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Reduced graphene oxide multilayers for gas and liquid phases chemical sensing

Marcos A. Gross, Maria J. A. Sales, Maria A. G. Soler, Marcelo A. Pereira-da-Silva, Mauro F. P. da Silva and Leonardo G. Paterno

Graphene oxide (GO) multilayers were produced by the layer-by-layer technique after successive immersions of quartz slides into aqueous suspensions of cationic poly(diallyldimethyl ammonium chloride) (PDAC) and anionic GO. The adsorbed amount of GO within the multilayers measured ex situ by UV-vis spectroscopy was found to increase linearly with the number of PDAC–GO bilayers. UV-vis and Raman spectra confirmed the conversion of GO to its reduced form, namely reduced graphene oxide (RGO), when the multilayers were subjected to hot hydrazine. According to AFM images, multilayers are flat with GO sheets forming edge structures. Additionally, impedance spectroscopy provided information regarding the multilayer growth mechanism, which starts with isolated GO sheets that bridge each other after deposition of five PDAC–GO bilayers. As a proof of principle, it was demonstrated that a sensor array composed by reduced multilayers deposited onto interdigitated microelectrodes and interrogated by impedance spectroscopy is capable of discriminating vapours of volatile solvents, including toluene, gasoline, ethanol, chloroform, and acetone, as well as chemicals in aqueous solutions, such as hydrochloric acid, sodium chloride, ammonium hydroxide, and sucrose. This capability was made possible only because the LbL assembly permitted one to tune the sensors’ sensitivity with the number of PDAC–GO bilayers. The results presented herein suggest that the reduced PDAC–GO multilayers are promising elements for non-specific chemical sensors.

Introduction

Graphene, a 2-D crystalline material formed by a single-layer of hexagonal arranged sp² carbons, has been long called attention for its outstanding properties including semiconductor behavior with zero band gap, high charge carrier mobilities in a near ballistic regime, high thermal conductivity and elastic modulus, and almost complete transparency to the visible light. All these features together make graphene a very attractive material for the new era of optoelectronic devices and chemical sensors. In the field of chemical sensors, graphene films may play a myriad of roles, spanning from direct transduction in conductometric gas sensors, to anchoring platform for catalyst nanoparticles and biomolecular recognition elements. The high electron transfer rate and high carrier mobility of graphene networks greatly favor the communication between analyte and the electrode’s surface, and, consequently, enhance sensitivity and shorten the response time of the chemical sensor system. However, the full exploitation of graphene properties in technological applications is still hampered by the low scalability of mechanical exfoliation and vacuum assisted production methods.

Alternatively, graphene-oxide (GO), a chemically derived of graphene, has partially overcome these drawbacks and is probably the most affordable source of graphene-based materials. GO is obtained by the chemical oxidation of graphite followed by exfoliation in water or polar organic solvents. The as-obtained GO sheets bear a significant amount of oxygen functionalities, such as hydroxyl, carboxyl, and epoxy that disrupt the pi-conjugated system of parent graphene and turn GO into an electrical insulating material. On the other hand, these same groups enable the preparation of very stable colloidal suspensions and also serve as sites for chemical derivatization and/or integration with several polymeric and inorganic matrices. Moreover, GO can be properly converted into a conducting form, namely reduced graphene oxide (RGO), whose optoelectronic properties closely resemble those exhibited by parent graphene. In aqueous alkaline suspensions, GO behaves as an anionic species due to deprotonation of its carboxyl groups. Therefore, GO is readily assembled with common cationic polyelectrolytes into ultrathin films via the electrostatic layer-by-layer (LbL) assembly technique. The LbL technique is a wet film...
deposition method based on the successive transfer of molecular layers to a solid substrate that is alternated dipped into cationic and anionic solutions. One of the main features of the LbL technique is that it allows one to control the film thickness at the molecular/nanometer level by setting-up the number of deposition cycles and the physicochemical conditions of the deposition solutions, such as concentration, pH, and ionic strength. Also, the method is quite inexpensive since it does not demand for sophisticated glassware or clean rooms, and films can be deposited onto any type of solid substrate.

