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Graphene Oxide Sheets at Interfaces

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Abstract: Graphite oxide sheet, now called graphene oxide (GO), is the product of chemical exfoliation of graphite and has been known for more than a century. GO has been largely viewed as hydrophilic, presumably due to its excellent colloidal stability in water. Here we report that GO is an amphiphile with hydrophilic edges and a more hydrophobic basal plane. GO can act like a surfactant, as measured by its ability to adsorb on interfaces and lower the surface or interfacial tension. Since the degree of ionization of the edge −COOH groups is affected by pH, GO's amphiphilicity can be tuned by pH. In addition, size-dependent amphiphilicity of GO sheets is observed. Since each GO sheet is a single molecule as well as a colloidal particle, the molecule−colloid duality makes it behave like both a molecular and a colloidal surfactant. For example, GO is capable of creating highly stable Pickering emulsions of organic solvents like solid particles. It can also act as a molecular dispersing agent to process insoluble materials such as graphite and carbon nanotubes in water. The ease of its conversion to chemically modified graphene could enable new opportunities in solution processing of functional materials.

Introduction

Surfactants are amphiphilic substances that can adsorb on interfaces and lower the surface or interfacial tension, and these are now used in numerous technologies such as detergents, emulsifiers, and dispersing agents.[1] Graphite oxide sheet, now called graphene oxide (GO), is the product of chemical exfoliation of graphite and has been known for more than a century.[2,3] It is essentially a graphene sheet derivatized by carboxylic acid at the edges and phenol hydroxyl and epoxide groups mainly on the basal plane.[4−7] GO has been known to disperse well in water since its first discovery over a century ago and thus has been routinely described as hydrophilic in the literature.[5−9] As shown in Figure 1a, GO's water dispersity and hydrophilicity has been mainly attributed to the ionizable edge −COOH groups.[4,6] However, its basal plane is essentially a network of hydrophobic polyaromatic islands of unoxidized benzene rings.[4,10,11] Therefore, GO should be viewed as an amphiphile with a largely hydrophobic basal plane and hydrophilic edges. On the other hand, GO is characterized by two abruptly different length scales. While its thickness is determined by a single atomic layer, the lateral dimension extends up to tens of micrometers. Since GO has the characteristics of both a molecule and a colloidal particle, would it behave like a molecular amphiphile or a colloidal surfactant?[12,13] To test the hypothesis, we studied the activity of GO at air−water, liquid−liquid, and liquid−solid interfaces.

Experimental Section

GO was synthesized by a modified Hummers method[3,14] from graphite powder (Bay Carbon, SP-1). For the CO_2 flotation experiment, GO was dispersed in commercially available carbonated water at a concentration of 0.01 mg/mL. A higher GO concentration hinders Brewster angle microscopy (BAM) observation of floating materials, as the GO sheets in the solution can generate a high-level background scattering. The experiment was carried out on a Langmuir−Blodgett (LB) trough (Nima Technology) equipped with a tensiometer and a BAM (Nima Technology). Fluorescence quenching microscopy (FQM) was performed as previously reported using fluorescein/polyvinylpyrrolidone (M_w = 55 000 D) as the fluorescent layer.[15] To create a stock dispersion with polydispersed sizes, a heavily sonicated GO was mixed with an unsonicated GO dispersion. The size-dependent amphiphilicity of GO was tested at an air−water interface using an LB assembly. A small aliquot of the stock dispersion was spread onto the water surface from a

