Langmuir−Blodgett Assembly of Graphite Oxide Single Layers

Laura J. Cote, Franklin Kim, and Jiaxing Huang*

Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

Received August 17, 2008; E-mail: Jiaxing-huang@northwestern.edu

Abstract: Single-layer graphite oxide can be viewed as an unconventional type of soft material and has recently been recognized as a promising material for composite and electronics applications. It is of both scientific curiosity and technical importance to know how these atomically thin sheets assemble. There are two fundamental geometries of interacting single layers: edge-to-edge and face-to-face. Such interactions were studied at the air−water interface by Langmuir−Blodgett assembly. Stable monolayers of graphite oxide single layers were obtained without the need for any surfactant or stabilizing agent, due to the strong electrostatic repulsion between the 2D confined layers. Such repulsion also prevented the single layers from overlapping during compression, leading to excellent reversibility of the monolayers. In contrast to molecular and hard colloidal particle monolayers, the single layers tend to fold and wrinkle at edges to resist collapsing into multilayers. The monolayers can be transferred to a substrate, readily creating a large area of flat graphite oxide single layers. The density of such films can be continuously tuned from dilute, close-packed to overpacked monolayers of interlocking single layers. For size-mismatched single layers, face-to-face interaction caused irreversible stacking, leading to double layers. The graphite oxide monolayers can be chemically reduced to graphene for electronic applications such as transparent conducting thin films.

Introduction

Graphite oxide (GO) is usually made by reacting graphite powder with strong oxidants such as a mixture of concentrated sulfuric acid and potassium permanganate.[1] After oxidation, the carbon sheets are exfoliated and derivatized by carboxylic acid at the edges, or phenol hydroxyl and epoxide groups mainly at the basal plane.[2−5] The reaction breaks the $\pi-\pi$ conjugation at those sites, which can be partially recovered by either chemical or thermal methods to yield graphene.[6−9] Recently, GO has rapidly become a promising material for polymer composite and graphene-related electronics applications.[6,9−14] A graphite oxide single layer (GOSL) consists of a hexagonal network of covalently linked carbon atoms with oxygen-containing functional groups attached to various sites (Figure 1a,b). It can be viewed as an unconventional type of soft material[15,16] in that it is a two-dimensional (2D) *membrane*-like single *polymer* molecule that also acts like a *colloid*. The colloidal "particle" is characterized by two abruptly different length scales, with the thickness determined by a single atomic layer and the lateral sheet extending to up to tens of micrometers. This gives GOSLs a very high aspect ratio and nominal surface area since a single layer is essentially completely surface. It is of both scientific curiosity and technical importance to know how these atomically thin sheets assemble and how they behave when interacting with each other.

The interaction between colloidal particles determines their colloidal stability. The three classical types of DLVO stability of charged colloidal particles are illustrated in Figure 1f by total energy (*U*) versus particle separation (*d*) curves.[15−17] A colloidal dispersion is stable if the electrostatic repulsion dominates. Its potential energy curve has a high energy barrier against flocculation or coagulation (dashed red line). If van der Waals

(1) Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 1339.
(2) Nakajima, T.; Mabuchi, A.; Hagiwara, R. *Carbon* **1988**, *26*, 357–361.
(3) Nakajima, T.; Matsuo, Y. *Carbon* **1994**, *32*, 469–475.
(4) He, H. Y.; Riedl, T.; Lerf, A.; Klinowski, J. *J. Phys. Chem.* **1996**, *100*, 19954–19958.
(5) Lerf, A.; He, H. Y.; Forster, M.; Klinowski, J. *J. Phys. Chem. B* **1998**, *102*, 4477–4482.
(6) Stankovich, S.; Dikin, D. A.; Dommett, G. H. B.; Kohlhaas, K. M.; Zimney, E. J.; Stach, E. A.; Piner, R. D.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2006**, *442*, 282–286.
(7) Stankovich, S.; Piner, R. D.; Chen, X. Q.; Wu, N. Q.; Nguyen, S. T.; Ruoff, R. S. *J. Mater. Chem.* **2006**, *16*, 155–158.
(8) Becerril, H. A.; Mao, J.; Liu, Z.; Stoltenberg, R. M.; Bao, Z.; Chen, Y. *ACS Nano* **2008**, *2*, 463–470.
(9) Li, X. L.; Wang, X. R.; Zhang, L.; Lee, S. W.; Dai, H. J. *Science* **2008**, *319*, 1229–1232.
(10) Dikin, D. A.; Stankovich, S.; Zimney, E. J.; Piner, R. D.; Dommett, G. H. B.; Evmenenko, G.; Nguyen, S. T.; Ruoff, R. S. *Nature* **2007**, *448*, 457–460.
(11) Gilje, S.; Han, S.; Wang, M.; Wang, K. L.; Kaner, R. B. *Nano Lett.* **2007**, *7*, 3394–3398.
(12) Eda, G.; Fanchini, G.; Chhowalla, M. *Nature Nanotech.* **2008**, *3*, 270–274.
(13) Li, D.; Muller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. *Nature Nanotech.* **2008**, *3*, 101–105.
(14) Ruoff, R. *Nature Nanotech.* **2008**, *3*, 10–11.
(15) Jones, R. A. L. *Soft Condensed Matter*, 1st ed.; Oxford University Press: Oxford, UK, 2002.
(16) Hamley, I. W. *Introduction to Soft Matter: Polymers, Colloids, Amphiphiles and Liquid Crystals*, 2nd ed.; Wiley: New York, 2007; p 340.
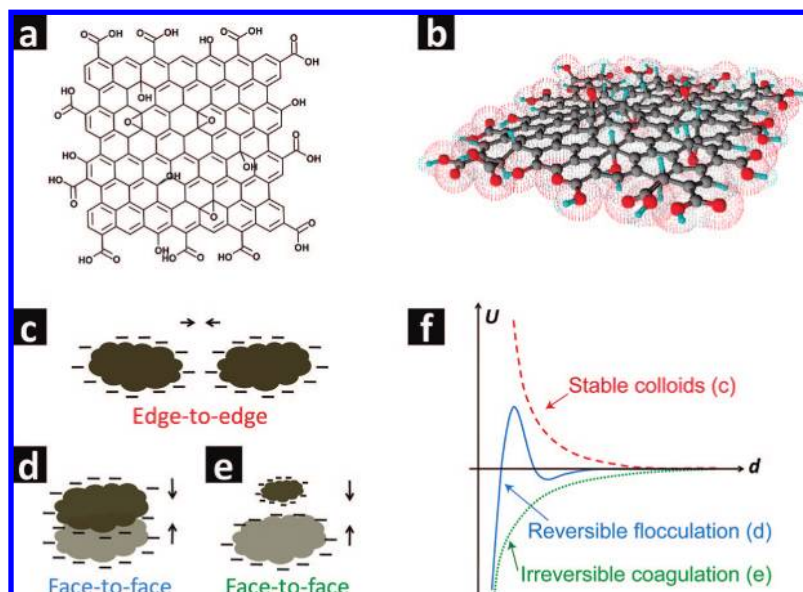(17) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: San Diego, 1992; p 450.

