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Photoreduction of Graphene Oxide Nanosheet by UV-light Illumination under H_2

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We have developed a new photoreduction process at room temperature for the graphene oxide nanosheet in order to increase its electrical conductivity, by illumination with UV light under H_2. This process will be useful for photopatterning conductive areas on insulator graphene oxide.

Much fundamental and applied research on graphene nanosheet has been done since Novoselov et al. reported unusual and very promising physical properties of these materials.[1] Graphene nanosheet is produced by various processes using graphite or SiC via its oxide.[1–8] However, the process via graphene oxide nanosheet is very simple and used on a large-scale at low cost.[9] Moreover, graphene oxide nanosheet can be used as nanoparts to fabricate nanohybrid materials such as layered functional materials by applying electrostatic principles, because the surface is negatively charged similar to metal oxide nanosheets.[10] Graphene oxide nanosheet with low conductivity must be reduced to highly conductive graphene or reduced graphene oxide in order to be used in electric devices. In this process, graphene oxide nanosheet is initially produced by exfoliation of graphite oxide and then reduced to graphene nanosheet. To prepare graphene or reduced graphene oxide nanosheet, the graphene oxide nanosheet is reduced with hydrazine, by heating in a reducing environment,[11–24] or TiO_2 photocatalysis.[25,26] It has been reported that reductions of epoxide and C=O proceed in the cases of hydrazine and thermal treatments respectively, while electron in conduction band produced under UV light reduces the graphene oxide in the case of TiO_2 photocatalysis. In any cases, detail mechanism is unknown. In this paper, a simpler reduction process under mild conditions (room temperature) using UV-light illumination under H_2 is demonstrated.

First, pure graphite (99.9999%, New Materials & Chemicals Ltd.) powder was oxidized by Brodie's method,[27] using fuming HNO_3 solution containing $NaClO_3$. The graphite powder was immersed and stirred in this solution for 6 h at 80 °C. After washing with pure water, the oxidized graphite was exfoliated in water with or without tetrabutylammonium (TBA) hydroxide (nanosheet solution). UV-light illumination using a 500-W high pressure Hg lamp was carried out for 2 h, unless otherwise stated, to the following four samples. The first (sample **1**) was nanosheet film prepared by applying nanosheet solution on a Pt substrate and drying in vacuum. This film, consisting of aggregated nanosheets, was analyzed by X-ray photoelectron spectroscopy (XPS, ThermoScientific SigmaProbe) and Fourier transform infrared spectroscopy (FT-IR, Perkin-Elmer, Spectrum One). The second (sample **2**) was single nanosheet film prepared as a Langmuir–Blodgett (LB) film on a mica substrate,[28] which was measured by atomic force microscopy (AFM, Veeco NanoScope V) to determine thickness. The third (sample **3**) was a single nanosheet film prepared by immersion of HOPG (highly oriented pyrolytic graphite) into nanosheet solution, which was then used for conductivity measurement by conductive atomic force microscopy (C-AFM, Veeco NanoScope V) using an AFM tip (Pt–Ir). The HOPG was freshly cleaved using cellophane tape before immersion. The last sample (sample **4**) was nanosheet solution. The solution was illuminated directly, and the produced black powder was then analyzed using XPS and C-AFM.

The C(1s) XPS spectra of sample **1** are shown in Figure 1. UV-light illumination under H_2 proved to be the most suitable for reduction, as can be seen from the minimized binding energy peak intensities of groups such as epoxide, carboxyl, carbonyl, and hydroxy in all samples. Even under UV illumination in N_2, the reduction proceeded as shown in this figure. In particular, the present photoreduction procedure is very effective for the reduction of C=O and/or C–O–C groups. The peak area ratio of oxygen-containing bonds[29] (C–OH, C=O, C–O–C, and O=C–OH) to C–C, C=C, and C–H bonds was about 1.5 for the oxidized sample before photoreduction, while those after photoreduction under N_2 and H_2 were about 1.2 and 0.75, respectively (Figure S1 in Supporting Information[30]). Atomic O/C ratios of the samples before (a) and after (c) the reduction were 0.36 and 0.32 respectively, although some errors will be contained because of thin film. XPS spectra of the samples photoreduced using various cut-off filters were also measured and shown in Figure S2.[30] From comparison of these spectra, it is clear that

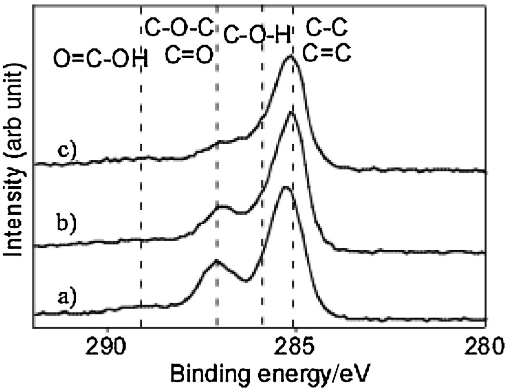

Figure 1. XPS spectra of C(1s) for the aggregated nanosheet samples: (a) graphene oxide nanosheet, (b) after photoreduction in N_2, and (c) after photoreduction in H_2.

