Preparation and Characterization of Surfactant-Exfoliated Graphene

Yeari Song, Hoik Lee, Jaehyoung Ko, Jungju Ryu, Minkyoung Kim, * **and Daewon Sohn** *

Department of Chemistry and Research Institute for Natural Sciences, Hanyang University, Seoul 133-791, Korea
E-mail: dsohn@hanyang.ac.kr (D. Sohn); kmk7300@hanyang.ac.kr (M. Kim)

An anionic surfactant, sodium dodecylbenzene sulfonate (SDBS), was introduced during the ultrasonication process for exfoliation of graphene. The surfactant plays the roles of exfoliator and stabilizer by binding to the graphene surface. The obtained modified graphene was characterized by Fourier-transform infrared spectroscopy (FT-IR) and solid state ^{13}C CP/MAS NMR to analyze the binding between molecules, and by X-ray diffraction (XRD) to characterize the bulk structure. The resulting graphene exhibited good dispersion stability in both water and organic solvents.

Key Words : Graphene oxide, Sodium dodecylbenzene sulfonate, Dispersity, Surfactant-exfoliation

Introduction

In recent years, graphene, a two dimensional hydrocarbon, has attracted considerable attention because of its unique electrical, optical, catalytic, and mechanical properties.[1-5] Graphene is not only a basic building block for graphitic materials, but it is also among the thinnest and strongest materials. Since Geim's research team first isolated single layer graphene from graphite in 2004, a large amount of research has been devoted to the synthesis of graphene. Many methods, such as mechanical exfoliation,[6] chemical vapor deposition (CVD),[7,8] and reduction of graphene oxide (GO),[9-11] have been reported for the preparation of high quality graphene. Since graphite is inexpensive and readily available, the chemical synthesis from graphite is regarded as the most cost effective and scalable method for the production of graphene.

Unfortunately, graphene does not remain uniformly dispersed as single or monolayer sheets in an aqueous environment, *i.e.* it precipitates after reduction due to its hydrophobic and organophobic characteristics. Since there is current interest in fabricating soluble graphenes to design graphene based devices, many studies of modified graphenes have been undertaken. One of these studies used proteins such as polydopamine to cap the terminal sites of graphene.[12,13] Another study employed an organic compound such as hexamethylenetetramine or butylamine as a one-step reductant.[14] These types of methods provided examples of techniques to synthesize water soluble graphenes.

Many investigations have attempted to discover suitable organic stabilizers for the improvement of concentrated and stable graphene colloidal dispersions. Among several methods, surfactants have been found to be suitable stabilization reagents.[15,16] Recent study reported sodium dodecylbenzene sulfonate (SDBS) to be admirable for dispersing graphene in an aqueous solution.[17] SDBS, an anionic surfactant was introduced as an exfoliator as well as stabilizer followed by *in situ* reduction with hydrazine to provide material with better solubility in aqueous solvents. With the aim of increasing graphene solubility by the ultrasonication process, we investigated a surfactant-stabilized graphene. In addition, the mechanism of surfactant binding to the graphene surface and an understanding of the stabilization process were investigated.

Experimental Section

Preparation of Graphene Oxide. Graphite powder from Kanto (Cica-reagent) was oxidized according to the modified Hummers method as originally presented by Kovtyuhova *et al*. to form graphene oxide.[18] Other reagents for the synthesis of graphene oxide (H_2SO_4, $K_2S_2O_8$, P_2O_5, $KMnO_4$, H_2O_2 and HCl) were obtained from Sigma-Aldrich. Typically, concentrated H_2SO_4 (50 mL), to complete the oxidation, was heated to 90 ^{o}C in a 500 mL beaker. P_2O_5 (10 g) and $K_2S_2O_8$ (10 g) were added with stirring until the materials were totally dissolved followed by cooling to 80 ^{o}C. Graphite powder (12 g) was added to this solution, the mixture was kept at 80 ^{o}C using a hotplate for 4.5 h, and the mixture was diluted with 2 L of DI water over 12 h. Next, the mixture was filtered using a 0.45 μm Millipore filter, and the residue was washed to remove all traces of acid. The solid was transferred to a drying dish and was left overnight. The next step was oxidation with H_2SO_4 (460 mL) while cooling in a 0 ^{o}C ice bath. The obtained graphite was added to H_2SO_4 and agitated. $KMnO_4$ (60 g) was slowly added to dissolve keeping the reaction temperature below 10 ^{o}C. The mixture was then allowed to react at 35 ^{o}C for 2 h followed by the addition of distilled water (920 mL), initially in 20-30 mL aliquots, while cooling in an ice bath to prevent an increase in the reaction temperature. After stirring for two hours, an additional 2.8 L of DI water and 50 mL of 30% H_2O_2 were added to the mixture, which produced a color change to yellow together with bubbling. The mixture was allowed to settle for at least a day, and the supernatant was decanted. The remaining mixture was centrifuged and then washed
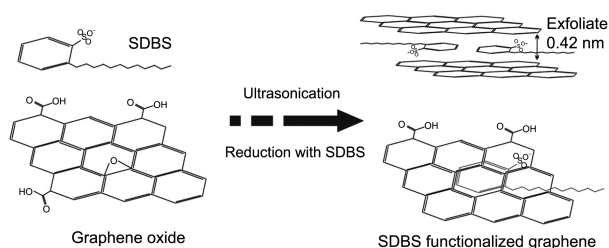
Figure 1. Preparation of SDBS functionalized graphene by ultra-sonication and reduction method.