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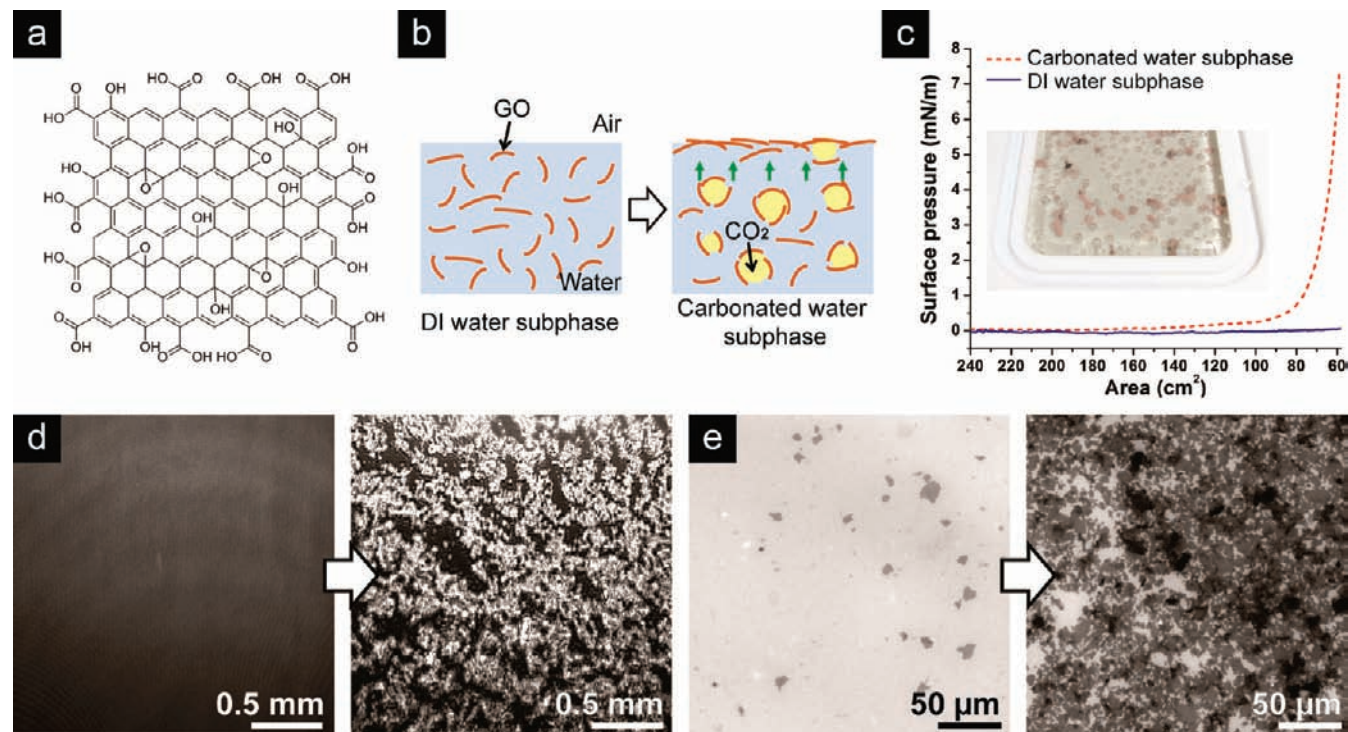(15) Kim, J.; Cote, L. J.; Kim, F.; Huang, J. *J. Am. Chem. Soc.* **2010**, *132*, 260–267.

Figure 1. GO at the air−water interface. (a) GO can be viewed as a two-dimensional molecular amphiphile, with hydrophobic π domains interspersed on its basal plane and hydrophilic −COOH groups on the edges as shown in the structural model.[4,10] (b) Schematic illustration showing the flotation of GO in carbonated water. GO is first captured by the rising CO_2 bubbles and then transported to the water surface. (c) Flotation experiment in an LB trough, in which boiling stones were added to promote the evolution of bubbles, as shown in the inset. After flotation, the increased surface pressure (dashed red line) during isothermal compression indicates the presence of GO at the water surface. In contrast, the surface pressure of GO in DI water remained nearly constant (solid blue line). Both (d) the *in situ* BAM images of the water surface and (e) the FQM images of GO sheets collected by dip coating show a massive increase of GO at the surface after flotation.

water−methanol mixture. Dip coating was performed from either between or outside of the barriers to collect GO sheets floating on the water surface or in the subphase, respectively. For Pickering emulsion experiments, organic solvent was mixed with GO water (i.e., GO dispersed in deionized (DI) water, 0.05 mg/mL) at half or equal volume and shaken by hand. Generally, a decreased volume ratio of organic solvent to GO water produced better emulsions. Microscopy images of the emulsion droplets were taken directly through the horizontally placed vials with a Nikon SMZ-1500 stereoscope. The diameters of >100 randomly chosen droplets (>20 for very large ones) were measured. The pH value of GO water was modified by adding HCl (1 M) or NaOH (1 M) solution. The ζ potential was measured with Malvern Instruments' Zetasizer Nano system. Drop shape analysis was performed with a Krüss DSA 100 instrument by creating a drop of aqueous GO dispersion with a volume of ∼35 μL in toluene. The drop volume was held constant for 40 min before being reduced by about 30% at a rate of 2.5 μL/min. For the solid dispersion experiments, graphite (Asbury, 3763) or carbon nanotubes (CNT, Strem Chemicals, multiwalled, diameter around 20 nm) powder was added into 10 mL of GO water at a mass ratio of 30:1 (graphite/GO) or 1:3 (CNT/GO), respectively. Then the dispersion was sonicated for 30 min using a Misonix S-4000 cup-horn ultrasonicator. A maximum amplitude of 80% was employed for graphite and 40% for CNT samples, respectively. After sonication, the supernatant was carefully collected and centrifugated at 1000 rpm for 5 min to remove undispersed chunks. For optical absorbance measurements, the CNT-GO water was diluted five times and measured on a UV−vis spectrometer (Beckman, DU 520). Scanning electron microscopy (SEM) images were taken on a Hitachi FE-SEM S-4800 instrument. Atomic force microscopy (AFM) images were acquired on a scanning probe microscope (Veeco, MultiMode V). CNT/GO thin films were prepared by vacuum filtration and transferred onto quartz substrates for sheet resistance measurement. To reduce GO, the film was

