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# Enhanced Solvent Exfoliation of Graphite to Graphene Dispersion in the Presence of Polymer Additive

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Enhanced solvent exfoliation of graphite to graphene dispersion is simply accomplished in the presence of various polymer additives. Use of poly(acrylic acid) (PAA) produces exfoliated graphene dispersion up to concentration of 13 μg mL$^{-1}$, which is much higher than the concentration of graphene dispersion without polymer stabilizer.

Graphene is a 2D carbon-based nanomaterial with outstanding electrical, thermal, and mechanical properties.[1–4] Graphene layers can be easily formulated by use of soluble graphene oxide (GO) which is an insulating precursor material of graphene and subsequent reduction to chemically reduced graphene oxide (RGO) in an indirect route.[5–9] Because chemical reduction of GO layer to graphene layer is difficult to complete, further thermal treatment is typically required for increasing electrical performance of prepared RGO layer by minimizing nonreduced defect sites.[8] But even after thermal treatment, prepared RGO layer is reported to often preserve several defect sites such as non-deoxygenated sp$^3$ carbons.[5] Recently, novel direct routes for exfoliation of graphite to graphene are demonstrated through either mechanical exfoliation[10] or solvent exfoliation of graphite.[11,12] While those direct exfoliations might not be so productive in the consideration of large-scale production, it is evident that exfoliated graphene through direct methods shows better electrical properties than RGO through indirect routes, because neither oxidation of graphite to GO nor reduction of GO to RGO is required. Among direct routes, solvent exfoliation of graphite to graphene is much more promising because this method produces stable graphene dispersion in solution; therefore, various wet processes can be applied for the production of graphene layer. But the concentration of graphene dispersion by solvent exfoliation is reported to be less than 8 μg mL$^{-1}$ even when good solvents for either graphite or graphene such as *N*-methyl-2-pyrrolidone (NMP) are used.[11] Such low concentration of graphene dispersion might result in decreased percolation of graphene plates during the graphene layer formation and resulting detrimental effects on graphene-based devices. Therefore, it is practically important to survey strategies to enhance concentration of graphene dispersion in solvent exfoliation of graphite. In indirect routes which utilize precursor GO, it is reported that various water-soluble polymers can assemble on RGO plates through noncovalent interactions such as $\pi$–$\pi$ interaction,[13,14] micellar encapsulation,[15] and hydrophobic interaction,[16–19] resulting in stable dispersion of RGO with high concentration up to 5 mg mL$^{-1}$ in water. Therefore, it is interesting to validate any enhancement effect on solvent exfoliation of natural graphite in the presence of polymer additives (Figure 1).

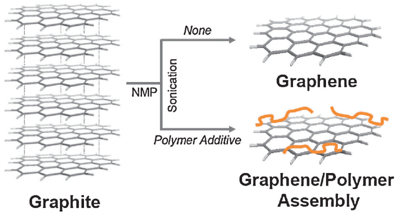

**Figure 1.** Schematic illustration for solvent exfoliation of graphite with or without polymer additive.

In this study, either hydrophilic polymers, such as poly(2-vinylpyrrolidone) (PVP), carbomethoxy cellulose (CMC), poly(acrylic acid) (PAA), and poly(styrene-4-sulfonate) (PSS), or hydrophobic polystyrene (PS) are tested to verify our assumption that polymer additive can enhance solvent exfoliation of graphite to graphene dispersion through the formation of graphene/polymer assemblies. At first, exfoliation of graphite without polymer additive was similarly attempted through a previously reported method.[11] Ultrasonication of natural graphite (2.5 mg) in NMP (20 mL) at 25 °C for 30 min produces transparent graphene dispersion with gray color after centrifugation (500 rpm for 90 min and 1000 rpm for 30 min). Concentration of exfoliated graphene dispersion can be calculated by measuring the absorbance of graphene dispersion at 660 nm and calibrating it with the reported calibration curve.[11] The calculated concentration of graphene dispersion in NMP exactly matches with the reported values, 4–8 μg mL$^{-1}$.

