Next Generation Solar Cells using Flexible Transparent Electrodes Based on Silver Nanowires and Graphene

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Abstract

Organic photovoltaic (OPV) devices have been developed extensively and optimised due to the use of nanomaterials in their construction. More recently, the demand for such devices to be flexible and mechanically robust has been a major area of research.

Presently, Indium Tin Oxide (ITO) is the material that is used almost exclusively for transparent electrode. However, it has several drawbacks such as brittleness, high refractive index and high processing temperature. Furthermore, the price of ITO has been highly volatile due to scarcity of indium resources and the increased consumption of the material. Therefore, cheap, flexible and solution-processed transparent conductors are required for emerging optoelectronic devices with flexible construction which can be promising for wearable or environmentally adaptable devices purposes such as flexible solar cells and displays.

Therefore, over the past decade an alternative material has been sought intensively, particularly in the need for producing large area flexible transparent electrodes. Many materials have been investigated but most investigations have focused on carbon nanotube (CNT), graphene flakes and metallic nanowires. Silver nanowires (Ag NWs) networks have been proven to show a high electrical conductivity with high optical transmittance. This special characteristic is desirable in transparent conductive electrodes in optoelectronic applications such as solar cells, light emitting diodes, and touch screen.

On the other hand, Polymeric substrates that act as a non-brittle scaffold as well as protective packaging of the OPV are an essential element for such an “All-plastic” device. However, for such applications where the coating should be relatively hard a bottleneck to fabricating large area homogeneous films is associated with the formation of cracks as a result of local mismatches in mechanical properties during film formation.

In this work, the fabrication and characterization of flexible transparent electrodes of Ag NWs on flexible substrates by spray deposition technique have been described. Furthermore, a way to enhance the electrical and mechanical properties of the Ag NWs transparent electrodes by incorporating a low density ensemble of graphene on top of the metal electrode networks using the Langmuir-Schafer has been achieved. Interestingly, the electrical conductivity in these hybrid electrodes is stable over relatively large strains.
during mechanical agitation indicating that such electrodes may have important application in future applications.

Finally, producing crack-free monolayer latex over large area has been fabricated and characterised. Therefore, the polymer latex thin film has promising applications as purposes of hard coatings.
Declaration

This thesis and the work to which it refers are the results of my own efforts. Any ideas, data images or text resulting from the work of others (weather published or unpublished) are completely recognized accordingly as such inside the work and ascribed to their originator in the text, bibliography or in footnotes. This thesis has not been submitted in entire or to some degree for whatever other scholastic degree or professional qualification. I agree that the university has the right to submit my work to plagiarism detection service Turnitin UK for originality checks. Whether or not drafts have been so-assessed, the university reserves the right to acquire an electronic version of the final document (as submitted) for evaluation as above.

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Sultan Alomairy
Acknowledgments

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Chapter 1 Introduction

Conversion of sunlight into electrical power via photovoltaic cells is considered to be a clean and renewable energy source, with the possibility of meeting a large percentage of future global energy needs. OPV has appeared as an emulator for inorganic materials based on photovoltaic cells, due to its potential of low cost, large scale production, its transparency or semitransparency, mechanical flexibility and light weight [1, 2]. Photovoltaic cells are constructed by sandwiching a very thin film of active organic material between two electrodes, one of which must be transparent to allow light to pass through. Photovoltaic cells have been designed in various ways and using different structures, which can contain single-layer, bilayer heterojunction or bulk heterojunction configurations [3].

The active layer includes an electron donor and an electron acceptor, producing a bulk heterojunction [4, 5] as shown in Figure 1-1. The morphological structure of the bulk heterojunction film is based on the operation principle. Firstly, the incident light will be absorbed in the active layer in the cell. In particular, the energy of the absorbed photon will transfer to electron existence in the highest occupied molecular orbital (HOMO) level of one of the active materials. This energetic electron will approach the lowest occupied molecular orbital (LUMO) energy level, leaving a positively charged hole in the HOMO. The excited electron and the created hole are not free but linked in a bound state, called an exciton [6]. Splitting an exciton is an important step which occurs at the interface between the donor and the acceptor to extract charge from the cell. Therefore, the electron lies on the acceptor and the hole in the donor. The most common problem to occur before the splitting stage is the recombination of the electron and the hole during the exciton diffusion to the interface where the exciton will be split. Therefore, according to the short lifetime of the exciton (a few hundred picoseconds) the diffusion length of the exciton to the interface should be 5-10 nm in order to avoid recombination [7, 8].
Figure 1-1 Schematic diagram illustrates device working principle from light absorption to charge collection. Adapted from [3].

Regarding enhancement of the efficiency of OPV, optimising the top electrode is a key factor. The performance of such devices depends critically on the properties of transparent electrodes [9]. Correspondingly, the optical transmittance (T) and the sheet resistance (Rs) are considered as the two essential parameters. In particular, the transmittance of the transparent electrode has to be large while the sheet resistance has to be small in order to minimize the loss of power due to resistive heating (Joule heating) [10]. In the past decade different types of transparent electrodes have been suggested based on a variety of nanomaterials [2]. Current commercial processes use metal oxides such as ITO for fabricating transparent electrodes [11]. However, despite its remarkable performance it has some disadvantages: it is an expensive material, it is naturally brittle, and is not considered to be environmentally friendly.

Cost is a major limitation; both the price of the raw material and the expense of fabrication. This limitation is especially critical for OPV, which depends on low cost to be competitive in the market [3]. The process of deriving rare indium from mining and refining it to purity is the main driving force behind the high price, as shown in Figure 1-2 [3].
The price of indium metal in dollars per kilogram from 2000 until 2014 [16].

ITO can reach sheet resistance as low as 20 Ω/sq with 90% transmittance on glass substrate. However for the flexibility and light weight necessary for OPV, it is necessary to build displays and others on plastics [5]. The idea of depositing ITO onto a flexible substrate is possible up to a width of 7 m, but the performance achieved is limited due to the heating procedure required to demonstrate low sheet resistance [5]. Additionally, ITO is inherently brittle, which limits its performance on flexible substrates. When the substrate is subjected to bending, microscopic cracks begin to generate which lead to an increase in sheet resistance [66-68]. Figure 1-3 shows scanning electron microscope (SEM) images of cracks caused by bending. ITO was deposited on a polymeric substrate, which then was bent and flattened again, with cracks forming as a result of this bending [6].

Figure 1-3 SEM images of crack formation in ITO as a result of substrate bending. Top: Tension, bottom: compression, adopted from [6].
Owing to this limitation, alternative materials are required. This issue is of particular importance for preparing large area flexible electrodes, and much work has been done to overcome these disadvantages. More recently, scientific investigations have focussed on materials as solution process transparent electrodes, such as CNTs [12], graphene flakes, metallic nanowires (NWs) [13] and others. These materials must meet minimum industry standards (T>90%, Rs<100Ω/sq), which will be discussed in the next chapter.

Another concern is the negative effects arising from interaction between environmental components and optoelectronic devices, which has generated an increase in the production of protective coatings. An example of these negative effects is the abrasion and scratching suffered by photovoltaic cells during manufacture installation and services. The principle, then, is to produce a coating which is hard, wear-resistant, and which can easily be deposited on a large scale. Increasing demand for waterborne coatings has fuelled extensive academic and industrial development, due to their promising potential applications and lower impact on our environment [16]. For applications where the coating should be relatively hard (i.e. with a high glass transition polymer) a bottleneck to fabricating large area homogeneous films is associated with the formation of cracks as a result of the mismatch of mechanical properties between the coating and the substrate during film formation [17]. To overcome this challenge, a proposal solution of fabricating crack-free monolayer latex coatings over large areas without any modification of the composition by means of the Langmuir-Blodgett (LB) technique. Particularly, it is shown that, by using the LB technique, not only is it possible to form a monolayer of polymer latex spheres at the air/water interface, but that these monolayers can also be deposited onto large area glass substrates (although applications to any substrate are possible).

1.1 Motivations and primary objectives of this thesis

The primary objective of this thesis is to utilise the advantages presented by the unique properties of silver nanowires and graphene, such as high electrical conductivity, high optical transparency, and high mechanical flexibility. The functionality of such materials for producing transparent flexible electrodes is needed to be part of the new generation of optoelectronic devices, such as photovoltaic cells. This need is based on the replacement of the current materials used, such as ITO, which have some drawbacks. Upon production of the Ag NWs electrode, identify and understand the weaknesses in the electrode and find a
route to overcome these issues are aimed, with the ultimate aim of improving electrode performance and therefore device performances. Final target is producing hard coating large scale film based on polymer latex for protective purpose of for instance solar cells.

1.2 Thesis outline

Chapter 1: Introduction

The introduction provides the framework of the research by explaining the problems and the primary objectives and the outlines of this thesis.

Chapter 2: Research background and literature reviews

In this chapter, a literature review is presented on the replacements on ITO. The replacement materials are focused on CNTs, graphene, conductive polymer, metal thin film, and metallic nanowires, the chapter also introduces some of their synthesis, fabrication method and properties. In the case of metallic nanowires, part of the chapter mentioned on the transparent electrode based on Ag NWs applications. Finally, latex polymer has been reviewed by identify the latex polymer and their film formation process.

Chapter 3: Experimental methods

The experimental methods and the characterisation techniques are presented in this chapter.

Chapter 4: Transparent flexible electrode based on Ag NWs and graphene

This chapter demonstrates the fabrication of Ag NWs electrode by using spraying deposition technique. The relationship between the optical transmittance and the sheet resistance is described. Also, this chapter illustrates the functionality of graphene for fabricating the hybrid electrode based on Ag NWs/graphene and presents the morphological, optoelectrical and mechanical properties of both pristine and the hybrid electrode.

Chapter 5: The influence of thermo-mechanical welding on Ag NWs and Ag NWs/graphene by three-point bending test
Chapter 6: Controlled Deposition of Latex Monolayer Film by Langmuir – Blodgett Technique for Hard coating Applications

This chapter demonstrates the novel approach of producing latex polymer monolayer over the large area by using Langmuir-Blodgett process. Optimisation and control of the deposition are presented. Optical and morphological properties of the produced film is also achieved.

Chapter 7: Summary and future prospective

Summary and suggestions for future research work are given in Chapter 7.
References


Chapter 2 Research Background and Literature Reviews

2.1 Light-Matter Interaction

Light interacts with matter in a number of ways. Whereas metals are shiny, water is transparent. Stained glass and gemstones transmit some colours but absorb others. Other materials, such as milk, appear white because they scatter incoming light in all directions. The following section will address a host of these optical phenomena in a wide range of solid state materials. However, it is first necessary to describe the ways in which the phenomena are classified, and the coefficients that are used to do so. Following this is an introduction of the materials studied, and clarification in general terms of how the solid state differs from the gas and liquid phases.

2.1.1 Classification of optical processes

The observed range of optical properties in solid state materials could be categorised into a number of general phenomena. Such as, reflection, propagation and transmission. Figure 2-1 illustrates the mechanism of light beam during hitting an optical medium. However, some of light is reflected from the front surface, this shows a light beam incident on an optical medium. Some of the light is reflected from the front surface, whereas the rest go into the medium and propagates throughout. There is a possibility if the light reaches the back surface to be reflected again or transmitted via the other side. There is a relation between the transmitted light amount and the reflectivity of the front and back surface, and also the propagation of the light way through the medium.
Figure 2-1 Schematic diagram illustrates reflection, propagation and transmission of incident light on an optical medium.

The phenomena that can occur while light propagates through an optical medium are illustrated schematically in Figure 2-2.

Figure 2-2 Phenomena which may occur as the light propagates through an optical medium. Refraction leads to reduce the wave velocity, while absorption causes attenuation. Luminescence can be combined with the absorption if the excited atoms emit again by spontaneous emission. Scattering causes redirection of the light.
Refraction causes the light waves to spread with a lower speed than in free space. This decrease of their speed prompts the twisting of light beams at interfaces, as portrayed by Snell's law of refraction. Refraction, in itself, does not influence the intensity of the light wave as it spreads.

Absorption happens amid the propagation if the light frequency is resonant with the move frequencies of the medium atoms. For this situation, the beam will be constricted as it propagates. The transmission of the medium is unmistakably identified with the level of absorption, on the grounds that just unabsorbed light will be transmitted. Specific absorption is in charge of the colouration of numerous optical materials. Rubies, for instance, are red in light of the fact that they absorb blue and green light, however not red light.

Luminescence is the process of spontaneous emission of light by excited atoms in a solid state material. One of the routes in which an atom can be raised into an excited state before the spontaneous emission is by the absorption of light. Luminescence can thus go with the propagation of light in an absorbing medium. In all direction, the light is emitted with different frequency to the incident light. Luminescence does not generally need to go with absorption. It takes an amount of time for the excited atoms to re-emit by spontaneous emission. Accordingly, the excited atoms possibly dissipate excitations energy as a heat prior to the re-emission process occurs. Therefore, the luminescence process efficiency relatively linked to the de-excitation dynamics in the atoms.

Scattering is referred to the process when light interacts with a medium and therefore changes its direction and possibly frequency. However, there is no change in the total photons number, but due to the change in the direction, the number going in the forward direction decreases. So, scattering is attenuated as absorption.

The scattering can be classified into two parts elastic and inelastic. If the light frequency remains unchanged the scattering is elastic, while the changing in the frequency leads to inelastic scattering. The difference in photon energy in an inelastic scattering process has to be taken away from the medium if the frequency increases, but given to the medium if the frequency decreases. A number of other phenomena can occur as the light.
2.1.2 Optical coefficients

Number of parameters which determine the medium properties in the macroscopic level can quantify the above optical phenomena. However, light reflection at the surface is defined by the reflection coefficient \( R \) which is described as the ratio of reflected power to the power incident on the surface, while the ratio of transmitted power to the incident power is defined the transmission coefficient \( T \). If there is no absorption or scattering, then by the principle of conservation of energy:

\[
R + T = 1 \quad 2.1
\]

The refractive index can describe the light propagation via the medium which is the ratio of the light velocity in free space \( c \), to the light velocity in the medium \( v \) as it is shown in this relationship:

\[
n = \frac{c}{v} \quad 2.2
\]

The light absorption by a medium can be quantified by its absorption coefficient. However, it can be described as the absorbed power fraction in unit length of the medium. For instance, in the light propagates in \( z \) direction with intensity of \( I(z) \) in that direction, then the thickness \( dz \) can be used to described the decrease in the intensity which is given by:

\[
dI = -\alpha dz \times I(z) \quad 2.3
\]

Also, this can be integrated to achieve Beer's law:

\[
I(z) = I_0 e^{-\alpha z} \quad 2.4
\]

where \( I_0 \) is the optical intensity at \( z = 0 \). Absorption coefficient is strongly dependent on the frequency, therefore optical materials might absorb one colour rather than another.

2.2 New Materials for Replacing ITO and its Transparent Electrodes

For considerations of cost and performance, there is a clear need for a replacement transparent conductor for optoelectronic devices. This material should have transparency
and conductivity figures of merit that meet or exceed the values of ITO while being more mechanically robust and not requiring expensive or high-temperature substrate processing. This material should perform equally well on any type of substrate, cost less than ITO, and be compatible with high-quality optoelectronic devices.

2.2.1 Carbon Nanotubes

CNTs can be defined as sheets of graphene that have been rolled up to a cylindrical shape with nanometer-scale diameter [1]. They are one dimensional materials with high aspect ratio (more than 1000). Depending on the synthesis process, CNTs exist as single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). The electron micrograph image in Figure 2-3 clearly shows the variation in the number of the nanotube walls. SWCNTs consist of one graphene layer rolled into a cylindrical form, and the MWCNTs consist of two or more graphene layers arranged around a central hollow, with van der Waals forces between the layers.

![Electron micrograph of MWCNTs with different numbers of layers](image)

Figure 2-3 Electron micrograph of MWCNTs with different numbers of layers, as observed by Ijima [1].

The term ‘tube chirality’ is used for specifying the atomic structures of the nanotubes. Therefore, chirality can be defined by the chiral vector, \( \vec{\tau} \), and the chiral angle, \( \theta \) as shown in Figure 2-4 (A). The chiral vector is defined by the following equation:

\[
\vec{c}_h = n\vec{a}_1 + m\vec{a}_2
\]
The integers \((n, m)\) are the number of steps along the carbon bonds of the hexagonal lattice, and \(\vec{a}_1\) and \(\vec{a}_2\) are the unit vectors of the graphene in real space [92]. Depending on the chiral angle \(\theta\) related to the twisting of the graphene sheet, three chiralities of tube can be found: armchair, zigzag and chiral. The structures of the nanotubes with different chiralities are presented in the Figure 2-4 (B). When the chiral angle is 0° then the \(m\) integer is equal to 0 and the nanotubes are called “zigzag”. In the case that the integers have the same value, \(n=m\), the chiral angle is 30° and the nanotubes are called “armchair”. For all other combinations of integers and chiral angles, the nanotubes are called “chiral”.

The chirality of the nanotubes has a serious influence on their electrical properties. For a certain \(n, m\) chirality of the nanotube, if \((2n+m)\) is a multiple of 3 then the tube is known as metallic, owing to the electrical properties that it develops. Alternatively, the nanotubes are known as semiconducting, their electrical properties being similar to those of a semiconductor. If no chiral angle is determined during the synthesis of CNTs, there should be twice as many semiconducting tubes as metallic. The diameter of the nanotubes can be calculated by using the chiral vector, as the interatomic spacing of the carbon atoms is known [1].

Figure 2-4 (A) Schematic graph showing the chiral vector and the different roll up chiralities. (B) Presents lattice structures for ideal armchair, zigzag and chiral and tubes.

2.2.1.1 Carbon nanotube electrodes

A single carbon nanotube can have electron mobilities higher than 100 000 cm²/V.s and CNTs have also been shown to have unique and beneficial optical and mechanical properties [2-4]. Films of CNTs appeared in the mid-2000s, being presented as a new material for transparent electrodes as illustrated in Figure 2-5. Initially, their use as an
alternative material for ITO was proposed due to their high mobility, but challenges emerged for these CNT films [4].

![Image](image.png)

**Figure 2-5** Transparent conductive network of carbon nanotubes [9].

The most important challenge relating to the conductivity of CNT random network is the junction resistance where nanotubes intersect. These junctions between nanotubes have high resistance, ranging from 200 kΩ - 20 MΩ [2]. Accordingly, the conductivity of CNT films is significantly lower than that of a single CNT. Some attempts have been made to reduce the sheet resistance of CNT films, for example by treating CNTs with acid and using longer CNTs [5]. **Figure 2-6** shows the sheet resistance as a function of CNT film transmittance before and after acid treatment [6]. Nevertheless, films of CNTs still have much lower conductivity than conventional ITO films.

A secondary issue related to junction resistance is that CNTs can be either metallic or semiconducting. In CNT fabrication, semiconductor and metal CNTs are produced at the same time, meaning that CNT films contain both kinds. The semiconductor nanotubes have lower conductivity than the metallic tubes, so do not contribute much to the overall conductivity [2]. However, the semiconductor nanotubes absorb light and, reducing transparency. In addition, metal-semiconductor junctions in CNT films create high contact resistance due to the Schottky barrier formation, resulting in higher sheet resistance [2]. It remains a significant challenge to separate metal and semiconductor CNTs or to produce purely metallic CNTs. Although some methods have been introduced to separate metal nanotubes, they are expensive and not suitable for commercial use [7].
Figure 2-6 Sheet resistance versus transmittance for SWNT films with varying thicknesses, before and after acid treatment [8].

Although acid treatment lowers the resistance of the films by reducing the junction resistance, the film’s overall sheet resistance is still much higher than that of ITO. The best results for CNT transparent electrodes are collated in Figure 2-7 [5] and show significant progress in recent years in fabricating transparent electrodes based on CNTs. Most applications, however, require lower sheet resistance and higher transparency than even the most favourable values shown in the plot. Therefore, CNT films at this time are not a suitable replacement for ITO [9-12].

