Chapter 4
Controlled deposition of fullerene derivatives within a graphene template by means of a modified Langmuir-Schaefer method

The scientific and technological potential of graphene includes the development of light, open 3D structures with high surface area, tunable pore size and aromatic functionalities. Towards this aim, we describe a bottom-up approach that combines self-assembly and Langmuir-Schaefer deposition for the production of fullerene-intercalated graphene hybrid materials. This method uses graphene nanosheets as templates for the attachment of two types of fullerene derivatives (bromo-fullerenes, \( \text{C}_{60}\text{Br}_{24} \) and fullerols, \( \text{C}_{60}(\text{OH})_{24} \)) in a bi-dimensional arrangement, allowing for perfect layer-by-layer growth with control at the molecular level. Our film preparation approach relies on a bottom-up process that includes the formation of a hybrid organo-graphene Langmuir film, which is transferred onto a substrate and then brought in contact with \( \text{C}_{60}(\text{OH})_{24} \) molecules in solution to induce self-assembly. In the case of grafting \( \text{C}_{60}\text{Br}_{24} \) molecules into graphene a further modification of the GO platelets was performed by bringing the surface of the transferred GO Langmuir film in contact with a second amino surfactant solution (capable to interact strongly with the \( \text{C}_{60}\text{Br}_{24} \)). By repeating these deposition cycles and thereby stacking numerous organo-graphene layers decorated with fullerene derivatives pillared structures were fabricated in thin films form. These fullerene-based hybrid thin films deposited on hydrophobic substrates were characterized by Raman and X-ray photoelectron (XPS) spectroscopies, X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and contact angle measurements.

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4.1 Introduction

Buckminster fullerene (C_{60}) was discovered in 1985 by Kroto, Curl and Smalley; it consists of 60 sp^2 carbon atoms arranged in pentagons and hexagons to form a spherical nanostructure (cage). Due to the size and electronic structure of C_{60} and larger fullerenes, derivatives can be formed by inserting atoms or molecules inside the cage (endohedral fullerenes) and by functionalizing with substituents outside the cage (exohedral fullerenes). Like most organic molecular materials, fullerenes and their derivatives can be insulators, semiconductors, or even superconductors when doped with other atoms or molecules. These tunable conductivity properties render them very attractive as active materials for electronic devices, such as light detectors, transistors, or solar cells.

Although halogenated fullerene derivatives are interesting for their outstanding physical and chemical properties, investigations of their potential for diverse applications are still scarce. However the presence of halogens in other carbon materials has been studied already decades ago. Doping with bromide was demonstrated to increase the electrical conductivity of graphite, and carbon nanotubes. More specifically, S. Tongay et al. fabricated a superconductive bromine-intercalated graphite by exposing highly ordered pyrolytic graphite (HOPG) to bromine vapour, with the same method N.Jung et al. achieved an enhancement of the conductivity for multilayered graphene films and thick graphite. Bromine derivatives of graphene that could be used for reversible bromine storage or as a starting material for further chemical modifications were synthesized by O. Jankovsky and co-workers in 2014. In the same year, K. Klouda et al. synthesized hybrid brominated nanostructures containing fullerene molecules within graphene oxide by reacting graphene oxide with brominated fullerene derivatives (C_{60}Br_{14-18}) and by direct bromination (with liquid bromide) of an oxidized GO-C_{60} mixture. Moreover Klouda’s group reported that the brominated materials thermally decomposed at higher temperatures than the unbrominated ones, due to the retarding action of bromine. A. E. Mansour et al. investigated the doping of graphene with bromine to develop high performance transparent conducting electrodes.
The functionalization of a fullerene cage can also be a first step in the synthesis of more complex derivatives with different physical and chemical properties. In this context the halogenation of fullerenes (with fluorine, chlorine, or bromine) is one of the most common chemical reaction to yield derivatives that can be either used as they are or serve as precursors in substitution reactions to sequentially attach aromatic groups to the fullerene cage. In the case of brominated fullerene the substitution of the bromine with OH groups results in derivatives with better solubility in water and in aqueous solutions. Polyhydroxylated fullerenes or fullerols \((C_{60}(OH)_n)\), have attracted much scientific and industrial attention in engineering, where they were found to improve the corrosion resistance and microhardness of coatings, to give better mechanical properties than \(C_{60}\), when incorporated in poly(styrene-co-4-vinylpyridine) for optical limiting performance or to reinforce and have anti-oxidation effects when mixed with natural rubber to inhibit the decrease of tensile strength after aging. Fullerols improve have been proposed for performing bio-oxidations. They have been tested as agents for Parkinson's disease (PD) prevention and therapy, and as active compounds in the preparation of skin rejuvenation cosmetic formulations, just to name a few of the many fields of science and technology where \(C_{60}(OH)_n\) have been considered.

