UNIVERSITY OF ZARAGOZA

NANOSTRUCTURED MATERIALS FOR NANOTECHNOLOGY

APPLICATIONS
(NANOMAT)

Carbonaceous Platforms for the Fabrication of Green Molecular Electronic Devices

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Contents

Abstract

The research on the development of electronic devices is growing as fast as ever. As new challenges arise with the continuous miniaturisation of electronic components, nanostructured and carbon-based materials have been become very promising for future developments and products. In this project, an all-carbon molecular electronic device, which is completely free of metals, is reported. A Langmuir film of graphene oxide (GO) was fabricated and characterised by using a Brewster angle microscope (BAM). Then, transferences of a GO Langmuir-Blodgett (LB) film onto mica substrate for different transference conditions were carried out. Morphology of the samples were characterised by using an atomic force microscope (AFM). Once the optimum transference conditions of GO LB film were determined, electrografting processes of Oligo(Phenylene Ethynylene) (OPE) derivatives onto highly oriented pyrolytic graphite (HOPG) substrate were carried out. After monolayers of OPE derivatives onto HOPG were confirmed by using various characterisation techniques such as Raman spectroscopy, AFM and cyclic voltammetry (CV), transferences of GO LB film onto modified HOPG substrates were carried out. Future work to achieve all-carbon molecular electronic devices is also explained.

Acknowledgements

Firstly, I would like to thank my supervisors, Dr. Santiago Martín Soláns and Dr. Pilar Cea Mingueza for all their support, patience and motivation.

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Last but not the least, I would like to thank my family and my friends for their continuous support during my master studies.

1. Introduction

This work constitutes the Final Master Project of the master on *"Nanostructured Materials for Nanotechnology Applications"* at University of Zaragoza for the 2016/2017 academic year. The objective of this project is to develop all-carbon electrode-molecule-electrode structures, completely free of metals, using bottom-up approaches as it will be explained in the upcoming sections.

During the master studies, the students are given both theoretical and practical lectures to help them gain and improve their skills regarding the fabrication and characterisation methods used in the field of nanotechnology. As research and development in nanotechnology has increased drastically, the ethical point of this increment has become a concern [1–4] and the students are expected to fulfil that need in their given tasks just as this final master project also aims to reduce the use of pollutant and/or scarce metals in electronics industry.

Nanotechnology mainly refers to manipulate the matter in nano scale, below 100 nm [5–7]. It is a multidisciplinary field [8–11] that concerns many researchers from different fields such as chemistry, physics, biology or engineering. Basically, there are two different approaches to manipulate matter in nano scale, bottom-up and top-down [6, 12]. Both approaches are used depending on the matter and the desired structure to obtain. In particular, this project focuses on fabricating carbon based components for their use in electronics by using bottom-up methods such as Langmuir-Blodgett (LB) technique and/or electrografting. In upcoming sections more information is given regarding to the development of electronics, the literature is reviewed, fabrication and characterisation techniques used in the work are looked upon, experimental procedure is explained in detail and finally, the project is concluded and the future work is mentioned.

1.1 Introduction to More Moore, More-than-Moore and Beyond CMOS

Miniaturisation of electronic components, mainly transistors, plays a key role in the development of the electronics industry and products available to society. Since early 1970s, the number of transistors in a chip has kept increasing by doubling almost in every 2 years. This trend has become known as *Moore's Law* [13, 14], years after Gordon E. Moore published his article named "Cramming more components onto integrated circuit" [15].

Before continuing any further, it is important to mention what a transistor is. The word, transistor, usually refers to *Field-effect transistor*, FET. It is a device that can be used as an amplifier or as an electrical switch. The transference of the charge is controlled by a *gate*, a unit of the transistor. Transistors are basically switches to have two states, *on* and *off* [16,17]. These two states are used to keep information which is converted to form a binary number as well as to create logic gates to process the information [18]. Today, transistors are deployed on a wide variety of products such as computers, vehicles, manufacturing machines, calculators, phones and any other product that includes electronic processors and/or variety of memory units (i.e. RAMs, flash memories, SSDs). As an example, *Qualcomm Snapdragon 835*, *Apple A11* and *Intel Cannonlake* processors, which are the current state-of-art chips, contain transistors of the size of 10 nm [19–21].

The continuous miniaturisation of transistors based on complementary metal oxide semiconductors (CMOS) is expected to struggle beyond the size of ∼5 nm. Below this size, short channel effects commence due to quantum tunnelling [22] as well as noise caused by heat dissipation [23]. Quantum tunnelling may cause electron to barrel through the channel, from the source to the drain, which would switch the transistor from an *off* to *on* state randomly and it would make the chip fails to function properly. Nevertheless, new alternatives for these logic units are being studied under the trend name of *beyond CMOS*. Efforts of *beyond CMOS* mainly include studies on placing more logic units in a chip, improving switching time, reducing power consumption and improving heat emission and dissipation. To develop new architectures of chips to obtain optimum performance from *beyond CMOS* devices is also a focus of the semiconductor

[24]. Some of these developments make transistor to work based on entirely different physical phenomena such as using spin, excitonic, photonic, magnetic or even heat domains to function instead of passing electrons [25].

Nevertheless, the electronics industry does not merely focus on developing faster and more efficient switches. Nowadays, the devices have to improve in many other ways, not merely by scale and processing power. Therefore, today's devices have to be capable to make a lot of functions and each day, devices with more capabilities are making their way into the market. For example, there are already cars which are able to park or even drive without the need of being controlled. These inventions were possible not only because processors are more capable today, but also because more specific and better sensors available. These capabilities are difficult to investigate under *More Moore* trend. Therefore, the term, *More-than-Moore* (MtM) is coined by "International Technology Roadmap for Semiconductors" (ITRS) with an aim to create the roadmap and standards for the evaluation of improvement in these functionalities. Research in both trends needed to develop higher value systems [13].

1.2   Review of the Literature

As it was mentioned in the previous section, Qualcomm Snapdragon 835, Apple A11 and Intel Cannonlake chips have made their way into the market, companies improving their 14 nm architecture to 10 nm architecture in 2017. However, R&D efforts to manufacture chips with smaller switches based on CMOS have not been over yet. For instance, IBM has already introduced their chip with 5 nm silicon nanosheet transistors with brand new architecture this year [26] as this technology inching its way to market more and more every year.

While CMOS based transistors are still being developed, the research on alternatives, *beyond CMOS* as well as on more functionalities, MtM are growing as fast as ever. A simple search of the keyword "*semiconductor*" can help us to see the change in number of publications (related the semiconductor) by year as it may be seen in Figure 1.1.
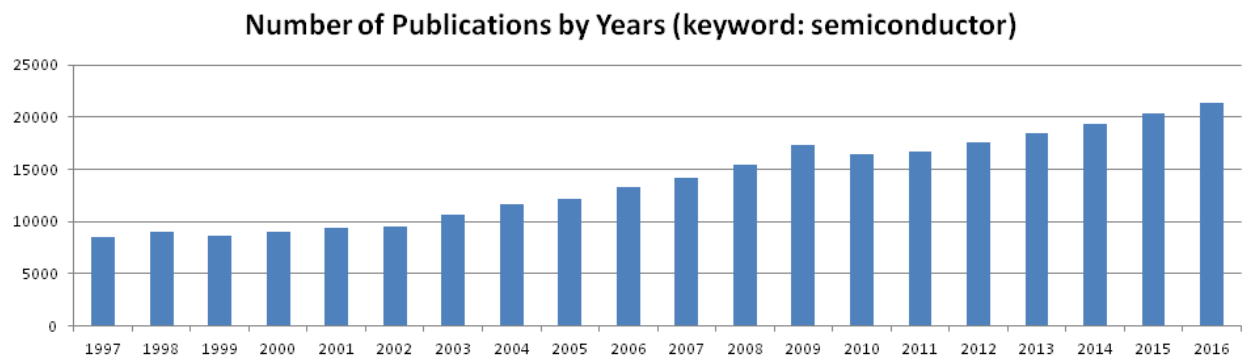
Figure 1.1: Data taken from "Web of Science" by searching the keyword "semiconductor".