Figure 2-7 Sheet resistance vs. transmittance for the highest conductivity CNT films. CNT film transmission at 550 nm versus sheet resistance for different data measured in the literature[13].
2.2.2 Graphene

Graphene is a two dimensional, atomically thick sheet of sp2-bonded carbon atoms packed in a honeycomb crystal lattice. Long-range \( \pi \)-conjugation in graphene yields extraordinary thermal, mechanical and electrical properties. Examples of the characteristics of graphene are the high current density, ballistic transport, chemical inertness, high thermal conductivity, optical transmittance and high hydrophobicity in nanometer scale [13]. Graphene is characterised as a semi-metal or zero-gap semiconductor and its optoelectrical characterisation has shown low absorption in white light and remarkably high electronic mobility at room temperature [14]. The corresponding resistivity of a graphene sheet is \( 10^{-6} \Omega \text{cm} \), considered to be the lowest resistivity substance at room temperature [15].

In order to benefit from its properties, the synthesis of a single layer of graphene on a suitable substrate is required. Therefore, the key factor is to be able to conduct controlled synthesis in a pure and isolated manner, which results in high yields of graphene sheets and which can be applied across the industry. The methods of graphene fabrication can be divided into two categories: solution processes (mechanical and liquid exfoliation, reduced graphene oxide) and the direct growth processes (epitaxial growth by chemical vapour deposition, unzipping of CNTs). Each approach has its own advantages and limitations.

2.2.2.1 Graphene Fabrication

Developments in methods of graphene preparation with high quality and in large quantities have taken considerable effort for research determinations as well as for applications [16, 17]. Since it was isolated in 2004, two general methods of fabricating the material have followed. Firstly, a top-down approach, based on breaking down graphite to graphene mechanically by the technique of mechanical cleavage or exfoliation. Secondly, a bottom-up approach characterised by synthesising the graphene using a technique such as chemical vapour deposition (CVD).

The process of expanding graphite has been in use for more than 100 years, originally being employed as filler for polymer resins [18, 19]. Moreover, recent developments have been increasingly and extensively more focussed toward preparing thinner flakes of graphene, known as graphite nanoplates (GNPs) [20]. Several techniques are able to produce these nanoplates, such as the exposure of acid-intercalated graphite to microwave
radiation, ball-milling and ultrasonication. The incorporation of GNPs to polymers has been shown to show significant enhancements in mechanical and electrical properties, which can be carried out at lower loadings than are required with expanded graphite [21, 22]. GNPs can be defined as a kind of graphite with a thickness from 100 nm to single layer graphene [20].

Mechanical cleavage (defined by repeatedly peeling off graphene with adhesive tape) is considered to be the simplest method for producing graphene with just one, or a few, layers. This graphene can typically be derived from good-quality natural graphite or from highly-oriented pyrolytic graphite [23]. Figure 2-8 presents an optical microscopic image of a single flake of graphene produced by mechanical cleavage and deposited onto polymeric substrate. In particular, these methods prepare graphene flakes with differing thickness up to a few layers, and have dimensions in the range of tens of micron.

![Figure 2-8](image.png)

**Figure 2-8** Photograph (in normal white light) of a relatively large multilayer graphene flake with thickness ∼3 nm on top of an oxidized Si wafer [20].

### 2.2.2.1.1 Chemical Vapour Deposition

The use of CVD to grow graphene is considered an important innovation which produces graphene films within macroscopic dimensions on the metal surface, which can be copper or nickel–copper, using a mixture of methane/H₂ [24, 25]. In the case of copper, graphene growth takes place on the foil of Cu through the process of surface catalysis and thin metal films do not need to be employed [25, 26]. Therefore, regarding nickel, thick graphite crystal is usually formed instead of graphene. However, this issue
has been solved by using deposited thin Ni layers with thickness less than 300 nm on SiO$_2$/Si substrates [24]. Nevertheless, it was found that for both metals the transferral of graphene can be done to other substrates [27]. This process has now been expanded to a roll-to-roll fabrication process where graphene can grow by CVD on copper-coated rolls. Following this, it can then be transferred to a thin polymer film backed with an adhesive layer to fabricate transparent conducting films [26, 28]. The resultant film has been found to present low sheet resistance at transmittance of the order of 97.4 %. In most cases, they have been found to be covered with a monolayer graphene film but also have some bilayer and few layer islands.

2.2.2.1.2 Unzipping Carbon Nanotubes

Graphene nanoribbons can be derived from carbon nanotubes, particularly by unzipping multi-walled carbon nanotubes. This process can either be carried out by the method of oxidative treatment in solution [29, 30], or by the method of Ar plasma etching upon nanotubes partially embedded in a polymer substrate [31]. Recently, this approach has been extended by using small clusters of metals such Co or Ni as nanoscalpels, which cut open nanotubes to produce graphitic nanoribbons [32]. The technique is able to cut graphene into pieces with well-defined shapes that can be used in different applications, including the fabrication of graphene devices [32].

2.2.2.1.3 Liquid Phase Exfoliation of Graphene

Exfoliation methods began to receive more interest as a method owing to increasing demands for a high-volume approach to production, for instance in composites [35, 36]. The most successful method was the exfoliation and dispersion of graphite in organic solvents such as N-methylpyrrolidone [37-39]. Very few defects have been observed on the fabricated graphene, which is also not oxidised. The produced dimensions, however, are typically limited to a few microns. Hernandez et al. [39, 40] have shown this method, and also demonstrated the possibility of disperse and exfoliate graphite to provide graphene suspensions in water-surfactant solutions. Moreover, they argued that this approach can be applied to inorganic materials which are based on layered compounds, such as molybdenum disulphide, MoS$_2$ [41]. By way of improving this method, they demonstrated a way to produce dispersions with higher concentrations of graphene by either sonicating the dispersion for long time [42] or by better controlling
centrifugation [43]. Additionally, other approaches to improve the graphene dispersion have been demonstrated. Increasing the mean lateral size of graphene flakes [44] or obtaining graphene dispersions in low boiling point solvents [45] can refine the exfoliation process. Therefore, these improvements can provide better deposition of the individual flakes on substrates.

2.2.2.2 Electrical Properties of Graphene

The electronic properties of graphene are the focus of most contemporary experimental research. The ability to tune the charge carrier from holes to electrons continuously was the notable feature in earlier research on graphene transistor, which exhibited the gate dependence in single graphene sheets. This dependence is more pronounced in the thinnest samples; while samples from multiple sheets present much weaker gate dependence other layers caused screening in electrical field [46].

The extraordinary mobility of graphene at high magnetic field and low temperature allows for observation of the quantum Hall effect for both electrons and holes [47]. This quantum Hall effect, due to the unique band structure of graphene, shows a slight difference from the conventional quantum Hall effect in that plateaus occur at half integers of $4e^2/h$ rather than the typical $4e^2/h$.

For more practical functions, the strong gate dependence of graphene can be used for either sensing or transistor applications. Therefore, corresponding changes in resistivity are small as graphene has no band gap. However, a graphene transistor is affected by a low on/off ratio, necessitating that graphene be carved into narrow ribbons in order to overcome this limitation. When the ribbon shrinks, the charge carrier momentum in the transverse direction quantises, which results in the opening of a band gap [48]. This band gap is proportional to the width of the ribbon [49]. A similar effect can be found in carbon nanotubes, where the band gap of the nanotube is proportional to its diameter.

2.2.2.3 Optical Properties of Graphene

Research has shown that graphene is optically transparent (70%–90% transparency depending on thickness) and has incredibly high electron, thermal transport and thermal conductivity properties [50]. These properties have enabled applications such as wear-resistant films, nanocomposites, OPV and transparent touch screens [24, 51]. One
inhibitor in these applications has been the difficulties with producing graphene in a commercially viable manner. It is impossible to make OPVs with tiny graphene flakes from scotch tape, so techniques such as epitaxial growth and copper foil were developed [25, 52]. As these techniques improve, and additional applications evolve, it is critically important to have a comprehensive understanding of the structure and properties of graphene.

2.2.2.4 Mechanical Properties of Graphene

Research on graphene has been wide ranging and regular, due largely to its incredible mechanical properties. Graphene has been shown to be the strongest material ever tested, with an elastic modulus of 1 TPa and a tensile strength of 130 GPa [53]. These results were obtained from a test conducted with graphene as a suspended sheet over nanoholes. In addition to testing for moduli, graphene’s frictional properties have been tested on suspended graphene sheets. Force friction microscopy (FFM) was used, and it was determined that frictional force decreased monotonically with increasing thickness [53]. Monolayer graphene’s frictional force was shown to be roughly twice that of bulk graphite, with tip-graphene adhesion constant [24, 54]. Another study, using Atomic Force Microscopy (AFM) on a corrugated substrate, investigated the interlayer shear strength of graphene, and concluded that it is greater than or equal to 5.6 MPa, a value orders of magnitude less than its tensile yield stress [55]. This research was prompted by the potential of graphene as a thin film and the fact that graphene’s mechanical properties have only been studied experimentally as suspended sheets and in polymer composites [51]. However, other mechanical properties of graphene, such as hardness, remain largely unexplored. In applications where graphene could be used as an electrode, it is critical to understand and quantify the load and impact that graphene can withstand. Recently in the Sandoz lab, a protocol was developed to determine the mechanical properties, specifically hardness, of thin films by using AFM nanoindentations [56].

2.2.2.5 Graphene Electrodes

The ability of graphene to form a high conductive network of flakes is one of its more interesting properties. Since graphene flakes’ thickness is a few nanometers, they are relatively transparent to visible light. However, the fabrication of a single, large-scale,
flake of graphene is the major concern. Accordingly, a network of graphene flakes has been fabricated, as shown in Figure 2-9, instead of a single layer. The sheet resistance of the fabricated electrode was very high (in the range of several kΩ) due to the high contact resistance value, which affected the electrical conductivity [57]. As shown in Figure 2-10, relation exists between film transparency and graphene layer thickness. Typically, the transparency depends on the thickness of the layer, hence a thinner film results in high transparency whilst maintaining high sheet resistance [58].

The graphene fabrication process, as well as that of incorporating them in electronic devices, has improved significantly. The production of a single sheet of graphene has been achieved, for instance by using CVD, but this method is relatively costly and the sheet resistance of the fabricating films of single sheets are not sufficient to make them practical in most applications [29].

![AFM height image of highly dense graphene film fabricated by the Langmuir-Blodgett process](image)

**Figure 2-9** AFM height image of highly dense graphene film fabricated by the Langmuir-Blodgett process [59].
Figure 2-10 Optical transmittance ($\lambda=550\text{nm}$) of CVD multilayer graphene. Red and blue dots are the experimental data showing a decrease in optical transmittance with an increase in graphene layer number [60].

2.2.3 Conductive Polymers

In 1977, conducting polymers and their ability to be doped were discovered [61]. Polymeric organic materials that have the electronic, magnetic, electrical and optical properties of a metal while at the same time retaining their processing ability and mechanical properties are called conducting polymers. Shirakawa et al. observed in 1977 that films of the semiconducting polyacetylene can undergo an increase in conductivity by doping with Br$_2$, I$_2$, or AsF$_3$ [62]. These discoveries made conducting polymers a promising material for several applications and attracted the interests of researchers, making them the most recent generation of polymers [63, 64]. Numerous conjugated polymers, mostly aromatic, were studied in the following years. These included poly(paraphenylene) (PPP), poly(thiophene) (PT), poly(pyrrole) (PPy), poly(aniline) (PANI), etc [65-67].

An important step in the development of conducting polymers was related to the doping process. Doping is an oxidation-reduction reaction in which the introduction of donors (doping of type n) or acceptors (doping of type p) into the material can be accomplished in a number of ways. It is worth noting that the doping of semiconducting polymers is not always reversible and easy to control. In brief, chemical doping involves a charge-transfer redox chemistry oxidation (p-type doping) or reduction (n-type doping). The major challenge of this method is that doping levels are not easily controlled. To deal with this difficulty, electrochemical doping was investigated, wherein the electrode
supplies the redox charge to the \( \pi \)-conjugate polymer and a polyelectrolyte plays the role of the counter ion. The doping level is easily controlled by the voltage that is applied on the polymer.

Similarly, conjugated polymers can be doped by photochemical oxidation and reduction, or by the injection of electrons and holes. In general, the doping process used is determined by the type of conjugated polymers, the required doping level and the application.

2.2.3.1 Conductive Polymers Electrodes

Transparent conductive polymers’ most attractive properties (namely their flexibility, low cost and lightweight) have attracted substantial interest since their discovery. Due to these properties, conductive polymer transparent electrodes have been applied as part of various optoelectronics devices [68, 69]. The most prominent example of this use is with PEDOT: PSS which is the combination of Poly (3, 4-ethylenedioxythiophene) and poly (styrene sulfonate) [70-72]. The degradation of PEDOT: PSS in air is, due to the absorption of oxygen and humidity, one of the major drawbacks as it affects their stability [73]. Intensive research has been carried out to overcome this issue, and has focussed on synthesizing a more stable conductive polymer; Fujitsu Company has used a type of polythiophene for their organic touch panels which is more stable in air [74]. Another drawback of PEDOT: PSS is that conductive polymer electrical conductivity cannot match that of ITO, which makes them unsuitable for the purpose of ITO replacement. There is, however, a possibility for conductive polymers to be combined with other nanomaterials like CNTs and graphene to improve their conductivity [75, 76].

2.2.4 Metal Nanostructured Electrodes

Metal nanostructured electrodes have been considered as an alternative for CNT films, graphene and transparent conductive polymers used as a solution to the low conductivity issue of the previous materials [77, 78]. Metals have the highest conductivity of all material types, however, the difficulty of fabricating transparent metallic electrodes lies in their low transparency in visible light [57]. The emergence of nanotechnology has offered an easier way for fabricating transparent metallic
nanostructured electrodes. Three common structures have been demonstrated to produce transparent metallic electrodes: metal nanogrids, thin metallic films, and metallic nanowire networks [57].

2.2.5 Metallic Nanowires

Nanowires can be considered as one dimensional (1D) material structure. Nanowires have been produced from a variety of elements including metals (e.g. Ag, Au), semiconductors (GaN, Si,), and insulators (SiO₂, TiO₂). Recently, metallic nanowires such as Ag NWs have shown great potential due to their unique physical properties [79], being attractive for different device applications. Electronic conduction in Ag NWs depends on both bulk conduction along the wire, and a tunnelling mechanism between wires. Ag NW networks have unique electrical, optical and thermal properties due to the high density of states (DOS) associated with the character of the metal [80]. In order to fully understand the carrier transport mechanism of Ag NWs and the importance of electron transport properties for electronic devices such as OPV, it is important to consider the effects of various parameters such as wire diameter, wire surface state, and chemical composition, among others.

2.2.5.1 Synthesis of Ag NWS

Ag NWs can be synthetized in solution with the polyol method. In this method, an ethylene glycol (EG) solution of poly (vinyl pyrrolidone) (PVP) and NaCl is heated to 170 °C and a mixture of AgNO₃ and EG is added gradually. Adding AgNO₃ into the solution leads to the creation of Ag⁺, which results in the formation of nanoparticles due to homogenous nucleation [42]. PVP has a strong interaction with {100} facets and passivates these surfaces, which slows down the addition of Ag. The interaction of PVP with {111} facets, however, is weaker. Thus, {111} facets grow faster in {110} direction [42, 81], which results in a 1D wire structure [82]. This method results in pentagonal shape silver nanowires, including a 5-fold grain structure as shown in Figure 2-11. The sidewalls are {100} planes. The two ends of the nanowires are bounded by {111} facets [82].
2.2.5.2 Metal Nanowire Electrodes

The nanostructured metal nanowires are considered as 1D with a wire shape. Typically, their diameter is less than 100 nm, with a length of 1 μm or more. In the case of silver and copper NWs, which can be produced in solution, it is possible to deposit the NW onto different substrates such as glass or polymeric to fabricate transparent conductive networks with random distribution. Metallic NW networks have further advantages, such as high transparency, mechanical flexibility, low sheet resistance, and cheap, easy abdication. For example, Ag NW transparency can reach 90% - a figure which, combined with sheet resistance below 10 Ω/sq, makes this kind of network more suitable for replacing ITO [79]. Moreover, these parameters can be controlled by varying the density of the deposited materials to produce electrodes with specific aspects. Figure 2-12 presents randomly-distributed silver nanowire electrodes produced with various densities.

Figure 2-11 Schematic illustration of silver nanowires growing in solution by the polyol method [82].
Figure 2-12 SEM images of Ag NW films with different densities. The different densities of Ag NW films lead to different sheet resistances: (a) 100, (b), (c) 50, and (d) 15 Ω /sq. The diameters of the Ag NWs are in the range of 40-100 nm [79].

Depositing Ag NWs can be undertaken through various simple, inexpensive techniques such as spin coating [80], spray coating [83], and Meyer rod coating [79]. Recently, Ag NWs have been considered as a strong candidate for producing transparent electrodes, due to silver’s unique high conductivity among metals [84]. Figure 2-13 presents a comparison of Ag NWs electrodes with other nanomaterials. In summary, Ag NWs exhibit a strong performance relative to graphene and CNTs.

While copper NWs have seen applications as transparent electrodes due to their cheap cost and high conductivity [85], there remain concerns over their instability in air resulting from a reaction with oxygen [86].
Figure 2-13 Transmittance (550 nm) plotted as a function of sheet resistance for thin films prepared from four nanostructured materials, graphene, single-walled carbon nanotubes, silver nanowires, and silver flakes. The dashed lines represent fits to the bulk regime, while the solid lines represent fits to the percolative regime [87].

2.2.5.3 Electrical Properties of Nanowire networks

Studying the electrical properties of nanowire networks is based on several characterisations of such networks, as well as the network morphology. Generally, the electrical resistance of the network is inversely proportional to the length of the nanowires, a relation linked with wire diameter [88, 89]. The increase in resistance with decrease in the diameter is due to the increase in the resistance of the individual nanowires. Bid et al. reported this phenomenon [90, 91], referring to the surface scattering of the electrons, as the reason for the increased resistance when nanowire diameter is reduced to close to, or below the mean free path of electrons of the bulk material. As such, the role of surface scattering becomes dominant, causing a reduction in the mean free path, which leads resistivity to increase above that of the bulk. Hecht et al [90] investigated the conducting mechanism of the metallic network by explaining the length dependent on the network resistance. However, the concept of this study was the required minimum number of nanowires to cross the network size being inversely proportional to the length of the nanowires. The achievement of a percolated network depends on the required number of interconnections of oriented nanowires. However, this required number is itself determined by the length of the wire. Therefore, longer nanowires require fewer wires to produce a conduction path across a given network,
meaning that they have fewer junctions, resulting in the lower resistances typically observed in networks made of long wires.

Moreover, nanowire density plays a role in the conductivity of the network. Many studies have investigated this issue and have reported that, by increasing the number of nanowires the resistance will decrease accordingly. However, this also decreases the optical transmittance of the network [79, 88, 92-94]. The materials used to fabricate the network play a large role in the overall resistance of that network, so silver and copper nanowire networks have shown more favourable electrical properties. Length and diameter also play an essential role in the required density for achieving percolation, and by extension the number of the conductive pathways through the network. Junction resistance is formed by the NWs-NWs junctions, which can also affect the conductivity of the network. In order to overcome this limitation, various procedures have been examined, including thermal annealing [58, 95, 96], high pressure [95], electrical annealing [96], and encapsulation [97]. These have all been shown to reduce the resistance of the network.

2.2.5.4 Optical Properties

The loss of optical transmittance in the network of Ag NWs mainly occurs by the reflection of incident light by the nanowires themselves [98]. Additionally, a remarkable reduction in the reflectance combines with the gradient of refraction index, which is an inherent factor in enabling better coupling of light to the material [99].

Optical haze, which is the ratio of diffuse transmission to direct transmission, is considered to be a critical factor for many applications [100]. The rate of scattered transmitted light is also an important parameter, alongside optical transparency and sheet resistance of the network. The degree of scattered transmitted light is a control on optical haze ratio. It is possible to produce a wide range of metallic nanowire networks with optical haze from lower than 2% to higher than 30% [101]. Within this range, electrodes based on metallic nanowires can be fabricated to suit many applications. In particular, a low haze ~ 2 % is preferred for display applications, while for solar cells higher haze is desirable as it increases the optical path length of light in the absorbing layer, thereby improving the efficiency of the photovoltaic [102]. Optical haze is also
dependent on other parameters such as NW density or diameter [101], deposition method and post-processing.

