PROCESSING OF ULTRA-THIN FILM OF UN MODIFIED C₆₀ FULLERENE USING THE LANGMUIR-BLODGETT TECHNIQUE.

EFFECT OF STRUCTURE ON STIFFNESS and OPTOELECTRIC PROPERTIES

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Materials Science and Engineering

By

HASANAIN BASIM ALTALEBI

B.S., BABYLON UNIVERSITY, 2008

2017

Wright State University

Maher S. Amer, Ph.D.
Thesis Director

Joseph C. Slater, Ph.D., P.E.
Chair, Department of Mechanical and Materials Engineering

Committee on final examination:

Maher S. Amer, Ph.D.

Ahsan Mian, Ph.D.

Allen Jackson, Ph.D.

Robert E. W. Fyffe, Ph.D.
Vice President for Research and Dean of the Graduate School
ABSTRACT

Monolayer films of C_{60} fullerene were for the first time produced successfully by using the Langmuir-Blodgett technique. The processing parameters were optimized and the structure of these films has been investigated using Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM). Film stiffness was measured to be in the range of 15 MPa to 32 MPa depending on the nature of the solvent used to process the films. Optical transparency and electrical performance have been measured and correlated to the film structure. While 100% transparent, the film measured conductivity was in the range of 10^{13} S/m, that is orders of magnitude higher than silver, copper, and even compacted graphene sheets. These films have great potential applications in many different fields including transparent electrodes, sensor, optoelectronic devices and photovoltaics.
# TABLE OF CONTENTS

1.0 Introduction .................................................................................................................. 1

1.1. The C₆₀ Fullerene Molecules ....................................................................................... 2

1.1.1. Electronic Transport Properties of C₆₀ Fullerene ................................................... 4

1.1.2. Optical Properties of C₆₀ Fullerene ......................................................................... 6

1.2. Langmuir Blodgett Technique ...................................................................................... 6

1.2.1. Langmuir Blodgett Instrument ................................................................................ 7

1.2.2. Formation of Langmuir Film .................................................................................. 12

1.2.3. Film Deposition ....................................................................................................... 12

1.2.4. Surface Tension ...................................................................................................... 17

1.2.5. Surface Pressure/Area per Molecule Isotherm ......................................................... 19

1.3. Scanning Tunneling Microscope .................................................................................. 21

1.3.1. Scanning Tunneling Microscope Instrument ............................................................ 21

1.3.2. Scanning Tunneling Microscopy Tips ..................................................................... 23

1.3.3. Mechanical Vibrations ............................................................................................ 23

1.3.4. Modes of STM Operation ....................................................................................... 23

1.4. Non-Contact Atomic Force Microscopy ...................................................................... 25

1.4.1. AFM Instrumentation .............................................................................................. 25

1.4.2. Image Formation ..................................................................................................... 27

2.0 Experimental Procedure ............................................................................................... 28
2.1. Langmuir Blodgett Instrumentation.................................................................28
2.1.1. Lab Environment .........................................................................................31
2.1.3. Film Formation Procedure ........................................................................33
2.1.4. Film Deposition. .........................................................................................35
2.2. Scanning Tunneling Microscope and Atomic Force Microscopy measurements...36
2.3. Electrical Conductivity and Transparency Measurements..............................36
3.0 Results and Discussion ..................................................................................41
3.1. Film Formation .............................................................................................41
3.1.1. Effect of C$_{60}$ Solution Concentration...................................................46
3.1.2. Effect of Solvent Evaporation Time. .........................................................51
3.1.3. Effect of Fullerene/Solvent Interaction......................................................51
3.2. Analysis of Optimum Films. .........................................................................60
3.2.1. Scanning Electron Microscopy (SEM) Micrographs....................................60
3.2.2. Atomic Force Microscopy and Scanning Tunneling Microscopy Images........60
3.2.3. Optical Transparency. ..............................................................................70
3.2.4. Electric Performance ..................................................................................70
4.0 Conclusions ....................................................................................................73
5.0 References ......................................................................................................74
LIST OF FIGURES

Figure 1.1. Schematic representation of C$_{60}$ molecule adapted from ref. [26] ........................ 3

Figure 1.2. The 1 nm effective diameter of the C$_{60}$ fullerene molecule adapted from ref. [5] .................................................................................................................. 5

Figure 1.3. Schematic of LB trough. The Wilhelmy plate monitors the surface through a microbalance interfaced with computer. Barrier movement is also controlled by computer. Adapted from ref [36] ...................................................................................... 8

Figure 1.4. Wilhelmy plate method adapted from ref. [41] .................................................. 10

Figure 1.5. The Langmuir Balance method adapted from ref. [38] ................................. 11

Figure 1.6. Langmuir-Blodgett deposition adapted from ref. [40] ............................ 13

Figure 1.7. Deposition process of different types of molecular films on solid substrate adapted from ref. [43] ........................................................................................................... 15

Figure 1.8. Langmuir-Schaefer deposition adapted from ref. [44] ............................. 16

Figure 1.9. A schematic depicting the force imbalances resulting in surface tension adapted from ref. [45] .................................................................................................................. 18

Figure 1.10. Surface pressure versus area per molecule isotherm adapted from ref. [43] ................................................................................................................................. 20

Figure 1.11. The Scanning Tunneling Microscope in a nutshell adapted from ref. [47] ........................ ........................................ 22

Figure 1.12. An STM can be operated in either the constant-current or the constant-height mode. The images are of graphite in air. Adapted from ref. [46] ........................................ 24

Figure 1.13. Schematic diagram of Atomic Force Microscope adapted from ref. [56] ................................................................................................................................. 26

Figure 2.1. Nima® Langmuir-Blodgett instrument model 1222D2 ............................ 29

Figure 2.2. Main screen of Nima® control screen ......................................................... 30
Figure 2.3. Isotherm for pure water showing minute pressure build-up as a proof of surface purity .................................................................32

Figure 2.4. Ultrasonic cleaner, Parafilm and sample of C_{60} solution .........................34

Figure 2.5. STM stage used in our experiment ............................................................37

Figure 2.6. AFM stage used in our experiment ............................................................38

Figure 2.7. Electrical measurements were performed by using an MN36 Digital Mini Multimeter (from EXTECH instrument) .................................................................39

