we can observe that the Tess-AuNP films include larger nanoparticles, between 20–50
nm in size, in addition to ensembles of smaller nanoparticles of $\sim$10 nm diameter.
Smaller nanoparticles may have a detrimental effect on the overall device efficiency. As
discussed by Fung et al.[28] a high density of small nanoparticles incorporated into the
PEDOT:PSS layer can result in a decrease in $J_{sc}$. However, in our Tess-AuNP solar cell,
small AuNPs are present at an overall density that is much lower than in the solar cell
with uniformly distributed AuNPs.
Figure 5-6 I–V curves of the prepared solar cells. (a) I–V curves under illumination. (b) I–V curve of Tess-AuNP cell measured in the dark.
Table 5-1 Series resistance ($R_{\text{series}}$), open circuit voltage ($V_{\text{oc}}$), short circuit current density ($J_{\text{sc}}$), fill factor and AM 1.5 photoconversion efficiencies ($\eta$) for the optimized solar cells studied in the present work compared to a reference cell with a PEDOT:PSS layer not containing gold nanoparticles

<table>
<thead>
<tr>
<th></th>
<th>$R_{\text{series}}$ (Ω)</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>$J_{\text{sc}}$ (mA cm$^{-2}$)</th>
<th>Fill factor (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tess-AuNP and PEDOT:PSS</td>
<td>78 ± 0.5</td>
<td>0.60 ± 0.01</td>
<td>6.98 ± 0.07</td>
<td>56.9 ± 1.2</td>
<td>2.36 ± 0.08</td>
</tr>
<tr>
<td>AuNP and PEDOT:PSS</td>
<td>174 ± 1</td>
<td>0.53 ± 0.01</td>
<td>3.5 ± 0.04</td>
<td>47.2 ± 0.9</td>
<td>0.88 ± 0.04</td>
</tr>
<tr>
<td>Reference</td>
<td>91 ± 0.5</td>
<td>0.59 ± 0.01</td>
<td>6.82 ± 0.07</td>
<td>53.7 ± 1.0</td>
<td>2.14 ± 0.07</td>
</tr>
</tbody>
</table>

Figure 5-6b shows the dark I–V curves of the Tess-AuNP cell. The cell with the Au enhancement layer shows a slightly lower series resistance ($R_s = 78 \pm 0.5$ Ω) in comparison to the corresponding control cell ($R_s = 91 \pm 0.5$ Ω) calculated by taking the slope of the dark I–V curve at 0.8 V bias voltage. Since the equivalent circuit of a solar cell consists of a current source in parallel with a diode and a shunt resistor we can estimate the series resistance of the cell from the slope of the I–V curve taken above the diode turn on voltage. The improved series resistance indicates that the tessellated AuNP layer is improving the electrical characteristics of the ITO contact in addition to the optical effects. Random distributions of AuNPs can also have this effect, but the interconnected nature of these nanoparticle networks provide percolating conductive pathways that yield a significant improvement in sheet conductivity. This decrease in series resistance then leads to an improvement in fill factor, increasing from 53.7 ± 1.0% to 56.9 ± 1.2%. Combined with the improved $J_{\text{sc}}$ we find a total improvement of solar cell efficiency from 2.14 ± 0.07% to 2.36 ± 0.08 for an increase of 10.2%.

EQE measurements were performed on the solar cells that showed a net improvement in cell efficiency. These are shown in Figure 5-7. The enhanced solar cell shows a small increase in the measured EQE across almost the entire spectrum, with the largest improvement showing around ~620 nm. The plasmonic resonance peak of the AuNP films typically rests at around ~530 nm so an enhancement indicates that the
Plasmonic resonance peak has possibly shifted due to a change in dielectric environment as the AuNPs are imbedded in PEDOT:PSS.[29] Additionally there is a redshift in the EQE data that shows a more efficient collection of light at higher wavelengths further suggesting a plasmonic enhancement.

Figure 5-7 Normalized EQE showing an increase due to an enhanced light trapping in the solar cell utilizing a Tess-AuNPs:PEDOT:PSS nanocomposite hole-transport layer. A redshift of the EQE spectrum is also noticeable for this device.

In conclusion, a simple way to fabricate an interconnected AuNP network by utilizing the solvent deposition dynamics of a Au$_{144}$(SCH$_2$CH$_2$Ph)$_{60}$ clusters dissolved in chlorobenzene is demonstrated. The fact that Au$_{144}$ clusters are soluble in many halogenated and aromatic organic solvents, such as chlorobenzene and toluene, gives them a wide range of possible uses as a AuNP precursor in comparison to precursors that can only dissolve in aqueous solution such as HAuCl$_4$·3H$_2$O. The utility of these films as a plasmonic enhancement layer in organic solar cells was also demonstrated as they yield a 10% improvement in cell efficiency when incorporated into the PEDOT:PSS layer.
Future work will focus on better understanding how all the different morphologies presented in this chapter influence thin film organic solar cells.


Chapter 6

6 Conclusions and future work

My work on organic solar cells is wide and ranges from examining the properties of graphene electrodes, to active layer degradation via oxygen and moisture incorporation, and ending with the use of Au clusters for the fabrication of metallic nanoparticles.