Contemporary studies have focussed on the importance and functionality of optical haze, rather than its contributions in the calculation of the figure of merit (FoM) [99, 101, 103]. Additionally, current discussions and comparisons of Ag NW-based electrodes’ optical haze are hampered by a lack of fair studies, owing largely to incongruous data in the literature.

2.2.5.5 Thermal Properties

The thermal characterisations of metallic nanowires are represented by the thermal conductivity of the nanowires, the electrical conductivity temperature dependence, and the thermal stability of the metallic network. Recently, many studies on electrical transport properties in nanostructure scale have been published [104]. Oxide or semiconductor nanowires hold the larger part of the research in this field, while many fewer studies are concerned with comparative investigations of thermal and electrical conductivities of metallic nanowires [105]. In brief, thermal and electrical conductivities of metallic nanowires adhere closely to the Wiedemann-Franz Law [105]. In one study, the thermal conductivity (K) of Pt nanowires was compared to their electrical conductivity (\(\sigma\)) at room temperature, then compared to the bulk data. Thermal and electrical conductivity of the metallic nanowires are decreased by 2.5 and 3.4 respectively. The proportional constant of this relation (L) was 25 % less pronounced in nanowires than in the bulk data [105]. This decrease is probably related to electron scattering at the grain boundaries. Some of these studies which compared electrical and thermal conductivity of metallic nanowires with bulk data have found other electrical properties of Au NWs similar to these of bulk without evidence of any polycrystalline grain structure [106] even with a diameter of 55 nm. Thermal conductivity was able to be increased by incorporating Ag NWs within the organic material [107]. Ag NW/polymer composites can be functionalised as a heat sink in electronic cooling applications by using the composite as thermal interface material [108].

Moreover, flexible transparent thin film heater can be produced by using Ag NW networks [108]. Above the percolation threshold of the randomly distributed network,
the combination of flexibility, transparency and high heating output is possible at low voltage (i.e. 12 V), which has many applications including but not limited to defrosting, defogging or fabrication of thermo-chromic displays [96]. Conversely, thermal properties play a crucial role in the topic of electrical resistance evaluation of Ag NWs networks during thermal annealing. Thermal annealing is an important method which is commonly used to fuse contacts at junctions between NWs-NWs and hence reduce their resistance. The accurate level of local annealing is one of the important parameters for any evaluation of the electrical properties, as above a certain level the metallic NWs tend to become unstable. It has been observed that a change upon morphological structures takes place during thermal annealing. Various metallic nanowires such as Au [109], Cu [33], Pt [110], or Ag [111] have recently been reported to suffer broken nanowires with more thermal annealing, which is consequently detrimental to network electrical conductivity. However, thermal annealing should be undertaken within controlled conditions in order to improve the electrical conductivity of the NWs network [112].

2.2.5.6 Structural and Mechanical Properties

Metallic nanowire morphology depends greatly on the fabrication methods of their network production. Accordingly, the majority of the current fabrication methods lead to the production of networks with rough surfaces which may lead to a reduction in device performance. Short circuits, current leakages and exciton recombination of photovoltaic may occur due to out-of-plane oriented wires. Some methods have been demonstrated for reducing the problems associated with stray nanowires. High mechanical pressure can be applied to increase uniformity in the geometry and minimise the morphology of 3D to 2D network [95]. Another method encapsulates the NWs network in a transparent conductive polymer, which has been proven to remarkably reduce surface roughness [113, 114].

Network structural behaviour has shown interesting results which allow such networks to feature prominently in contemporary research. One of the advantages of electrodes based on nanowire networks is their mechanical properties. Metallic nanowires have displayed excellent properties when subjected to mechanical stress [92, 94, 115].
Applications to solar cells, OLEDs, and thermal heaters have shown that they can be produced on flexible substrate nanowire electrodes. The capability of flexible electrodes to resist external stress is far greater than that of many conventional transparent conductive materials [96]. Lee et al [116] investigated the flexibility of Ag NWs network with transmittance of ~90% and sheet resistance between 9 and 70 Ω/sq. The network was stable over 460% strain without any substantial increase in the electrical resistance [116]. The adhesion of the nanowires network layer to the substrate is the greatest weakness of the flexible electrode under mechanical stress. Particularly, direct applied friction or the application of adhesive tape to the network causes elemental failure, affecting performance. However, encapsulation of the network can reduce this weakness.

2.2.6 Ag NWs/Graphene Hybrid Structure

Despite the electrical, optical, mechanical advantages of Ag NWs-based transparent electrodes, they still suffer from some drawbacks associated with their fabrication. Among these drawbacks are low breakdown voltage, oxidisation, high contact resistance between the network and the active materials, and the typical NW-NW junction resistance. Concerning junction resistance, it is well known that electrical conductivity in Ag NWs networks is dominated by percolation through junctions. Therefore, the inherently large junction resistance associated with the transportation of electrons at the junction leads to an increase in sheet resistance. Post-treatment approaches including thermal annealing, high mechanical pressure and welding may limit the applicability of flexible substrates, in particular for large area, flexible optoelectronic devices. An approach which may present opportunities regarding the restriction on flexible substrates is the combination between Ag NWs and other nanomaterials such as CNTs and graphene [117-120]. Graphene is the foremost candidate due to its unique features: Sp² hybridisation carbon atoms, excellent transport properties with charge carrier mobility ~20 000 cm² V⁻¹ s⁻¹ at room temperature and absorption of only 2.3% of visible light. Furthermore, graphene flakes provide 2D conductive paths for the electrons to pass through, so, according to percolation theory graphene could bridge non-percolated nanowires and also improve the percolation network by decreasing the inter-wire resistance of nanowires, especially at
intersections. Yun et al. [121] demonstrated a hybrid transparent flexible electrode based on graphene oxide (GO)/Ag NWs with sheet resistance ~150 $\Omega$/sq and transmittance of 86 %. The polycrystalline graphene grown by CVD is considered to be the most common material used for forming the hybrid structure. Incorporating CVD graphene to Ag NWs films can obtain $T$ above 90% and $R_s = 64\Omega$/sq.

Traditionally, GO, reduced GO and CVD-grown graphene were the most used for producing hybrid electrodes. However, the CVD method involves a very complicated and time-consuming transfer process, which limits its application in polymer composites. However, the liquid phase exfoliation of graphite in organic solvent by sonication without oxidation is seen as a promising method to obtain high quality graphene sheets.

2.3 Applications of Transparent Electrodes based on Ag NWs

Transparent electrodes based on Ag NWs are a strong candidate for being incorporated into current device application due to their low sheet resistance and high transparency. This positions supported by their mechanical properties, which offer opportunities for use in emerging flexible optoelectronic applications. As has been mentioned previously, the technology for producing these applications is compatible with low-cost and large-scale processes. Therefore, a solution has to be found which will overcome the current limitations, thereby enabling successful industrial integration into devices.

Economic analysis can confirm that the use of Ag NWs is not an issue. Indeed, the provided PV cost analysis modules clarify that Ag NWs are three times less expensive compared to ITO on PET substrate [34].

Regarding the applications, controlling Ag NWs surface roughness is a major challenge which has to be taken into account with great consideration [27]. Its status as a major issue comes from the effects of surface roughness, which can include electrical shorts or leakage in devices, especially in multi-layered systems. Ag NWs surface roughness has been investigated and evaluated to be in the order of hundreds of nm [52, 97]. In the literature, different methods have been developed to tackle the issue of electrode roughness. For instance, surface roughness has been reduced by mechanical pressing [52, 96], thermal annealing [27], polymer coating [96, 97] surface peeling and transfer
processes [96, 97, 133]. It has been reported that the flattening of the Ag NW networks not only reduces the surface roughness but also improves the electrical conductivity by lowering the sheet resistance.

As described previously, the weak adhesion of Ag NW networks to the substrate is also a disadvantage of its electrode. However, the suggested solution was based on encapsulating that electrode within a thin layer of organic materials (Teflon, PEDOT: PSS) [11, 52]. In particular, the device can be designed in such a way that the adhesion of Ag NWs to the substrate becomes less important by incorporating that network into multi-layered devices.

Finally, the evaluation of devices is not directly related to Ag NW’s electrode, but will be dependent on the overall device architecture and not exclusively on the Ag NW network. In addition, device optimisation should also tune the stability against different conditions such as oxidisation, as well as mechanical stability under mechanical stress.

2.3.1 Photovoltaic Applications

Recently, flexible organic photovoltaic cells have attracted attention as a method of next-generation energy harvesting, and have also been intensively studied due to their low-cost fabrication, light weight and great flexibility [122-124]. A randomly distributed Ag NWs network was recently a candidate for this application due to Ag NW’s unique advantages, including inherent low resistivity, high transmittance, and great flexibility, all of which make it suitable for high performance OPV. Many studies have incorporated Ag NWs as a primary electrode for photovoltaic applications [115, 125, 126]. Ag NWs networks can be produced with optical haze varying between 1 and 30%, according to experimental conditions [101]. As reported earlier, the low haze value is desirable for display applications around 2 %, while the high optical haze value of approximately 30% is accepted for photovoltaic applications. Moreover, in photovoltaic systems a high optical haze is implied by light scattering into the device, leading to a high rate of absorption across sections [101]. Lee et al. [127] investigated OPV with Ag NWs network and reported high performance of those cells. Comparing Ag NWs-based OPV with ITO-based device, they found that devices with Ag NWs showed a higher short circuit current due to high optical transmittance and lighter scattering, which can improve the absorption of the light by the active layer and surface
roughness. Chih-Hung et al. [102] have demonstrated that the increase in efficiency is proportional to the increase in the haze value. Additionally, Gaynor et al [126] reported that conversion efficiency is increased by approximately 10% in Ag NWs composite electrode against the ITO standard (η = 3.4% using ITO on plastic and η = 3.8% for Ag NWs composite). The flexibility advantage of Ag NWs networks is demonstrated in the fabrication of flexible photovoltaic cells, which cannot be achieved on any transparent conductive oxide [128]. Flexible photovoltaic cells display a remarkable capability for producing electricity when curved, even when bent up to an angle of 120°, as demonstrated in Figure 2-14. These photovoltaic cells are organic polymer cells which use Ag NWs electrode embedded in PEDOT: PSS, a conductive polymer.

![Figure 2-14](image)

**Figure 2-14** Flexible solar cell in operation (left) and the I-V curves at different angles [128].

2.3.2 Transparent Heaters

Transparent heater applications have several uses, such as defrosting windows in aeroplanes. Indeed, this application was one of the first which enabled high-altitude flight [129]. The majority of transparent devices for defrosting or defogging are produced by using layers of ITO, which do not significantly resist mechanical constraints. Therefore, Ag NWs random networks appear to be compatible for use as transparent film heaters on flexible surfaces. Joule’s law is the underlying principle to which governs the operation of this device. It is also known as Joule’s heating, and it describes the heat produced as a result of the flow of electrical current through a
transparent electrode. If an electrical current passes through the transparent electrode, the electrical energy will be converted to heat as resistive losses in the materials. This principle can be expressed by the following equation:

\[ P = \frac{V^2}{R} \]

Where \( V \) is the applied voltage, \( R \) the total resistance and \( P \) the dissipated power.

Concerning the applicability of Ag NWs in this to this end, many devices have been reported with excellent properties based on Ag NWs, particularly on plastic [96, 130]. Interestingly, the remarkable optoelectronic properties of Ag NW networks allow the supply of significant power at low voltage (typically below 12 V) which opens many more possibilities for application.

2.3.3 Displays

Organic light emitting diodes (OLEDs) have the advantage of being able to be fabricated by a solution process and therefore are more appropriate for low-cost, large-area flexible displays and white lighting panels. In particular, to operate OLED, electrical current is needed to flow through its active layer to start lighting. In this process, the charge carrier transport properties play an important part in such devices. Therefore, in addition to the importance of the active layer itself, the interface with their neighbouring layers and electrodes are also crucial [131]. Metallic nanowire-based OLEDs have been examined by a few studies, presenting significant electroluminescent properties [94, 114, 132]. Particularly, Yu et al. have integrated Ag NWs polymer composite electrodes in large angle bending PLEDs [114].

As in OPV devices, Ag NWs-based OLED performance increased slightly though higher-power efficiency when contrasted with conventional ITO [94, 133]. This is largely attributed to an improved scattering of emitted light by Ag NWs. Gaynor et al have recently proved very high-efficiency ITO-free white OLEDs [134]. These initial studies have opened the way to large-scale integration of Ag NWs-based electrodes in emerging flexible display devices.
2.3.4 Touch Panels

Touchscreen technology has dramatically become ubiquitous in a great number of electronic products. It is extensively employed for smartphones, tablet PCs and other technologies. Current industrial products are based on the approach of resistive or capacitive touch panels. The front electrode of this device is the conduit for emitted light, so it requires high transparency and low resistance, as well as low diffusivity (optical haze). In the near future, many devices using touchscreen technology will become flexible, hence demand for flexible (bendable and stretchable) transparent electrode for these applications will increase. The random network of Ag NWs-based electrode is a promising candidate, as presently reported using resistive-type panels [135, 136]. Therefore, fabricated capacitive touch sensors [137], these investigations showing clearly that Ag NW-based technology offers high performance for across many applications, and has the potential to replace ITO in the short term for future flexible touch-screen panels [138]. Lee et al. [135] investigated flexible electrode touch panels based on very long Ag NWs. In this study, a vacuum transfer method was used to produce touch panels by coating Ag NW networks on glass substrates. ITO is sputtered on PET substrate, which is placed as the flexible top as well as the bottom transparent electrodes. The produced touch panel is a resistive type, which is inserted between Ag NW’s upper electrode on glass and ITO lower electrode on PET substrate. This touch panel has been demonstrated successfully, and shows good transparency and performance in an LCD screen. This study summarised that the used of long Ag NWs is promising in many optoelectronics applications.

2.4 Polymer Latex

The stable colloidal dispersion of polymer particles in an aqueous medium (usually water) is defined as latex - it is synthesized via emulsion polymerisation by using a variety of initiators, surfactants and monomers [139]. There are a variety of applications where latex dispersions are used to produce mechanically coherent films. Some of these include paints, coatings, adhesives, caulks and sealants[140]. In addition to these common products, there are many other industrial applications, such as pressure sensitive adhesives, carpet backing, floor polish, textiles and textile sizing, coatings for drug delivery and sustained/controlled release[141, 142].

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2.4.1 Latex Film Formation

The concept of latex film formation refers to a process comprising different stages or steps such as compaction, deformation, and interdiffusion of polymers across particle-particle boundaries (coalescence). The formation of a continuous film (i.e. transparent and crack-free) is dependent on the minimum film formation temperature (MFFT) which can be defined as the lowest temperature at which the process of formation can take place. Formation undertaken below this temperature can be result in cracking or whitening [140]. The process of film formation is experimentally divided into a number of stages, as indicated in Figure 2-15 [143]. In the first stage, which corresponds to the wet initial stage, the inter distance is reduced and the concentration rises until a dense packing of spheres is achieved. This packing occurs as a result of surface tension (water-air interfacial tension) and capillary forces [144], Stage II, involving particle deformation, is an essential part of film formation. In order to produce a uniform void-free film, it is necessary to first dry latex above the MFFT. The formation of latex particles into rhombic dodecahedra structures results in the reduction of interfacial energy and capillary forces. However, in the event that the drying process of latex has taken place below MFFT, the polymer particles will not be deformed and the interstices will be filled with air, resulting in a non-transparent powdery film. In stage III, called coalescence, interdiffusion of polymers across particle-particle boundaries occurs, producing homogeneous optically clear films [140].
Figure 2-15 Schematic illustrates the mechanism of latex film formation: stage I Evaporation and particle concentration, stage II Particle deformation, and stage III Polymer chain diffusion across particle boundaries. Redrawn from [151].

2.4.2 Driving Force for Latex Film Formation

As mentioned, at the second stage of the film formation the deformation will start to take place. The causes of such a deformation have been extensively researched and it is therefore highly probable there are several driving forces in operation in that stage. However, the proposed driving forces for latex film formation include dry sintering, wet sintering, capillary deformation and capillary ring [145].

*Wet sintering* at the polymer-water level: Interface tension is considered as the driving force for deformation, and consequently the interfacial free energy will decrease due to the elimination of the interfacial area between particles.

*Dry sintering* at the dry sintering level: The main force for deformation is the surface tension between the polymer and air, which leads to a reduction in the surface area between particles [146].
Capillary deformation at the water-air interface: In the wet film the meniscus will occur. Therefore, the meniscus will create negative pressure which is called capillary pressure, thus leading to compression of the particles.

2.4.3 Cracking of the Polymer Latex Film

Cracking of polymer latex films has received considerable attention in recent years due to its undesirable outcomes in many important applications such as paints and coatings. As mentioned in 2.4.1, a thin film of latex dispersion is applied on a water resistant substrate during the second stage of film formation. Water is evaporated, which subsequently leads to an increase in solid contents. In the state of stable dispersion, the strong interparticle repulsive forces are sufficient to disperse the particles, overcoming the tendency of attractive forces to bring them together. The continued evaporation of water leads the particles being concentrated into a closed packed array, which is accompanied by the development of stresses in the wet film [147, 148].

Depending on the polymer glass transition temperature (Tg) and ambient temperature, the final film may be homogeneous or it may contain a large number of cracks. It has been observed that if the polymer particle’s Tg is higher than the ambient temperature, the state of the polymer will be glassy and suitable for making a hard coating system. However, the latex particles’ deformation and coalescence will not take place under these conditions. Hence, the final film inevitably includes a large number of cracks [145, 149].

In addition, the liquid meniscus will undergo a large degree of bending at the top layer of the particle network during the evaporation. Compressive capillary force will therefore be more pronounced on that network [150]. Ambient conditions are also found to affect the way cracks form and grow. In an experimental study by Lecocq and Vandewalle [151], it was found that the drying rate has a strong effect on crack nucleation and growth, with fast drying generating a large number of small cracks and slow drying resulting in a small number of larger cracks.

In order to obtain a crack-free coalesced film, the film formation temperature (Tff) must be higher than the Tg. There are two ways to carry out the film formation: firstly, by adding a volatile plasticiser to reduce the polymer’s Tg to below the Tff. This process,
however, is undesirable for health and environmental reasons. The second approach involves sintering the latex film through applying the $T_f$ (which must be greater than the polymer’s $T_g$) onto the film by placing the film in the oven or under infrared (IR) sources [152].
References


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Chapter 3  Experimental Techniques

3.1 Deposition Technique

3.1.1 LB Deposition Technique

3.1.1.1 LB of Amphiphilic Molecules

There has recently been more demand for increasingly smaller devices with higher speed and performance. In this regard, the development of thin film technologies plays an essential role in the process of realising molecular-level devices. There are various techniques available for producing high quality thin films, such as sputtering [1], molecular beam epitaxy [2], electrodeposition [3], self-assembly [4] and LB [5]. The most promising technique which can provide real monomolecular assembly for different applications is the LB technique. Some of LB’s advantages over others techniques are:

1- Controlling the thickness of the monolayers;
2- The enablement of a homogenous deposition of the monolayer film over large area;
3- The possibility of building multilayer structures with potentially varied compositions;
4- Low cost.

3.1.1.2 Short History of the LB Technique

In 1774, Benjamin Franklin reported to the British Royal Society that small amounts of oil dropped onto a large pond spread well, covering about half of the area of the pond’s surface [6]. A German researcher named Agnes Pockles, roughly 100 years later, [7] improved upon Franklin’s demonstration by relating surface contamination of a water layer to the type of oil used, publishing his findings in Nature in 1891. However, the first researcher to perform a significant investigation on floating monolayers at the air/water interface was Irwing Langmuir in 1910, research which earned him a Nobel prize [8]. Katherine Blodgett, several years later, detailed sequential monolayer transfer
onto a solid substrate. The resulting technique is therefore known as LB film deposition, after its two pioneers [5]. Currently the LB process is one of the most widely-used techniques for producing monolayer films.