Figure 1. (a) Structural model and (b) 3D view of a GOSL showing carboxylic acid groups at the edge, and phenol hydroxyl and epoxide groups mainly at the basal plane.[3,5] There are two fundamental interacting geometries when two single layers meet: edge-to-edge (c) and face-to-face (d,e). The sheets are negatively charged on their edges due to ionized carboxylic acid groups. The competition between electrostatic repulsion and van der Waals attraction determines the colloidal stability of such interacting systems. Edge-to-edge interaction (c) should be stable against flocculation or coagulation due to strong repulsion and weak attraction. With increased van der Waals attraction, face-to-face interaction may lead to reversible flocculation of (d) GOSLs of comparable sizes, or irreversible coagulation of (e) GOSLs of very different sizes. These scenarios correspond to the three classical types of DLVO colloidal stability, for which schematic total potential energy versus separation profiles are shown in (f):[15−17] dashed red line, strongly repelling colloids; solid blue line, kinetically stable colloids forming reversible flocculation; dotted green line, unstable colloid forming coagulation.

attraction dominates, the colloids are unstable and tend to coagulate irreversibly since there is no repelling barrier on the total energy curve (dotted green line). If the sum of repulsion and attraction generates a secondary minimum (solid blue line), the colloids remain kinetically stable. Their flocculation (the state at the secondary minimum) can be reversed by agitation. GO is known to form a colloidal solution in water due to electrostatic repulsion between the ionized carboxylic and phenol hydroxyl groups. These groups are located mainly at the edges, and so are the charges. When two GOSLs approach each other, they experience both electrostatic repulsion and van der Waals attraction. Their total energy (U) is a sum of these two potentials. Due to their highly anisotropic shape, the total potential energy of two interacting GOSLs should depend on the geometry in which they approach each other. There are two fundamental interacting geometries between GOSLs: edge-to-edge and face-to-face (Figure 1c−e). Note that the scaling law of van der Waals potential versus separation ($1/d^n$) depends on the geometry of the interacting bodies.[17]

two points	two parallel chains	two parallel planes
$W \sim 1/d^6$	$W \sim 1/d^5$	$W \sim 1/d^2$

Therefore, the colloidal stability of GOSLs should also depend on their interacting geometry. When two flat sheets are brought together in an edge-to-edge manner (Figure 1c), their van der Waals potential should scale in a way between those of two atoms ($1/d^6$) and two chains ($1/d^5$), which rapidly decays as the separation increases. Therefore, the electrostatic repulsion should dominate, leading to a potential energy curve without minimum, similar to the dashed red line in Figure 1f. This suggests that GOSLs would form a stable colloidal dispersion against flocculation or coagulation if they are confined in 2D

space. If the sheets are brought together in a face-to-face manner, their van der Waals potential now scales with ($1/d^2$). In addition, the residual π-conjugated domains in the sheets can contribute to the attraction, too. It should then be possible to see a shallow energy minimum before the repelling barrier on the curve, similar to the solid blue line in Figure 1f. This would lead to reversible stacking when GOSLs are forced to overlay with other. It is indeed in agreement with the observation that GO colloidal solutions usually form flocculation during storage, which can be redispersed by shaking or gentle sonication (Supporting Information, Figure S1). The face-to-face interaction should also depend on the relative sizes of the sheets. When two GOSLs with very different sizes meet this way, the separation between the charges, which are mostly on the edges, is no longer represented by the physical separation of the layers. Therefore, the repulsive potential has a finite minimum value due to the size mismatch, while the attractive potential can still scale continuously as the face-to-face separation decreases. This would lead to a potential energy curve without a repelling barrier (Figure 1f, dotted green line). The colloidal system would be unstable; therefore, two such GOSLs should tend to stack nearly concentrically to form a double layer.