With regards to *beyond CMOS* devices, many of them have been studied such as Tunneling FETs (TFETs), Graphene *pn*-junctions, BisFET, SpinFET etc. [24]. Not to mention, all these devices only represent a small part of development in electronics and semiconductors. Smallest transistor, with a size of 1 nm, has been developed by Desai et al. whereas single-wall carbon nanotubes (SWCNT) have been used as the gate and MoS_2 has been used as the channel material [27]. The use of carbon as a part of the device is not limited to previously mentioned study and it is used in many other forms as well. For example, Luisier et al. have investigated graphene nanoribbon (GNR) TFETs [28], Low et al. have investigated the transport properties of graphene *p-n* junction, Reddy et al. have proposed a BisFET which operates on tunnelling of electron between two graphene layers for high power operations (1000 times higher than CMOS devices) [29]; similarly, Banerjee et al. have proposed another BisFET using graphene for lower voltage/power operations which would not be possible with a CMOS transistor [30].

As it was mentioned previously, the fabrication of high value products not only requires better logic units but also requires developing more functionalities. For the last few decades, many new functionalities introduced in many devices and also these functionalities have opened new doors for the invention of brand new products. Sensing materials such as touch screens, better proximity sensors for a variety of products, transparent screens/devices, better batteries are merely some results of these researches on MtM devices. On this regard, carbon-based compounds, especially graphene being transparent, flexible and conductive material, are being studied widely

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to develop these kind of devices. Also being one of the most abundant element on Earth and the increasing capacity of the production of high-value carbon based materials such as graphene, carbon nanotubes (CNTs), fullerenes etc. have boosted the applications of carbon. H. Sohn et al. have investigated optical and electrical properties of dual-doped graphene. They have found out that p/p doped graphene gives the best results in terms of sheet resistance (R_s) and optical transmittance (TT). They have used HNO_3 as p-type dopant for graphene and also doped it with Ag NWs. The results are promising to replace indium tin oxide (ITO) which is brittle and offer limited optical transmittance, on the contrary of dual-doped graphene [31]. Similarly, B. Zhang et al. have studied the electrical and optical performance of Ag NWs/rGO structures. They have obtained very low sheet resistance (15.33 Ω /sq) and an optical transmittance close to ITO (80.1% at 550 nm) [32].Additionally, Sangiao et al. have used LB technique and FEBID to obtain all-carbon molecular electronic devices [33]. Li et al. used chemical vapor deposition (CVD) to grew single-walled CNTs (SWCNTs) onto reduced graphene oxide (rGO) and obtained results better than growing these SWCNTs onto metal electrodes. While some problems occur in metal electrodes due to high temperature operations (which could be the case with CVD process), rGO has shown great stability and even improved its electrical properties by reducing itself even further [34]. The economical advantage, that carbon-based electronic devices provide by eliminating the use of valuable metals, should not be underestimated. Wang et al. has achieved increasing the utilisation efficiency of Pt in proton exchange member fuel cells (PEMFCs) by growing CNT arrays on carbon paper and electrodepositing Pt onto these CNTs, therefore reduced the amount of Pt used in these systems drastically [35]. Similarly, carbon based electrodes were also used by Mitchell et al. for high energy $Li-O_2$ batteries, by Lee et al. for lithium-ion batteries as well as electrochemical capacitors and by Ramuz et al. for fabricating all-carbon fuel cell [36].

2. Objectives

The objective of the master program is to train the students in the methodologies used in the field of nanoscience and nanotechnology. Throughout the studies, students are aimed to gain skills to search and obtain information, to analyse and interpret the information, to apply their knowledge

in given tasks, as well as to be aware and responsible for the work they conduct. On this regard, the students are given:

- Theoretical lectures regarding fabrication, assembly and characterisation of nanostructured materials.
- Practical lectures and opportunity to gain experiences in using advanced tools for nanotechnology.
- Various projects to help them to gain both interdisciplinary working experience,and to improve their management and communication skills throughout the presentation with their involvement.
- Optional tasks such as those involving in external industrial practices, multidisciplinary joint educational projects and fabrication of micro/nano-devices.

Meanwhile the main objective of this project is to construct a molecular electronic device by using physicochemical fabrication methods. The fabrication of an all-carbon electrode-molecule-electrode structure is desired. In order to obtain this structure, Oligo(Phenylene Ethynylene) (OPE) derivatives with different terminal groups will be assembled onto an highly oriented pyrolytic graphite (HOPG) substrate by electrografting and on top of these monolayers a GO LB film as the top contact electrode was incorporated. Since graphene has better electrical properties than GO, the reduction of the GO LB film will be carried out and the characterisation of the electrical properties of these structures is encouraged for further studies.

3. Experimental part

In this section, all equipments and materials used in this project are given, the fabrication and the characterisation techniques used in this project are described and the experimental procedure is explained in detail.

3.1 Equipments and Materials

Equipments and materials used in order to conduct the study are given in this section.

Equipments

The equipments used in this project are given below.

- A NIMA Langmuir trough, with the dimensions of 100 mm x 720 mm . It is located in the Department of Physical Chemistry of University of Zaragoza.
- A homemade Langmuir trough, with the dimensions of 210 mm x 460 mm . This one is also located in the Department of Physical Chemistry of University of Zaragoza. It was used mainly to transfer Langmuir films onto a substrate(Langmuir-Blodgett films).
- A micro-BAM KSV-NIMA Brewster Angle Microscope (50 mW, 659 nm), with a lateral resolution better than 12 μm . It was used together with the NIMA Langmuir trough to characterise *in situ* the formation of a Langmuir film at the air-water interface.
- An AUTOLAB PGSTAT302N model Potensiostat; used for carrying out the electrografting processes and cyclic voltammetry experiments.
- An SPM Multimode 8 Environmental AFM from Bruker-Veeco that belongs to the Laboratory for Advanced Microscopies (LMA) and it was used to characterise the morphology of the films formed by using either the LB technique or electrografting.
- A confocal Raman Imaging from Witec, model ALPHA300M+, with an excitation wavelength of 633 nm; belonging to the Institute of Nanoscience of Aragon (INA) and used to characterise electrografting process.

Substrates

Mica, highly oriented pyrolytic graphite (HOPG) and gold substrates (from Arradee, Germany) were used throughout this project.

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Compounds used

The solution of graphene oxide (GO) used in this project was provided by Dr. A. Benito and Dr. W. Maser from Institute of Carboquímica de Aragón (ICB-CSIC). A mixture of water/methanol, with a ratio of 1:5 is used as a stabilising solvent for GO sheets.