Figure 2.8. Optical measurements were performed by using a Fluke 941 light micrometer ........................................................................40

Figure 3.1. Early trial isotherm using toluene solvent ...............................................42

Figure 3.2. Same isotherm as in Figure 3.1 with film length instead of area per molecule.............................................................................43

Figure 3.3. Stress/Strain curve for the solid phase of the film shown in Figure 3.1......44

Figure 3.4. Schematic presentation of film Stress/Strain curve calculations.............45

Figure 3.5. Isotherm obtained for toluene solvent with 0.025 mg/mL concentration. Film average thickness 1.17nm .................................................................47

Figure 3.6. Stress/Strain curve for film shown in Figure 3.5. Film stiffness 26.58 MPa........................................................................48

Figure 3.7. Isotherm for 0.025 mg/ml in toluene with 500 µL total solution ..............49

Figure 3.8. Stress/Strain curve for a HCP monolayer of C_{60} in toluene. Stiffness 32.1 MPa........................................................................50

Figure 3.9. Effect of solvent evaporation time for C_{60} in chlorobenzene. True HCP structure is observed with 1/2 hour solvent evaporation time ........................................52

Figure 3.10. Isotherm for C_{60} monolayer with HCP structure from benzene ..........53

Figure 3.11. Isotherm for C_{60} monolayer with HCP structure from toluene ..........54

Figure 3.12. Isotherm for C_{60} monolayer with HCP structure from chlorobenzene ...55

Figure 3.13. Stress/Strain curve for a HCP monolayer of C_{60} in benzene. Stiffness 15.36 MPa........................................................................56
Figure 3.14. Stress/Strain curve for a HCP monolayer of C_{60} in toluene. Stiffness 32.1 MPa ................................................................. 57

Figure 3.15. Stress/Strain curve for a HCP monolayer of C_{60} in chlorobenzene. Stiffness 15.1 MPa ................................................................. 58

Figure 3.16. Dependence of film stiffness on fullerene/solvent interaction strength as indicated by solution limit ................................................................. 59

Figure 3.17. SEM micrograph for C_{60} film out of benzene ........................................ 61

Figure 3.18. SEM micrograph for C_{60} film out of toluene ........................................ 62

Figure 3.19. SEM micrograph for C_{60} film out of chlorobenzene ........................................ 63

Figure 3.20. AFM-3D image of benzene sample of one layer ........................................ 64

Figure 3.21. AFM-3D image of toluene sample of one layer ........................................ 65

Figure 3.22. AFM-3D image of chlorobenzene sample of one layer ........................................ 66

Figure 3.23. STM-3D image of benzene sample of one layer ........................................ 67

Figure 3.24. STM-3D image of toluene sample of one layer ........................................ 68

Figure 3.25. STM-3D image of chlorobenzene sample of one layer ........................................ 69

Figure 3.26. Correlation between film conductivity and solvent dipole moment ........... 72
LIST OF TABLES

Table 3.1. The stiffness of the produced HCP monolayer films.................................51
Table 3.2. Optical transparency of the produced films................................................70
Table 3.3. Electric performance of the produced films .............................................70
ACKNOWLEDGMENTS

My thesis would not have been possible without the help of my family, friends and colleagues. I would like to first give thanks to my family for their unconditional love and support throughout my life. My mother and father have taught me to work hard for what I believe in and I hope I can continue to live up to their standards. My work is dedicated to my biggest role model, my father, who passed away while I was working on my Thesis. He will always be missed and never forgotten.

My advisor professor Maher Amer has been vital to my success in my master’s studies. I am so blessed to have the opportunity to work so closely with professor Amer, truly a wealth of knowledge in our field of materials. Professor Amer was like a father to me and I forever owe a debt of gratitude for his patience and guidance. He supported me personally and academically through all the ups and downs of my research. I have learned a great deal about materials science from him and have grown simultaneously as a student and a person.

Also, I would like to thank my sponsor, Higher Committee for Education Development in Iraq (HCED) for their support and for giving me the chance to finish my master’s degree in the United States, at Wright State University.

Finally, many thanks to my best friend, Patrick Cleaver for his encouragement and believing in me. It was an honor to work with him and his help won’t be forgotten.
DEDICATION

This thesis is dedicated to my mother and to the memory of my beloved father

Dr. Basim Abduljabbar Altalebi
1.0 Introduction

Zero-dimensional Fullerene also known as C$_{60}$ or Buckminster fullerene is considered the third allotrope of the carbon element. It has received a great deal of attention from material scientists and researchers since its discovery by Robert F. Curl, Jr., Richard E. Smalley, and Sir Harold W. Kroto in 1985 [1-5]. Specifically, thin films of fullerenes are important because they show many outstanding features such as superconductivity, superconductivity upon reduction, photo-electrochemical response, and unique electrochemical behavior [6]. Also, it was found that C$_{60}$ particulates and ultrathin films could be super solid lubricants, due to the fact that C$_{60}$ molecules have a spherical shape which is similar to that of ball bearings [7]. One of the most commonly utilized techniques to create films with ordered structures is the Langmuir technique, creating films at the air-water interface that can be transferred to a solid substrate [8]. It has been proven that LB films can be used in many nanotechnology areas such as liquid crystal devices, semiconductors, sensors, optoelectronic devices and photovoltaics [9]. Producing such monolayer fullerene films is not that simple or straightforward especially with pristine, un-modified C$_{60}$. The first investigations by Obeng and Bard regarding the deposition of stable Langmuir films of C$_{60}$ has been unsuccessfully replicated by several teams, who report that such films are unstable and very hard to reproduce [10-15]. Successful attempts could only be achieved with surface modified C$_{60}$ or C$_{60}$ derivatives due to the well-known hydrophobic nature of the unmodified nano-carbon spheres [16-21].
In this work, we conduct a systematic study to investigate the parameters affecting the formation of mono-layer unmodified C\textsubscript{60} fullerene nano-films and report about their electrical and optical properties. Langmuir-Blodgett films will be produced and characterized using both Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM).

