Graphene Oxide Thin Films: Influence of Chemical Structure and Deposition Methodology

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Supporting Information

1. INTRODUCTION

Graphene has emerged as a new material with a bright future due to its unique properties that include high charge mobility, high thermal conductivity, transparency, and good mechanical properties. Due to these extraordinary properties, graphene has been suggested as a promising candidate for the manufacture of transparent conducting electrodes, transistors, and O₂−O₂ reductions. However, each application requires a different set of properties. Thus, graphene synthesized by physical methods such as chemical vapor deposition (CVD) or micromechanical exfoliation renders high-quality sheets suitable for electronic applications, while these materials cannot be used for the fabrication of inks or composites because they do not present functionalized groups.

In these cases, chemical graphene is preferred because it contains reactive oxygen functional groups that can attach small molecules, polymers, or nanoparticles to the graphitic surfaces for potential use in polymer composites, gas sensors, or photovoltaic applications.

Chemical graphene, also known as graphene oxide, GO, is usually synthesized by oxidation of graphite or carbon nanofibers by the method of Staudenmaier or Hummers and Offeman. The graphene oxide thus obtained is often reduced by chemical agents or thermal annealing to restore the graphene structure. However, GO reduced by chemical agents, also called reduced graphene oxide (RGO), retains some O-groups attached to the basal plane of GO.

Despite the great interest raised by graphene oxide, its chemical structure is still subject to debate. The variability of the starting material, even in the case of graphite, and the oxidation protocols seem to be the main cause for discrepancies. The best-known GO structure consists of two main regions constituted by hydrophobic π-conjugated Csp² and Csp³ domains. The latter are mainly constituted by alcohol and epoxy groups located at the basal plane and carboxylic acid groups at the edges.

Moreover, the chemical structure of GO has been revisited because it has been demonstrated that oxidation of carbon-based materials originated highly oxidized organic fragments, referred to as oxidative debris (OD). These fragments are strongly adsorbed on the graphitic sheets through π–π stacking interactions and can be removed by alkaline washing of GO. The purified material contains a lower amount of O-groups than nonpurified ones and presents a similar oxidation degree to that achieved by chemical reduction of GO. According to this information, the structure of purified graphene oxide is quite different from the nonpurified one. However, although the presence of OD represents a clear disadvantage when applications demand chemical purity of graphene materials, it can play an important role in anchoring nanoparticles or polymers to the GO sheets across the carboxylic or epoxy and hydroxyl groups.

Another important issue is related to the implementation of chemical graphene into devices, because it requires uniform and...
reproducible deposition techniques. Several techniques such as drop-casting \(^{29}\) or spin-coating \(^{30}\) often result in nonuniform films due to uncontrolled capillary flow and dewetting processes during solvent evaporation. These processes force the sheets to fold and wrinkle, \(^{11}\) losing the excellent properties of graphene. \(^{1}\) An alternative method is the Langmuir–Blodgett technique (LB), based on the transfer process of Langmuir films from the air–water interface onto solids by vertical dipping of the substrate in the Langmuir monolayer. \(^{32}\) The LB technique allows continuous variation of particle density, spacing, and arrangement by compressing or expanding the film by use of barriers. Consequently, it offers the possibility of preparing reproducible films with the control of interparticle distance necessary to exploit the nanocomposites in technological applications. Despite the fact that this methodology has been successfully used for transferring water-insoluble molecules \(^{32}–^{34}\) and nanoparticles, \(^{35}–^{39}\) it was less commonly employed to transfer graphene oxide onto solid substrates. However, some works reported results for LB films of GO synthesized from graphite \(^{30,31,40}–^{43}\) and from nanofibers. \(^{14}\) In most of these works, LB films were prepared with nonpurified graphene oxide; however, in the case of graphene oxide obtained from nanofibers, LB films of purified and nonpurified graphene oxides were prepared. \(^{14}\) The results proved that the purified graphene oxide presented less adsorption on the solid substrate (SiO\(_2\)) than the nonpurified one. \(^{14}\) This behavior was attributed to elimination of an elevated number of carboxylic acids attached to the organic fragments (OD).

