

論文の内容の要旨

論文題目 Study on New Reduction Methods of Graphene Oxide

(酸化グラフェンの新しい還元手法に関する研究)

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1. Introduction

Graphene is a one-atom thick sheet of graphite and composed of sp^2 carbon atoms arranged in a regular hexagonal lattice. Since graphene was first isolated, it has attracted attention due to its remarkable electronic, mechanical and chemical properties. As well as graphene, graphene derivatives such as graphene oxide (GO) and heteroatom doped graphene are also attractive materials. GO is the oxidized form of graphene and functionalized with hydroxyl, epoxy, carboxyl groups and so on. Due to these functional groups, GO can be dispersed in various solvents and form nanocomposites with various materials. For these properties, wide application of GO has been expected. GO was used as a precursor of graphene for mass production. Graphene produced from GO, however, has a problem that reduced graphene oxide (rGO) retain many defects which were formed in the oxidation process. In the present study, I have developed a method to reduce GO effectively by using a thin metal overlayer as a catalyst and heating the GO with catalyst in vacuum. By changing the conditions, the fabricated form of graphene could be controlled. In order to produce graphene in large quantity at low cost, I also developed a method of solution processed GO reduction by using radical reaction. Furthermore, I also fabricated sulfur-doped graphene, which is expected as a catalyst of oxygen reduction reaction, from GO by solution process.

2. Graphene Preparation from Graphene Oxide by Annealing on Metal Surfaces

2.1. Annealing Graphene Oxide at the Interface between a Ni Layer and SiO₂

Graphene was formed from GO by annealing GO at the interface between a Ni layer and SiO₂ substrate. Procedure of this method is as follows. First, GO synthesized by modified Hummers method was deposited onto the SiO₂ substrate by

spin coating method from methanol suspension. Typically the GO was a single layer and the coverage was less than unity. Then the 20 nm Ni film was deposited on the GO/SiO₂/Si substrate by using Knudsen cells. Next, the Ni/GO/SiO₂ sample was annealed at 800 °C for 10 min in vacuum and cooled to room temperature at a rate of about 30 °C/s. After that, the Ni film was etched by immersing the sample into FeCl₃ aqueous solution and the sample was washed with deionized water and methanol. Figure 1 shows SEM image of this sample after etching the Ni film and washing. The area circled by white line is where the Ni film was not deposited and the shape of GO was unchanged (sample A). In the area circled by white dashed line, large sheet whose lateral size was about 1 mm can be seen (sample B). On the other hand, in the area circled by black line, threadlike material whose lateral size was about 10 μm was observed (sample C). Figure 2 shows the Raman spectra of samples A, B and C, together with that of GO. In sample B and C, 2D band (~2700 cm⁻¹) appeared, FWHM of G band (~1580 cm⁻¹) sharpened and the peak intensity ratio of the D band (~1350 cm⁻¹) to the G band ; I_D/I_G was smaller than that of GO. Judging from these results, sample B and C were graphene and sample A was rGO with many defects. Thus, graphene was prepared from GO at relatively low temperature without using flammable gas.

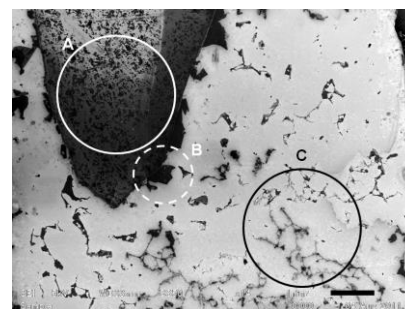


Figure 1. SEM image of graphene prepared from GO by annealing between a 100 nm Ni layer and SiO₂. The scale bar is 1 mm.

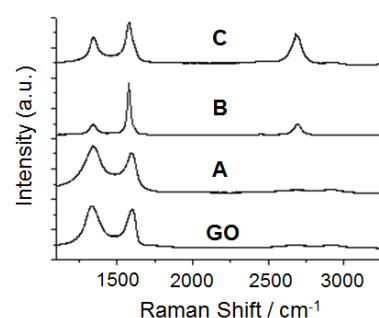


Figure 2. Raman spectra of GO, sample A, B and C.

2.2. Dependence of the Shape of Graphene on the Quantity of Graphene Oxide, the Kind of Metal Overlayer and Annealing Temperature

To investigate the factor to decide the shape of graphene, preparation conditions of graphene were changed variously. The quantity of GO suspension deposited onto SiO₂ was 1 drop or 10 drops. The kind of metal overlayer was 100 nm Ni or 50 nm Pd. Annealing temperature was 800 °C or 1000 °C. This result is shown in Table 1. Large area graphene and threadlike graphene were formed under these conditions. When the GO (1 drop or 10 drops) covered with 50 nm Pd film was annealed at 1000 °C, the Pd film evaporated mostly and graphene was not formed. It is reported that carbon solubility to Pd is higher than to Ni. And generally carbon solubility to a metal increases with temperature. From these facts and Table 1, mechanisms of graphene forming were suggested. For the low carbon solubility, the deposited GO was not decomposed entirely and some GO fragments were left. Then carbon atoms segregated around the remaining GO fraction and grew as graphene in a cooling process. Thus large area graphene was formed. For the high carbon solubility, on the other hand, carbon atoms were decomposed and dissolved into a metal entirely. Then in a cooling process, carbon atoms segregated preferentially at grain boundaries and threadlike graphene was formed. By these mechanisms, 2 types of graphene were prepared.

