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Role of poly(*N*-vinyl-2-pyrrolidone) as stabilizer for dispersion of graphene via hydrophobic interaction

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Abstract Stable aqueous dispersion of chemically reduced graphene is simply obtained by reducing GO solution in the presence of PVP. Prepared aqueous graphene dispersion was optically clear and stable for several months without any aggregation or precipitation. Graphene/PVP assembly shows decreased optical transmittance (47% at 600 nm) and quenching of photoluminescence of parent GO (8.5% at 375 nm) after reduction. Raman analysis confirms that reduction of GO to graphene is efficient in the presence of PVP. Both DLS and AFM analysis confirm that there is efficient and overall interaction between chemically reduced graphene plates and PVP chains. Hydrophobic interaction between graphene and PVP might be responsible for this solubilization of chemically reduced graphene in solution.

Introduction

Carbon nanomaterials such as carbon nanotube and graphene have received intensive research interests due to their fascinating mechanical and electrical properties. For practical application, carbon nanomaterials must retain enough solubility in organic or aqueous solvents because various wet processes such as spin-coating, spraying, and ink-jet printing are easily applicable through using solubilized carbon nanomaterials [1–7].

While solubilization methods using various surfactants such as sodium dodecyl sulfate (SDS) and polymers such as poly(*N*-vinyl-2-pyrrolidone) (PVP) have been well established in carbon nanotube research [8], those methods are not effective for solubilizing graphene in solution. Graphene has single 2D sp_2-carbon conjugated structures and has limited solubility in solvent due to their strong dispersion forces between hydrophobic graphene plates. Therefore, water soluble precursor, graphene oxide (GO) has been utilized for device fabrication and further reduction was done to render isolating GO into conducting graphene [9–12]. To solubilize chemically reduced graphene in solution, only block copolymer with high molecular weight such as Pluronic has been reported to be effective for the solubilization of graphene in water through micellar encapsulation [13]. Recently, various noncovalent chemistries have been developed to formulate solubilized chemically reduced graphene. Graphene could be solubilized through either π–π interaction with water soluble π-rich molecules such as pyrene derivative, poly(4-styrenesulfonate) (PSS), polyethynylenephenylene having negative charges in their structures (Fig. 1c) [14–17]. In these cases, π–π interaction supports the formation of graphene/(poly)electrolyte assembly, and then charge repulsion among interacting (poly)electrolytes on graphene plates disrupts strong dispersion force of graphene components. Also, covalent chemistry can be utilized for solubilizing graphene in various solvents. Introducing of pendant groups is known to be effective for solubilization of substituted graphene via esterification, amidation, and amidation reactions with GO (Fig. 1b) [18–25]. But, this covalent chemistry renders some of sp_3 carbons of graphene plates into sp_3 carbons due to the presence of covalent linkages, and therefore deterioration of electrical properties of pristine graphene is often observed.

Recent researches demonstrate simple methods for the solubilization of chemically reduced graphene through

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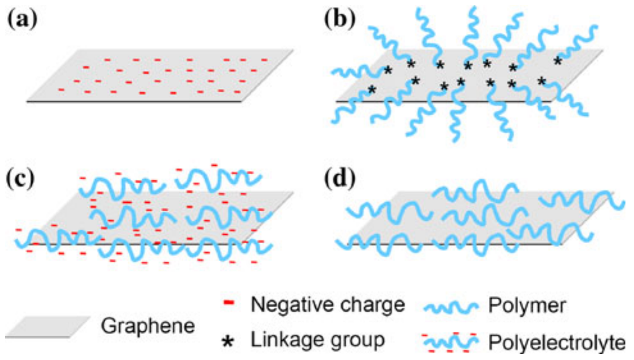

Fig. 1 Schematic illustration of methods for the solubilization of chemically reduced graphene in solvent through **a** the introduction of negative charges, **b** the formation of covalent linkages, **c** π–π interaction with π-rich (poly)electrolytes, and **d** hydrophobic interaction with non-(poly)electrolytes