Figure 2. FT-IR data for (a) SDBS, (b) GO, (c) RGO, and (d) SDBS-g.

with 10% HCl solution followed by DI water to remove residual acid. The resulting solid was dried in air and dialyzed for two weeks to remove any remaining metal.

Synthesis of SDBS Functionalized Graphene. For the synthesis of SDBS functionalized graphene, SDBS and hydrazine hydrate were purchased from Sigma-Aldrich. In the pretreatment step, 1.75 g (5 mmol) of SDBS was dissolved in 100 mL of DI water over 20 minutes. It is higher concentration than the CMC of SDBS, 3.72 mmol. The prepared graphene oxide (0.01 g) was added to this solution and was ultrasonicated for 90 minutes. The mixture was chemically reduced by heating with hydrazine at 98 °C for 24 h. The black suspension was cooled to room temperature, then diluted with DI water (500 mL), followed by filtration through cellulose-treated Millipore filter paper (0.45 μm). Finally, the obtained powder was dried at 80 °C. Figure 1 shows the SDBS functionalization process.

Results and Discussion

Characterization of Functionalized Graphene. The obtained SDBS functionalized graphene was examined through various techniques to confirm its bonding interactions. FT-IR spectra are shown in Figure 2. Figures 2(a-c) are SDBS, GO (graphene oxide), and RGO (reduced graphene oxide), respectively. The GO spectrum has hydroxyl, carbonyl, and ether bond absorptions at approximately 3600, 1727, and 1042 cm^{-1}.[9] For GO reduction to RGO, oxygen atoms are almost completely removed by hydrazine hydrate, as residual C-O-C bonds could be observed at 1633 cm^{-1}. In the SDBS spectrum, three peaks at 2958, 2928, and 2856 cm^{-1} are due to C-H vibrations of alkyl chains, and a phenyl vibration peak is seen at 1600 cm^{-1}. Peaks related to the sulfur atom in SDBS appear at 1043 cm^{-1} for S=O stretching and at 834 cm^{-1} for C-S stretching. In the SDBS-g spectrum, two notable peaks stand out compared to the SDBS spectrum. The three peaks around 2900 cm^{-1} from SDBS were red shifted approximately 8-10 cm^{-1}, due to interactions between the alkyl chain of SDBS and the graphene surface. Intermolecular interactions lead to an increased force constant reflected in an increase in the frequency. Another shifted peak at 1569 cm^{-1} for the phenyl vibration of SDBS was attributed to π-π interactions between the two molecules. The broad absorption peak from 1183 to 1112 cm^{-1} is typical for C-O-C bonds in chemically reduced graphene.[19] The FT-IR spectral data support SDBS being chemically
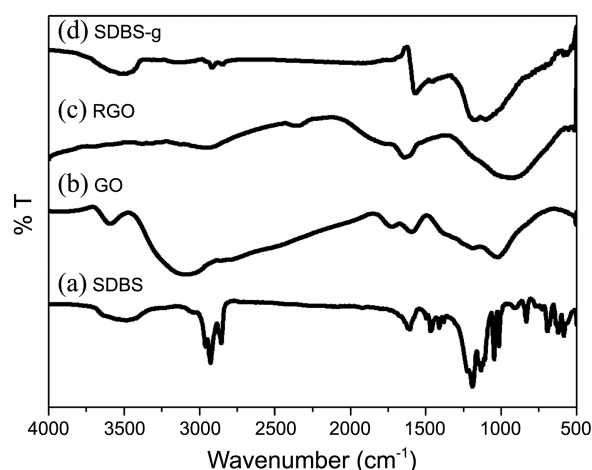
bonded to the graphene surface.

