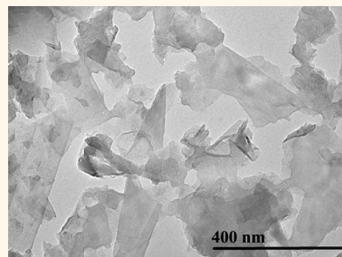


Conductive Thin Films of Pristine Graphene by Solvent Interface Trapping

Steven J. Woltornist,^{†,‡} Andrew J. Oyer,^{‡,‡} Jan-Michael Y. Carrillo,^{‡,§} Andrey V. Dobrynin,^{‡,§} and Douglas H. Adamson^{†,‡,*}

[†]Department of Chemistry, [‡]Institute of Materials Science, Polymer Program, and [§]Department of Physics, University of Connecticut, Storrs, Connecticut 06269, United States. [‡]These authors contributed equally.

ABSTRACT Graphite's insolubility in conventional solvents is a major obstacle to its utilization. This challenge is typically addressed by chemical modification such as oxidation, followed by reduction. However, pristine graphene possesses superior properties as oxidation and reduction lead to degradation of the graphene. Here we demonstrate the use of an interfacial trapping technique to assemble laterally macroscopic films of pristine graphene that are up to 95% transparent. This is accomplished by modest sonication of natural flake graphite in a water/heptane mixture to form continuous films at the interface between two immiscible liquids. Furthermore, the graphene sheets readily climb hydrophilic solid substrates, forming a homogeneous thin film one to four layers thick. These films are composed of a network of overlapping graphene sheets and shown to have long-range structure with conductivities on the order of 400 S/cm.



KEYWORDS: graphene · interfacial self-assembly · transparent conductor · solution processing · natural flake graphite

The availability of inexpensive,¹ transparent, and conductive pristine graphene films has the potential to revolutionize solar power harvesting, photonics, and flexible electronics technology.^{2–4} Graphene insolubility and the intrinsic tendency to aggregate, however, have necessitated the use of either reduced graphite oxide^{5–8} or chemical vapor deposition (CVD)^{9–12} sources of graphene. Chemical modification of graphene significantly reduces film conductivity,¹³ while vapor deposition requires high production costs. It would be tremendously advantageous to use pristine graphene to lower the cost and boost film conductivity.

In this paper, we describe for the first time a one-step technique to produce laterally macroscopic, transparent, and conductive films from pristine (untreated and unmodified) natural flake graphite with well-controlled thickness. The films are one to four graphene layers thick and inexpensive to produce. Furthermore, there are no theoretical limitations to film lateral dimensions, and such films can be easily transferred to various substrates. This technique is the first step in the widespread utilization of natural graphene as a substitute for materials such as indium tin oxide (ITO) in applications such as solar panels, organic electronics, and batteries. The conductivity of graphene

films formed by our interface trapping method (see Supporting Information for details) shows conductivity on the order of 400 S/cm.

RESULTS AND DISCUSSION

The film formation occurs at the interface of a phase-separated mixture of water and heptane. While graphene does not form a stable suspension in either water or heptane, when placed in a mixture of the two, with mild sonication, the graphene sheets assemble at the heptane/water interface to form a uniform macroscopic film that remains stable for an indefinite period of time. Figure 1 shows graphene film formation at the water/heptane interface, with graphene shells stabilizing a water/heptane emulsion. The size of the drops is a function of the volume fraction of water and heptane.

When placed in a water/heptane solvent mixture of approximately 1:1 mass composition, the graphite, after mild sonication, exfoliates at the solvent interface. In addition, the graphene sheets climb the sides of the hydrophilic glass vial. As the glass of the vial is hydrophilic, a thin layer of water is present on the surface and is in contact with the heptane vapor, leading to a high-energy interface. Graphene sheets “climb” this surface to minimize the interfacial energy, leading to thin graphene films. This phenomenon

* Address correspondence to adamson@uconn.edu.

