

Notes

Synthesis and Characterization of Soluble Alkylalcohol-derivatized Graphene Oxide

Seunghyun Jang, Honglae Sohn, and Young Chun Ko^{†,*}

Department of Chemistry, Chosun University, Gwangju 501-759, Korea

[†]Graduate School of Education, Sehan University, Chonnam 526-702, Korea. *E-mail: ycko@sehan.ac.kr

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Graphene oxide, a two-dimensional sheet-shaped nanostructure mainly composed of sp^2 carbon skeleton bonds, has recently attracted explosive worldwide interests.¹⁻⁹ And so, many effective synthetic methodologies have been developed for graphene oxide. Since the successful synthetic methods of graphene oxide were invented by Brodie in 1859 and by Hummers and Offeman in 1958, during eight years of the modern period studies graphene oxide synthesis have been achieved considerably by modifying Brodie's, and Hummers and Offeman's methods.^{10,11} Most exfoliation of graphite oxide has been possible either by sudden thermal expansion or ultrasonic dispersion of graphite to obtain graphene.¹²⁻¹⁶ Graphene oxide is a water-insoluble nanomaterial containing carboxylic, epoxy, and hydroxyl groups. That is, graphene oxide is an oxidized nanomaterial with acidic functional group and the oxidants intercalated in the inter-thin layer space. This guides to a route for exfoliation of graphite by rapid de-intercalation.¹⁷ The graphene oxide is considered as a special and new material possessing a high area to volume ratio and violent charge transport properties. These novel properties can be made graphene oxide greatly promising for the diverse applications including high functional batteries, sensors, solar energy system, and highly sophisticated micro-electrical devices such as field-effect transistors and electro-mechanical resonators.¹⁸⁻²⁷ Here, therefore, we report a synthesis on derivatization of graphene oxide with alkylalcohol to give soluble graphenes. Because the soluble alkoxy-derivatized graphene oxides may be presented a particular electronic transport properties. In this paper we study to yield a basic optical properties data of the soluble graphene oxides.

Experimental Section

Measurements. FT-IR spectra of samples (as KBr pellets) were obtained on a Nicolet 5700 Spectrometer. UV-Vis spectra were obtained by UV-vis spectrophotometer (Shimadzu Co. model S-3100). Scanning electron microscope (SEM) images were obtained by a cold field emission scanning electron microscope (FE-SEM, S-4700, Hitachi). Fluorescence emission and excitation spectra were recorded on a Perkin-

Elmer Luminescence Spectrometer LS 50B. 4-(Dimethylamino)pyridine (DMAP) and alkylalcohol ($(CH_3(CH_2)_nOH$: $n = 7$ (octyl alcohol), 11 (dodecyl alcohol), 14 (1-pentadecanol), 18 (1-nonadecanol), and 21 (1-docosanol)) were purchased from Sigma-Aldrich, and used without further purification. *N*-Hexane and *ortho*-dichlorobenzene were purchased from Sigma-Aldrich and purified by fractional distillation. All the solvents were rigorously purified to be free of emitting impurities prior to use.

Synthesis of Graphene Oxide. Black microcrystalline graphite (Sigma-Aldrich, 5 g) was exfoliated in 120 mL of 1:3 ratio of concentrated nitric acid and sulfuric acid for above 120 min using a high power ultrasonicator at 480 watt at the constant bath of 40 °C. The dispersion was left untouched at room temperature for 4 days during which time the dispersion was changed to purple-brown color. After the dispersion was subject to the centrifugal separation at the speed of 5,000 rpm for 2 h, the upper layer of the solution was decanted. After the solute at the lower layer was taken with distilled water up to the marked-volume line of the glass tube, it was rotated by centrifugal separator at the speed of 5,000 rpm for 1 h. This washing procedure was repeated five times. The graphene oxide was then filtered through a 0.2 μ m PTFE membrane with ethyl alcohol and toluene (Sigma-Aldrich). The product was dried *in vacuo* overnight in a vacuum line. The resulting graphene oxide had a grayish colors and not shiny like the graphite.