Nanotechnology can tune and control the fundamental physicochemical properties of fullerenes and their derivatives by ordering them into molecular thin films for the use in diverse applications including optoelectronics, photovoltaics and solar cells, sensors, biological applications and many more. The possibility to control the size and the orientation of (functionalized) fullerene molecules in 2D arrays can lead to new functional and low-dimensional materials with interesting and promising properties.

Here we report a bottom-up layer-by-layer approach for the production of fullerene-graphene oxide hybrid materials that combines the self-assembly with the Langmuir-Schaefer (LS) deposition technique. Graphene oxide nanosheets were used as a template for integrating \(C_{60}\) derivatives (fullerol with chemical formula \(C_{60}(OH)_{24}\) and bromo-fullerene with chemical formula \(C_{60}Br_{24}\)) in 2D arrays. More specifically, a dilute water suspension of chemically oxidized graphene (GO) was used as subphase in a Langmuir-Blodgett trough and an amino surfactant, which
covalently binds to GO, was applied for the formation of hybridized GO platelets in the air-dispersion interface. After the transfer of the hybrid GO Langmuir film using the Langmuir-Schaefer method (horizontal dipping), the substrate was dipped into a solution of fullerols \( \text{C}_60(\text{OH})_{24} \) to induce self-assembly (SA). Instead, in the case of grafting \( \text{C}_60\text{Br}_{24} \), after the transfer of the hybrid GO Langmuir film using the Langmuir-Schaefer method (horizontal dipping), the substrate was first brought in contact with another amino surfactant solution to induce functionalization by self-assembly and then, as the final step, lowered in the solution of the bromo-fullerene to complete the self-assembly with the \( \text{C}_60\text{Br}_{24} \) molecules. Hybrid graphene oxide multilayer thin films hosting fullerene-derivatives molecules within their interlayer space were fabricated by repeating these two procedures, as illustrated in Scheme 4.1. The samples were characterized by Raman and X-ray photoelectron spectroscopies, X-ray diffraction, Atomic Force Microscopy and contact angle measurements.

4.2 Experimental Section

4.2.1 Materials

Buckminster fullerene (99.8%), octadecylamine (ODA, \( \geq 99\% \)), hexamethylenediamine (HEX, \( \geq 99\% \)), acetone, methanol and ethanol were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH) pellets were obtained from Vioryl. Ultrapure deionized water (18.2 M\( \Omega \)) produced by a Millipore Simplicity® system was used throughout. The Si wafers (P/Bor, single side polished, purchased from Si-Mat) used as substrates were cleaned prior to use by ultrasonication in water, acetone and ethanol for 15 min each. All reagents were of analytical grade and were used without further purification.

4.2.2 Synthesis of Graphene Oxide

Graphene oxide (GO) was synthesized using a modified Staudenmaier method, as described in Chapter 3 (see section 3.2.2).
4.2.3 Synthesis of fullerene derivatives

In a typical synthesis of polybrominated fullerene\textsuperscript{22} (C\textsubscript{60}Br\textsubscript{24}), 300 mg of Buckminster fullerene were dissolved in 2 mL of elementary bromine, in the presence of a catalytic quantity of FeBr\textsubscript{3}. The mixture was stirred for 40 min at room temperature. When the reaction was completed, the excess of unreacted bromine was evaporated and the catalyst was separated by dissolving in a mixture of ethanol/H\textsubscript{2}O (1:2, v/v).

Polyhydroxylated fullerene (fullerol, C\textsubscript{60}(OH)\textsubscript{24}) was synthesized by using polybrominated fullerenes as precursor.\textsuperscript{22} More specifically, fullerol was obtained by reacting 50 mg of C\textsubscript{60}Br\textsubscript{24} with 5 mL of NaOH 2 M (pH = 13) for 2 h at room temperature. After completion of the reaction, the solvent was evaporated at 40 °C; then the mixture was filtered and washed 5 times with 10 mL of ethanol (purity 70 %). The dark brown powder product obtained after the filtration was soluble in polar solvents like water.\textsuperscript{22}

