XX IMEKO World Congress
Metrology for Green Growth
September 9–14, 2012, Busan, Republic of Korea

NONCOVALENT FUNCTIONALIZATION OF GRAPHENE BY WATER SOLUBLE POLY (ETHER ETHER KETONE)

[1]Tapas Kuila, [2]Nam Hoon Kim, [1]Partha Khanra, and [1,2]Joong Hee Lee

[1]WCU Program, Department of BIN Fusion Technology, Chonbuk National University, Jeonju, Jeonbuk, 561-756, Republic of Korea
[2]Department of Hydrogen and Fuel Cell Engineering, Chonbuk National University, Jeonju, Jeonbuk, 561-756, Republic of Korea

Abstract: Water dispersible graphene has been prepared by noncovalent functionalization of graphene oxide using sulfonated poly(ether ether ketone) (SPEEK). Both the chemical and electrochemical method has been employed to noncovalently attach the SPEEK macromolecules on the surface of graphene. In chemical methods, SPEEK macromolecules are attached on the surface of graphene oxide followed by reduction using hydrazine monohydrate. On the contrary, electrochemical exfoliation of graphite to graphene occurs in presence of SPEEK macromolecules in aqueous medium under a potential difference of 30 V. The functionalized graphene has been characterized successfully to confirm the attachment of hydrophilic functionalities on to graphene.

Keywords: Sulfonated poly(ether ether ketone); Graphene; Noncovalent functionalization; Water dispersion

1. INTRODUCTION

Graphene has attracted a significant research interest in the field of physics, chemistry, bio-science, materials science, etc. since its discovery in 2004 by Geim et al. [1]. Its exceptional electrical conductivity, mechanical flexibility, and high transparency makes graphene an ideal choice for the use in polymer composites, biosensor, drug delivery system, p-n junction materials, supercapacitor device, solar cell, etc. [2-7]. However, pristine graphene cannot be used for this purpose due to its tendency to agglomerate at ambient temperature [7]. The superior properties of graphene are loosed when it is agglomerated to form graphitic structure. The dispersion stability of pure graphene in a solvent or in a matrix is also very poor due to the absence of functional groups [8,9]. Moreover, the use of pristine graphene in transistor device is also problematic due to the absence of band gap in graphene. Graphene based field effect transistors cannot be turned off effectively due to the absence of band gap in pristine graphene [5]. Therefore, the problems associated with the agglomeration, dispersion stability, band-gap, etc. should be removed to access the inherent properties of graphene for the benefits of mankind. Molecular level doping of organic functionalities on the surface of graphene enables to remove the afore-mentioned problems and helps to process graphene by solvent-assisted techniques, such as layer-by-layer assembly, spin-coating, and filtration [10].

2. EXPERIMENTAL

2.1 Materials

Natural flake graphite purchased from Sigma Aldrich, Germany was used as the starting material. High purity graphite rods were supplied from Qingdao Xinlei Graphite Product Co. Ltd., China. Potassium permanganate (TCI, Japan) and sulfuric acid (Samchun Pure Chemical Co. Ltd., Korea) were used as oxidizing agents. Hydrochloric acid, hydrogen peroxide, silver nitrate, barium chloride and were purchased from Samchun Pure Chemical Co. Ltd., Korea. Poly (ether-ether-ketone) (Victrex 450G) was received from Victrex plc, UK and used for the surface modification of graphene after sulfonation. Hydrazine monohydrate (TCI, Japan) was used as reducing agent.

2.2 Sulfonation of poly(ether ether ketone)

Poly (ether ether ketone) (PEEK) (5 g) were added to 100 ml of concentrated H_2SO_4 (95-98 wt.%) at room temperature under nitrogen atmosphere. The dissolved PEEK was stirred vigorously at 55 ^{o}C for 5 hours. The reaction mixture was then added to ice cold water and washed repeatedly with DI water until reaching to neutral pH. The product was then dried at 70 ^{o}C under vacuum to obtain sulfonated PEEK (SPEEK).