Synthesis of Alkoxy-Derivatized Graphene. Graphene oxide (GO, 1.5 g), DMAP (0.20 g, 1.64 mmol), and alkylalcohol ($CH_3(CH_2)_nOH$: $n = 7, 11, 14, 18,$ and 21) (26.8 mmol) were slowly added in order at room temperature to a Schlenk flask containing *ortho*-dichlorobenzene (120 mL). The reaction mixture was refluxed at 180 °C for 3 days. After removal of solvent *in vacuo*, the organic layer was washed with *n*-hexane. The removal of volatiles at *in vacuo* yielded tacky product, alkoxy-derivatized graphene. Each the products was identified as an alkoxy-derivatized graphene. Among them, the dodecyloxy-derivatized soluble graphene is used as a representative for exploring this paper (dodecyloxy-graphene: DDO-G). Because each the data of UV-vis and IR spectroscopy, and the surface morphology of SEM among

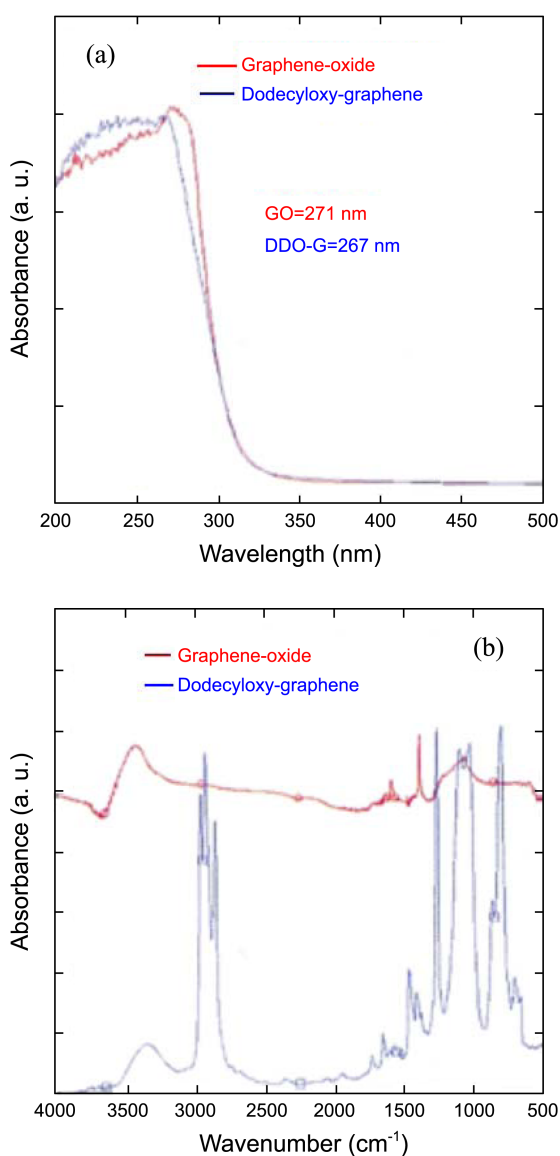


Figure 1. (a) UV-vis absorption spectra and (b) FT-IR spectra of graphene oxide and dodecyloxy-graphene, respectively.

them was about the same.

Results and Discussion

The absorption spectra of each graphene oxide (red line) and dodecylalcohol-graphene (blue line) in THF are shown in Figure 1(a). The broad peaks in the vicinity of 233 nm is considered due to $\pi \rightarrow \pi^*$ of C=C. And the sharp peaks at 270-300 nm is due to $n \rightarrow \pi^*$ transition of C=O.²⁸ The FT-IR spectra of each graphene oxide and dodecylalcohol-graphene are shown in Figure 1(b). Qualitative analyses were conducted by FT-IR spectroscopy in order to investigate the chemical composition of each graphene oxide and dodecyloxy-graphene (Figure 1(b)). The red (upper) line in Figure 1(b) shows the FT-IR spectrum of graphene oxide. To verify our synthesized graphene oxide, the FT-IR analysis was conducted. The broad bands shown at 3400 cm^{-1} is ascribed to O-H stretching vibration. The band at 1735 cm^{-1}

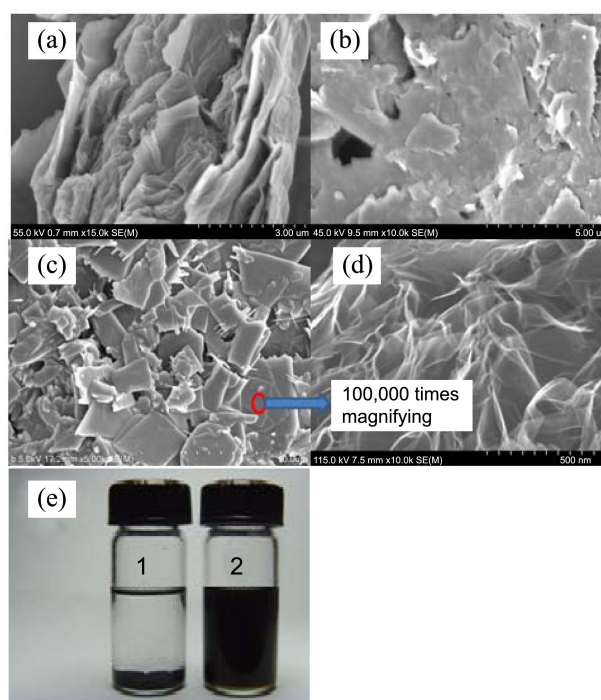


Figure 2. SEM images of (a) graphite, (b) graphene oxide, (c) dodecyloxy-graphene, (d) 100,000 times magnifying image of dodecyloxy-graphene; (e) photo image of graphene oxide (1) and dodecyloxy-graphene (2).

