Processable aqueous dispersions of graphene nanosheets

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Graphene sheets offer extraordinary electronic, thermal and mechanical properties and are expected to find a variety of applications. A prerequisite for exploiting most proposed applications for graphene is the availability of processable graphene sheets in large quantities. The direct dispersion of hydrophobic graphite or graphene sheets in water without the assistance of dispersing agents has generally been considered to be an insurmountable challenge. Here we report that chemically converted graphene sheets obtained from graphite can readily form stable aqueous colloids through electrostatic stabilization. This discovery has enabled us to develop a facile approach to large-scale production of aqueous graphene dispersions without the need for polymeric or surfactant stabilizers. Our findings make it possible to process graphene materials using low-cost solution processing techniques, opening up enormous opportunities to use this unique carbon nanostructure for many technological applications.

Graphene, a new class of two-dimensional carbon nanostructure, has attracted tremendous attention from both the experimental and theoretical scientific communities in recent years[1]. This unique nanostructure holds great promise for potential applications in many technological fields such as nanoelectronics, sensors, nanocomposites, batteries, supercapacitors and hydrogen storage[1]. However, a lack of an efficient approach to producing processable graphene sheets in large quantities has been a major obstacle to exploiting most proposed applications.

Like carbon nanotubes and many other nanomaterials, a key challenge in the synthesis and processing of bulk-quantity graphene sheets is aggregation. Graphene sheets, which have a high specific surface area, unless well separated from each other, tend to form irreversible agglomerates or even restack to form graphite through van der Waals interactions. This problem has been encountered in all previous efforts aimed at large-scale production of graphene through chemical conversion or thermal expansion/reduction[2–5]. The prevention of aggregation is of particular importance for graphene sheets because most of their unique properties are only associated with individual sheets. Aggregation can be reduced by the attachment of other molecules or polymers onto the sheets[4–6]. However, the presence of foreign stabilizers is undesirable for most applications. New strategies to produce relatively clean graphene sheets in bulk quantity while keeping them individually separated are required.

Graphite, consisting of a stack of flat graphene sheets, is inexpensive and available in large quantities from both natural and synthetic sources. This ordinary carbon material is likely the most readily available and least expensive source for the production of bulk graphene sheets. Mechanical cleavage of graphite originally led to the discovery of graphene sheets[7] and is the process currently used in most experimental studies of graphene[1]. However, the low productivity of this method makes it unsuitable for large-scale use. Chemical conversion from graphite appears to be a much more efficient approach to bulk production of graphene sheets at low cost[2–5].

As recently demonstrated by Ruoff and co-workers[2,4], the solution-based route involves chemical oxidation of graphite to hydrophilic graphite oxide, which can be readily exfoliated as individual graphene oxide (GO) sheets by ultrasonication in water (Fig. 1). Graphene oxide, which is electrically insulating, can be converted back to conducting graphene by chemical reduction, for example, using hydrazine. Unfortunately, previous work[2,4] has shown that, unless stabilized by selected polymers, chemically converted graphene (CCG) sheets obtained through this method precipitate as irreversible agglomerates owing to their hydrophobic nature. The resulting graphene agglomerates appear to be insoluble in water and organic solvents[2], making further processing difficult.