4.2.4 Preparation of hybrid multilayers of graphene oxide and C\textsubscript{60}-derivatives

A Langmuir Blodgett (LB) trough (KSV 2000 Nima Technology) was cleaned with ethanol and distilled-deionized water. GO suspensions in ultrapure water (0.02 mg mL\textsuperscript{-1}) were prepared and used as subphase. To achieve the hybridization of the GO sheets in the LB trough, 200 μL of a 0.2 mg mL\textsuperscript{-1} ODA dissolved in a chloroform/methanol mixture (9/1, v/v) were spread onto the water surface using a microsyringe. After a waiting time of 20 min to allow for solvent evaporation and GO-surfactant functionalization to occur, the hybrid ODA-GO layer was compressed at a rate of 5 mm min\textsuperscript{-1} until the chosen stabilization pressure of 20 mN m\textsuperscript{-1} was reached. This pressure was maintained throughout the deposition process. The hybrid Langmuir layers (ODA-GO) were transferred onto the Si-wafer substrates by horizontal dipping (Langmuir Schaefer technique), with downward and lifting speeds of 10 and 5 mm min\textsuperscript{-1}, respectively.\textsuperscript{44, 64}

\textsuperscript{1} Fullerene derivatives samples were provided by Dr. Panagiota Zygouri (University of Ioannina, Greece)
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Scheme 4.1. Schematic representation of the synthetic procedures for fabricating the hybrid films of left: graphene oxide and C$_{60}$(OH)$_{24}$ (ODA-GO-C$_{60}$(OH)$_{24}$) or right: graphene oxide and C$_{60}$Br$_{24}$ (ODA-GO-HEX-C$_{60}$Br$_{24}$). Both procedures consist in a Langmuir Schaefer deposition combined with with one self-assembly step (left) or two self-assembly steps (right).

After the horizontal lift of a substrate, the ODA-GO film was dipped into an aqueous solution of fullerols (0.2 mg mL$^{-1}$). A hybrid graphene/C$_{60}$(OH)$_{24}$ multilayer film was constructed by repeating this procedure for 60 times, as shown in Scheme 4.1 (sample denoted as ODA-GO-C$_{60}$(OH)$_{24}$). For the formation of the hybrid graphene oxide film hosting polybrominated fullerene in its interlayer space, a further surface modification of the GO nanosheets was performed by bringing the surface of the transferred Langmuir film (ODA-GO) in contact with an amino surfactant, HEX dissolved in methanol (0.2 mg mL$^{-1}$) and making use of a self-assembly step.$^{44, 65}$ After this functionalization, in a final stage, the hybrid organo-GO (ODA-GO-HEX) film was lowered into a solution of polybrominated fullerene (0.2 mg mL$^{-1}$) dissolved in an ethanol/H$_2$O mixture (2/1, v/v) to induce the formation of a hybrid ODA-GO-HEX-C$_{60}$Br$_{24}$ layer by self-assembly. By repeating this procedure 60 times, a hybrid multilayer film was constructed as shown in Scheme 4.1 (sample denoted as ODA-GO-HEX-C$_{60}$Br$_{24}$). Each time when the substrate was lowered, it was allowed to...
touch the air-water interface or the solution surface in a very gentle dip of max 0.5 mm below the liquid surface for 90 s. After each deposition step samples were rinsed several times by dipping into ultrapure water (to eliminate any weakly attached cations or molecules that remained from the deposition steps) and dried with nitrogen flow (to avoid contaminating either the LB air-water interface or the other solutions).41,44,66

4.3 Results-discussion

4.3.1 Structural characterization of C\textsubscript{60} derivatives\textsuperscript{2}

FTIR spectra of polybrominated fullerene (C\textsubscript{60}Br\textsubscript{24}) and fullerol (C\textsubscript{60}(OH)\textsubscript{24}) are shown in Figure 4.1. In the case of polybrominated fullerene, the stretching vibrations of the C-Br groups were observed in the range of 500-610 cm\textsuperscript{-1} (515 cm\textsuperscript{-1}, 545 cm\textsuperscript{-1} and 609 cm\textsuperscript{-1}).\textsuperscript{67} Based on the Sadtler Handbook of Infrared spectra\textsuperscript{68} bands in the region of 1000-1200 cm\textsuperscript{-1} can be attributed to vibrations of C-Br groups; for C\textsubscript{60}Br\textsubscript{24}, these bands appear at 1045 cm\textsuperscript{-1}, 1086 cm\textsuperscript{-1}, 1144 cm\textsuperscript{-1}, 1180 cm\textsuperscript{-1}.

