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ORIGINAL PAPER

Large-scale preparation of graphene sheets and their easy incorporation with other nanomaterials

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Abstract Graphene dispersions with concentrations up to 0.5 mg/mL were produced by dispersion in *N,N*-dimethylformamide with the aid of polyacrylic acid. Graphene oxide could also be dispersed with even higher concentration (17 mg/mL), and this advantage was used for the large-scale synthesis of graphene. The good dispersion of graphene sheets also facilitated the preparation of a new hybrid material of graphene and Fe_3O_4 nanoparticles, which exhibited interesting magnetic properties.

Keywords Graphene · In situ polymerization · Large-scale · Nanomaterial · Polyacylic acid

Introduction

Graphene is a flat monolayer of carbon atoms in a hexagonal arrangement [1]. The novel electronic properties of graphene have attracted increasing attention from different scientific research fields, and offered potential applications in many technological areas [2–8]. The incorporation of graphene sheets into composite materials is a promising route to harnessing their properties. At the very beginning, single sheets of graphene were isolated by simply tracing a sample of bulk graphite across a substrate in a process known as micromechanical cleavage [1]. Other methods have also been reported, including thermal annealing of SiC [9], chemical reduction of graphite oxide [4], intercalative expansion of graphite [6], bottom-up growth [10], chemical vapor deposition [11], and liquid-phase exfoliation [12]. The

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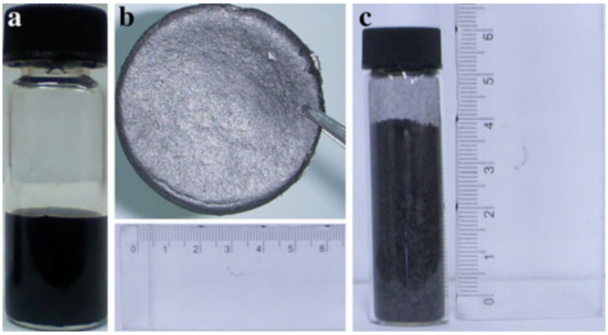

Fig. 1 The photographs of graphene product. **a** Water dispersion of the prepared graphene; **b** graphene paper prepared by vacuum filtration of its dispersion (after being washed with water for many times); **c** the final product of graphene as powder (0.83 g)

most welcome method so far for chemists should be the exfoliation of graphene oxide (GO), followed by the chemical reduction in dispersion solutions. However, similar to carbon nanotubes (CNT), a key challenge to handle graphene is aggregation, which hampers the processing of it into composite materials and its preparation in large-scale through the wet chemical methods mentioned above. Thanks to the efforts of scientists, soluble or dispersible graphene sheets could be prepared by chemical modification or non-covalent functionalization approaches, for example, reduction of alkylamine-modified GO, to conduct the reduction of GO in the presence of poly(sodium 4-styrenesulfonate) or ammonia solution, and the introduction of carboxylic or sulfonate groups onto their basal planes [13–18]. In general, the concentration of the graphene dispersions is about 0.02 mg/mL, not high enough for the further processing, for example, being incorporated into composite materials. Thus, to exploit the special properties of graphene, convenient methods for the mass production of graphene and the preparation of their composite materials are still required. Here, we demonstrate that the graphene dispersion with a concentration up to 0.5 mg/mL, could be produced by dispersion with the aid of polyacrylic acid (PAA) in *N,N*-dimethylformamide (DMF). GO could also be dispersed with even higher concentration (17 mg/mL), which was used in the large-scale preparation of graphene (Fig. 1). The good dispersion of graphene sheets also facilitated the preparation of a new hybrid material of graphene and Fe_3O_4 nanoparticles.

Experimental

Materials and instruments

Benzoyl peroxide (BPO) was recrystallized in methanol/chloroform. DMF was dried over and distilled from CaH_2. Acrylic acid was distilled under reduced pressure. Fe(II) chloride tetrahydrate (99 %), Fe(III) chloride hexahydrate (97 %), and other solvents and chemicals were used as received.