It is well known that exfoliated graphite oxide (or GO) can form well-dispersed aqueous colloids[8–12]. Our study on the surface charge (zeta potential) of as-prepared GO sheets shows that these sheets are highly negatively charged when dispersed in water (Fig. 2a), apparently as a result of ionization of the carboxylic acid and phenolic hydroxyl groups that are known to exist on the GO sheets[13,14]. This result suggests that the formation of stable GO colloids should be attributed to electrostatic repulsion, rather than just the hydrophilicity of GO as previously presumed[2]. Given that carboxylic acid groups are unlikely to be reduced by hydrazine under the given reaction conditions[2], these groups should therefore remain in the reduced product as confirmed by our FT-IR analysis (Fig. 2b). The presence of carboxylic acid groups suggests that the surface of the graphene sheets in aqueous solution should still be charged after reduction. We surmised that the electrostatic repulsion mechanism that makes GO colloids stable could also enable the formation of well-dispersed graphene colloids.
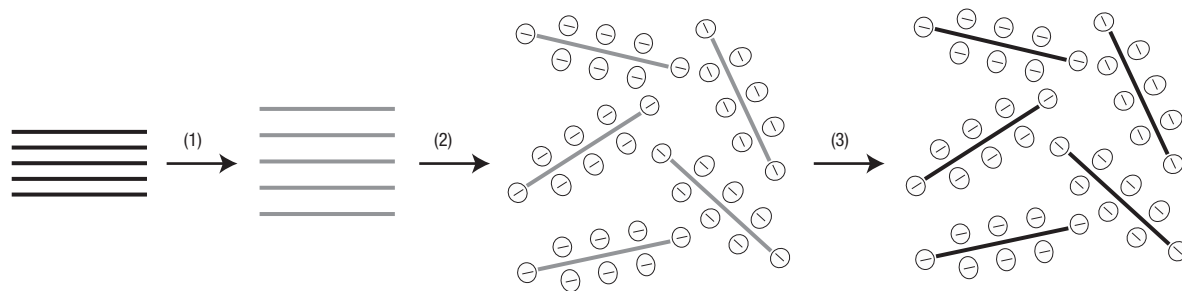
Figure 1 Scheme showing the chemical route to the synthesis of aqueous graphene dispersions. 1, Oxidation of graphite (black blocks) to graphite oxide (lighter coloured blocks) with greater interlayer distance. 2, Exfoliation of graphite oxide in water by sonication to obtain GO colloids that are stabilized by electrostatic repulsion. 3, Controlled conversion of GO colloids to conducting graphene colloids through deoxygenation by hydrazine reduction.
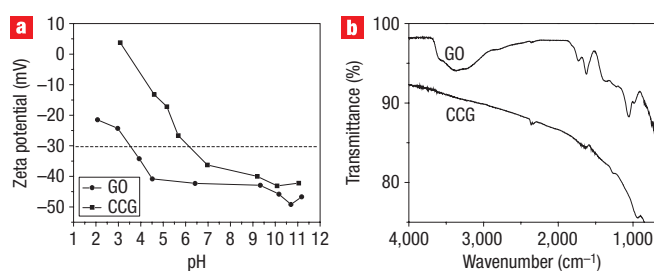
Figure 2 Surface properties of GO and CCG. **a**, Zeta potential of GO and CCG as a function of pH, in aqueous dispersions at a concentration of ~0.05 mg ml^{-1}. **b**, FT-IR spectra of GO and CCG. The absorption band at around 1,700 cm^{-1} is attributed to carboxyl groups. The absorption of CCG sheets at this range is observable but not as prominent as that observed for GO, likely due to the overlapping of the strong absorption of graphene sheets in this region.