2.3 Surface modification of graphene

Graphite oxide was prepared my modified Hummers method [11]. For the surface modification of graphene, at first stable aqueous dispersion of single layer graphene oxide (GO) was obtained by sonication and centrifugation. Then the weighed amount of SPEEK solution in water was added to the GO dispersion followed by stirring at 70 ^{o}C for 24 hours. Hydrazine monohydrate was then added and the mixture was refluxed for additional 24 hours at 100 ^{o}C. Finally, it was filtered using 0.2 μm cellulose acetate membrane papers and dried under vacuum. The SPEEK modified graphene was termed as SPG. In order to compare the dispersion stability of SPG, GO was reduced to graphene (CRG) in absence of SPEEK macromolecules.

2.4 Electrochemical exfoliation of graphite

Electrochemical exfoliation of graphite was carried out in aqueous medium in presence of SPEEK macromolecules. Two graphite rods were used as cathode and anode at a potential difference of 30 V. After 30 minutes of current flow, the anode rod started to corrode and the transparent solution became black. Anode rod was totally corroded after 24 hours and the current flow between the two electrodes dropped to 0 A. The bigger size particles were separated by centrifugation and the excess of SPEEK were removed by filtration through 0.2 μm cellulose acetate membrane papers. Electrochemically prepared graphene was designated as SEG.

2.5 Characterization

The dispersion stability of pure GO and surface modified graphene (SPG and SEG) in water were tested at room temperature using a UVS-2100 SCINCO spectrophotometer. Fourier transform infrared (FT-IR) spectroscopy was performed with a Nicolet 6700 spectrometer (Thermo Scientific, USA) over a wavenumber range of 4000-400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed using Axis-Nova, Kratos Analytical Ltd, Manchester, UK. Transmission electron microscopy (TEM) (JEOL JEM-2200 FS, Japan) was employed to analyze the nanostructure of the SPG and SEG. Raman spectra of pure GO and SPG were obtained on a Nanofinder 30 (Tokyo Instruments Co., Osaka, Japan).

3. RESULTS AND DISCUSSION

Fig. 1 shows the digital image of GO, SPG, SEG, and CRG dispersed in water and dimethylformamide (DMF). Pure GO, SPG, and SEG form stable dispersion both in water and DMF after mild sonication. However, CRG does not disperse either in water or in DMF. The surface of GO contains varieties of oxygen functionalities such as hydroxyl, carboxyl, epoxy, etc. which accounts its good dispersion in water and DMF. After reduction, all these oxygen functionalities were removed and the CRG float on the top of the water due to poor hydrophilicity. On the contrary, the noncovalently attached SPEEK macromolecules on the surface of SPG and SEG help to obtain the stable dispersion in water and DMF.

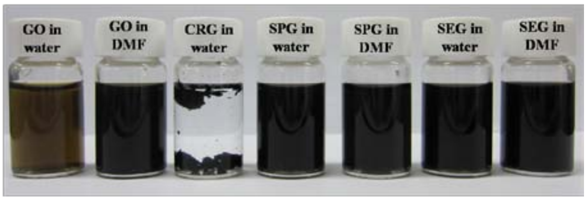

Fig. 1: Digital image of pure GO, CRG, SPG and SEG dispersed in water and DMF

UV-Vis spectra of pure GO, SPG, and SEG are shown in Fig. 2. Pure GO exhibits a broad band centred at 230 nm, corresponding to the $\pi \rightarrow \pi^*$ transition of C=C of GO. The appearance of a peak at 300 nm is attributed to the $n \rightarrow \pi^*$ transitions of C=O, suggesting the presence of oxygen functionalities in GO [12]. However, both of these peaks are absent in the functionalized graphene. Appearance of a new peak at ~ 265 nm and ~292 nm are observed for SPG and SEG, respectively. This is attributed to the reinstallation of the π-electron conjugation after reduction of GO. The appearance of this peak relatively at higher wavelength for SEG is attributed to the direct exfoliation of graphite to graphene in a one-step. Electrochemical exfoliation precludes the destructive oxidation process. Therefore, π-electronic orbital remains intact even after the separation of single layer from the stacks of graphite.