**Figure 3-1** The LB trough is designed for the deposition of LB layers by conventional vertical or horizontal dipping onto substrates.

3.1.1.3 Fundamentals of Surface Chemistry

In order to understand how the LB technique works, it is important to understand fully the fundamentals of surface chemistry and the underlying theory. Surface tension is an important property that must be understood. Forces acting on molecules in bulk and molecules at the surface are totally different. In the bulk of the liquid, the molecule is surrounded by other molecules in all directions and experiences equally balanced forces from the surrounding molecules. Molecules on the surface, however, act as an interface between two phases (liquid and air). From one side, molecules are subjected to a strong attractive force from other molecules below in the bulk, while from the upper side there is little or no attractive force from the gaseous phase (Figure 3-2 [9, 10]).
Figure 3-2 Schematic shows interaction of molecules at a gas-liquid interface.

3.1.1.4 LB Forming Materials

Amphiphilic materials can be considered as a class of compounds that can form a stable monolayer on the subphase. These kinds of material contain both hydrophobic and hydrophilic constituents. Typically, the hydrophilic part is represented by small functional head groups, and the hydrophobic part is formed by long tail groups which contain aliphatic chains. Spreading these materials onto the water subphase leads to the immersion of the hydrophilic heads in the water and causes them to distribute evenly on the available surface area. Importantly, the molecules will not dissolve when in water due to the existence of hydrophobic tails [11].

3.1.1.5 Isotherms of Amphiphilic Materials

The characteristics of the monolayer material on the water surface are analysed by measuring changes in surface tension in terms of the surface area per molecule (surface area available to each molecule) upon compression of a monolayer. Surface pressure-area (P-A) isotherm is performed by applying compression at a constant pressure.

\[ P = \gamma^o - \gamma \]  \hspace{1cm} 3.1

where \( \gamma^o \) is the surface tension of the pure subphase and \( \gamma \) is the surface tension after applying the dispersion. The shape of the isotherm provides the two dimensional signature characteristic of the molecules that make up the monolayer film. Many physical parameters such as temperature, composition and pH play a part. Consequently, barrier speed, relative humidity and the solvent used to deposit the surfactants may all affect the shape of the isotherm [11]. As such, it is crucial to
perform the isothermal compression in a controlled environment such as a clean room. For a typical surface pressure-area isotherm, there are a number of distinct regions or phases of the isotherm, displayed in Figure 3-3. Initially, when the surfactants are transferred on to the surface of the subphase, the monolayer will find sufficient area. The molecules can at this point be considered to be in a two-dimensional gaseous phase. Under this condition, the molecules have very little effect on the surface tension of the subphase. As the surfactant molecules on the subphase are compressed, the mean distance between molecules starts to decrease and they begin to exert stronger forces on each other. The surface pressure of the system increases, and it can then be considered to be in a two-dimensional liquid phase. Further compression will cause the molecules to draw closer together and become more compact. The surface pressure starts to increase steeply and linearly. The molecules are now in a two dimensional solid phase. With continued closing of the barrier, the forces acting upon the molecules become too strong for confinement in two dimensions and the molecules start to slip either into the subphase or onto the monolayer. The surface pressure corresponding to this point is called the Collapse pressure. The film irreversibly loses its mono-molecular form [12].

![Figure 3-3 Schematic representing surface pressure-area Langmuir isotherm of amphiphilic material showing three phases: gas, liquid and solid.](image)

**Figure 3-3** Schematic representing surface pressure-area Langmuir isotherm of amphiphilic material showing three phases: gas, liquid and solid.

### 3.1.1.6 Film Deposition of Amphiphilic Molecules

At the solid phase stage, the floating molecules are arranged compactly where the surface pressure has to be high enough to form a cohesive monolayer. With the proper mechanism, the monolayer-thin film can be transferred onto a solid substrate which can later be used for
characterizing or for fabricating monolayer devices. The deposition procedure is controlled by moving the substrate up and down while keeping the surface pressure at a constant value, as shown in **Figure 3-4** (A). It is crucial that the surface pressure during the deposition process is high so that the attractive force between the molecules remains sufficient to prevent them from de-aggregating during the transfer process. Multilayer structures will be produced by repeating successively the dipping and withdrawing process [12]. However, LB will be used for depositing latex polymer which will be discussed in chapter 6.

Furthermore, since LB film is done by dipping the substrate vertically onto the trough. A Langmuir-Schaefer (LS) film can be defined as one or more monolayers of material deposited from a liquid surface onto a solid substrate. The way of deposition can be done by dipping the substrate horizontally through a floating monolayer as shown in **Figure 3-4** (B). LS will be used for depositing graphene on the top of Ag NWs electrodes as will be discussed in chapter 4.

**Figure 3-4** Schematic representation of (A) LB and (B) LS for transfer amphiphilic monolayer to a substrate.
3.1.2 Spray Deposition Technique

There are a wide variety of solution-based techniques for producing thin films. Spray deposition is one technique which has been applied in the production of various optoelectronics devices, such as organic photovoltaic, sensors and organic light emitting diodes [13]. The most attractive features of the spray deposition technique lie in its simplicity and the low cost in terms of the equipment. Moreover, it also allows for the production of a more homogenous and uniform film with a large area [14].

The simple spray system is comprised of an airbrush and air compressor. However, the optimisation of preparation conditions is the main controlling variable on the quality of fabricated samples. Namely, the distance between the nozzle and the sample, the deposition pressure and the substrate surface temperature are parameters which can negatively influence film quality if they are not optimised [15].

3.1.3 Spin Coating

Spin coating is one of the most common techniques used for the deposition a variety of materials, especially soluble organic materials [16]. The typical procedure of spin coating involves centring a substrate on the stage of the spin coater and covering it with a solution. The film is then fabricated by centrifugal force, as the solution spreads over the stage [17]. Spin speed, solution concentration and molecular weight are the main parameters which control film thickness [17].

3.1.4 Drop Casting Technique

Drop casting is considered to be the simplest method for fabricating thin film [18]. By casting a solution on a horizontal substrate, the film is fabricated and the solvent evaporates. The main disadvantage of this method is that there is no degree of control over film thickness [18].

3.2 Characterisation Techniques

3.2.1 UV-Vis Spectroscopy.
Materials analysis by absorption, emission or scattering of electromagnetic radiation is called spectroscopy. This field is concerned with the interaction of radiation with matter, which can lead to the redirection of the radiation or cause energy transitions of the molecules or atoms. Absorption is the transition of a state (i.e. rotation, vibration or electronic) from a low to a higher level with the transition energy of electromagnetic radiation of molecules or atoms. In contrast, the transition from a higher to a lower level is called emission (either radiative or non-radiative), while scattering is the result of redirecting light due to inelastic or elastic interaction with matter.

Absorption spectroscopy, in keeping with the principles mentioned above, is based on electronic transitions. According to Beer’s law, the absorbance depends on the incident light intensity \( I_0 \) and the transmitted light intensity \( I \), indicated in Beer-Lambert Law:

\[
A = \log \frac{I_0}{I} = \varepsilon c \tag{3.2}
\]

\( \varepsilon \) is molar absorptivity, \( l \) is path length of the sample and \( c \) is the solution sample’s concentration. Therefore, by plotting absorption as a function of wavelength, one obtains an absorption spectrum.

UV-Visible spectroscopy is an important technique for investigating the electronic and optical properties of nanomaterials. Figure 3-5 shows the diagram of a typical spectrometer which contains a light source, monochromator for dispersing the light, sample and reference, detector and a computer.
3.2.1.1 Integrating Sphere

The aim of using the Integrating Sphere Accessory is allowing the light beam in transmission mode to pass straight through samples without being spread out by scattering or diverted by refraction. The opaque samples are analysed by placing them in the back of an integrating sphere, so that light is reflected off them, allowing the bounced scattered light to be gathered. Conversely, transparent samples which allow light to pass through, but scatter it, can be analysed by placing that sample in the front of the integrating sphere, allowing transmitted light to be gathered. The two methods of analysis are similar in that the emergence of the scattered light takes place from the hemispherical pattern, as shown in Figure 3-6.

The integrating sphere is presented as a kind of Diffuse Reflectance Accessory (DRA). Diffuse reflectance refers to the reflectance which occurs when light is reflected off a matte surface. This is in contrast to specular reflectance, which occurs from mirror-like surfaces. The internal surface of the integrating sphere accessory is coated with a material with very high diffuse reflectance.
Figure 3-6 (A) Spectrometer with attached integrating sphere. (B) Integrating sphere-based UV.

3.2.2 Atomic Force Microscopy

AFM is a sophisticated technique for the study of the topography of a sample in x, y as well as z direction. It utilizes a sharp tip at the end of a cantilever that moves over the sample in a raster scan and bends in response to the force between the tip and the sample. An optical lever technique is employed for the operation, as shown in Figure 3-7. As the cantilever bends, light from the laser is reflected onto the photodiode. The difference in the signal is used as a measure of bending of the cantilever. The bending of the cantilever obeys Hooke’s law [19]:

\[ F = -kz \]  

For small displacements, the force between the tip and the sample can be calculated. Figure 3-7 presents a diagram of a typical AFM. The forces which can be measured with this technique are: van der Waals, capillary forces, contact forces and electrostatic forces.
Figure 3-7 Schematic illustration of Atomic Force Microscope (AFM).

The scanner is capable of sub-Angstrom level resolution in the x, y or z direction, z being the direction perpendicular to the sample. The AFM can be operated in two modes, namely a feedback control mode and a control mode without feedback. The feedback control mode works with constant force between the tip and the sample, where the piezo which moves the sample (or the tip) responds to any change in the force between the sample and tip and alters the separation between the two to restore the original value of force. This measurement is known as height mode measurement and enables reliable topographical analysis of the sample. When the feedback control mode is off, the measurement is performed at constant height (deflection mode), which is useful in high-resolution analysis of samples that are extremely flat. AFM incorporates several refinements such as sensitive detection, flexible cantilever, sharp tips, high-resolution precise tip-sample positioning and force feedback, which enables it to achieve atomic level resolution. Since the imaging process uses the force of interaction of the atoms on the tip to that of the sample, AFM is used for imaging even the non-conducting samples.

AFM measurements can be performed in contact, semi-contact or non-contact modes, the difference being the extent of tip-sample interaction during the measurement. Contact mode AFM is the most commonly-used method, where the tip remains in close contact with the sample during the scanning process. The repulsive regime in the intermolecular force curve represents the interaction force between the tip and the sample as it illustrated in Figure 3-8.
Semi-contact mode can be applied for studying soft materials, biological matter and other samples which are weakly bound to their substrates. Figure 3-8 shows the state of force interaction which takes place between the tip and the sample. The tip oscillates at its resonating frequency and is positioned over the sample so that it makes contact with the sample for a short time interval during oscillation. The topography of surface is shown as a height image. Furthermore, the shifting phase of the oscillating cantilever is recorded and provides some idea about the quality of material properties such as chemical composition, adhesion or elasticity and friction. Non-contact AFM mode is also a non-destructive mode, being performed by using large-range interactions where the oscillation of the cantilever is above the sample’s surface. Non-contact mode will be operated in the attractive regime of the inter-molecular force curve. Notably, soft surfaces can be studied in this mode, but its major disadvantage lies in the fact that it is sensitive to any condensed water on the surface [15].

![Interatomic forces vs. distance curve](image)

**Figure 3-8** Interatomic forces vs. distance curve, where the repulsive part is dominated by electrostatic interactions and the attractive part is dominated by dipole-dipole interactions.

3.2.3 Scanning Electron Microscopy (SEM)

SEM is a form of electron microscopy which obtains images by focusing a primary electron beam on the sample’s surface. The interaction between the beam and the atoms
takes place in 3-dimensional space, known as the interaction volume. In the interaction volume the scattered electrons can be divided into two interaction types: inelastic scattering and elastic scattering. During the inelastic scattering, where the electrons transfer energy and change direction with every interaction of atom, the production of secondary electrons, backscattered electrons and X-rays occurs. By analysing the detected singles of secondary electrons, high-resolution images of the morphology of the sample’s surface will be gained. This can also be completed by using backscattered electrons. Both of these are able to provide information from a few nanometres of a sample’s surface [20].

![Figure 3-9](image.png)

**Figure 3-9** SEM’s schematic representation of the interaction between an electron beam and the sample [21].

### 3.2.4 Contact Angle Measurement

Contact angle is defined as the angle which is formed by the intersection of liquid-vapour and liquid-solid interfaces. For example, if a liquid droplet on a horizontal flat surface spreads on that surface, a small contact angle will be observed. In contrast, a large contact angle is observed when the drop does not spread on the surface. Measurement of the contact angle is essential for the study of wettability; contact angle is a clear indicator for the wettability degree during the interaction of solid and liquid. In particular, full wettability occurs at $0^\circ$ contact angle for hydrophilic surfaces, while
the greater 90° contact angle reflects low wettability for hydrophobic surfaces, as illustrated in Figure 3-10.

Furthermore, the liquid droplet shape is governed by the surface tension. Every molecule in a pure liquid is pulled in all directions equally by neighbouring molecules, resulting in an overall force of zero. However, molecules located on the surface have an unbalanced net force in every direction, as they are not surrounded by other molecules in every direction. In this sense, they are pulled inward by neighbouring molecules.

Experimentally, the equipment used for contact angle measurement consists of a flat stage, a micrometre syringe to apply a liquid drop, a light source, and an integrated camera and telescope. The motorised syringe can be controlled to apply the appropriate amount of liquid. The measurement is achieved by aligning the tangent of the sessile drop profile at the contact point with the surface, and allowing the software to compute the contact angle.

![Figure 3-10] Schematic diagram illustrating wetting of different fluids. (A) Shows a fluid with more wetting and a small contact angle < 90°, (B) medium wetting contact angle=90° and (C) little wetting large contract angle > 90°.

3.2.5 Electrical Measurements

3.2.5.1 Sheet Resistance

Resistivity is one of the elementary parameters of a conducting material. The symbol ρ with the unit Ω.cm represents the resistivity of a material. Resistance is related to resistivity, shown as:

\[ R = \rho \frac{L}{wt} \]
Where \( L \) is the length of the sample, and \( w \) and \( t \) are the width and thickness of the sample respectively. Since the thicknesses of films is often difficult to measure, sheet resistance is defined to represent resistance per square area of a thin film with the unit \( \Omega/\square \) (Ohms per square) and is given by

\[
R_s = \frac{\rho}{t} \quad 3.5
\]

So

\[
R_s = R \frac{w}{L} \quad 3.6
\]

Thus, the total resistance of a film is proportional to the number of squares that can be drawn on the conducting surface area.

3.2.5.2 Two Point-Probe Measurement

The simplest method of characterizing a material electrically is by using the two-probe method. This method only requires current flow between two connections and the measurement of the voltage between the same probes. Two adjustable probes were used to connect the electrodes of the sample and the set of data was plotted. The sheet resistance is obtained as the reciprocal of the slope in the I-V curve.

3.2.6 Mechanical Analysis

3.2.6.1 Three-point Bending Test

It is necessary to measure the influence of deflection on the electrical properties of the flexible transparent electrode based on Ag NWs and graphene due to the applied bending moments. The three-point bending test is widely used to characterize such mechanical behaviours of materials.

Conducting the test involves placing the sample with rectangular shape on two parallel supports. The sample will be subjected to an external load applied perpendicularly to the longitudinal axis of the sample [22]. Displacement is applied at its centre and the resulting force is recorded.
In this work, the Dynamic Mechanical Analysis (DMA) technique is used to study the influence of the applied mechanical deflection on the optical conductivity of the flexible transparent electrode. DMA is viewed as one of the most versatile and reliable experimental techniques available, and has been used for decades to study the rheology of many kinds of polymers and polymer matrix composites. It uses a highly specialized optical encoder to measure displacement that enables it to achieve a resolution of 1nm [23] Its precision in identifying mechanical transitions of polymers makes it the most favourable material characterization technique for this study. The accuracy and reliability of experimental results can, however, be affected by the quality of the prepared samples.

3.2.6.2 Strain Tensile and Bending Test

The strain tensile test can provide important information about the strength of materials, and is an accepted test to specify the material. By pulling a sample, the reaction of the sample to tension can be measured relatively simply. Additionally, the degree to which the pulled material will elongate can be determined. Moreover, a complete tensile profile can be obtained for the materials that are subjected to the test. The resulting curve shows the reaction to the force being applied. Figure 3-11 shows a typical stress-strain curve.

Figure 3-11 Typical stress-strain curve of a polymeric material. A is the proportional point (The point where the behaviour starts to be non-linear), B the yield point (The local maximum in the stress-strain curve) and C the break point.

In order to study bending and stretching of the flexible electrode and investigate the electrical stability of this electrode under these conditions, a strain-tensile experiment
for bending test was carried out in cycling mode, which was sufficient to bend the sample for a large number of bending cycles. In order to test stretching, a normal strain tensile test was also carried out.

**Stress**

Stress is a quantity that is proportional to the force causing a deformation; stress (σ) is the external force (F) acting on an object per unit across sectional area (A).

\[
\sigma = \frac{F}{A} \tag{3.7}
\]

When a sample is stressed, separation or orientation of the molecular structure occurs, bringing about a change in its dimensions. However, to describe the change in the sample’s size, one must monitor the associated strain.

**Tensile strain**

Applying force to a sample with initial length \((l_0)\), results in a change to a new length \((l)\) after stretching. Therefore, the tensile strain (ε) is the ratio of the difference between the initial length \((l_0)\) and the final length \((l)\) relative to the initial length, as in the following relationship:

\[
\varepsilon = \frac{l - l_0}{l_0} \tag{3.8}
\]

The relationship between the stress and the strain can be described by Hooke’s law, which states that the strain is proportional to the stress, by the following relationship.

\[
\varepsilon \propto \sigma
\]

This can be rewritten as:

\[
\sigma = \text{constant } \varepsilon
\]

So, the constant is defined by the elastic or Young’s modulus. Young’s modulus can be extracted from the initial part of the slope of stress-strain curve in the elastic region. However, this expressions will be used to analyse the mechanical properties during the mechanical test which will be performed on Ag NWs and Ag NWs with graphene in chapter 4 and 5.
References


Chapter 4 Transparent Flexible Electrode Based on Ag NWs and Graphene

4.1 Introduction

Transparent electrodes are a crucial part of many electronic devices, including organic solar cells, displays (Liquid Crystal Displays (LCDs), and touch panels. Transparent electrode thin films are optically transparent to visible light and are also electrically conductive, enabling their use in applications where light needs to enter or leave a device. Organic solar cells, for example, use transparent electrodes as either anodes or cathodes to complete the solar cell circuit, at the same time allowing visible light to pass through the film and generate charge carriers [1].

The most common materials used for transparent electrodes are metal oxides, particularly ITO, which is the most popular material for transparent electrodes. ITO can provide highly transparent electrodes (80-95%) with low sheet resistances (10-1000 Ω/sq). Metal oxides owe their transparency to their band gap energies, which are larger than the energies of photons in the visible range. The band gap of ITO, for example, is 3.8 eV [4].

For a particular application, the transparency and sheet resistance of an ITO film can be controlled through the film’s thickness [2]. Therefore, there exists a trade-off between transparency and resistance; a film with lower resistance requires a thicker ITO layer, which results in lower transparency. In addition, new device technology has necessitated new features for transparent electrodes, such as flexibility, low cost, light weight, and an easy fabrication processes [2].

As established in the introduction of the first chapter, ITO cannot meet all the new expected qualifications for the innovative next generation of electronics. ITO has ceramic properties, meaning that it is not flexible; a small amount of strain as low as 2-3% can initiate cracks in ITO film on flexible substrates, which reduces electrode conductivity and dramatically affects device performance [3]. Secondly, indium is a rare material, the price of which is volatile and with an overall upward trend [4]. Thirdly, the fabrication of ITO is costly; it requires high temperatures and a high vacuum to enable control over thickness and doping concentration [4]. Additionally, its
production relies on sputter deposition, which can damage the underlying layers of organic devices. An additional coating needs to be applied to solve this problem, a process which further elevates production costs.