thermally annealed at 200 or 400 °C for 1 h in a muffle furnace. GO was also chemically reduced by exposing to hot hydrazine vapor (hydrazine monohydrate, Sigma Aldrich) at 200 °C for 1 h. Sheet resistance was measured by a four-point probe setup.

Results and Discussion

GO at the Air−Water Interface. In prior work, we first discovered that GO can float on the water surface during LB assembly without the need for structural modification or extra surfactant.[14] This suggests that GO should be surface active, just like molecular amphiphiles. If this is true, the surface of GO water should be covered with a layer of sheets, which can be directly observed by BAM—a surface selective imaging technique.[16] As shown in Figure 1d (left), BAM observation of freshly prepared GO water revealed little surface-active material. However, GO sheets started to appear after a few hours. This is attributed to the slow diffusion of GO sheets, which are typically micrometer-sized, to the surface due to their large "molecular" mass. To accelerate their migration to the surface, we designed a flotation process using commercially available carbonated water (Figure 1b, right). Boiling stones were added to release the solvated CO_2 (Figure 1c, inset). If GO sheets are indeed surface-active, they would adhere to the rising CO_2 bubbles and become thermodynamically trapped after they reach the air−water interface to minimize the surface energy (i.e., lower the surface tension). The experiment was carried out in an LB trough equipped with a tensiometer to monitor the surface tension and a BAM to watch the surface. To facilitate the

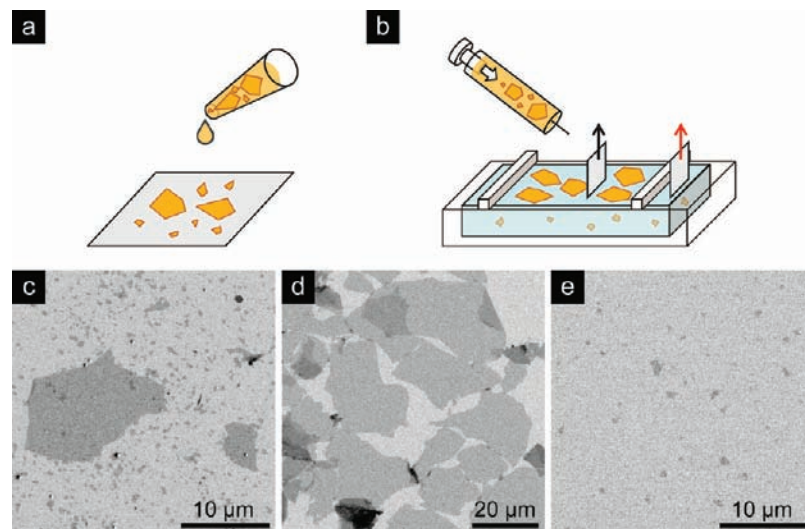(16) Marshall, G.; Dennin, M.; Knobler, C. M. *Rev. Sci. Instrum.* **1998**, *69*, 3699–3700.

Figure 2. Size-dependent amphiphilicity of GO and spontaneous *in situ* size separation during LB assembly. GO sheets were deposited on Si wafer from the same stock dispersion by (a) drop casting and (b) LB assembly. In (b), samples were collected by dip coating from both the surface (between the barriers, black arrow) and the subphase (outside the barriers, red arrow). (c) An SEM image of the drop-casted sample reveals both large (>5 μm) and small GO pieces (≤1 μm) in the stock dispersion. However, during LB assembly spontaneous size separation occurred, in which the air−water interface had effectively acted as a filter to support the large sheets on the surface (d) while sinking the small pieces into the subphase (e). This implies that smaller GO pieces are more hydrophilic.