Solid-state ^{13}C NMR spectra were employed to explore structural changes by the functionalization. Similar trends as
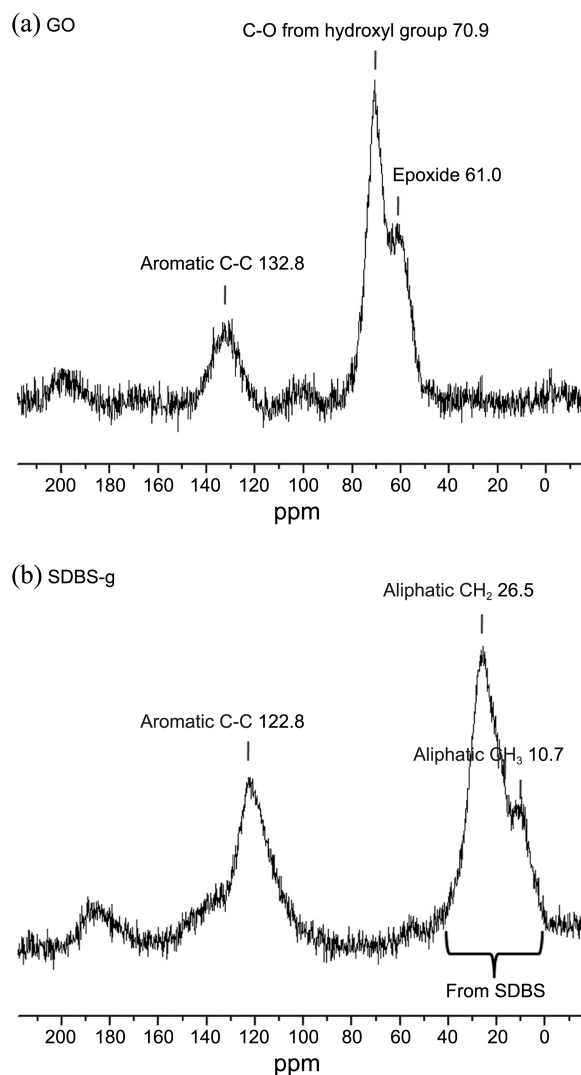

Figure 3. ^{13}C CP NMR spectra for (a) GO and (b) SDBS-g.

Surfactant-Exfoliated Graphene Oxide

Bull. Korean Chem. Soc. **2014**, Vol. 35, No. 7   2011

seen by FT-IR were observed in the NMR spectra. The peaks for GO (Figure 3(a)) show general trends. Epoxide, a C-O bond from a hydroxyl group, and aromatic C-C bonds were apparent at 61.0, 70.9, and 132.8 ppm, respectively.[19,20] For the SDBS functionalized graphene oxide, peaks were shifted as seen in Figure 3(b). The peak at 10.7 ppm is from a terminal aliphatic CH_3, and the peak at 26.5 ppm is from intermediate CH_2 groups in the alkyl chain.[21] The SDBS NMR plot supports this result with upfield peaks between 14-36 ppm. A significant peak shift was observed for the aromatic C-C bond, which had a chemical shift of 122.8 ppm. The reason for this shift is a shielding effect induced by the close proximity of the phenyl group of SDBS and aromatic rings of graphene. Since the aromatic rings shield each other, the absorption frequency as well as the chemical shift becomes lower resulting in an upfield shift of the absorption peak in the NMR.

To confirm the structures, XRD patterns of GO, RGO, and SDBS-G were measured as presented in Figure 4. Calculation of the d-space distances are based on Bragg's equation ($2d·sinθ = n·λ$). The sharp peak at 9.9° in Figure 4(a) corresponds to an 8.96 Å interlayer spacing due to the oxygen functional groups of GO and water molecules held in the interlayer space of hydrophilic GO.[22,23] In the case of SDBS-g in Figure 4(c), the broad peak position at 21.52° indicates a 4.12 Å interlayer distance. Amorphous states are easily drawn through a broad range of peaks. There are two points for further discussion, reasons for the amorphous state and the larger SDBS-g d-space. First, the amorphous state was extrapolated from a broad range of XRD plots. Moreover, it can be thought that initially tangled SDBS chains become partially straightened as they absorb to the graphene surface; thus, the shape of SBDS-g is amorphous. Second, the reason for the increased interlayer is presumed to be the result of the repulsive force between negatively charged SDBS coated layers.