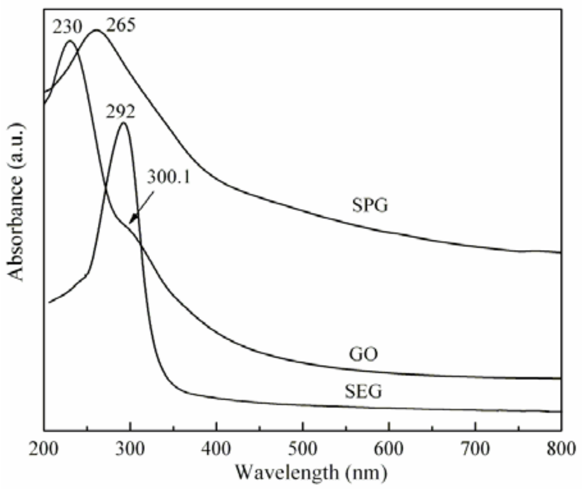

Fig. 2: UV-Vis spectra of pure GO, SPG, and SEG in water

FT-IR measurements were carried out to confirm the reduction of GO and the attachments of SPEEK macromolecules on the surface of graphene. Table 1 summarizes the major peak positions found in the pure GO, SPEEK, SPG, and SEG. The appearance of peaks at 1224, 1162, 1078, and 684 cm^{-1} in the FT-IR spectra of SPEEK confirm the successful sulfonation of the PEEK polymer [13,14]. It is seen that the characteristics peak for GO such as carboxyl (-COOH), hydroxyl (-OH), epoxy (-C-O-C-) are almost absent in the SPG. The absence of these peaks confirm the reduction of GO to graphene. On the contrary, some new peaks related to the characteristics peak of SPEEK are appeared in the SPG. This further confirms that SPEEK has been doped on to the surface of graphene. In the case of SEG, almost identical peaks are observed as in the case of SPG. All these findings suggest the functionalization of graphene sheets using SPEEK.

Table 1: FT-IR data's of pure GO, SPEEK, SPG, and SEG

Peak positions (cm^{-1})	*Functional groups*
3416, 1404	Stretching vibration of -OH
2932, 2856	Stretching vibration of –CH and -CH_2
1734	Stretching vibration of -COOH
1628	-C=C-
1490, 1224, 1078	Presence of –SO_3H
1231, 1051	Stretching vibrations of epoxy and alkoxy
1456	Stretching vibration of –C-N
1560	Bending vibration of –N-H

The XPS of pure GO, SPG, and SEG have been performed to analyze the chemical composition of their surfaces and the results are summarized in Table 2. It shows that pure GO contains ~31.3% oxygen including –OH, -COOH, -C-O-C-, etc. functionalities. After reduction and chemical functionalization, SPG contains only 12.3% oxygen. This suggests that most of the oxygen functionalities have been removed during the reduction process. Moreover, pure GO does not contains sulphur and nitrogen. But SPG contains ~1.5% sulphur and 2.2% oxygen. The SPG is contaminated with nitrogen due to the use of hydrazine monohydrate as a reducing agent. SEG contains only 3% of sulphur but no nitrogen.

Table 2: Elemental composition of GO, CRG, SPG, and SEG

Sample	*Carbon (at.%)*	*Oxygen (at.%)*	*Sulfur (at.%)*	*Nitrogen (at. %)*	*C/O ratio*
GO	68.5	31.3	------	-------	2.2
CRG	89.2	8.2	-------	2.2	10.9
SPG	83.9	12.3	1.5	2.2	6.8
SEG	79.2	19.6	1.3	-------	4.1

Fig. 2 shows the TEM images of the water dispersion of SPG and SEG. The TEM images of SPG and SEG are lamellar structures. It also shows that there is almost no morphological difference in SPG and SEG. The appearance of transparent sheets of SPG and SEG may be due to the strong binding of SPEEK molecules to the surface of graphene sheets by π-π interaction. The –SO_3H groups of SPEEK doped on to the surface of graphene also help in preventing restacking by strong electrostatic repulsion. High resolution TEM (HR-TEM) has been performed to determine the number of layers in the functionalized graphene. The folding of the layers of functionalized graphene films appear as dark line. For single layer of graphene, one dark line should appear; for bilayer graphene, two lines should appear and so on. The appearance of few lines in our TEM image analysis suggests the formation of few layer graphene.