I have examined various solution processing methods suitable for preparing thin film graphene electrodes for the purposes of using them in organic solar cells. Specifically I have modeled a simple relationship between thin film transparency and sheet resistance. This is done by first utilizing percolation theory to determine a relationship between sheet resistance, $S$, and fractional area coverage. We then determine an approximate relationship between fractional area coverage and average graphene layer thickness, which is then ultimately related to the film transmittance. In this way we determine the following relationship,

$$ S = S_0 \cdot [(M/A) \cdot \ln(1/T) - f_0]^x \approx S_0 \cdot [(50/A) \cdot \ln(1/T) - 0.3]^x $$  \hspace{1cm} (6.1)

where, $S_0$ is the sheet resistance of individual flakes, and $A$ is a unit less measure of the flake quality. I used this relationship to fit to several sets of data obtained in the literature. Good analytical fits were obtained in all cases which demonstrates the utility of this relation. This relation is specifically useful for evaluating the performance of different graphene exfoliation and thin film deposition methods in a way that allows an easy comparison between methods. Future work related to this should involve taking into account the contact resistance between sheets.

My work on solar cell degradation tested to see how the morphology, elemental content, and power conversion efficiency changed during controlled accelerated degradation. We were able to determine that during the "70-70-70" test, where a solar cell is exposed to 70°C and 70% humidity for up to 70 hours, significant separation of the P3HT and PCBM phases is observed in conjunction with a dramatically increased surface

...
roughness. This is confirmed by both RBS measurements and AFM measurements. The elemental content was determined by RBS measurements. Specifically, the oxygen content of the active layer was determined to stay relatively constant during the entire experiment. Meaning that if oxygen does play a strong role in the degradation of solar cells the actual quantity of oxygen that participates in active layer degradation is relatively small in comparison to the total amount of oxygen in the film. EPR measurements are then used to determine the fraction of oxygen that create paramagnetic centers. In addition, we found that the spin density of the active layer tends to increase with exposure and that the resulting power conversion efficiency has an exponential relationship with active layer spin density. That is,

\[ \eta = \eta_0 \exp \left( - \frac{N_D}{N_{CD}} \right) \]  

(6.2)

with \( \eta \) the power conversion efficiency, \( \eta_0 \) is a constant of proportionality, \( N_{CD} \) is a critical spin density, and \( N_D \) is the spin density of the active layer. The continuation of this work would be to determine the relationship between \( \eta \) and \( N \) in different bulk heterojunction systems and to ultimately determine if a general relationship exists. Similar relationships exist in other photovoltaic systems. Specifically, amorphous silicon has a general relationship between spin-density, efficiency, and other fundamental device parameters, as seen in chapter 3 Eqn. (3.5) and in reference [1]. It is possible that the constant of proportionality \( \eta_0 \) is a function of fundamental device parameters and this possibility should be investigated.

Our work on Au molecular nanocluster nucleation, presented in chapter 4, shows that it is possible to form Au nanoparticles directly inside of a polymer from molecular gold precursors. This was attained by mixing Au molecular clusters with the polymer and then curing at moderate temperatures. We determined that Au nanoparticles can easily be created by this method by annealing with temperatures as low as 150 °C. The Au nanoparticles were observed to cluster into spheres ranging in sizes from 500 nm to a few microns across. It was determined that this is a result of non-heterogeneous nucleation due to the thin film nature of the film. The specific mechanisms for the generation of Au nanoparticles were determined by examining the elemental content of the films. It was
found that during the annealing process the sulfur content of the film is greatly reduced. This shows that the removal of the stabilizing ligands of the Au molecular clusters leads to the nucleation of the resulting Au. Indeed when these samples are annealed in atmosphere a much different nucleation process is observed. Specifically, a larger quantity of Au nanoparticles is found with a very strong plasmonic response in comparison to samples annealed in N₂. This process allows Au nanoparticles to be deposited inside of a polyimide matrix when previously methods to achieve such a structure relied on either layer by layer methods[2] or by utilization of a high energy Au⁺ beam to implant Au into the polymer[3].

This work was originally intended for use making resistive memory devices such as those described by Tseng et al [4]. By suspending Au nanoparticles in a polymer it is possible to create a memory device that changes its resistive properties when an electric field is applied across it. This should be pursued as these Au nanoparticle and polymer systems are remarkably durable and could show performance enhancements beyond current technologies. Specifically, work should be done to prevent the characteristic aggregation of Au nanoparticles that is seen in these films. The knowledge gained from this study is then utilized in chapter 5 where we develop the method further.

I show that a similar process can be used to create thin films of Au nanoparticles which have practical applications in the enhancement of organic solar cell electrodes. An Au molecular nanocluster was dissolved in a solvent which is then spin-coated on top of an ITO substrate. The substrates are then heated to create the Au nanoparticles much in the same way they were formed in chapter 4. We found that by exploiting the spin-coating dynamics we could create Au nanoparticles in unique patterns of Voronoi tessellation patterns. Uniform layers of nanoparticles can also be created in this way by simple changing the solvent used in processing to toluene instead of chlorobenzene. Similar to the work done in chapter 4 we find that sulfur content of the films tends to decrease with increased annealing time. Longer annealing time results in Au nanoparticles that are free from sulfur and so they should give better performance when used in a plasmonic application.
Indeed, we find that these films do produce a small improvement in power conversion efficiency when incorporated into an organic solar cell. By analyzing the current-voltage measurements in conjunction with EQE measurements, it was determined that this enhancement is due to a combination of plasmonic light harvesting and an improvement in sheet conductivity of the ITO electrode.

In summary, I have investigated a new way to model the sheet conductivity and transmittance of graphene films so they can be optimized for use in organic photovoltaics, done work on oxygen related paramagnetic centers in organic solar cells, and have done significant work on the nucleation of Au nanoparticles by the use of Au molecular clusters. These Au nanoparticles where then used to enhance the performance of thin film organic solar cells.


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**Scholarships**