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Figure 1. Pickering emulsion of water in heptane stabilized by pristine, natural flake graphene. The ratio of heptane to water is 19:1.

is shown in Figure 2A. The graphene film, even after centrifugation at forces greater than 300,000*g*, remains stable at the interface below the heptane and above the water. If, however, the heptane is allowed to evaporate, the heavier graphite will fall through the water and precipitate at the bottom of the vial, showing that the graphene is not simply suspended on the water by surface tension.

When a glass slide is introduced to the system, the film also climbs both sides of the slide. As the glass provides a hydrophilic surface necessary to form the water/heptane interface, a hydrophobic surface will not lead to climbing. Polyethylene vials show graphene at the liquid interface, but no climbing. The same effect is seen by treating the inside of a glass vial with trimethylsilyl chloride to make the walls of the vials hydrophobic. As seen in Figure 2B, the graphene no longer climbs the vial walls, instead partially coating the now hydrophobic walls in contact with the water phase. Placing an untreated glass slide in the treated vial, as shown in Figure 2C, results in graphene climbing the slide. Figure 2D illustrates such a film on a glass slide, with a graphene layer on both the back and front of the slide.

The formation of the graphene films is explained by reassembly of graphene sheets at the oil/water interface driven by minimization of interfacial free energy of the system. Indeed, the surface energy of graphene $\gamma_g = 54.8 \text{ mN/m}^{14,15}$ lies nearly in the middle between the surface tension of water, $\gamma_w = 72.9 \text{ mN/m}$, and the surface tension of heptane, $\gamma_h = 20.1 \text{ mN/m}$, at 20 °C.¹⁶ This results in a positive spreading parameter value of $S \cong 6.6 \text{ mN/m}^{17}$. The climbing of the graphene indicates that the corresponding Hamaker constant of the glass/water/graphene/heptane vapor system is negative.¹⁷ The capillary forces holding the graphene at the interface of the two liquids is substantially stronger than the gravitational force as long as the graphene film is thinner than the corresponding capillary length of $\sim 0.7 \text{ mm}^{18}$.

The strong affinity between graphene and the water/heptane interface is also seen in detailed molecular dynamics simulations performed with several graphene sheets dispersed at a water/heptane

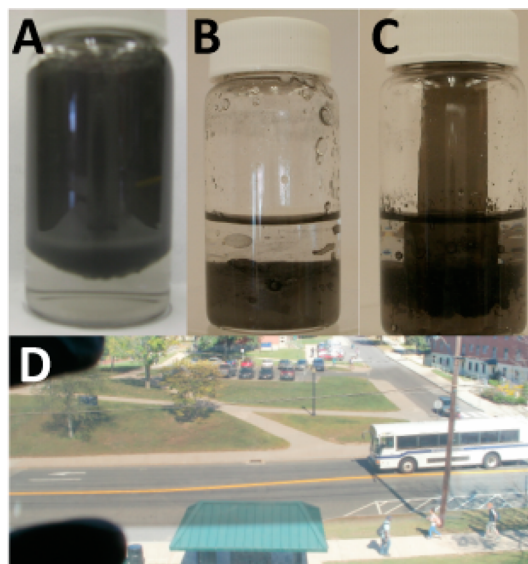


Figure 2. Images of graphene film. (A) Glass sample vial containing water, heptane, and graphene showing graphene film climbing the glass from the water/heptane interface to the top of the vial. (B) Glass vial whose interior surface has been made hydrophobic by treatment with a chlorosilane. Graphene is observed at the water/heptane and water/hydrophobic glass interface of the lower phase, but no climbing is observed above the water layer. (C) Vial as in panel B, but with an untreated glass slide inserted. The graphene climbs the slide even as it does not climb the hydrophobic glass vial. (D) Macroscopic transparent film of graphene on a glass slide formed by interface trapping.

interface (see Supporting Information for detail). During simulations, graphene sheets move along the interface, forming stacks two and three sheets thick. Figure 3A shows the number fraction distribution normal to the interface (*z*-axis) in simulations with nine graphene sheets. Graphene stacks are located at the water/heptane interface with a slight preference toward the heptane phase. We never observe the formation of stacks with more than three sheets. The further restacking of graphene flakes is suppressed by an increase in aggregate bending energy.