Raman spectroscopy was performed on the LabRAM HR 800UV (Horiba Jobin Yvon Company) using 632.8 nm laser excitation. Scans were taken on an extended range (150–3,400 cm^{-1}) and the exposure time was 50 s. The sample was viewed under a maximum magnification of × 10. Transmission electron microscopy (TEM) was performed on a JEM-2010 at an accelerating voltage of 200 kV. The TEM samples were prepared by drying a droplet of the dispersion on a carbon grid. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 at an accelerating voltage of 1,000 V. We used two different methods to prepare the SEM sample, one was liquid phase and the other was solid phase. For the liquid phase, the sample was dispersed in deionized water with sonication for 10 min, a droplet of the dispersion was dropped on an aluminum foil, and the aluminum foil was fixed on an SEM stage using the conductive adhesive. The other way was to simply fix the sample on an aluminum foil with the aid of the conductive adhesive. Because of the good conductivity of graphene, we did not plate gold during the sample preparation. Infrared (IR) spectra (400–4,000 cm^{-1}) were measured using a Nicolet 380 FT-IR with pure KBr as the background. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min in argon atmosphere at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA). The X-ray powder diffraction (XRD) analyses were performed on a Bruker D8 Advanced X-ray diffraction with Cu Kα radiation ($\lambda = 1.5418$ Å). The diffraction data were recorded for 2θ angles from 5° to 60°. UV–Vis spectra between 200 and 800 nm were measured on a Shimadzu UV-2550 Spectrophotometer.

Preparations

Synthesis of GO

Graphite oxide was synthesized from natural graphite by the modified Hummers method [19]. H_2SO_4 (70 mL) was added into the 250 mL flask filled with graphite (1 g) at room temperature, followed by the addition of solid $KMnO_4$ (7 g) slowly below 20 °C (ice bath). Then, the temperature was increased to 35 °C and the mixture was stirred for 2 h. Excess water was added into the mixture at 0 °C (ice bath) and then H_2O_2 (30 wt%) was added until there was no gas produced. The mixture was filtered and washed with 1 M HCl aqueous solution and deionized water for several times. Exfoliation was carried out by sonicating under ambient condition for 40 min.

Synthesis of graphene with the aid of PAA

Graphite oxide (20 mg) and DMF (10 mL) were added into a 100 mL Schlenk tube, and the tube was evacuated under vacuum and then flushed with argon three times through the sidearm. After sonicated for 40 min, BPO (10 mg) was added to the tube and stirred for 15 min, and then acrylic acid (3 mL) was added dropwise into the mixture. The mixture was heated to 60 °C and stirred for 24 h under an atmosphere of argon. When the reaction was finished, it was centrifuged and washed with petroleum ether to remove the excess acrylic acid. The solid in the bottom were added to a 100 mL flask, and then deionized water (20 mL) and hydrazine hydrate (2 mL) were added. It was heated to 95 °C and stirred for 24 h. The well-dispersed black suspension was filtrated and washed with petroleum ether, tetrahydrofuran (THF) and deionized water for several times. The final filtrate cake was dried under vacuum at 40 °C.

Synthesis of graphene with the aid of PAA (large-scale)

Graphite oxide (1.3 g) and DMF (50 mL) were added into a Schlenk tube, and the tube was evacuated under vacuum and then flushed with argon three times through the sidearm. After sonicated for 40 min, BPO (20 mg) was added to the tube and stirred for 15 min, and then acrylic acid (20 mL) was added dropwise into the mixture. The mixture was heated to 60 °C and stirred for 24 h under an atmosphere of argon. When the reaction was finished, it was centrifuged and washed with petroleum ether to remove the excess acrylic acid. The solid in the bottom were dispersed into water (450 mL), hydrazine hydrate (5 mL) was added, and the mixture was heated to 95 °C and stirred for 24 h. The well-dispersed black suspension was filtrated and washed with petroleum ether, THF, and deionized water for several times. The final filtrate cake was dried under vacuum at 40 °C.

Synthesis of Fe_3O_4 nanoparticles

$FeCl_2 \cdot 4H_2O$ (0.198 g, 1 mmol), $FeCl_3 \cdot 6H_2O$ (0.406 g, 1.5 mmol), PAA (0.106 mg), and deionized water (50 mL) were added into a 150 mL flask. Then ammonium hydroxide was added dropwise to the mixture with stirring until the pH value of the solution reached 9. Thereafter, the solution was kept stirring for additional 30 min under an atmosphere of argon, and then heated to 80 °C and stirred for 1 h.