However, more efforts must be carried out to understand the role of chemical composition on the properties of graphene oxide films since this information is critical to develop new materials that may be used in technological applications. With this objective in mind, we focus our attention on analyzing the effect of the chemical structure of graphene on the properties of films deposited on SiO\(_2\) substrate. To synthesize graphene oxide of different chemical compositions, two starting materials, graphite and GANF nanofibers, were used. The oxidation procedure was previously reported by our group and consists of a slight modification of the Hummers method, \(^{14,19}\) combined with alkaline washing. Graphene oxide materials were characterized by X-ray photoelectron spectroscopy (XPS), \(\zeta\) potential measurements, and dynamic light scattering (DLS). All these techniques make it possible to determine the chemical composition, surface electric charge and size of the different materials. After characterization, graphene oxides were deposited at the air–water interface and subsequently transferred from the air–water interface onto the substrate by two deposition methodologies, vertical dipping (LB) and horizontal dipping, also known as Langmuir–Schaefele methodology (LS). The LS method has successfully been employed to obtain surfactants, polyelectrolytes, and nanoparticles films, \(^{44}–^{47}\) but to the best of our knowledge, it has not yet been used to build graphene oxide films. We choose these two deposition methodologies because the contact between the substrate and GO materials takes place across different groups for the two techniques; therefore we expect that this fact shall provide an excellent way to analyze the influence of chemical composition on the properties of graphene oxide thin films.

2. MATERIALS AND METHODS

2.1. Materials. NaNO\(_3\) (99%), H\(_2\)SO\(_4\) (98% w/w), K\(_2\)MnO\(_4\) (>99%), H\(_2\)O\(_2\) (30% w/w), NaOH, and HCl (35%) were provided by Sigma–Aldrich and used without further purification. Millipore ultrapure water was obtained by a combination of ROIs and Milli-Q systems from Millipore and was used to prepare solutions, reaction media, and the subphase of the Langmuir trough. The solid substrate is As-doped silicon wafers (100) with 300 nm of dry thermal SiO\(_2\) thin film, and it was supplied by CENER (Spain). Acid subphase pH was adjusted by addition of HCl (Sigma–Aldrich) and of sodium hydroxide solutions (1 N) Normex from Carlo Erba.

Graphite flakes (99.02 fixed C) were from Qingdao Super Graphite Co., Ltd., and the commercial GANF nanofibers have been supplied by GRAnPH Nanotech (Grupo Antolina Ingeniería). GANF consists of a stacked cup of carbon nanofibers composed of graphic sheets of approximately five graphene layers, rolled along the fiber axis to develop a continuous spiral. The material presents a low number of stacked graphene layers in its structure and constitutes an excellent starting material to obtain a few layers of graphene oxide.

2.2. Synthesis of Graphene Oxide. Graphite oxide (GO) was synthesized by a modified Hummers method developed by our group. \(^{19}\) Using this method, highly oxidized GO nanodevices of a few layers are obtained. Synthesis of graphene oxide from GANF nanofibers was reported in a previous work. \(^{14}\) The purification procedure used in the current work was reported by Roukke et al. \(^{24}\) to purify graphite oxide and was previously used by our group to purify graphene oxide obtained by oxidation of GANF. \(^{14}\) Briefly, graphene oxide is dispersed in water (0.1 mg mL\(^{-1}\)) and sonicated in an ultrasonic bath for 10 min. A 1 M solution of NaOH is added dropwise until the solution becomes turbid. Then the solution is kept at reflux for 1 h. In a typical experiment, 50 mL of graphene oxide solution requires around 1 mL of NaOH solution to observe the color change from brown to black. Purified graphene oxide solutions were neutralized at reflux with HCl (1 M) for at least 1 h. The solution thus obtained was centrifuged (5 min) at 1900g and the supernatant was discarded, while black aggregates were dispersed in water. The washing procedure was repeated at least 10 times.

2.3. Experimental Methods. Pressure–area isotherms of graphene oxide materials were recorded on the Langmuir mini-trough (KSV, Finland) placed on an antivibration table. A KSV2000 system 2 was used for LB and LS deposition. Holder model KN 0006 from KSV was used for LS deposition. Surface pressure was measured with a Pt–Wilhelmy plate connected to an electrobalance. Subphase temperature was maintained at 20.0 ± 0.1 °C by flowing thermostatted water through jackets at the bottom of the trough. The temperature close to the surface was measured with a calibrated sensor from KSV, while the water temperature was controlled by means of a thermostat/cryostat, Lauda Ecoline RE-106.