The LbL technique has been employed to produce GO films for different application purposes including, but not limited to, transparent conducting films, field effect transistors, lithium ion batteries, supercapacitors, solar cells, sensors, and polymer nanocomposites. As already mentioned, graphene and GO films can be used in chemical sensors to exert different tasks. In the present contribution, we describe for the first time the use of poly(diallyldimethylammonium chloride) and graphene oxide or else PDAC–GO multilayers assembled under the LbL technique as sensing units of electronic nose and tongue systems. These systems are comprised by an array of non-specific sensing units whose electrical signals, as caused by the interaction with analytes, are decoded by a pattern recognition method, usually a multivariate data analysis tool. The LbL assembly permitted us to tune the sensing units’ sensitivity by varying the number of PDAC–GO layers and thus to provide unique electrical fingerprints for different types of chemicals in either liquid or gas phases. In order to harness the electrical features of GO alone, we propose the use of the electrical isolating PDAC. Also, PDAC is quite stable against the hydrazine treatment, which is used to convert GO into RGO. Firstly, the structure, morphology and electrical properties of GO-based LbL films were assessed by UV-vis and Raman spectroscopy, atomic force microscopy and impedance spectroscopy. Later, as a proof of principle, the sensors were exposed to vapours of volatile solvents (chloroform, acetone, toluene, ethanol, and gasoline) and aqueous solutions containing sodium chloride, ammonia, hydrochloric acid, and sucrose. After impedance measurements and principal component analysis we could confirm that the present GO-based sensor array is capable of detecting and discriminating different analytes in either liquid or gas phases.

**Experimental**

**Materials**

The cationic polyelectrolyte, poly(diallyldimethylammonium chloride) (PDAC, \(M_w = 450,000 \text{ g mol}^{-1}\)) and all other chemicals, unless stated, were purchased from Sigma-Aldrich (MO, USA) and used without any additional purification step. Ultrapure water (18.2 MΩ cm) purified by a Milli-Pore Milli-Q system was used throughout all procedures. Graphene oxide (GO) was obtained by oxidative chemical exfoliation of graphite powder (Ciba Geigy) in a mixture of 1 : 2 : \(H_2SO_4\)-HNO_3 (2 : 1 v/v) and KClO_3 as originally described by Staudenmaier with some modification as described elsewhere. The as-obtained graphic oxide was suspended in \(NH_4OH\) aqueous solution (pH 10) under sonication (150 W, 1 h). The resulting GO suspension was centrifuged at 15 000 rpm for 20 min to remove remaining solids and stored for film depositions. Quartz and optical glass slides (10 × 25 × 1 mm\(^2\)) used as substrates for multilayer depositions were previously cleaned in “piranha” solution followed by RCA solution (\(H_2O-H_2O_2-NH_4OH\), 5 : 1 v/v).

**Multilayers deposition**

The deposition of multilayers was performed at room temperature (~25 °C) following a LbL procedure according to the following steps: (i) immersion of the glass substrate into the cationic solution (PDAC, 1 g L\(^{-1}\), pH 10) for 3 min; (ii) immersion of the substrate–PDAC into a stirring bath of deionized water for 20 s; (iii) drying of the substrate–PDAC with air flow; (iv) immersion of the substrate–PDAC into the anionic GO suspension (0.2 g L\(^{-1}\), pH 10) for 3 min; (v) immersion of the substrate–PDAC–GO into a stirring bath of deionized water for 20 s; (vi) drying of the substrate–PDAC–GO with air flow. The steps (i) to (vi) produce a single PDAC–GO bilayer film and were cyclically repeated up to 20 bilayers. Henceforward, the multilayers will be represented as (PDAC–GO)\(n\), where \(n\) stands for the number of bilayers. After depositions, films were immersed for 5 min in hot (~50 °C) aqueous hydrazine (25%) to reduce oxygen functionalities.