Synthesis of graphene–Fe_3O_4 hybrid

Fe_3O_4 solution (5 mL) and RGO–AA solution (5 mL) were added into a 25 mL flask, followed by stirring at room temperature for 30 min. The well-dispersed suspension was filtrated and washed with ethanol for three times. The final product was dried under vacuum at 40 °C.

Synthesis of the complex of graphene and PAA

Graphene (4 mg) and DMF (5 mL) were added into a Schlenk tube, and the tube was evacuated under vacuum and then flushed with argon three times through the sidearm. After sonicated for 40 min, BPO (10 mg) was added to the tube and stirred for 15 min, and then acrylic acid (3 mL) was added dropwise into the system. The mixture was heated to 60 °C and stirred for 24 h under an atmosphere of argon. The well-dispersed black suspension was filtrated and washed with petroleum ether, THF, and deionized water for several times. The filtrate cake was dried under vacuum at 40 °C.

Results and discussion

Our idea of dispersion of graphene with the aid of PAA was inspired by the fact that CNT became soluble with the aid of polymer (actually the polymer chain wrapped the nanotube tightly) [20]. After failed several times in other polymer systems, the graphene sheets could be well dispersed with the aid of PAA (in situ polymerization of acrylic acid in the presence of graphene sheets) (labeled as system G–AA). The resultant dispersion was very stable, and its deep black color remained unchanged after being stored for several weeks or centrifuged at a speed of 4,000 revolutions per minute (rpm) for 15 min. Without the presence of PAA or just to mix the graphene sheets and PAA together (labeled as system G–PAA), the resultant dispersion was unstable (Supplementary Figs. S1, S2). This indicated that the formed PAA in the polymerization process could wrap the graphene sheets much better. Also, it was possible that some polymer chains were grafted onto the graphene sheets, although no spectroscopic evidence could confirm this point.

Considering that GO was hydrophilic and contained some polar groups, such as carboxyl acid moieties, it was expected that GO should be well dispersed in water with the aid of PAA. Really, GO could be well dispersed with the aid of PAA (in situ polymerization of acrylic acid in the presence of GO) (labeled as system GO–AA). Without the presence of PAA or just to mix GO and PAA together (labeled as system GO–PAA), after 5 min, GO precipitated from the dispersion (Supplementary Figs. S3, S4). Further increasing the concentration of GO–AA to 17 mg/mL, the dispersion still did work (Supplementary Fig. S5). This result prompted us to prepare graphene sheets through the reduction of GO–AA in large-scale. According to the similar procedure reported in the literatures [13, 19], the good dispersion of graphene sheets was produced as shown in Fig. 1a and Supplementary Fig. S6 (labeled as system RGO–AA). After filtered and washed with water for several times, a thick film was obtained (Fig. 1b) and the grinded powder was 0.83 g (Fig. 1c). For comparison, the mixture of RGO and PAA (labeled as system RGO–PAA) was prepared. Also, the reduction of GO (labeled as system RGO) without the presence of PAA was conducted (Supplementary Fig. S7). However, the yielded graphene precipitated from the reaction solution during the reduction of GO without the presence of PAA, while the suspension of the mixture of GO and PAA was only stable less than half an hour. It should be pointed out that during our research, there was a report concerning the layer-by-layer self-assembly of graphene sheets, in which PAA was used for the dispersion of graphene [21]. However, in this article, we used PAA to aid the dispersion of GO for the synthesis of graphene in large-scale, and we also applied the good dispersion of graphene for the production of graphene-based hybrid material.

The produced graphene sheets have been well characterized by different methods. Nearly the same IR spectra of RGO and RGO–AA were obtained (Supplementary Fig. S8), no absorption peak centered at about 1,723 cm^{-1} (originated from PAA) could be found in the spectrum of RGO–AA. This indicated that the amount of PAA possibly presented in RGO–AA was very little, or perhaps there were no PAA present. Similar phenomena were observed in their XRD spectra (Supplementary Fig. S9). The Raman spectra were recorded using red laser radiation (632.8 nm), along with that of GO for comparison (Supplementary Fig. S10). The spectrum of GO was in well accordance with that reported previously. The graphene samples demonstrated Raman signals as a broad D-band centered at 1,331 cm^{-1} and a G-band at 1,593 cm^{-1}, with the ratio of 1.40 (I_D/I_G) for RGO–AA, while 1.07 for RGO. These results were in good agreement with those reported in the literatures [22], indicating that GO has been well deoxygenated in both of RGO and RGO–AA.