observation, the floating materials were concentrated by compressing the water surface using barriers. In a control experiment, the surface pressure of GO water, which is essentially a measure of decreased surface tension,[17] remained unchanged even after full compression (Figure 1c, solid blue line). However, increased surface pressure after flotation was clearly observed (Figure 1c, dashed red line). Meanwhile, BAM revealed a large amount of material on the surface right after the evolution of bubbles (Figure 1d, right). The floating materials were collected on a glass substrate, which can be conveniently imaged by an FQM technique we recently developed.[15] Figure 1e confirms the much increased surface density of GO sheets after flotation. Flotation can be achieved with other gases such as nitrogen and air through DI water.[18] Upward convection flows induced by heating or evaporation were also found to accelerate the surface enrichment of GO sheets, as revealed by BAM observation. The surface activity of GO thus confirmed that it is indeed amphiphilic. This new insight is important for understanding the processing and assembly of GO-based materials. For example, now it is clear why GO tends to form a thin film at the water surface during evaporation.[19,20]

Size-Dependent Amphiphilicity. The hypothesis that GO is an amphiphile with a largely hydrophobic basal plane and hydrophilic edges implies that its amphiphilicity should be size dependent. As the size decreases, the edge-to-area ratio would increase. Therefore, smaller sheets should be more hydrophilic due to higher charge density resulting from the ionizable edge −COOH groups. To test this idea, GO water was heavily sonicated to reduce the size of GO sheets. Indeed, increased ζ potential of the GO dispersion was observed after sonication. The dispersion of smaller GO sheets was then mixed with an unsonicated sample to create a new stock dispersion. The GO

sheets were then deposited on a Si wafer by drop casting (Figure 2a) and imaged to evaluate their sizes. The SEM image in Figure 2c reveals both large (>5 μm) and small (≤1 μm) GO pieces in the stock dispersion. The stock dispersion was then spread onto the air−water interface for LB assembly.[14] If GO has size-dependent amphiphilicity, larger sheets should float on the water surface while smaller ones could sink due to increased hydrophilicity. This was indeed observed. As shown in Figure 2b, GO sheets floating on the surface were collected by dip coating from the area between the two barriers, while those in the subphase were collected by dip coating from the area outside the two barriers. SEM images (Figure 2d,e) of samples thus collected clearly show that spontaneous size separation did occur during LB assembly. The density of GO sheets collected from the subphase was low, due to much lower GO concentration in the bulk of the subphase than on the surface. The results support the hypothesis that GO becomes more hydrophilic as its size decreases, which could be used to design methods of size separation as demonstrated in Figure 2. It is also quite intriguing that the water surface itself acts as a size-separation filter for GO sheets, which could be potentially extended to other colloid systems.

GO at an Oil−Water Interface. Next we found that GO can act as an emulsifier to create submillimeter-sized organic solvent droplets (e.g., toluene) that are stable in water for months (Figure 3). This is characteristic of particle stabilized Pickering emulsions,[21−24] suggesting that GO is acting like a colloidal surfactant.[12,13] The size of the toluene droplets was found to depend on the concentration of GO water. Figure 3a−g shows that as the GO concentration is reduced, the volume of the emulsion phase is decreased. Meanwhile, the average sizes of the droplets increase (Figure 3h), which is consistent with

