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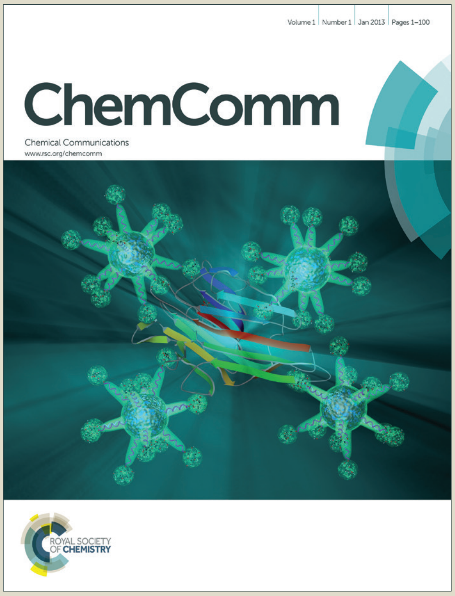

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Urea-assisted aqueous exfoliation of graphite for high-quality graphene

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Urea-assisted aqueous exfoliation of graphite was found to be more efficient than exfoliation in N, N-dimethylformamide (DMF), and high-quality graphene was obtained with a yield up to 2.4%. The mechanism that primary amine facilitate aqueous exfoliation was proposed and experimentally validated, which may inspire new strategies for efficient liquid exfoliation.

Graphene, because of its outstanding properties, has attracted considerable attention from both fundamental and applied science communities over the past decade.[1] High-quality graphene can be prepared through bottom-up routes, such as micromechanical exfoliation, chemical vapour deposition, epitaxial growth, ball milling of graphite and chemical synthesis; but all of these methods produce a very limited quantity of graphene.[2] In recent years, liquid exfoliation of graphite, a typical top-down technique, has been developed to be the most promising method for mass production of single- and few-layered graphene sheets with high quality.[3] In particular, aqueous exfoliation is more advantageous than the organic solvents owing to its extremely low cost and minimal environmental issues.[4]

For efficient aqueous exfoliation, the dispersing stability of the exfoliated graphene (EG) flakes is one of the key factors because pristine graphene is hydrophobic by nature and the flakes tend to restack together in water.[5] Therefore, a stabiliser is generally introduced to prevent aggregation in aqueous exfoliation, through modifying the surface of EG and affording intersheet steric/electrostatic repulsion. Various types of organic stabilisers have been explored, including surfactants,[6] polymers[7] and polycyclic aromatic hydrocarbons,[8] and some of these organic chemicals have been proven to be highly efficient for graphene fabrication. For example, using the triblock copolymer Pluronics P-123, aqueous graphene dispersions as high as 1 mg mL^{-1} can be achieved after sonication for only 2 h.[9] However, residuals of the organic stabilisers, which are generally electrically insulating, can seriously compromise the ultimate electrical performance of graphene-based devices. Unfortunately, removal of these stabilisers is often not a trivial task because these molecules are elaborately selected for their strong binding to the graphene surface[4] and many of them are even toxic. In addition, disposal of these organics also significantly increases the manufacturing cost and the environmental impact.

Easy-to-remove inorganic alternatives, such as NaOH, Na_2CO_3, and K_2CO_3, have recently been reported to be suitable for aqueous exfoliation owing to the electrostatic stabilisation of EG provided by the basic aqueous solution.[4] Although these chemicals are inexpensive and safe to handle, the efficiency of this approach requires further improvement for scalable fabrication of graphene.

Therefore, inexpensive stabilisers that give high exfoliation efficiency and can be easily removed with minimal environmental impact will largely facilitate the industrialisation of aqueous exfoliation technology. Herein, we report the use of urea, a cheap and environmentally friendly reagent, as a stabiliser for highly efficient aqueous exfoliation of natural graphite to prepare high-quality graphene sheets. Exfoliated graphene with a yield of up to 2.4% is achieved in water with the presence of urea, which outperforms the exfoliation in N, N-dimethylformamide (DMF) under similar conditions. In addition, filtration of the dispersions can readily remove the introduced urea and yield graphene paper with high electrical conductivity ($1.5\pm0.1\times10^4$ S m^{-1}). Finally, we propose and experimentally validate a primary amine-based exfoliation mechanism that is expected to inspire new strategies for efficient liquid exfoliation.