The strength of attraction between graphene stacks and heptane/water interfaces is evaluated by calculating the potential of the mean force between a three-sheet stack and interface in a system with a total of nine graphene sheets (see Figure 3B). The minimum of the potential is located at the water/heptane interface. The potential is steeper toward the water phase, confirming that the water is a poorer solvent for graphene than is heptane. In the heptane phase, the potential saturates at distance *z* larger than 4 Å. The magnitude of the potential in the plateau regime is on the order of 4.5*RT* (where *R* is the gas constant and *T* = 300 K). This confirms a strong affinity of graphene stacks for the water/heptane interface. Note that, in a real system, consisting of larger graphene sheets, this energy difference should be even greater, pinning graphene to the interface even more strongly. Also, for larger sheets, the formation of thick aggregates is suppressed

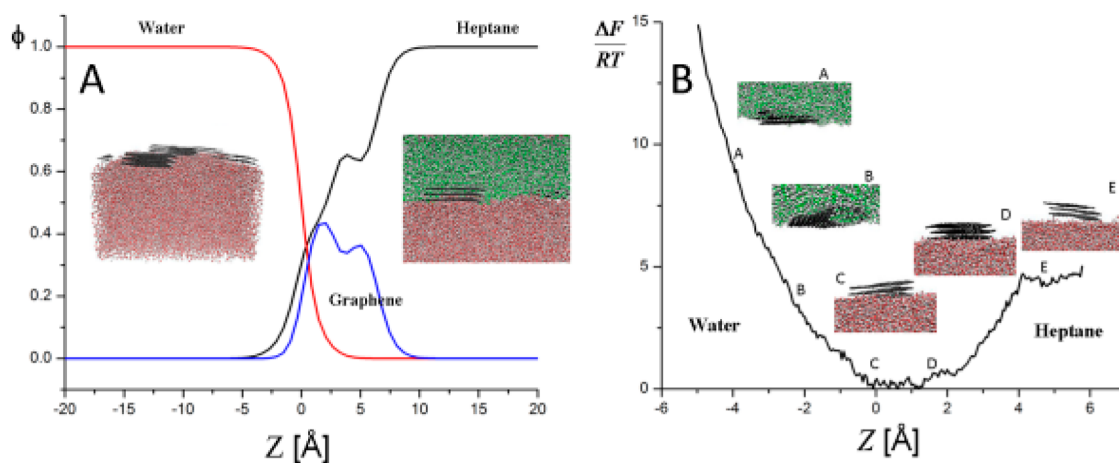


Figure 3. Computational study of graphene films. (A) Number fraction distribution of water, heptane, and graphene along the z-axis, normal to the water/heptane interface. Insets show snapshots of the simulation box. In the left inset, heptane is transparent. In the insets, hydrogen atoms are shown in light gray, oxygen atoms are colored in red, carbon atoms belonging to graphene are black, and carbon in heptane is green. (B) Potential of the mean force for three-layer graphene flake assembly. Insets show typical configuration of the graphene flakes. The solvent into which the graphene assembly is pulled is transparent.

due to both the necessity of diffusing large distances along the interface and the aggregate bending energy penalty to add a new sheet to a stack. This lack of restacking traps graphene at liquid–liquid interface.