The compound 4-(4-(4-(trimethylsilylethynyl)phenylethynyl)phenylethynyl) aniline (TMS-OPE-NH$_2$) was provided by Dr. Paul J. Low from University of Western Australia; meanwhile the compound 4-(2-(4-(2-(4-aminophenyl)ethynyl)phenyl)ethynyl)benzenamine (NOPEN) was provided by the group of Prof. Jose Luis Serrano, in particular this molecule was synthesised by Lucia Herrer, from University of Zaragoza. The chemical structure of these compounds used for fabricating films by electrografting are shown in Figure 3.1. TMS-OPE-NH$_2$ compound was selected in order to generate the diazonium salt from the NH$_2$ group which enables the covalent bonding between the molecule and the HOPG substrate while TMS group prevents the multilayer formation. On the other hand, the NOPEN was chosen for producing the diazonium salt and for improving the interaction between the other NH$_2$ group and the GO LB film as it will be explained in upcoming sections.
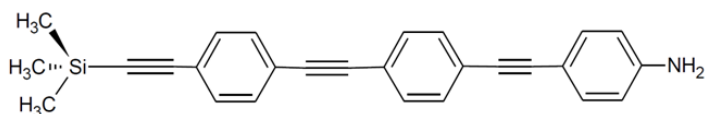
a) Chemical structure of 4-(4-(4-(trimethylsilylethynyl)phenylethynyl)phenylethynyl) aniline (TMS-OPE-NH2)
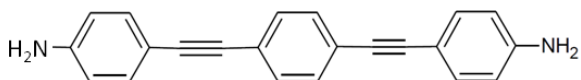
b) Chemical structure of 4-(2-(4-(2-(4-aminophenyl)ethynyl)phenyl)ethynyl)benzenamine (NOPEN)

Figure 3.1: Chemical structure of (a) TMS-OPE-NH$_2$ and (b) NOPEN.

Chemical compounds

Other chemical compounds used in this project are given in Table 3.1.

Table 3.1: Table of compounds

Compound	CAS-number	Provider
Ethanol	64-17-5	VWR Chemicals
Methanol	67-56-1	Sigma-Aldrich
Chloroform	67-66-3	Macron Fine Chemical
Acetone	67-64-1	Fisher Chemicals
Acetonitrile	75-05-8	Sigma Aldrich
Tetrahydrofuran	109-99-9	Scharlau
Nitric acid	7697-37-2	NORMAPUR
Sulfuric acid	7664-93-9	Fisher Chemicals
Hydrogen peroxide	7722-84-1	Panreac
2,2-Diphenyl-1-picrylhydrazyl	1898-66-4	Sigma-Aldrich
Tert-butyle nitrite	540-80-7	Sigma-Aldrich
Tetrabutylammonium tetrafluoroborate	429-42-5	Sigma-Aldrich
Millipore MilliQ-Water		Science Faculty, Distillator

3.2   Fabrication and Characterisation Techniques

Before explaining the methodology followed in this study, brief information is given regarding the fabrication and characterisation techniques used throughout this project. Fabrication techniques such as Langmuir-Blodgett method, electrografting and characterisation techniques such as Brewster Angle Microscopy (BAM), cyclic voltammetry (CV), Raman spectroscopy, Atomic Force Microscopy (AFM) are briefly explained in the following sections.

3.2.1 Fabrication Techniques

The fabrication techniques used in this study are briefly explained in this section.

Langmuir-Blodgett Technique

The Langmuir-Blodgett (LB) technique, Figure 3.2, is a technique to form a monolayer of amphiphilic molecules at the air-water interface which can be transferred onto a solid substrate. The hydrophilic part of the molecule, ideally, consists of groups such as carboxylic acid, sulphates, amines, alcohols meanwhile the hydrophobic part consists of groups such as hydrocarbon chains or lipids [37]. Placing these molecules on the water surface is achieved by solving these molecules in an immiscible solvent and the following spreading of this solution onto the water surface [38]. After waiting for some time for allowing the solvent to evaporate, these molecules are compressed by fusing a mobile barrier/barriers while surface pressure is monitored by using a Wilhelmy plate [39]. This action causes molecules to come together and eventually form a monolayer [37]. Once the monolayer is formed, a solid substrate is used to pass through the air-water interface and the monolayer formed on the water surface is transferred to the substrate. The direction of the deposition or number of layers on the substrate can be controlled by adjusting the starting position of the substrate and by how many times the substrate passes through the interface.
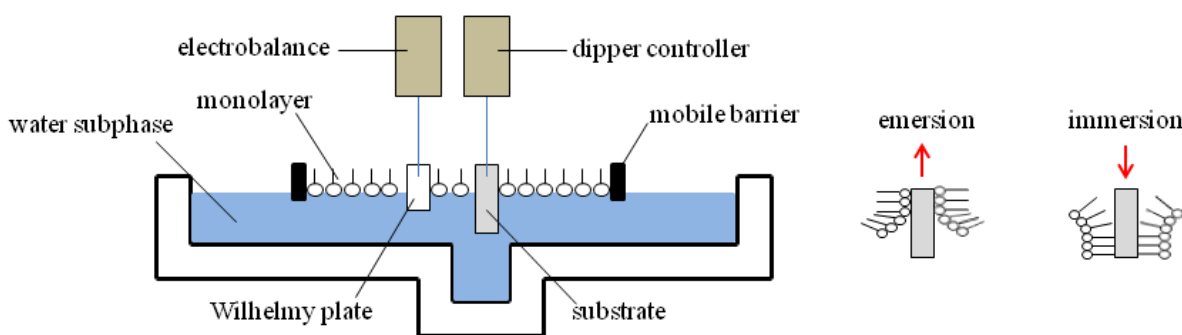

Figure 3.2: Schematic of a Langmuir trough as well as the sequence followed to fabricate an LB film [40].

Electrografting

Electrografting is an electrochemical process where organic molecule attaches to solid conducting substrate as result of electron transfer due to reduction or oxidation. This attachment can be also achieved with non-conducting substrates if reducing or oxidising reagenst are used. The resulting bonding is a strong covalent bond, also often termed as chemisorption. The technique is used to form layers of the organic molecule onto the substrate [41]. The electrografting mechanism to form a covalent bond between the compound and the substrate once a radical is formed by the reduction of a diazonium salt can be seen in Figure 3.3.
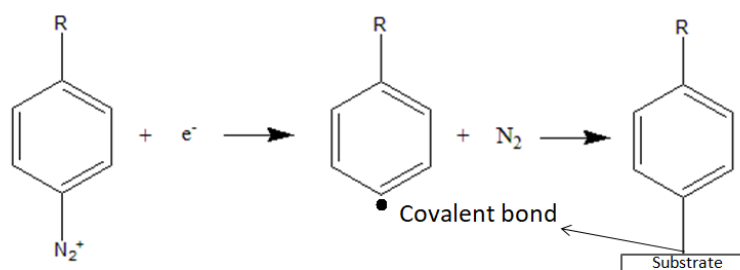

Figure 3.3: Electrografting process of a diazonium salt onto a conducting substrate.

3.2.2   Characterisation Techniques

The characterisation techniques used in this study are briefly explained in this section.

Brewster Angle Microscopy

When a *p*-polarised light comes to an air-water interface with a specific angle, α, it is not reflected. However, when a thin LB film is formed at the air-water interface,a part of the light is reflected. This fact is the principle of a Brewster angle microscopy (BAM), Figure3.4. In that case, while the air-water interface without a thin film will be seen dark on the images registered by the microscope, the interference of the thin film will cause a very small reflection and it could be seen

in lighter colors on the microscope. This phenomena can be used to observe *in situ* the formation of films at the air-water interface [42] .
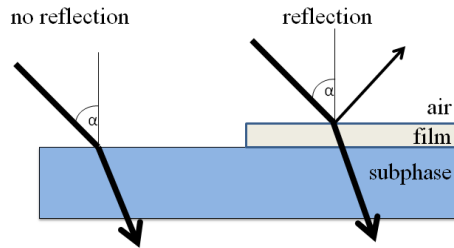
Figure 3.4: Principle of the Brewster angle microscopy.