Chemicals and detailed experimental procedures are described in the electronic supplementary information (ESI). It should be noted that probe ultrasonication rather than variable bath ultrasonication was used to ensure a fixed power delivery into the aqueous system. Temperature during the exfoliation was well controlled through an external circulating cooling system (see Fig. S1, ESI†). In a typical experiment, natural graphite was added into the urea/water solution and then subjected to probe ultrasonication (output of approximately 14 W) for a period of time. The resulting black suspension was left to stand overnight and then centrifuged to remove the un-exfoliated graphite. The top two-thirds of the centrifuged suspension was then gently extracted for further characterisation. Fig. 1a presents 20 mL of homogeneous black solution obviously exhibiting the Tyndall effect when a red laser beam is passed through it, suggesting the formation of a uniform dispersion. Fig. S2a depicts a typical ultraviolet-visible (UV-Vis) spectrum of the dispersion, where a π-π^* transition peak is found at around 270 nm while the spectrum is featureless in the visible region, sharing the characteristics of

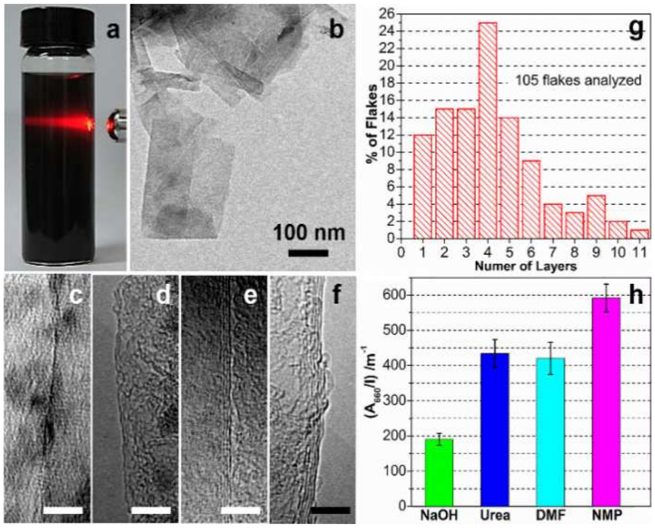

Fig. 1 (a) Photograph of the aqueous dispersion containing EG flakes. (b) TEM of urea-assisted EG sheets. HR-TEM images of (c) monolayer, (d) bilayer, (e) trilayer, and (f) four-layer graphene sheets. The scale bars are 5 nm. (g) Statistical thickness analysis of EG by HR-TEM. (h) Average A_{660}/l for various dispersions prepared in an analogous manner. The error bars correspond to the statistical error obtained by averaging the data of three independent experiments.

previously reported graphene dispersions.[4] The absorbance per unit cell length at 660 nm (A_{660}/l) undergoes only a minimal decrease with sediment time (Fig. S2b, ESI†), indicating a good stability at room temperature. Both scanning electron microscopy (SEM, Fig. S3, ESI†) and transmission electron microscopy (TEM, Fig. 1b) images reveal the microstructures of the exfoliated sheets in the dispersion. Similar to general liquid exfoliations,[3] the reductions in sheet thickness (mono-layer and few-layer) and lateral size (100-700 nm) are evident compared with the graphite flakes. According to statistical analysis (Fig. 1g) based on high-resolution TEM images (HR-TEM, Fig. 1c-1f) of 105 pieces of isolated sheets, monolayer graphene accounts for 11.4 % of the sheets, and those with fewer than five atomic layers amount to 63.8 % of the sheets in the dispersion. Atomic Force Microscopy (AFM, Fig. S4, ESI†) also confirm that most graphene sheets possess lateral size at submicron scale. Interesting, we also observed graphene sheets with size up to 5 µm in the samples (Fig. S4b). All of these results demonstrate the feasibility of urea as an additive to assist aqueous exfoliation.

Exfoliation efficiency is crucial, and especially for mass production of high-quality graphene. To evaluate the efficiency of this newly developed method, the content of graphene in the dispersions should be determined. A direct but tedious method to determine the content is to weigh the completely dried graphene powder extracted from the dispersions via thorough wash and filtration (see ESI†). Alternatively, UV-Vis absorption spectroscopy provides a convenient way to solve this problem by correlating the concentration of the solid in liquid and the absorbance. As shown in Fig. S2c, A_{660}/l exhibits a positive linear correlation with the corresponding graphene concentration determined by the weighing method. According to our data, this Lambert-Beer behaviour with an absorption coefficient (α_G) of 3517 mL mg^{-1} m^{-1} allows concentrations to be measured rapidly by UV-vis spectra. Hereby, we investigate the effects of different exfoliation parameters, including exfoliation time, ultrasound bath temperature, initial graphite concentration and urea dosage, on the concentration of the EG dispersions (Fig. S5, ESI†) to systematically evaluate and optimise the exfoliation efficiency. Amazingly, as shown in Fig. 1g, we find that urea/water gives a performance even better than DMF and NaOH/water under similar conditions. A graphene concentration of up to 0.15 mg mL^{-1} and a maximum yield of 2.4 % are obtained under the optimised conditions. It should be noted that the concentration and yield are larger than those obtained in aqueous exfoliation assisted by most surfactants.[9]