Figure 4.1: FTIR spectra of (a) polybrominated fullerene (C\textsubscript{60}Br\textsubscript{24}) and (b) fullerol (C\textsubscript{60}(OH)\textsubscript{24}).

\textsuperscript{2} The structural characterization of fullerene derivatives samples was provided by Dr. Panagiota Zygouri (University of Ioannina, Greece)
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The spectrum of $C_{60}(OH)_{24}$ shows characteristic bands due to the presence of hydroxyl groups at 1065 and 1458 cm$^{-1}$ (bending vibrations of C–OH groups), as well as at 685 cm$^{-1}$, 849 cm$^{-1}$ and 905 cm$^{-1}$ (wagging vibrations of OH). The bands at 3465 cm$^{-1}$ (stretching vibration) and 1690 cm$^{-1}$ (bending vibration) are instead indicative of the presence of water molecules. The band at 3465 cm$^{-1}$ corresponds to the stretching vibration of the -OH bond and is observed also in liquid water.$^{69}$

Raman spectra of pristine and polybrominated fullerene ($C_{60}Br_{24}$) are shown in Figure 4.2. $C_{60}$ is characterized by high $I_h$ symmetry and presents 46 vibrational modes distributed over the 174 vibrational degrees of freedom. From the 46 vibrational modes, 4($T_{1u}$) are active in the infrared region and 10 ($2A_g + 8H_g$) are active in Raman, while the remaining are optically inactive.$^{70}$

$$\Gamma_{\text{vib}} (C_{60}) = 2A_g (\text{Raman}) + 3F_{1g} + 4F_{2g} + 6G_g + 8H_g (\text{Raman}) + A_u + 4F_{1u} (\text{IR}) + 5F_{2u} + 6G_u + 7H_u$$

In the case of polybrominated fullerene, the bromines are attached to the twelve six-membered rings of the fullerene structure at the 1 and 4 position induce a “boat” conformation, while for the remaining 8 six-membered rings, the bromine atoms bound to the carbons 1, 3 and 5, create a “chair” conformation.$^{71}$ The active vibrations of the C-Br groups are five, more specifically stretching vibrations of these groups are observed at 505 cm$^{-1}$, 516 cm$^{-1}$, 549 cm$^{-1}$, 562 cm$^{-1}$ and 585 cm$^{-1}$.

![Figure 4.2](image_url)

**Figure 4.2:** Left: Raman spectra of (a) Pristine Buckminster fullerene and (b) polybrominated fullerene ($C_{60}Br_{24}$). Right: typical structure of $C_{60}Br_{24}$. 

The presence of the band at 1463 cm\(^{-1}\) in the spectra of the C\(_{60}\)Br\(_{24}\), which is due to the Ag symmetry of the fullerene, indicates that the icosahedral structure remains unaffected after the functionalization (Figure 4.2 right). The appearance of a new band at 308 cm\(^{-1}\) can be attributed to a neutral molecular Br\(_2\) in a charge transfer complex between C\(_{60}\) and Br\(_2\). The absence of any \(\nu_{\text{Br-Br}}\) signal renders the C\(_{60}\)Br\(_{24}\) a real derivative of fullerene.\(^{72,73}\)

Thermogravimetric analysis (TGA) and thermal analysis (DTA) measurements for polybrominated and polyhydroxylated fullerene are presented in Figure 4.3. The TGA curve of C\(_{60}\)Br\(_{24}\) (a) presents a 9\% weight loss up to 100 °C corresponding to absorbed water and unreacted molecular bromine (Br\(_2\)). At the temperature range between 100 and 180 °C, a mass loss (~31\%) is observed, which can be attributed to the removal of functional groups. The curve of DTA shows an exothermic peak at 430 °C related to the combustion of the fullerene carbon cage, which is followed by the total weight loss of the sample (~60 wt\%). In the case of fullerols (b), a mass loss of ~20 wt\% in the temperature range up to 120 °C, points to the presence of naturally absorbed water molecules and demonstrates the hydrophilic character of the C\(_{60}\)(OH)\(_{24}\). The removal of the hydroxyl groups occurs between 150 and 320 °C and corresponds to a weight loss of ~13\%.

Figure 4.3: Thermogravimetric analysis (TGA) and thermal analysis (DTA) measurements of (a) polybrominated (C\(_{60}\)Br\(_{24}\)) and (b) polyhydroxylated fullerenes (C\(_{60}\)(OH)\(_{24}\)).
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Above 350 °C the decomposition of the graphitic lattice resulting in a weight loss close to 37%. The removal of the hydroxyl groups and the decomposition of the fullerene are not separated in the DTA curve, indicating an interdependence of these two phenomena and consequently testifying to the successful chemical functionalization of the fullerene.