As demonstrated in many colloid experiments[15], including our previous work on the synthesis of stabilizer-free conducting polymer aqueous colloids[16], the colloidal stability of an electrostatically stabilized dispersion is strongly dependent on pH, the electrolyte concentration, and the content of dispersed particles. By controlling these parameters, we now find that chemically converted graphene sheets are indeed able to form stable colloids through electrostatic stabilization. Graphene oxide dispersions can be directly converted to stable graphene colloids through hydrazine reduction under controlled conditions (Fig. 1). The use of polymeric or surfactant stabilizers is not required. We have found that the complete removal of metal salts and acids, which often remain in the starting graphite oxide, is critical to stability. These residual electrolytes can neutralize the charges on the sheets, destabilizing the resulting dispersions.
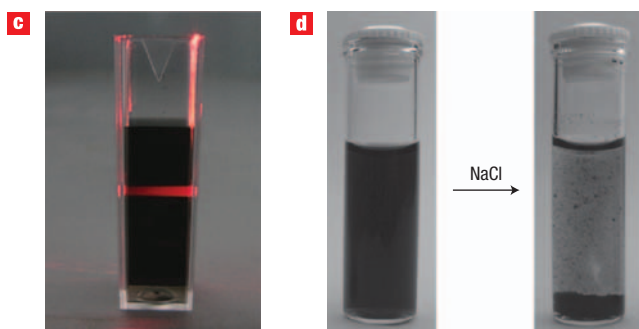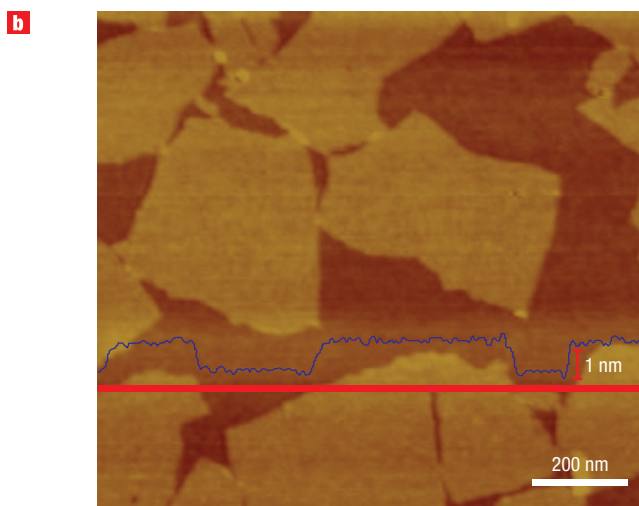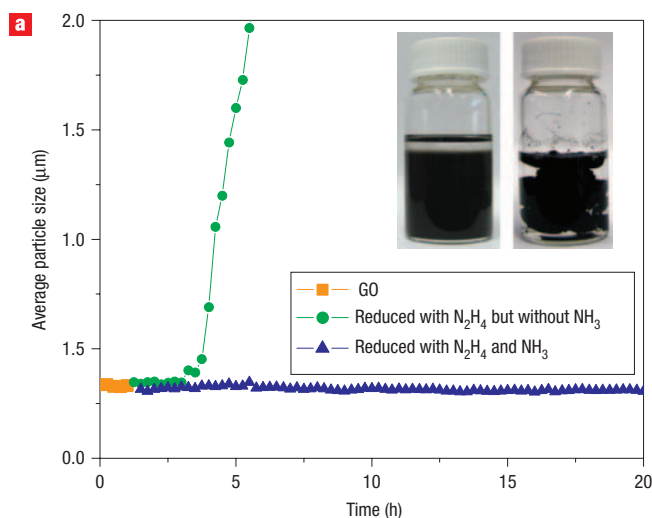
In order to obtain maximal charge density on the resulting graphene sheets, ammonia is added to the reaction solution to increase the pH to around 10. Volatile ammonia can be easily removed after the graphene sheets are processed into solid films or composites. The use of excess hydrazine also renders the dispersion basic. However, hydrazine is highly toxic and its use should be minimized. Additionally, we find that during the reduction process, the graphene sheets at the water/air interface tend to agglomerate upon water evaporation and a layer of black solid gradually appears on the liquid surface. This problem can be effectively avoided by adding a layer of water-immiscible liquid (such as mineral oil) to the solution to eliminate the air/water interface.

We note that if GO dispersions with concentrations less than 0.5 mg ml^{-1} are reduced by hydrazine under appropriate conditions (see Methods), the particle size of the resulting CCG sheets does not increase after the reduction is complete (Fig. 3a). No sediment is observed even after the dispersion has been centrifuged at 4,000 r.p.m. for several hours. Atomic force microscopy (AFM) shows that the resulting CCG sheets that are cast on a silicon wafer are flat, with a thickness of ~1 nm (Fig. 3b). These results indicate that, similar to the original GO dispersion, the as-prepared CCG sheets remain separated in the dispersion.
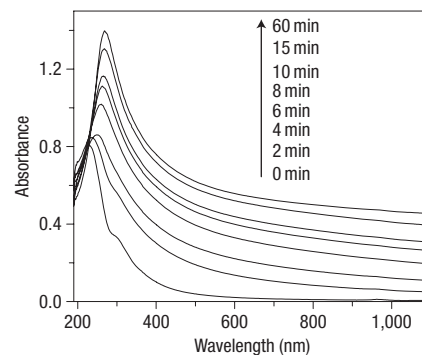
The colloidal nature of the resulting CCG dispersions is further confirmed by two experiments typically conducted in colloid science: investigations of the Tyndall effect and the salt effect. A diluted CCG dispersion gives rise to the Tyndall effect, in which a laser beam passing through a colloidal solution leaves a discernible track as a result of light scattering (Fig. 3c). Adding an electrolyte solution such as sodium chloride into a CCG dispersion leads to immediate coagulation (Fig. 3d). These observations are characteristic of a lyophobic colloid stabilized through electrostatic repulsion and can be explained using the classical Derjaguin–Landau–Verwey–Overbeek theory[15].

