

GRAPHENE OXIDE SHEETS AT AIR-WATER, LIQUID-WATER AND SOLID-WATER INTERFACES

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Introduction

Graphene oxide (GO) sheets has been known to disperse well in water since its first discovery [1-2], and thus has been routinely described as hydrophilic. GO's water dispersity and hydrophilicity has been mainly attributed to the ionizable edge -COOH groups. However, its basal plane is essentially a network of hydrophobic polyaromatic islands of unoxidized benzene rings. Therefore, GO should be viewed as an amphiphile with a largely hydrophobic basal plane and hydrophilic edges. Meanwhile, 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 both the characters of a molecule and a colloidal particle, would it behave like molecular amphiphiles or colloidal surfactants? To test the hypothesis, we studied the activity of GO at air-water, liquid-liquid, and liquid-solid interfaces.

Experimental

GO was synthesized by modified Hummers method [2-3]. For the CO₂ flotation experiment, GO was dispersed in carbonated water at a concentration of 0.01 mg/ml. The experiment was carried out on a Langmuir-Blodgett (LB) trough equipped with a tensiometer and a Brewster angle microscope (BAM). For Pickering emulsion experiments, organic solvent was mixed with GO water (*i.e.*, GO dispersed in deionized water, 0.05 mg/ml) at half or equal volume and shaken by hand. pH value of GO water was modified by HCl (1M) or NaOH (1M) solution. For the solid dispersion experiments, graphite or multi-walled CNTs (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 minutes using a Misonix S-4000 cup-horn ultrasonicator. After sonication, the supernatant was carefully collected and centrifugated at 1000 rpm for 5 minutes to remove undispersed chunks. SEM images were taken on a Hitachi FE-SEM S-4800.

Results and Discussion

We first discovered that GO can float on water surface during LB assembly without the need for structural modification or extra surfactant [3]. This suggests that GO should be surface active 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. As shown in Figure 1c (left), BAM observation of freshly prepared GO

water revealed little surface active materials. However, GO sheets started to appear after a few hours. This is attributed to the slow diffusion of micron sized GO sheets to the surface due to their large “molecular” mass. To accelerate their migration to surface, we designed a flotation process using carbonated water (Fig. 1a, right). In this process, GO sheets were dispersed in carbonated water and boiling stones were added to release the solvated CO₂ (Fig 1b, inset). If GO sheets are indeed surface active, they would adhere to the rising CO₂ bubbles, and become thermodynamically trapped after they reach the air-water interface to minimize the surface energy. Indeed, increased surface pressure after flotation was clearly observed (Fig. 1b, dashed red line). However, in the control experiment, the surface pressure of GO water remained unchanged (Fig 1b, solid blue line). BAM images also revealed a large amount of materials on the surface right after the evolution of bubbles (Fig. 1c, right).

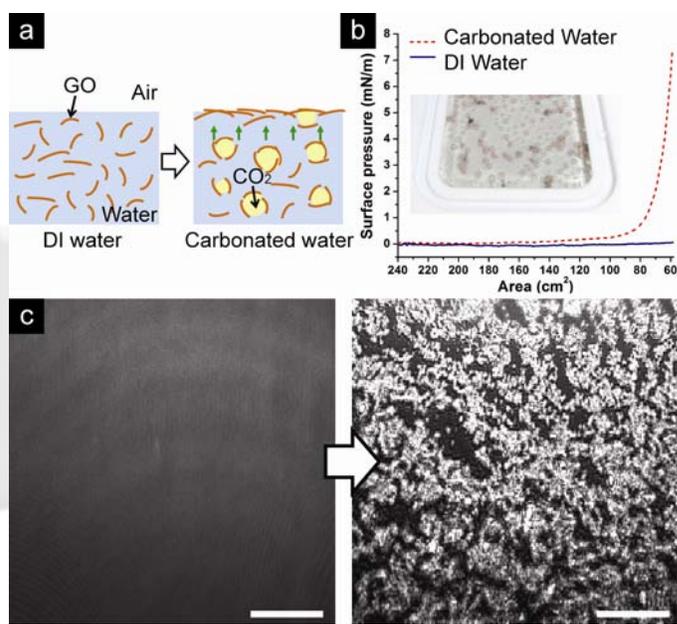


Fig. 1 GO at air-water interface. (a) Schematic illustration showing the flotation of GO in carbonated water. (b) After flotation, the increased surface pressure (dashed red line) indicates the presence of GO at the surface. (c) *in-situ* BAM images of the water surface before and after flotation. Scale bars = 0.5 mm.

Next we found that GO can act as an emulsifier to create sub-millimeter sized organic solvent droplets (*e.g.*, toluene) stabilized in water for months (Fig. 2d). This is characteristic of particle stabilized Pickering emulsions [4], suggesting that GO is acting like a colloidal surfactant. The amphiphilicity of GO can be tuned by changing pH as it affects the degree of ionization of the edge -COOH groups. High pH values promote the deprotonation of the -COOH groups, which would make GO more charged (Fig. 2a). Therefore, GO sheets should become more hydrophilic as the pH is increased.