4.3.2 Structural control of hybrid monolayers

To demonstrate the attachment of ODA to the GO flakes, we recorded the surface pressure-molecular area (π-A) isotherms while compressing the Langmuir film by means of the movable barriers of the LB trough. Figure 4.4 displays the π-A isotherms of an ODA monolayer on pure water and on a GO dispersion. The curves show changes in slope corresponding to the phase transitions from two dimensional gas to condensed liquid and then to solid during the compression process. The fact that the compression of ODA on the GO suspension gives rise to an increase of the surface pressure much earlier during the compression that for ODA on pure water, indicates that GO has hybridized by covalent bonding via the amide functionality of ODA and a hybrid floating layer of ODA-GO has been formed.44

![Image](image-url)

**Figure 4.4.** π-A isotherms recorded during the compression of ODA monolayers on pure water and on an aqueous dispersion of 20 ppm GO.
Representative AFM images of hybrid Langmuir monolayers (ODA-GO) transferred onto the Si-wafer at different surface pressures in the LB trough, namely 5, 10, 15 and 20 mN/m, are shown in Figure 4.5. The topographic images revealed that the substrate surface coverage of the hybrid ODA-GO monolayers is higher as the surface pressure increases. GO nanosheets with well-defined edges are easily observed in the AFM micrographs, verifying the formation of a hybrid Langmuir film at the air-dispersion interface. More specifically, when the Langmuir film was compressed at 5 mN m\(^{-1}\) (Figure 4.5a), the GO platelets appear isolated with an empty space between them. When the Langmuir film was further compressed at 10 mN m\(^{-1}\) (Figure 4.5b), the GO platelets contact each other, with still rather large voids between them and at even higher surface pressure of 15 mN m\(^{-1}\) (Figure 4.5c), the nanosheets become more closely packed.

**Figure 4.5.** AFM height images of ODA-GO monolayers deposited on Si-wafer substrates at different surface pressures of a) 5 mN m\(^{-1}\), b) 10 mN m\(^{-1}\), c) 15 mN m\(^{-1}\) and d) 20 mN m\(^{-1}\) during the compression process.
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When deposited at 20 mN m\(^{-1}\) the hybrid film becomes very dense but with only very few overlaps between adjacent flakes (Figure 4.5d). Furthermore, the GO layers exhibit wrinkles that may be related to water-GO interaction and are formed during dipping and drying. GO sheets can become wrinkled during water evaporation due to surface tension.\(^{74, 75}\) The average thickness of the flakes is 1.1.5±0.2 nm as derived from topographical height profile (section analysis) corresponding to the size of single graphene oxide layers, which is 6.1 Å.\(^{76, 44}\)

Detailed AFM images of single ODA-GO-HEX-C\(_{60}\)Br\(_{24}\) and ODA-GO-C\(_{60}\)(OH)\(_{24}\) hybrid layers deposited on Si-wafer are shown in Figure 4.6. The micrographs reveal the presence of quite uniform and nearly spherical particles decorating several micrometer size layers indicating the successful attachment of the C\(_{60}\) derivatives on the graphene oxide surface. More specifically, the C\(_{60}\)Br\(_{24}\) decoration in the hybrid ODA-GO-HEX monolayer is relatively uniform revealing small particles in all over the surface of the GO sheets while wrinkled sheets were also observed.

![AFM images](image)

**Figure 4.6.** AFM height images and cross section analysis profile of ODA-GO-HEX-C\(_{60}\)Br\(_{24}\) (left) and ODA-GO-C\(_{60}\)(OH)\(_{24}\) (right) hybrid single layers.
In the other hand, the hybrid ODA-GO-C$_{60}$(OH)$_{24}$ layer exhibit a smoother distribution and higher coverage of C$_{60}$(OH)$_{24}$ molecules on the graphene oxide layers as compared to C$_{60}$Br$_{24}$ in the hybrid ODA-GO-HEX-C$_{60}$Br$_{24}$ layer. This different morphology is due to the direct attachment of C$_{60}$(OH)$_{24}$ to the polar oxygen-containing groups homogeneously distributed on the graphitic surface (without interposed surfactant like in the case of brominated fullerene). The average size of decorating C$_{60}$Br$_{24}$ and C$_{60}$(OH)$_{24}$ molecules was about 3±0.2 nm and 1.8±0.2 nm respectively as deduced from the height profile analysis. The larger size of the C$_{60}$Br$_{24}$ moieties arises probably from the presence of the adsorbed HEX molecules attached to C$_{60}$Br$_{24}$.