It is worth pointing out that in water, ammonia and hydrazine dissociate to generate ionic species that act as electrolytes. Therefore, as with the addition of sodium chloride (Fig. 3d), the overuse of the two chemicals can result in destabilization of the resulting dispersions. We note that if the amount of hydrazine exceeds the optimal level described in the Methods section (hydrazine:GO = 7:10 by weight), the stability of the dispersion decreases with increasing concentration of hydrazine. For example, if the weight ratio of hydrazine to GO is increased to 7:1, agglomeration occurs in about one day. In order to obtain stable dispersions in this case, excess hydrazine must be immediately removed from the resulting dispersions. Additionally, like other lyophobic colloids, the colloidal stability of the resulting dispersions is also dependent on the concentration of CCG. The reduction of GO dispersions with a concentration greater than 0.5 mg ml^{-1} leads to gelation over time.

The feasibility of forming stable graphene dispersions through electrostatic stabilization is further supported by our zeta potential analysis. As shown in Fig. 2a, the zeta potential of the reduced graphene dispersion is pH dependent, which is consistent with the fact that the ionization of carboxylic acid groups is strongly related to pH. Although the magnitude of the zeta potential is lower than that of the original GO sheets at the same pH, the zeta potential is below −30 mV when the pH is greater than 6.1 and can reach −43 mV when the pH approaches 10. Zeta

Figure 4 UV-vis absorption spectra showing the change of GO dispersions as a function of reaction time. The absorption peak of the GO dispersion at 231 nm gradually redshifts to 270 nm and the absorption in the whole spectral region ($>$231 nm) increases with reaction time, suggesting that the electronic conjugation within the graphene sheets is restored upon hydrazine reduction.

Figure 3 Colloidal and morphological characterization of CCG dispersions. a, Effect of the addition of ammonia on the dispersion state of CCG sheets, characterized by measuring average particle sizes over a long period of time. The photographs shown in the inset were taken two days after the reduction reaction was complete with (left) and without (right) the addition of ammonia. The concentration of the starting GO solution is $\sim$0.5 mg ml^{-1}. **b**, Tapping-mode AFM image of CCG sheets with a height profile (blue curve; scale bar, 1 nm) taken along the red line. The sample was prepared by drop-casting a dilute CCG dispersion onto a silicon wafer. **c,d**, The Tyndall effect and the salt effect confirming the colloidal nature of the CCG dispersions. The salt effect experiment highlights the importance of complete removal of residual salts and acids from the starting GO solution.

potential values more negative than -30 mV are generally considered to represent sufficient mutual repulsion to ensure the stability of a dispersion, as is well known from colloidal science[15].

The formation of stable graphene dispersions enables the reaction process to be monitored using UV-vis spectroscopy. As shown in Fig. 4, the absorption peak of the GO dispersion at 231 nm gradually redshifts to 270 nm and the absorption in the whole spectral region ($>$231 nm) increases with reaction time, suggesting that the electronic conjugation within the graphene sheets is restored upon hydrazine reduction. Little increase in absorption is found after 1 h, indicating completion of the reduction within that period. This experiment also suggests that, like conjugated polymers, the electronic conjugation level of graphene is chemically controllable, offering possibilities to tailor the optical and electrical properties of graphene sheets. We find that graphene sheets with different reduction levels can all form stable dispersions if they are prepared using the procedure described in the Methods section.

