

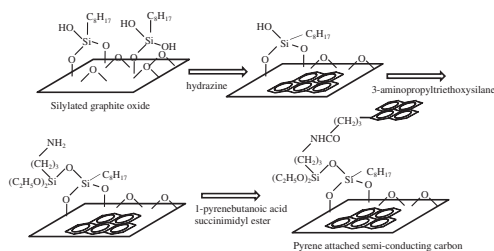
Preparation of Semiconducting Graphene-based Carbon Films from Silylated Graphite Oxide and Covalent Attachment of Dye Molecules

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Dye molecules were attached to the layers of semi-conducting graphene-based carbon film by reacting the reduced silylated graphite oxide containing amino groups with active ester of dye.

Since a report by Geim et al., graphene which is a single layer of graphite has attracted much attention because of its excellent electrical properties.¹ Graphite oxide (hereafter abbreviated as GO) prepared from graphite is a promising precursor materials to obtain graphene in a large quantity, for example, by reducing it by using sodium borohydride, concentrated sulfuric acid and finally hydrogen gas.² Upon the reduction of GO using hydrazine monohydrate, it changes from insulator to semi-conductor and then to semimetal.³ On the other hand, semi-conducting carbon materials have been tested as solar cell electrodes.⁴ In the analogy of dye-adsorbed semi-conducting titanium dioxide used for dye-sensitized solar cells, it would be very interesting if dye molecules are attached to the semiconducting carbon layers. In this study, therefore, a procedure to attach dye molecules to the layers of semiconducting carbon was developed using reduced silylated GO as a precursor. Amino groups were first attached to the layers of reduced silylated GO, and then active ester was reacted with the resulting material in a similar manner to that reported for the attachment of dye to silylated magadiite.⁵

Graphite oxide ($C_8H_{3.9}O_{4.7}$) was prepared, based on the Brodie's method.⁶ GO was silylated with octyltrichlorosilane according to our previous studies.⁷ The content of silylating reagent was determined based on the amount of residual silica after thermogravimetric analysis, and 0.72 per GO unit was obtained. The *n*-hexadecylamine molecules were intercalated into the resulting silylated GO (hereafter C_8SiGO) in order to make it disperse well in organic solutions.⁸ It was dispersed in a chloroform/cyclohexane (1 mg mL^{-1}) solution and was cast on the quartz or silicon substrates (0.05 mL cm^{-2}). The solvent was evaporated slowly at 2°C and thin film samples were obtained.⁸ The intercalated *n*-hexadecylamine was then removed by washing the film with ethanol. The thickness of the film was about 200 nm estimated by AFM measurement. The obtained thin films were exposed to the vapor of hydrazine monohydrate at 60°C for 30–180 min. It was then reacted with 3-aminopropyltriethoxysilane (APS) in cyclohexane (30 mL) at 80°C for 1 day. The product was immersed in the dimethylformamide solution of 1-pyrenebutanoic acid succinimidyl ester (PyBA-S; 10 mL, 25 mM) at 60°C for 1 h. The obtained sample was analyzed by X-ray diffraction (Rigaku Rint-2100, Cu $K\alpha$ radiation), Infrared (Nicolet Avatar 360), UV-vis (Hitachi U-3010), and fluorescence spectroscopy (Hitachi F-7000, excitation wavelength of 330 nm).