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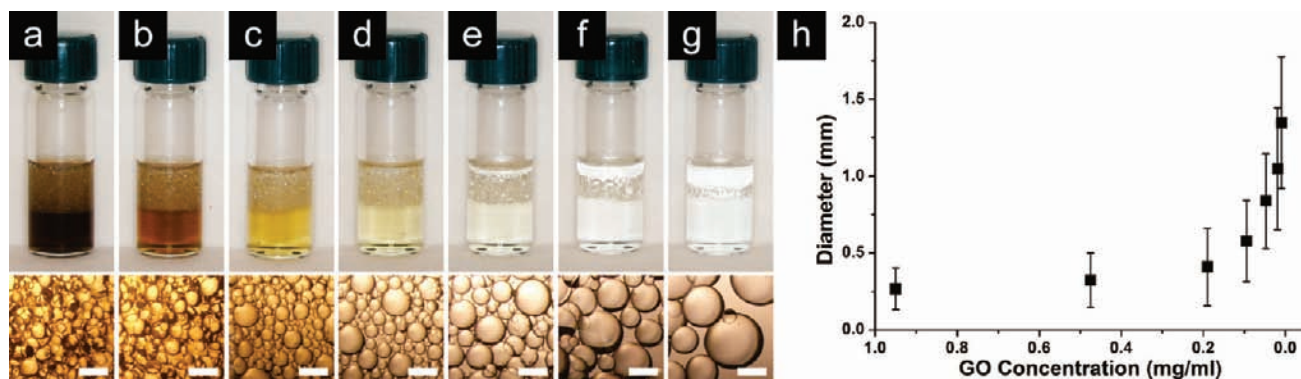
Figure 3. GO at the liquid−liquid interface. GO sheets can stabilize oil droplets in water by adsorbing at the oil−water interface, forming Pickering emulsions. (a−g) Toluene droplets formed upon shaking a tolune/GO water mixture, where the concentration of GO was varied from (a) 0.95 mg/mL to (b) 0.47, (c) 0.19, (d) 0.095, (e) 0.047, (f) 0.019, and (g) 0.0095 mg/mL, respectively. The bottom row shows microscopy images of the toluene droplets. All scale bars are equal to 1 mm. (h) As the concentration of GO was decreased, the volume of the emulsion phase decreased (a−g, top), while the size of oil droplets increased from (a) 0.267 mm to (b) 0.323, (c) 0.409, (d) 0.578, (e) 0.838, (f) 1.047, and (g) 1.347 mm in diameter, respectively (a−g, bottom, h).
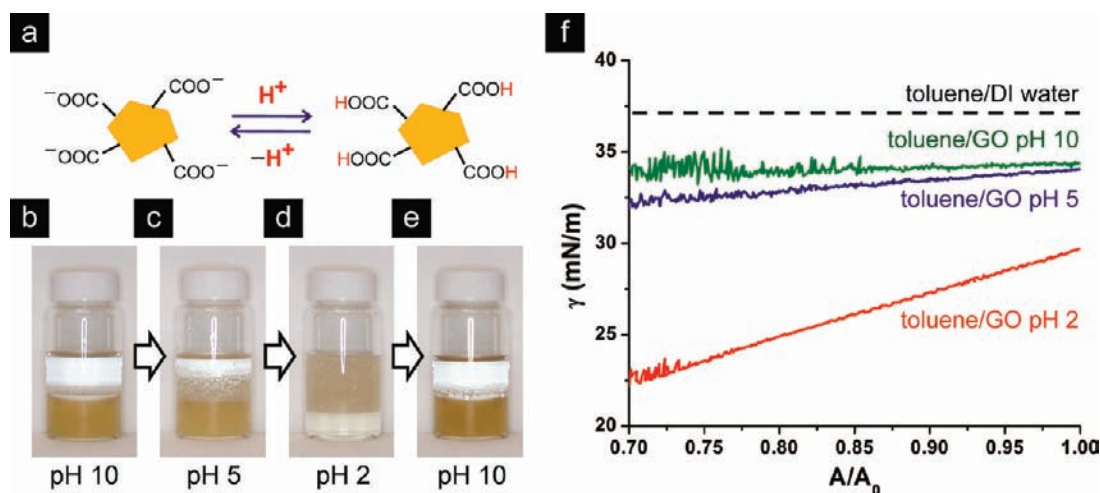

Figure 4. pH-dependent amphiphilicity of GO and its Pickering emulsions. (a) The edge −COOH groups can be reversibly protonated and charged, rendering pH-dependent amphiphilicity of GO. Parts (b)−(e) show the toluene−GO water biphasic mixtures at different pHs. (b) In base solution, GO is deprotonated, charged, and more hydrophilic and therefore remains in the aqueous phase. (c, d) In acidic solutions, GO becomes more protonated, less charged, and more hydrophobic. Therefore, it prefers the oil−water interface, helping to stabilize the Pickering emulsion droplets. At around pH 2 (d), GO can be completely extracted from water to the oil−water interfaces. (e) The emulsion is destabilized when the pH is raised back to 10, returning GO to the aqueous phase. (f) Interfacial tension (γ) between toluene and aqueous GO dispersions at different pH values. Data are obtained by shrinking a suspended aqueous droplet so that the overall interfacial area decreases from an initial value of A_0 to a lower value of A. A decrease in interfacial tension was observed for all pH values but became more pronounced at lower pH, confirming the pH-dependent amphiphilicity of GO.