As shown with carbon nanotubes[17–20], the dispersion of nanomaterials in solution is crucial to advancing many technological applications. Owing to their hydrophobic nature, the direct dispersion of graphite or graphene sheets in water has been generally considered unattainable. This work, for the first time, suggests that ordinary natural graphite, when treated appropriately by chemical means, can readily disperse in water to generate stable graphene colloids without the need for any polymeric or surfactant stabilizers. Of great significance is that the successful formation of relatively pure graphene dispersions enables the use of conventional low-cost solution-phase processing techniques to create new graphene-based materials and devices. For example, we have observed that a single layer of CCG sheets can be deposited on a substrate by simply drop-casting from a dilute CCG dispersion (Fig. 3b), which provides a facile approach to obtain single graphene sheets for device fabrication or studies on the properties of individual sheets. Recent work has demonstrated that the graphene sheets obtained by hydrazine reduction of GO sheets appear to act as a p-type semiconductor[21] and the electrical conductivity exhibits a field-effect response[21,22], suggesting that our processable CCG sheets could be an exciting material for use in future nanoelectronics.

Uniform graphene films can also be readily formed on a membrane filter by vacuum filtration of as-reduced dispersions.
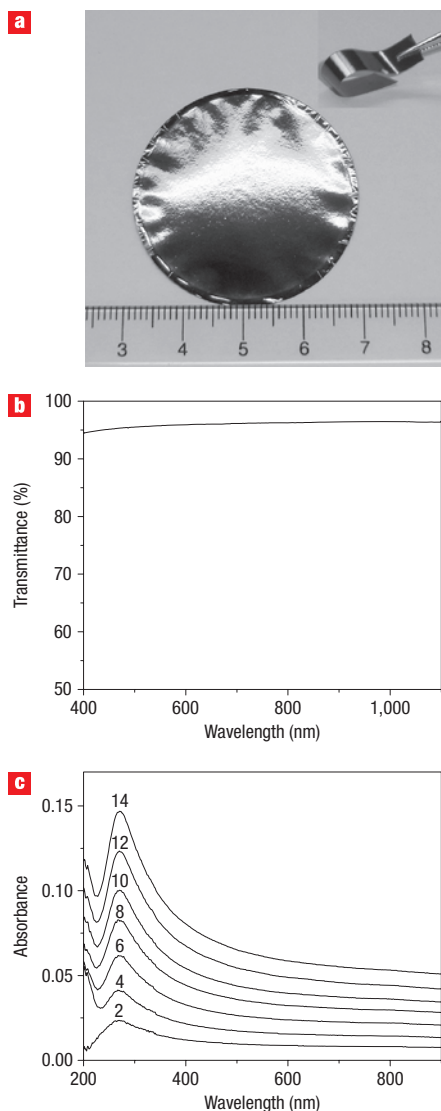
Figure 5 Examples demonstrating that films made of CCG sheets can be easily fabricated from CCG dispersions using various solution-phase processing techniques. a, A 10-μm-thick CCG film or paper prepared by vacuum filtration of a CCG dispersion through an alumina membrane. The film exhibits a shiny metallic lustre. A CCG strip (top-right inset) cut from the film is bent to demonstrate its flexibility. **b**, A transmission spectrum of a CCG coating deposited on a glass slide by air-brush spraying of a CCG solution. The transmittance in the visible light range is greater than 96%. **c**, UV–vis spectra of polycation/CCG films prepared by a layer-by-layer electrostatic self-assembly technique. The absorbance increases linearly with an increase in the number of assembly cycles (denoted above each curve), indicative of the successful assembly of CCG sheets on the substrate.