1.1 The C\textsubscript{60} Fullerene Molecules

C\textsubscript{60} fullerenes are the zero-dimensional form of graphitic carbon that can be described as rolling up a graphene sheet by adding pentagons to its structure [22]. The C\textsubscript{60} molecule has a truncated icosahedron shape which is similar to a soccer ball having 12 pentagons and 20 hexagons [23] (Figure 1.1). The name of Buckminsterfullerene was given to C\textsubscript{60} molecules, named after the architect Buckminster Fuller who created the geodesic cage in the 1960's [24]. The structure of buckminsterfullerene C\textsubscript{60} consists of sixty sp\textsuperscript{2} hybridized carbons [25]. Investigation of the C\textsubscript{60} structure displays that each pentagon is surrounded by five hexagons. This makes C\textsubscript{60} the smallest fullerene having no touching pentagons. There are two classes of C-C bonds that can be observed in the fullerene structure which are C-C bonds between a hexagon and a pentagon and C-C bonds between two hexagons [5]. This geodesic and electronic bonding are responsible for the stability of C\textsubscript{60} molecules [26]. C\textsubscript{60} molecules have a significant feature which is its high degree of symmetry. The geometry of the C\textsubscript{60} molecule allows for 120 symmetrical operations, including axial rotation and planar reflection; mapping the molecule onto itself. This is the reason why the C\textsubscript{60} is the most symmetrical molecule [23].
Figure 1.1. Schematic representation of C\textsubscript{60} molecule adapted from ref. [26].
In order to quantify the effective diameter of the C₆₀ fullerene molecule, the sphere diameter must be approximated and combined with the effective thickness of the pi-electron orbitals that make up the molecule. The spherical approximation results in a diameter of 6.88 Å. The thickness of the molecule can be approximated by the well-known thickness of graphene, which is 3.37 Å. Combining these two factors results in an effective diameter of C₆₀, approximately 1 nm, truly a nano material, as shown in Figure 1.2 [5]. The centers of the C₆₀ molecules form a FCC lattice, with a nearest-neighbor C₆₀ – C₆₀ distance that corresponds to the diameter of the molecule. At room temperature, the size of the cubic unit cell is 14.17 Å, and the nearest-neighbor distance is 10.02 Å [27].

1.1.1. Electronic Transport Properties of C₆₀ Fullerene

Electronic transport properties of individual C₆₀ molecules have been studied by using a scanning tunneling microscope (STM). In order to understand the electrical resistance, an experiment was set up. In this experiment, a C₆₀ molecule was introduced between the STM tip and a clean Au surface at 300 K in a high vacuum. At relatively low applied bias voltages, the C₆₀ molecule showed linear current-voltage behavior. This indicates that C₆₀ behaves like a metal–vacuum–metal tunnel junction at a low bias voltage within the C₆₀ HOMO-LUMO gap of 1.7eV [28].
Figure 1.2. The 1 nm effective diameter of the C₆₀ fullerene molecule adapted from ref. [5].
1.1.2. Optical properties of C_{60} Fullerene

Optical properties of C_{60} fullerene are basically spectroscopic properties which include the infrared (IR) absorption spectrum, the absorption spectrum in the visible and ultraviolet (UV) ranges, and Raman scattering spectra (RS). First, Infrared (IR) absorption spectrum consists of four active modes at 527, 576, 1183, and 1429 cm\(^{-1}\). Second, the absorption spectrum in the visible and ultraviolet (UV) ranges contains peaks relating to optical transitions at 3.5–5.6 eV and to excitons at energies below 3 eV. Measurement of the absorption in the visible region as a function of temperature, hydrostatic pressure, and magnetic field has demonstrated spectral features near the absorption edge are as a result of excitons. Generally, the UV and visible absorption spectra show characteristic features of molecules in the gas or liquid phase. This means that fullerenes can be thought of a single molecular crystal. Finally, Raman scattering spectra (RS) contain two “breathing” Ag-modes indicating symmetric oscillations of the molecule (497 cm\(^{-1}\)) and of pentagons (1469 cm\(^{-1}\)), and eight Hg-modes: 270, 433, 709, 773, 1103, 1253, 1424, and 1576 cm\(^{-1}\). Fullerenes have both intermolecular and intramolecular processes, which effect their optical properties [29].

1.2. Langmuir Blodgett Technique

There are many different methods to create monolayers of fullerene molecule. A few examples include vacuum sublimation, solvent evaporation from a fine suspension, self-assembly, and Langmuir –Blodgett (LB) deposition. The LB method is especially convenient because it enables the creation of very uniform multilayers, with control over molecular orientation, and with good control over the film thickness, uniformity, and architecture [30]. The LB method is relatively more economical when compared to other
methods due to the ability of constructing two-dimensional molecular sheets of large areas at low cost [31]. It is beneficial to create high quality films having remarkably enhanced molecular order and a uniform surface [32]. The production of ultrathin Fullerene films having ordered structure helps to increase understanding of fullerene and also has practical applications [33].

Historically, in 1774 Benjamin Franklin was the first who observed the effect of the spreading of the oil droplets on a pond’s surface. Later, Lord Rayleigh estimated that an oil layer on the water’s surface was 10 and 20 Å thick, very close to the thickness of monomolecular film of fatty acids. In 1891, Agnes Pockels studied the variation in the surface tension of oil by designing a device with a movable strip that allowed change to the area of the water surface. In 1917, Irving Langmuir studied, in depth, the floating monolayer and developed many techniques such as the surface film balance. In 1919, Katherine Blodgett reported the transferring of monolayers and multilayers onto a solid substrate. The building up and the deposition, together is known as the Langmuir – Blodgett technique [34].

1.2.1. Langmuir Blodgett Instrument

Basically, Langmuir Blodgett devices consist of five main parts: a trough, a subphase, a compression system, a sensor and a dipping system as illustrated in Figure 1.3. The trough is a subphase container of rectangular or circular geometry can be used. The materials used for the trough required to be inert, resistant to organic solvents, and easy to clean and formed. Polytetrafluoroethylene (PTFE) is very widely used material for this purpose [34, 35]. The subphase can be water, mercury, hydrocarbons or glycerol.
Figure 1.3. Schematic of LB trough. The Wilhelmy plate monitors the surface through a microbalance interfaced with computer. Barrier movement is also controlled by computer. Adapted from ref. [36].
Water subphase of highest purity is commonly used. It can be either of distilled or deionized water [35]. The compression system includes movable barriers of PTFE material connected to a motor with a controlled speed to compress the film [35].