The 2D water surface serves as an ideal platform to investigate the above-mentioned interactions of GOSLs. First, the interface is geometrically similar to GOSL, making it ideal to accommodate the flat sheets. Second, the soft, fluidic "substrate" should allow free movement of GO sheets upon manipulation, which should facilitate interactions between the flat GO sheets in both edge-to-edge and face-to-face geometries. Here we report Langmuir−Blodgett (LB) assembly of GOSLs. We discovered that GOSLs can float on a water surface without the need for surfactants or stabilizing agents. The GOSL monolayers exhibit remarkable reversibility against isothermal compression−expansion cycles. In contrast to molecular and

hard colloidal particle monolayers, GOSLs tend to fold and wrinkle to resist collapsing into multilayers. We successfully made monolayers of flat GOSLs over large areas with continuously tunable density, which can be chemically converted to graphene for electronic applications such as transparent conductor thin films.[8,11,18]

Molecular monolayers floating at the air–water interface have been a subject of extensive interest since the 18th century.[19] In a typical process for preparing LB monolayers, amphiphilic molecules are first dissolved in a volatile organic solvent and then spread onto the water surface. As the solvent evaporates, the molecules are trapped on the water surface, forming a monolayer. A moving barrier is then used to change the area of the monolayer, thus effectively tuning the intermolecular distance. As the film is compressed, it can undergo phase transitions from gas to liquid to solid phases before collapsing into a multilayer. The film can be transferred to a solid substrate (e.g., by dip-coating), forming a monolayer coating over a large area. The LB technique is not limited by small molecules; monolayers of polymers[20,21] and nanomaterials[22–25] have been prepared in similar manner. Single-layer graphite oxide itself can be viewed as a cross-linked molecular monolayer.[26] If these monolayers are placed on a water surface, they can be collectively manipulated by the moving barrier. The GO sheets can then be pushed together edge-to-edge by compression. Face-to-face interaction may be induced *in situ* by overcompression, forcing GOSLs to slide on top of each other, or *ex situ* through sequential, layer-by-layer dip-coating. These types of interactions are important for understanding the properties of GO thin films, as they affect surface roughness, porosity, packing density, etc. On the other hand, for the practical use of GO for graphene-based electronics, it is critical to make large-area, flat, single-layer GO films. LB would be an ideal approach to achieve this.

Experimental Section

Graphite Oxide (GO) Synthesis and Purification. GO was prepared using a modification of Hummers and Offeman's method from graphite powders (Bay carbon, SP-1).[1,7,11,27] In a typical reaction, 0.5 g of graphite, 0.5 g of NaNO$_3$, and 23 mL of H$_2$SO$_4$ were stirred together in an ice bath. Next, 3 g of KMnO$_4$ was slowly added. All chemicals were purchased from Sigma-Aldrich and were used as received. Once mixed, the solution is transferred to a 35 ± 5 °C water bath and stirred for about 1 h, forming a thick paste. Next, 40 mL of water was added, and the solution was stirred for 30 min while the temperature was raised to 90 ± 5 °C. Finally, 100 mL of water was added, followed by the slow addition of 3

mL of H$_2$O$_2$ (30%), turning the color of the solution from dark brown to yellow. The warm solution was then filtered and washed with 100 mL of water. The filter cake was then dispersed in water by mechanical agitation. Low-speed centrifugation was done at 1000 rpm for 2 min. It was repeated until all visible particles were removed (about 3–5 times) from the precipitates. The supernatant then underwent two more high-speed centrifugation steps at 8000 rpm for 15 min to remove small GO pieces and water-soluble byproduct. The final sediment was redispersed in water with mechanical agitation or mild sonication using a table-top ultrasonic cleaner, giving a solution of exfoliated GO.

Langmuir–Blodgett (LB) Assembly of GO. When the as-prepared aqueous solution of GO is directly applied onto a water surface, most material sinks into the subphase. However, we found that methanol is a good solvent for the LB experiment since it disperses GO well and spreads on a water surface rapidly. A deionized (DI) water/methanol mixture with an optimal ratio of 1:5 was used for most LB experiments. After addition of methanol, the solution was sonicated for 30 min using a table-top ultrasonic cleaner. The average size of the GO sheets can be controlled by the time of sonication, and detailed studies are ongoing. Two centrifugation steps were taken to further purify the sample. First, the solution was centrifuged at 8000 rpm for 20 min to further remove smaller GO sheets and byproduct from the supernatant. The precipitate was collected and redispersed with 1:5 = water/methanol solution. The solution was then centrifuged at 2500 rpm for 10 min to remove aggregates and larger GO sheets. The final supernatant contained well-dispersed GO sheets with sizes in the range of 5–20 μm.