Atomic Force Microscopy

An Atomic Force Microscope (AFM) is a tool to measure intermolecular forces at the nanoscale with atomic resolution. It is used to characterise the morphology of several materials such as, semi-conductors, polymers or biomaterials. A typical AFM includes the following parts: a microcantilever, a laser, a piezoelectric (PZT) actuator and a position sensitive photo detector. A feedback loop lies in the heart of the working principle of an AFM. There are many modes and purposes that an AFM can be used for such as non-contact mode, contact mode or tapping mode. Nevertheless, for the main use, the working principle depends on the force or height between the tip and sample. While keeping one of these values constant, the change in other value is evaluated to form topographical images (Figure 3.5) [43].
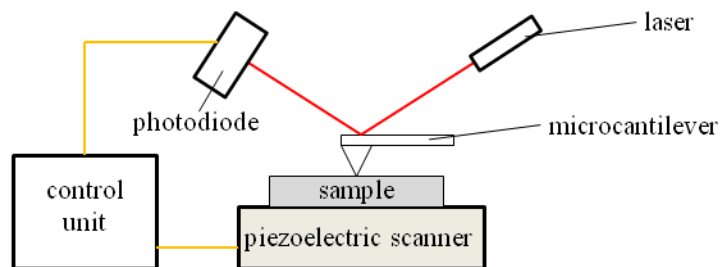
Figure 3.5: Schematic of AFM components [43].

Cyclic Voltammetry

Cyclic voltammetry (CV) is a technique that allows the measurement of the current which is the result of a cycling potential of the working electrode. A CV system consists of the following units: an electrochemical cell with the electrodes, a potentiostat, a current-to-voltage converter and a data acquisition system. The electrochemical cell consists of a working electrode, counter electrode, reference electrode and an electrolyte solution [44]. When a voltamperogram is registered,the potential of the working electrode is changed linearly with time meanwhile reference electrode maintains a constant potential. Counter electrode (also called auxiliary electrode) serves as a source or as a sink for electrons and electrolyte solution provides ions to the electrodes during the measurement [45]. CV can be used for redox processes [46], electron transfer kinetics [47] or for study the reversibility of a reaction [48].

Raman Spectroscopy

Raman spectroscopy is a technique that allows the interpretation of unique vibrational characteristics (in other words, fingerprints). In this technique light is used to strike to molecules. As a result of this action, inelastically scattered light is produced. The frequency of the scattered light is shifted compared to the inducing light. If the frequency of the scattered photon is lower than the frequency of the inducing light, then this case is known as stokes Raman scattering. The opposite case, which means the frequency of the scattered photon is higher than the inducing light's, is known as anti-stokes Raman scattering. The measurment of these shifts in the frequency and using the information which exists in the literature (which are the fingerprints as these shifts are unique) allow to identify the structure [49].

3.3   Experimental Procedure

In this section, the experimental procedure followed in this project is given in detail.

### 3.3.1 Fabrication, Characterisation and Transference of LB films of GO

Fabrication and characterisation of a Langmuir film of GO

The first experiments performed in this project were the fabrication and characterisation of graphene oxide (GO) films by using LB technique. The concentration of the solution is assumed to be 0.9 mg/mL and it was stabilised in a mixture of Milli-Q water:methanol, with a ratio of 1:5. Later on, chloroform was also added to the mixture in terms to avoid the dilution of solution into the subphase until achieving a concentration of 0.18 mg/mL. Under these conditions, the mixture of Milli-Q water:methanol:chloroform had a ratio of 1:5:6, respectively. The solution was sonicated for 10 minutes before spreading. The LB trough was cleaned firstly with acetone and then with chloroform. 20 minutes of wait is required after each cleaning step for allowing the evaporation of solvents. Afterwards, the Langmuir trough was filled in with Milli-Q water and drained 3 times.

After this cleaning procedure, 6 mL of the GO solution was carefully spread onto the water with the speed of 0.1 mL per minute. BAM was also used to characterise *in situ* the formation of the film. The take off of the isotherm occurs when the molecules were compressed to 100 cm^2. After that, the surface pressure increases until a surface pressure of 14 mN/m was achieved when the molecules were compressed to 50 cm^2. According to BAM images, a subtle formation of the film was possible to observe when the surface pressure reaches to 2.6 mN/m. The resulting isotherm and BAM image can be seen in Figure 3.6. When the surface pressure increases to 0.4 mN/m, a very faint, string-like formation of the GO film becomes possible to see. At surface pressure of 2.6 mN/m (image (c)), the film is almost completely formed and continuing the compression beyond this point does not cause a decent improvement. The bright spots (dot-like spots) that can be seen in Figure 3.6 (in images of (c) and (d)) are the result of the impurities and the organic materials, which could be the part of the GO solution to begin with.
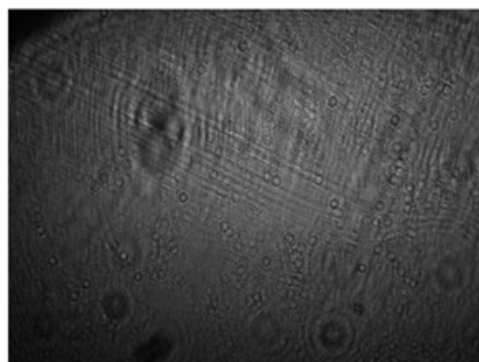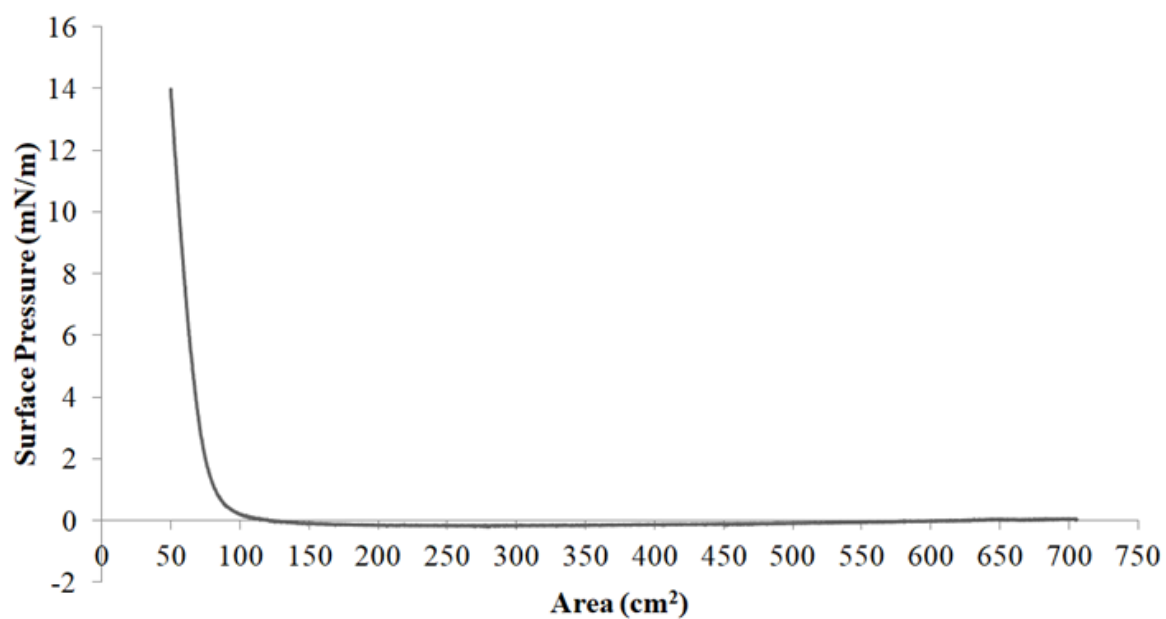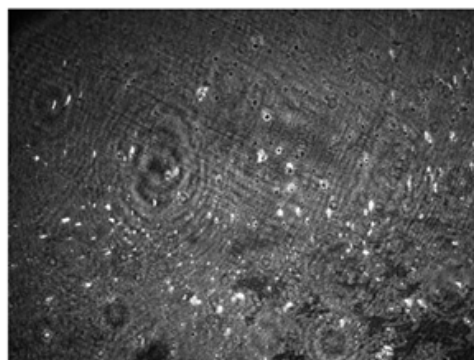
a) Surface pressure is 0 mN/m
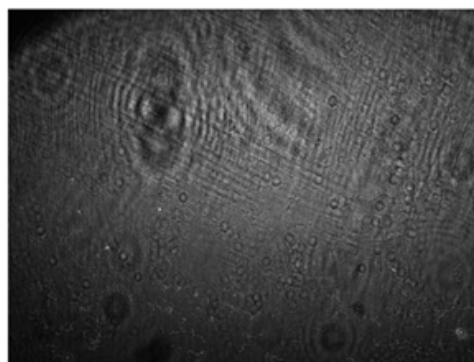
b) Surface pressure is 0.4 mN/m
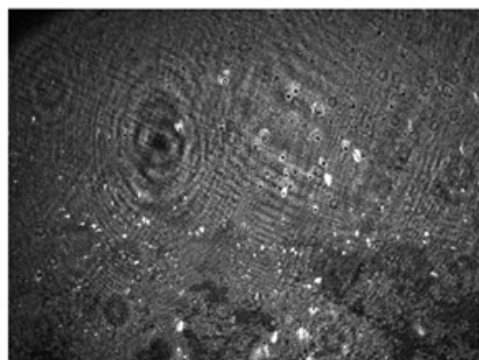
c) Surface pressure is 2.6 mN/m