The absorption peak of GO–AA appeared at 263 nm, perhaps owing to the functionalization of GO by PAA, which was in accordance with literatures reported previously [23, 24]. After the reduction, the peak red-shifted to 274 nm, accompanying with a shoulder peak at 291 nm (Supplementary Fig. S11), indicating that the electronic conjugation within the graphene sheets was restored upon reduction. TEM images further exhibited the visual proof of the production of graphene sheets (Fig. 2, Supplementary Fig. S12), while SEM images were shown in Fig. 3 and Supplementary Fig. S13. There were many white dots in the pictures of RGO, however, much better photos with nearly no white dots were obtained for RGO–AA. The white dots might be the defects without fully reduction, since a significant amount of hydroxyl and epoxide groups without being reduced were found previously in the graphene prepared through the chemical oxidation/reduction approach [25]. If it was the case, our method might provide a good method to produce graphene more similar to pristine graphene.

We could not see any polymer chain in RGO–AA, indicating the amount of the possible present PAA should be less. The dispersion behavior of the prepared graphene was similar to that reported previously (Fig. 4). The TGA thermograms demonstrated that the trend of RGO–AA was similar to that of graphene obtained from other method (Supplementary Fig. S14). PAA was not very stable, indicating that PAA, possibly present in RGO–AA, could be removed upon annealing. Thus,

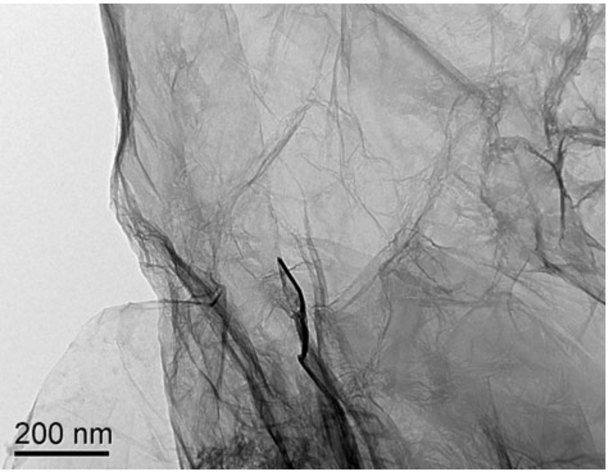

Fig. 2 TEM image of RGO–AA

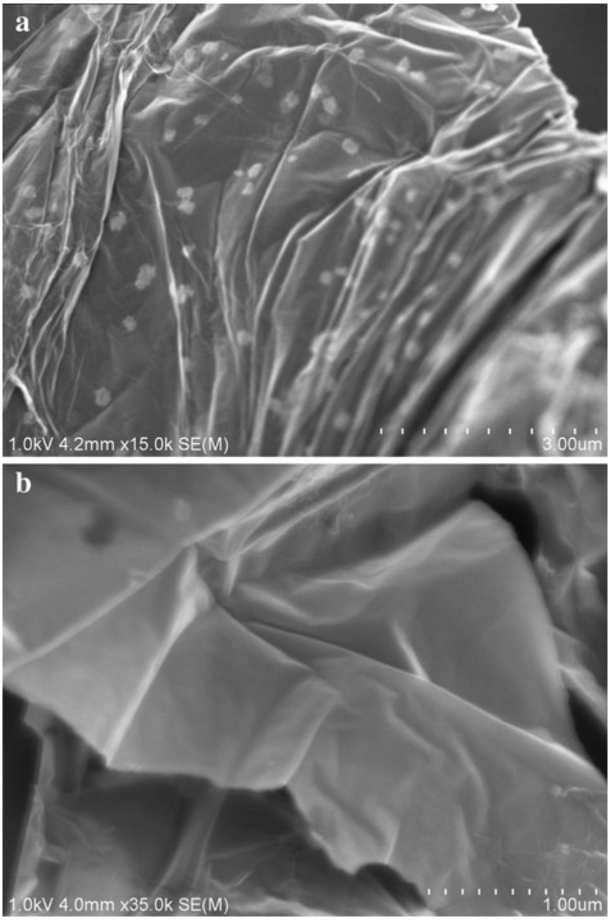

Fig. 3 SEM images of **a** RGO and **b** RGO–AA. The SEM samples were fixed on an SEM stage with the aid of the conductive adhesive

our method for the synthesis of graphene in large-scale could be an alternative approach to the present ones [10, 26–30].