charge repulsion between negatively charged graphene plates in the absence of π–π interaction (Fig. 1a) [26, 27]. Ammonia and hydroxide was reported as effective reagents for introducing negative charge on graphene plates, but this is also covalent chemistry and leaves some sp_3 carbons in graphene structure. PVP is reported to increase the stability of above negatively charged graphene dispersion [28, 29]. But PVP itself has not been utilized for the solubilization of chemically reduced graphene. Because PVP is not ionic in nature, the only possible interaction with graphene plate is the hydrophobic interaction. This hydrophobic interaction between graphene plates and PVP chains is reported to enable direct solvent exfoliation of natural graphite to graphene dispersion in the presence of PVP in water [30]. But this direct solvent exfoliation of natural graphite is difficult to provide graphene dispersion with higher concentration more than 8 μg/mL [31]. Therefore, it is quite interesting to verify that above hydrophobic interaction between chemically reduced graphene plate, and PVP is strong enough for solubilizing chemically reduced graphene in water with higher concentration (Fig. 1d). In the case of carbon nanotube, wrapping of PVP chains on the surface of carbon nanotube is well documented and it is reported that the presence of PVP can increase solubility of carbon nanotube up to 1.4 mg/mL in water [32]. 2D structural features of graphene plates might hamper efficient wrapping of PVP chains on graphene plates but the hydrophobic interaction between graphene plates and PVP chains is regarded to be maintained similarly to carbon nanotube. This type of preparation of soluble graphene has several advantages. First, it is completely noncovalent chemistry, and therefore it can minimize build-up of any undesirable sp_3 carbons in chemically reduced graphene. Next, this method does not require molecular design for π-rich polyelectrolyte which requires extensive synthetic efforts. Various commercial polymeric structures can be utilized instead of expensive polyelectrolytes. Recently, our research has revealed that various commercially available water soluble polymers which are not polyelectrolytes can successfully produce stable aqueous graphene solution via noncovalent chemistry [33, 34]. Therefore, simple solubilization of chemically reduced graphene using PVP is attempted without any other reagents or additives. Because most biomolecules are not π-rich in their structures, our approach can be easily utilized for the formation of soluble graphene/biomolecule assembly with high stability and graphene concentration.

Experimental

Materials and instruments

All the chemicals were purchased from Sigma–Aldrich Corporation. Graphite powder was purchased from Bay Carbon Inc (SP-1). PVP having weight average molecular weight of 40,000 Da was used after reprecipitation. UV–VIS spectra were obtained from UV–VIS spectrometer of Hewlett Packard. Photoluminescence spectra were obtained from L550B luminescence spectrometer of Perkin Elmer. FT-IR spectra were obtained from IR100/IR200 spectrometer of Thermoelectron Corporation. Raman analysis was done from LabRAM high resolution UV/VIS/NIR dispersive Raman microscope of Horiba John Yvon. DLS data were obtained from particle size analyzer (ELS-Z) of Otsuka Electronics Corporation. SEM images were obtained from JSM-6700 field emission scanning electron microscope of GELO Corporation. AFM images were obtained from XE-100 atomic force microscope of PSIA.

Synthesis of graphene oxide (GO)

Graphene oxide was prepared from natural graphite by a modified Hummers method [15, 35, 36]. In the first step, pre-oxidized graphite powder was synthesized through reaction of graphite powder (3 g), sulfuric acid (12 mL), $K_2S_2O_8$ (2.5 g), and P_2O_5 (2.5 g). This pre-oxidized graphite powder (2 g) was further oxidized by sulfuric acid (120 mL), $KMnO_4$ (15 g), and water (250 mL). After dilution with water (700 mL), decomposition of excess $KMnO_4$ by H_2O_2 (30%, 20 mL) and complete removal of metal ions by HCl (10%, 1 L), the resulting GO solution was filtered and washed with water several times. The resulting GO powder was shortly dried in air and then transferred into 1 L of water to make bright brown GO solution. The GO solution was dialyzed (molecular weight cut-off membrane, MWCO with 1,000,000 Da) in deionized water for 1 week and brown fibrous GO powder was finally obtained after freeze-drying under reduced pressure. For experiments, fresh GO solution (2 mg of GO in 15 mL of water) was prepared and used with minimum sonication (not more than 30 min) just before use.

Preparation of graphene/PVP assembly

100 mg of PVP was simply mixed with aqueous GO solution (2 mg in 15 mL of deionized water). To reduce GO into chemically reduced graphene, hydrazine monohydrate (30% aqueous solution, 4 drops) was added into the mixture and temperature was maintained at 80°C for 24 h. The GO solution with initially bright brown color is getting darker in the progress of reduction to graphene solution. Prepared solution of graphene/PVP assembly did not show any visible precipitation for more than 6 months. For comparison, reduction of GO solution was done without PVP. This produced insoluble graphite-like precipitation within a few hours.