d) Surface pressure is 9 mN/m

Figure 3.6: A representative isotherm recorded during the compression of GO at the air-water interface and BAM images registered simultaneously at surface pressure given below the images.

Fabrication and characterisation of a LB film of GO

As a next step, the homemade Langmuir trough was used for the transference of the GO film onto a mica substrate. Mica substrate was exfoliated a few times before using. Due to homemade Langmuir trough is having larger minimum compressed area than NIMA Langmuir trough, 15 mL of the same solution was spread, keeping all other conditions constant. The transferences of a GO film were carried out at different surface pressures in terms to optimise the best surface pressure to be used as well as several transferences were done to improve the surface coverage. As it can be seen in Figure 3.7, optimum tranference pressure was 4mN/m because the coverage of the GO sheets was better than the rest as well as comperatively larger GO sheets was obtained. Also in the case of multiple transferences, which was 3 transferences (Figure 3.8), no improvement was observed in terms of the coverage or the GO sheet sizes. A section analysis of an AFM image, for the optimum case, reveals that around three GO sheets stack up to form the GO film in general and single layer of a GO sheet has a thickness of $\sim$1 nm (Figure 3.9). Nevertheless, under these experimental conditions and even when a high surface coverage and large GO sheets were obtained, there were parts of substrate without covering. This result limits the use of these GO films as bottom electrode but not as the top electrode as it was used in this project. The results are in agreement with the results obtained by Li et al. [50].
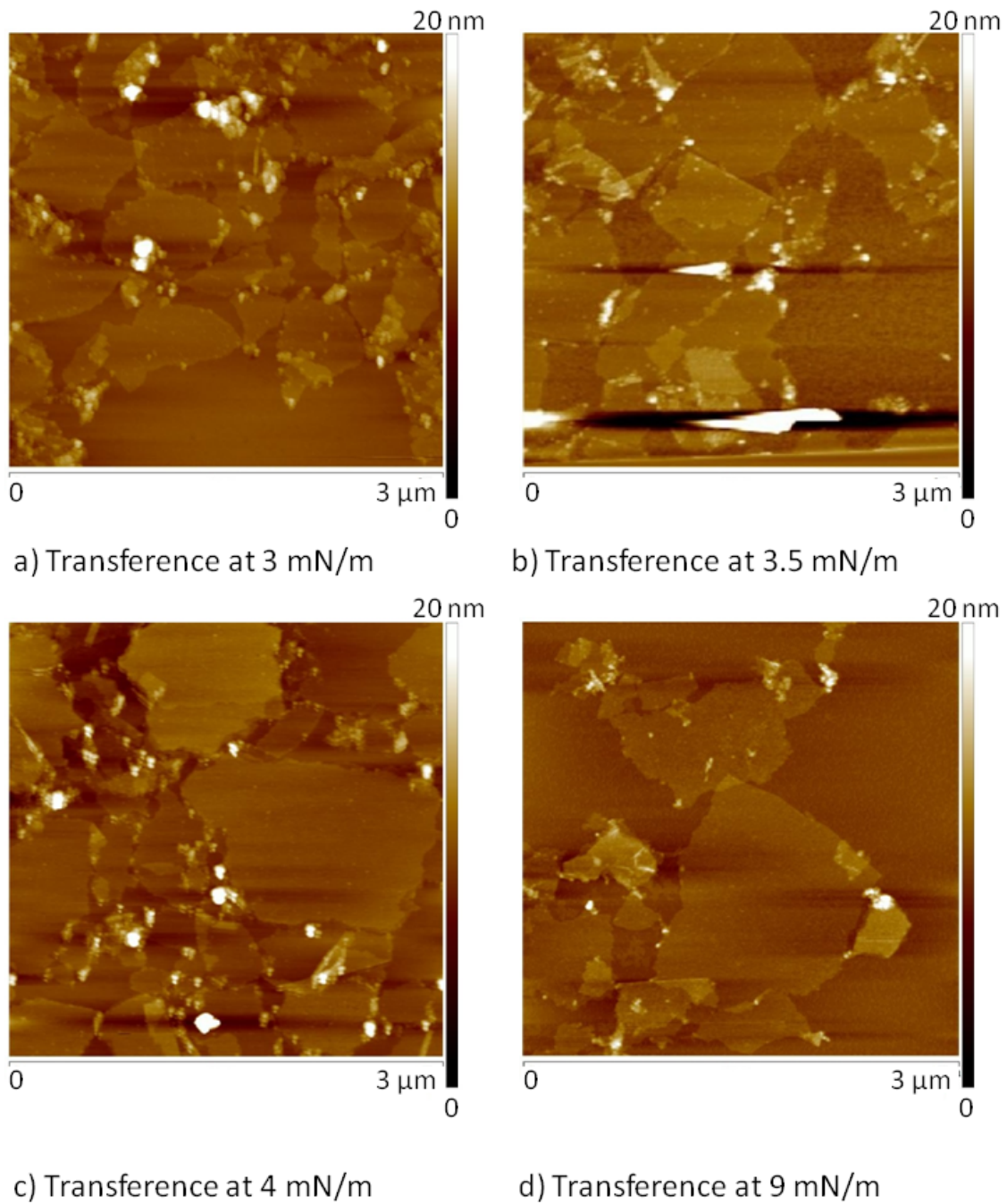
a) Transference at 3 mN/m

b) Transference at 3.5 mN/m

c) Transference at 4 mN/m

d) Transference at 9 mN/m

Figure 3.7: AFM images of the mica samples covered with LB film of GO transferred at different surface pressures.