The spreading solution was prepared with water/methanol mixtures (1:5 v/v) as solvent, because it was demonstrated to be a good spreading solvent for graphene oxide. \(^{40}\) We use two different spreading solutions for GO synthesized from graphite (0.18 mg mL\(^{-1}\)) and from GANF (0.5 mg mL\(^{-1}\)). Graphene oxide materials were dispersed by sonication for 30 min and then deposited onto the slightly acid water subphase with a micrometer Hamilton syringe. The pH of the aqueous subphase ranges from 2 to 3. We selected these pH values because when materials with acid groups are spread on an alkaline subphase the functional groups are ionized, exhibiting greatly enhanced solubility in water as compared with the corresponding uncharged monolayers. \(^{48}\) In this pH range, GO materials are in nonionic form (\(pK_a \approx 4\)) and consequently are irreversibly pinned to the interface. \(^{49,50}\) Monolayer stability was checked by the procedure previously reported. \(^{14}\) Briefly, after deposition of spreading solution at the aqueous interface, the isotherm was recorded until it reached a given surface pressure value; then the barriers stopped and the surface pressure was recorded for at least 10 min. Results showed that the surface pressure remained constant with time, proving the stability of these monolayers. \(^{52}\) On the other hand, surface pressure isotherms in the pH range studied are averaged from at least three curves.

Nanoplatelets were transferred from the air–water interface onto silicon wafers by symmetric barrier compression (20 mm/min) with the substrate into the trough by vertical (LB) and horizontal (LS) dipping at 2 mm/min.
X-ray photoelectron spectra of powder samples were measured in a VG Escalab 200R spectrometer (Fisons Instruments) equipped with an excitation source of Mg Kα (hν = 1253.6 eV) radiation and a hemispherical electron analyzer. High-resolution spectra were recorded at 20 eV analyzer pass energy. The residual pressure in the analysis chamber was maintained under 4 × 10⁻⁷ Pa during data acquisition.

ζ Potential and dynamic light scattering measurements were carried out on a Zetasizer Nano ZS device (Malvern, U.K.). The concentration of graphene oxide dispersions was 0.12 mg·mL⁻¹. For ζ potential experiments, the electrophoretic mobility was measured at 20.0 °C in the DTS 1060C disposable cell and converted into ζ potential via the Smoluchowski relationship. DLS experiments were performed at 20.0 °C and the intensity autocorrelation function was obtained at 13° and transformed into electric field autocorrelation functions according to the Siegert relationship.

SEM images were taken with a Carl Zeiss Evo HD microscope with an accelerating voltage of 5 kV.

3. RESULTS AND DISCUSSION

3.1. Characterization of Graphene Oxide. Prior to film preparation, it is necessary to characterize the graphene oxide materials by XPS spectroscopy. Figure 1 presents two illustrative examples of the C₁s core-level spectra for purified (PGO) and nonpurified (GO) graphene oxide obtained by oxidation of graphite.

In both samples, the C₁s core-level spectrum is an asymmetric band that can be fitted by three components centered at 284.8, 286.4, and 287.9 eV, where the first two are more intense than the third one. These peaks are assigned to C=C bonds of the aromatic carbon bonds (284.8 eV), to C–O bonds of alcohol or epoxy groups (286.4 eV), and to COO⁻ groups (287.9 eV). From the areas of these peaks, the atomic percentages of the different groups were determined. Table 1 collects band position, percentage of different species, and C/O and Csp²/Csp³ ratios. For comparative purposes, the values corresponding to nanofiber graphene oxide (NGO) and purified nanofiber graphene oxide (PNGO) are also presented in Table 1. These values were taken from our previous work.

Results in Table 1 show significant differences between the chemical composition of graphene oxide obtained by oxidation of graphite or GANF nanofibers. Thus, although the percentage of Csp² is quite similar for nonpurified materials GO and NGO, the percentage of COOH groups attached to NGO is twice that for GO. Conversely, the percentage of hydroxyl or epoxy groups localized at the basal plane is higher for GO than for NGO. We have observed this behavior in a previous work, in which it was hypothesized that it could be related to differences between the size of nanoplatelets obtained from graphite and GANF. This is because the carboxylic groups are mainly localized at the edge of sheets, while the hydroxyl or epoxy groups are attached to the basal plane; consequently, one expects that the smallest sheets, such as those provided by oxidation of GANF nanofibers, rendered the highest number of carboxylic groups at the edges. To confirm this assumption, we estimate the size of nanoplatelets by dynamic light scattering (DLS; see below).