As mentioned above, the incorporation of graphene sheets into composite materials was a promising route to harnessing their unique properties [31]. The good dispersion of RGO–AA in water enabled the possibility of its incorporation with other nanoparticles dispersed in water. With the interest to obtain multifunctional materials with both good conductivity and high magnetism, Fe_3O_4 was selected as the second component. Another reason was that Fe_3O_4 nanoparticles could be easily prepared and well dispersed in the aqueous solution of PAA. Just simply mixing the two dispersion solutions of graphene and Fe_3O_4 together, stirring for several minutes, then filtrating, the hybrid powder of graphene and Fe_3O_4 could be obtained. Although the preparation method was only a physical mixing process, once formed, the obtained hybrid powder could not be separated by applying the

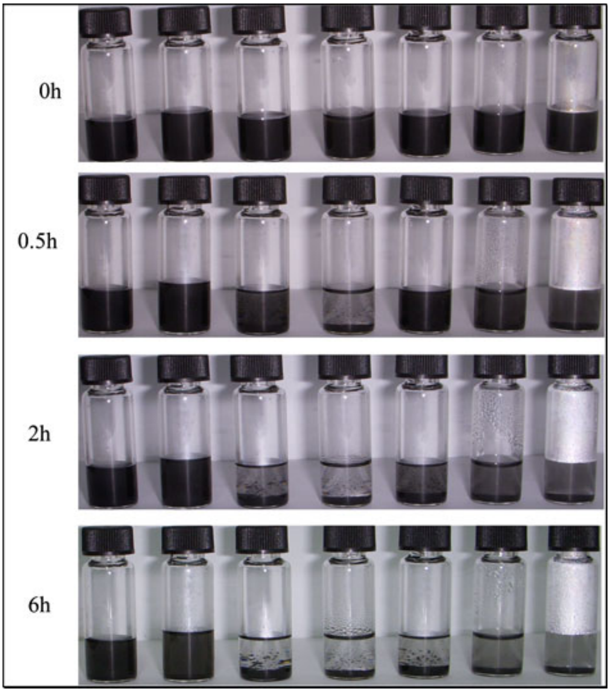

Fig. 4 Photographs of graphene dispersed in different solvents with sonication for 20 min. From *left* to *right*: *N*-methyl pyrrolidone (NMP), DMF, *o*-DCB (1,2-dichlorobenzene), dimethyl sulfoxide (DMSO), toluene, THF and H_2O

Fig. 5 Photographs of RGO–AA–Fe_3O_4 without (*left*) and with (*right*) the placement of a lodestone

magnetic field: as shown in Fig. 5, all the powder was attracted to the bottle wall immediately upon the placement of a lodestone, no trace powder remained at the bottom. This phenomenon indicated that there should be some interactions between

