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Wrinkles and overlaps: on the structure-property relationship of tiled graphene oxide monolayers. False coloured AFM images of tiled graphene oxide monolayers showing much higher surface roughness of wrinkles (front) than overlaps (back), resulting in greater light scattering.
Tunable assembly of graphene oxide surfactant sheets: wrinkles, overlaps and impacts on thin film properties

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Graphene oxide (GO) sheets are a unique type of soft building block for creating functional graphene based materials and devices. Rapid progress has been made in the chemistry and applications of GO. However, there is a pressing need for rational assembly strategies of these two-dimensional (2D) sheets, which is crucial for determining the microstructures and thus final properties of bulk GO or graphene materials. For example, wrinkles and overlaps are the two fundamental morphologies between flexible, interacting sheets that are usually convoluted in solution-processed thin films. Based on the recent discovery of the surfactant-like property of GO sheets and their pH dependent amphiphilicity, now we are able to control the tiling of such 2D sheets to obtain thin films with either a wrinkled or overlapped type of microstructure, thus allowing us to deconvolute how these two basic microstructures affect the electrical and optical properties of the final thin films. The work here provides a well-defined example of the materials science paradigm, the microstructure-properties relationship, for this new soft material.

Introduction

Graphite oxide sheets, now known as graphene oxide (GO), are the liquid phase oxidation-exfoliation product of graphite, which was first synthesized over a century ago.1,2 GO consists of a single atomic layer of sp2 hybridized carbon atoms derivatized by phenol hydroxyl and epoxide groups mainly on the basal plane and ionizable carboxylic acid groups at the edges,3,4 as shown schematically in Fig. 1a. Charge repulsion of the ionized edge acid groups allows GO to form stable single layer aqueous dispersions.5 In recent years, rapid progress has been made in the chemistry6–8 and applications of GO as a graphene precursor.9–12 However, there is a pressing need for rational assembly strategies of these two-dimensional (2D) sheets, especially when they are processed and used beyond the single layer level. Assembly plays a key role in the structure-properties relationship of bulk graphene materials since it controls the microstructures of the resulting materials which determine their final properties.

In addition to the hydrophilic hydroxyl and carboxyl acid groups on the edge, there are unoxidized hydrophobic polyaromatic nanographene domains remaining on the basal plane (Fig. 1a), which makes GO a unique tethered 2D surfactant sheet. Indeed, a recent discovery showed that GO does behave like surfactants.13–15 GO was found to be enriched at interfaces without being modified by surfactants,16 capable of lowering the interfacial energies and dispersing insoluble materials such as carbon nanotubes in water.17 In addition, GO’s amphiphilicity can be tuned by pH since it affects the degree of ionization (Fig. 1b) or the number of charges on the sheets, as shown in zeta potential measurements (Fig. 1c).

These surfactant-like properties of GO sheets suggest that one could potentially control how they assemble at interfaces by tuning their amphiphilicity. Here we report one such example, using pH as a tuning parameter to guide the assembly of GO sheets at the air–water interface. Interacting sheets can be coaxed to form a continuous film with two distinct types of microscopic morphologies, namely wrinkles and partial overlaps. These microstructures were found to have different effects on the electrical and optical properties of the resulting graphene based monolayers. The processing-microstructure-properties relationship reported here could provide a model system for designing better graphene based technologies such as transparent conductor thin films16–22 since wrinkles and overlaps are the two fundamental morphological features of graphene based thin films.

Experimental

Graphene oxide synthesis and purification

GO was prepared with a modified Hummers’ method2 from graphite powders (Bay carbon, SP-1). Briefly, 2 g of graphite, 1 g of NaNO3, and 46 mL of H2SO4 were stirred together in an ice bath. Next, 6 g of KMnO4 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 h while the temperature was raised to 90 °C. Finally, 200 mL of water was added, followed by the slow addition of 6 mL of H2O2 (30%). The warm solution was then filtered and washed with 3 × 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 as measured by filtration.

Footnotes

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Langmuir-Blodgett (LB) assembly of GO

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 chloroform and acetone 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 cm²/min. The dimensions of the trough are 10 cm × 25 cm with a volume of 300 mL. Typical initial and final surface areas were around 240 and 60 cm², respectively. Initial isotherms were taken after the film was allowed to equilibrate for at least 20 min after the spreading. The pH was altered by the addition of 1 M HCl or 1 M NaOH and measured with an Accumet Basic AB15 pH meter. The GO monolayer was transferred, typically midway and at the minimum area, by vertically dipping the substrate into the trough and slowly pulling it up (2 mm/min). Either glass or silicon substrates treated with 1 : 1 : 5 NH₃OH:H₂O₂:DI were used. Isotherms in figures have a zeroed baseline.