Pickering emulsions stabilized by colloidal particles.[25] Although the submillimeter-sized toluene droplets (Figure 3a−d) are much larger than the typical Pickering emulsions stabilized by colloidal particles (e.g., silica[25]), they were remarkably stable against coalescence due to the high surface area of GO, which allows them to be kinetically trapped at the interface. The areas of GO sheets used in our experiments are typically in the range of hundreds to thousands of square micrometers, which is many orders of magnitude higher than the cross-sectional areas of typical colloidal particles.

   pH-Dependent Amphiphilicity. The amphiphilicity of GO can be tuned by changing the pH, as it affects the degree of ionization of the edge −COOH groups. For example, high pH values promote the deprotonation of the −COOH groups, which would make GO more charged (Figure 4a). In fact, the ζ potentials of GO water were measured to be −50.2 mV at pH

10 and −22.7 mV at pH 2, respectively, which were consistent with a prior report in literature.[6] Therefore, GO sheets should become more hydrophilic as the pH is increased. Indeed, when the pH was tuned to 10, GO was found to stay in the water phase and no Pickering emulsions were created even after vigorous shaking (Figure 4b). However, as the pH was decreased, GO-coated toluene droplets started to form. Figure 4c shows the emulsion phase obtained at around pH 5. In comparison to Figure 4b, the color of the water phase was paler, since some GO was transferred to the emulsion phase. When the pH was lowered to 2, nearly all the GO was extracted, leaving the water phase clear of color (Figure 4d). Meanwhile, the emulsion phase reached its maximum volume. When the pH was adjusted back to 10, the droplets coalesced into a continuous phase, ejecting GO back to water (Figure 4e). Therefore, GO can be reversibly shuttled between water and the emulsion phase, which could make it useful for extraction or phase transfer applications. The pH-dependent activity of GO

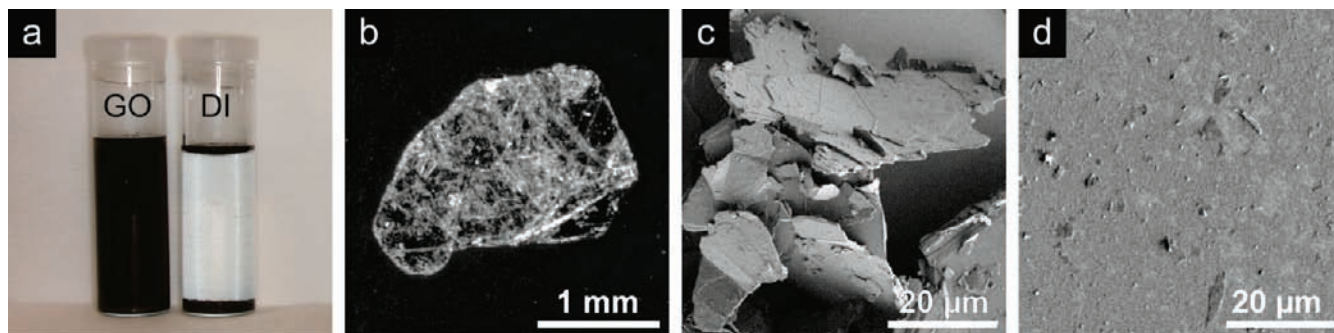(25) Frelichowska, J.; Bolzinger, M. A.; Chevalier, Y. *Colloid Surf. A* **2009**, *343*, 70−74.

Figure 5. GO can act as a surfactant to disperse insoluble solid in water. (a) Graphite powder turns into a stable colloidal dispersion in GO water after sonication (left vial). In contrast, it does not disperse at all in DI water (right vial). Microscopy images (b, optical microscopy; c and d, SEM) of untreated graphite powders and samples sonicated in DI and GO water, respectively, show orders of magnitude size reduction after sonication in GO water.

was confirmed by drop shape analysis of the interfacial tension between GO water and toluene.[26] Figure 4f shows that a decrease in interfacial tension during compression was observed at all pH values but was much more pronounced for the acidic GO dispersions. In control experiments, the GO water was filtered once more and redispersed in DI water. Drop shape analysis showed that the reduction of interfacial tension by the filtrate was not as significant as that induced by the purified GO. Therefore, GO indeed acted as a surfactant for the oil−water system, as measured by its ability to adsorb at the oil−water interface (Figure 4d) and reduce the interfacial tension (Figure 4f). It was also found that GO can stabilize aromatic solvents more efficiently than aliphatic solvents (see the Supporting Information, Figure S1), presumably due to stronger π−π interactions.

Although the reduction in interfacial tension was modest, Pickering emulsions in GO water appeared stable for an extended period of time (at least months). The large surface areas of the GO sheets can help them to be kinetically trapped at the interface, rendering long-term emulsion stability, if they indeed adopt the extended, flat-sheet geometry at the interface. The morphology of GO sheets on the droplet was indirectly examined by transferring them to a substrate. This was done by dip coating from the emulsion phase. When the substrate was in contact with the oil droplets, it tended to break the oil droplets and "peel off" the interfacial GO sheets, in a way similar to contact transfer[27] or Langmuir−Shaffer deposition.[17] FQM imaging revealed that although there were many multilayer islands, the underlying layer was largely a monolayer of flat GO sheets (see the Supporting Information, Figure S2). This implies that a monolayer of GO is sufficient to stabilize the oil−water interface. The multilayer domains were likely due to secondary deposition from collapsing droplets as they were broken by the substrate. Since GO is much enriched at the oil−water interfaces, dip coating from the emulsion always produces films much denser than those from the original GO water, which turns out to be a facile method for making GO films with high coverage.

