doi:10.1246/cl.2010.1160
Published on the web October 5, 2010

Solubilization of Reduced Graphene in Water through Noncovalent Interaction with Dendrimers

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Solubilization of reduced graphene is simply attempted through in situ reduction of graphene oxide (GO) solution in the presence of poly(propylene imine) dendrimers **G4** or **G5** with terminal amine groups through noncovalent interaction. Interestingly, porous graphene film was formed by filtration of these dendrimer-stabilized reduced graphene solutions.

Graphene has received increasing interests due to its fascinating electrical and structural properties in various applications.[1] Generally, graphene oxide (GO) is used for device fabrication instead of graphene because reduced graphene itself is not soluble in any solvents due to its strong dispersion force between graphene plates. But GO is insulating and, therefore, an additional reduction step is required to convert GO to graphene to provide electrical properties.[2] To overcome this problem, several approaches have been attempted to formulate soluble graphenes through either covalent or noncovalent chemistry. Covalent modification of GO with incoming small molecules or polymers through the formation of ester, amide, amine, and urethane linkages has been reported to give reduced graphene with enough solubility in organic solvents or water.[3] Recently, novel noncovalent chemistries were uncovered, and solubilization of reduced graphene was possible without any covalent chemistry. π–π Interaction with molecules having rich π electrons and micellar encapsulation using polymer surfactants were reported to solubilize reduced graphene in solvents. These noncovalent chemistries are more promising because the electric properties of parent graphene are not affected by the presence of any sp^3 carbons which are inevitably present in covalent chemistries.[4]

In this communication, we report simple noncovalent chemistry to solubilize reduced graphene in water using poly(propylene imine) dendrimers with terminal amine groups. 10 mg of DAB-*dendr*-$(NH_2)_x$ ($x = 32$ and 64 for **G4** and **G5** dendrimers, respectively) was added into aqueous GO solution (1 mg in 30 mL of water), and then hydrazine monohydrate (4 drops) was added. On heating at 80 °C more than 24 h, the reaction mixture with initial bright brown color became darker in the progress of reduction to graphene. When dendrimers are in excess compared with GO, all the reduction reactions produced completely homogeneous aqueous reduced graphene solutions which are stable more than six months. UV–vis spectroscopy shows much decreased transmittance after reduction (Figure 1). The size of GO and graphenes was estimated by dynamic light scattering (DLS) and AFM. We noticed that GO plate dimension decreases with increasing sonication time. Regardless of size of the initial GO, solubilized reduced graphene which is stabilized in the presence of amine-terminated dendrimers showed similar plate dimensions after reduction.

To confirm the detailed noncovalent interactions between reduced graphene and amine-terminated dendrimers, the stability of prepared graphene solutions was monitored under various conditions. While they are stable in either neutral or acidic conditions, high pH above 11 made reduced graphene instantly precipitate from the solution. Adding excess salts such as NaCl did not form any aggregation or precipitation. Reduction of GO with similar hydroxy-terminated dendrimers produced insoluble graphite precipitation. These results show that the presence of terminal amine groups is one key factor for solubilization of graphene in water and support that the interaction between amine-terminated dendrimers and reduced graphenes is not fully electrostatic.[3d] Amine-terminated dendrimers can be easily transferred into organic phase with the use of long fatty acids such as dodecanoic acid.[5] When the above reduced graphene solution was mixed with 1 wt % dodecanoic acid solution in toluene, solubilized graphene precipitated from aqueous solution into the water/toluene interface due to complete transfer of dendrimers into toluene. This again supports that the interaction between reduced graphene and amine-terminated dendrimers is not covalent. Combination of hydrogen bond with ion pairing might contribute to solubilization of graphene/dendrimer conjugates in water. There might be a small amount of remaining carboxylic acid groups on the surface of reduced graphenes. Dendrimers with terminal amine groups can interact with these carboxylic acid groups through either ion pairing or hydrogen bonds. Aggregation of graphene plates into insoluble graphite structures can be minimized in the presence of these bulky dendrimer cations. From some of our recent studies to solubilize reduced graphene via noncovalent chemistries, various water-soluble polyelectrolytes with different backbone structures and pendent functional groups seem to be effective to make reduced graphene solutions. Further studies might help to elucidate the detailed interaction parameters between reduced graphene plate and water-soluble polyelectrolytes such as dendrimers in detail.

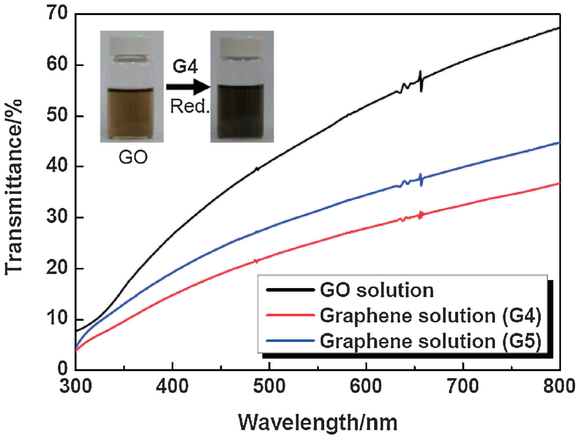

Figure 1. UV–vis spectra of GO solution and reduced graphene solution with either **G4** or **G5** dendrimers.