The Sensor is for surface pressure measurement. In this regard, there are two different approaches to record the surface pressure: Langmuir balance and Wilhelmy plate (more popular) [34, 35]. In the Wilhelmy plate method, a plate is suspended from a sensitive balance and partially immersed in the subphase. The forces that act on the plate are gravity, buoyancy and surface tension [35] as shown in Figure 1.4. Many different materials can be used such as mica, etched glass, and platinum, but a paper plate of high quality filter or chromatography paper are more common [37]. However, Langmuir balance method is a differential measurement, in which the magnitude of force that acts on a movable barrier that separates a pure water surface from the film is determined [38] as shown in Figure 1.5. The dipping system consists of a solid substrate and a well for LB deposition. Substrates of various materials can be used [34].
Figure 1.4. Wilhelmy plate method adapted from ref. [39].
Figure 1.5. The Langmuir Balance method adapted from Ref. [38].
1.2.2 Formation of Langmuir Film

Typically, Langmuir films are insoluble monolayers that are created at the gas/liquid interface in such a way that their free energy is minimized. First, this is done by dissolving material under investigation in a suitable solvent. Basically, the candidate materials are recognized of having amphiphilic features, which means they have a hydrophilic (water-loving) head group which is easily soluble in water and a hydrophobic (water-hating) tail group. The balance between these groups will lead to the creation of the monomolecular layer. A variety of different materials can be used such as fatty acids, aromatic compounds, dyes, fullerenes, charge-transfer complexes, polymers, and biological compounds. Regarding the solvents, they should be capable of dissolving enough monolayer material, not reactive chemically with materials, not soluble with the subphase and able to evaporate within acceptable time to avoid creating contaminations. Second, a certain amount of the solution is spread on the subphase (usually water) and left for a suitable time to ensure the evaporation of the solvent is achieved completely. This will result in a monomolecular layer of one-molecule thick, with head groups immersed in the water and tail groups remaining outside (pointing towards the gas phase). Finally, movable barriers work on compressing the monolayer film where it will go through different phases as a function of compression [34, 35].

1.2.3 Film Deposition

This process can be defined as the chemical reaction between the monolayer of the desired material and a substrate of a certain type. The way to do that is by moving a solid substrate vertically through the monolayer/air interface, while the pressure is held constant [34, 35] as shown in Figure 1.6. Based on the materials’ nature of the utilized
Figure 1.6. Langmuir – Blodgett deposition adapted from Ref. [40].
substrate, two cases of deposition can happen. First, if the substrate is hydrophilic, the deposition occurs on the down path mode, this is when the substrate is raised through the water. For this reason, it is preferable to immerse the substrate before the spreading and compressing the film. This will help to avoid the aggregation of the deposited film.

Second, if the substrate is hydrophobic, the deposition takes place on the up path, this is when the substrate is lowered to the water subphase [41]. There are three types of depositions that can be achieved which are Y-, X-, Z- types as illustrated in Figure 1.7. Y-type is widely used for monolayer deposition on the down and up path, in which the molecules are arranged in head to head and tail to tail pattern. In the X- and Z-type, the deposition takes place on the down path or on the up path, respectively [42].

Besides holding the temperature and surface pressure constant during the deposition process, the deposition can be affected by chemical composition and physical structure of the substrate surface [35]. However, for very rigid monolayers, the Langmuir – Schaefer method can be used. In this method, monolayers at the air-water interface are deposited horizontally onto a hydrophobic substrate as shown in figure 1.8. Typically, this method can be used to deposit monolayer films or multilayers films of X type in certain cases [42].
Figure 1.7. Deposition process of different types of molecular films on solid substrate adapted from ref. [43].
Figure 1.8. Langmuir–Schaefer deposition adapted from Ref. [44].
1.2.4 Surface Tension

The air/liquid interface has high free energy caused by the difference in environment between the surface molecules and those in the bulk. The creation of a monolayer as a result of spreading an amphiphilic material on a liquid subphase has an influence on the surface tension. The surface tension can be understood as a negative pressure which can be explained based on the fact that the attractive interaction of the water molecules at the interface, will be minimized by accumulation of the amphiphilic material at the air/liquid interface. The existence of monomolecular film on a liquid surface will lead to the reduction in the free energy of the system due to the interactions that initiate between the hydrophilic polar group and the water surface molecules. For this reason, the reduction in the surface tension occurs. This reduction will cause an expansion of the air/water interface in the presence of monolayer. When the surface area per molecule of the monolayer film is large and the volume of the spreading is low enough to restrict the interactions between neighboring amphiphilic molecules, then there is very little effect by the monolayer on the surface tension of the liquid. However, the reduction of surface area per molecule due to the compression by the movable barriers result in decreasing the intermolecular distance, thus surface tension is reduced. The amphiphilic molecules begin to interact and show a repulsive effect on each other [38] (Figure 1.9).
Figure 1.9. A schematic depicting the force imbalances resulting in surface tension adapted from Ref. [45].
1.2.5. Surface Pressure/Area per Molecule Isotherm.

The two-dimensional film will go through several phase transformations as a function of compression as illustrated in Figure 1.10. These phases are similar to three-dimensional gas, liquid, and solid states. In the gas phase, the area per molecule is high and molecules are far apart on the liquid subphase, hence, there is no interaction between molecules. As the film compresses, the area per molecule is reduced and molecules start to interact with each other causing an increase in the surface pressure, indicating a phase transformation to liquid expanded (LE) state. With even more compression, the pressure starts to increase sharply indicating the transition from the liquid expanded phase to a condensed phase known as the solid phase. Upon extrapolation of this phase of the isotherm to zero surface pressure, the x-intercept provides the area/molecule expected for a hypothetical uncompressed close-packed monolayer. Further compression will lead the film to be collapsed in which molecules are forced out of the monolayer, causing disordered multilayer film. This collapse is highly dependent on the compression rate and film history [34, 35].
Figure 1.10. Surface pressure versus area per molecule isotherm adapted from ref. [43].
1.3 Scanning Tunneling Microscope

The discovery of the scanning tunneling microscope (STM) was achieved by Binning and Rohrer in 1981 at the IBM Zurich Research Laboratory in Switzerland. STM was developed by Binning, Rohrer, Gerber, and Weibel. Binnig and Rohrer won a Nobel Prize in Physics in 1986 for their invention [46, 47]. The working concept of the STM is based on a quantum mechanical effect known as tunneling, where electrons exhibit wave properties [48]. The STM provides images regarding the topography of the material’s surface with sub-atomic resolution [49].

