Experimental report

15/09/2018

Proposal: 9-10-1551 **Council:** 4/2018

Title: In situ study of the effect of chemical composition on the morphologyof Graphene oxide films

Research area: Chemistry

This proposal is a new proposal

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Samples: Purified graphene oxide PGO
Graphene Oxide GO

Instrument	Requested days	Allocated days	From	To
FIGARO Langmuir trough	2	2	05/09/2018	07/09/2018

Abstract:

Graphene oxide (GO), is usually synthesized by oxidation of graphite or carbon nanofibers as an attractive route to prepare graphene based devices. However, controlling the chemical structure and deposition as thin films remains an unsolved problem. It has been shown recently [Langmuir 31, 2697 (2015)] that by using Langmuir-Blodgett technique one can control the film coverage with the percentage of CO groups attached to GO sheets. However,the microscopic mechanism of the increase in the coverage has not been understood. Therefore, the main objective of this Neutron Reflectometry study is to develop microscopic understanding of the effect of GO chemical composition on morphology, thickness and coverage of graphene oxides films on air-water and on solid substrate (Si/SiO2) interfaces. Graphene oxides selected will be obtained by graphite oxidation and using the purification procedure previously reported.

IN-SITU STUDY OF THE EFFECT OF CHEMICAL COMPOSITION ON THE MORPHOLOGY OF GRAPHENE OXIDE FILMS

Scientific Background and Objectives

Graphene oxide (GO), is usually synthesized by oxidation of graphite or carbon nanofibers as an attractive route to prepare graphene-based devices (1). However, controlling the chemical structure and deposition as thin films remains an unsolved problem (2-7). It has been shown recently that by using Langmuir-Blodgett technique one can control the film coverage with the percentage of CO groups attached to GO sheets (4,5). However, the microscopic mechanism of the increase in the coverage has not been understood.
Therefore, the main objective of the Neutron Reflectometry proposal 9-10-1551 was to develop microscopic understanding of the effect of GO chemical composition on morphology, thickness and coverage of graphene oxides films on air-water interface.
Graphene oxides selected were obtained by graphite oxidation and using the purification procedure previously reported (4,5,7). Thus, films of graphene oxides with two different chemical composition and structures were obtained and deposited at the air-water interface.

Experimental details

Specular neutron reflectivity (SNR) experiments were performed to study the interfacial structure of the Graphene Oxides GO sheets during the LB deposition process; initially, as Langmuir layers. The SNR measurements were made on the time of flight (TOF) reflectometer on the FIGARO beam line at the ILL, Grenoble, France. Data were collected at two incident angles 0.613° and 3.77°. Calibration of FIGARO was performed using a pure D_2O sub-phase. Backgrounds were subtracted from the data by the simultaneous acquisition of off-specular data for each measurement on the area detector. No off-specular scattering was observed for the monolayers under the conditions of the experiment. All SNR experiments were performed at a temperature of 20°C by using a thermostatic bath.

Graphene oxides, synthesized from graphite (GO) and graphene oxide purified by alkaline washing (PGO), Langmuir monolayers at the air/water interface were made in a Teflon trough. Both graphene oxide materials were well dispersed in water/methanol mixtures (1:5 v/v) by sonication for 30 min and then deposited onto a slightly acid water subphase (pH = 2-3) with a micrometer Hamilton syringe. Subphase temperature was maintained at 20.0 °C. Then, SNR profiles of the GO and PGO monolayers were obtained using two different H/D contrasts, namely D_2O and air contrast matched water ACMW (a mixture of composition 92% H_2O and 8% D_2O by volume) as shown Fig 1. We performed a full-Q structural NR analysis of the graphene oxide sheets, at two different compositions, with the aim to evaluate the differences in thickness and interfacial density at two different surface pressure values for each material (3 and 10 mN/m). Since GO and PGO exist in different 2D states monitored by the surface pressure values we selected two surface pressure values corresponding to the beginning and onset of the LE state (between 2 and 10 mN/m) (5) for both GO and PGO. Above this surface pressure value, the monolayer is constituted by overlapped sheets becoming instable. Therefore, we selected the LE region of monolayers to obtain information of stable monolayers.
The SNR profiles plotted in Fig. 1 were analyzed by the Abeles matrix method using Motofit (8) assuming a stratified structure including the air, the graphene oxide layer and the bulk phase. To find the parameters that show the most realistic model, the SNR data obtained for the two contrast at each experimental condition were simultaneously fitted with a genetic algorithm with least