For LB, the trough (Nima Technology, model 116) was carefully cleaned with chloroform and then filled with DI water. GO solution was slowly spread onto the water surface dropwise using a glass syringe. Generally, the solution was spread with speed of 100 μL/min up to a total of 8–12 mL. Surface pressure was monitored using a tensiometer attached to a Wilhelmy plate. A GO film with faint brown color could be observed at the end of the compression. The film was compressed by barriers at a speed of 20 cm^2/min. The dimensions of the trough are 10 cm × 25 cm. Typical initial and final surface areas were around 240 and 40 cm^2, respectively.

The GO monolayer was transferred to substrates at various points during the compression by vertically dipping the substrate into the trough and slowly pulling it up (2 mm/min). As with the LB deposition of other materials, effective transfer occurs when the meniscus spreads on the substrate during dip-coating. We discovered that hydrophilic surfaces are necessary for effectively collecting the graphite oxide single layers from the LB film. Poor deposition was observed on hydrophobic surfaces obtained by silane treatment on silicon or glass. Therefore, only hydrophilic substrates were used in this work. Typically silicon wafers were treated with 1:1:5 = NH$_4$OH:H$_2$O$_2$:DI solution for 15 min to be more wettable by water. Other substrates used include glass, quartz and mica. Double layer GO was prepared by depositing the first layer using the method described above, drying the substrate in an oven at 80 °C for 1 h, and then doing the second deposition on the substrate using the same conditions.

Characterization. Brewster angle microscopy study was carried out on a homemade setup, which was described in great detail elsewhere.[28] The deposited film was characterized using scanning electron microscopy (SEM; Hitachi S-4800-II) and atomic force microscopy (AFM; Digital Instrument, MultiMode scanning probe). We have identified the proper set of conditions for reliably seeing single layers under SEM. All the SEM images were taken with low acceleration voltage (e.g., 0.8 kV) and high current (e.g., 20 μA). Under these conditions, single layers were readily visible and the contrast between single layer, double layer, and multiple layers

(18) Eda, G.; Lin, Y.-Y.; Miller, S.; Chen, C.-W.; Su, W.-F.; Chhowalla, M. *Appl. Phys. Lett.* **2008**, *92*, 233305.

(19) Franklin, B.; Smyth, A. H. *The writings of Benjamin Franklin*; Macmillan: New York/London, 1905; p 10 v.

(20) Sun, F.; Castner, D. G.; Mao, G.; Wang, W.; McKeown, P.; Grainger, D. W. *J. Am. Chem. Soc.* **1996**, *118*, 1856–1866.

(21) Reitzel, N.; Greve, D. R.; Kjaer, K.; Hows, P. B.; Jayaraman, M.; Savoy, S.; McCullough, R. D.; McDevitt, J. T.; Bjornholm, T. *J. Am. Chem. Soc.* **2000**, *122*, 5788–5800.

(22) Collier, C. P.; Saykally, R. J.; Shiang, J. J.; Henrichs, S. E.; Heath, J. R. *Science* **1997**, *277*, 1978–1981.

(23) Kim, F.; Kwan, S.; Akana, J.; Yang, P. *J. Am. Chem. Soc.* **2001**, *123*, 4360–4361.

(24) Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R.; Sun, Y.; Xia, Y.; Yang, P. *Nano Lett.* **2003**, *3*, 1229–1233.

(25) Whang, D.; Jin, S.; Wu, Y.; Lieber, C. M. *Nano Lett.* **2003**, *3*, 1255–1259.

(26) Abraham, F. F.; Goulian, M. *Europhys. Lett.* **1992**, *19*, 293–296.

(27) Kovtyukhova, N. I.; Ollivier, P. J.; Martin, B. R.; Mallouk, T. E.; Chizhik, S. A.; Buzaneva, E. V.; Gorchinskiy, A. D. *Chem. Mater.* **1999**, *11*, 771–778.

(28) Danauskas, S. M.; Ratajczak, M. K.; Ishitsuka, Y.; Gebhardt, J.; Schultz, D.; Meron, M.; Lin, B. H.; Lee, K. Y. C. *Rev. Sci. Instrum.* **2007**, *78*, 103705.

was apparent. AFM images recorded on the same samples confirmed the SEM observation. AFM images were taken with tapping mode at a scanning rate of 1 Hz. The apparent heights of all the GO sheets observed were around 1 nm, which is consistent with previously reported values.[11,32] GOSL films collected from the overpacked region (region d in Figure 2e) on a glass slide were reduced to graphene by exposure to hydrazine vapor. The samples were placed in a sealed Petri dish with 100 μL of anhydrous hydrazine (98%, Sigma-Aldrich) for 18 h at room temperature. They were then rinsed by DI water and dried in an 80 °C oven for 1 h. Four gold electrodes with dimensions of 1.5 mm × 7.5 mm × 40 nm and 1.5 mm separation were patterned on the slides using a thermal evaporator and a shadow mask. The $I-V$ curves were obtained using a Keithley 2400 source meter on a homemade probe station. The transmission spectrum was measured in the areas between the electrodes using a fiber optics spectrometer (Ocean Optics, USB 2000). Spectroscopy data acquired at five different points were averaged to plot the spectrum in Figure 6a (below). Average transmittance was calculated by averaging all the data points between 400 and 800 nm on the spectrum.