Figure 1 shows the X-ray diffraction patterns of C_8SiGO reduced for various times. With the increase in reaction time, the diffraction peak becomes broader and shifts to higher angle and reaches $2\theta = 7.4^\circ$ ($d = 1.19 \text{ nm}$). Since the diffraction peak of unreacted C_8SiGO was not observed, the sample was almost uniformly reduced by hydrazine, probably because the diffusion of them between GO layers was facilitated by the large interlayer spacing of

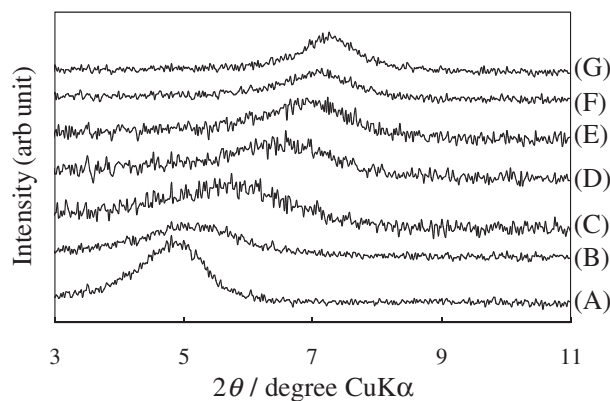


Figure 1. X-ray diffraction patterns of C_8SiGO films (A): before and after reduction by hydrazine for (B): 30, (C): 60, (D): 90, (E): 120, (F): 150, and (G): 180 min.

C_8SiGO . The interlayer spacings of the resulting samples were still larger than that of graphite and even GO (0.70 nm). At the same time, in the infrared spectra of the samples prepared on the Si substrate, the absorption peak observed at 2920 cm^{-1} due to the $-(CH_2)-$ groups for the pristine C_8SiGO was still observed, though it became somewhat weaker. The alkylsilyl groups bonded to GO layers via two Si–O bondings⁷ could survive even after reaction with hydrazine. The absorption peak at 1020 cm^{-1} due to C–O–C groups also became smaller as suggested from the reaction proposed in the literature.⁹ These indicate that GO layers were reduced and that alkylsilyl groups still remained in the reduced C_8SiGO samples, and further functionalization on the silanol groups on alkylsilyl groups was expected.

In the UV-vis absorption spectrum of the pristine C_8SiGO , the absorption peaks at 300 and 227 nm were observed, which are typically observed for GO before silylation as shown in Figure S1.¹⁰ This suggests that silylation of GO had no influence on the electronic structure. After reaction with hydrazine, the peak at 300 nm assigned to the carbonyl groups at the edge of GO layers disappeared, and that at 227 nm shifted to longer wavelengths, indicating the reduction of GO. This peak slightly shifted to longer wavelength with the increase in the reaction time, and the peak position reached a constant value of 265 nm after 120 min. At the same time, the absorption in the region of visible light also increased. This indicates that the number of carbon atoms participating in the π -conjugating system increased as the result of reduction of oxygen containing functional groups in GO layers. Figure 2 shows the optical band gap of the above samples estimated by Tauc's plot.¹¹ The band gap of C_8SiGO was 1.7 eV which was similar to that reported for GO in the literature.¹² It greatly decreased to -1.5 eV for the sample reduced for 30 min. Then, it increased with the increase in reaction time and reached a constant value of 0.5 eV after 150 min. The decrease in the optical band gap indicates the increase in the number of fused sixfold rings in the

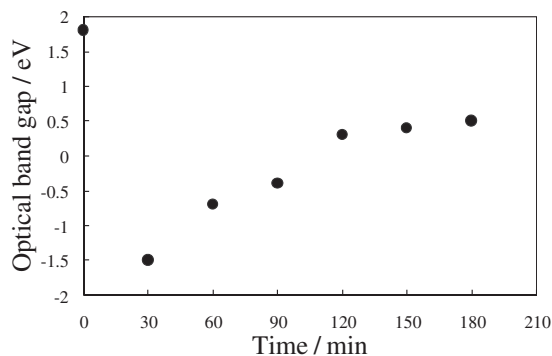


Figure 2. Optical band gap of the reduced C_8SiGO as a function of reaction time.