4.3.3 Characterization of graphene/C$_{60}$-derivative hybrid multilayers

The X-ray diffraction patterns of the produced ODA-GO-HEX-C$_{60}$Br$_{24}$ and ODA-GO-C$_{60}$(OH)$_{24}$ hybrid multilayers (60 layers) are shown in Figure 4.7. The hybrid multilayer with C$_{60}$Br$_{24}$ shows a 001 diffraction peak at 2θ=2.3° from which a $d_{001}$-spacing of 38.4 Å is deduced.

![XRD patterns and schematic illustration (inset) of ODA-GO-HEX-C$_{60}$Br$_{24}$ and ODA-GO-C$_{60}$(OH)$_{24}$ hybrid multilayers (60 layers).](image)

**Figure 4.7.** XRD patterns and schematic illustration (inset) of ODA-GO-HEX-C$_{60}$Br$_{24}$ and ODA-GO-C$_{60}$(OH)$_{24}$ hybrid multilayers (60 layers).
This $d_{001}$ value corresponds to an interlayer space of $\Delta = 38.4 \pm 6.1 = 32.3 \text{ Å}$, where the value of 6.1 Å represents the thickness of the GO single layer,\textsuperscript{76} indicating the successful insertion of the C$_{60}$Br$_{24}$ molecules as pillars between GO sheets. Moreover, the presence of higher order (00l) reflections in the XRD pattern of ODA-GO-HEX-C$_{60}$Br$_{24}$ suggests very high order in the stacking of the GO layers. On the other hand, the ODA-GO-C$_{60}$(OH)$_{24}$ hybrid multilayer shows a 001 diffraction peak at $2\theta=2.7^\circ$, resulting in a smaller $d_{001}$-spacing of 32.7 Å. This value corresponds to an interlayer space of $\Delta = 32.7 \pm 6.1 = 26.6 \text{ Å}$, testifying to the presence of C$_{60}$(OH)$_{24}$ molecules in the interlayer space.\textsuperscript{77} This value is smaller as compared to the $d_{001}$-spacing of ODA-GO-HEX-C$_{60}$Br$_{24}$ because the C$_{60}$(OH)$_{24}$ molecules are directly attached to the graphene oxide layers without an interposed surfactant.

The Raman spectra of the produced ODA-GO-HEX-C$_{60}$Br$_{24}$ and ODA-GO-C$_{60}$(OH)$_{24}$ hybrid multilayers deposited on a Si wafer are shown in Figure 4.8. Spectra of graphene-based thin films exhibit the characteristics bands. The second order D band at around 1350 that is connected to sp$^3$ hybridized carbon arising from lattice defects and distortions while the first order G band at around 1600 cm$^{-1}$ is linked with sp$^2$ hybridized carbon atoms of the graphitic lattice.\textsuperscript{78, 79}

![Raman spectra of ODA-GO-HEX-C$_{60}$Br$_{24}$ and ODA-GO-C$_{60}$(OH)$_{24}$ hybrid multilayers (inset: Raman spectrum of graphene oxide).](image)

**Figure 4.8.** Raman spectra of ODA-GO-HEX-C$_{60}$Br$_{24}$ and ODA-GO-C$_{60}$(OH)$_{24}$ hybrid multilayers (inset: Raman spectrum of graphene oxide).
The ratio of the D- to G-band intensities ($I_D/I_G$) is indicative of the quality of the graphitic lattice and was found to be 0.81 for the pristine GO (Figure 4.8, inset). The ratio of the D- to G-band intensities ($I_D/I_G$) for the hybrids ODA-GO-HEX-C$_{60}$Br$_{24}$ and ODA-GO-C$_{60}$(OH)$_{24}$ multilayers is at least 1.1 and 1.06 respectively. This increase of the $I_D/I_G$ ratio in the case of the hybrid films could be assigned to the relative increase of the D' band (1620 cm$^{-1}$), which exceeds the intensity of the G band suggesting the hybridization of GO due to the covalent bonding of the amide functionality of ODA. Moreover, both spectra display three broad bands in the 2D region at ~2700, ~2930 and ~3200 cm$^{-1}$, which are typical of GO materials. These are related with the 2D (or else G') vibrational mode, the D+D' mode and the 2D' mode in that order.\footnote{78, 79, 81, 82}