Next, various polymer additives (PS, PVP, PSS, PAA, and CMC) were introduced in the process of solvent exfoliation of graphite. To screen out any size effect of used graphite powder, a large quantity of graphite (25 mg) was sonicated in NMP (200 mL) for 30 min and the whole mixture was equally separated into each volume (20 mL) while continuing sonication. Then, polymer additive (0.1 g) was immediately added into each sample with additional sonication for 60 min. As a control, sonication of graphite was similarly performed without any polymer additive. In addition, because all polymer additives in tests (0.1 g in 20 mL of NMP) do not show any absorbance at 660 nm, it is regarded that any change of optical absorption in solution only correlates with the concentration of exfoliated graphene plates. Enhanced exfoliation of graphite to graphene dispersion is clearly observed with the use of PVP, CMC, and PAA (Figure 2a). Overall solvent exfoliation of graphite with or without polymer additive was repeated five times, and the concentration profiles of prepared graphene dispersions were averaged and summarized (Figure 2b). Definitively, PVP, CMC, and PAA show increase of concentration of graphene dispersion. In the case of PAA, graphene dispersion up to concentration of 13 μg mL$^{-1}$ was observed. But PS and PSS show similar or slightly decreased concentration. The best choice of polymer additive in our study seems to be PAA. This is rather surprising because PAA has very limited solubility in NMP less than

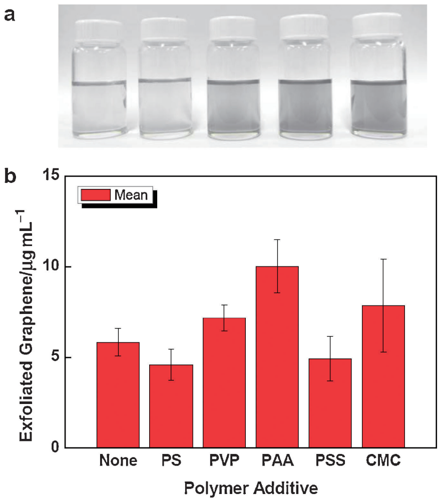

**Figure 2.** (a) Photo images of graphene dispersions with polymer additives in certain experimental set (none, PS, PVP, CMC, and PAA, from left to right). (b) Averaged concentration profiles of graphene dispersions with or without polymer additive in repeated experiments (the bar in each column shows distribution on average).

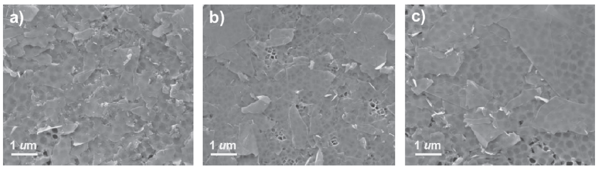

**Figure 3.** E-SEM images of graphene films from (a) graphene/PAA assembly, graphene/CMC assembly, and graphene only dispersion.

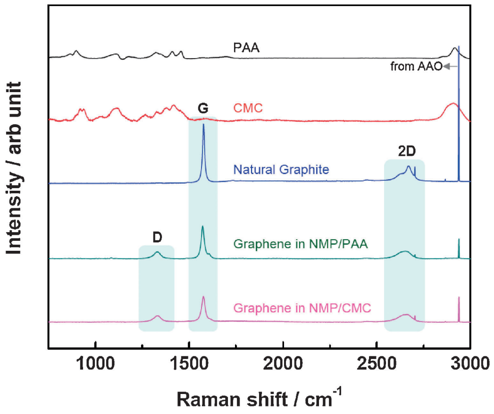

**Figure 4.** Dispersive Raman spectra of PAA, CMC, natural graphite powder, vacuum-filtered films from graphene dispersions with or without polymer additive in NMP.