Results and discussion

Solubilization of chemically reduced graphene in water

To prepare solution of chemically reduced graphene in the presence of PPV, aqueous solution of GO was simply obtained by using Hummer's method from natural graphite. Reduction of resulting GO solution (2 mg in 15 mL of water) by hydrazine monohydrate with PVP (100 mg) produced clear black-colored reduced graphene solution, while insoluble graphite-like precipitation was formed from the direct reduction of GO solution without PVP. Graphene/PVP assembly showed reduced optical transmittance (47% of GO transmittance at 600 nm) and was optically clear, while no aggregation or precipitation was found even after 6 months. Ultracentrifugation over 20,000 rpm did not result any sedimentation. UV–VIS spectroscopy showed evidently decreased transmittance over all wavelengths due to the recovery of sp_2-conjugation structures which are partially broken in insulating GO as shown in Fig. 2a. Photoluminescence (PL) spectra were obtained from each solution with irradiation wavelength of 300 nm before and after reduction of GO/PVP solution as shown in Fig. 2b. The broad emitting peak around 370 nm of GO solution was almost quenched after reduction. Reduced graphene showed just 8.5% of photoluminescence of parent GO at 375 nm. While the origin of photoluminescence of GO is unclear, recovered conjugation length of chemically reduced graphene may result this quenching of PL after reduction.

Non-covalent interaction between graphene and PVP

To understand the role of PVP as a stabilizer for dispersion of graphene in water, prepared graphene/PVP solution was filtered through AAO membrane (pore size of 0.2 μm) to remove any non-interacting PVP chains from the solution. PVP has been known to solubilize SWNT or MWNT in water together with surfactants such as SDS by wrapping [32]. Single graphene has not tube-like but planar 2D structure. Wrapping of PVP chains with graphene looks unfeasible because the plate dimension of planer graphene (typically 1 μm) exceeds chain length of PVP. PVP chains may partially interact with graphene on surface not through wrapping. While the detailed molecular structure of interacting graphene/PVP assembly is unclear in this stage, it will form assembled structure with less interacting energy compared with wrapping in the case of carbon nanotubes. Actually, PVP was not observed in graphene film after filtration. FT-IR spectrum of filtered graphene film showed complete disappearance of PVP as shown in Fig. 3a. Instead, obtained spectrum was almost matched with that of insoluble graphite precipitation, showing the absence of carbonyl stretching peak around 1750 cm^{-1} of GO and the

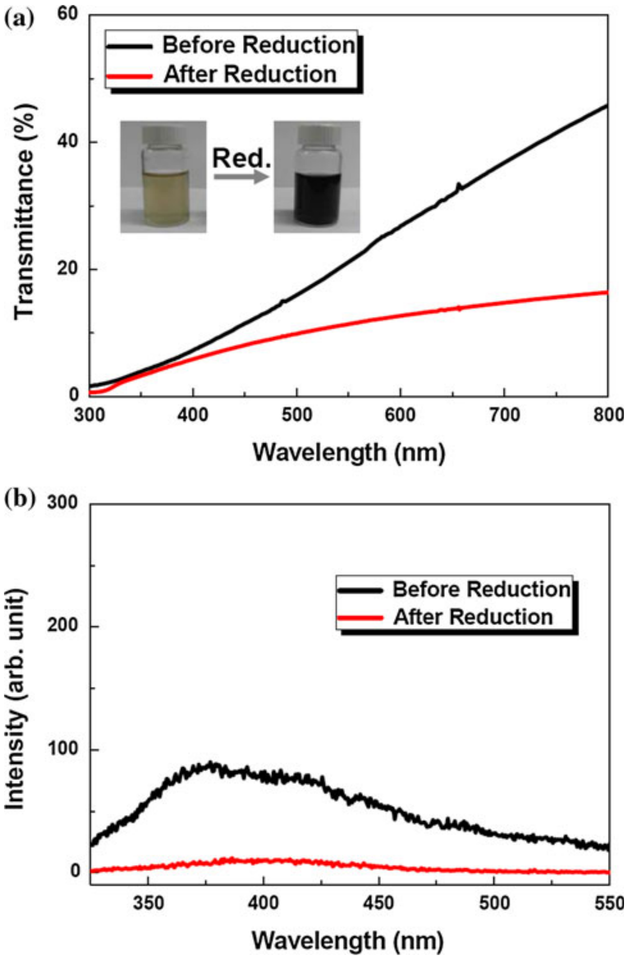

Fig. 2 **a** UV–VIS spectra (insects are images of GO/PVP and graphene/PVP solutions, respectively) and **b** PL spectra of GO/PVP solution before and after reduction