GO as a Dispersing Agent for Graphite and Carbon Nanotubes. One of the major applications of surfactants is as dispersing agents for the solution processing of solids.[1] Inspired by the surfactant behaviors of GO at the air−water and

liquid−liquid interfaces, we proceeded to the solid−liquid interface to see if GO could act as a molecular dispersing agent. As a proof of concept, we chose graphite and CNTs as the model system, both of which are known to be difficult to process in water. Since GO has many π-conjugated aromatic domains in its basal plane, it should be able to strongly interact with the surface of graphite and CNTs through π−π attractions. Some earlier reports also showed that GO was capable of adsorbing drug or dye molecules through π−π interactions.[28−30] Therefore, the excellent water processability of GO could be inherited by forming complexes with graphite particles or CNTs. Figure 5a shows that GO can effectively disperse graphite powders in water. The starting powders were hundreds of micrometers to millimeters in diameter (Figure 5b). After being sonicated in water, they broke into thinner pieces of tens of micrometers (Figure 5c) but still settled down right afterward (Figure 5a, right). However, in GO water, much smaller particles were obtained with diameters of only a few micrometers (Figure 5d). This represents reduction in size of nearly 3 orders of magnitude. In addition, the particles were found to be covered by GO sheets. The graphite dispersion in GO water stayed stable for days. Even though a large portion of the suspended particles eventually settled down, they could be readily redispersed by gentle shaking or mild sonication. The greater size reduction in GO water is likely a result of surface functionalization by GO, which makes the graphite particles better suspended and more effectively sonicated. On the other hand, the presence of GO sheets should greatly retard the motion of graphite particles in water during sonication. Therefore, when ultrasound induced microjets impinge on the particles, their kinetic energies can be better directed to break the particles.

A tremendous amount of effort have been devoted to making CNTs water processable through wrapping by water-soluble materials.[31−34] Since many surfactants for dispersing CNTs have

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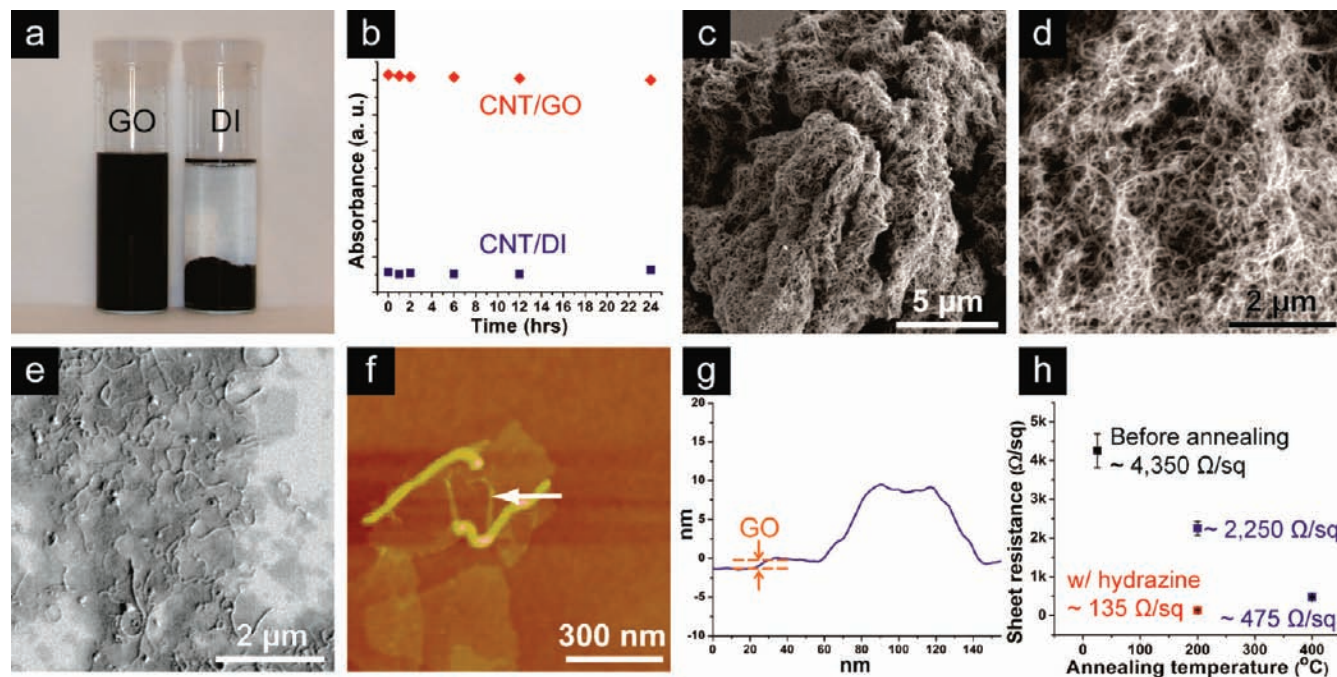(34) Vaisman, L.; Wagner, H. D.; Marom, G. *Adv. Colloid Interface Sci.* **2006**, *128*, 37–46.