As far as the influence of the purification process on chemical functionalization of graphene oxide is concerned, our results confirm that alkaline washing increases the Csp²/Csp³ ratio. It is also interesting to point out that the Csp²/Csp³ value is the same for the two purified materials. Another interesting result was that the percentage of alcohol or epoxy groups becomes similar for the two purified materials, although it differs for the nonpurified materials. To interpret this behavior, it is necessary to take into account theoretical and spectroscopic results regarding the removal of the oxygenated groups from GO nanoplatelets at low temperatures, 350–400 K. According to those results, the surface density of epoxy groups seems to be critical for the selective elimination of O-groups. Thus, high coverage of epoxy groups creates precursors for the release of CO/CO₂ mixtures from the epoxy groups, while low surface density of epoxy groups favors the elimination of O atoms from other O-groups. Our results confirm theoretical predictions since GO contains a higher percentage of epoxy groups than NGO, and consequently it loses a higher number of epoxy groups than NGO during alkaline washing at 373 K.

<table>
<thead>
<tr>
<th>bond</th>
<th>max binding energy (eV)</th>
<th>composition (%)</th>
<th>C/O</th>
<th>Csp²/Csp³</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>284.8</td>
<td>51 ± 3</td>
<td>1.6</td>
<td>1.04</td>
</tr>
<tr>
<td>C–O</td>
<td>286.4</td>
<td>42 ± 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COO⁻</td>
<td>287.9</td>
<td>7 ± 0.4</td>
<td></td>
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</tr>
</tbody>
</table>

PGO

| C=C  | 284.8                  | 72 ± 4          | 4.3 | 2.6       |
| C–O  | 286.4                  | 20 ± 1          |     |           |
| COO⁻ | 288.2                  | 8.0 ± 0.4       |     |           |

NGO

| C=C  | 284.8                  | 60 ± 3          | 1.6 | 1.5       |
| C–O  | 286.4                  | 26 ± 1          |     |           |
| COO⁻ | 287.9                  | 14.0 ± 0.7      |     |           |

PNGO

Calculated from XPS. Data taken from ref 15.
Our results demonstrated that the chemical composition of GO sheets can be tuned by a combination of starting material and purification procedure. Accordingly, in order to analyze the influence of chemical functionalization of GO on the properties of films, the next step will be to transfer the materials from the air–water interface to the solid substrate by LB and LS methods. However, since solid coverage and sheet wrinkles can be influenced by nanoplatelet size\(^{22}\) and electric charge,\(^{53}\) \(\zeta\) potential and nanoplatelet size were previously determined. In a previous work,\(^{14}\) \(\zeta\) potential values of NGO and PNGO aqueous solutions were determined and they showed a bimodal distribution for NGO, centered at \(-34\) and \(-50\) mV, and a broad distribution centered at \(-20\) mV for PNGO. In the current work, the \(\zeta\) potential values obtained for GO and PGO, shown in Figure 1c, present a similar trend: a bimodal distribution centered at \(-34\) and \(-65\) mV for the nonpurified sample, GO, and a broad distribution centered at \(-34\) mV for PGO, although the electric charge of graphene oxide synthesized from graphite is higher than that of sheets obtained from GANF. The \(\zeta\) potential values of our graphene oxides are similar to those found by other authors.\(^{14}\) Comparison between the \(\zeta\) potential values of purified and nonpurified sheets allows us to conclude that the electric charge is higher for the nonpurified materials than for the purified ones. This fact is consistent with the elimination of highly oxidative debris reported from XPS measurements.

We use dynamic light scattering measurements to obtain information about the effect of purification procedure on nanoplatelet size. It is necessary to consider that, in order to calculate the hydrodynamic radius by DLS, our equipment uses the Stokes model, which considers a spherical geometry the graphene sheets lack; therefore, our results are just a raw estimation that acceptably agrees with the size values estimated from the SEM images (see below). All the DLS experiments present nonexponential correlation functions that when analyzed by use of regularized inverse Laplace transforms, (ILT) CONTIN, yield complex distribution functions; see more details in Figure S1 of Supporting Information. The distribution functions on the apparent hydrodynamic diameter scale, \(d_h\),\(^{99}\), presented as insets in Figure S1, are asymmetric and very broad; this is indicative of populations of different size. On the other hand, the maximum position of the distribution functions is different for each material. Thus, nanoplatelets of graphene oxide synthesized by oxidation of graphite (GO and PGO) are bigger than those obtained from GANF (NGO and PNGO). This result confirms our previous assumption.\(^{14}\) Moreover, sheets of purified graphene oxide are smaller than those of nonpurified ones. This fact has been reported for graphene oxide obtained from graphite and was attributed to breaking of the sheets due to the sonication procedure used to disperse purified materials.\(^{22}\) However, in our case the same sonication methodology was applied for all samples, and consequently we expect that breaking cannot be the main reason for this difference in our graphene oxides, although it is possible that the sonication process did not affect purified and nonpurified sheets in a similar way. An alternative explanation is to consider that the washing procedure eliminates the OD adsorbed on the basal plane of the graphene oxide sheets, decreasing the apparent size of nanoplatelets determined by DLS. We think that a combination of all these factors could interpret the observed behavior.