Therefore, many researchers have focussed on finding an alternative material over the past decade. This issue is of particular importance where preparation is concerned, as the ability to prepare a large area of flexible electrodes, which are compatible with the flexible nature of organic materials over inorganic ones, enables a wide array of potential applications for organic optoelectronic devices. Much work has been done to overcome the difficulties presented by the current methods. More recently, scientific attention has been focussed on networks of CNTs [5-7], graphene flakes [8-10], and metallic NWs [3, 11-16]. Regarding the minimum industry standards (T>90%, Rs<100Ω/sq), CNTs and graphene flakes fall below the threshold; the inherently large junction resistances associated with nanotube and graphene junctions preclude their use in this field [17]. Therefore, metallic nanowires are at present the most promising nanomaterial - in particular, Ag NWs and Cu NWs. However, in the case of Cu NWs, their application is limited by their low aspect ratio [18]. Electrospinning has been explored as a way to produce continuous 1D copper nanofibers, requiring complex fabrication methods including high temperatures [18]. Ag NWs, however, do not suffer from such a disadvantage, making them excellent candidates for transparent, highly conductive electrodes [13].

Recent years have seen the incorporation of other 2D materials in order to overcome some of the drawbacks of Ag NWs, such as the contact resistance of inter-nanowire junctions [19, 20]. Accordingly, graphene has been used to enhance the electrical response of electrodes; it is also effective in producing flexible transparent electrode stretching, which may see major advances in future device structures [21-23].

In transparent conductor research, it is crucial to compare the performance of new materials against known standards. Transparent conducting materials are generally compared using FoM [24]. A FoM is determined by comparing the material’s transmittance to its electrical conductivity, and relates how they are affected by the physical properties of the electrode. The optical properties of a thin film can be
analysed using the Lambert-Beer law, which relates optical transmittance to the thickness of the material:

\[ T = e^{-\alpha t} \]  \quad 4.1

Where \( \alpha \) is the absorption coefficient and \( t \) is the film thickness. For a bulk-like metal system it is well-recognised that optical transmittance is directly related to the electrical properties of the material, as light transmission is determined by the interaction of impinging photons with the plasmonic states in the metal. Hence the above expression can be modified to reflect this inference, and the transmittance can be directly related to the sheet resistance:

\[ R_s = (\sigma_{DC,B} t)^{-1} \]  \quad 4.2

Where \( \sigma_{DC,B} \) is the DC conductivity of a thick (bulk-like) network. Here \( t \) can be eliminated from the equation, by using the relationship between \( T \) and \( R_s \):

\[ T = e^{-\alpha / \sigma_{DC,B} R_s} \]  \quad 4.3

However in nanostructured transparent conductors, the following Equation is often used to calculate the relation between \( T \) and \( R_s \) [24-26]:

\[ T = \left(1 + \frac{Z_0}{2} \sigma_{Op} t \right)^{-2} \]  \quad 4.4

where \( Z_0 = 377 \ \Omega \) is the impedance of free space, and \( \sigma_{Op} \) is the electrical conductivity of such a network in the presence of an alternating electric field (optical conductivity) [25]. This equation could be rewritten to directly relate \( T \) and \( R_s \) as:

\[ T = \left(1 + \frac{Z_0 \sigma_{Op}}{2R_s \sigma_{DC,B}} \right)^{-2} \]  \quad 4.5

Surprisingly, when one approaches the monolayer limit where the electrode structures are very thin, the networks tend to exhibit sheet resistances considerably higher than
predicted by equation 4.2. This is explained by the DC conductivity, which in thin networks is no longer thickness independent but follows a percolation-like thickness dependence [27]. According to percolation-like behaviour, \( \sigma_{DC} \propto (t-t_c)^n \), where \( t \) is the estimated thickness of the network, \( t_c \) is the minimum thickness required to form the first conducting path, and \( n \) is the percolation exponent. This leads to a new relationship between \( T \) and \( R_s \) which applies to very thin, transparent networks.

\[
T = [1 + \frac{1}{\Pi} \left( \frac{Z_0}{R_s} \right)^{1/(n+1)}]^{-2}
\]

where \( \Pi \) is the percolative FoM

\[
\Pi = 2\left[ \frac{\sigma_{DC,B}}{\sigma_{Op}} \right]^{1/(n+1)}
\]

Here, \( t_{min} \) is the thickness below which the DC conductivity becomes thickness dependent and \( \Pi \) is a dimensionless number. It is clear from analysis of the above expression that large values of \( \Pi \) give low \( R_s \) coupled with high \( T \). Hence, a high value of \( \Pi \) but low values of \( n \) are optimal to achieve low resistance coupled with high transmittance [26, 27]. Achieving the highest value for the ratio of optical conductivity to electrical conductivity is a driving goal in producing functional electrodes.

Solution process techniques such as spraying deposition [28, 29], drop casting [14, 29], spin coating [30, 31] or rod-coating [32] offer simple and inexpensive production of the random structure of NW networks. The spraying deposition technique is more readily applicable, and is able to produce film with more homogeneity.

In this chapter, a novel method of fabrication and characterisation of a flexible transparent electrode based on Ag NWs and Ag NW/graphene is described. To my knowledge, this is first time that this kind of electrode on PMMA substrates has been produced. Initially, the spray deposition technique was used for producing Ag NW electrodes on PMMA flexible substrates with different densities. Subsequently,
however, a way to enhance the electrical and mechanical properties of Ag NW transparent electrodes was also developed - depositing graphene on the top of the flexible Ag NWs electrodes via the LS process. In this chapter, both fabricated electrodes will be characterised morphologically, optically, electrically and mechanically. The overall aim of this work is the production of transparent conductive electrodes with attractive flexible, optical, electrical and stable features, as well as low production costs.

4.2 Experimental method

4.2.1 Ag NWs Dispersion

Ag NWs were supplied by Cambrios as suspensions in water. Typically, 0.75 ml of the dispersion was added to 10 ml of IPA (isopropyl alcohol) to give a concentration of 0.075mg ml\(^{-1}\). Figure 4-1 shows a photograph of a vial containing a typical dispersion of Ag NWs in IPA. The dispersions are stable for extended periods with no appreciable sedimentation witnessed over days.

![Figure 4-1 A photograph of Ag NWs dispersion of 0.075mg ml\(^{-1}\) in IPA.](image)

4.2.2 Graphene Dispersion

Graphene dispersion was prepared by collaborators from Trinity College Dublin. In a typical dispersion procedure, 2.5g of graphite powder, purchased from Sigma Aldrich (product number 332461), was added to 100ml of aqueous surfactant solution (0.5 mg/ml triton X-100) to give an initial graphitic concentration of 25 mg/ml. This mixture was sonicated using a sonic tip (Sonics VX- 750 ultrasonic processor with flat head tip).
for 4 hours at 75% of maximum power (i.e. 75% of 750 W nominal max power). The dispersion was left to stand overnight. The top 50 ml was decanted into 2 x 28.5ml vials and centrifuged (Hettich Mikro-22R) for 90 minutes at 1500 rpm. The top 14mls were then decanted into a 14ml vial.

1 ml of the original NMP dispersion (5 mg ml\(^{-1}\)) was added to 50 ml of chloroform and sonicated by bath sonicator for 30 minutes. The mixture was then divided into 4 dispersion samples in order to centrifuge them at different times: 0, 30, 60, and 90 min.

### 4.2.3 Spraying Deposition

The spray system comprises an airbrush, air compressor, and a movable stage where the substrate is placed. By pouring the silver nanowire dispersion into the cup and pressing the main lever, a stream of sprayed dispersion emerges. Notably, the spraying pattern depends largely on the distance between the airbrush and substrate (15 ±2 cm) and the air pressure (4bars), as illustrated in Figure 4-2.

**Figure 4-2** A photograph of the spray system which comprises an airbrush, air compressor, and movable stage where the substrate is placed.

### 4.2.4 Preparing LS Method of Graphene Monolayer

The LS graphene monolayer was prepared using the Langmuir technique (Nima technology). A graphene dispersion of 0.04mg/ml was spread in the trough by dropping 8-10 ml slowly in a drop-by-drop manner. The solvent was allowed to evaporate for approximately 10 minutes before the barriers were closed at a speed of 15mm/min, with the result that the P-A isotherm was obtained. The monolayer was transferred from a film formed by a cycling method: comprising and expanding the PMMA substrate
(electrode of Ag NWs) by the LS method with the rising speed of 1mm/min and three different pressures - 5, 10 and 15 mN/m.

### 4.3 Characterisations

The surface morphologies of Ag NW and the hybrid films of Ag NW/graphene were observed by SEM (JEOL JSM-7100F), AFM (semi-contact mode using NT-MDT AFM (Moscow, Russia)) and optical microscopy. The measurements of optical haze and reflectance of pristine Ag NWs electrodes with different densities were carried out using an integrating sphere (Cary 5000 UV-Vis-NIR Spectrophotometer Varian). In addition, optical transmittance of both pristine Ag NWs and the hybrid Ag NWs/graphene was undertaken using UV-Vis-NIR Spectrophotometer (Cary 5000 UV-Vis-NIR Spectrophotometer Varian). Mechanical characterisations of both Ag NWs and Ag NWs/graphene hybrid electrodes were carried out using a commercial instrument (Stable MicroSystems Texture Analyzer, Godalming, UK) which was utilised in stretching and bending tests.

I-V characteristics were obtained using a standard two-probe technique (Keithley Model 4200). Silver paint was deposited at the edges of the rectangular glass substrates with a conductive film on top.

### 4.4 Results and Discussions

#### 4.4.1 Fabricating Ag NW Networks on PMMA Substrate

The spraying deposition technique was used to produce an Ag NW randomly distributed network on PMMA substrate, as illustrated in Figure 4-3. Ag NWs in IPA dispersion (0.07mg/ml) were prepared and sprayed down in a controlled procedure, as described in 4.2.1. In order to manage the production of a conductive Ag NW network, a range of electrodes with varying density of Ag NWs was prepared by altering the spraying time. Figure 4-4 illustrates height images of AFM and optical micrographs images of the three different densities achieved: low, medium and high. In this figure, (a, d) represent the low density Ag NW networks with Rs of 30 KΩ/sq, while (d, e) show the medium density of the network where Rs is 1300 Ω/sq. High density is represented by (c, f) with Rs of 35 Ω/sq.
Figure 4-3 Schematic diagrams of (a) Spray system comprising an airbrush, which is vertically mounted onto a controlled plate, movable in the x and y directions, and (b) the sample Ag NWs on PMMA substrate with contacts.

![Figure 4-3](image)

As the density was increased, the network become more conductive, and the transmittance decreased accordingly. 1D structure Ag NWs were placed randomly, creating an arbitrary network which allowed charge carriers to pass in different directions.

Figure 4-4 (a-c) AFM height images (20x20µm) and (d-f) Optical micrographs of sprayed sliver nanowires at three different densities of Ag NWs: high, medium and low.

![Figure 4-4](image)
directions. AFM and optical microscopic images describe the Ag NWs network densities, which were achieved by varying the number of spray repetitions. By increasing the density of the film, the network becomes thicker, resulting in increased conductivity and decreased transmittance.

Therefore, to demonstrate the Ag NWs network density’s effect on conductivity and transparency, Figure 4-5 is provided, showing the relationship between the optical transmittance and the sheet resistance. As described in the above expression in equation 4.7, the percolative FoM $\Pi$ should be as large as possible to give low Rs coupled with high T. Furthermore, it is desirable if the high value of $\Pi$ is combined with low percolation exponent n. The fitting of T-Rs data gives $\Pi = 91.19$ and $n = 2.25$.

In most cases, percolation behaviour begins to occur for the Ag NWs electrode with $T > 90\%$, meaning that the expected bulk-like behaviour does not take place in this region – a feature desirable for the optoelectronics device industry. In particular, to compare the value of $\Pi$ and n, Sukanta De et al. reported that the FoM $\Pi = 31.7$ and $n = 1.9$ for Ag NWs network [24]. So, the $\Pi$ and n values obtained in Figure 4-5 show a remarkable enhancement in the Ag NW’s electrode conductivity. As reported, the n value is taken as a variant range from 1-4 which lies within the expected limits of the percolation exponent.

![Figure 4-5 Transmittance (550 nm) plotted as a function of sheet resistance for thin films prepared from Ag NWs networks deposited at different densities.](image)

4.4.2 Optical properties of silver nanowires on PMMA substrate
4.4.2.1 Optical Haze

Optical haze is the scattering of light by a medium, leading to low clarity of any objects observed through said medium. In short, optical haze is the amount of light which is diffusely [33] scattered by a transparent surface, given as a percentage of total transmitted light.

Optical haze is a quality which is maximised for some applications and minimised for others. In the case of photovoltaic devices, a large haze value leads to enhancement of the optical path length, where light-trapping structures are required to improve light absorption in the active layer. On the other hand, when applied for displays, optical haze is generally preferred to be kept at a low level, usually <1%.

In this work, the scattering of individual silver nanowire is considered to be the initial point from which to start broadening the investigation of light scattered by the entire Ag NWs network. As mentioned in 3.2.1.1, the haze can be measured by fitting the integrating sphere accessory into the standard UV/Vis spectrophotometer. In practical terms, this is done by determining four transmission scans at different configurations of the integrating sphere for the sample (illustrated in Figure 4-6) and substituting these values into the following equation:

\[
\text{Haze} = [(T4/T2) - (T3/T1)] \times 100\% 
\]

Where T1 is background checking, T2 is total transmitted illumination, T3 is beam checking, and T4 is pure diffusive transmittance.
Figure 4-6 Experimental haze measurement setup: (a) total forward scattered illumination; (b) total transmitted illumination; (c) and (d) are the corrections for the experimental setup.

Many research groups have incorporated Ag NWs as a top electrode for photovoltaic devices [34-36]. It has been shown that Ag NW networks can be produced with optical haze values between 1 and 30% in the visible range [37]. The variant optical haze range which is achieved with Ag NWs networks makes it suitable not only for photovoltaic applications, but also acceptable for display applications [37, 38].

The magnitude of the optical haze in Ag NW network electrodes is reported to be related to the diameter of the wire [39, 40]. In addition, most reports mention that high aspect ratios are obtained by small diameter / long length wires, whereas larger diameters show more scattered cross-sections. To my knowledge, this is the first study which investigates optical haze in Ag NW electrodes on PMMA, which is governed by the density of Ag NWs network.

Optical haze was calculated and compared to the electrodes of each Ag NW density variant. This comparison was undertaken in order to understand the relationship between haze and Ag NW density, highlighting which variant can provide the best enhanced scattering. As discussed in 4.4.1, there is a relation between low sheet resistance and high transmittance of Ag NW electrodes: Figure 4-7 shows that optical haze appears to increase with increasing density of Ag NWs, meaning that conductivity...
is also increased proportionally. Typically, the electrodes with lowest sheet resistance of 39.8 – 337.08 Ω/sq with highest haze of ~ 6.5% – 4.5% are considered as very dense electrodes, while maintaining high transmittance percentages of 97% - 98% at a wavelength of 550 nm, as presented in Figure 4-8 (a, b). For the remaining electrodes, which have sheet resistance from 3.4×10^5 Ω/sq – 1.4×10^6 Ω/sq, low haze value from 1.5 % until 0.5 % are shown.

The aim of the study focuses on the production of a high-conductivity electrode which is conditioned to also hold high transparency percentage values. However, the relationship between the optical haze and Ag NWs network density reveals that the Ag NW network can be fabricated to produce a significant optical haze value. This naturally leads to improvements in light absorption efficiency of solar cells from the increased path of light transmitted into the active layer, resulting in an enhanced short circuit current density.

Figure 4-7 Optical haze (%) as a function of wavelength of Ag NWs electrodes with different sheet resistance.
4.4.2.2 Optical Reflectance

The optical path of the incident light can be varied by the scattering effect. It has been reported that the light reflection caused by the specular and diffuse is considered a significant problem for the light transmitted through Ag NWs electrodes [13, 14, 24].

Figure 4-8 (a) Transmittance (at 550 nm) as a function of optical haze (at 550 nm), and (b) optical haze (at 550 nm) as a function of sheet resistance.
However, the reflectance measured by the standard method, which presents only specular reflection (mirror-like), cannot alone provide sufficient evaluation of Ag NW networks. Therefore, specular and diffusive reflectance were measured by using the integrating sphere accessory, which was fitted onto the spectrophotometer, as illustrated in Figure 4-9.

**Figure 4-9** Experimental setups during reflectance measurement. (a) Position 'S' measures total reflectance by including the specular component and (b) Position 'D' measures diffuse reflectance only.

**Figure 4-10** (a) shows the comparison between total (specular and diffusive) reflectance, diffuse reflectance and specular reflectance of different Ag NW densities as presented at the wavelength of 550 nm. It was observed that the total reflectance (specular and diffusive) increases with Rs. The significant increase was in observed close to the region of the medium density of Ag NWs network and sharply increased until it reach the very conductive network with Rs of ~40 Ω/sq with total reflectance of ~17 %. This increase in reflection may be caused by a change in Ag NWs morphology, which in turn is due to increase density of Ag NW networks. In addition, diffusive reflectance, which was measured separately, exhibits the same behaviour as that observed in total reflectance. However, specular reflectance can be calculated by subtracting the diffusive reflectance from the total reflectance as shown in the same figure as well. Comparing diffusive and specular reflectance reveals that, as specular (mirror-like) reflectance is not caused by scattered reflection, the majority of reflected light can be classified as diffusive reflectance; hence Ag NW networks reflection is dominated by scattering.
It has been discussed in 4.4.2.1 that enhancement of the optical haze as a product of increased Ag NWs network density is possible. As such, Ag NW networks show promise as a top electrode on photovoltaic devices as light concentrator. Generally speaking, reflected light means no captured energy, however in this case the diffusive reflectance of light due to random distribution of Ag NW networks may in fact increase their ability to capture incident light. In other words, their ability to harvest photons would be enhanced. This enhancement by reflectance mainly comes from the multiple reflection of light among the Ag NWs network, which can lengthen or increase the optical path in the active layer of solar cell [41].

Figure 4-10 (a) Total, diffusive and specular reflectance Ag NWs electrode as a function of sheet resistance. (b) Percentage of incident light which is reflected specularly and diffusely varying Ag NW electrodes sheet resistances. (c) Dashed lines correspond to percentage of incident light reflected diffusely.
4.5 Fabrication the Hybrid Transparent Flexible Electrode Based on Ag NWs and Graphene.

As mentioned in 4.1, the conductivity of Ag NW networks is governed by percolation theory; moreover the conductivity also depends on or is limited by other parameters such as nanowire length, diameter and junction resistance. Concerning junction resistance, there is a high possibility of a gap forming in the random geometry between NW-NW junctions, which limits the conducting pathway of charge carriers [24]. Consequently, post-process treatment such as mechanical [13, 42], thermal [11, 43] and plasmonic welding [44] are required to reduce junction resistance. As a result of this, thermal treatment values of 180-200 °C or high mechanical press forces of 81 GPa are considered to be essential [42]. These conditions, then limit the applicability of flexible substrates, in particular for large area, flexible optoelectronic devices.

However, it remains necessary to find an approach for utilising the high efficiency of Ag NWs networks without being bound by the post-process treatment. Such an approach could lift the restriction on using flexible substrates. This approach is a simple method which integrates Ag NWs with graphene to produce a hybrid transparent flexible electrode.

In order to realise the aforementioned approach, a low concentration of graphene is required. Therefore, achieving high quality of graphene dispersion is an important step in this process. Optical characterisation of graphene is the best way to characterise the dispersion, so by measuring the absorption coefficient (α) which is related to the absorbance per unit path length (A/l) via the Lambert-Beer law:

\[ A = \alpha l C \quad 4.9 \]

In order to ascertain this value for graphene, the absorption coefficient must be experimentally determined. Thus, graphene dispersion was prepared by adding 1 ml of graphene in NMP to 50 ml chloroform, so the concentration of the resulting mixture dispersion was 0.1 in NMP/chloroform. This dispersion was put in the bath sonicator for 30 minutes in ice bath. After sonication, the dispersion was divided into four samples in order to centrifuge them for different time periods. Figure 4-11 shows the
absorption spectra of four graphene dispersion samples which were centrifuged at 0, 30, 60 and 90 minutes. In all cases, spectra of the absorbance were featureless in the visible region as is expected in two dimensional materials [45]. A significant relationship was obtained between graphene concentration and absorbance per unit path length, as presented in Figure 4-12. The linear fitting of these points provides an absorption coefficient at 660 nm of $\alpha = 839.75 \text{ L g}^{-1} \text{ m}^{-1}$, as shown in Figure 4-12.