Characterization

In situ Brewster Angle Microscopy (Nima, MicroBAM) snapshots were taken during isotherm cycles. The deposited films on silicon were characterized using atomic force microscopy (AFM; Digital Instrument, MultiMode scanning probe), scanning electron microscopy (SEM; Hitachi S-4800-II) and fluorescence quenching microscopy. Optical microscopy images of the wrinkles and overlaps were taken using Nikon Eclipse E600 POL with Nikon LU PlanFlour 50x/0.80 A objective and Diagonostic Instruments Inc. Spot insight QE camera. The contrast of images of wrinkles and overlaps was enhanced using Photoshop to make them more visible.

Water contact angle was measured using a Kruss DSA100 drop shape analyzer. The contact angle of water drops of pH 10 and pH 2 were measured on a close packed GO film deposited by the Langmuir–Blodgett technique on a quartz slide. Zeta potential was measured with Malvern Zetasizer Nano ZS with a 5 mM NaCl background electrolyte in the dispersions.

For reduction, the films were placed in a dish containing hydrazine and were heated to 100 °C for two hours or by heating at 500 °C in an Ar atmosphere for 1h. Electrodes were patterned using a thermal evaporator and a shadow mask. The electrode length is 4 mm and channel widths are 2.5 and 0.25 mm for the wide and narrow respectively. Resistance was measured using a Keithley 2400 and a probe station at ambient conditions.

The transmission of the samples were measured by a TE-cooled CCD (Princeton Instruments, PIXIS 400B) coupled on an Acton SP-2356 spectrograph. A 1200 G/mm grating with 750 nm blaze wavelength was used. At least 20 local areas were randomly chosen from each sample through an optical microscope (Nikon TE-2000U), and the transmission of each region was measured over the visible wavelength range and averaged to yield given values.

Local scattering measurements were made on single sided reduced wrinkled and overlapped graphene oxide films on glass as well as uncoated glass as a control. The back side of the glass substrate is attached to the hypotenuse face of right angle prism with index matching oil. The laser is incident normal to the orthogonal face of the right angle prism and subject to total-internal-reflection (TIR) at sample/air interface. An inverted
optical microscope is placed underneath the sample and is used to collect the light scattered from the sample surface. The light was measured by a coupled grating spectrometer with matched EMCCD camera (Shamrock 303, Andor Technology).

Results and discussion

The hydrophilicity of GO can be tuned by the degree of ionization of the carboxylic acid groups through pH, which directly affects their surface activity. This can be conveniently observed using Brewster Angle Microscopy (BAM, Fig. 1d).15 BAM uses $p$-polarized light incident on the water surface at the Brewster angle, such that there is no reflection from the surface and the image appears dark.23,24 When a surface layer is introduced, in this case GO, the index of refraction is changed, thus reflection is allowed and the sample appears bright. BAM images in Fig. 1e-1g confirmed that GO can migrate to the air–water interface from the bulk dispersion by stirring. A significant number of bright spots appeared on the surface of a pH 2 dispersion after stirring (Fig. 1e). Fewer spots were seen when the pH was increased to 5.5 (Fig. 1f). Very little surface materials were seen when the pH was 10 (Fig. 1g).

The change in surface activity motivates the exploration of the pH dependent assembly behavior of GO at the air–water interface. A Langmuir–Blodgett trough was used so that GO sheets can be rapidly deposited on water surface, manipulated by barriers, monitored by a surface pressure tensiometer and visualized by a BAM. Typically, a monolayer of GO sheets was prepared by spreading a 5:1 methanol:water GO dispersion drop wise onto the water surface.15 Surface pressure-area isotherms were then recorded upon compression of the film (Fig. 2a, curve 1). Typically the surface pressure is a measure of material density at water surface. Fig. 2a shows the isotherm plots of a GO monolayer when the pH value of the subphase was changed from 5.5 (curve 1) to 10.5 (curve 2) and back to 5.5 (curve 3). After adding base (1 M, NaOH) to the subphase, the maximum surface pressure was greatly reduced, typically from over 20 mN/m to a few mN/m. When the pH was restored to 5.5 by adding HCl to neutralize the base, the surface pressure was largely recovered but still smaller than the initial value (Fig. 2a, curve 3). The incomplete recovery of surface pressure suggests that there was a loss of material at the interface under basic conditions. It was also noted that a higher degree of compression was needed to restore the surface pressure. As seen in Fig. 2b, the isotherm plots after (curve 2) pH cycling has a similar shape to the initial curve 1, but reaches the same final pressure at a smaller area. SEM images of films collected at equal surface pressures before and after the pH cycle (Fig. 2b, insets) reveal a similar packing density and morphology. Since the GO sheets packed in the same way before and after pH cycling, it confirms that the incomplete recovery observed in Fig. 2a was indeed due to material loss in the monolayer. As a control, an equal amount of salt (NaCl) to that produced during a pH cycle (~3 mM) was added to a pure water subphase which resulted in little change in the isotherms or morphology of the deposited sheets, indicating the increased ionic strength during pH cycling does not significantly affect the assembly.