1.3.1 Scanning Tunneling Microscope instrument

In the STM device as illustrated in Figure 1.11, a conductive sharp tip (usually made of W or Pt–Ir alloy) is mounted on a piezoelectric translator which consists of three elements ($p_x, p_y, p_z$). The piezoelectric translator provides precise atomic scale control of the $x, y, z$ motion based on the transverse piezoelectric effect, which means that the crystal is elongated perpendicular to the applied electric field. The tip is placed 0.3–1 nm to the surface of the conductive material under investigation. A bias voltage is applied between the tip and the sample surface which will enable electrons to tunnel between them, generating a current that can be measured. The direction of current flow depends on the polarity of the bias voltage ($V$). If $V > 0$, the electrons in the occupied states of the tip will penetrate to the empty states of the sample. If $V < 0$, the electrons in the occupied states of the sample will penetrate to the empty states of the tip [46, 47]. The tunneling current is highly dependent on the distance between the tip and sample’s surface[50]. Feedback electronics are used to keep the tunneling current constant.
Figure 1.11 The scanning Tunneling Microscope in a nutshell adapted from ref.[47].
The way to do that is by comparing the tunneling current to a reference current. Then, the difference is amplified and converted into a voltage $V_z$ [46, 47]. The voltage $V_z$ is applied to the piezo, $p_z$, element which moves the tip up and down to maintain a constant tunneling current when the tip is scanned at $p_y$ and $p_x$, over the surface [50].

1.3.2 Scanning Tunneling Microscopy Tips

The creation of a good tip has a big impact on the quality of obtained images by scanning tunneling microscopy. The operating features of the STM depend on using the single, outermost atom at the tip. Basically, the tips are made of a relatively hard material to avoid the probability of contacting between the tip and the sample surface. Materials that can be used as a tip are Tungsten (W), platinum, gold, Pt-Ir alloys, carbon nanotube (CNT) and diamond coated. The most widely used among these materials is Pt-Ir alloys due to high hardness and oxidization resistance [51].

1.3.3 Mechanical Vibrations

The presence of mechanical vibrations around the sample or tip can make an atomic resolution with STM very difficult since these vibrations may have a larger amplitude than the atomic dimensions. Getting rid of these vibrations can be done by placing the STM instrument on a soft rubber mattress to dampen vibrations of high frequency. This mattress rests on a two-kilogram block of granite with foam-rubber feet to dampen vibrations of low frequency. This damping system will result in achieving high atomic resolution [52].

1.3.4 Modes of STM Operation

There are two different modes that can be used to operate the STM (Figure 1.12). Constant current mode, in which a feedback loop changes the height of the
Figure 1.12. An STM can be operated in either the constant-current or the constant-height mode. The images are of graphite in air. Adapted from Ref. [46].
tip to maintain a constant tunneling current. The height of the tip is adjusted by applying a voltage to the piezoelectric drive which results in a map of topography of the surface. However, in the constant height mode, the tip’s height does not change, instead the current changes as the distance between the tip and sample changes [46].

1.4. Non-contact Atomic Force Microscopy

Atomic Force Microscopy (AFM) was invented by Binnig et al. in 1986[53]. It is used to observe the surface’s shape in which information regarding the three-dimensional (3D) structure down to the nanometer level can be obtained. A variety of materials can be imaged by using AFM under different circumstances such as air, liquid and sometimes under vacuum. These materials can be hard or soft, synthetic or natural regardless of opaqueness or conductivity [54].

1.4.1 AFM Instrumentation

The most important parts of an AFM are the microscope stage, control electronics and a computer as shown in Figure 1.13. The microscope stage consists of the scanner that provides the system of the AFM tip’s movement with respect to the sample, sample holder, and a force sensor, to hold and monitor the AFM tip. The stage can be interfaced with an optical microscope to examine the sample and tip. Normally, the stage is mounted on a table that provides a vibration free level that decreases noise and enhances the resolution. The control electronics typically have the shape of a large box connected to both the microscope stage and the computer. The purpose of the electronics is to create signals that operate the scanner and any other parts with a motor in the microscope stage. Also, the electronics work on converting the signals from the AFM into a digital form
Figure 1.13. Schematic diagram of Atomic Force Microscope adapted from ref. [55].
so that they can be processed by the computer. Moreover, the control electronics are responsible for managing the feedback between the signals to and from the AFM stage based on the entered information in the computer.

The computer has a certain software that enables the user to process and analyze the acquired images [56].

1.4.2. Image Formation

In non-contact mode of AFM, a very sharp tip attached to the end of a flexible cantilever is placed very close and precisely to the sample’s surface. A piezoelectric material is responsible for this precise movement. Typically, the tip-cantilever assembly is made from silicon or silicon nitride. The close proximity will result in measuring the van der Waals attractive forces that cause a change in the resonant frequency of the cantilever leading to deflection. The cantilever deflection is measured by detecting the position of a laser beam reflecting from the cantilever and directed to a quadrant photodiode. The photodiode is a semiconductor sensor that converts the light intensity into an electrical current. A feedback loop from the AFM electronics manages the movement of the tip up and down during imaging the sample’s surface so that the interaction forces are kept constant [57, 58].

In this study, we conduct a systematic investigation to identify the processing parameters controlling the formation of unmodified- C_{60} Fullerene. The parameters to be investigated are; the nature of the solvent used (the effect of solvent/Fullerene interaction), the evaporation time of the solvent used, and the initial concentration of the C_{60} solution used to produce the films. In the following chapter, we will discuss the experimental procedures followed in this work.
2.0 Experimental Procedure

2.1. Langmuir Blodgett Instrumentation

The Nima® model 1222D2 rectangular Langmuir trough was used for all film compression experiments. The trough consists of two compression barriers and two pressure sensors as illustrated in Figure 2.1. The pressure sensors are Wilhelmy plates, small pieces of chromatography paper which measure the surface pressure.