**Structure, morphology, and chemical sensing properties of multilayers**

Structural and morphological characterizations were carried out by UV-vis (Varian Cary 5000) and Raman (Jobin Yvon model T64000, 514 nm laser line) spectroscopies, and tapping mode AFM (dimension ICON with Nanoscope V controller, Bruker, Santa Barbara, CA, USA, Software Nanoscope 8.15.R3). Impedance spectroscopy was performed with an impedance analyzer (Agilent Precision LCR Meter 4284A) in the frequency range of 20 Hz to 1 MHz, with an excitation voltage of 50 mV. Multilayers with \(n = 1, 2, 3, 4, 5, 10, 20\) were deposited onto gold interdigitated microelectrodes of the same type as described elsewhere, and were then labeled as sensing units S1, S2, and so on. The sensing performance was tested in both liquid and gas phases using an experimental setup described elsewhere. For the liquid phase testing, the sensing units were immersed into 60 mL of individual, aqueous solutions (20 mmol L\(^{-1}\)) of sodium chloride, ammonium hydroxide, hydrochloric acid, and sucrose. The conditioning step was set in 5 min before impedance measurements were taken. For the gas phase testing, the sensing units were exposed to the headspace gas phase generated by 20 mL of chloroform, acetone, toluene, ethanol, and gasoline contained in a rubber capped glass vessel (150 mL). The conditioning step was set in 10 min before impedance measurements were taken. In both cases, the temperature of the measurement cell was kept controlled by a heating/cooling bath at 25.0 ± 0.5 °C. Impedance data were further processed by principal component analysis (PCA) using a homemade algorithm implemented in MatLab with the Statistical Toolbox. In the present experiment, a data matrix was generated by setting columns for each sensing unit (PDAC–RGO films with different
numbers of bilayers) and rows for the electrical responses (R or C) for the different analyzed samples. The PCA method uses orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components. The starting data matrix is reduced to a smaller matrix (Z), which is obtained through the variance and covariance matrix (S). Based on S one can calculate the autovalues (λ) and the autovectors matrix (U). λ represents the variance of each principal component (PC) and is expressed in percentage (the greater the value the greater the importance of that PC). The scalar product of autovectors indicates the angle that the new coordinate system (PC) establishes with the latter one. Lastly, with the product of the initial data matrix by U one obtains Z. The result of a PCA is a plot (2- and/or 3-D) where the axes represent the PC’s and data are the component scores, the transformed variable values corresponding to a particular data point. Each data point has an associated loading, which corresponds to the weight by which each standardized original variable should be multiplied to get the component score. PCA plots were generated by measurements performed in triplicates.

Results and discussion

The main feature of the LbL technique is its precise control of film thickness, which scales linearly with the number of deposited bilayers (n). This control is made possible because in the electrostatic driven LbL assembly the adsorption process is self-regulated. Initially, substrate’s surface charges are gradually compensated by the upcoming adsorbate species, and then, finally reversed (or overcompensated). When the net substrate’s surface charge is reversed, it begins to repelling adsorbate species from the surrounding solution and the adsorption ends at its own. In order to deposit more layers, the next adsorbing material must exhibit a signal charge opposite to the previous one and the adsorption process takes place in the same way as before. In a preliminary experiment, we have determined the time for “charge reversion” in the PDAC–GO system, which corresponds to the adsorption equilibrium condition. We have concluded that three minutes of immersion of substrates into either PDAC or GO solutions were sufficient for reaching this condition.

Fig. 1a displays UV-vis spectra registered after every odd deposited PDAC–GO bilayer as a way to monitor the multilayer growth. As one can see in the inset, absorbances at 225 nm and 300 nm increase linearly with the number of PDAC–GO bilayers and confirms that the multilayer growth takes place step-by-step, or else, a same amount of PDAC–GO is adsorbed per deposited bilayer. This deposition is made possible by the electrostatic interaction between quaternized nitrogen atoms in the PDAC chains and the carboxylate groups in GO sheets. All spectra feature the same electronic transitions, attributed to GO only since PDAC does not absorb in the UV-vis region. In accordance to the literature, the prominent peak at 225 nm is ascribed to the π → π* transition in C=C bonds from the remaining graphitic regions whereas the subtle shoulder at 300 nm represents the n → π* in C=O bonds that originate upon graphite oxidation. Fig. 1b shows the effect of hydrazine treatment on (PDAC–GO)GO sample. The two initial absorption peaks are converted to a single and stronger one located at 267 nm. That one is ascribed to the π → π* transition in C=C bonds. The position is red shifted in comparison to the one of the non-reduced, as-made multilayer, because of partial reestablishment/enlargement of the pi-conjugated system. This is a clear evidence for the GO → RGO conversion.