The next question to address is the cause of the large difference in the final surface pressure of curves 2 and 3 in Fig. 2a, which could be due to a difference in material density or the microstructures of the GO monolayer (i.e., the packing of GO sheets). To investigate this, we collected the monolayer at the end of compression under both acidic and basic pH values. The samples were thus termed “acidic” and “basic” monolayers, respectively, and evaluated using three microscopy techniques, namely fluorescence quenching microscopy (FQM),25,26 scanning electron microscopy (SEM)25,26 and atomic force microscopy (AFM) in order to image the samples at millimeter to submicron length scales. The large area overviews obtained by FQM (Fig. 3a, 3d) show that the coverage of both types of monolayers was comparable. However, some parallel wrinkles can be seen in the acidic monolayer as depicted by the darker lines in Fig. 3a. The wrinkles are perpendicular to the direction of compression, indicating that the tiled monolayer buckled as a whole membrane during compression. More detailed viewing by SEM (Fig. 3b) revealed that there are many smaller wrinkles on individual GO

![Fig. 2](image-url)

**Fig. 2** Effect of pH values on the LB assembly of GO sheets. (a) Surface pressure-area isothermal plot of a LB monolayer of GO sheets on DI water subphase (pH = 5.5, black solid line 1). After increasing the subphase pH value to 10.5, the same compression ratio yielded a greatly reduced final surface pressure (red dashed line 2). When the pH was adjusted back to 5.5, the final surface pressure was only partially restored (blue dotted line 3). (b) After the pH cycling, the final surface pressure can be completely restored by more compression. SEM images of the monolayers collected at the highest surface pressure by dip coating show similar packing behavior and density before (inset 1) and after (inset 2) pH cycling. (a-b) suggest that some GO sheets were squeezed into the subphase during the pH cycling. Scale bars represent 25 μm.
sheets. Since the GO sheets are irregularly shaped polyhedrons with polydisperse sizes, they would squeeze each other from random directions when the monolayer is compressed. As a result, the wrinkles seem to be disoriented, too. However, many wrinkles near the edges of the GO sheets were found to be aligned with the contact lines of neighboring sheets, suggesting that they were also buckling structures developed under in plane compressive forces. AFM images (Fig. 3c) on individual wrinkles show that they are typically thicker than 3 nm, often reaching 5 to 10 nm. Note that the apparent thickness of GO is around 1 nm, these wrinkles effectively create many 5 to 10-layer islands in the monolayer, thus increase the films surface roughness. In contrast, wrinkles are not observed in the basic film. Rather, the sheets slide on top of one another forming partial overlaps, as seen in the FQM, SEM and AFM images (Fig. 3d-f). The overlapped areas were typically only 2-layers thick, making the basic monolayer much smoother than the acidic one.

This change in packing behavior is likely due to the difference in hydrophilicity of GO under different pH values. Under basic conditions, GO sheets are more hydrophilic and more wettable by water, which is measured by an increase in the water contact angle on a GO film of 60° for basic to 70° for acidic water. Therefore, they could acquire a water lubricating layer, which would allow them to slide on each other upon compression during LB assembly. However, under acidic conditions, GO sheets are more hydrophobic, which would force the sheets to squeeze each other when compressed, leading to buckling structures. Hydrogen bonding between the carboxylic acid edge groups may also contribute to the wrinkling behavior since it can help to fix the interacting sheet edges, preventing them from sliding. The transition from the overlapping to wrinkling state accounts for the sharply increased surface pressure when the basic subphase was neutralized (Fig. 2a, curves 2 and 3) since the wrinkled microstructure requires higher surface pressure to maintain than the overlapped state.

Wrinkles and overlaps are the two fundamental morphologies of interacting sheets in GO based bulk materials. For example, they are the common features found in solution processed GO or the subsequent reduced GO (r-GO, a.k.a. chemically modified graphene) films. pH dependent LB assembly can now offer model systems to deconvolute the effects of these two types of micro-structures on material properties. As a proof of concept, we chose to study how wrinkles and overlaps affect the sheet resistance and optical transmission, the two most important performance parameters of GO based transparent conductor thin films.