Figure 6. Dispersing CNTs in GO water. (a) After sonication, CNTs (multiwalled) form a colloidal dispersion in GO water (left vial), while in DI water they rapidly aggregate (right vial). (b) The stability of the CNT dispersion was monitored by its absorbance in the visible range, which stayed nearly constant over 24 h. Such dispersions remained stable for at least a couple of months. The absorbance of the supernatant of a CNT/DI water sample was negligible, which is consistent with the poor dispersity of CNT in water. SEM images of the sample (c) before and (d) after sonication in DI water reveal that it does not disentangle the CNTs. (e) In contrast, after sonication in GO water, the CNTs are well dispersed and disentangled. (f) AFM image of GO stabilized CNTs deposited on a SiO_2/Si substrate. (g) Height profile data along the arrow drawn in (f) reveal that the CNT is adhered to a GO single layer. (h) Increased electrical conductivity of the CNT/GO films after thermal (blue dots) or chemical treatments (red dot).

polyaromatic components (e.g., pyrene[35]), GO should be able to adhere to CNTs and disperse them in water as well. Figure 6a shows that CNTs indeed dispersed well in GO water with a 1:3 mass ratio after sonication. As is the case with graphite, sonication alone does not disperse CNTs in water. The colloidal stability of the CNT-GO water was monitored by its optical absorbance over a period of 24 h (Figure 6b), which remained nearly constant after sonication. The dispersion was found to be stable for at least a few months. Microscopy analysis revealed that the initial CNTs samples were heavily entangled (Figure 6c), which remained largely unaffected by sonication in water (Figure 6d). In contrast, CNTs sonicated in GO water were completely disentangled. Extensive microscopy observations by SEM (Figure 6e) and AFM (Figure 6f,g) revealed that almost all the CNTs in the sample were adhered to GO (Figure 6e), which is consistent with our hypothesis. Although the CNTs shown in Figure 6 were multiwalled, we have found that GO can also effectively disperse single-walled CNTs in water.

GO can also better disperse other π-conjugated materials such as conducting polymer polyaniline powders. Since it can be readily reduced to conductive, chemically modified graphene,[5,7] GO could be a particularly attractive dispersing agent for solution processing of materials for electronic applications, since now the surfactant itself is a functional component as well. Commonly used dispersing agents such as molecular surfactants,[33,34] polymers,[36] and DNA[37] are usually insulating materials, which

need to be removed afterward to avoid decreased conductivity. However, GO can actually provide more conducting pathways in the final complex after it is reduced.[38,39] Figure 6h shows that the sheet resistance of a vacuum-filtered GO−CNT film indeed decreased significantly after either hydrazine vapor treatment or thermal annealing.

Conclusion

In conclusion, despite its excellent dispersity in water, GO is an amphiphile that can adsorb onto interfaces and lower surface and interfacial tension. Its amphiphilicity can be tuned by changing pH as it shuttles between water and the oil−water interface. Size-dependent amphiphilicity was also observed, leading to spontaneous interfacial size separation. GO is essentially a single atomic sheet, while its lateral dimension extends to the size of colloidal particles, which renders it a unique material exhibiting molecule−colloid duality. It creates highly stable Pickering emulsions of organic solvents like colloidal particles and disperses insoluble solids in water like molecular surfactants. This new insight echoes our earlier view that GO is an unconventional soft material.[14,18] It should help to better understand and improve the solution processing of GO-based graphene materials and open up opportunities to design new functional GO-based hybrid materials.

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Supporting Information Available: Emulsion droplets of common organic solvents in water stabilized by GO at different pH (Figure S1) and FQM images of GO sheets dip-coated from the emulsion phase (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

JA102777P

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