The use of an interface to produce nontransparent oxidized and reduced graphite films has been demonstrated elsewhere.^{19–22} The formation of transparent conductive graphene films from modified graphitic precursors was reported recently; however, in all previous investigations, dispersing the graphitic materials in one of the solvent phases was the initial step.^{23–26} The requirement of first forming a dispersion is the major reason for the widespread use of the water-dispersible graphene oxide despite the damage caused to the graphene by oxidation.²⁷ Unlike the previous studies, we have used the lack of graphite solubility to our advantage. Placing graphene at the interface of two immiscible liquids results in a condition where the graphene stabilizes the liquid/liquid interface and lowers the total energy of the system. We have found that using systems in which the graphitic material can be dispersed in one of the solvents does not lead to the climbing phenomenon that forms our transparent films. The use of functionalized graphene sheets produced by the thermal exfoliation and reduction of graphene oxide does not result in climbing graphene nor does the use of solvents such as NMP or DMF.

The graphene film is formed on a glass slide simply by placing the slide in the vial where it intersects the water/heptane interface. After film climbing, the slide is removed and the heptane allowed to dry. The film can also be floated off of the glass slide onto the surface of water, as illustrated in Figure 4A. This allows for the transfer of the film to other surfaces, an important aspect of the system for both applications and characterization. This lift-off technique can be repeated several times to produce thicker films.

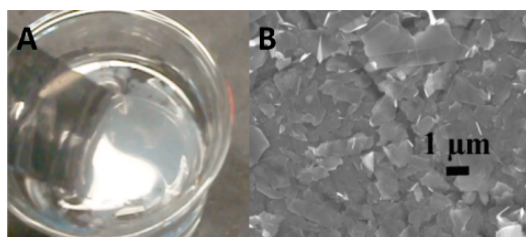


Figure 4. Images of pristine graphene films. (A) Graphene film formed on a glass slide by climbing being floated onto a water surface. (B) FESEM image of pristine graphene film. The sheets have lateral dimensions on the micrometer size scale and form an overlapping arrangement consistent with TEM images. The valleys seen are from the sample holder.

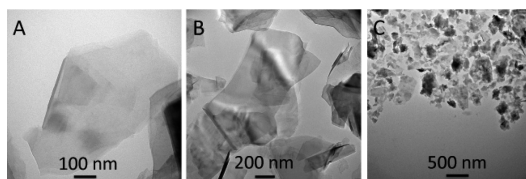


Figure 5. TEM images of graphene film. (A–C) One to four layer, overlapping network morphology of the graphene films. The films contain open regions, single sheets, and stacked sheets.

By lifting the film onto an SEM stub, images such as that shown in Figure 4B are obtained. The film is shown to be composed of overlapping graphene sheets with roughly micrometer lateral dimensions. These large sheets are possible due to only brief, mild sonication being required for the graphene exfoliation. The trenches in Figure 4B are characteristic of the aluminum stub used to mount the sample.

The float-off technique is also employed to obtain TEM images such as those shown in Figure 5A–C. The film is observed to be composed of a network of overlapping graphene sheets. Spaces containing no graphene are also observed, and analysis of the TEM