Figure 4-11 Absorption spectra per unit path length for graphene dispersed in NMP/chloroform mixture and centrifuged at different time (0, 30, 60, and 90 min).

Figure 4-12 Absorbance per unit path length ($\lambda=660$ nm), A/l, as a function of concentration of graphene (inset: optical photograph of the high to low concentrations of graphene dispersion in NMP/chloroform mixture).
Furthermore, the quality of the dispersion was investigated statically by analysing the length and the thickness distributions of the exfoliated graphene flakes via AFM images. Samples were prepared by spin coating on mica substrate at 3000 rpm for 10 seconds. AFM results are used widely for evaluating dispersion quality, so typical AFM height images show numbers of exfoliated graphene flakes which are distributed easily on the mica, due to the low boiling point of chloroform, presented in Figure 4-13 (a). Therefore, in the AFM height image in Figure 4-13 (b) two cross sections show two different flakes thicknesses ~ 1nm and 1.9 nm Figure 4-13 (c). These indicate the presence of monolayer or at most bilayer flakes.

**Figure 4-13** (a) A typical AFM height image (10x10 µm) shows numbers of graphene flakes. (b) AFM height image (2x 2 µm) of selected graphene flakes for analysis study. (c) Section analysis of the line in (b).

A histogram analysis was performed based on the large number of graphene flakes collected by AFM, providing the static analysis shown in Figure 4-14. The thickness of graphene histogram shows that mean thickness is ~ 2.2 nm, thus the vast majority of the flakes are within the range of monolayer graphene. However, flakes with multilayers are also presented in the histogram. Mean length is ~ 351 nm, indicating small flakes - a probable reason for this is the further sonication and centrifugation of the mixture of graphene in NMP and chloroform.
Figure 4-14 Statistical analysis of AFM images showing histograms of flake thickness (a), flake length (b), and the aspect ratio between the length and the thickness of graphene flakes deposited from NMP/chloroform mixture (c).
4.5.1 Optimising the Surface Coverage of Graphene Film Deposited onto PMMA Substrate

4.5.1.1 LS Deposition at Different Surface Pressures

The graphene solution is placed on the water surface owing to the insolubility of the chloroform solvent, which gives the water high surface tension at room temperature. As such, the solution spreads rapidly over the available area of the Langmuir trough. The initial stage, which takes place after the evaporation of the solvent, can show weak interaction between graphene flakes in terms of the dispersion’s low concentration. During this stage the effect on the surface tension is negligible; flakes only interface with the aqueous phase and the air, thus this stage can be considered as a gas phase. By moving the barriers across the surface area which is not occupied by graphene, the monolayer will be decreased. However, at this point the graphene flakes start to interact repulsively with each other, leading to reduced surface tension. Further compression leads the monolayer to transition from gas phase to liquid, and finally to solid phase before starting collapse. Figure 4-15 (a) represents the typical surface pressure area isotherm, which displays phase transitions and a collapse pressure above 20 mN/m. Three graphene thin films were deposited by LS technique at surface pressures of 0, 10 and 20 mN/m as shown in Figure 4-15 (b). As discussed previously, the aim is to fabricate graphene monolayer-thin film with low density but high surface coverage in order for it to be deposited in the top of Ag NWs electrode homogenously. So, by investigating the relationship between the optical transmittance and the fractional surface coverage of the fabricated films (A, B and C) weak coverage can be observed. Inherent increase in the fractional surface coverage is observed with an increase in surface pressure from 0-20 mN/m. The maximum fractional surface coverage is around 0.16 at the pressure of 20 mN/m, as shown in Figure 4-16. Weak coverage can refer to the weak distribution of graphene flakes or the weak packing of these flakes during barrier compression. Moreover, observation of the optical photographs of deposited films reveals that the distribution is not homogeneous, as presented in Figure 4-15 (b). These optical photographs also reveal that graphene flakes accumulate on top of each other, represented by white colouring. This accumulation is not a result of the collapse in the monolayer during barrier compression, because it can be observed even in the
film which is deposited at the lowest surface pressure of 0 mN/m. On the other hand, the inhomogeneous distribution and the accumulation are responsible for the drop in the optical transmittance from 93.8 % at the pressure 0 mN/m to 90.2 % at the pressure 20 mN/m.

Figure 4-15 (a) Representative surface P-A isotherm of graphene monolayer deposited from chloroform/NMP mixture at the air–water interface. (b) Optical photographs of a graphene film at the air/water interface deposited from chloroform/NMP mixture at different surface pressure (0, 10 and 20 mN/m).

Figure 4-16 Optical transmittance as a function of the fractional surface coverage of graphene film deposited By LS at three different the surface pressure ((A) 0 mN/m, (B) 10 mN/m and (C) 20 mN/m).
4.5.1.2 LS Deposition by Cycling (Compression-expansion) at Different Surface Pressures

In order to improve the surface coverage of the LS graphene films, deposition by compression-expansion cycles was prepared. Three different surface P-A isotherm cycles were adhered to, presented in Figure 4-17 as a, b and c, where A is the cycle at the pressures of 1, 1 and 1 mN/m, B is the cycle at the pressures 3, 6 and 10 mN/m, and C is the cycle at the pressure 5, 10 and 20 mN/m. Their optical photographs indicate the improvement in the quality of the deposited films. The improvement in the distribution can be explained by the absence of accumulations. Increases in surface coverage with every cycle are obvious, practically in the last cycles of 5, 10 and 20. Figure 4-18 shows the increase in fractional coverage compared with that before the cycling procedure. Improvement is also visible in overall optical transmittance. Typically, there is no observed drop similar to that in the surface P-A without cycles. This is due to the even distribution and the absence of graphene flake accumulation.
Figure 4-17 Surface pressure-area (P-A) isotherms of graphene monolayer deposited by LS via cycling (Compression-expansion) LS graphene film on PMMA substrate for three cycling; (a) at pressure 1, 1 and 1 mN/m, (b) at pressure 3, 6 and 10 mN/m and (c) at pressure 5, 10 and 20 mN/m.
Figure 4-18 Optical transmittance as a function of the fractional surface coverage of graphene film deposited by LS at three different the surface pressures by cycling process (Compression-expansion), (A) at pressure 1, 1 and 1 mN/m, (B) at pressure 3, 6 and 10 mN/m and (c) at pressure 5, 10, 20 mN/m.

4.5.1.3 Morphology of the Hybrid Electrode

The fabrication of the hybrid electrode by depositing the graphene flakes via the LS technique on the top of Ag NWs networks has been illustrated schematically in Figure 4-19 (A). As previously discussed in 4.5.1.2, to optimise the graphene film, it is deposited by spreading ~10 ml of graphene dispersion on the Langmuir trough and then subsequently completing compression-expansion isotherm cycles at the selected surface pressures of 5, 10 and 20 mN/m as described above. The graphene monolayer is then transferred horizontally onto Ag NWs networks on the PMMA substrate, which will have been prepared previously by the spraying technique.
Figure 4-19 Schematic illustration of the fabrication of Ag NWs network and Ag NWs/graphene hybrid electrode on PMMA substrate at room temperature. (B) AFM (20x20µm), (C) and (D) SEM images show unwrapped and wrapped junctions of Ag NWs by graphene flakes (100 nm scale bar).

The morphological structure of the fabricated hybrid electrode was investigated by AFM and SEM. AFM height images as well as SEM images show the state of the hybrid structures that were assembled by graphene covering on top of the Ag NWs network, as shown in Figure 4-19 (B-D). In this way, closer contact can be achieved as Ag NWs can be wrapped by graphene flakes, possible due to graphene’s flexible and stretchable properties. The graphene flakes provide two dimensional conductive paths for the electrons to pass through by enhancing charge transfer between Ag NWs and the flakes, thus improving the conductivity of the hybrid film. Therefore, according to the percolation theory, graphene could bridge non-percolated nanowires and also improve the percolation network by decreasing the inter-wire resistance of nanowires. This bridging is especially significant at the interface, where the force applied by graphene
flakes acts to compress the Ag NWs network. In contrast, in the absence of graphene, the macroscopic conductivity of the nanowire assembly may be limited by the air gap (different dielectric constant) at the interface.

On the other hand, from AFM and SEM images it can be observed that some NW-NW junctions are still not wrapped by graphene. This can be explained by the use of low-density graphene with a uniform homogenous film, chosen to avoid any loss in transmittance, which can be reduced by 2.3 % of the white light for every single layer of graphene.

**Figure 4-20** shows the relationship between the optical transmittance at 550 nm as a function of sheet resistance for various densities of Ag NWs networks, both before and after depositing graphene – this is presented by the seven samples fabricated. Optical transparency was recorded at higher than 90 % for all the samples of the hybrid electrode where the transmittance was reduced in total by ~ 2 %. Therefore, the resulting hybrid electrodes still satisfy the requirement for optical properties of transparent electrode.

A reduction in sheet resistance occurs after incorporating the graphene. This remarkable decrease, proportional to low densities of Ag NWs network, is observed, especially with the lowest density (sample 1) where the Rs was reduced from 19.6 M Ω/sq to 65.3KΩ/sq. A clear example for Ag NWs is sample 2 (original Rs = 79.9 kΩ/sq and T = 98.6 %) shifting after the deposition of graphene to the value of Rs = 11.8 kΩ and T = 95.1 %. This sample is considered to be within the region of the low density of Ag NWs as well. For medium density sample 5 with the value of Rs = 1067 Ω/sq reduced to 665.7 Ω/sq, the transmittance was reduced from 98.1 to 95.6 %. Sample 7 represents the high density network with Rs = 100.9 Ω/sq which decreased to 74.2 Ω/sq and T = 97.6 to 94.8 % after deposition of graphene.

The most significant changes in resistance, then, are related to lowered densities of Ag NWs network. **Figure 4-21** shows the differences in the values of the sheet resistance and the transmittance at 550 nm before and after the depositing the graphene. This figure indicates that the largest improvements are observed at low-density samples and the size of these improvements decreases with increasing Ag NWs network density. The reason for this is that graphene flakes directly affect the top layer of the Ag NWs.
by wrapping or bridging the nanowires together. Conversely, they have little or no interaction with the Ag NWs that exist under the top layer [46].

![Graph](image)

**Figure 4-20** Transmittance plotted versus sheet resistance for pristine Ag NW networks and Ag NW/graphene hybrids.

![Graph](image)

**Figure 4-21** Change in sheet resistance and change in the transmittance of the Ag NWs after depositing graphene as a function of the initial sheet resistance of the pristine Ag NWs.

Furthermore, the deposited graphene flakes act as a protective layer, potentially preventing oxidation and increasing adhesion. This is particularly relevant for application in photovoltaic cells operating in undesirable environmental conditions.
4.5.2 Mechanical Behaviour of Flexible Transparent Conductive Electrodes based on Ag NWs and Graphene

Many optoelectronic devices are subjected to mechanical stress or deformation; therefore mechanical characteristics are of great importance for the performance of these devices. Thus, Ag NWs are considered as alternatives to ITO, which cannot meet the flexibility requirements of optoelectronic devices due to its brittleness. The flexibility of transparent electrodes implies the withstanding of the functions of that electrode to mechanical stress. Ag NWs have shown remarkable results for flexible transparent electrodes. Therefore, Carmichael et al. [47] investigated the stability of Ag NWs and ITO electrodes under mechanical tests such as bending and tensile strain, showing that the Ag NWs electrode compares favourably with ITO in terms of stability of the ratio of change in resistance divided by initial resistance. In this section, bending and stretching tests were performed for Ag NWs and Ag NWs/graphene hybrid electrodes.

4.5.2.1 Bending Test of Ag NWs and Ag NWs/graphene Hybrid System on PMMA Substrates

Studying the mechanical properties of thin film is important in optoelectronics, particularly, where flexibility of the film and the potential to be applied in flexible or wearable optoelectronics devices is concerned. In the previous section, Ag NWs and Ag WNs/graphene hybrid electrodes were shown to be an effective replacement for ITO when used as thin film optoelectronic devices. Following from this, this section will investigate the flexible properties of the Ag NWs and Ag NWs/graphene hybrid electrodes on PMMA substrates. The technique for investigating the properties of both Ag NWs and Ag NWs/graphene electrodes is a bending test. This test has the advantage of showing both the mechanical stabilities of both electrodes and comparing their flexibility under the bending cycle test. Samples were prepared as previously discussed in the experimental section in dimensions of 50x12.7x0.7 mm, and the test was performed by a texture analyser (illustrated in the Figure 4-22).

**Figure 4-23** shows the bending test results of the Ag NWs and Ag NWs/graphene hybrid electrodes on PMMA substrates. The change in resistance of the flexible
electrode was expressed as \((\Delta R/R_0)\) 100\%, where \(R_0\) is the initially measured resistance before carrying out the test and \(R\) is the measured value after electrode bending by radius curvature of 7.5 mm at each bending cycle. The test results showed that the change in the electrical resistance of both electrodes remained constant during 30 cycles of bending. After 30 bending cycles the change in the pristine Ag NWs electrode increased suddenly by the value of \(~ 10\%\) and continued to increase gradually with each bending cycle, until reaching the rate of change of \(~ 18\%\) at 100 bending cycles.

In contrast, the hybrid electrode exhibited more constant behaviour, even after 30 bending cycles. When 100 cycles were reached, a change of \(~ 7\%\) had been recorded. Both electrodes, then, show significant electrical stability under the mechanical test due to the inherent flexibility of Ag NWs. The remarkable improvement in the stability of the electrical conductivity in the hybrid electrode under this test was due to the presence of graphene, sufficient to overcome the degradation in Ag NWs conductive pathways. That degradation, following the application of mechanical bending, could be overcome by graphene wrapping junctions and building new conductive paths serves to highlight the hybrid electrode’s excellent mechanical flexibility.

![Photograph during bending test](image-url)

**Figure 4-22** Photograph during bending test of a specimen’s strips of Ag NWs and Ag NWs/graphene by using texture analyser.
4.5.2.2 Stretching Test of Ag NWs and Ag NWs/Graphene Hybrid Electrodes on PMMA Substrate

A typical tensile test of PMMA substrate by stretching a specimen’s strips was carried out using a texture analyser instrument as well. The tensile stress strain curve of PMMA shows that stress is proportional to strain, as illustrated in Figure 4-24. The curve initially behaves linearly, and the Young modulus can be extracted by linear fitting of the initial portion of that curve at the value of ~ 6.17 MPa. At this stage, polymer chains are randomly oriented and heavily cross linked, and thus behave in an elastic manner. The elastic region is followed by increasing stress beyond a certain limit fracture of polymer matrix which is mainly caused by crazing. Therefore, by maintaining the application of stress, the curve reaches a yield point resembling a shoulder, associated with permanent or plastic deformation. This causes reorientation of these chains until they become anisotropic, before failure takes at strain 9.8 % and stress 54.5 MPa.
Figure 4-24 Stress-strain curve of PMMA substrate showing the elastic region and the failure point.

Figure 4-25 shows the mechanical stretchability of the Ag NWs and Ag NWs/graphene hybrid electrodes that were fabricated. The average of the resistance changing rate of both electrodes is plotted against elongation when under stretching. The resistance of both electrodes remained almost unchanged up to ~ 2 % elongation especially within the elastic region of the substrate. Furthermore, increasing elongation to ~3 % caused an increase in the resistance of Ag NWs electrode, which was sufficient to distinguish it from the hybrid electrode’s behaviour which was only slightly increased. Pristine Ag NWs electrode resistance rate continued to increase proportionally with further elongation until the cessation of conductivity takes place as a result of the failure point of the PMMA substrate at 9.5 % elongation, where the maximum resistance change was recorded at ~ 27 %. According to percolation theory, the change in the resistance value should remain constant with stretching, as long as the wires are connected through the conductive path. The increase in the resistance change with further elongation may be due to the increase in the conductive path length, causing difficulties for the electrons to pass through. Eventually, the conductive path broke and resulted in the cessation of conductivity. In the case of the hybrid electrode, the increase in resistance change rate was slight after 3 % elongation and that increase was almost at a constant level of about 7 %, until the substrate broke at 9.5 % elongation. Therefore, the presence of the
graphene is expected to form more 2D conductive paths, and thus maintain conductivity with increased elongation.

![Image](Figure 4-25) Stretchability of Ag NWs and Ag NWs/graphene electrodes representing the change in resistance as a function of elongation.

4.5.3 Stability of Ag NWs And Ag NWs/graphene hybrid electrodes

The oxidation stability evaluation test of Ag NWs and Ag NWs/graphene electrodes was completed by exposing them to air for almost one month. Figure 4-26 presents the oxidation stability test for both electrodes and shows the change in the resistance for both samples. Ag NWs are well-known to oxidise easily when are exposed to air. Therefore, the resistance of Ag NWs increased by a ratio of almost 10 % after one month. Junction resistance and electrical resistivity of Ag NWs after oxidation would increase due to the formation of silver oxides on Ag NWs surface [19, 48].

Hybrid electrodes, in contrast, exhibited a resistance increase of less than 3 % in one month. Graphene can impede environmental oxidants from affecting the Ag NWs and their junctions by wrapping around the Ag NWs-NWs junctions and increasing the stability of the hybrid electrode. Therefore, the significant difference in the change of the resistance between pristine Ag NWs and Ag NWs with graphene electrodes verifies that the graphene can act as protection layer or as a gas barrier, as it is impermeable to oxygen molecules.
4.6 Conclusion

In this chapter, Ag NWs flexible transparent, very conductive electrodes, which were fabricated with large area with controlled density by the spraying deposition technique on PMMA substrates, have been prepared and shown as a promising option for ITO film replacement. The characteristics and performance of the electrodes have been illustrated. The opto-electrical properties were measured by studying the relationship between optical transmittance and sheet resistance of the produced electrodes. This relationship high value of FoM $\Pi = 91.19$ combines with low percolation exponent $n = 2.25$ have been achieved which is a desirable feature for the optoelectronics device industry. Additionally, optical haze of Ag NWs electrodes with different densities was investigated, and it has been shown that the optical haze rate remains within the acceptable level < 30%, marked as the level desirable to enhance the optical path length or act for light-trapping purposes in photovoltaic applications.

The junction resistance formed at Ag NWs electrodes was reduced by depositing graphene on top of Ag NWs electrodes. In this case, the graphene film was produced by the LS process, and optimised by producing graphene film at three different surface pressures: 5, 10 and 20 mN/m through the cycling method (compression-expansion cycles) to increase surface coverage. A remarkable reduction in sheet resistance has been recorded after transferring graphene flakes to all sprayed Ag NW electrodes, with
a slight decrease in optical transparency also being noted. A greater reduction was observed in the higher sheet resistance electrodes.

For the application of flexible optoelectronic devices, both pristine Ag NWs and the hybrid electrodes were characterised mechanically by performing bending and stretching tests. Both of electrodes appeared to be reliable for flexible optoelectronic applications, but the hybrid electrode proved to be more reliable under these tests. Finally, the hybrid electrode was shown to be more stable in the oxidation stability test, proving that graphene can act as protection layer or as a gas barrier due to its impermeability to oxygen molecules.
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The influence of Thermo-Mechanical Welding on Ag NWs and Ag NWs/Graphene by Three-Point Bending Test

5.1 Introduction

The exceptional mechanical, optical, electrical, and thermal properties of low-dimensional materials [1-4] such as nanowires, nanoparticles, and nanotubes have long occupied the attention of academics and industry workers alike. They have been functionalised to suit different fields such as optical electronics [5], energy storage [6] and sensors [7]. The recent increased demand for transparent conductive electrodes as well as flexible devices has seen the rise of some nanomaterials such as CNTs [8, 9], graphene [10, 11] and metallic nanowires as replacements for ITO [12-14]. Particularly, Ag NWs transparent electrodes are considered as a potential candidate due to their high transparency and high electrical conductivity for optoelectronic applications such as solar cells, LEDs and touch panels – characteristics supported by their potential high throughput, low-cost fabrication, flexibility, and solution-processability.