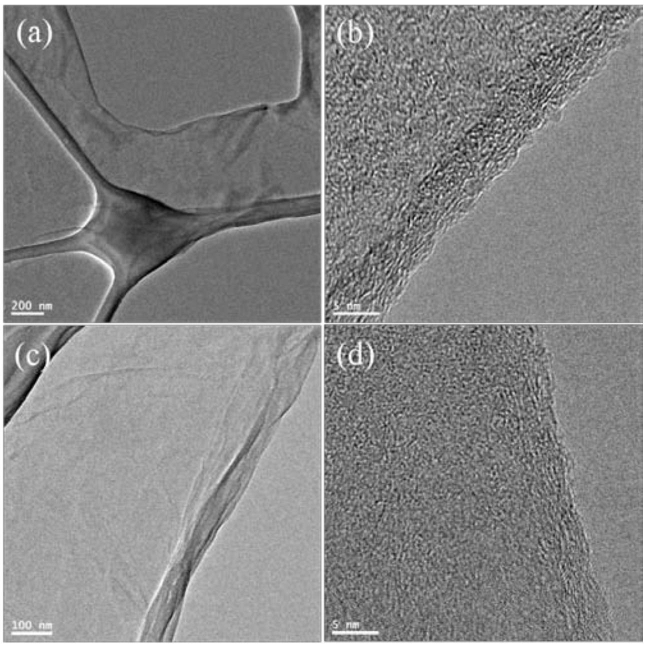

Fig. 3: TEM and HR-TEM images of (a,b) SPG and (c,d) SEG.

Fig. 4 shows the Raman spectra of pure GO and SPG. In pure GO, the G band appears at 1596 $cm^{-1}$and D band at 1348 cm^{-1}. After reduction and functionalization, both the bands shift to lower region. The appearance of D and G bands at higher region is due to the breakage of π-electronic conjugation in GO. Moreover, the intensity ratios of the D to G (I_D/I_G) band is less than 1 in pure GO. This is attributed to the extensive oxidation and generation of oxygen functionalities on the surface of GO. However, the I_D/I_G has increased to 1.03 in the SPG. This is ascribed to the attachment of SPEEK on the reduced GO.

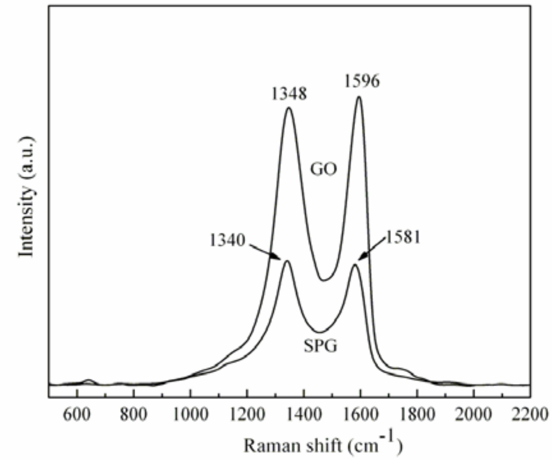

Fig. 4: Raman spectra of pure GO and SPG

Raman spectra of pure GO and SEG are shown in Fig. 5. The major peaks appear at 1575 cm^{-1} (G band) and 1348 cm^{-1} for both pure graphite and SEG. However, in the case of graphite, both the peaks are sharp and highly intense. On the contrary, after electrochemical exfoliation and functionalization, the peak intensities have been decreased significantly in the SEG. This is attributed to the attachment of SPEEK macromolecules and generation of oxygen functionalities on the surface of graphene [13,14].