Raman spectra presented in Fig. 2 give an additional support to the effective conversion of GO into RGO after the hydrazine treatment. As seen in Fig. 2, spectra of the (PDAC–GO)GO multilayer film before and after hydrazine treatment exhibit the typical graphene spectral signature with two intense bands at ~1340 and ~1600 cm⁻¹. In accordance to the literature they are respectively ascribed to the D-band, which corresponds to the breathing mode of k-point phonons of A₁g symmetry and the G-band, which corresponds to the first-order scattering of the E₂g phonon of sp² carbons. The relative Raman D/G intensity ratio (I_D/I_G) is inversely proportional to the average size of sp² domains and can be used to estimate the graphite oxidation extension. For the as-produced (PDAC–GO)GO multilayer film (Fig. 2a), I_D/I_G = 0.99, while for the hydrazine treated sample, noted as (PDAC–RGO)GO (Fig. 2b), I_D/I_G = 1.48. This increase
upon hydrazine treatment corresponds to reduction reactions of the GO phase. The increase is due to creation of new graphitic domains that are smaller than those present in GO before reduction, but more numerous. In summary, part of the pi-conjugated system is recovered and is consistent with the GO → RGO reduction.

The morphology of PDAC–GO multilayers was assessed by AFM. Fig. 3 provides AFM topographic images of [PDAC–GO]$_5$ and [PDAC–GO]$_{20}$ samples. As it can be seen in Fig. 3a and b, the GO sheets are assembled on each other with their edges highlighted by white arrows. The flat morphology of GO sheets is a predominant feature of PDAC–GO multilayers. The surface roughness is relatively high (~4.5 nm) in multilayers with few bilayers (up to 4) and decreases to a constant value of 2 nm from 5 bilayers. The multilayers’ thicknesses was also assessed by AFM and was found to increase linearly ($R^2 = 0.998$) with the number of PDAC–GO bilayers, in the range between 5 to 20 bilayers. This result is in agreement with the UV-vis data displayed in Fig. 1a, which showed that equal amounts of each component were adsorbed per each assembly cycle. The thickness per bilayer, as estimated from the linear fitting, is 1.4 nm. This value is consistent with the 1 nm thick single GO sheets as determined by Stankovich et al. However, the initial bilayers (up to 4 bilayers) still leave a considerable number of empty spaces, which suggests a 3-D island nucleation growth. Therefore, the linear increase is only ascribed to GO–PDAC islands and does not account for the empty spaces. As more PDAC–GO bilayers are being deposited, GO sheets bridge each other and fill these empty spaces. This growth model will be corroborated further by impedance measurements, as we shall see.

Despite the high conductivity of parent graphene, the PDAC–GO multilayers also exhibit a prominent capacitive behavior because of the dielectric nature of both components. However, the multilayers become conducting when the GO phase is properly converted into RGO upon hydrazine treatment. Therefore, impedance spectroscopy appeared as a suitable tool to study the electrical properties of PDAC–GO multilayers, since it can probe both behaviors by taking advantage on the vast range of measurable frequencies allowed by common instruments. When a sinusoidal excitation potential in the form of $V(t) = V_m \sin(\omega t)$ is applied to the system (an electric circuit or a material specimen), a steady state current $I(t) = I_m \sin(\omega t + \theta)$ develops. The angle $\theta$ expresses the phase difference between the voltage and the current. It is zero when the system is purely resistive. $V$ and $I$ are time-dependent while $\omega$ is the angular frequency of the electric field, expressed by $\omega = 2\pi f$, with $f$ given in Hertz. The electrical impedance $Z$ is a frequency-dependent resistance. As a vector quantity, $Z$ is represented as a complex number, composed by a real part, $Z'$, and an imaginary one, $Z''$, as follows:

$$Z(\omega) = Z' + jZ'' = \frac{V}{I}$$

(1)

where $j = \sqrt{-1}$. The coordinates are given by:

$$\text{Re}(Z) \equiv Z' = |Z| \cos \theta$$

(2)

$$\text{Im}(Z) \equiv Z'' = |Z| \sin \theta$$

(3)

with the phase angle

$$\theta = \tan^{-1}(Z''/Z')$$

(4)