The graphics screen on the Nima device has series of menus that control the entire process while running the experiments (Figure 2.2). The software menus included in the menu bar are the graph menu, barrier menu, dipper menu, calibration menu, and variables menu. The control screen enables the user to view the isotherm and control the deposition by accessing the various software options.

In our experiments, the original open area of the trough was 500 cm², the closed area was 50 cm², and the speed of barrier was set to 100 cm²/min. All these parameters were kept constant in our study.
Figure 2.1. Nima® Langmuir-Blodgett instrument model 1222D2.
Figure 2.2. Main screen of Nima® control screen.
2.1.1 Lab Environment

Performing experiments by using Langmuir-Blodgett technique requires working in a well-controlled environment. The trough must be kept very clean, hence, for all experiments the operator wears polyethylene gloves to keep contaminations such as dust particles, grease, and other materials far away from the trough. The trough was cleaned with a Kimwipe tissue soaked in methanol. After cleaning 15 minutes was allowed for the methanol to completely evaporate. The trough was filled with pure, clean distilled water (commercially available). The cleanliness of the water subphase is visually inspected for any unwanted contaminations. An isotherm plot, surface pressure vs. area per molecule, of the water subphase was recorded to ensure that the water surface gives a near-zero surface pressure, indicating the surface cleanliness is acceptable. The maximum recorded surface pressure was less than 0.5 mN/m, indicating an extremely clean water surface as shown in Figure 2.3. Additionally, the LB trough is enclosed in an isolated laminar flow cabinet to ensure a scale 100 clean room. A thermocouple was used to record the water subphase temperature ensuring a constant value of 21±1°C. Moreover, a steel frame laboratory bench for holding the LB instrument was used to reduce any unwanted vibrations. Taking measures to control these factors ensure accurate and reliable results.
Figure 2.3. Isotherm for pure water showing minute pressure build-up as a proof of surface purity.
2.1.3. Film Formation Procedure

\(\text{C}_60\) fullerene sublimed 99.9% crystalline powder was obtained from Sigma – Aldrich. The \(\text{C}_60\) powder was dissolved into three different solvents, namely, toluene, benzene, and chlorobenzene. Toluene (anhydrous, 99.8%), chlorobenzene (for HPLC, 99.9%) were obtained from Sigma-Aldrich and benzene was obtained from Burdick & Jackson Laboratories Inc. For all experiments, diluted solutions were prepared for each sample of 10 mL volume with a concentration 0.025 mg/ml, which was found to be optimal in obtaining uniform and stable monolayers of \(\text{C}_60\) fullerene. The procedure of film formation can be summarized in a few steps. First, 0.005 grams of \(\text{C}_60\) powder are weighed using an analytical balance. Then, this powder is deposited into a glass flask and 10 mL of solvent (toluene, benzene, or chlorobenzene) is added to prepare a concentrated solution. After that, a sonication was performed for 1 hour which helps to ensure that all the particles are dissolved completely. Next, the solution was diluted by taking 1 mL of the concentrated solution and adding 9 mL of the appropriate solvent. The diluted solutions were then sonicated for 1 hour. The samples are stored in clean containers which are sealed firmly by Para film as shown in Figure 2.4.

The \(\text{C}_60\) solution was deposited onto the area between the measuring barrier and the moving barriers. This step is done by spreading 500 \(\mu\)L of the diluted solution on the trough by using an air – displacement pipette. 100 \(\mu\)L of solution was placed in five different regions on the trough. The experiments were held for 30 minutes which was enough to assure that all the solvent was evaporated and \(\text{C}_60\) was evenly dispersed. Plotting the isotherm for the \(\text{C}_60\) film indicated an area per molecule of ~ 91 Å\(^2\) (0.9 nm\(^2\)), indicating a hexagonal closed packed monolayer.
Figure 2.4. Ultrasonic cleaner, parafilm, and sample of C\textsubscript{60} solution.
All experiments were carried out at room temperature. The Langmuir film was compressed with a barrier speed of 100 cm²/min and the isotherm plot showed a steep rise with no collapse pressure, indicating a good surface spreading and stability of the film.

2.1.4. Film Deposition

Monolayers of C₆₀ fullerene can be transferred onto a solid substrate by using the Langmuir Blodgett technique. Basically, the deposition can be performed directly after the isotherm plot indicates a stable film of C₆₀ fullerene. The deposition process is done in the solid phase since the monolayers at this phase are stable enough to be transferred to the solid substrate. This will enable successful deposition of high quality homogeneous films. Langmuir Blodgett films were deposited onto both hydrophilic glass slides (37 mm × 19 mm × 1.08 mm) and steel disks, allowing for characterization by atomic force microscopy and scanning tunneling microscopy, respectively. Prior to deposition, substrates are completely cleaned and immersed under the water interface. Langmuir–Blodgett film deposition was undertaken using a vertical dipping at a speed of 20 mm/min under constant pressure. In the dipping experiment, the film was compressed up to a specific target pressure between (10-15) mN/m. The dipping process is completely controlled by an automated system where dipping depth, speed, and number of dipping successions can be programmed. When the required number of layers have been deposited, the dipper will stop. The samples are suspended in air for 1 hour to dry completely and stored in clean containers for further characterization.
2.2. Scanning Tunneling Microscope and Atomic Force Microscopy Measurements

The STM and AFM, manufactured by Nanosurf®, were used for surfaces imaging at the atomic level as shown in Figure 2.5 and Figure 2.6, respectively. Both instruments are placed on fiberboard box to reduce vibrations that would impact the accuracy of the measurements. The samples were imaged at room temperature and atmospheric pressure. Images were acquired in both constant-current mode and Z out mode with a tip-sample bias of 0.080 V and a scan range of 6.25 nm.

In STM measurements, samples deposited on steel disks are scanned using sharpened tips made of Pt/Ir wire. However, in AFM measurements, samples deposited on glass slides are scanned using sharp tips made of silicon.