For comparison purposes, we have calculated the size of graphene oxide sheets from SEM images of films transferred onto the solid using ImageJ 1.46 software. Details of calculations are presented in Supporting Information. Comparison between frequency analysis of sheets and DLS curves (Figure S3 of Supporting Information) shows good correspondence between the sizes obtained by the two methodologies, DLS and SEM. This gives strong support to the values of nanoparticle size determined by DLS measurements.

3.2. Graphene Oxide Thin Films. Our results show that the oxidation and purification procedures reported in this work provide graphene oxide of different chemical composition and nanoplatelets of different size and electric charge; therefore, the next step was to study the effect of these factors on the morphology of graphene oxide films.

To study the effect of chemical structure of GO on Langmuir monolayers, surface pressure–area isotherms were recorded (Figure 2a). In this work we have recorded only the isotherms of graphene oxide obtained by oxidation of graphite, because the isotherms of NGO and PNGO were reported in a previous paper.\(^{14}\) We determine the compressional elastic modulus, \(K\), to obtain information about the surface state of materials at the air–water interface. The compressional elastic modulus was calculated from surface-pressure isotherms and eq 1, and the values are plotted against surface pressure in Figure 2b.

\[
K = -A \left[ \frac{\partial \pi}{\partial A} \right]_{\Pi, \theta}
\]

Surface pressure and compressional elastic modulus isotherms present similar morphology to that obtained for NGO and PNGO.\(^{14}\) Therefore, we interpret the isotherms of GO and PGO in a similar way. Accordingly, monolayers of surface pressure value close to 0 were assigned to surface states in which the nanoplatelets are isolated in a two-dimensional gas state. When the surface area is further decreased, the nanoplatelets are pushed closer to each other, resulting in small domains that grow until the maximum of compressional elastic modulus is reached. This two-dimensional region is commonly assigned to the liquid expanded (LE) state.\(^{50}\) Beyond the compressional elastic modulus maximum, the nanoplatelets form wrinkles, overlaps, and 3D structures.\(^{50,55}\)
Comparison between compressional elastic modulus isothersms of purified and nonpurified materials shows that $K$ values are higher for PGO than for GO monolayers (Figure 2b). Similar behavior was observed for NGO and PNGO monolayers. Some authors related this behavior to the increase of electrostatic repulsions between COO$^-$ groups attached to the graphene oxide nanoplatelets; however, this is not our situation, since we deposited the graphene oxide sheets on an acidic subphase, pH 2–3, in which the carboxylic groups were in the nonionized form, COOH. Therefore, in order to analyze the origin of these interactions, we used the Volmer model adapted for nanoparticle monolayers to interpret the surface pressure isothersms of NGO and PNGO, respectively. This model was proposed to interpret the isothersms of monolayers within the two-dimensional LE state. Therefore, we have selected results corresponding to this state, from 0.6 to 21 mN·m$^{-1}$ for GO and from 1.8 to 27 mN·m$^{-1}$ for PGO. Briefly, the model describes the interface as a mixture of different components in which the cohesion pressure, $\Pi_{coh}$, is the parameter related to different interactions between water molecules in the aqueous subphase, between water and nanoplatelets, and between nanoplatelets. The model relates surface pressure to minimum area occupied by nanoplatelets in the LE state ($\omega$) to area occupied by water molecules in this state ($\omega_0$), and to cohesion pressure ($\Pi_{coh}$) through the following equation:

$$\Pi = \frac{kT(\omega/A)}{\omega_0(1 - (\omega/A))} - \Pi_{coh}$$

(2)