Free-standing films or graphene paper can be peeled off the membrane. The films are bendable and exhibit a shiny metallic lustre (Fig. 5a). The conductivity of graphene paper prepared using the procedure described in the Methods section is found to be $\sim$7,200 S m^{-1} at room temperature, which is comparable to that of chemically modified single-walled carbon nanotube paper[23]. We note that Ruoff and co-workers have recently demonstrated that strong GO paper can be prepared using a similar filtration strategy[24]. The resulting paper could find use in many fields, including membranes, anisotropic conductors and supercapacitors[24]. Our preliminary measurements show that the graphene paper obtained from direct filtration of our stable CCG dispersions gives a tensile modulus up to 35 GPa, which is close to that of the GO paper. We expect that our strong, conductive, flexible and thermally stable graphene paper should be more attractive than non-conductive, less thermally stable GO paper for practical applications.

Spraying techniques such as air-brushing can also be used to produce conductive graphene coatings on various substrates. Like many other lyophobic colloids, once the graphene colloids are dried, they are not redispersible in water, rendering as-prepared graphene coatings water-resistant. Of particular significance is that, owing to the high aspect ratio of the graphene sheets, a very thin graphene coating, which is almost transparent, can result in the formation of a continuous conducting network. Figure 5b shows a transmittance spectrum of a sprayed CCG coating on a glass slide. The coating gives a sheet resistivity of $2.0 \times 10^7 \Omega \square^{-1}$ at room temperature, and the transmittance in the visible wavelength range is higher than 96%. The conductivity of this as-sprayed coating is sufficient for antistatic applications. Antistatic coatings are vital to the safety of materials, machinery and individuals across many different industries[25]. Our work may lead to the development of a new generation of antistatic coatings that can combine electrical conductivity with transparency, excellent thermal and chemical stability, water resistance and low production cost. Graphene dispersions may thus find immediate practical uses.

Additionally, the highly charged state of the CCG sheets in water makes it possible to use the well-known layer-by-layer electrostatic assembly technique[26–29] to build up complex and controllable graphene-based nanosystems with other functional molecules, polymers and nanostructures. We have demonstrated the feasibility of this process by alternately immersing a quartz slide in a dilute CCG dispersion and a typical cation polyelectrolyte—poly(diallyldimethylammonium chloride). As confirmed by the absorption spectra (Fig. 5c), CCG sheets can be successfully assembled using this simple approach. Note that thin films of graphite oxide sheets have been previously prepared using this technique[8–12]. However, to make the resulting graphite oxide film conducting, an additional reduction step is needed. This reduction process is likely to be detrimental to composites containing more delicate molecular structures such as biomolecules or conjugated polymers. It has been extensively demonstrated that self-assembled multilayered electroactive films hold great potential in many applications such as sensors and neuroprosthetic devices[26–29]. It would be reasonable to expect that the successful formation of graphene colloids will open up possibilities to use this powerful electrostatic assembly technique to manipulate graphene sheets for creating many new and potentially useful nanosystems.

In summary, we have demonstrated that aqueous graphene dispersions can be readily formed by controlled chemical conversion of GO colloids without the need for either polymeric or surfactant stabilizers. Chemically converted graphene can now be viewed as a special water-soluble conducting macromolecule that can be simply obtained from graphite. Graphene sheets should be superior to normal synthetic conducting polymers in terms of thermal and chemical stability and mechanical strength, and more competitive than carbon nanotubes in terms of production cost. Furthermore, as shown with carbon nanotubes[18–20], the successful dissolution of graphene sheets in solution as well as the residual carboxylic groups on the sheets enables the use of solution-phase chemistry to further modify graphene sheets for achieving new functionalities.

The dispersant-free feature offers a great deal of flexibility in the creation of novel graphene-based nanocomposites with many other molecules and nanostructures. The ease of synthesis and the exceptional solution-phase processability of CCG sheets make this inexpensive and conductive nanostructure attractive not only for future nanoelectronics, but also for large-scale applications in both conventional technological fields, such as transparent antistatic coatings and electrochemical devices, and emerging areas such as flexible/transparent electronics, high-performance nanocomposites, nanomedicines and bionic materials. We believe that the work presented here will provide a significant step forward to bringing graphene materials much closer to real-world applications.