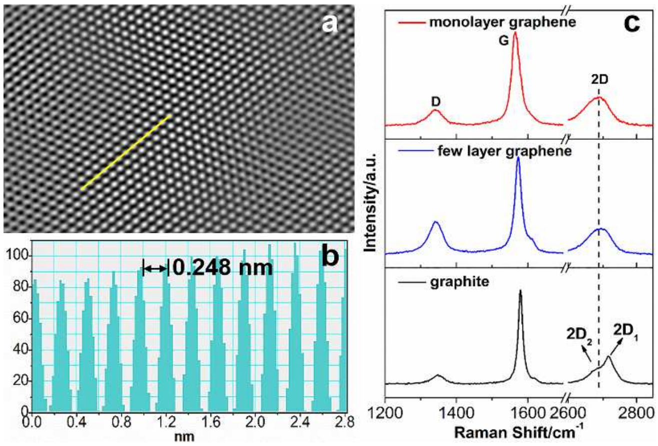

Fig. 2 (a) A digitally filtered HR-TEM image of the EG sheet. (b) Intensity analysis along the yellow line in (a). (c) Typical Raman spectra of EG prepared in urea/water solution and graphite.

Graphene prepared by liquid exfoliation is characterised by high quality, which is also embodied in graphene sheets exfoliated in the urea/water system. As shown in Fig. 2a, the filtered HR-TEM image of a few-layered graphene flake clearly reveals the hexagonal nature of the graphitic structure. Intensity analysis (Fig. 2b) along the yellow line in Fig. 2a determines the hexagonal width to be 0.248 nm, close to the expected value of 0.25 nm,[6] which strongly suggests that the pristine structure of the graphene were remained during ultrasonication. Raman spectra further confirm the intact structure of the EG flakes. Quite different from graphite (Fig. 2c), single symmetrical 2D peaks (ca. 2690 cm^{-1}) for extracted EG powder sample demonstrates the presence of monolayer and few-layer graphene and helps distinguish them from each other. A sharp G peak (ca. 1570 cm^{-1}) is evidently separated with the D peak (ca. 1340 cm^{-1}) without any overlap, which is consistent with the typical Raman signal of high-quality graphene.[10] The small D peak is associated with edge defects[3a] and the average intensity ratio of the D peak to G peak (I_D/I_G, ca. 0.26) is significantly lower than that of EG prepared in other solvent systems (Fig. S6, ESI†). This may indicate that exfoliation in urea/water tends to form EG with higher quality. To test the practical performance, the extracted EG is redispersed via mild bath ultrasonication and subsequently processed into free-standing papers (Fig. S7, ESI†). The papers with an average apparent density of 1.5 g cm^{-3} give a mean electrical conductivity of $1.5 \pm 0.1 \times 10^4$ S m^{-1}, which is distinct from the papers fabricated from EG in a surfactant/water solution whose good electrical performance can only be achieved after removal of surfactants under high temperature. In contrast, urea can be readily eliminated by a simple wash, which is demonstrated by X-ray photoelectron spectroscopy (XPS) analysis (Fig. S8, ESI†) of the extracted EG powders.

The mechanism underlying the efficient exfoliation, i.e., the role of urea, is investigated to obtain a more comprehensive understanding of this technique. Stable dispersing of EG in water is a basic prerequisite for effective aqueous exfoliation and EG dispersions, as previously described, and to explore the origin of this stability, the zeta potential of the graphene dispersions with urea is

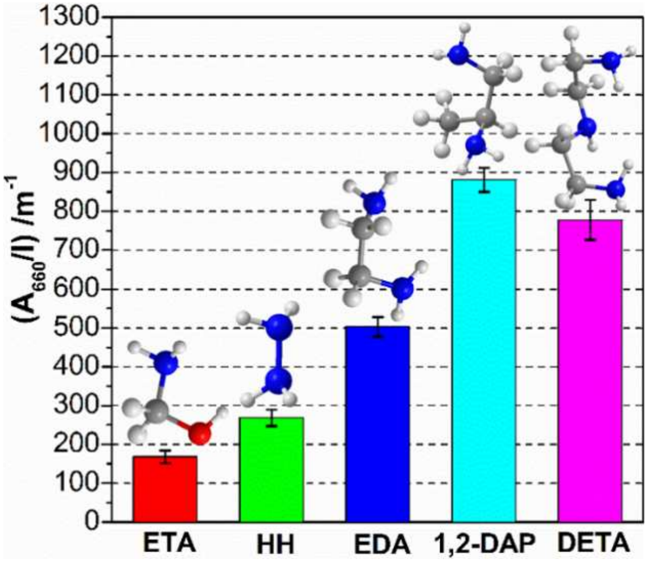

Fig. 3 A_{660}/l of the EG dispersions exfoliated in water assisted by various molecules and chemical structures of corresponding molecules. The error bars correspond to the statistical error obtained by averaging the data of three independent experiments. Atom key: blue: N atom, white: H atom, black: C atom, red: O atom.