In order to gain further information for the type of bonding between the graphene oxide layers and the C$_{60}$ derivatives we employed X-Ray photoelectron spectroscopy measurements. Figure 4.9 displays the C1s and N1s core level regions of the ODA-GO-C$_{60}$(OH)$_{24}$ hybrid multilayer. Four contributions located at binding energies of 284.6 eV, 286.1 eV, 287.2 eV and 288.6 eV can be identified. The peak at 284.6, which accounts for 61.1\% of the total carbon intensity, originates from the carbon-carbon bonds of graphene oxide and of the fullerene cage, as well the C-C of ODA. The peak at 286.1 eV is due to C-O of GO and of the hydroxyl groups of fullerol. The same peak also contains contributions from C-N bonds of ODA molecules when reacted with the epoxy groups of graphene oxide. The contribution at 287.2 eV is due to C=O (carbonyl) as well C-O-C (epoxy) functional groups and accounts for 10.7 \% of the total carbon intensity. A last peak centred at 288.6 eV stems from carboxyl groups of graphene oxide (3.1\%). Additionally there is no characteristic shake up peaks of C$_{60}$\footnote{83} are observed because the π electrons are no longer delocalized over the whole molecule.\footnote{84, 85}

In the Nitrogen 1s photoelectron spectra we identify three contributions, one at 399.3 eV attributed to C-N-C bond of ODA with the epoxy groups of graphene oxide, a second one at 400.8 eV corresponding to the primary amines that may interact with the GO surface by non-covalent bonding and a third one, which originates from the protonated amines of ODA-GO-C$_{60}$(OH)$_{24}$.
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**Figure 4.9.** C1s (left) and N1s (right) core level photoemission spectra of a ODA-GO-C$_{60}$(OH)$_{24}$ hybrid multilayer film.

Figure 4.10 shows the C1s and N1s photoemission spectra of the ODA-GO-HEX-C$_{60}$Br$_{24}$ hybrid multilayer. The main contribution to the C1s line at 284.6 eV binding energy results from carbon-carbon bonds of graphene oxide and of the fullerene cage, as well as from the C-C bonds of ODA and accounts for 57.4% of the total carbon intensity.

**Figure 4.10.** C1s (left) and N1s (right) core level photoemission spectra of the ODA-GO-HEX-C$_{60}$Br$_{24}$ hybrid multilayer film.
A less intense peak (17.1%) arises from the C-O of GO and the C-Br bond of fullerene derivative and contains also contributions from C-N bonds of ODA molecules due to the chemical grafting of the amino groups of ODA with the epoxy groups of GO. The contribution at 287.2 eV is due to the C=O (carbonyl) as well C-O-C (epoxy) functional groups and accounts for 8.9 % of the total carbon intensity while the presence of carboxyl groups is demonstrated from the peak located at 288.6 eV (7.7%). The additional peaks at 290.0 eV and 291.5 eV in the ODA-GO-HEX-C\textsubscript{60}Br\textsubscript{24} spectrum are due to C1s shake up features of C\textsubscript{60}\textsuperscript{86,87} resulting from π–π* transitions excited in the photoemission process and therefore gives proof to the presence of fullerene derivatives in the hybrid multilayer.

In the Nitrogen 1s photoelectron spectrum of ODA-GO-HEX-C\textsubscript{60}Br\textsubscript{24} we identify three contributions like in the case of ODA-GO-C\textsubscript{60}(OH)\textsubscript{24}, one at 399.4 eV attributed to C-N-C bond of ODA and/or HEX molecules with the epoxy groups of graphene oxide, a second one at 400.8 eV corresponding to the primary amines that may interact with the GO surface by non-covalent bonding or physisorb to the graphene surface unreacted and a third one, which derives from the protonated amines of ODA-GO-HEX-C\textsubscript{60}Br\textsubscript{24} system. Furthermore we observe an increase of the NH\textsubscript{3}\textsuperscript{+} amines for ODA-GO-HEX-C\textsubscript{60}Br\textsubscript{24}, implying that a higher percentage of NH\textsubscript{3}\textsuperscript{+} amines interacts electrostatically with the graphene surface; this results in a lower C-N-C peak (32.9 % of the total N1s intensity) as compared to the C-N-C peak (38.3 % of the total N1s intensity) of the ODA-GO-C\textsubscript{60}(OH)\textsubscript{24} hybrid film.