Results and Discussion

The as-made GO colloidal dispersion was purified by several centrifugation and/or dialysis steps. The size of the GOSLs in thus-treated samples was polydisperse but typically larger than 5 μm in diameter. With minimal sonication treatment, large sheets of tens of micrometers can be obtained. In order to transfer the GO onto a water surface, a volatile spreading solvent is needed. However, common water-immiscible spreading solvents, such as chloroform or toluene, are not good for dispersing the hydrophilic GO. In addition, prior studies showed that GO tends to collapse and adopt three-dimensional compact conformations in "poor", less polar solvents such as acetone.[29,30] Therefore, we chose the simplest polar protic alcohol—methanol—as the spreading solvent. The purified GO dispersion was therefore transferred into a 1:5 water/methanol mixture before spreading, and the GO colloids were found to be stable in this solution. Since a LB monolayer is very sensitive to surface-active impurities, all parts of the LB trough were thoroughly cleaned and tested before each experiment. Plasticware and rubber were avoided during the storage and handling of both the solvent and the dispersion to minimize contamination. The GO dispersion was carefully spread on the water surface drop-by-drop using a glass syringe. Usually a faint brown color could be observed. The monolayer was then stabilized for about 20 min before isothermal compression. Surface pressure was monitored using a tensiometer equipped on the LB trough. The monolayer was transferred to silicon wafers, glass slides, or mica disks by vertical dip-coating and imaged by SEM and AFM.

As the monolayer is compressed, slight darkening of the monolayer color can be observed, which is consistent with increased material density at the water surface. To confirm that the GO sheets were indeed supported by the air–water interface rather than suspended near but beneath the surface, the monolayer was examined *in situ* by surface-selective Brewster angle microscopy.[28,31] Highly reflective shining pieces were observed, indicating the presence of micrometer-sized, flat GO sheets (Supporting Information, Figure S2) at the surface. The density of the sheets can be reversibly altered during the compression–
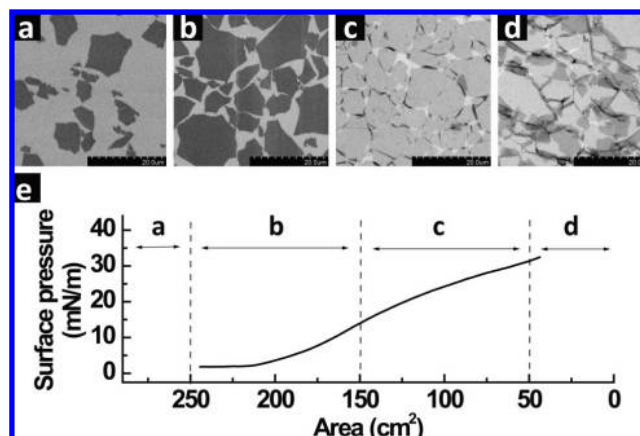

Figure 2. Langmuir–Blodgett assembly of graphite oxide single layers. (a–d) SEM images showing the collected graphite oxide monolayers on a silicon wafer at different regions of the isotherm. The packing density was continuously tuned: (a) dilute monolayer of isolated flat sheets, (b) monolayer of close-packed GO, (c) overpacked monolayer with sheets folded at interconnecting edges, and (d) over packed monolayer with folded and partially overlapped sheets interlocking with each other. (e) Isothermal surface pressure/area plot showing the corresponding regions a–d at which the monolayers were collected. Scale bars in a-d represent 20 μm.

expansion cycles. A gradual increase in surface pressure was recorded as the barrier was closed, as shown in the isothermal surface pressure–area plot in Figure 2e. SEM images of the monolayers collected at different stages of the plot clearly show four types of GO assembly. There was an initial gas phase where the surface pressure essentially remained constant during compression (region a in Figure 2e). Monolayer collected at this stage consisted of dilute, well-isolated, individual GO sheets (Figure 2a). It is worth noting that most of the GO sheets were larger than 5 μm in diameter, yet all of them were flat. Prior methods for making GO thin films, such as drop-casting, spin-coating,[8] spraying,[11] or filtration,[10,12] usually produced wrinkled sheets even with submicrometer sizes.

As the area was decreased, the surface pressure started to rise and the GO sheets were pushed closer to each other. A few turning points were observed on the isotherm plot as the monolayer entered the condensed phase, reflecting different types of interactions of the single layers. At the first stage of pressure increase (region b in Figure 2e), the GO sheets started to "touch" each other and eventually formed a close-packed monolayer, where they tiled the entire 2D surface (Figure 2b). The increase in surface pressure is likely due to the electrostatic repulsion between the GO sheets. AFM images of the same monolayers on a silicon wafer show uniform thickness of the GO sheets around 1 nm (Figure 3a), which is consistent with previous reports.[11,32] In close-packed films, the gaps between two GO sheets were often too small to resolve using our AFM. This suggests that LB assembly may be used for making nanogaps between GO or graphene sheets. When the monolayer was further compressed beyond the close-packed region, a further increase in surface pressure was observed. This is in contrast to monolayers of small molecules or hard colloids, which would collapse into multilayers, leading to constant or

(29) Hwa, T.; Kokufuta, E.; Tanaka, T. *Phys. Rev. A* **1991**, *44*, R2235–R2238.

(30) Wen, X.; Garland, C. W.; Hwa, T.; Kardar, M.; Kokufuta, E.; Li, Y.; Orkisz, M.; Tanaka, T. *Nature* **1992**, *355*, 426–428.