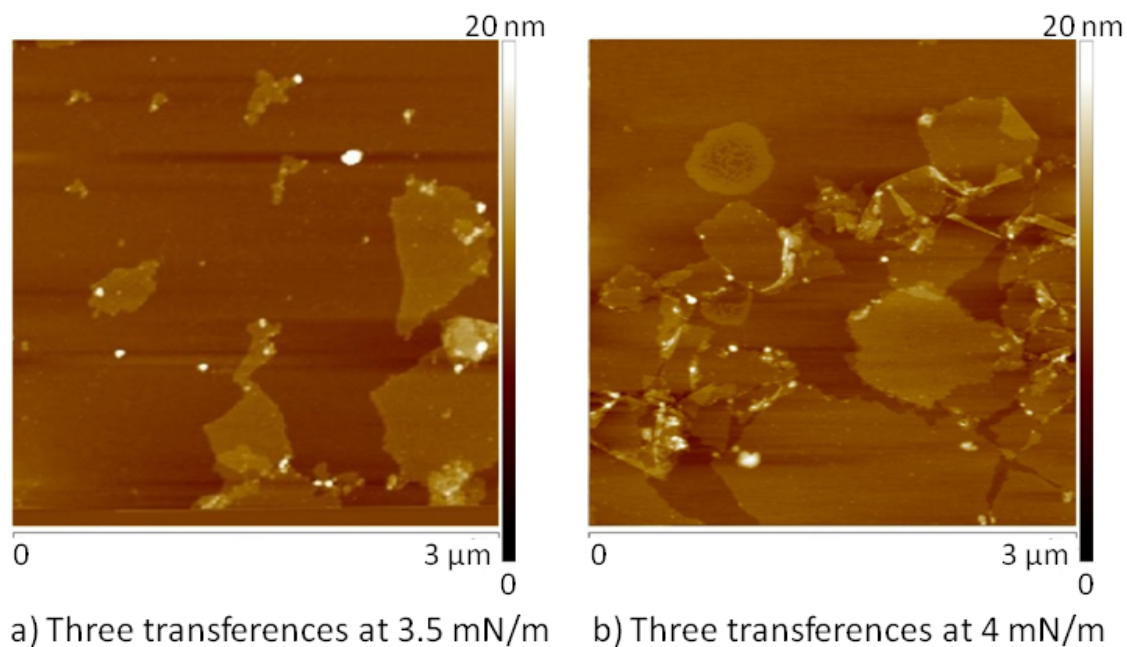a) Three transferences at 3.5 mN/m   b) Three transferences at 4 mN/m

Figure 3.8: GO LB film was transferred onto bare mica in three transferences at the surface pressures indicated below the images.
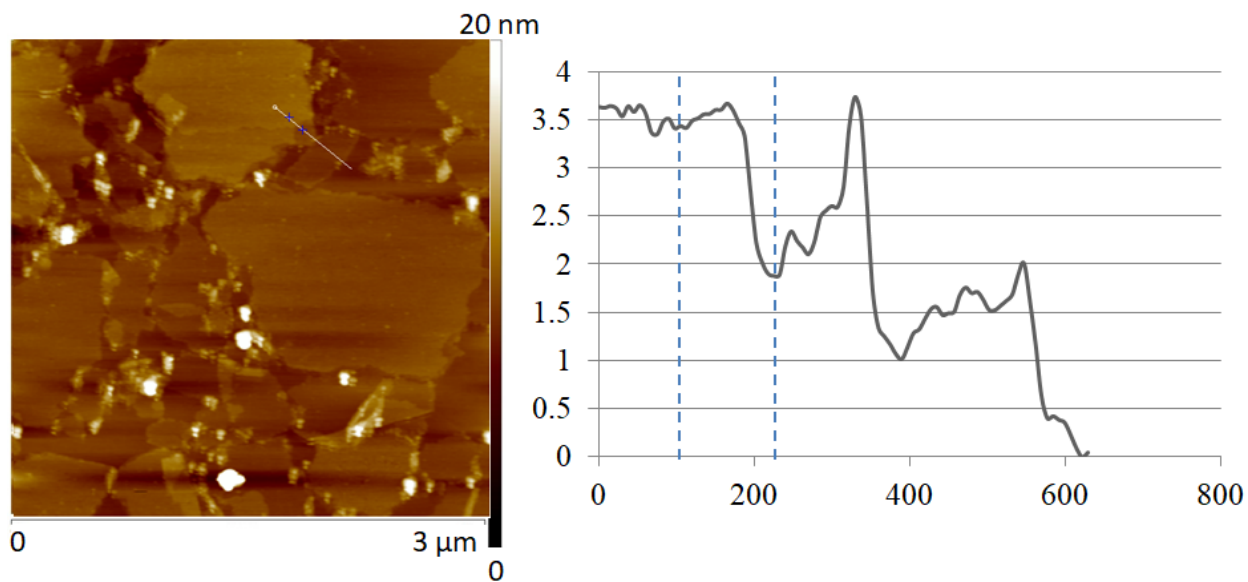

Figure 3.9: AFM image of the GO film at the optimum surface pressure, 4mN/m and the section analysis.

3.3.2 Fabrication of the HOPG-OPE-GO Structures

As it was mentioned in section 2, the main objective of this project was to fabricate an all-carbon molecular electronic device. In this section, the fabrication of films of the two OPE derivatives by electrografting, the deposition of a GO film onto these OPE films and their characterisation are explained.

Methodology used for cleaning a HOPG substrate

As a first step the HOPG substrate was exfoliated. Afterwards, the substrate was sonicated firstly, in a HNO_3:water solution, with a ratio of 1:1 and secondly, in mixture of H_2O_2, H_2SO_4 and water solution for 10 minutes for each mixture. Then, the substrate was sonicated in ethanol,acetone and acetonitrile, each one for 5 minutes. Finally, the HOPG was again exfoliated to obtain a surface as flat as possible.

Electrografting of OPE derivatives onto HOPG substrate

To perform the electrografting of TMS-OPE-NH_2 compound, diazonium salt was synthesised *in situ* in the electrochemical cell as it was explained by Garcia, in his final master project [51]. Briefly, 20 mL acetonitrile (ACN) was used as solvent. A 3mM tert-butyle nitride solution as reductor, a 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as electrolyte and reagent (once it was dried for 24 hours) as well as 2.5 mM TMS-OPE-NH_2 compound were added in solution. The solution was stirred for 30 minutes before reaction took place while a nitrogen flow was passed to have an inert atmosphere. Once the synthesis was completed, the electrografting process was conducted at a scan rate of 50 mV/s and with a step potential of 0.01 V. As it can be seen in Figure 3.10, the peak at the potential of -0.4 V disappeared after the first cycle which means the surface of the substrate was coated by the organic compound.
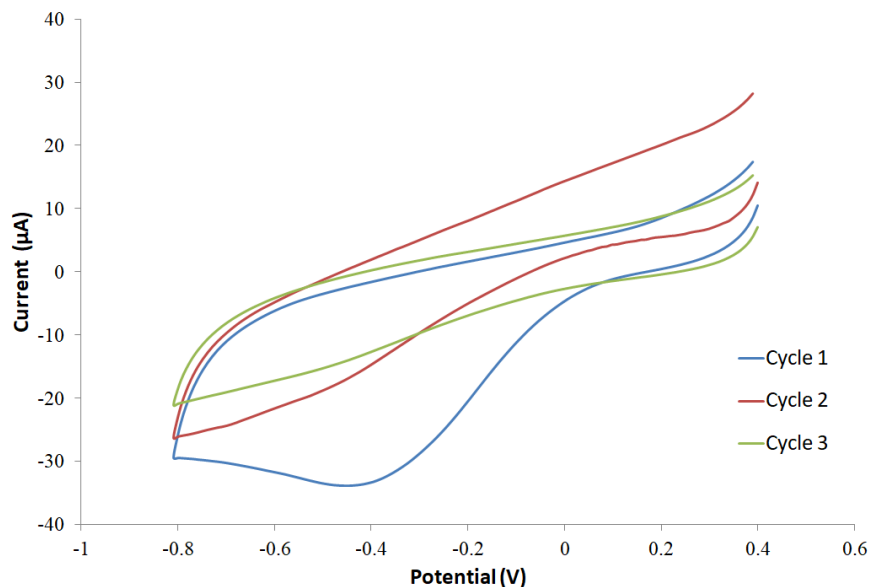
Figure 3.10: Cyclic voltammograms recorded during the electrografting process.