Water contact angle (CA) measurements are presented in Table 4.1. The CA for the ODA-GO-C\textsubscript{60}(OH)\textsubscript{24} hybrid multilayer film results systematically higher than that of the ODA-GO-C\textsubscript{60}Br\textsubscript{24} hybrid multilayer film, with the first exhibiting CA=85° and the latter CA=55°, ca. 1 min after the droplet touches the surfaces. Both advancing and receding CA are higher for the ODA-GO-C\textsubscript{60}(OH)\textsubscript{24} system.

Despite the fact that C\textsubscript{60}(OH)\textsubscript{24} molecules are considered to be more hydrophilic than of C\textsubscript{60}Br\textsubscript{24} due to the -OH functional groups, our CA results revealed that the ODA-GO-C\textsubscript{60}(OH)\textsubscript{24} hybrid system exhibits a more hydrophobic character than ODA-GO-HEX-C\textsubscript{60}Br\textsubscript{24}. 
Table 4.1. Water contact angle measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>CA (t=0)</th>
<th>CA (t=1min)</th>
<th>Advancing CA</th>
<th>Receding CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODA-GO-HEX-C_{60}Br_{24} (30 layers)</td>
<td>59±1º</td>
<td>55±1º</td>
<td>64±1º</td>
<td>&lt;20±1º</td>
</tr>
<tr>
<td>ODA-GO-C_{60}(OH)_{24} (30 layers)</td>
<td>98±1º</td>
<td>85±1º</td>
<td>103±1º</td>
<td>40±1º</td>
</tr>
</tbody>
</table>

This difference can be attributed to the different synthesized nanostructures. Microscopy studies revealed that the distribution of the grafted C_{60}(OH)_{24} molecules on the graphene oxide layer is more dense and homogeneous comparing the ODA-GO-HEX-C_{60}Br_{24} hybrid multilayer, resulting in a different morphology. Moreover the hydrophilic behaviour of the ODA-GO-HEX-C_{60}Br_{24} film, compared to the more hydrophobic behaviour of the ODA-GO-C_{60}(OH)_{24} is corroborated by the XPS data discussed above. As was observed from Fig. 4.9 and Fig. 4.10 the contributions of the hydrophilic C(O)O (7.7% of the total C1s intensity) and NH_3^+ (24.8% of the total N1s intensity) groups for ODA-GO-HEX-C_{60}Br_{24}, are more dominant than the corresponding ones for ODA-GO-C_{60}(OH)_{24} (3.1% of the total C1s intensity and 19.5% of the total N1s intensity), while the contribution due to aliphatic/hydrophobic carbon bonds (C-C) is higher for ODA-GO-C_{60}(OH)_{24} (61.1% of the total C1s intensity) than for ODA-GO-HEX-C_{60}Br_{24} (57.4% of the total C1s intensity).

4.4 Conclusions

C_{60}(OH)_{24} and C_{60}Br_{24} fullerene derivatives were effectively inserted between graphene oxide layers through a layer-by-layer synthetic approach, which combines Langmuir-Schaefer deposition and self-assembly steps. The effectiveness of this method in terms of coverage, uniformity and single-layer level control of the assembly was confirmed by π-Α isotherms and AFM measurements. X-ray diffraction measurements revealed the successful insertion of C_{60}Br_{24} and C_{60}(OH)_{24} molecules.
between the graphene oxide nanosheets resulting in hybrid multilayer structures. The existence of $C_{60}(OH)_{24}$ and $C_{60}Br_{24}$ in the hybrid system was revealed by X-ray photoelectron spectroscopy, while Raman spectroscopy showed that the insertion of the fullerene derivatives between the graphene oxide nanosheets caused an increase of the $I_D/I_G$ ratio, confirming the covalent bonding of the amide functionality of ODA to GO. Corroborating the XPS results, contact angle measurements revealed that the hybrid film of graphene oxide and $C_{60}(OH)_{24}$ exhibits a more hydrophobic character, while the hybrid film of graphene oxide and $C_{60}Br_{24}$ is more hydrophilic, suggesting that the hydrophobicity doesn’t depend on the functional groups of the pristine nanomaterials but on the morphology of the hybrid systems. These novel fullerene-based hybrid films could be candidate nanomaterials for potential applications in photovoltaics, sensors, or optoelectronic devices as well as in photocatalysis and drug delivery.
Controlled deposition of fullerene derivatives within a graphene template by means of a modified Langmuir-Schaefer method

4.5 References

Controlled deposition of fullerene derivatives within a graphene template by means of a modified Langmuir-Schaefer method

Controlled deposition of fullerene derivatives within a graphene template by means of a modified Langmuir-Schaefer method