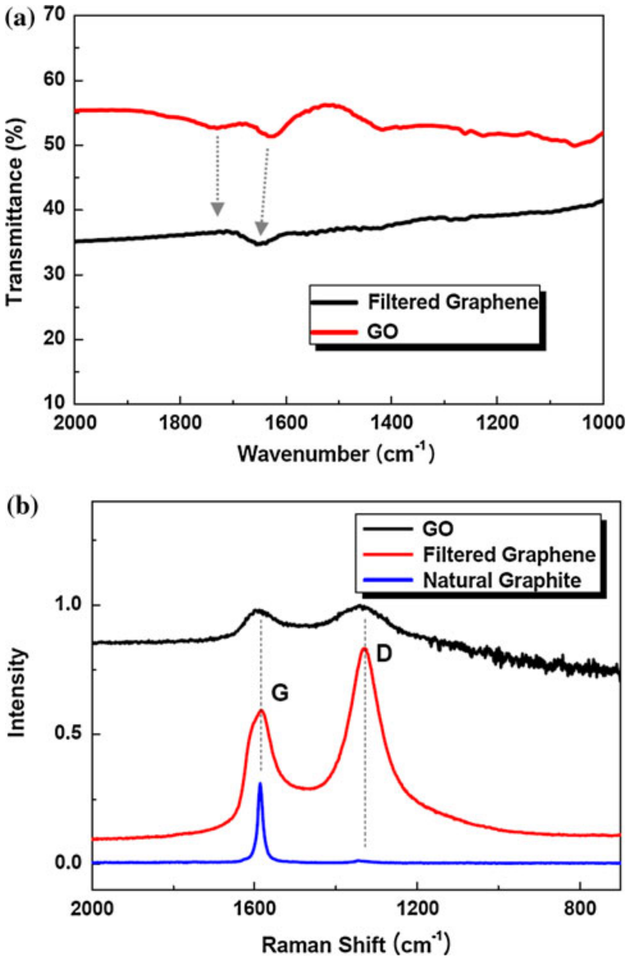

Fig. 3 **a** FT-IR spectra of prepared graphene film and GO powder and **b** Raman spectra of GO powder, prepared graphene film, natural graphite

presence of sp_2 stretching of conjugated carbons. This result confirms that reduction to graphene from GO is almost completed. Prepared graphene film is not soluble in water again. This supports that PVP is not covalently linked with graphene plate because physical filtration/washing procedure cannot break any covalent linkages between PVP and graphene. The disappearance of PVP chains in prepared graphene film might originate due to weakened hydrophobic interaction between graphene plates and PVP chains in solid state. In addition, Raman spectrum of filtered graphene film was monitored using a 633 nm He–Ne laser beam as shown in Fig. 3b. While pristine natural graphite shows only well-known G band at 1585 cm^{-1}, both GO and prepared graphene film show both G and D bands around 1580 and 1330 cm^{-1}, respectively. The appearance of D band and the increase of D band intensity compared with G band intensity support that prepared film are mainly composed of not only graphite grains but also graphene plates. This Raman result agrees well with the report by Stankovich, confirming that GO is well chemically reduced to graphene in this graphene/PVP assembly solution [37].

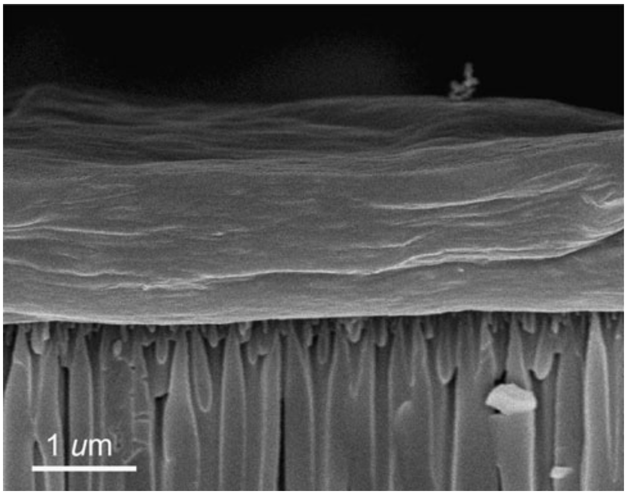

Fig. 4 FE-SEM image of filtered graphene film with a thickness of 1.5 μm (underlying pore structure is from AAO membrane)