With this previous background, we can go through with the impedance spectra of PDAC–GO multilayers. Fig. 4 shows the impedance spectra (Z and phase angle) of the [PDAC–GO]$_{20}$ sample before and after hydrazine treatment. As seen in Fig. 4a, the complex impedance $Z$ (see eqn (1)) of the [PDAC–GO]$_{20}$ sample before the hydrazine treatment (in black) is on the order of $10^4$ ohms (in the limit of DC regime, or else when $\omega \to 0$) and decreases continuously with the frequency as typical of a dielectric material. On the other hand, after the hydrazine treatment (in red) the sample’s impedance decreased to 500 ohms and is constant for the whole frequency range. This behaviour is typical of a conducting material (or else with predominant resistive behaviour). To corroborate this conclusion, in Fig. 4b is shown how the phase angle changes as the
frequency is varied. As expected, for the sample before the hydrazine treatment (in black), the phase angle is about −90° in almost the whole frequency range whereas is near 0° for the sample submitted to hydrazine (in red).

The impedance data can also be represented in Nyquist plots, where semicircles have coordinates in real ($Z'$) and imaginary ($Z''$) impedance components. From the semicircles is possible to estimate the parameters, resistance ($R$) and capacitance ($C$). The Nyquist plots for the impedance behavior of multilayer films after being submitted to the hydrazine treatment, namely from now on as PDAC–RGO, are given in Fig. 5a. The highlighted numbers refer to the number of PDAC–RGO bilayers. The inserted graphic shows an enlarged view of the spectra for multilayers with 5, 10, and 20 bilayers.

It is possible to note that the size of semicircles is smaller for multilayers with more PDAC–RGO bilayers. It means that, as more bilayers are being deposited, less resistive the multilayers become. Besides the size decrease, the semicircles' center is shifted, from right to left, from low to high frequency region. This effect is expected as the multilayers become more conducting with more bilayers and the impedance behavior becomes less frequency-dependent. This observation can be quantitatively seen in Fig. 5b that shows the complex impedance measured in 20 Hz and 1 kHz of multilayers with different numbers of PDAC–RGO bilayers. For either low (20 Hz) or high (1 kHz) frequency, the complex impedance decreases monotonically with the number of PDAC–GO bilayers. At both frequencies, the impedance reaches the lowest value around 5 bilayers and does not decrease significantly after that point. We propose that the initial bilayers do not coat the entire substrate and leave empty spaces, following a 3-D island growth model. Thus, at the very beginning of the deposition GO sheets remain isolated from each other and electrical contacts are poorly established in the film. As the deposition continues with more bilayers those initial nuclei enlarge until bridging each other (coalescence) and, finally, they establish an effective electrical contact. After that, the adsorption of more bilayers will not affect the multilayer’s resistance so significantly. This adsorption mechanism is typically found during the Lbl assembly of conducting materials, such as polyaniline. For polyaniline films, the electrical contact is fully attained after 13 bilayers.

In order to ascertain the potential use of hydrazine-treated multilayers, PDAC–RGO, in chemical sensing, we submitted them to vapor of volatile solvents and immersed them into...
aqueous solutions of different chemicals while registering the complex impedance at different frequencies. In accordance with our previous contributions,\textsuperscript{23,24} we verified that at 1 kHz the difference between the responses of different PDAC–RGO films for a same analyte was the largest, so that the ability of the sensor array in discriminating samples was the best at this frequency. Furthermore, this frequency range is easily attained by simpler circuits, which thus enable one for the development of lower cost instrumentation. Therefore, the results presented from now on will refer only to impedance measurements taken at 1 kHz. To process the data, we first calculated the values of \( \text{R} \) and \( \text{C} \). For a parallel \( RC \) circuit, \( \text{R} \) and \( \text{C} \) were calculated from impedance data as follows:

\[
\text{R} = \frac{|Z|}{\cos \theta} \quad (5)
\]

\[
\text{C} = -\frac{\sin \theta}{\omega|Z|} \quad (6)
\]

The idea of using \( \text{R} \) and \( \text{C} \) instead of \( Z \) (or \( Z' \) and \( Z'' \)) is that they represent clearer the two more general mechanisms for the interaction between the sensoactive layer (PDAC–RGO multilayer) and the analyte species. For a charge-transfer mechanism the figure of merit is the electrical resistance. On the other hand, when the analyte species causes polarization of the sensoactive layer, the capacitance represents the observed effect.