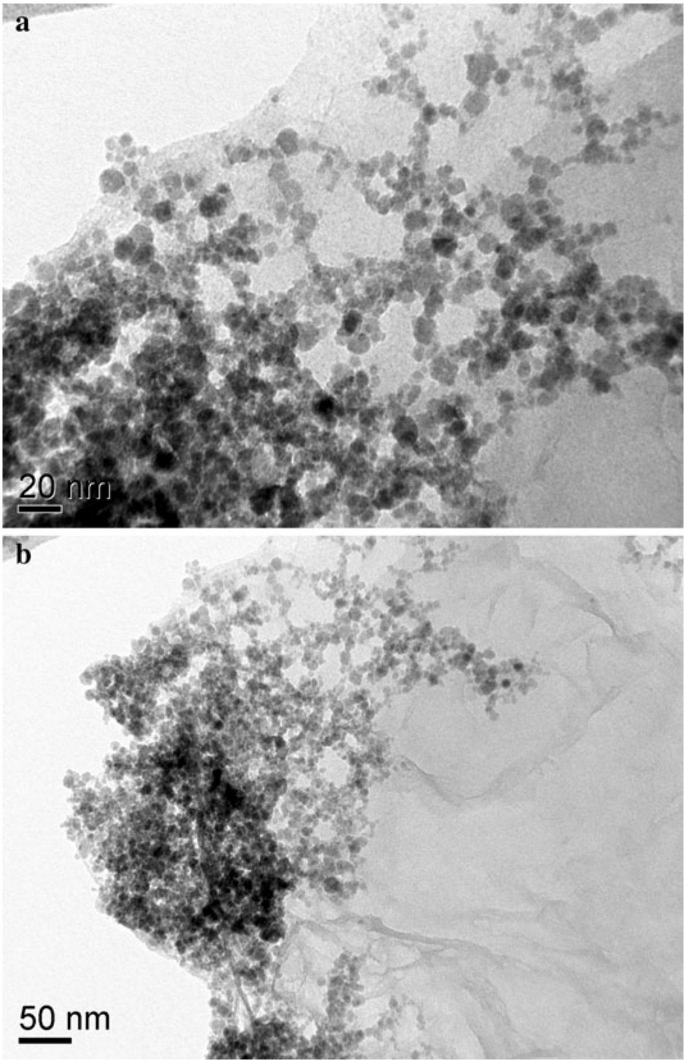

Fig. 6 TEM images of RGO–AA–Fe_3O_4

the two composites, graphene and Fe_3O_4, in addition to the simple physical dispersion.

TEM images demonstrated that the nanoparticles of Fe_3O_4 mainly appeared on the edge of graphene sheets, and nearly no particles were observed about 400 nm away from the edge, though the size of the graphene sheets was as large as several microns (Fig. 6). Thus, the dispersion of the Fe_3O_4 nanoparticles should not be a randomly physical process, but had something to do with the chemical nature of the edges of graphene sheets. As reported by Radovic and Bockrath [32], the zigzag

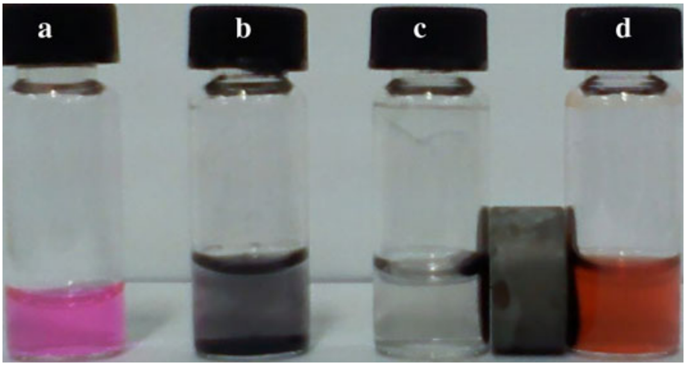

Fig. 7 Photographs of rhodamine B. **a** The solution in water, after the addition of **b** RGO–AA, **c** RGO–AA–Fe_3O_4 and with the aid of a lodestone, and **d** Fe_3O_4 and with the aid of a lodestone

sites of the edges were carbene-like, with the triplet ground state being most common, which could explain the puzzling ferromagnetic properties of some impurity-free carbon materials. Thus, the existence of the Fe_3O_4 nanoparticles near the edges of graphene sheets might be ascribed to the edge effect of graphene sheets.

We also considered the possible applications of this hybrid material with interesting magnetic property. It was known that graphene sheets possessed good absorbing ability toward organic dyes due to their large surface area. As demonstrated in Fig. 7, the red solution of rhodamine B was faded to colorless upon the addition of graphene and the hybrid material of RGO–AA–Fe_3O_4. With the aid of a lodestone, the latter could be easily collected and removed from the solution for recovering. For comparison, the addition of Fe_3O_4 nanoparticles did not lead to the colorless solution. This experiment just exhibited one possible application of the hybrid material, but the practical applications should not only be limited to this.

Conclusions

We have demonstrated a method to disperse graphene sheets in solvents with the aid of PAA, and a concentration could be achieved as high as 0.5 mg/mL in DMF. Also, by using the good dispersion of graphene, we have prepared a hybrid material of graphene and Fe_3O_4 nanoparticles with interesting magnetic and absorbing properties, which opened up a new avenue for the incorporation of graphene sheets with other nanomaterials to produce new functional materials. Also, with the aid of PAA, GO demonstrated even better performance with a dispersion concentration as high as 17 mg/mL, which was used in the large-scale synthesis of graphene.

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