Before sheet resistance, the GO monolayers were thermally reduced at 500 °C in an Ar atmosphere for 1h. Gold electrodes were patterned on the resulting r-GO films by evaporation. Typically two sets of electrode separations were formed – a narrow one of 0.25 mm and a wide one of 2.5 mm (Fig. 4a, inset). Since the r-GO films were made by tiled smaller pieces, the distribution of sheet resistance values measured at different spots and different electrode separations directly reflects the uniformity of sample coverage. If the coverage is uniform, sheet resistance values measured should be consistent and insensitive to the electrode geometries. Otherwise, the values measured would scatter, especially with narrower
electrode gaps. As shown in Fig. 4a, the sheet resistance values measured on the acidic monolayer (solid and hollow squares) have very wide range of distribution, especially for those measured with narrower electrode gaps (solid black squares), which scattered over nearly two orders of magnitude. In contrast, values obtained with the basic monolayer (Fig. 4a, solid and open circles) were much more focused and consistent regardless of the electrode separation. FQM observation revealed that the acidic monolayers were less uniform than the basic ones with many pin holes free of r-GO sheets. In fact, before transferring to the substrate, the uniformity difference of the monolayers on water surface can also be seen by in situ BAM observations.

Fig. 4 Effect of pH on the sheet resistances of annealed GO monolayers. (a) Sheet resistances of r-GO monolayers collected from a pH 5 (black squares) and pH 10 (red circles) subphases. Inset shows samples with patterned gold electrodes of wide and narrow separations of 2.5 and 0.25 mm, respectively. For the “acidic monolayer”, the sheet resistance values measured at different spots and different electrode separations were very scattered, suggesting uneven coverage of GO sheets. The resistance values for the “basic monolayer” were much more uniform and consistent, suggesting uniform GO coverage. Indeed, at medium compression, BAM images show (b) aggregated islands structure in the “acidic monolayer” with many empty areas. (c) In the “basic monolayer”, GO sheets appeared to be much more evenly distributed. Scale bars = 0.5 mm.

Fig. 5 Effect of wrinkles and overlaps on the monolayer transparency. Optical microscopy images of monolayers taken under bright-field transmission mode (a, d) and dark-field scattering mode (b, e) reveal that wrinkles (a, b) cause higher optical loss than overlaps (d, e) due to stronger light scattering (c, f). In (c) and (f), the white and blue arrows depict incident and scattered/reflected light paths in the dark field objective, respectively. All scale bars = 20 μm.
Fig. 4b shows the acidic monolayer at moderate compression ratio. GO sheets were found to form islands linking together into a network-like structure. This is likely due to stronger hydrogen bonding between the sheets at lower pH. Even when the network structure was compressed, gaps between the islands cannot be completely eliminated, leading to less uniform thin film deposition. Upon addition of base, these islands quickly disperse (Fig. 4c) due to increased charge repulsion, resulting in a more even film. Overall, the sheet resistance values of the acidic r-GO monolayers were only slightly higher but much more scattered than those of the basic monolayers.

The optical properties of the wrinkled and overlapped samples also differ. Optical loss is greater in the wrinkled structures, which have an average percent transmission of 94.1% compared to 96.1% for the partially overlapped, hydrazine reduced GO monolayers. Bright field transmission optical microscopy images (Fig. 5 a, d) of a reduced wrinkled film show darker features (i.e., increased loss) at the wrinkled sites. The cause of the increased loss is revealed in dark field images. As shown schematically in Fig. 5 c, f, in the dark field imaging mode, light is incident on the sample at an oblique angle, such that only scattered light will enter the front lens to form the image. In the dark field image (Fig. 5b), wrinkles can be clearly seen as bright scattering centers on the black background. The overlaps are essentially featureless in both bright field and dark field modes of imaging. In Fig. 5d and 5e, an aggregated GO cluster was shown, only to focus the camera. Local laser scattering measurements results indeed confirmed that wrinkles are much stronger scatterers than the overlaps. The averaged scattering from wrinkled areas is around 3.7 times that of the overlapping areas.

Conclusion

The properties of a tiled graphene based thin film will not only be determined by the quality of each single layer, but also how they assemble. As for the electronic properties and transparent conductor applications, there has been extensive effort in making chemically modified graphene as conductive as possible. Much less known is how the thin film microstructures affect the overall material performance. Utilizing pH dependent LB assembly of GO sheets, we were able to prepare graphene based monolayers with microstructures dominated by wrinkles or overlaps – the two basic morphological features usually convoluted in graphene films. For the first time, we were able to isolate their effects on the electrical and optical properties. For making a better, tiled graphene based transparent conductor, thin films with the partially overlapped sheets would be preferred due to more uniform coverage and lower optical scattering loss. The study here provides a model system illustrating how assembly controls the microstructures, and determines the properties of bulk graphene-based materials.

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Notes and references