Pure graphene films with different thickness were obtained by simple filtration of above graphene solutions using anodized aluminum oxide (AAO) membranes with pore size of 0.2 µm. After several washing steps (100 mL of water, three times) with deionized water to remove any noninteracting dendrimers, the

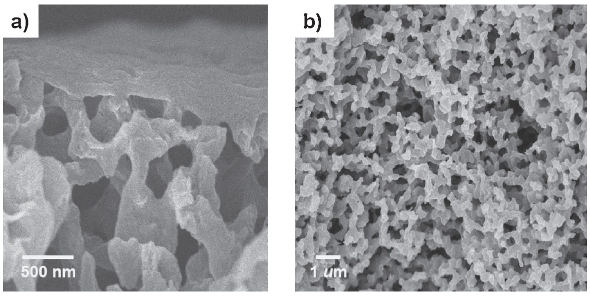

Figure 2. Side-view FE-SEM images of filtered graphene film using **G4** dendrimer a) in top region and b) in the middle.

structure and composition of prepared graphene films were monitored by FT-IR and FE-SEM analyses. From FT-IR analysis, the presence of dendrimer in the filtered graphene films was not observed. This is probably because the interaction of dendrimer and reduced graphene is noncovalent and repeated washing with water breaks interaction between reduced graphenes and dendrimers completely. None of the prepared graphene films were soluble in water any longer. In contrast, spin-coated or drop-cast graphene/dendrimer films were resoluble in water due to the presence of interacting dendrimers. Interestingly, unusual porous film structures were observed in FE-SEM images of graphene films which were prepared by filtration (Figure 2). This is in great contrast with the usual horizontally layered structures of graphene or GO films in the literature.[2c] We think that initial filtration produces membranes of weak graphene/dendrimer composites and that further filtration and several washing steps remove all the remaining dendrimers which are weakly bound with graphene plates. Dendrimer-rich domains in composite films may produce porosity in the final graphene films after removal. The porous structure of these graphene films did not deteriorate electrical properties of the reduced films because the contact between neighboring graphene plates is still preserved. The surface resistance of porous graphene films was in the range of 10^4–10^6 Ω/sq depending on the thickness (1–20 μm) of the membranes.

The structural features of graphene plates with dendrimers were monitored by either AFM or FE-SEM images. Diluted reduced graphene solutions were spin-coated or drop-cast for sample preparation. Both AFM and FE-SEM showed increased graphene plate thickness around 12 nm probably due to the presence of interacting dendrimers.[6] The plate dimensions were in the range between 200 and 400 nm. Both **G4** and **G5** did not show any significant difference. The overall structural rearrangement from natural graphite to GO and then to reduced graphene was monitored in Raman analysis (Figure 3). FT-Raman spectra of filtered graphene film using **G5** dendrimer showed characteristic G and D bands at 1589 and 1320 cm^{-1}, respectively. While GO also shows broad G and D bands in a similar range, the D/G intensity ratio of reduced graphene film is much higher than GO. This Raman result agrees well with a report by Stankovich, confirming that GO is well reduced to graphene in this graphene/dendrimer solution.[7]

In summary, aqueous graphene solution was simply prepared by using dendrimers having terminal amine groups via noncovalent interaction between reduced graphene plates and dendrimers. Interestingly, graphene films having porous structures were prepared by filtration of these graphene solutions. Various wet processes can be directly applied by using prepared solubilized graphene to formulate graphene-based electrodes or other devices.

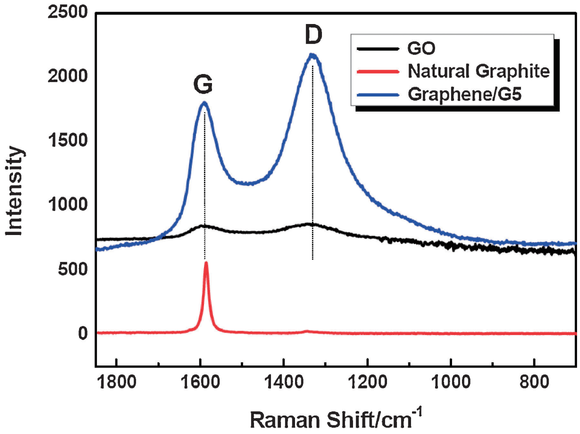

Figure 3. FT-Raman spectra (using a 633 nm He-Ne laser beam) of GO, natural graphite, and filtered graphene film using **G5** dendrimer.

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (No. 2010-0004806) and supported by a grant from the Academic Research Program of Chungju National University in 2010. We also specially thank Ms. Hee Won Seo in Research Support Team (KAIST, Central Research Instrumental Facility) for kind help with Raman experiment.

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