Table 1. The shape of graphene under various conditions.

	Ni 100 nm		Pd 50 nm	
	1 drop	10 drops	1 drop	10 drops
800 °C	a, b	a	b	a
1000 °C	b	a, b	c	c

a : Large area graphene, b : Threadlike graphene

c : rGO (graphene was not formed)

2.3. Dependence of the Shape of Graphene on the Thickness of Ni Film and Cooling Rate

Large area graphene and threadlike graphene were prepared by above method. However, judging from 2D band of Raman spectra, these 2 types of graphene were thick. To fabricate thin graphene sheet, the thickness of the Ni film were changed from 20 nm to 60 nm. The samples were cooled to room temperature at ~ 10 °C/s (slow rate) in addition to ~ 30 °C/s (rapid rate). In the following Gr (X, s(r)) denotes the sample, which was formed by depositing a Ni film of X nm thickness and cooling with a slow (rapid) rate. Figure 3a and 3b show SEM images of GO after 20 nm Ni deposition and Gr (20, r) after etching of the same GO sheet respectively. The lateral size of Gr (20, r) is approximately several tens μm and the shape of product seems similar to that of the original GO. In the case of slow cooling, the shape of Gr (20, s) was also similar to that of GO. From these results, the cooling rate had little effect on the shape and size of product. On the other hand,

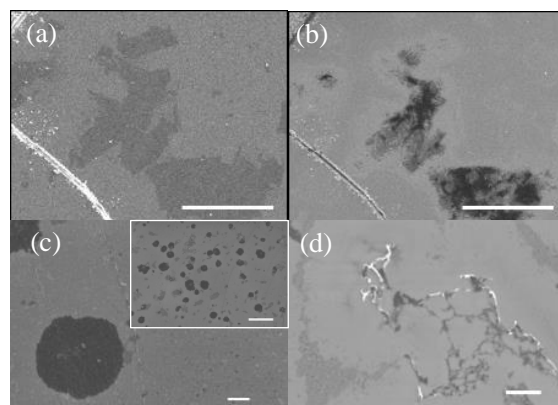


Figure 3. Typical SEM images of (a) GO sheet after 20 nm Ni deposition, (b) Gr (20, r) after etching Ni film, (c) Gr (50, s), and (d) Gr (50, r). All scale bars are equal to 10 μm . The scale bar in the inset of (c) is 100 μm .

in the case of Gr (50, s) (Figure 3c), circular graphene whose lateral size was about 50 μm was observed. As shown inset in Figure 3c, only circular graphene were obtained. In the case of Gr (50, r) (Figure 3d), threadlike graphene with a typical length of several μm were obtained. In contrast to the case of 20 nm Ni film, cooling rate affected the shape of graphene. Graphenes formed in cases of 20, 30 and 60 nm Ni film were also investigated. When the Ni film was 20 to 40 nm, the shapes of graphene resembled that of the original GO sheets. When the Ni film was over 50 nm, the products have the different shapes from the original GO sheets. These results suggested the mechanism of graphene growth from GO (Figure 4). In the case of thin Ni film, part of the isolated carbon atoms could not be dissolved into the Ni layer and would suppress decomposition of GO sheets. In cooling process, the carbon atoms which have diffused into the Ni film would segregate at the interface between Ni and GO sheets. These carbon atoms would repair the defects of GO sheets. Thus, graphene with the similar shape of GO sheets is formed (Figure 4a). In the case of thick Ni film, all carbon atoms of GO sheets are dissolved into Ni and no GO sheet remain between Ni and SiO_2 interface. In cooling process, the dissolved carbon atoms are segregated. When the cooling rate is rapid, duration of carbon segregation is short so that segregation occurs mainly at such defective sites as grain boundaries of the Ni film on SiO_2 . In this way, threadlike graphene is formed. On the other hand, when the cooling rate is slow, duration of carbon segregation is long and the segregated carbon atoms could diffuse laterally at the Ni/ SiO_2 interface (Figure 4b). Thus the shape of graphene is controlled by the quantity of carbon atoms which can be dissolved into Ni layer and cooling rate.