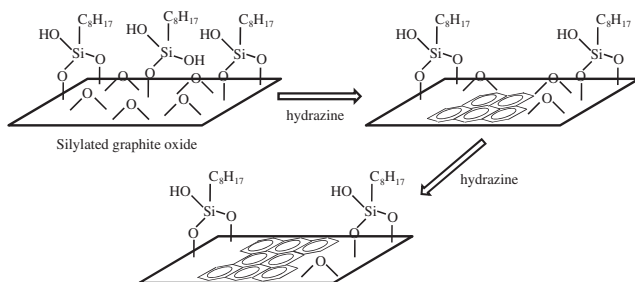


Figure 3. Schematic reaction pathway for the reduction of silylated graphite oxide.

samples¹³ formed as the result of the reduction of the oxygen-containing groups. The negative optical band gap is physically meaningless; however, in the case of copper ion implanted carbons, it has been suggested that it is related to the additional absorption due to the defects formed in each fused sixfold ring or graphite-like nanoclusters.¹⁴ In the present case, the remaining oxygen-containing groups within the GO layers are the possible candidates for such defects. A possible reaction pathway for the reduction of C_8SiGO is schematically shown in Figure 3.

Figure 4 shows the X-ray diffraction patterns of C_8SiGO reduced for 60 min before and after reaction with APS and then Py. The diffraction peak at $2\theta = 5.74^\circ$ ($d = 1.54$ nm) shifted to lower angle of $2\theta = 3.86^\circ$ ($d = 2.29$ nm) and 3.52° ($d = 2.51$ nm) after reaction with APS and Py, respectively. This strongly indicates that APS and Py were introduced between the layers of reduced C_8SiGO . For the sample reduced for longer than 90 min, the diffraction peak was not observed after reaction with APS, indicating the layered structure of C_8SiGO was destroyed.

Figure 5 shows the UV-vis spectra of APS-attached reduced C_8SiGO sample before and after reaction with PyBA-S. The spectrum before reaction with APS was almost the same as that observed for reduced C_8SiGO . After reaction with PyBA-S, several absorption peaks around 345–230 nm due to pyrene chromophores were clearly observed. In addition, in the IR spectrum of APS-attached reduced C_8SiGO after reaction with PyBA-S, absorption peaks due to amino groups at 1654 and 1518 cm^{-1} due to the amide groups were observed as shown in Figure S2.¹⁰ These indicate that the pyrene chromophores were successfully attached to the semi-conducting carbon layers.

Finally, the authors believe that the present method is very useful to prepare dye molecule-attached graphene-based semi-conducting carbons.

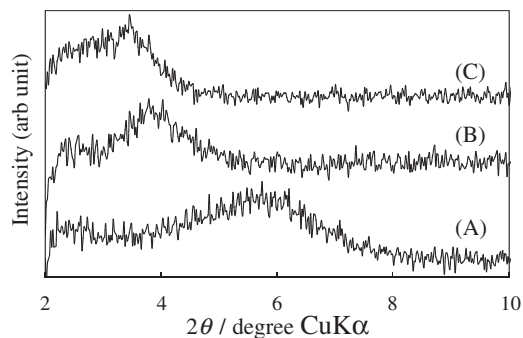


Figure 4. X-ray diffraction patterns of (A) C_8SiGO reduced for 60 min and APS-attached reduced C_8SiGO , (B) before and (C) after reaction with PyBA-S.

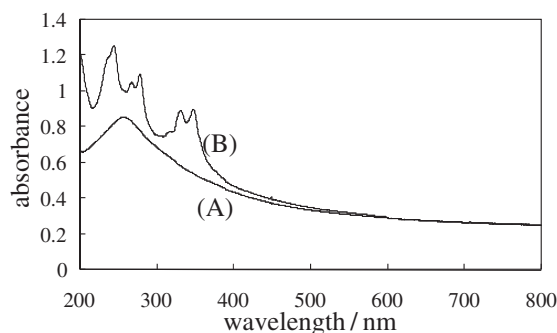


Figure 5. UV-vis spectra of APS-attached reduction C_8SiGO : (A) before and (B) after reacted with PyBA-S.

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