The values calculated from eq 2, using the best-fit parameters collected in Table 2, are plotted as lines in the insets of Figure 2c, the cohesion pressure values, $\Pi_{coh}$, against the percentage of COOH groups obtained by XPS measurements. As can be seen in Figure 2c, the cohesion pressure linearly increases with the percentage of COOH groups. This behavior points to attractive interactions between carboxylic acids as the main contribution of the surface cohesion pressure parameter. In an attempt to confirm this fact, we have analyzed the effect of oxygen functionalities on the surface cohesion pressure parameter by modifying the pH of the water subphase. Recent results reported three pK values for graphene oxide: 4.3, 6.6, and 9.8. These pK values were assigned to carboxylic groups in close proximity to a hydroxyl group (4.3), to the remaining carboxylic groups (6.6), and to phenolic groups ionized to give phenolate anions, (9.8). According to these pK values, the pH range selected in this work was 2–14; however, monolayers adsorbed on alkaline subphases (pH ≥ 9) present high solubility in the subphase, and consequently their isothersms are not reproducible. Therefore, we present results corresponding to stable monolayers, pH ≤ 9. On the other hand, to minimize GO dissolution in the aqueous subphase, we have chosen graphene oxide synthesized from graphite because it renders the most stable Langmuir monolayer. This is because it presents the most accurate charge/size ratio to remain pinned at the interface.

Isothersms of GO adsorbed on water subphases of different pH are presented in Figure S4 of Supporting Information. The LE region of isothersms was fitted to the Volmer model, eq 2, and the best-fit parameters are collected in Table S1 of Supporting Information. The surface cohesion pressure parameter, $\Pi_{coh}$, is plotted against pH in Figure 2d. Results clearly show that $\Pi_{coh}$ decreases when the pH of the aqueous surface increases. According to pK values of the carboxylic groups, 4.3 and 6.6, respectively, when the pH increases, the carboxylic group percentage decreases, decreasing the hydrogen bonds between graphene oxide sheets, and as a consequence the $\Pi_{coh}$ value also decreases. On the other hand, when the pH value increases, the carboxylate anions also increase, providing electric negative charge to sheets. In this situation, repulsions between sheets can also contribute to the decrease of the $\Pi_{coh}$ value. All results allow us to demonstrate that hydrogen bonds between carboxylic groups at the edges of sheets are one of the most important contributions of the surface cohesion pressure parameter, $\Pi_{coh}$.

We have demonstrated the important role of the carboxylic group in assembly of Langmuir monolayers of graphene oxides. Therefore, the next step is to study the role of O-functional groups in the morphology and coverage of films prepared by Langmuir–Blodgett and Langmuir–Schaefer methodologies. We expect that differences between these two deposition methodologies will make it possible to understand the role of the chemical composition of graphene oxide on structure and coverage of graphene oxide thin films. We have transferred graphene oxide monolayers at the liquid expanded state because they provide films of interconnected sheets without wrinkles, overlaps, and 3D structures, which are responsible for the low quality of films. Accordingly, we transfer Langmuir monolayers at the surface pressure value of 5 mN·m$^{-1}$. Figure 3 collects SEM images of LB films of different graphene oxide sheets. Magnification of some regions is presented as insets in these figures. The SEM images show some differences between films. Thus, simple visual inspection of images seems to indicate that solid coverage increases for nonpurified films. On the other hand, the nanoplatelets of nonpurified materials are bigger than

| Table 2. Parameters Obtained from Fit of Experimental Isothersms to Equation 2$^a$
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<tbody>
<tr>
<td>sample</td>
<td>$\omega$ (cm$^2$)</td>
<td>$\omega_0$ (nm$^2$)</td>
</tr>
<tr>
<td>GO</td>
<td>13.6 ± 0.1</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td>PGO</td>
<td>14.2 ± 0.1</td>
<td>0.10 ± 0.01</td>
</tr>
<tr>
<td>NGO$^b$</td>
<td>57 ± 3</td>
<td>0.13 ± 0.01</td>
</tr>
<tr>
<td>PNGO$^b$</td>
<td>53.0 ± 0.2</td>
<td>0.23 ± 0.01</td>
</tr>
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$^a$See text for details. $^b$Data from ref 15.
those of purified ones, and nanoplatelets corresponding to graphene oxide synthesized by oxidation of GANF are the smallest ones. These facts are consistent with DLS measurements.

Figure 4 shows SEM images of graphene oxide films obtained by Langmuir−Schaefer methodology. As can be seen, the film morphology presents similar trends to LB films, although the highest coverage seems to be reached by means of the Langmuir−Blodgett method.