(31) Lipp, M. M.; Lee, K. Y. C.; Zasadzinski, J. A.; Waring, A. J. *Rev. Sci. Instrum.* **1997**, *68*, 2574–2582.

(32) Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. *Carbon* **2007**, *45*, 1558–1565.
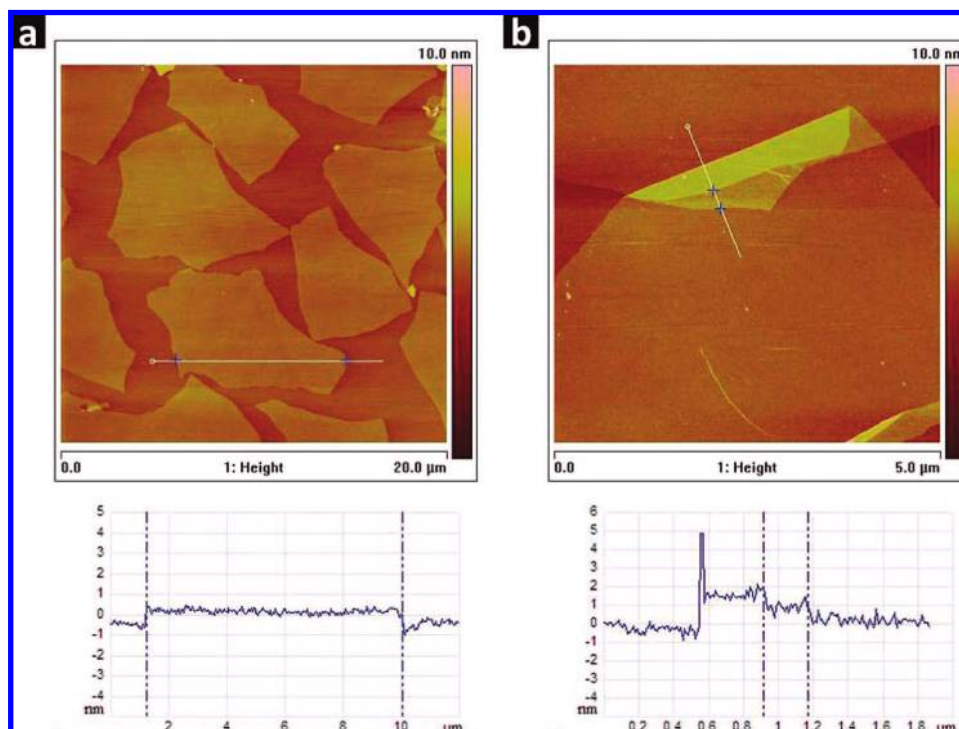
Figure 3. AFM images showing (a) a close-packed graphite oxide monolayer and (b) two touching GO sheets with folded edges on silicon wafer. The thickness of the graphite oxide sheets was measured to be around 1 nm, as shown in the line scans. Images (a) and (b) were recorded on the same samples used for Figure 2b,c, respectively.

reduced surface pressure.[33] A striking interaction between the GO sheets was revealed by the SEM images (Figure 2c). Instead of overlapping with each other, the GO sheets started to fold at the touching points along their edges. Since the single layers are soft and flexible, the increased surface pressure is thus dissipated by the folding and wrinkling of the edges, leaving the interior flat and essentially free of buckling or wrinkling. As shown in the AFM image (Figure 3b), the folds or wrinkles were usually much more than 2 nm, which would be the height for overlapped edges. They also produced a much higher contrast in the SEM images, marking the boundaries of the sheets. At this stage, the coverage of GO over the surface was much increased, yet the majority area of the monolayer was still flat. At even higher pressure, partial edge-overlapping was observed, leading to a nearly complete monolayer of interlocked GOSLs (Figure 2d). This edge-to-edge interaction mechanism continued to prevent the center of the GO sheets from wrinkling up to a point where there was no free space left in the monolayer. With the GO sheets interlocked with each other, the entire monolayer buckled like a whole piece of thin film upon further compression. Macroscopic wrinkles at millimeter scale, which can be seen by the eye, eventually led to the collapse of the monolayer.

Based on the total potential energy analysis (Figure 1c,f), LB films of GOSLs should be stable against flocculation or coagulation. The observed GOSL tiling behavior in Figure 2 is in good agreement with the hypothesis. The strong edge-to-edge repulsion resisted stacking or overlapping between layers, even when the monolayer was compressed. In addition, the 2D GO monolayers did show excellent stability, as they were