0.1 mg in 10 mL of NMP. Actually, significant amount of insoluble polymer powders are observed during solvent exfoliation process with PAA. But after centrifugation, most of insoluble polymer powders are removed together with non-exfoliated graphite powder, resulting in transparent graphene dispersion. Noncovalent interaction between polymer additive and graphene plate might contribute to such enhanced solvent exfoliation of graphite to graphene dispersion. In the case of PAA, hydrophobic interaction is the only possible interaction between graphene plates and PAA chains because other noncovalent interactions such as $\pi$–$\pi$ interaction and ionic interaction is not feasible in this case. Recently, we formulated soluble RGO/PAA assembly through noncovalent interaction and proposed that hydrophobic interaction might be the key interaction parameter for anchoring of PAA chains on RGO plates.[20] In solvent exfoliation, similar hydrophobic anchoring of PAA chains on graphene plate might be feasible even though the medium is not aqueous here. Efforts to examine assembly structures of graphene/polymer additive was unsuccessful by using atomic force microscopy (AFM) after applying and drying of graphene dispersion. Only aggregated structures with height of 20–25 nm were observed in AFM images. It is thought that solvent evaporation during sampling preparation induces aggregation of exfoliated graphene.

To monitor the detailed structural features of graphene/polymer assemblies, graphene dispersions were vacuum-filtered through anodized aluminium oxide (AAO) membrane. Environmental scanning electron microscopy (E-SEM) images of prepared graphene films from graphene/PAA or graphene/CMC dispersion show aggregated or separated graphene flakes with different shapes and sizes up to 1–2 µm while E-SEM image of graphene film from graphene only dispersion shows bigger plate dimension around 1–4 µm (Figure 3). Definitely, addition of polymer additive seems to decrease plate dimension of exfoliated graphene. Interestingly, the above E-SEM images reveal AAO pore structures under overlaying graphene plates. It is unclear why graphene plates are transparent in E-SEM analysis even after gold sputtering. Ultrathin structural feature of graphene plates might result in this "transmittancy" of graphene plates in E-SEM analysis. But, it is difficult to verify that observed graphene plates in E-SEM images are single-layered or not.

Layered structures of prepared graphene films were examined in detail by dispersive Raman spectroscopy of samples with a 633-nm 20-mW He-Ne laser (Figure 4). While pristine natural graphite shows only G band at 1586 cm$^{-1}$, prepared graphene films in the presence of polymer additive show both G and D bands at 1580 and 1331 cm$^{-1}$, respectively. This appearance of D band is known to come from edges not from diffuse structural orders in the graphene films.[21] Because laser spot size of Raman analysis is around 1–2 µm similar to the graphene flake dimension in Figure 3, Raman analysis of above ultrathin graphene film is likely able to expose edge regions to the laser beam spot, resulting in the appearance of D band. Much more important structural information on the thickness of graphene flakes is obtained from the shapes of 2D bands at around 2630–2670 cm$^{-1}$. While pristine graphite shows a distinct shoulder band at 2634 cm$^{-1}$ together with sharp 2D band at 2670 cm$^{-1}$, all prepared graphene films show broad single 2D bands at 2655 cm$^{-1}$. This appearance of a broad single 2D band supports that all prepared graphene films consist of graphene flakes with less than 5 layers.[11] Therefore, it is confirmed that solvent exfoliation of natural graphite in the presence of polymer additive results in stable dispersion of graphene flakes with less than 5 layers thickness. From all these results, it is clear that the presence of polymer additive definitely enhances solvent exfoliation process of graphite into exfoliated graphene dispersion while inducing little detrimental effects.

In summary, enhanced solvent exfoliation of graphite into graphene dispersion (up to 13 $\mu$g mL$^{-1}$ in NMP) was demonstrated by the use of polymer additive. While the detailed interaction mechanism between graphene plates and polymer additive is not fully understood in this state, hydrophobic interaction between graphene plates and polymer chains might enhance solvent exfoliation of graphite in the presence of polymer additive, resulting in graphene dispersion with graphene plates less than 5 layers thick.

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