The microstructure of prepared graphene film was monitored in FE-SEM images as shown in Fig. 4. The usual layered structure was observed in obtained graphene film [2]. Individual graphene plates are not observable due to the extensive overlapping of neighboring graphene plates and instead usual wrinkled structures were found in top surface of graphene film. The thickness of graphene film can be easily controlled by changing volume or concentration of graphene/PVP solution. The sheet resistance of graphene films depends on the film thickness and was in the range of 10^6–10^5 ohm/square. For example, 30 nm thick graphene film with a transmittance of 50% shows a sheet resistance of 1.7×10^6 ohm/square. The calculated conductivity of this sample is around ~2 S/m which is comparable to the conductivity value of chemically reduced graphene film before any thermal treatment in other report [6].

DLS and AFM study

The as-prepared GO/PVP solution showed broad size distribution between 1 and 8 μm in DLS analysis as shown in Fig. 5a. After reduction, prepared graphene/PVP solution showed decreased size distribution between 800 nm and 2 μm as shown in Fig. 5b. Extensive dialysis more than 1 week was done to remove any non-interacting PVP from the solution. While reduced graphene is soluble even after dialysis, further decrease of particle size distribution was monitored in DLS study between 300 nm and 1 μm as shown in Fig. 5c. Probably, GO/PVP might form micelle-like loosely packed superstructure before reduction.

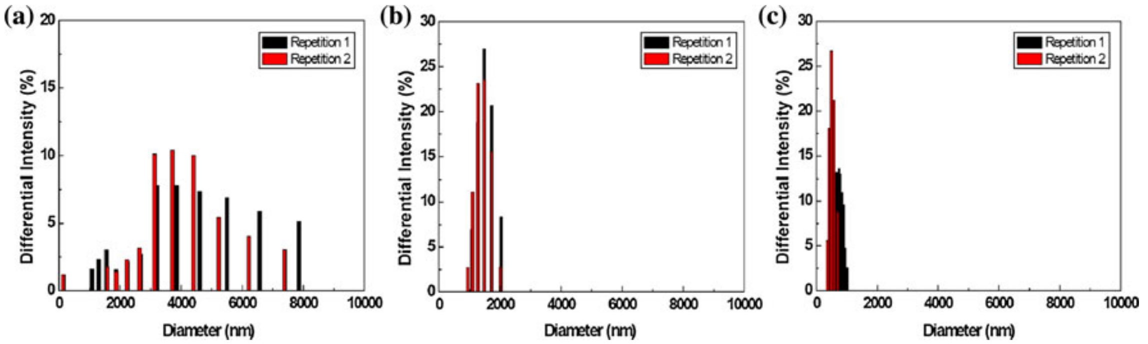

Fig. 5 Plots of diameter versus intensity plots of **a** GO/PVP solution, **b** graphene/PVP solution, and **c** graphene/PVP solution after dialysis

Reduction of GO to graphene will start to induce relatively strong hydrophobic interaction between graphene plates and PVP chains, resulting in much densely packed graphene/PVP assembly structure in solution. In last, dialysis of graphene/PVP solution will remove any free or loosely interacting PVP chains from graphene/PVP solution, showing smallest particle dimension in DLS analysis. We believe that there is no free PVP in graphene/PVP solution after dialysis. Therefore, correlation between DLS and AFM analysis was tried in next.