2.3. Electrical Conductivity and Transparency Measurements

Carbon conductive double-faced adhesive tape (Nonwoven Fabric Core) was obtained from Nisshin EM Co., Ltd and used as an electrode material in electrical measurements. Glass slide substrates, of varying number of C₆₀ fullerene layers, were placed between the carbon tape electrodes. Electrical conductivity measurements perpendicular to the film plane were performed using an MN36 Digital Mini Multimeter from EXTECH instruments (Figure 2.7). Optical measurements at room temperature were performed in the dark and under illumination of a 27 W lamp of. A Fluke 941 light micrometer was used to measure light intensities in lux units with the sensor connected by a 1m coiled lead (Figure 2.8).
Figure 2.5. STM stage used in our experiment.
Figure 2.6. AFM stage used in our experiment.
Figure 2.7. Electrical measurements were performed by using an MN36 Digital Mini Multimeter (from EXTECH instruments).
Figure 2.8. Optical measurements were performed by using a Fluke 941 light micrometer.
3. Results and Discussion

3.1. Film Formation

Figure 3-1 depicts an early trial for the processing of fullerene [60] Langmuir-Blodgett films. For this film, we used a fullerene/toluene solution with a concentration of 0.0025 (mg/mL), the solution volume put in the trough was 200 (μL) making the total number of C\textsubscript{60} molecules equal to 4.18264\times10^{14}, the barrier speed of 100 (cm\textsuperscript{2}/min.), and the trough substrate temperature was 22°C. As shown in Figure 3-1, the film showed a gas phase, a liquid phase, and a solid phase. Upon extrapolation of the solid phase region, the line intersection showed that the average area per fullerene molecule is 2375 Å\textsuperscript{2}/molecule. Realizing that the average area per a fullerene molecule in a closed packed hexagonal lattice structure is 91 Å\textsuperscript{2}. This indicates that the produced film has a very open structure and not a mono-layer compact film.

Figure 3-2 shows the same isotherm with the x-axis in terms of film length instead of area per molecule. From the slope of the solid phase region in this isotherm and the trough geometry, the stress/strain curve of the solid film can be obtained as in Figure 3.3. Simply, we convert the surface pressure (N/m) into force by considering the constant width of the trough. By dividing the force over the film cross-sectional area (film thickness is determined from Figure 3.1), we can determine the stress. The strain is determined by the change of the solid film length over the initial solid film length as determined from Figure 3.2. Figure 3.4 depicts a schematic presentation of the calculation process.
Figure 3-1. Early trial isotherm using toluene solvent.
Figure 3-2. Same isotherms as in Figure 3-1 with film length instead of area per molecule.
Figure 3.3. Stress/Strain curve for the solid phase of the film shown in Figure 3.1.
Figure 3.4. Schematic presentation of film Stress/Strain curve calculations.
3.1.1 Effect of C\textsubscript{60} Solution Concentration

Solution concentration effect was investigated by changing the initial solution concentration while keeping the other two parameters (i.e., solvent evaporation time and nature) constants. Figure 3.5 depicts the isotherm obtained for fullerene [60] in toluene with a concentration of 0.025 (mg/mL) that is an order of magnitude larger than the concentration used to produce the isotherm shown in Figure 3.1. The solution amount used in this experiment was 400 µL making the total number of molecules equal to 8.36528*10\textsuperscript{15}. The area per molecule calculated was found to be 107 Å\textsuperscript{2} indicating that the film is a monolayer with slightly open structure. Figure 3.6 shows the stress/strain curve for such a film with a stiffness value of 26.58 MPa.

As we increased the amount of solution to 500 µL (total number of C\textsubscript{60} molecules equal to 1.04566*10\textsuperscript{16}), we obtained the isotherm shown in Figure 3.7. The process resulted in a real mono-layer film with an average area per molecules of 92 Å\textsuperscript{2}. This indicates that the film is a true mono-layer with exactly a HCP structure. Figure 3.8 shows the stress/strain curve for the film with a stiffness value of 32.11 MPa. It is important to note the increase in film stiffness as the film structure became HCP.

These results allowed us to fix the solution concentration to 0.025 mg/mL and the amount added to the trough to 500 µL.
Figure 3.5. Isotherm obtained for toluene solvent with 0.025 mg/mL concentration. Film average thickness 1.17 nm.

At zero pressure:
Area per molecule = 107 Å²
Average film 1.17 layers (1.17 nm)

(A mono-layer with slightly open structure)
Figure 3.6. Stress Strain curve for film shown in Figure 3.5. Film stiffness 26.58 MPa.
Figure 3.7. Isotherm for 0.025 mg/mL in toluene with 500 µL total solution.

\[ y = 52.375 - 0.56686x \quad R^2 = 0.99923 \]

At Zero pressure
Average area per molecule = 92 Å²
Monolayer with HCP structure
Figure 3.8. Stress/Strain curve for a HCP monolayer of $C_{60}$ in toluene. Stiffness 32.1 MPa.
3.1.2. Effect of Solvent Evaporation Time

The second processing parameter tested was the solvent evaporation time. Figure 3.9 shows over-laid isotherms for fullerene [60] in chlorobenzene. The isotherms represent evaporation times of ½, 1, and 4 hours. As shown in the Figure 3.9, the corresponding area per fullerene molecule is 90, 83, and 85 Å², respectively. This indicates that as the solvent is left for half an hour to evaporate, the resulting film is a monolayer with HCP structure. If the film is left longer than half an hour, the fullerene molecules start to climb and the film starts to lose its structure and starts to form multi-layers. This is very important observation since it indicates that some solvent molecules are needed to stabilize a mono-film of such hydrophobic spherical molecules.

3.1.3. Effect of Fullerene/Solvent Interaction

Figures 3.10 to 3.12 show isotherms of HCP structured C₆₀ monolayer films out of the three aromatic solvents used in this study, namely, benzene, toluene, and chlorobenzene, respectively. Figures 3.13 to 3.15 show the stress strain curves for the films processed from the three solvents as well. Table 3.1. Summarizes the stiffness of the produced HCP monolayer films.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Film Stiffness (MPa)</th>
<th>Solubility limit (mg/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>15.36±0.45</td>
<td>1.7</td>
</tr>
<tr>
<td>Toluene</td>
<td>32.1±1.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>15.1±1.0</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 3.1. The stiffness of the produced HCP monolayer films.
Figure 3.9. Effect of solvent evaporation time for C$_{60}$ in Chlorobenzene. True HCP structure is observed with ½ hour solvent evaporation time.
Figure 3.10. Isotherm for C\textsubscript{60} monolayer with HCP structure from benzene.
Figure 3.11. Isotherm for C₆₀ monolayer with HCP structure from toluene.

