

# LANGMUIR-BLODGETT ASSEMBLY OF GRAPHENE OXIDE SHEETS

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## Introduction

Graphene oxide is the liquid oxidation of graphite powder, and consists of a single atomic carbon network derivitized by phenol hydroxyl and epoxide groups on the basal plane and carboxylic acid groups at the edges[1, 2]. The chemical functionalization breaks the extended  $\pi$ - $\pi$  conjugation of graphene, resulting in an insulating material. However the conductivity may be partially restored through reduction methods such as chemical or thermal treatments [3, 4]. The oxygen functionalizations make the sheet more hydrophilic and the ionizable carboxylic acid groups induce an electrostatic repulsion between the sheets, allowing GO to readily form a stable single layer colloidal dispersion in water [5], making possible large scale solution processing of the material. GO is therefore thought of as a promising precursor to graphene based materials. It will then be important to understand how to assemble the sheets into the desired structures. Furthermore, since GO is a unique soft layered material which could be considered of both a molecule and colloid, it is of fundamental scientific curiosity to understand the interactions between the sheets. In order to gain insight into the inter-sheet interactions of these highly anisotropic sheets, they were assembled at the air-water interface using the Langmuir-Blodgett technique and pH was used to tune the packing behavior of compressed films.

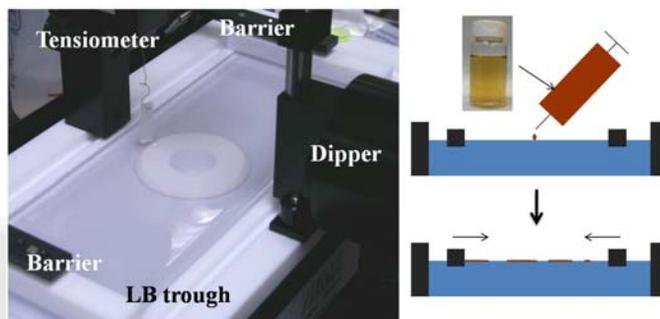
## Experimental

GO was prepared using a modification of Hummers method[6] from graphite powders (Bay carbon, SP-1). Briefly, 2 g of graphite, 1 g of  $\text{NaNO}_3$ , and 46 mL of  $\text{H}_2\text{SO}_4$  were stirred together in an ice bath. Next, 6 g of  $\text{KMnO}_4$  was slowly added. All chemicals were purchased from Sigma-Aldrich and were used as received. Once mixed, the solution was transferred to a 35°C water bath and stirred for about 1 h, forming a thick paste. Next, 80 mL of water was added, and the solution was stirred for 1 hr while the temperature was raised to 90 °C. Finally, 200 mL of water was added, followed by the slow addition of 6 mL of  $\text{H}_2\text{O}_2$  (30%), turning the color of the solution from dark brown to yellow. The warm solution was then filtered and washed with 3x 200 mL of 10% HCl followed by 200 mL water. The filter cake was then dispersed in water by mechanical agitation and stirred overnight. The dispersion was then allowed to settle and the top clear yellow dispersion was subjected to dialysis for 1 month resulting in a stock solution with a concentration of about 0.17 mg/ml.

The as prepared GO was diluted to a ratio of 5:1 methanol/water solution. The trough (Nima Technology,

model 116) was carefully cleaned with acetone and then filled with deionized water (DI). GO solution was spread onto the water surface dropwise using a glass syringe to a total volume of 10-15 mL. The surface pressure was monitored using a tensiometer attached to a Wilhelmy plate. The film was compressed by barriers at a speed of 50  $\text{cm}^2/\text{min}$ . The dimensions of the trough are 10 cm  $\times$  25 cm. Initial isotherms were taken after the film was allowed to equilibrate for at least 20 minutes after the depositions. The GO monolayer was transferred to either glass or silicon substrates treated with 1:1:5  $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{DI}$  by vertically dipping the substrate into the trough and slowly pulling it up (2 mm/min).

In-situ Brewster Angle Microscopy (Nima, MicroBAM) snapshots were taken during isotherm cycles. The deposited films on silicon were characterized using scanning electron microscopy (SEM; Hitachi S-4800-II) and Fluorescence Quenching Microscopy.[7]

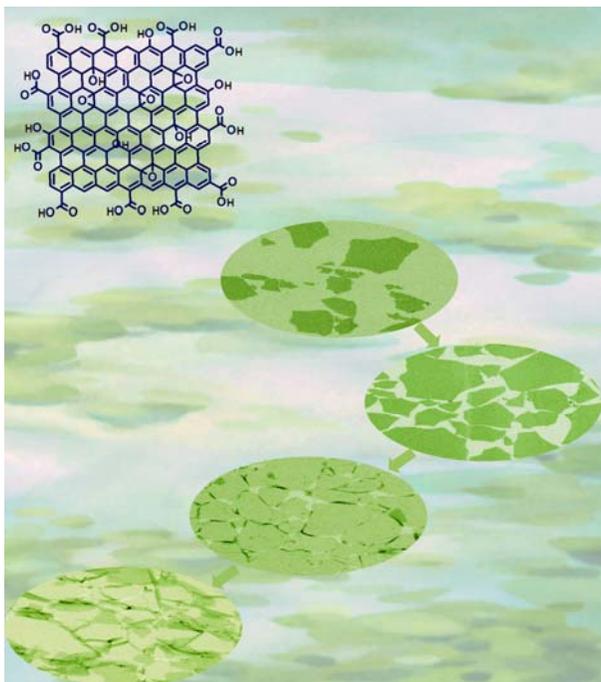


**Fig. 1** Langmuir-Blodgett trough and schematic. GO can be spread on the water surface from a methanol dispersion, leaving the sheets trapped between movable barriers. The tensiometer measures the surface pressure and the dipper allows for transfer of the monolayer onto a solid substrate.

## Results and Discussion

Although GO readily disperses in water, the sheets can be spread on the water surface from a methanol-water dispersion, leaving the two-dimensional single layers floating at the interface. The LB technique can then be used to compress the sheets together by movable barriers and the layer at the water surface can then be transferred to a solid substrate at various points along the compression cycle by dip-coating. SEM viewing of dip-coated samples on silicon revealed four distinct packing behaviors. As shown in figure 1, the density of sheets can be continuously tuned from isolated flat sheets, which then tile together as they closely packed. It is noteworthy that these sheets remain flat, since this would be difficult to achieve with other deposition methods, such as spin coating or drop-casting. Since the sheets are soft, further compression results in folding at the interaction edges and finally results in an over-packed layer with interlocked structure. These interactions were found to be reversible, as the packing behavior before and after cycling was found to be similar[8]. The interactions and film morphology may be further tuned. GO sheets have ionizable carboxylic acid groups at the edges

allowing the degree of charge and hydrophilicity to be altered simply by altering the pH of the subphase.



**Fig. 2** Schematic of a graphene oxide sheet showing aromatic regions functionalized by oxygen containing groups, including ionizable carboxylic acid groups at the edges. GO sheets floating at the air-water interface, much like water lilies on a pond, are shown in the SEM images with increasing GO density from top to bottom.

### Conclusions

Graphene oxide layers can be assembled at the air-water interface and transferred to solid substrates with a continuously tunable density of sheets over a large area. The packing behavior of the sheets can be further tuned by altering the pH of the subphase. These techniques can help to improve thin film morphologies and coverage and allow for further studies into the effect of structure on the overall film properties. The large area coverage of graphene oxide monolayers provides a processing technique for graphene-based transparent conductor applications.

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