Fig. 6 displays the electrical response of sensing units made of PDAC–RGO films with different number of bilayers (where S1 refers to a sensing unit with one PDAC–RGO bilayer, S2 = 2 bilayers and so on) for analytes in the gas phase. In Fig. 6a it is shown the percentual change in \( \text{R} \) (where \( \Delta \text{R} = \text{R} - \text{R}_0 \), the difference between resistances, after \( \text{R} \) and prior \( \text{R}_0 \) to vapor exposure) of each sensing unit. This choice for resistance measurements was made because the capacitance of all sensors was essentially the same for different vapours, which thus disables the sensor array to discriminate the vapours. All sensing units, except by S10, respond to all solvents by exhibiting an increasing of \( \Delta \text{R}/\text{R}_0 \). The responses of each sensing unit were systematically reproduced in different runs, with less than 20% of standard deviation of the mean value. The increase in \( \Delta \text{R}/\text{R}_0 \) is lower for thicker multilayers. On the other hand, thinner multilayers are more sensitive because their surface area is comparatively larger than their volume. Thus, small concentrations of analytes are sufficient to cause a significant change on their electrical properties. However, we see that S1 and S2 respond almost with the same \( \Delta \text{R}/\text{R}_0 \) value for different solvents, which compromises the analytes’ distinction. On the other hand, sensing units made of thicker multilayers can distinguish better different solvents, since they provide greater differences in \( \Delta \text{R}/\text{R}_0 \). As the multilayer thickness increases, the access for analytes’ molecules inside the sensing layer gradually worsens. This apparently drawback provides the sensing unit with a possible mechanism for analytes distinction. Hence, the size the size and structure of analyte’s molecules begin to playing a role.

Studies conducted by different research groups have ascribed the charge transfer between analyte and sensoactive layer as the main sensing mechanism for graphene-based gas sensors.\textsuperscript{4,5,33,34} This mechanism is more clearly manifested when the gas molecules display strong electron donating or withdrawing character, as for example NO\textsubscript{2} or NH\textsubscript{3}. In the case of our analytes, this character is less pronounced. It is more likely that our analytes swell the PDAC–RGO multilayers and enlarge the distance between neighbour RGO domains, which thus increases \( \Delta \text{R}/\text{R}_0 \). The PCA plot of Fig. 6b shows that the sensor array distinguishes the solvents while separating them into two groups. One group contains toluene (2.4; 11 mmHg), gasoline (~2.1), chloroform (4.8; 110 mmHg), and acetone (20.7; 110 mmHg) and the other one contains only ethanol (24.3; 40 mmHg). The solvents in the first group, except by acetone, are all hydrocarbons with quite similar polarities (as expressed by dielectric constants, first data in parenthesis) while ethanol is a highly polar molecule. Despite the lack of a straightforward relationship between the score’s positioning and PC’s, the array is still capable to performing vapours distinction.

Fig. 7 presents the electrical response (in terms of capacitance) of the PDAC–RGO sensor array for analytes in the liquid phase. We have used \( C \) as a figure of merit based on the well accepted model for the electronic tongue based on impedance measurements.\textsuperscript{26,35,36} According to that model, the sensor response is accounted for by the impedance of an equivalent
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Multilayered thin films of poly(diallyldimethyl ammonium chloride) (PDAC) and graphene oxide (GO), or else PDAC–GO, are prepared by immersing solid supports (quartz slides and interdigitated electrodes) into their respective aqueous suspensions. The GO sheets provide to the multilayers a very flat surface morphology after deposition of few PDAC–GO bilayers. The as-prepared multilayers when properly reduced with hot hydrazine solution exhibit electrical impedance dependent on the chemical composition of the surrounding environment and can be readily employed in non-specific sensor arrays for detection of chemicals in either gas or liquid phases. The ability of the layer-by-layer technique in depositing multilayers with variable thickness that is precisely controlled at the nanometer level enables one for the production of sensing units displaying different levels of chemical sensitivity. This feature is unique and paramount for the development of sensor arrays of low cost and widespread use in chemical sensing.

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