Deprotection step to remove TMS group and characterisation via Raman analysis

Once the electrografting process was carried out, a deprotection step was applied in order to remove TMS groups to obtain alkyne end groups, considering they would provide better interaction with the GO film. For that, the modified HOPG was immersed in an ACN solution with 50 mM tetra-n-butylammonium fluoride (TBAF) for an hour [51].

Afterwards, the HOPG was characterised by Raman spectroscopy. The D-peak at 1336 cm^{-1} corresponds the covalent functionalisation of the HOPG (result of the conversion of sp^2 hybridized surface lattice of carbon to sp^3); in this case, it is the covalent bond between TMS-OPE-NH$_2$ monolayer and the HOPG. The G-band and 2D-band peaks at 1576 and 2679 cm^{-1}, respectively, are corresponded to the HOPG itself. The ratio of the intensity at D-peak and G-peak, I_D/I_G is a measure of the concentration of covalent defect sites [52]. I_D/I_G ratio for the sample was 0.3 which indicates that a very compact monolayer was formed. The Raman spectra can be seen in Figure 3.11.
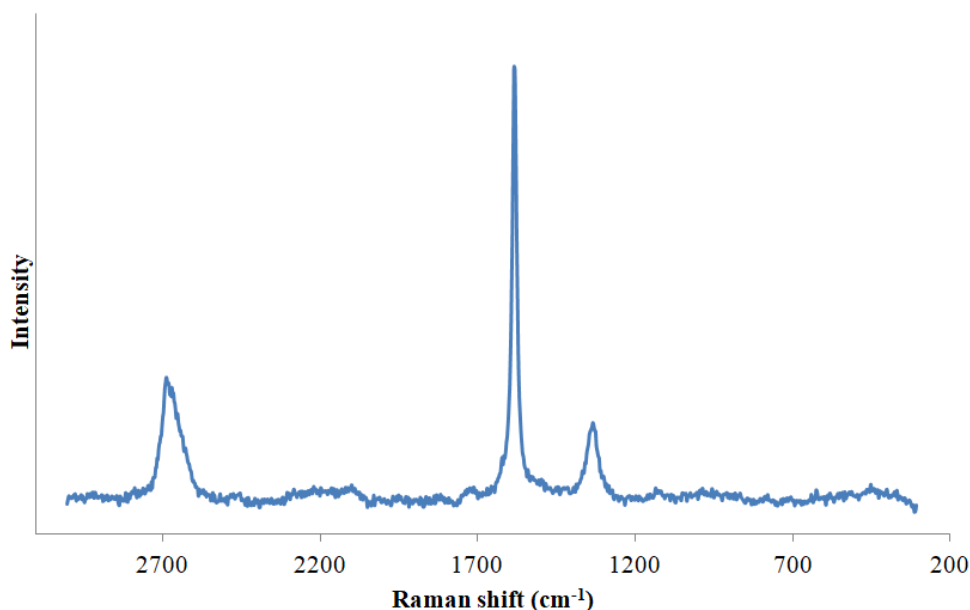
20

Figure 3.11: Raman spectroscopy of TMS-OPE-NH$_2$ monolayer onto HOPG.

Transference of the GO film on top of the TMS-OPE-NH$_2$ monolayer

Once it was demonstrated the formation of a homogeneous and compact monolayer of TMS-OPE-NH$_2$, the sample was taken for the transference of a LB film of GO. For comparison, bare mica was also used. After performing the transference, the substrates were analysed by AFM. It was possible to observe the presence of GO sheets on the bare mica, however these GO sheets were not observed on the modified HOPG with the TMS-OPE-NH$_2$ monolayer.This outcome points out that there was not an interaction between the GO and the alkyne group of the TMS-OPE-NH$_2$ monolayer, once the TMS group was removed.

Since it was not possible to incorporate the GO onto the alkyne group presents in the TMS-OPE-NH$_2$ monolayer once the TMS group was removed, other OPE derivative was used to achieve this challenge. In this case, the OPE derivative selected was NOPEN compound. As it was said above, this compound has two amine end groups, which will be used to generate *in situ* the diazonium salt during the electrografting process and the other one to make the interaction with the GO. Nevertheless, before doing the electrografting process, a self assembly monolayer of

NOPEN onto a gold substrate was used in terms to check in a first step the interaction between the amine group and GO. A gold substrate was incubated in a tetrahydrofuran (THF) solution with 0.1mM NOPEN compound. After waiting for 48 hours, the gold sample was taken off and washed with THF to eliminate all the physisorbed material and dried with a flow of nitrogen. The modified gold substrate was used to make the transference of a GO by using the LB technique. AFM was used to characterise this monolayer (Figure 3.12). As it can be observed, the GO was incorporated to the NOPEN monolayer.
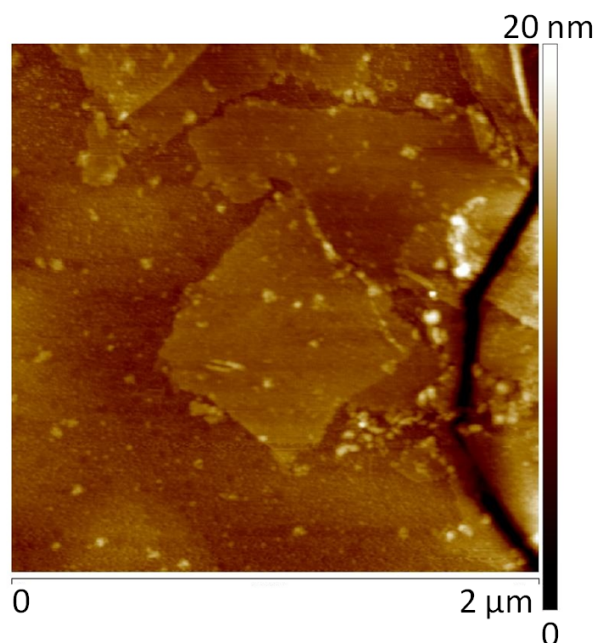

Figure 3.12: AFM image of a modified gold substrate with a NOPEN monolayer and the incorporation of a GO LB film.