measured. A potential ranging from -38 to -41 mV implies that electrostatic repulsion is responsible for the stable dispersing. Whereas, redispersing of the extracted EG in water without urea lead to suspension with zeta potential in the range of -8 to -15 mV (Fig. S9, ESI†) and obvious sediments after standing for 1 day. The significant reduction of the zeta potential and degraded stability after the elimination of urea highlights the importance of the urea molecule for graphene stabilisation in water. The reported pH-related stability in the case of NaOH-assisted exfoliation[4] can be excluded because all of our EG dispersions have a pH value of 6–7, independent of the amount of urea. The attractive interaction between the graphene surface and the primary amine groups (-NH_2) has been revealed through theoretical calculations.[11] However, -NH_2 group cannot ionize to afford negative surface charge for stable dispersing. Therefore, we suppose that after absorption through one of the two -NH_2 groups in urea molecule, the remained -NH_2 group may undergo reaction with CO_2 dissolved in the water, forming -NHCOOH group[12] that readily ionizes and renders the graphene surface negatively charged. Therefore, we suppose that after absorption through one of the two -NH_2 groups in urea molecule, the remained -NH_2 group may undergo reaction with CO_2 dissolved in the water, forming -NHCOOH group[12] that readily ionizes and renders the graphene surface negatively charged. This type of transformation is in fact a well-established route to achieve CO_2 capture using various kinds of amines.[12] To confirm the occurrence of reaction between urea and CO_2, we monitor the electrical conductivity of urea/water solution (360 mg mL^{-1}) under different conditions (See ESI†). As can be seen in Fig. S10, the conductivity of urea/water solution with CO_2 feeding shows significant linear increase when subjected to ultrasonication. Ionization of H_2CO_3 derived from dissolved CO_2 is unlikely to cause the continuous increased conductivity, because feeding of CO_2 leads to rapid increase and maximization of conductivity to a much smaller value (Fig. S10, ESI†). Therefore, with the activation by ultrasonication, a chemical reaction must occur between urea and CO_2, producing reagent that is ready to ionize and increases conductivity of the solution. Under ultrasonication and no feeding of extra CO_2, a significant and steady increase of electricity conductivity is also detected (Fig. S10, ESI†). This is exactly the case of the aqueous exfoliation, in which CO_2 from air serves as the CO_2 resource and can be readily dissolved into the solution with the help of ultrasonication agitation. Therefore, the exfoliation mechanism can be described as follows: When subjected to ultrasonication, thick graphite flakes are exfoliated into thinner sheets with large area of the fresh graphite surface exposed to water. An -NH_2 group in every dissolved urea molecule then rapidly absorbs onto the newly formed surface, reducing the interface energy with water. Reaction of the remained -NH_2 group of the absorbed urea molecule reacts with CO_2 forms -NHCOOH group, which ionizes in water and stabilises the exfoliated sheets by the electrostatic repulsion. Repetition of this process during prolonged ultrasonication results in the continuous thinning of graphite flakes and the final formation of graphene sheets.

Undoubtedly, for the proposed mechanism, primary amine group is the key to realise efficient exfoliation. To further experimentally validate the mechanism, aqueous exfoliation is also performed in an analogous manner with the presence of other molecules containing primary amine group (see ESI†). Five chemicals, i.e., ethanolamine (ETA), hydrazine hydrate (HH), ethidene diamine (EDA), 1, 2-diaminopropane (1, 2-DAP) and diethylenetriamine (DETA) are investigated, and the results (Fig. 3) show that exfoliation is effective in all cases and the mixture of water and 1, 2-DAP or DETA even gives an exfoliation efficiency even higher than NMP, which strongly supports that the exfoliation mechanism is based on the primary amine. Despite their high exfoliation efficiency, however, these five chemicals are not suitable for aqueous exfoliation considering the safety and environmental impact. Nevertheless, we believe that this proposed mechanism will inspire new strategies for more efficient liquid exfoliation towards high-quality graphene.

In conclusion, by introducing urea as stabiliser, we develop a novel exfoliation approach to prepare high-quality graphene directly from graphite in water. The approach is more efficient than exfoliation in DMF, achieving a high graphene yield of ca. 2.4%, which is a technical breakthrough for surfactant-free aqueous exfoliation. The proposed exfoliation mechanism based on a primary amine is experimentally validated and expected to inspire new strategies for more efficient liquid exfoliation.

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Notes and references

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