Mechanism of SDBS Functionalized Graphene. On the basis of the analysis results, it is possible to predict how

Figure 5. Comparison of the dispersion stability of SDBS-g and RGO (a) in aqueous solution, (b) in various solvents after 60 sec, and (c) after 6 h.

SDBS adsorbs on graphene oxide. SDBS is an aliphatic reagent that has both hydrophilic (sulfonate) and hydrophobic (benzene ring and alkyl chains) sites. This surfactant forms micelles that are dissolved in water. When graphene oxide is ultrasonicated in SDBS solution, each functional group generates appropriate interactions. Na cations are strongly electron-withdrawing, which induces SDBS molecules to interact with electron-donating groups on graphene oxide such as the hydroxyl and aromatic ring. Therefore, the phenyl group of SDBS binds to the carboxyl group or -OH bond and the long alkyl chains position themselves on the graphene surface because of hydrophobic interactions or an electron-donating inductive effect. By contrast, SDBS binding to the edge of graphene oxide functional groups can have alkyl chains oriented away from the surface to interact with excess SDBS in water solution to form micelles. This structure allows SDBS to play the role of exfoliator for graphene.

Dispersion Stability of Functionalized Graphene. Figure 5 shows photographs of vials containing dispersions of SDBS-g in different solvents (0.1 mg/mL). From a comparison of SDBS-g and RGO, it is clear that SDBS-g was well dispersed in aqueous solvents due to the presence of SDBS on the graphene surface. Six dispersion solvents were examined for up to about 6 h: water, DMF, ethanol, THF, chloroform, and acetone. Immediately after mixing SDBS-g in each solvent (60 sec), the dispersities were fairly similar except for the acetone mixture, which had some precipitate. After six hours, the dispersions were more visibly different. The chloroform solution hardly changed, while the DMF and water solutions retained most of the SDBS-g in solution. On the other hand, with ethanol and THF, the solvent became clear with readily apparent precipitation. The acetone solution was slightly more transparent, but the clarity was not very different. The reason for the good dispersion stability in chloroform is presumed to be due to strong hydrophobic interactions between the material and solvent.
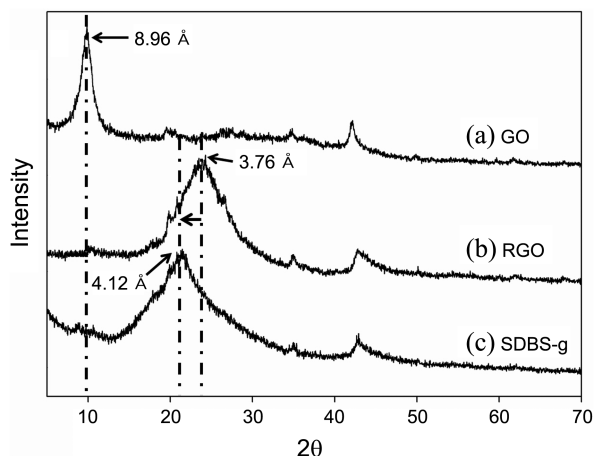
Figure 4. XRD plots of (a) GO, (b) RGO, and (c) SDBS-g. SDBS-g has a larger d-space distance than RGO because of the repulsive force between negatively charged layers.
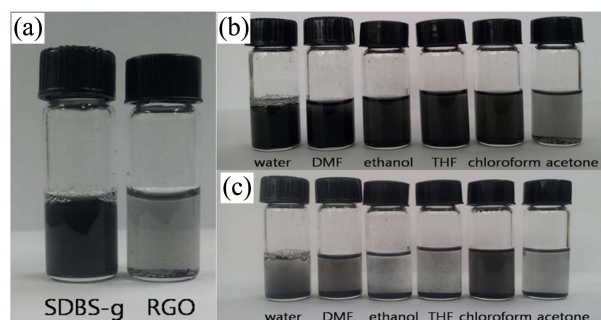
Conclusion