The structural features of graphene/PVP assembly were monitored by AFM analysis. The plate dimension of graphene is much smaller in graphene/PVP assembly compared with GO. This result correlates with the decreased size of graphene/PVP assembly after reduction in DLS analysis. In addition, while the parent GO showed thickness around 1.2 nm as shown in Fig. 6a, graphene/PVP assembly showed increased thickness around 2.2 nm as shown in Fig. 6b. In this stage, it is unclear whether observed graphene/PVP assembly in Fig. 6b is monolayer or not. But because even highly diluted graphene/PVP solution shows similar images in AFM analysis, it is believed that most of graphene/PVP assemblies in solution are monolayers. Increased monolayer thickness of

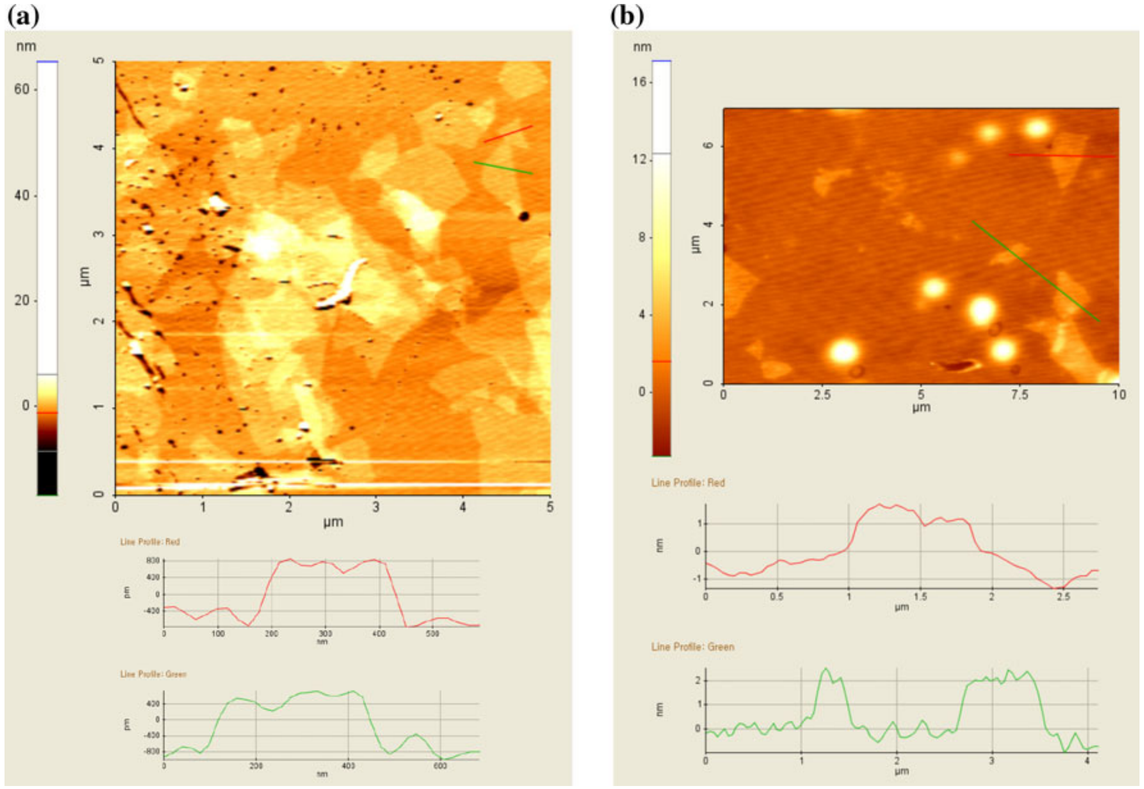

Fig. 6 AFM images of **a** GO and **b** graphene/PVP assembly after intensive dilution of both solutions (*bottoms* are height profiles for *inserted lines*)

graphene/PVPV assembly compared with GO supports the presence of interacting PVP chains on graphene plate. From the structural feature of graphene/polymer assembly in Fig. 1d, thickness of graphene/PVP assembly is expected to be slightly increased compared with GO.

Conclusion

Stable aqueous dispersion of chemically reduced graphene was obtained by reducing GO solution in the presence of PVP. Prepared aqueous graphene solution was optically clear and stable for several months without any aggregation or precipitation. Hydrophobic interaction between reduced graphene plates and PVP chains are responsible for this stabilization of reduced graphene in solution. This approach is versatile and simple compared with other approaches which require covalent chemistries or π-rich molecules with negatives charges. Systematic examination of other water soluble polymers for graphene solubilization is required to elucidate the detailed hydrophobic interaction between water soluble polymers and reduced graphene plates. The solubility of reduced graphene in this method approaches solubility of GO in water (4 mg/mL), while PVP is known to solubilize carbon nanotube in a concentration of 1.4 mg/mL when PVP is used together with surfactant. The increased solubility of chemically reduced graphene in the presence of PVP supports efficient and overall interaction between graphene plate with PVP chain.

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