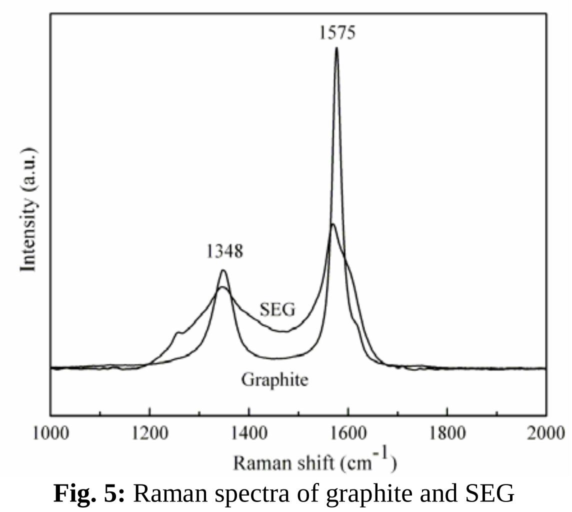

Fig. 5: Raman spectra of graphite and SEG

4. CONCLUSIONS

Chemical and electrochemical exfoliation techniques have been employed to prepare water dispersible graphene using SPEEK as functionalizing agent. The SPEEK macromolecules noncovalently attach on the surface of graphene through π-π interaction. The functionalized graphene (SPG and SEG) can disperse well in water and DMF and are stable for more than 90 days. UV-Vis spectra have been performed to check the formation of graphene. It suggests that the quality of the electrochemically exfoliated graphene is much better as compared to that of the graphene obtained by chemical oxidation-reduction techniques. XPS analysis suggests that a small extent of oxygen functionalities have been generated during the electrochemical exfoliation as evidenced by elemental composition study. The formation of few layer graphene is also clearly visible from the TEM image analysis. Raman spectra analysis also suggests the attachment of SPEEK on the surface of graphene by chemical and electrochemical ways.

5. ACKNOWLEDGEMENT

This study was supported by the Human Resource Training Project for Regional Innovation, the Converging Research Center Program (2011K000776), and the World Class University (WCU) program (R31-20029) through the National Research Foundation (NRF) funded by the Ministry of Education, Science, and Technology (MEST) of Korea.

6. REFERENCES

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov. “Electric field effect in atomically thin carbon films,” Science, vol. 306, no. 5696, pp. 666-669, October 2004.

[2] T. Kuila, S. Bose, C. E. Hong, M. E. Uddin, N. H. Kim, P. Khanra, and J. H. Lee. “Preparation of functionalized graphene/linear low density polyethylene composites by a solution mixing method,” Carbon, vol. 49, no. 3, pp. 1033-1037, March 2011.

[3] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, and B. H. Hong, “Large-scale pattern growth of graphene films for stretchable transparent electrodes,” Nature, vol. 457, pp. 706-710, February 2009.

[4] Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay, and Y Lin, “Graphene based electrochemical sensors and biosensors: a review,” Electroanalysis, vol. 22, no. 10, pp. 1027-1036, May 2010.

[5] F. Xia, D. B. Farmer, Y. M. Lin, and P. Avouris, “Graphene field-effect transistors with high on/off current ratio and large transport band gap at room temperature,” Nano Letter, vol. 10, no. 2, pp. 715-718, January 2010.

[6] Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach, and R. S. Ruoff, “Carbon-based supercapacitors produced by activation of graphene,” Science, vol. 332, pp. 1537-1541, June 2011.

[7] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, and R. S. Ruoff, “Graphene based polymer composites,” vol. 442, pp. 282-286, January 2006.

[8] J. I. Paredes, S. V. Rodil, A. M. Alonso, and J. M. D. Tascon, “Graphene oxide dispersions in organic solvents,” Langmuir, vol. 24, no. 19, pp. 10560-10564, August 2008.

[9] C. Shan, H. Yang, D. Han, Q. Zhang, A. Ivaska, and L. Niu, “Water-soluble graphene covalently functionalized by biocompatible poly-l-lysine,” Langmuir, vol. 25, no. 20, pp.12030-12033, September 2009.

[10] H. Bai, Y. Xu, L. Zhao, C. Li, and G. Shi, “Non-covalent functionalization of graphene sheets by sulfonated polyaniline,” Chemical Communication, pp. 1667-1669, January 2009.

[11] W. S. Hummers and R. E. Offeman, “Preparation of graphitic oxide,” Journal of American Chemical Society, vol. 80, pp. 1339, 1958.

[12] Z. Luo, Y. Lu, L. A. Somers, and A. T. C. Johnson, “High yield preparation of macroscopic graphene oxide membranes,” Journal of American Chemical Society, vol. 131, no. 3, pp. 898-899, January 2009.

[13] T. Kuila, P. Khanra, S. Bose, N. H. Kim, B. C. Ku, B. Moon, and J. H. Lee, “Preparation of water-dispersible graphene by facile surface modification of graphite oxide,” Nanotechnology, vol. 22, pp. 305710, July 2011.

[14] T. Kuila, P. Khanra, A. K. Mishra, N. H. Kim, and J. H. Lee, “Functionalized-graphene/ethylene vinyl acetate co-polymer composites for improved mechanical and thermal properties,” Polymer Testing, vol. 31, no. 2, pp. 282-289, April 2012.