squares and refined with a Levenberg-Marquardt optimization. We have estimated the SLD parameter from data in literature for materials of similar composition (9).
Results in Fig. 1 show a clear change in the SNR profiles in ACMW for GO and PGO. We analyzed both the D_2O (results not shown) and ACMW profiles by a simple 1-layer model. The SNR profiles and the resultant fits are plotted in Fig.1. From the data analysis, the remarkable difference between the thickness of GO and PGO films can be explained if one considers that the purification procedure consists in the elimination of oxidative impurities obtained by oxidation of graphite. It has been postulated that these impurities are adsorbed on the graphene oxide basal plane, therefore, the elimination of impurities drives to films thinner, as demonstrated by our results and with different roughness.

Conclusions.
We collected several complete NR datasets of GO and PGO at different lateral pressures. The initial analysis clearly demonstrated that structural changes could be directly observed by neutron reflectometry (see Fig.1). We provided, therefore, a quantitative characterization of the interfacial thickness and structure of graphene oxide layers spread on the air/water interface.

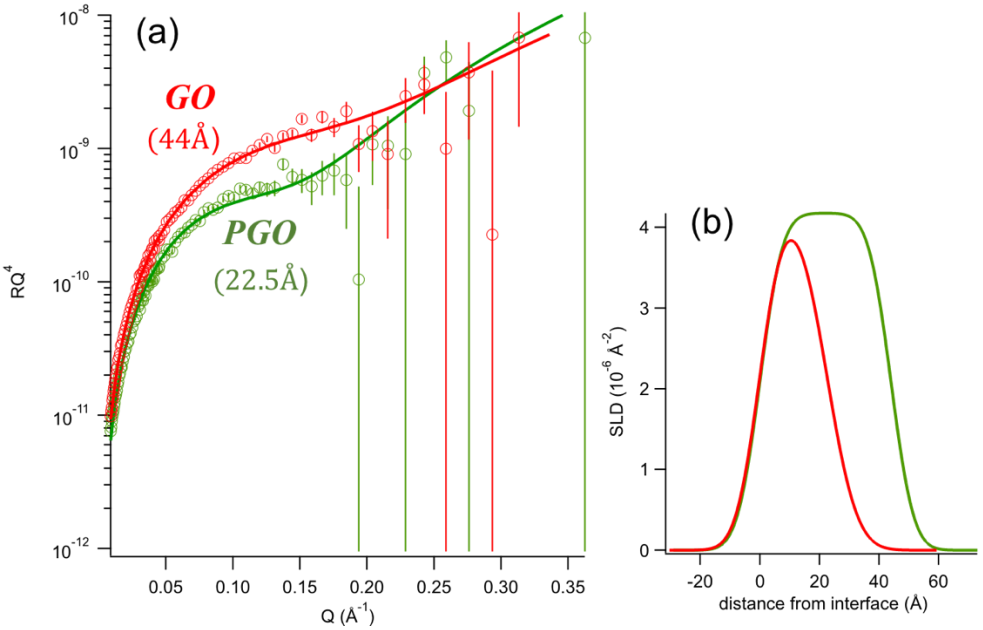

Figure 1. Full Q Structural analysis of graphene oxide layers. (a) Specular Neutron Reflectometry profiled for GO and PGO in ACMW at surface pressures of 10 and 9.8 mN/m, respectively. A one-layer model fit is shown as a solid line on each sample. (b) Scattering length density profiles calculated from the fit to the data shown in (a).

References

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