Surfactant modified graphene was successfully synthesized with SDBS via a simple ultrasonication method. The basic bondings of SDBS-g were investigated through FT-IR

data that indicated the existence of SDBS on the graphene surface, which caused red shifting of the peaks from conjugation between the two molecules. The structure of functionalized graphene was found to be amorphous by XRD data with a wide range of 2θ degree. From the calculation of d-space distance, it was found that SDBS-g had a larger interlayer spacing than simply reduced graphene because of the repulsive force between layers. The product dissolved well in hydrophobic solvents, especially chloroform. However, SDBS-g showed improved dispersion stability in water than pure reduced graphene oxide, even six hours after the solution had been mixed. The anionic surfactant, SDBS, acts as an exfoliator as well as stabilizer in this process. The use of surfactant functionalized graphene could provide quite practical utility for spin coating or solution casting due to its improved dispersion properties in aqueous solution.

References

1. Park, H.; Han, T. H. *Bull. Korean Chem. Soc.* **2013**, *34*, 3269.
2. Zhang, Y. B.; Tan, T. W.; Stormer, H. L.; Kim, P. *Nature* **2005**, *438*, 201.
3. Tung, N. T.; Khai, T. V.; Lee, H.; Sohn, D. *Synthetic Metals* **2011**, *161*, 177.
4. Yim, J.; Jeong, G. H.; Shin, J.; Lee, J.-H.; Kim, J.-H.; Kim, S.-W. *Bull. Korean Chem. Soc.* **2013**, *34*, 3181.
5. Zhao, X.; Zhang, Q. H.; Chen, D. J.; Lu, P. *Macromolecules* **2010**, *43*, 2357.
6. Novoselov, K. S.; Geim, A. K.; Morozoy, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666.
7. Srivastava, S. K.; Shukla, A. K.; Vankar, V. D.; Kumar, V. *Thin Solid Films* **2005**, *492*, 124.
8. Reina, A.; Jia, X.; Ho, J.; Nezich, D.; Son, H.; Bulovic, V.; Dresselhaus, M. S.; Kong, J. *Nano Lett.* **2009**, *9*, 30.
9. Si, Y.; Samulski, E. T. *Nano Lett.* **2008**, *8*, 1679.
10. Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlahaas, K. A.; Kleinhammes, A.; Jia, Y. Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. *Carbon* **2007**, *45*, 1558.
11. Kim, C. D.; Min, B. K.; Jung, W. S. *Carbon* **2009**, *47*, 1610.
12. Waite, J. H.; Tanzer, M. L. *Science* **1981**, *212*, 1038.
13. Xu, L. Q.; Yang, W. J.; Neoh, K. G.; Kang, E. T.; Guo, D. *Macromolecules* **2010**, *43*, 8336.
14. Shen, X.; Jiang, L.; Ji, Z.; Wu, J.; Zhou, H.; Zhu, G. *J. Colloid Inter. Sci.* **2011**, *354*, 493.
15. Islam, M. F.; Rojas, E.; Berhey, D. M.; Johnson, A. T.; Yodh, A. G. *Nano Letters* **2003**, *3*, 269.
16. Goak, J. C.; Lee, S. H.; Han, J. H.; Jang, S. H.; Kim, K. B.; Seo, Y.; Seo, Y. S.; Lee, N. *Carbon* **2011**, *49*, 4301.
17. Takayanagi, T.; Morimoto, M.; Yabutani, T. *Analytical Sciences* **2013**, *29*, 769.
18. Tung, V. C.; Chen, L. M.; Allen, M. J.; Wassei, J. K.; Melson, K.; Kaner, R. B.; Yang, Y. *Nano Letters* **2009**, *9*, 1949.
19. He, H.; Riedl, T.; Lerf, A.; Klinowski, J. *J. Phys. Chem.* **1996**, *100*, 19954.
20. He, H.; Klinowski, J.; Forster, M.; Lerf, A. *Chem. Phys. Lett.* **1998**, *287*, 53.
21. Moon, H. G.; Chang, J. H. *Polymer* **2011**, *35*, 265.
22. Buchsteiner, A.; Lerf, A.; Pieper, J. *J. Phys. Chem. B* **2006**, *110*, 22328.
23. Park, S.; An, J.; Poitts, J. R.; Velamakanni, A.; Murali, S.; Ruoff, R. S. *Carbon* **2011**, *49*, 3019.