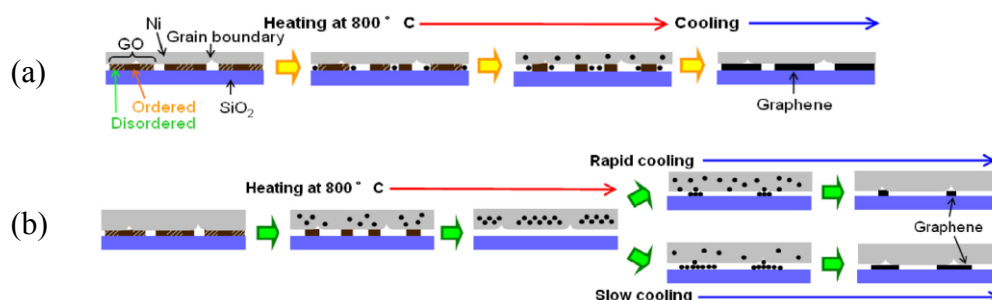


Figure 4. Model of graphene growth in the case of (a) thin Ni and (b) thick Ni layers.

3. Reduction of Graphene Oxide by Radical Treatment

GO was reduced by radical treatments such as methyl radical, ethyl radical, bromoethyl radical and benzyl radical. Radical treatments were performed by the following method. Azobisisobutyronitrile (AIBN), tris(trimethylsilyl)silane (TTMSS), one of CH_3I , $\text{C}_2\text{H}_5\text{Br}$, $\text{BrC}_2\text{H}_4\text{Br}$ or PhCH_2Br were added into GO/DMF suspension and heated at 80°C for 2 h. In all cases, GO was aggregated and the color of GO changed to black. Therefore, GO was reduced by these radicals. Raman spectra of these sample were measured and can be deconvoluted into G band ($\sim 1590\text{ cm}^{-1}$), D band ($\sim 1330\text{ cm}^{-1}$) and D^{**} band ($\sim 1500\text{ cm}^{-1}$) (Figure 5a). The FWHM of the G band; Γ_G , the FWHM of the D band; Γ_D and the peak intensity ratio of D^{**} band to G band; $I_{\text{D}^{**}}/I_G$ are plotted in Figure 5b in each specimen. These results indicate that the improvement of crystallinity was achieved in the following order; $\text{CH}_3\text{I} > \text{BrC}_2\text{H}_4\text{Br} > (\text{N}_2\text{H}_4) > \text{C}_2\text{H}_5\text{Br} > \text{PhCH}_2\text{Br}$.

4. Reduction and Sulfur-Doping of Graphene Oxide by Solution Process

Sulfur-doped graphene was prepared by solution process as follows. GO aqueous suspension was added to $(\text{NH}_4)_2\text{S}_x$ and kept for 2 h at room temperature. Then this GO treated with $(\text{NH}_4)_2\text{S}_x$ (SG) was washed with deionized water and methanol. SG was aggregated and the color of SG was black. These phenomena are seen when GO is reduced. Figure 6 shows XPS spectrum of SG in the region of S2p. S2p peak was observed and this result indicates that sulfur exist in SG. S/C was 3.8 atom%. This S2p peak can be deconvoluted into 3 peaks at 164.2, 165.4 and 168.7 eV respectively. The peak of 168.7 eV should arise from some oxidized sulfur (SO_x). The peaks of 164.2 and 165.4 eV correspond to the split peak of sulfur of sulfide or elemental sulfur.

5. Conclusion

I developed three reduction methods of GO, which are useful for preparation of graphene and S-doped graphene. The first method is annealing of GO at the interface of metal layer and SiO_2 . By this procedure, graphene was formed from GO and the shape of graphene depended on the quantity of carbon atoms dissolved into the metal layer. The second method is radical treatment of GO. By this treatment, GO was reduced. When CH_3I or $\text{BrC}_2\text{H}_4\text{Br}$ was used, GO was reduced more effectively than hydrazine. The third method is reduction and sulfur doping of GO by solution process. From XPS, sulfur was doped in GO successfully. S/C was 3.8 atom%.

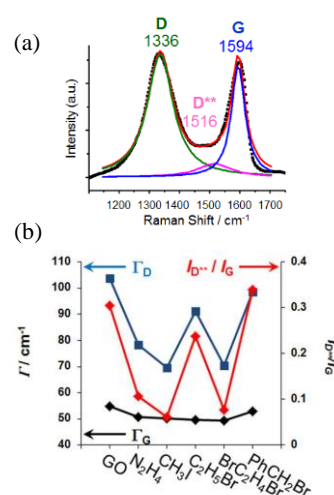


Figure 5 (a) Raman spectrum of GO. (b) Γ_G , Γ_D and $I_{\text{D}^{**}}/I_G$ for each reducing reagent.

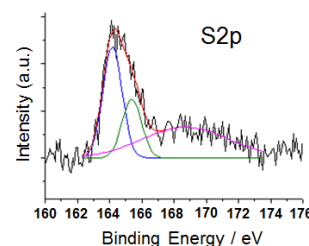


Figure 6 XPS spectrum of S2p in SG.