METHODS

SYNTHESIS

Graphite oxide was synthesized from natural graphite (SP-1, Bay Carbon) by a modified Hummers method as originally presented by Kovtyukhova and colleagues[10,30]. As-synthesized graphite oxide was suspended in water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids. Ultrapure Milli-Q® water was used in all experiments. As-purified graphite oxide suspensions were then dispersed in water to create a 0.05 wt% dispersion. Exfoliation of graphite oxide to GO was achieved by ultrasonication of the dispersion using a Brandson Digital Sonifer (S450D, 500 W, 30% amplitude) for 30 min. The obtained brown dispersion was then subjected to 30 min of centrifugation at 3,000 r.p.m. to remove any unexfoliated graphite oxide (usually present in a very small amount) using an Eppendorf 5702 centrifuge with a rotor radius of 14 cm. In a typical procedure for chemical conversion of graphite oxide to graphene, the resulting homogeneous dispersion (5.0 ml) was mixed with 5.0 ml of water, 5.0 μl of hydrazine solution (35 wt% in water, Aldrich) and 35.0 μl of ammonia solution (28 wt% in water, Crown Scientific) in a 20-ml glass vial. The weight ratio of hydrazine to GO was about 7:10. After being vigorously shaken or stirred for a few minutes, the vial was put in a water bath (∼95 °C) for 1 h. Unless specifically stated, graphene dispersions prepared according to the above procedure were used for further characterization and film fabrication in this work. Note that the concentration of hydrazine in the reduction mixture can be varied from 0.0175 wt% (used in the above procedure) to 1.75 wt%. However, in order to obtain stable dispersions when the concentration is greater than 0.0175 wt%, excess hydrazine in the resulting dispersions must be removed by dialysis against a ∼0.5% ammonia solution once the reduction is complete. A $R_{\mathrm{N_2H_4/GO}}$ ratio of 7:10 appears to be an optimal ratio for producing stable dispersions of highly conducting graphene sheets (see Supplementary Information).

The graphene paper, shown in Fig. 5a, was made by filtration of a dispersion through an Anodisc membrane filter (47 mm in diameter, 0.2 μm pore size; Whatman), similar to the method reported for making GO paper[24]. The graphene paper was cut by a razor blade into rectangular strips of approximately 4 mm × 15 mm for mechanical testing.

CHARACTERIZATION

UV-vis absorption and/or transmission spectra were obtained using a Shimadzu UV 1601 spectrophotometer. The spectra were taken from the reaction mixture (diluted by a factor of 30) at different times. The dispersion/aggregation state of CCG sheets in water was monitored by measuring their average particle size using a Malvern Zetasizer Nano-ZS particle analyser. Note that the particle size measurement on this instrument is based on the assumption that the particles are spherical, so the instrument is unable to give the absolute sizes of graphene sheets. Nevertheless, the measurements obtained provide a means of monitoring dispersion stability. Attenuated total reflectance FT-IR spectra of free-standing films prepared by vacuum filtration were recorded on a Nicolet AVATAR 360 FTIR spectrometer with a Smart OMNI Sampler with a germanium crystal. AFM images were taken in tapping mode with the SPM Dimension 3100 from Veeco. Conductivity measurements of free-standing CCG films prepared by vacuum filtration were carried out on a Jandel RM3 Test Unit using a four-point-probe head with a pin-distance of about 1 mm. Mechanical tensile tests were conducted with a Q800 Dynamic Mechanical Analyzer (TA Instruments). The samples were gripped using film tension clamps with a clamp compliance of about 0.2 μm N^{-1}. The tensile tests were performed in the controlled strain rate mode with a preload of 0.001 N and a strain ramp rate of 0.01% min^{-1}.

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Author contributions

D.L. conceived and designed the experiments, R.B.K. and G.G.W. were involved in discussions on the design and interpretation of the experiments, and D.L., M.B.M. and S.G. performed the experiments. D.L., R.B.K. and G.G.W. co-wrote the paper. All the authors discussed the results and commented on the manuscript.