In an attempt to quantify these differences, we have calculated the solid coverage from SEM images by using ImageJ 1.46 software. Details of calculations and some illustrative images are presented in Supporting Information. The solid coverage values thus calculated were plotted against the percentage of Csp² obtained from XPS in Figure 5a. Error bars represent the standard deviation determined from at least 10 images.

Results in Figure 5 show that LB films present higher coverage than LS ones. Moreover, the solid coverage reached by LB methodology is almost independent of the percentage of aromatic carbon, while it decreases as the Csp² percentage increases for films prepared by the LS technique. In an attempt to interpret this behavior, we analyze the influence of the O-groups attached to graphene oxide sheets on solid coverage. Therefore, we plot the solid coverage against the percentage of C−O groups determined by XPS in Figure 5b. We choose these groups because they can be responsible for interactions between SiO₂ of the solid substrate and nanoplatelets. It is necessary to consider that some authors prefer to use the optical contrast of graphene oxide normalized to the optical...
Figure 5. Variation of solid coverage of films, built by (●) LB and (▲) LS methods, with (a) percentage of aromatic carbon Csp² and (b) percentage of epoxy or hydroxyl groups, C−O.

The contrast of pristine graphene as an indicator of the relative surface density of C−O groups. 60 This choice is the most correct one. However, the percentage of C−O groups determined by XPS also can be used, considering that such percentage is directly correlated to the optical contrast. 60 This determination by XPS also can be used, considering that such percentage is directly correlated to the optical contrast. 60 This latter choice is, in this case, more suitable because of the lower uncertainty that XPS measurements exhibit.

Data in Figure 5b show that the solid coverage of LB films weakly increases when the percentage of C−O groups attached to sheets increases; however, it increases with the percentage of C−O groups for films prepared by LS methodology. This behavior can be understood by considering the different orientation of the substrate relative to the monolayer in the two deposition techniques. In the case of LS deposition, the solid substrate is horizontally dipped in the air–water interface and the contact between solid substrate and nanoplatelets is mainly across the epoxy and hydroxyl groups attached to graphene oxide sheets 57 and the silanol groups. Consequently, when the percentage of C−O groups increases, attractive interactions between substrate and graphene oxide also increase, favoring the adsorption of sheets. In contrast, when deposition is carried out by LB methodology, the solid is vertically dipped in the interface, and the contact between silanol groups of the solid and graphene oxide sheets is across all the O-groups of graphene oxides; consequently, the solid coverage presents less dependence on C−O groups. The diagram in Figure 6 illustrates this explanation.

4. CONCLUSIONS

Results in this work demonstrated that it is possible to tune the chemical composition of graphene oxide sheets by combining the chemical oxidation of two different starting materials, graphite or GANF nanofibers, with purification by alkaline washing. Our results demonstrated that the influence of starting material on the chemical composition of graphene oxides is greater for nonpurified materials than for purified ones. We also proved that graphene oxide sheets obtained from graphite are bigger and present higher surface electric charge than those synthesized from GANF nanofibers. The surface pressure isotherms were interpreted according to the Volmer model, and the parameters obtained from the fit of experimental isotherms to the model point to the existence of attractive interactions between the carboxylic acids of nanoplatelets. 57 The solid coverage of graphene oxide depends on the chemical composition of graphene oxide and on the deposition methodology employed to build the film. Our results demonstrate that the LB methodology renders the highest solid coverage and does not present significant dependence on chemical structure. On the contrary, the solid coverage found for films prepared by the LS methodology increases when the amount of C−O groups attached to the basal plane of sheets increases. In summary, our results proved that it is possible to modulate the coverage of graphene oxide films by modifying the chemical composition of graphene oxide sheets and the deposition methodology. This strategy could be presented as an easy way to obtain reproducible graphene oxide films of different morphology and coverage.

ASSOCIATED CONTENT

Supporting Information
Additional text describing nanoplatelet size determination from DLS measurements and SEM images, isotherms of graphene oxide at different pH subphases, and determination of solid coverage from SEM images; eight figures showing time ACFs and relaxation time distribution peaks obtained by DLS, SEM image of GO nanoplatelets, size frequency analysis of different samples obtained from SEM images, surface pressure isotherms for GO at different pH values, and determination of solid coverage from SEM images; one table listing parameters obtained from fitting experimental isotherms to eq 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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