At Zero pressure
Average area per molecule = 92 Å²
Monolayer with HCP structure

Surface pressure (mN/m)

Area per molecule (Å²)

y = 52.375 - 0.56686x  \quad R^2 = 0.99923
Figure 3.12. Isotherm for C\textsubscript{60} monolayer with HCP structure from chlorobenzene.
Figure 3.13. Stress/Strain curve for a HCP monolayer of C$_{60}$ in benzene. Stiffness 15.36 MPa.
Figure 3.14. Stress/Strain curve for a HCP monolayer of C\textsubscript{60} in toluene. Stiffness 32.1 MPa.
Figure 3.15. Stress/Strain curve for a HCP monolayer of C$_{60}$ in chlorobenzene. Stiffness 15.1 MPa.
Figure 3.16. Dependence of film stiffness on fullerene/solvent interaction strength as indicated by solubility limit.


Optimum monolayer HCP structured films were observed by scanning electron microscopy (SEM). Due to resolution limitation, only uniform smooth surface of the substrate could be observed as shown in Figures 3.16-3.18. It is important to note that the apparent granular structure belongs to the substrate. Hence, we utilized STM and AFM to get high quality images.

3.2.2. Atomic Force Microscopy and Scanning Tunneling Microscopy Images.

Figures 3.19 to 3.21 show AFM images for HCP monolayer C_{60} films prepared using benzene, toluene, and chlorobenzene, respectively. Each image shows a 2X2 µm three dimensional map of the film. All image shows uniform monolayer films with some parts of multilayers. On the other hand, Figures 3.22 to 3.24 show STM images of the same films. Each image shows a 6X6 nm three dimensional map of the films. The images also confirm that our films are very uniform with double layer ridges one to three C_{60} molecule wide.
Figure 3.17. SEM micrograph for C$_{60}$ film out of benzene.
Figure 3.18. SEM micrograph for C$_{60}$ film out of toluene.
Figure 3.19. SEM micrograph for C₆₀ film out of chlorobenzene.
Figure 3.20. AFM - 3D image of benzene sample of one layer.
Figure 3.21. AFM -3D image of toluene sample of one layer.
Figure 3.22. AFM -3D image of chlorobenzene sample of one layer.
Figure 3.23. STM-3D image of benzene sample of one layer.
Figure 3.24. STM 3D image of toluene sample of one layer.
Figure 3.25. STM-3D image of chlorobenzene sample of one layer.
3.2.3. Optical Transparency

The measurements of optical transparency are summarized in Table 3.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th># layers</th>
<th>Light Intensity</th>
<th>Transparency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>0</td>
<td>313±5 LUX</td>
<td>100%</td>
</tr>
<tr>
<td>Benzene</td>
<td>1</td>
<td>311±5 LUX</td>
<td>100%</td>
</tr>
<tr>
<td>Benzene</td>
<td>2</td>
<td>310±5 LUX</td>
<td>100%</td>
</tr>
<tr>
<td>Toluene</td>
<td>1</td>
<td>313±5 LUX</td>
<td>100%</td>
</tr>
<tr>
<td>Toluene</td>
<td>3</td>
<td>310±5 LUX</td>
<td>100%</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1</td>
<td>319±5 LUX</td>
<td>100%</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>3</td>
<td>318±5 LUX</td>
<td>100%</td>
</tr>
</tbody>
</table>

Table 3.2. Optical transparency of the produced films.

3.2.4. Electric Performance

The measurements of electric performance are summarized in Table 3.3.

\[ \text{Solvent} \] \hspace{1cm} \text{layers} \hspace{1cm} \text{R (ohm)} \hspace{1cm} \text{Resistivity} \hspace{1cm} \text{Conductivity} \hspace{1cm} \text{Solvents Polarity} \times 10^3 \text{ Cm} \\
\begin{align*}
\text{Benzene} & 2 & 5 \times 10^{-5} & 16.5 \times 10^{-14} & 6 \times 10^{12} & 0.0 \\
\text{Toluene} & 3 & 11 \times 10^{-5} & 5 \times 10^{-14} & 20 \times 10^{12} & 1.00 \\
\text{Chlorobenzene} & 3 & 2 \times 10^{-5} & 3 \times 10^{-14} & 33 \times 10^{12} & 5.6 \\
\end{align*}

Table 3.3. Electric performance of the produced films.

It is clear from table 3.3. that the electrical conductivity of HCP C\textsubscript{60} films is much higher than that of bulk silver, for which the conductivity is 6.20*10\textsuperscript{7}(S/m) and bulk copper, for which the conductivity is 5.85*10\textsuperscript{7}(S/m) [63]. The values measured are also higher than those reported for sublime C\textsubscript{60} films [64, 65] and even higher than the value reported for compacted graphene powder [66]. It is interesting to realize that the electrical
conductivity values of double and triple layers of HCP C$_{60}$ films are also much higher than the value for graphene sheets that was reported to range between $8 \times 10^3$ and $2 \times 10^5$ (S/m) depending on the exact method of graphene structure and production method [67].

It is very well known that the electrical conductivity of nano-films depends on the exact structure of the film. Here we show that the polarity of the solvent residues in the produced film also affects the film electrical conductivity as shown in Figure3.26.
Figure 3.26. Correlation between film conductivity and solvent dipole moment.

\[ y = 25.348 + 4.0089 \log(x) \]

\[ R^2 = 0.68088 \]
4.0 Conclusions

Based on our current research and results, the following conclusions can be drawn:

1. We managed for the first time to produce mono-layer films of C₆₀ with all processing parameters controlled and understood.

2. The produced films show a stiffness that does depend on the level of solvent/fullerene interaction and there is an optimum value for such dependence.

3. The films up to 3 layers with thickness of 3 nm were completely transparent to visible light.

4. The HCP C₆₀ films with 2 to 3 layers demonstrated a very high value of electrical conductivity exceeding that of graphene films. This result brings the attention to the importance of controlling the nano-fullerene film structure in order to controlling its optoelectrical properties.
5.0 References


52. STM teachers manual.