Indeed, when the pH was tuned to 10, GO were found to stay in the water phase and no Pickering emulsions were created (Fig. 2b). However, as the pH was decreased, GO coated toluene droplets started to form. Figure 2c shows the emulsion phase obtained at pH=5. Compared to Figure 2b, the color of 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 (Fig. 2d). Meanwhile, the emulsion phase reached its maximal volume. When the pH was adjusted back to 10, the droplets coalesced into a continuous phase, ejecting GO back to water (Fig. 2e). Therefore, GO can be reversibly shuttled between water and the emulsion phase, which could make it useful for extraction or phase transfer applications.

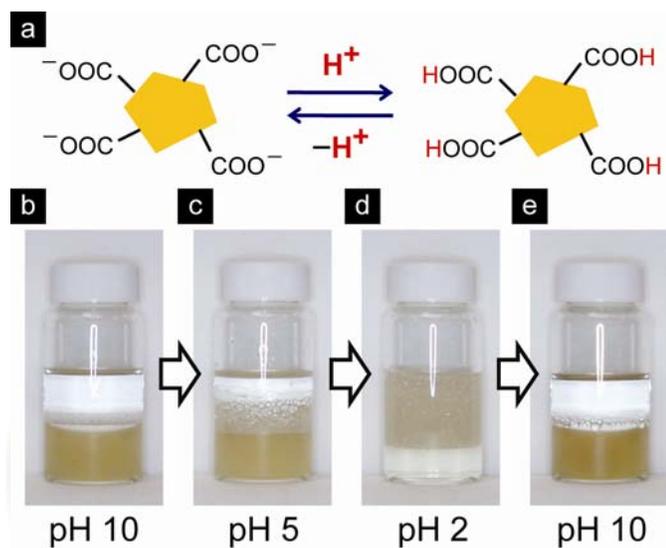


Fig. 2 Pickering emulsion stabilized by GO. (a) The edge COOH groups can be reversibly protonated, rendering pH dependent amphiphilicity of GO. (b-e) show the toluene-GO water biphasic mixtures at different pH.

We then proceeded to the solid-liquid interface to see if GO can act as a molecular dispersing agent. 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. Figure 3a shows that GO can effectively disperse graphite powders in water. When sonicated in DI, graphite particles broke into thinner pieces of tens of microns (Fig. 3b), which settled down right afterwards (Fig. 3a, right). However, in GO water, much smaller particles were obtained with diameters of only a few microns (Fig. 3c). 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. Figure 3d shows CNTs dispersed well in GO water, which was found to be stable for at least a few months. Microscopy analysis revealed that the initial CNTs samples were heavily entangled which remained largely unaffected by sonication in water (Fig. 3e). In contrast, CNTs sonicated in GO water were

completely de-bundled (Fig. 3f). Since it can be readily reduced to conductive, chemically modified graphene [5], GO could be a particularly attractive dispersing agent for solution processing of materials towards electronic applications.

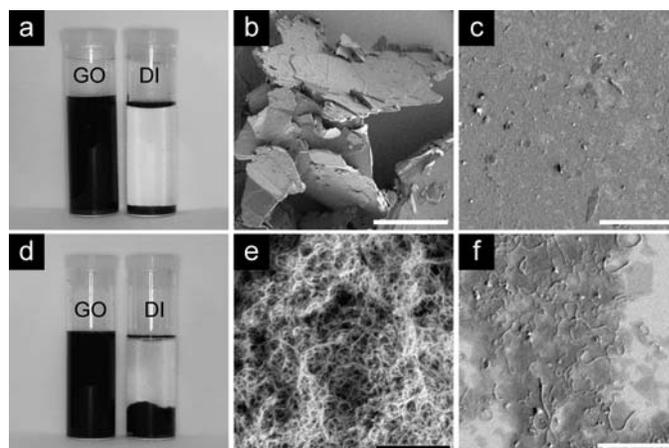


Fig. 3 Dispersing (a-c) graphite and (d-f) CNT in DI (b, e) or GO (c, f) water. Scale bars in b, c = 20 μm ; e, f = 2 μm .

Conclusions

In conclusion, despite of its excellent dispersibility in water, GO should be better described as an amphiphile, which can adsorb onto interfaces and lower surface and interfacial tension. Its amphiphilicity can be tuned by pH. GO can act like colloidal particles to create highly stable Pickering emulsions of aromatic solvents, and can disperse insoluble solids in water like molecular surfactants. This new insight should help to better understand and improve the solution processing of GO based graphene materials, and open up opportunities to design new functional hybrid materials.

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