essentially fully reversible after many cycles of compression–expansion (Figure 4). SEM study confirmed that the folds, wrinkles, and partial overlapping observed during compression (Figure 2c,d) completely disappeared when the film was opened (Figure 4). Since the folding and overlapping would lead to partial face-to-face interaction, the disappearance of such structures upon monolayer expansion suggests that such interaction is not stable. Figure 4a shows representative surface pressure plots of three cycles of compression/expansion without sample collection. The curves have nearly the same shape and final pressure. However, there was a small shift of the gas–liquid phase transition point toward smaller area as the cycles continued (Figure 4b). This indicates the loss of a small amount of material from the monolayer after each cycle. Close examination of the monolayer before and after cycling revealed many double-layer structures consisting of a small GO sheet (<5 μm) on top of a much larger one (Figure 4c,d). Note that the small layer tended to completely overlap with the larger underlayer. No partially overlapped double layers were observed. These small sheets were probably pushed onto the neighboring larger ones at high surface pressure. This introduced the face-to-face type of interaction as discussed in Figure 1e. Once a small GO piece was pushed onto a large one, the electrostatic repulsion between the edges of the two sheets would lock them into completely overlapped or even nearly concentric arrangement. This double-layer structure is further stabilized by van der Waals and residual π–π stacking between the faces of each sheet. The absence of double layers of similarly sized sheets and partially overlapped double layers after the surface pressure was released suggests that face-to-face interaction (Figure 1d) between similarly sized single layers should be either unfavorable or reversible. Since GO samples obtained by oxidizing graphite particles are naturally polydisperse in size, one can take advantage of this unusual stacking behavior to make double

(33) Ybert, C.; Lu, W. X.; Moller, G.; Knobler, C. M. *J. Phys. Chem. B* **2002**, *106*, 2004–2008.
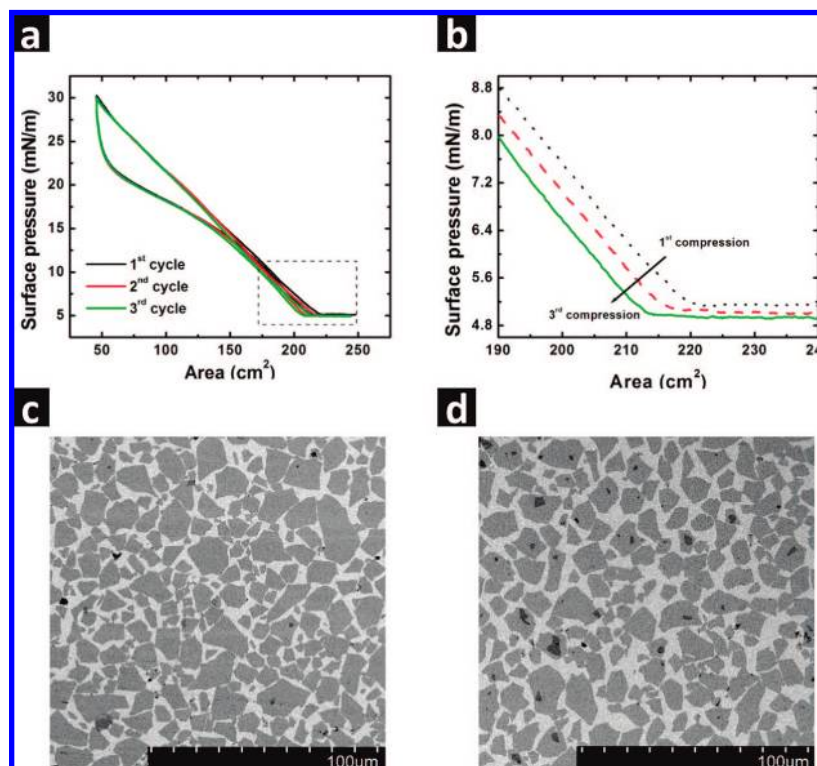
Figure 4. GOSL monolayer was highly reversible and stable against compression. (a) Isotherm plots of three sequential compression−expansion cycles. The three plots essentially overlapped with each other, except in the early stage of compression, as indicated with the dotted-line box. (b) Close-up view of the initial stage of compression, revealing a shift of the plots to the lower area direction, indicating materials loss at the air−water interface after isotherm cycles. The SEM images of the monolayers (c) before and (d) after cycling show that smaller graphite oxide sheets were pushed onto larger ones, thus effectively reducing the amount of materials at the air−water interface. It also creates double layers of graphite oxide sheets.
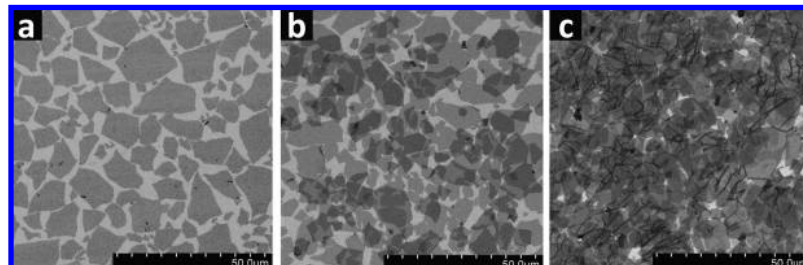
Figure 5. SEM images showing layer-by-layer assembly of graphite oxide double layers of similar sizes. (a) Close-packed single-layer graphite oxide monolayer as the first layer. (b) Double layers with dilute top layer. (c) Double layers with high-density top layer. The heavy degree of folding and wrinkling of the second layer in (c) suggests strong repulsion between the two layers.

layers or possibly even multilayers of GO by isothermal pressure−area cycling. Double layers were also made by sequential, layer-by-layer dip-coating. The first layer, collected at close-packed density, was either aged in air overnight or baked in an oven for 1 h to enhance its adhesion to the substrate. The second layer was then deposited at various pressures. Double GO layers were successfully made. However, the second layer of GO sheets experienced repulsion from both their neighbors and those in the underlayer. As a result, the newly deposited second layer tended to be wrinkled, especially at high density (Figure 5c). The density of the second layer was also lower than that of the first layer when deposited at the same surface pressure (Figure 5b).