is attributed to C=O stretching vibration. The vibrational bands of three peaks at 1390 , 1253 , and 1056 cm^{-1} are due to the deformation of O-H, stretching of C-OH, and stretching of C-O, respectively. The broad bands shown at 3346 cm^{-1} is ascribed to O-H stretching vibration. The emergence of the vibrational band at $2854\text{--}2961\text{ cm}^{-1}$ is due to C-H group formed from synthesis of dodecylalcohol-graphene. The vibrational bands of peaks at 1374 , 1260 , and 1037 cm^{-1} are due to the deformation of O-H, stretching of un-reacted C-OH, and stretching of C-O, respectively. The significant differences in FT-IR spectra between graphene oxide and dodecyloxy-graphene are the change of relative peaks intensity and the chemical shift of peaks, except C-H group formed because of formation of dodecyloxy-graphene. Figure 2(a, b, c, and d) shows the SEM images of each graphite, graphene oxide, and dodecylalcohol-graphene. Figure 2(a) shows a graphite monolith having a blunt shapes. In Figure 2(b) graphene oxide is thickly covered with two-dimensional nanostructure with *ca.* 20-3,000 nm in diameter. Figure 2(c) indicates dodecyloxy-graphene is covered with two-dimensional nanostructure with *ca.* 20-3,000 nm particles in diameter. Herein the particle sizes of graphenes are dependent on the extent of sonication. Figure 2(d) indicates 100,000 times magnifying image as large as dodecyloxy-graphene in Figure 2(c). The Figure 2(e) presents the photo images of graphene oxide and dodecyloxy-graphene in THF. Graphene oxide (GO) shows very pale purple-brown color, while dodecyloxy-derivatized graphene (DDO-G) displays rich purple-brown color. Figure 3 shows the photoluminescences (PL) of graphene oxide and dodecyloxy-graphene in THF.

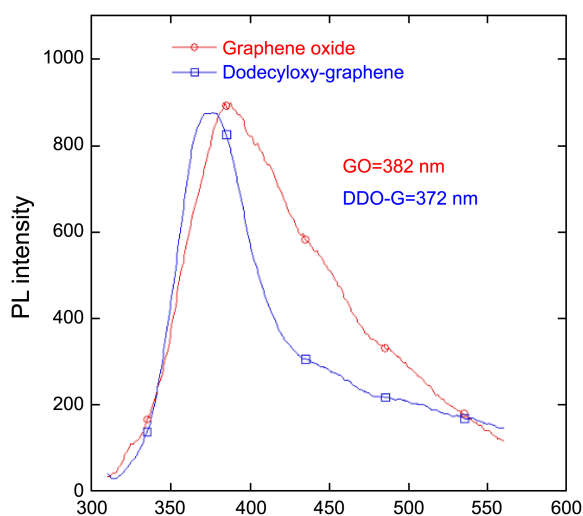


Figure 3. Fluorescence spectra of graphene oxide and dodecyloxy-graphene.

As-prepared graphene oxide exhibits an emission band at 382 nm with an excitation wavelength of 325 nm. However, an emission band at 372 nm for the dodecyloxy-derivatized graphene shifts to shorter wavelength by 10 nm. Although dodecyl alcohol doesn't have the properties of chromophore, that acts as an auxochrome (-OH). Recently, PL from chemically derivatized GO has been demonstrated.²⁹⁻³² The characteristics of the PL indicates that it originates from the recombination of electron-hole (e-h) pairs, localized within small sp^2 carbon clusters. Dodecyl alcohol is transparent in the emission spectrum. However, in graphene oxide the emission spectrum is observed by possessing the properties of chromophore by many conjugation relations and auxochrome by -OH, -O-, and -COOH. For dodecyloxy-graphene the emission spectrum is observed with a blue shift and a decrease in the intensity of the bands. Herein, in dodecyloxy-graphene the appearance of the blue shift is different with what initially expected. Because, when -OH group of n -orbital is reacted with chromophore groups, the increase in the intensity of the bands should be generally observed. Consequently, we consider an obvious fact that the blue shift is due to well unknown graphene properties up to now. The special property of alkyloxy-graphene will be used for areas of applications to increase emission intensity and electron transfer.

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