Nevertheless, since the aim of this project is to fabricate all-carbon structures, the electrografting process was used to assemble the NOPEN onto HOPG substrate. The same conditions to these used for carrying out the electrografting process of the TMS-OPE-NH$_2$ were used,except a 1mM NOPEN solution was used instead of TMS-OPE-NH$_2$ compound and a 2mM 2,2-Diphenyl-1-picrylhydrazyl was added to the solution as an inhibitor. The purpose of adding the inhibitor to the solution was to protect an amine end group of NOPEN molecule to exploit it for the incorporation of GO LB film as it was explained before. The peak at -0.1 V was disappeared

after the first cycle because the surface was covered with the NOPEN monolayer. Additionally, the peak at ~0.2 V corresponds to the inhibitor.
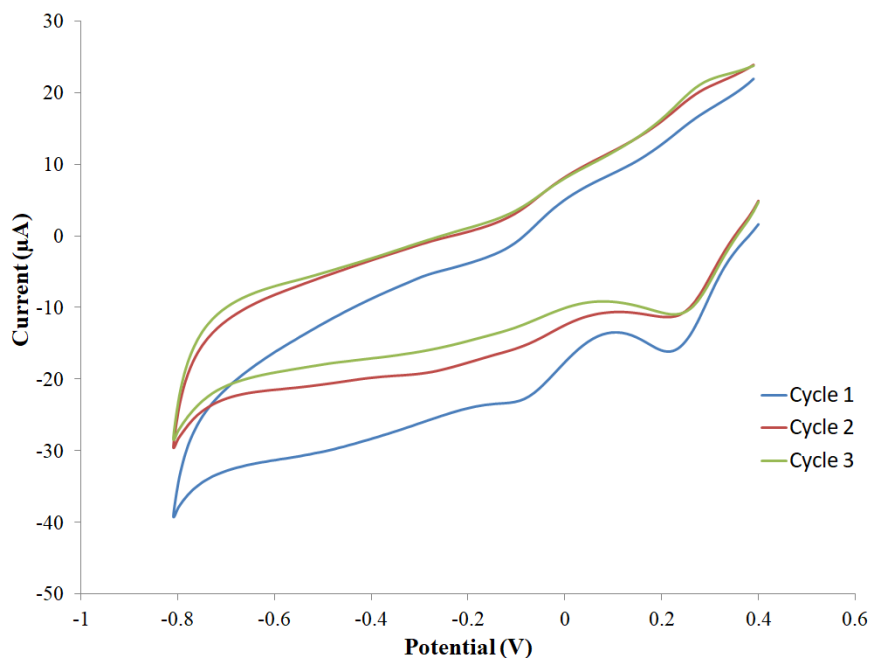

Figure 3.13: Cyclic voltammograms recorded during electrografting process is given for all 3 cycles.

After performing the electrografting process, a transference of a LB film of GO was carried out and it was characterised by AFM in terms to check the incorporation of GO. However, it was not possible to observe the presence of GO sheets on top of NOPEN monolayer, even though it was possible to observe GO sheets on the part of the HOPG without covering the NOPEN monolayer (Figure 3.14). Since it was demonstrated the incorporation of GO LB film on top a NOPEN monolayer, the lack of incorporation of GO in this case means that the amine group is not the end group. Probably, even when an inhibitor was used, the amine was converted into a N_2^+ which shoud be investigated in future works.

a) AFM image of GO LB film on top of NOPEN monolayer onto the HOPG

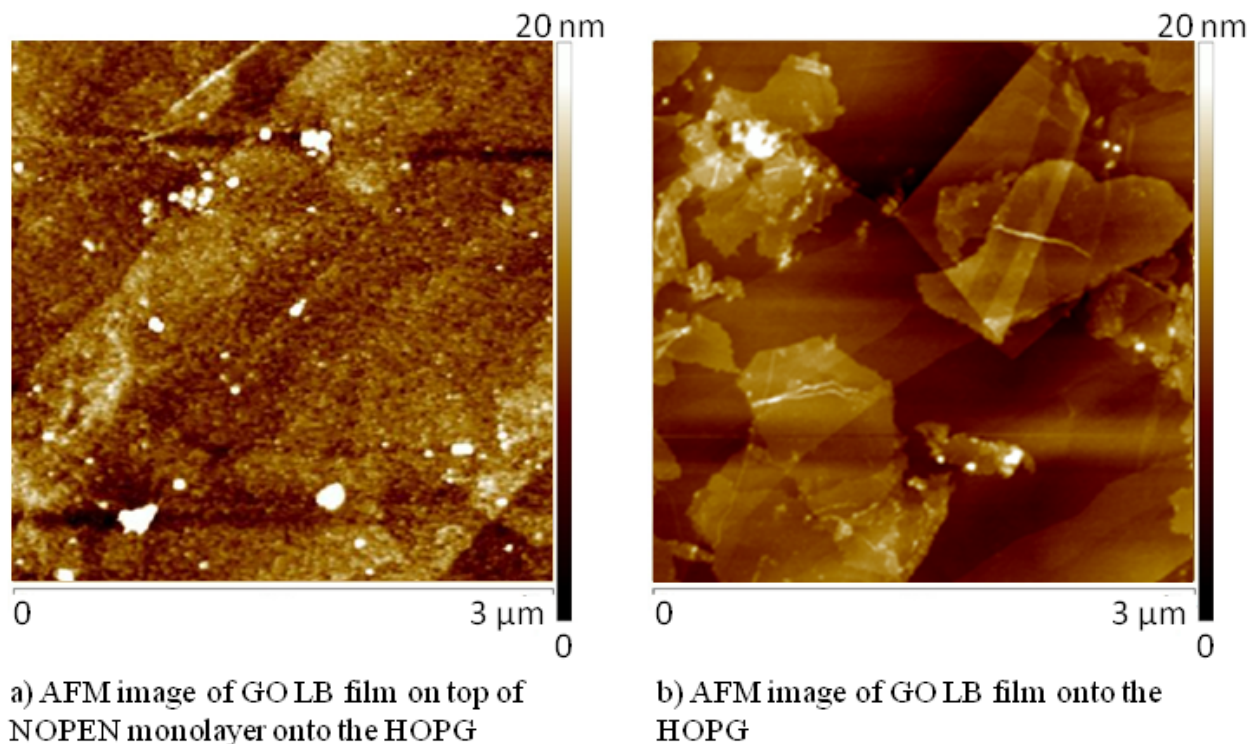b) AFM image of GO LB film onto the HOPG

Figure 3.14: AFM image of the HOPG sample.

4. Conclusion

In this final master project, fabrication and transference conditions for GO LB films were explored in order to fabricate carbon-based electrodes for molecular electronic applications; in addition, electrografting processes of OPE derivatives were performed and GO LB film were deposited onto these monolayers to be used as top contact electrode. Incorporation of GO LB film onto films prepared from TMS-OPE-NH$_2$ films onto HOPG electrode was not accomplished. This result was interpreted in terms of the lack of interactions between the molecules in the film and GO. Subsequently electrografted films from NOPEN were fabricated. The transference was also inhibited. Despite GO was not successfully deposited onto the two monolayer films studied in this final master project, this work has paved the way for future investigations for fabricating all carbon molecular electronic devices and investigations to obtain a OPE derivative monolayer with

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a compatible terminal group is recommended as it would finally make the fabrication of all carbon molecular devices using GO as top contact electrode possible.

5. Future works

The HOPG sample modified with NOPEN monolayer can be characterised by XPS to confirm the existence of a N_2^+ end group. As it was explained previously, substituting N_2^+ with proper end group is required to incorporate GO LB film onto the organic monolayer. In theory, this substitution may be achieved by placing the sample in a warm water bath to replace the end group by hydroxylic group (-OH) [53, 54]. Once the HOPG-OPE derivative-GO structure is fabricated, GO will be reduced to graphene to improve its electrical properties. Afterwards, the characterisation of electrical properties of the sample will be carried out.

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