The electrostatic repulsion between the GOSLs leads to the above-mentioned edge-to-edge and face-to-face assembly behaviors. Both stacking and overlapping appeared to be unfavorable, which is actually beneficial for forming GOSL monolayers. It makes LB assembly a fairly robust 2D tiling technique for

making high-quality monolayers. In fact, the area of the surface monolayer in our experiment was on the order of 100 cm^2, which is already at the scale of a 4 in. wafer. Large areas of GO single layers can be collected at the desired surface pressure, yielding uniform coverage of different types of monolayers (Supporting Information, Figure S3). Additional density control can be achieved by varying the pulling speed during LB transfer (Supporting Information, Figure S4). The GO single layers can be reduced by known methods (hydrazine, hydrogen, or thermal annealing) to graphene.[7,8] The close-packed monolayers (Figure 2b) would readily produce graphene wafers for large-scale device fabrication. The overpacked monolayers (Figure 2c,d) already constitute continuous electrical pathways that can be potentially useful for transparent conductor applications.[8,12,34,35]

(34) Wang, X.; Zhi, L. J.; Mullen, K. *Nano Lett.* **2008**, *8*, 323−327.
(35) Wang, X.; Zhi, L. J.; Tsao, N.; Tomovic, Z.; Li, J. L.; Mullen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2990−2992.
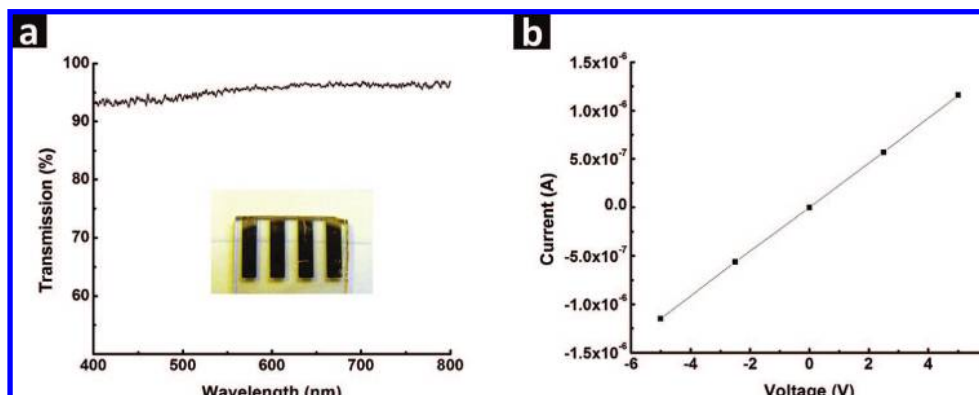
Figure 6. Transparent conducting thin film obtained by chemical reduction of an overpacked, interlocking GOSL monolayer such as those collected from region d of the isotherm plot in Figure 2. (a) Transmission spectrum of such a thin film deposited on a glass slide (inset), showing an average of 95.4% transmittance in the visible region. (b) Current−voltage plot of the same film obtained by four-point measurement.

As a proof of concept, we collected a GOSL monolayer at the overpacked region of the pressure−area plot (region d in Figure 2e) on a glass slide. The film was chemically reduced to graphene by exposure to hydrazine vapor. Four gold electrodes were patterned onto film for electrical measurement (Figure 6a, inset). Transmission measurement showed that the film has an average of 95.4% transmittance in the visible region of the spectrum (Figure 6a). Figure 6b is the current−voltage plot obtained by four-probe measurement. The sheet resistance was 1.9×10^7 Ω, which is comparable to previous reports on chemically reduced GO films.[8] The resistance can be reduced further by thermal treatment.[8]

Conclusion

We have successfully demonstrated Langmuir−Blodgett assembly of GOSLs and made the following discoveries. Water-supported monolayers of GOSLs can be made without any surfactant or stabilizing agent. The single layers formed stable dispersion against flocculation or coagulation when confined at the 2D air−water interface. The edge-to-edge repulsion between the single layers prevented them from overlapping during monolayer compression. The layers folded and wrinkled at their interacting edges at high surface pressure, leaving the interior flat. GOSL monolayers can be readily transferred to a solid substrate with density continuously tunable from dilute, close-packed to overpacked monolayers of interlocking sheets. When single layers of very different sizes are brought together face-to-face, they can irreversibly stack to form double layers. The monolayers can be readily imaged by SEM with high contrast between single and multilayers. The geometry-dependent GOSL interaction revealed here should provide insight into the thin-film processing of GO materials since the packing of GOSLs affects surface roughness, film porosity, packing density, etc. In addition, LB assembly readily creates a large-area monolayer of GOSL, which is a precursor for graphene-based electronic applications.

Supporting Information Available: Figure S1, pictures of GO colloidal solution; Figure S2, BAM images of GOSL monolayer; Figure S3, low-magnification SEM images showing GOSL monolayers corresponding to those in Figure 2; Figure S4, SEM images showing the effect of pulling speed on the GOSL monolayer density. This information is available free of charge via the Internet at http://pubs.acs.org.

JA806262M