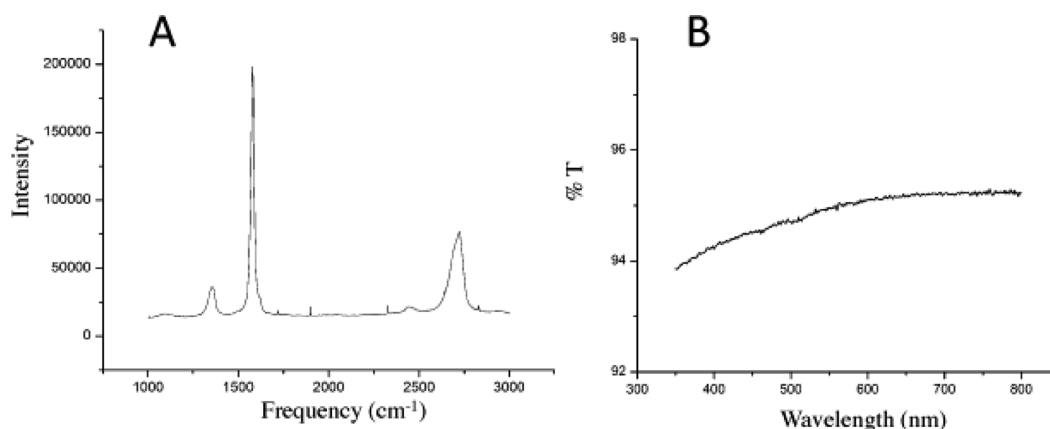


Figure 6. Spectroscopy of pristine graphene films. (A) Raman spectra of graphene film. The shape of the 2D peak is consistent with two layers of graphene. (B) UV-vis spectra of the graphene film on a glass slide. Lower transparency at shorter wavelengths is thought to arise from the adsorption of hydrocarbons on the surface.

images indicates that nearly 20% of the film surface contains no graphene. The overlapping graphene sheets serve to hold the film together. The thickness of the film is also analyzed by Raman spectroscopy. Comparing the spectra of our films, as shown in Figure 6A, with literature examples indicates a stacking of approximately two sheets.²⁸ The transparency of the graphene films is as high as 95% (Figure 6B). A single graphene sheet has been shown to absorb 2.3% of incident white light, with hydrocarbon contamination causing slightly lower transmission below 500 nm.²⁹ Four graphene sheets would be expected to lead to ~91% transmittance. With 20% of the surface free of graphene, the transmittance is expected to be ~93%. As shown in the TEM images and indicated by Raman spectroscopy, the film averages less than 4 sheets, thus the observed value of ~95% transmittance is consistent with these observations.

We find experimentally that the films formed by graphene climbing are consistently composed of four or fewer graphene sheets normal to the substrate. The films formed at the bulk solvent interface, however, can be much thicker depending on the

concentration of graphite. This discrepancy is due to the climbing phenomena being driven by lowering the interfacial energy between the water absorbed on the hydrophilic glass walls and the heptane vapor in the headspace of the vial. Once graphene occupies the interface, the driving force for climbing is diminished and no additional sheets are drawn up.

CONCLUSIONS

We have demonstrated the formation of a transparent and conductive macroscopic graphene film by trapping exfoliated graphene sheets at a liquid interface. Computational studies have shown that this interface trapping process is the result of the strong affinity of the graphene sheets to the interface. The film deposition technique is simple, inexpensive, applicable to a wide range of surfaces, scalable, utilizes pristine, natural flake graphite with no prior treatment, and requires no post-treatments such as chemical reduction or heating. It will revolutionize the application of graphene films in transparent electrodes in solar panels and organic electronic devices.

METHODS

Sample Preparation. To prepare graphene films, a typical procedure is as follows: 2 mg of bulk pristine graphite was first put into a 20 mL glass scintillation vial. Then, 5.0 mL of *n*-heptane (Fisher Scientific, HPLC grade) was added, and the system was briefly bath sonicated (Branson 80W B2510DTH) to break up any large particles. It was then tip sonicated (Cole-Parmer 750 W Ultrasonic processor) for 15 min at 40% power to exfoliate the graphite and disperse it into the heptane. After the sonication, 5.0 mL of water was added and the system was bath sonicated again briefly to help move the graphene sheets to the interface. The mixture was then tip sonicated with the tip right above the main liquid–liquid interface a second time for 15 min at 40% power to further exfoliate the graphene sheets and to distribute the sheets about the interface. After the second tip sonication, the system may be shaken to create emulsion spheres, which upon coalescence generate a film that climbs the walls of the vial.

To transfer the film, using the method above, but before the water dried under the graphene layer, the slide was dipped into

a beaker of water. The film detached from the slide and floated on the top of the water. Depending on the substrate, the film was transferred by either putting it under the water and lifting the film onto it or pushing the substrate under while near the film.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Simulation details, Raman spectroscopy, transmission electron microscopy, and conductivity measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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