The mechanical characteristics of Ag NWs also play an important role where the reliability of performance of their applications is concerned. Many applications of Ag NWs see them subjected to mechanical stresses and deformations during usage [13]. Therefore, Ag NWs flexible electrodes should be stable and replicable under such applied conditions. This stability of Ag NWs electrodes is considered desirable in various applications where the basic functionalities are dependent on their stability under such conditions. For instance, a large degree of bending is required to guide light in the nanophotonics. Additionally, it has been found that discontinuities such as cracks resulting from bending can strongly affect the surface plasmon resonance and light propagation in waveguides in Ag NWs networks [15, 16]. Therefore, a more profound understanding of Ag NWs elasticity, plasticity and fracture is crucial to ensure the reliability and performance of their applications. Several methods have been employed to characterise Ag NWs mechanically, such as nanoindentation, the three point bending test and tensile test. Lucas et al. [17] investigated plastic deformation of Ag NWs by using nanoindentation through AFM. Wu et al. [18] and Jing et al. [1] used three point double beam bending tests. In this method, Ag NWs were fixed from both ends and
subjected to bending by an AFM tip at the midpoint, where Young modulus and yield strength were calculated. Zhu \textit{et al.} carried out tensile tests for Ag NWs using SEM by fixing NWs [19] between the nanomanipulator tip and AFM cantilever and then pulling until the failure point was reached. Therefore, with a known spring constant, Young’s modulus, yield strength, and ultimate strength were measured from the deflection of the AFM cantilever. In particular, it has been demonstrated that Young modulus and yield strength of Ag NWs investigated through all previous methods were typically higher than for bulk silver. Dependence of mechanical properties on size was reported for diameters smaller than 100 nm [1, 19].

As mentioned in the previous chapter, the gap formed between NW-NW in randomly distributed Ag NWs networks caused high contact resistance at junctions. This junction resistance remains a critical issue in Ag NWs networks. Consequently, post-process treatments such as mechanical [20, 21], thermal [22] and plasmonic welding [23] are required to reduce junction resistance. These conditions limit the applicability of flexible substrates, in particular for large area, flexible optoelectronic devices. However, an alternative approach, demonstrated in the previous chapter, of depositing graphene on the top of Ag NWs network overcame this limitation. Graphene sheets wrapped the NWs at the junction, minimising the formed gap and bridging between NWs to generate a 2D conductive path.

Recently, individual low-dimensional nanostructures such as CNTs [24-26], metallic nanowires [27-30] and NPs [31-33] have been able to be joined successfully by several methods such as applying voltage/current [25, 28, 34], heating the sample stage [27, 32, 35], or by focusing high-intensity electron or laser beams onto the joining part [31, 36, 37]. These methods undoubtedly have their own particular advantages, but are all linked by their reliance on local heating process; these are difficult to control precisely at significant length scales, and may bring about changes in the underlying substructures.

Two decades ago, Whitesides \textit{et al.} showed that two thin gold films on elastomer substrates can be welded together under laboratory ambient conditions with significant low loads [38]. They did conclude, however, that the mechanism was not fully understood. The cold welding process was extended by this finding, emerging into the
production of various optoelectronic devices including OLED devices and PV cells [39].

Cold welding is a solid state welding process in which the welding can be achieved without fusion at the interface. Lu et al. demonstrated the welding of single crystalline Au NWs with diameters between 3 and 10 nm by only mechanical contact under relatively low applied mechanical pressure [40]. The resulting welding structure is characterised by the same crystal orientation, strength and electrical conductivity. It is also mentioned that the quality of the welding is attributed to the dimension of the sample nanoscale, the mechanism of the orientation and the assisted fast surface atom diffusion. This process is applicable to other kinds of metals such as gold/silver and silver/silver.

The proposed approach uses the DMA instrument to apply mechanical stress in an oscillatory manner by performing the three point bending test and studying the expected influence on the pristine Ag NWs network and the hybrid Ag NWs/graphene network.

In this chapter, the observed enhancement in the conductivity of the pristine Ag NWs electrode will be investigated electrically and morphologically to determine the resultant welding between NWs in the investigated networks.

5.2 Experimental Method

Samples were prepared initially by cutting PMMA substrates with specific dimensions to suit the DMA three point bending clamp geometry. The dimensions of the cut substrates were 50 mm in length and 12 mm in width. The test was applied for both pristine Ag NWs flexible transparent electrodes and the hybrid Ag NWs/graphene flexible transparent electrode; hence the fabrication of both samples followed the same procedure as outlined in the previous chapter. Subsequently, samples were placed on the DMA three point bending clamp (Q800 DMA, TA Instruments, Newcastle, DE) on top of two support bars. Particular care was taken to ensure that they were parallel to the length axis of the clamp, as shown in Figure 5-1 (b) with opened furnace on DAM. Three mechanical stresses were applied to different specimens separately: 0.1, 0.24 and 0.4 MPa. During the test, the Keithley 2400 Model 2400 Source Meter & Instrument was connected to both ends of the specimen for measuring the resistance with time.
5.3 Characterisations

The I-V characteristics of Ag NW pristine and the Ag NWs/graphene hybrid electrodes were obtained by using a two point probe (Keithley Model 4200) during the test. Additionally, characterisation of I-V of the Ag NWs electrodes at different positions along the length of the electrode was carried out before and after the test. This will be described later in greater detail.

The surface morphology of the Ag NWS electrode was compared with the affected surface morphology before and after by AFM, which was performed in semi-contact mode using the NT-MDT AFM (Moscow, Russia), and SEM to quantify the affected position of the electrode through mechanical welding.

5.4 Results and Discussions

The behaviour of conductive transparent pristine Ag NWs and hybrid system based on Ag NWs/graphene was investigated. Both fabricated transparent flexible electrodes of Ag NWs and hybrid Ag NWs/graphene on PMMA substrates were placed on the DMA three point bending clamp, as shown in the schematic diagram of the experimental setup in Figure 5-1 (a). The randomly distributed Ag NWs network was fabricated by the
spraying deposition technique, and the hybrid electrode was prepared by depositing graphene on the top of Ag NWs network (described in detail in the previous chapter).

These samples were subjected to oscillation sweep mechanical stress by the DMA three point bending clamp. In this study, different stresses were applied during the test. This selection was adjusted to prevent the failure of PMMA substrates. Therefore, the maximum stress was 0.4 MPa, beyond which substrate failure will occur. The minimum value was 0.1 MPa - the limitation of DMA instrument - to ensure the effectiveness of the test. Finally, the stress value of 0.25 was selected in order to provide the expected influence between the maximum and the minimum stresses.

The relative resistance change of the pristine Ag NWs was investigated as a function of the test duration time under the three different stresses, as shown in Figure 5-2 (a). It was observed that the overall behaviour of the three similar densities of Ag NW networks was significantly reduced by percentage. As shown, under the minimum stress of 0.1 MPa, the reduction was ~ 1%, while under the stress of 0.25 MPa the reduction was ~1.8 % and at the maximum stress the reduction was ~ 3 %. The reduction in the electrical resistance of the Ag NWs electrodes was directly proportional to time. In particular, with 0.4 MPa the reduction took place at the time of ~ 50 sec, while the reduction in the electrode resistance which was subjected to 0.25 MPa came after ~125 sec. This trend continued, with the lowest stress of 0.1 MPa being observed at around 150 sec, as illustrated in Figure 5-2 (b).
Figure 5-2 (a) Relative resistance change of Ag NWs electrode as a function of the test duration time under three different stresses: 0.1, 0.25 and 0.4 MPa. (b) The magnified section shows when the reduction in the resistance starts as a function of time duration, at stress of 0.1 MPa reduction starts ~ 150 sec, stress of 0.25 MPa the reduction starts at ~ 125 sec, and with highest stress of 0.4 MPa reduction starts at ~ 50 sec.

Compared with these pristine Ag NWs flexible transparent electrodes, the hybrid Ag NWs/graphene electrodes behave entirely different under the same experimental procedure. Figure 5-3 represents relative resistance change as a function of time subjected to mechanical oscillation sweep stress. In this figure, three hybrid electrodes
with similar densities exhibit stability without any significant change in resistance under the three different stresses throughout the test duration. This behaviour (of graphene being found to maintain the stability of the Ag NWs networks mechanically and electrically) was expected, as it had been observed performing the same function during the normal bending and the stretchability test in previous chapter. The observed enhancement was generated by wrapping the Ag NWs networks with graphene flakes, especially at the junctions between NW-NW and also bridging unconnected NWs. As such, a 2D conductivity path was formed, improving electrode conductivity as well as the mechanical stability of the hybrid network.

![Figure 5-3](image)

**Figure 5-3** Relative resistance change of Ag NWs/graphene hybrid electrode as a function of the test duration time under three different stresses 0.1, 0.25 and 0.4 MPa.

Regarding the pristine Ag NWs electrodes, the most probable explanation of the reduction in electrical resistance lies in the welding of Ag NWs during the mechanical test. This finding is considered to build upon the existing findings of Whiteside *et al.*, where two gold films were welded together by contact under low load in ambient laboratory conditions. Additionally, recent investigations of Lu *et al.* have demonstrated welding by mechanical contact alone at room temperature of Au NWs, as well as between Ag NWs with diameters of 3 - 10 nm [40]. They identified atomic diffusions as
the process underlying this welding. Moreover, this welding can be achieved easily and instantaneously between NWs, which have the same growth orientation. In this study, the applied load which hits the targeted area in the electrode may have led nanowires to interact or attach when stress was being applied. Therefore, junction resistance in the network can be reduced by achieving NW welding.

Although atomic diffusion is considered an important factor, diffusion energy barriers also need to be taken into account. It has been reported that the diffusion barrier in the single atom on metal surfaces is quite low (~ 1 ev), which can be activated thermally even at room temperature [41].

Once sufficient mechanical stress is applied in the system, welding at the junctions occurs by surface and bulk diffusion of silver atoms. The size of the contact area depends on the diffusion magnitude. Furthermore, the tendency of Ag NWs to weld could be described by the relation between free energy and nanowire diameter. The Gibbs-Thomson theory, where Gibbs free energy increases rapidly with smaller particle dimensions as a result of an increased contribution from the Gibbs-Thomson potential, supports this assertion. The theory is shown in the following equation:

$$\Delta G = 2\gamma\Omega m/r$$

where $\gamma$ is the surface energy, $\Omega m$ is the volume per atom of investigated material, and $r$ is the radius of the nanowires. In this equation, the NW diameter is inversely proportional to the free energy, so smaller diameter Ag NWs will be subjected to greater potential energy. This potential energy declines with increasing NW diameter. Moreover, the findings of Lu et al. regarding welding Au NWs, explained above, affirm that atomic diffusion in such welding can be activated thermally at room temperature when Au NWs or Ag NWs come into contact with each other. So, further applied mechanical stress, which leads NWs to interact at junctions, may generate thermal energy, hence increasing the opportunity for NWs to achieve large area contact at NWs-NWs junctions.
5.4.1 The Influence of Mechanical Three-Point Bending Test on Ag NWs Network

In order to further understand whether the aforementioned mechanically assisted surface-atom diffusion alone could facilitate the cold welding of nanowires, a sample of Ag NWs was prepared using a different setup with respect to the two silver paint contacts at the end of the sample. Instead of painting the two ends as above, the proposed design is to paint the sample on the width side, or perpendicular (transverse), to the axis of the DMA clamp as shown in Figure 5-4 (b). The purpose of this is to use the transverse contacts to verify that the welded area is in the centre of the electrode, where the clamp beam hits. As mentioned above, the more significant reduction in electrical resistance was observed with the highest applied stress of 0.4 MPa, so this experiment was carried out under the highest stress; this affords the sufficient information without the need to repeat at all stresses. In particular, two pristine Ag NWs samples with the same density were painted by silver contact in two different ways; the first in the transverse direction described, and the second in the same longitudinal direction as in the initial work. Figure 5-4 (c) shows relative resistance change as a function of test duration for both Ag NW electrodes with longitudinal contacts and transverse contacts. The electrical resistance of each decreased during the test time (1400 sec, significantly longer than the previous duration of 800). A reduction of ~ 2 % in resistance was recorded during the test time of the longitudinal electrode, while ~ 4 % of resistance was noted for the transverse electrode. The close to 100 % reduction of the transverse was more than in the state of the longitudinal electrode which indicates that the position that was targeted by the hitting of the clamp beam is the area influenced by welding. Another notable feature in this figure is the mechanism, or process, of the reduction. This can be divided into two regions; the reduction and the saturation region. In the case of the longitudinal electrode, the resistance was observed to decrease gradually until 1000 seconds: This can be considered as the saturation time, during which change in resistance occurs consistently. In contrast, resistance of the transverse electrode dropped rapidly from the beginning until almost 400 seconds by ~ 3.5 %, followed by the saturation region. This drop in the resistance of the transverse electrode may validate the contribution of mechanical applied stress for the welding of the nanowires; a probable cause is the oscillation of the clamp beam, which is the centre
of the sample. The rapid reduction in electrical resistance reveals that the Ag NWs network located between these two painted contacts was affected more than the longitudinal contacts.

![Image](image1.png)

**Figure 5-4** (a) and (b) longitudinal and transverse electrodes respectively. (c) Comparing the relative resistance change of Ag NWs electrodes during the longitudinal and transverse setup as a function of the test duration time under the stress of 0.4 MPa.

For more quantitative support for this hypothesis, the change in the resistance was investigated at different positions along the length of sample as illustrated in the schematic in **Figure 5-5**. This diagram shows how resistance was measured between every two points (referred to as a measurement pair) before and after the three point bending test, and plotted as a function of the length between those two points.

![Image](image2.png)

**Figure 5-5** Illustrated schematic diagram of different positions of the electrical resistance measurement.
Figure 5-6 shows the actual measured resistance before the test and after the applied mechanical test. The resistance measured between the closest pair exhibits the most notable reduction, where resistance decreased from 144.5 to 111 Ω, with the remaining measured resistances were: from 259 to 242 Ω, 303 to 289 Ω, 433.8 to 292 Ω and 666 to 655 Ω between the farthest pair. So, this change in the resistance is plotted as a function of the distance between the points, presented in Figure 5-7. This figure reflects the magnitude of the change in electrode resistance as distance from the centre increased, moving further in both directions until the end of the electrode.

**Figure 5-6** Comparison between the electrical resistance at different positions along the length of the electrode before and after the mechanical three point bending test.

**Figure 5-7** Relative resistance change as a function of length between different contact positions along the length of the electrode, where the measurements start from the centre of the sample.
It is clear that the magnitude of the reduction in resistance decreases with increase in distance between the points of the pair. However, to understand the direct influence of mechanical applied stress, Figure 5-6 has been re-plotted as the actual resistance before and after the mechanical applied stress between each pair, divided by the length between them and plotted as a function of the length. This is shown in Figure 5-8. In particular, during the measurements for all resistances at every pair, the previous resistance measurements are included in the following points. Therefore, the comparison between resistance before and after the mechanical test in this figure provides the exact reduction in resistance at every position.

![Figure 5-8](image)

**Figure 5-8** Comparison between the resistance at different position on the electrode before and after the mechanical three points bending test.

5.4.2 The Morphology of Ag NWs Network before and After the Mechanical Three-Point Bending Test

SEM was carried out to characterise the Ag NW networks before and after the mechanical welding process which was performed by the three point bending test. SEM images of the Ag NW electrode centre before the welding process are shown in figure 5-10, revealing that the wires lie on top of each other, as was expected. The resultant gap between NW-NW leads to increased resistance of the network. Additionally, the shape of NWs at NW-NW junctions is clearly sharp at the interface. After mechanical welding occurs as a result of mechanical stress, the morphology of the targeted area in
the centre of the electrode was altered, as shown in Figure 5-9. In the case featuring in Figure 5-9, the sample under stress of 0.4 MPa was found to be welded in its centre, the area targeted by the clamp beam. Moreover, in the welded contact the top electrode had deformed toward the bottom wire, resulting in significant symmetric contact morphology. Therefore, the gap formed during the fabrication of Ag NWs network, observable in the image before applied mechanical welding, has been eliminated and an improvement in electrical conductivity results.

In order to further investigate the welded contact at the NW-NW junctions, AFM was performed in the affected area. The resulting image, Figure 5-10, is a 3D AFM height image which shows that the mechanical welding process brings wires into contact by welding them together. Hence, the gap formed between NWs is reduced, which manifests as an improvement in electrical conductivity by minimising the junction resistance.

![Figure 5-9 SEM images represent Ag NWs electrode before (left) and after (right) the mechanical three point bending test.](image)

![Figure 5-10 3D AFM height image 2X2 µm of Ag NWs electrode after the three point bending test.](image)
5.5 Conclusion

In this chapter, the influence of the applied mechanical test on flexible transparent Ag NWs and Ag NW/graphene electrodes was investigated. The electrical characterisation performed during the three point bending test showed that the pristine Ag NWs electrodes appeared to be enhanced (in response) as a result of the applied different mechanical stress. However, the reduction in electrical resistance was directly proportional to the applied mechanical stress by DMA, while the Ag NWs/graphene was stable electrically during the applied test.

The interesting enhancement in the electrical conductivity on the pristine Ag NWs electrode led to further study of said electrode. The targeted position in the electrode by the three point bending clamp beam was investigated in order to verify the hypothesis of Ag NWs electrode welding at the affected area. Accordingly, the transverse contact electrode was compared with the longitudinal contact electrode, and it was shown that the reduction in its electrical resistance was more than the reduction in the longitudinal state. For the same purpose, the electrical resistance of the Ag NWs electrode was measured at different positions along the electrode before and after the test, and it was noted that the reduction magnitude was increased by moving closer to the electrode centre.

Finally, SEM and AFM were performed and confirmed the welding between NW-NW at the junction, which resulted in reduction of junction resistance in the network. The ability of NW-NWs to connect was attributed to the atomic diffusion between Ag NWs, stimulated by the frequent oscillatory contact under the applied load.
References


6.1 Introduction

Increasing demands for producing waterborne coatings have been extensively developed academically and industrially due to their promising potential applications and lower impact on our environment. For applications where the coating should be relatively hard (i.e. the glass transition of the polymer is high) a bottleneck to fabricating large area homogeneous films is associated with the formation of cracks as a result of the mismatch of mechanical properties between the coating and the substrate during film formation.

The earlier discussion in 3.1.1.1 concerned using the LB technique to deposit amphiphilic molecules. Besides using amphiphilic molecules some researchers have demonstrated the formation of Langmuir monolayers of latex particles. However, by spreading latex particles on the subphase there is a challenge related to counteracting the obvious solubility of the latex particles in the subphase. Reculusa and Ravaine [1] have used the LB technique successfully for deposition of silica based colloidal crystals achieving well organised 2D/3D silica multi arrays with controlled thickness by adding salt or surfactant during the LB process. Szekeres et al. [2] demonstrated the processing of silica particles into monolayers (357,450 and 550 nm in diameter) on water by modulating the ionic character of their surface. Moreover, they reported how the quality of particle ordering can be affected by the type and parameters associated with the surfactant (concentration, type and chain length) and by changing the medium (chloroform, methanol or mixture of both). Recently, SchohMeijer et al. [3] diluted PMMA and poly (butyl methacrylate) (PBMA) with methanol by various concentrations to produce LB thin films. Cong Qian et al. [4] used ethanol as a dispersion medium in the absence of surfactant in a polystyrene latex dispersion which cannot be dispersed very well with pure water without a surfactant.

In these studies the observed drawbacks of using alcohols were related to the resulting aggregation which is dependent on two factors. Firstly, the decrease in the electrostatic
repulsion force between the particles due to the lower permittivity of certain alcohols relative to the water. Secondly, the viscosity of the particle surface is affected, due to the decrease in the glass transition temperature of the particles’ external layer through alcohol swelling.

Regarding producing latex monolayers via other techniques, Qingfen et al. have recently prepared a monolayer of polystyrene (PS) and annealed it directly on the air-water interface to achieve controlled interstice size. The resulting film can be transferred to arbitrary substrate which was used for nanosphere lithography applications [5].

In this study, using the LB technique, it is shown how it is possible to form a monolayer of polymer latex spheres at the air/water interface without any modification to the composition and secondly it is possible to deposit these monolayers onto large area glass substrates. AFM studies indicate that the resulting coatings consist of hexagonally close packed particles that form crack-free monolayers over large areas. Moreover, the homogeneity of the monolayer can be increased further by a further step involving thermal annealing of the films. The resulting transparent homogeneous coatings are ideal systems to act as packaging for plastic electronic applications.

6.2 Experimental Details

6.2.1 Materials

Latex 1 and 2 are based on styrene (St), butyl acrylate (BA) and acrylic acid (AA). They were synthesized at the University of the Basque Country, in Spain. Sodium lauryl sulfate (SLS) was used as a surfactant and potassium persulfate (KPS) as an initiator. AA was employed to increase electrostatic colloidal stability as it modifies the kinetics of the emulsion polymerisation. It also alters interactions between polymer particles, changing their packing behaviour and improving film performance. Two different monodispersed, polymer latex samples, prepared by emulsion polymerisation, were used in this work (summarised in Table 1).
The LB films of the latex particles were prepared in the LB trough (Nima) by controlling the surface pressure and the volume instead of changing the area of the trough as the barrier movement was found to disrupt the buoyancy of the polymer particles at the interface causing instability in the film. The latex particle (295nm and 80nm) dispersions having volumes of 800µl for latex 1 and 1200µl for latex 2 respectively were spread over the subphase (pure water which purified Milli-Q system) until a surface pressure of 9mN/m and 12 mN/m was reached for latex 1 and 2 respectively. The formed monolayer was transformed immediately onto a glass substrate which was already cleaned by detergent and repeatedly washed by DI water before being treated for 30 min by ultraviolet-ozone. This treatment results in creating a hydrophilic surface for the glass substrate. Vertical dipping at a speed of 25 mm/min was used during the deposition method.

### 6.3 Characterisations

#### 6.3.1 UV-Vis Optical Study

A UV-Vis transmission spectrum was performed over the range 300-900nm using a Camspe M350 UV-Vis spectrophotometer.

#### 6.3.2 Contact Angle Measurements

To perform the contact angle measurement, a drop of deionized water was applied to each treated substrate (by UV-ozone for 30min) and compared to an untreated substrate. An optical camera was used to capture the side view of substrates to measure their contact angles. Measuring a contact angle can be performed by Kruss software.
accompanied with Kruss contact angle measurement instrument (Kruss Co.Ltd, Hamburg, Germany). Side view images of both substrates with a water drop on each of them is shown with their contact angles in Figure 6-5.

6.3.3 Atomic Force Microscopy

AFM (NT-MDT) was used for the topographical study, by performing in semi-contact mode. The latex thin film was prepared by LB the technique on a glass substrate. This was attached to the metal disk with double sided sticky tape and placed on the AFM stage to study morphology.

6.4 Results and Discussions

6.4.1 Mechanism of the Formation of Polymer Latex Monolayers on the Water Subphase

As mentioned in 3.1.1.1, the LB technique generally needs amphiphilic molecules to be trapped at the air–water interface with the hydrophilic head group immersed into the subphase, while the hydrophobic tail group preventing the molecules being dissolved in the subphase.

Previous literature reports have shown that to deposit latex particles onto a glass substrate by the LB method, a modification to their composition needs to be done (for example by adding alcohol). However, here we show that the Langmuir deposition can be successfully performed without any modifications to the latex composition and consequently to deposit these monolayers onto large area glass substrates. This will be discussed in the next section. Figure 6-1 presents a schematic diagram which reveals the suggested spreading mechanism of latex particles on the subphase.
6.4.2 Surface Pressure-Volume Isotherms

Generally, a P-A isotherm is a graph which is achieved by recording the surface pressure as a function of surface area. Figure 6-2 shows P-A isotherm’s behaviour of latex 1 monolayer which revealed that by increasing the surface pressure is associated with reducing the surface area and the monolayers undergo a pseudo phase transition as discussed previously. In the typical P-A isotherm, three transition regions can be distinguished.

However, during the isotherm compression cycle, as latex particles are highly hydrophilic, they have the tendency to be solubilized in water causing them to disappear from the water surface migrating towards the bottom of the trough.

![Figure 6-1 Suggested spreading mechanism of the latex particles on air water interface.](image)

![Figure 6-2 Surface pressure-area isotherm of latex1 monolayer.](image)
To overcome this problem, a different isotherm approach has been chosen. In this approach, instead of changing the area, the volume of latex dispersion deposited on the water subphase was changed. Figure 6-3 shows a pressure-volume isotherm for the latex which reveals that by spreading the initial volume, the surface pressure slightly increased followed by a gradual increase in pressure as additional latex is added to the subphase. However, at a pressure of 12mN/m the isotherm reaches a saturation point which is an indication that the trough’s area is saturated by the dropped latex volume. It shows that saturation level at the surface of 9mN/m produces the optimised conditions for depositing the resulting thin film.

Figure 6-3 Surface pressure- volume isotherm of latex 1 monolayer.

Figure 6-4 Surface pressure-volume isotherm of latex 2.
Figure 6-4 represents the pressure-volume isotherm of the latex 2 of smaller particles (80nm). It is evident for these experiments that the behaviour is different. A large increase is evident in the pressure for small increases in the dispersion volume dropped on the surface. The isotherm markedly changes gradient after the volume of 500µl is reached. After this transition, the pressure gradually increases linearly with volume added. However, the probable explanation of this behaviour is relevant to the saturation concept already mentioned for the latex of large particles (295nm). From the shape of the isotherm one can somewhat tune density and homogeneity of the monolayer to be deposited onto a substrate.

6.4.3 Deposition of Latex Films on Glass Substrates

6.4.3.1 Contact Angle Measurements

Surface properties, such as hydrophobicity and hydrophilicity are frequently used for describing the behaviour of surfaces investigated. A surface is hydrophobic if it tends not to adsorb water or not be wetted by water. On the other hand, a surface is hydrophilic if it tends to adsorb water or be wetted by water.

Practically, both hydrophobicity and hydrophilicity are intimately related to each other, so contact angle measurement can be a quantitative method to both measure wettability and differentiate between both characteristics.

Figure 6-5 shows the contact angle study for two different glass substrates, untreated and treated with the UV-Ozone treatment. It is clear that the treatment increases the hydrophilicity of the substrate with the contact angle measured being markedly reduced. In extreme hydrophobic case, the water droplet can be spherical on the surface and roll away from its original places. On the other hand, treatment of the substrate for 30min produces a surface with excellent spreading.
Figure 6-5  Contact angle measurements before and after the UV-ozone treatment of the glass substrates.

6.4.3.2  Surface-Polymer Interactions

The effect of UV-ozone treatment has on increasing hydrophilicity of the surface. However, to understand thin film stability on substrate after deposition. Figure 6-6 shows the interaction between substrates (both untreated and treated substrates by UV-ozone) and the latex particles. It is observed from that figure the deposited LB film on the untreated substrate was discontinuous and randomly distributed. Hence, a non-uniform film will result. On the other hand, the treated substrate shows in the same figure also a relatively homogeneous deposited LB film which may lead to the production of a high quality uniform film.

Figure 6-6  microscopic images show the interaction between latex 1 particle and before and after treatment of substrates by UV-Ozone.
6.4.4 Particles Presence at Air Water Interface as a Function of Time

The interface is a surface separating two phases of matter, each of which may be solid, liquid, or gaseous. To focus precisely on this concept, the presence of the latex particles has been investigated as a function of time via two different ways. Firstly, a Petri dish has been used to see the diffusion of the particles at the air /water interface. A small amount of the latex particles dispersion was collected from the dispersed phase in the Petri dish at different times. A UV-Vis study has been performed on the collected latex dispersion that results from the diffusion of particles from the surface to the bulk over time. Figure 6-7 shows the absorbance at $\lambda=450$nm as function of time for two different latex particles size (295nm and 80nm). A marked increase in absorption was observed of the latex 1 at short times (between 1min and 3min) after which the rate decreases. To explain these two different behaviours, a schematic diagram in Figure 6-7 (b) is shown. From the schematic diagram it can be explained that the diffusion rate at the initial time was higher than in the proceeding time. On the other hand, the absorbance change associated with the presence of the latex 2 is almost invariant with time which means that the amount of particles reaching the bulk does not change. A possible reason for the differing behaviour for the different particle sizes may be related to difference in density and the amount of the surfactant used for stabilization which is illustrated in Figure 6-7 (d) that some particles are suspended in different position in the medium.

The second investigation was done by using surface tension measurements as a function of time for the latex 1 and 2. Figure 6-8 shows a gradual increase in the surface tension of latex 1 from the initial time of 1min to the 18min where the surface tension was very close to the surface tension of the water. However, this measurement simply reveals how long the latex particles stay at the air/water interface. One can measure the change in surface tension as a function of time and relate it to the reference surface tension of pristine water to indicate how much material remains at the air water interface. Again one can see large differences between the behaviour of latex 1 and latex 2 respectively. The data suggests that even after long time periods some latex particles remain at the interface. The apparent discrepancy in the data obtained from spectroscopy and surface tension for the large particles may be explained by the fact that the particles dispersed in the bulk are not evenly distributed within the volume of the liquid. Moreover, when
the latex particles come under the influence of buoyancy, they have a tendency to float or to sink depending on their size and density. However, as long as the particles remain separate the process is called creaming [6].

**Figure 6-7** Absorbance of latex 1 and 2 as a function of time. (a & d) image of the diffusion of latex 1 & 2 respectively. (b & c) schematic diagrams show the diffusion mechanisms of the latex 1 & 2 respectively.

**Figure 6-8** Surface tension of latex 1 and latex 2 as function of the time.

**6.4.5 The Effect of Surface Pressure**

As discussed above in section 6.4.2 during the pressure-volume isotherm measurement of the latex 1, four LB films have been deposited at various pressures (3, 6, 9, 12 mN/m). The obtained films have been analysed by AFM. **Figure 6-9** presents a series of AFM
images which show that the resulting surface coverage is not particularly sensitive to deposition pressure. In the next discussion, it will become clear that the most important parameter for homogeneous surface coverage is dipping speed.

Figure 6-9 AFM images (height & phase 50µm×50µm) of latex 1 at different surface pressure (3, 6, 9 and 12mN/m).

6.4.6 The Influence of Deposition Velocity of the Substrate Motion on Coverage

Optimising the coverage rate of the LB films is very sensitive to the influence of the velocity of the substrate motion. To show this, samples have been prepared by using two different deposition speeds (5mm/min and 25mm/min). Figure 6-10 shows AFM images of two different LB films that are deposited at the speed mentioned above. It is clearly evident that the efficiency and uniformity of deposition is greatly enhanced for the higher speed. In contrast, weak coverage is observed for the slower speed.
In order to improve the coverage of the resulted LB films, a new approach has been followed. This can be easily achieved by sequential repeat dippings. Due to the hydrophillic nature of the latex, they will efficiently adsorb on the treated glass substrates thus filling the voids. **Figure 6-11** shows the AFM and microscope images of latex 1 as a function of increased immersion time. The increase in the coverage density is quite evident at increased numbers of immersions. Therefore, with each immersion, new particles are added to voids in the deposited film area. After 6 immersions, the covered area approached 100%.
Figure 6-11 AFM images (height & phase 50µm×50µm) and microscopic images (10µm) of latex 1 LB films deposited by (1, 3 & 6 immersions).

The same procedure was followed for the case of the small latex particles (latex 2), the initial surface pressure chosen to be 12mN/m. Figure 6-12 shows the series of AFM images (height and phase) of LB films of latex 2 deposited using sequential dipping (1, 3 and 10 times). As latex 2 contains a large amount of surfactant, it is clear from the images that its presence has an appreciable effect on the quality of the films. In this situation, even when the latex particles are concentrated and closely packed, as the water evaporates, the surfactants have the tendency to trap small volumes of water in the drying films [7]. Hence, a non-uniform and incomplete coverage is found for the first and third immersions. By increasing the immersion number to 10 times, the coverage density is increased, although the films are still relatively non-uniform. Therefore, it can be concluded that the latex 2 has not produced the expected quality of the LB film which is promising for coatings purposes.
AFM images (height & phase 50µm×50µm) of latex 2 LB films deposited by (1, 3 & 10 immersions).

6.4.8 Sintering of Micro-Cracks in the Latex 1 Thin Film

Latex film cracking is a major issue in the use of high Tg polymers for thin coating applications. Despite the high density of the latex 1 LB thin film deposited at the optimised conditions. It is seen that there are a large number of cracks present due to local mismatches in the polymer packing. This has been discussed in the literature review section 2.3.3. Film uniformity can be increased by sintering the film above the glass transition temperature. In the sintering experiment, the film was placed in an oven at 60°C to ensure sufficient polymer chains mobility and be capable for distinguishing any morphological changes in films structures. At various times of the sintering process, AFM was carried out with height images which are presented in Figure 6-13. Due to particle deformation, this series of AFM height images shows the fading stage of formed cracks in the film. In this figure the image before sintering shows the latex monolayer with almost perfect close packing, but deep cracks w appeared in the surface and subsequently led to form island of particles, in which the particles are still lying next to each other.
Therefore, a comparison of this series of images (before and after annealing) reveals the effect of the sintering process, where the particles have flattened as a result of the reduction in capillary stresses during the process. The surface roughness has been characterised before and after the sintering experiment.

Furthermore, it is obvious that, the latex particles in the sintering process up to 4 hours still have spherical shape but with decrease in their diameter. Beyond that the particles start disappear until eventual deformation at 12 hours. The surface roughness has been characterised before and after the sintering experiment and found to show continuous decrease with sintering time. Figure 6-14 displays exponential decay behaviour in the surface roughness. This behaviour of decay has been observed in other studies [8-10].
Figure 6-13 AFM height images (10x10 µm) of latex 1 particle monolayer sintered at 60 °C.
Figure 6-14 Surface roughness of latex 1 monolayer during annealing at 60 °C.

6.5 Conclusion

Producing crack-free monolayer latex over large area has been discussed in this chapter. Fabrication of polymer latex thin film has promising applications in the purposes of hard coatings. Deposition process has been optimised by different investigations such as substrate treatment, contact angle measurements, surface tension study, and particles diffusion at the interface. The surface coverage was optimised by different parameters such as surface pressure, deposition velocity during raising the substrate from the LB trough, and the immersion time. However increasing time was more effective parameter with latex 1 in terms of producing the highest surface coverage which was achieved after 6 immersing times.

The crack-free latex 1 film was achieved by sintering that film for different time at 60 °C. The desire film was demonstrated after placing it in the oven for 12 hrs at 60 °C, AFM studies confirmed the homogeneity of the produced LB film over large areas.
References


Chapter 7 Summary and Future prospective

7.1 Summary

Producing an alternative transparent flexible electrode which can be incorporated in different optoelectronic applications as a replacement for ITO was the main aim for this work. Also, finding a way to protect the fabricated electrode such as using hard coating film based on polymer latex. Thus, to fulfil this objective of this work a transparent flexible electrodes was produced based Ag NWs. This conductive network was investigated and developed to ensure its applicability as an alternative for ITO and its reliability to be suitable as a part of flexible devices such as wearable photovoltaic devices or environmentally adaptable devices.

In chapter 4, the random Ag NWs network which was deposited on PMMA substrate by the spray deposition technique showed remarkable electrical, optical and mechanical properties which can allow Ag NWs to be a promising candidate for replacing ITO. The addition of graphene flakes which were deposited by the LS process on the top of the Ag NWs led to the enhancement of the electrical conductivity of the Ag NWs network where graphene acted to reduce the influence of formed junction resistance between NW-NW by wrapping them together or/and bridge unconnected NWs. Moreover, this enhancement of electrical conductivity was achieved without affecting the standard industrial condition of the optical transmittance of the fabricated hybrid electrode. In addition, the deposited graphene led also to modify the mechanical properties of Ag NWs electrode in terms of bending and stretching tests. This finding indicated reliability of the Ag NWs, but the hybrid Ag NWs/graphene electrode exhibited to be more reliable under the applied stress.

In chapter 5, the pristine Ag NWs transparent flexible electrode was showing an improvement in the electrical conductivity after applying the three point bending test which was carried out by DMA instrument. It was found that the reduction in the electrical resistance was directly proportional to the applied load. The probable reason of this reduction was resulted by the joining between NW-NW when the electrode was targeting by the oscillatory hitting which was performed by the test clamp beam. The
morphological structures showed that NWs were welded at the junctions between NW-NW. The metallic atomic diffusion was activated by the applied mechanical stress during the experiment time.

In chapter 6, a novel method for producing a large area crack-free hard coating based on polymer latex was achieved. This is an environmentally friendly high performance protection coating with no hazardous materials deposited by LB deposition technique. The fabrication of the latex monolayer was optimised to be produced over large area with high surface coverage. AFM morphological studies confirmed the homogeneity of the produced LB film.

7.2 Future prospective

Increasing the light absorption in the active layer at a limited thickness of film still remains a challenge in the fabrication of solar cells. Increasing harvesting incident light is one of the important key to increase the efficiency of the organic solar cells for instance. Therefore, the main aim of light trapping is to increase the optical light path within the solar cell system. However, harvesting light by scattering light behaviour by plasmonic effect is one of the desirable ways. Plasmonic effect has the potential to be applied in organic solar cells. Hence light can be concentrated and ‘folded’ into an active layer to convert more light into solar energy, resulting in higher efficiency. The suggested plan is to incorporate metallic nanowires into the active layer to increase light absorption by active layer materials. Luping Yu et al demonstrated the increase in the active layer absorption by incorporating a mixture of Ag and Au nanoparticles [1]. The achieved enhancement was not only in the light absorption, but also in the charge carrier density and the lifetime. Therefore, the key point is to benefit from the local surface plasmonic resonance (LSPR) metallic nanoparticles. So, the potential work in based on incorporating Ag NWs in the active layer.

Also, for the same purpose of improving the efficiency of solar cells, the light optical path length is desirable to be increased within the solar cell active layer. Therefore, one of the suggested ways is light trapping concept. As my group has demonstrated 3D photonic crystals based on polymer latex can be incorporated with the solar cell to
increase the probability of higher absorption which lead to increase photocurrent density in the cell.

Photonic crystals are defined as the periodic structure with lattice period similar to the wavelength of the light. Some phenomena may occur such as reflection and diffraction as a result of the light interaction with photonic crystal structure. However, 3D photonic crystals can provide a potential opportunity to enhance the output of solar cells, but as the polymer suffered from low transmittance in higher photon energies, photonic crystals with controlled thickness may show good transmittance in that band. In case of placing photonic crystal, the following schematic diagram shows photonic crystal is either placed on the top of the solar cell (angular-selective case), in between two solar cells (energy-selective case) or on the back of a solar cell (resonant light trapping) as showing in Figure 7-1.

![Schematic diagram of the three areas of application of 3D photonic crystals.](image)

**Figure 7-1** Schematic diagram of the three areas of application of 3D photonic crystals. For angular-selective applications on the top of a solar cells (a), as intermediate reflector (b) or for enhanced light trapping (c). While visible and IR spectrum wavelength are comparable to the particle size, particle size range from 300-1200 nm can be considered to be incorporated.

Finally, basic photovoltaic structure whereby an active material such as a conjugated polymer (PPV) will be sandwiched by in a configuration. In this final piece of work I will study the interface between the silver nanowire/graphene electrodes and the optically active layer. Using photoconductivity measurements will be able to look at the effectiveness of charge transfer at the interface and give the first indications of the relevance of our novel device structures for novel solar applications. Also, these
measurements could be shown for stretched samples which would allow for the realization of wearable photovoltaic devices or environmentally adaptable devices

References