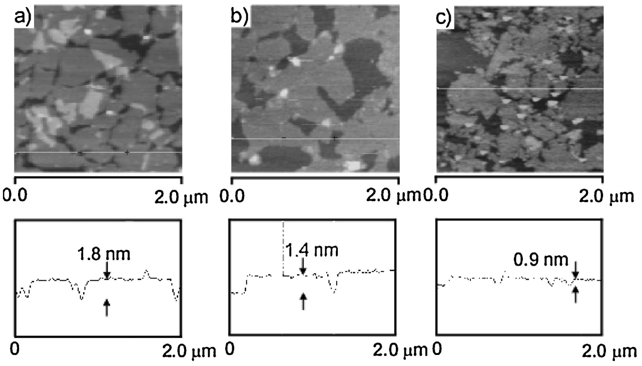

Figure 2. AFM images of the single nanosheets: (a) graphene oxide nanosheet, (b) after photoreduction under N_2, and (c) after photoreduction in H_2. The thicknesses of the nanosheets a, b, and c were about 1.8, 1.4, and 0.9 nm respectively.

UV light around 300 nm is more effective on the present photoreduction. Thus, the UV-light illumination proved very useful for the reduction of the graphene oxide nanosheet, especially under H_2, although reduction was not complete under the present conditions.

FT-IR spectra of the samples before and after the reduction are shown in Figure S3.[30] Peaks around 1700, 1400, 1200, and 1050 cm^{-1} are based on carbonyl and carboxyl C=O, carboxyl C–O, epoxy C–O–C, and alkoxy C–O groups, respectively. The speaks of C=O and C–O–C disappered by the photoreduction. These results are in harmony with those in XPS mesurements as stated above. Initially, C=O and C–O–C bonds at the graphene oxide surface will be destroyed by UV light, and then H_2 will react with O to produce H_2O in the present mechanism.

The AFM images of the single nanosheets (sample **2**) are shown in Figure 2. The thickness of the graphene oxide nanosheet before the photoreduction was about 1.8 nm, while those after were about 1.4 and 0.9 nm under N_2 and H_2 respectively. The thickness of the nanosheet increases with increase in the degree of oxidation, because of the presence of oxygen-containing functional groups at the graphene surface.[29] Consequently, the decrease in thickness after UV-light illumination results from photoreduction.

Figure 3 shows the *I*–*V* curves of the graphene oxide nanosheets (sample **3**) measured by C-AFM. Small currents are based on very small contact area (10–10^2 nm^2) of the AFM tip at substrate. The current was zero for single graphene oxide nanosheet in the applied voltage region from 0.5 to −0.5 V as shown in Figure 3. It should be noted that the conductivity of the nanosheet dramatically increases after UV photoreduction, especially for samples irradiated under H_2. This is due to the increase in π conjugation in the two-dimensional carbon networks.

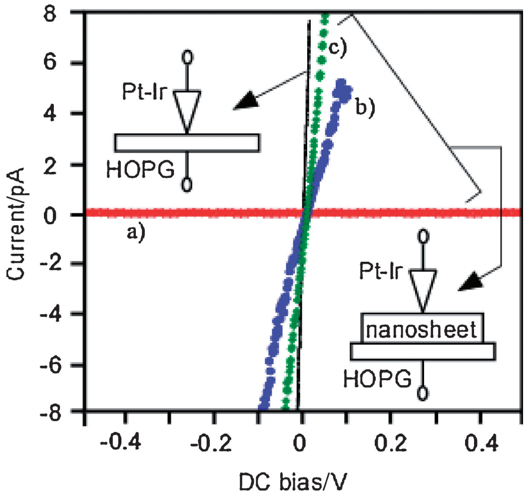

Figure 3. *I*–*V* curves of the single nanosheets: (a) graphene oxide nanosheet, (b) after photoreduction under N_2, and (c) after photoreduction in H_2. The conductivity increased after UV photoreduction, especially under H_2. The graphene oxide nanosheet photoreduced in H_2 (c) shows a semimetallic behavior.

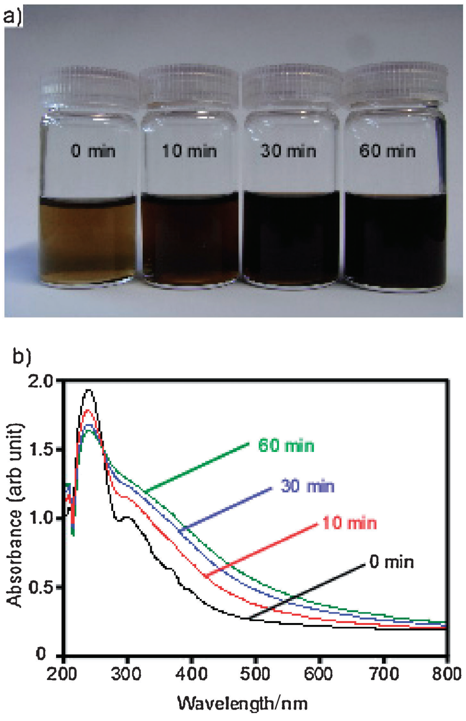

Figure 4. Color of the nanosheet solution as a function of illumination time under N_2: (a) color depth and (b) UV–vis spectra. The color changed to black by the UV photoreduction. The color of black and the increase in the visible absorption are based on the photoreduction of the graphene oxide nanosheets.

The above photoreduction occurred even in the nanosheet solution (sample **4**). The color of the solution changed from pale brown to black, and the depth of the color increased with illumination time as shown in Figure 4, where the UV–vis absorption spectra of the nanosheet solutions are also shown. The black color results from aggregation of photoreduced graphene oxide nanosheets[19] of various thicknesses (2–20 nm, not single nanosheet), determined by AFM observation. The aggregation occurs by hydrophobic interaction between the photoreduced nanosheets in water, while sufficiently oxidized graphene nanosheet is hydrophilic.[16,31]

Figure 5 shows the *I*–*V* curves of the aggregated photoreduced nanosheets on HOPG. The conductivities of all the aggregated nanosheets are much higher than that of the starting

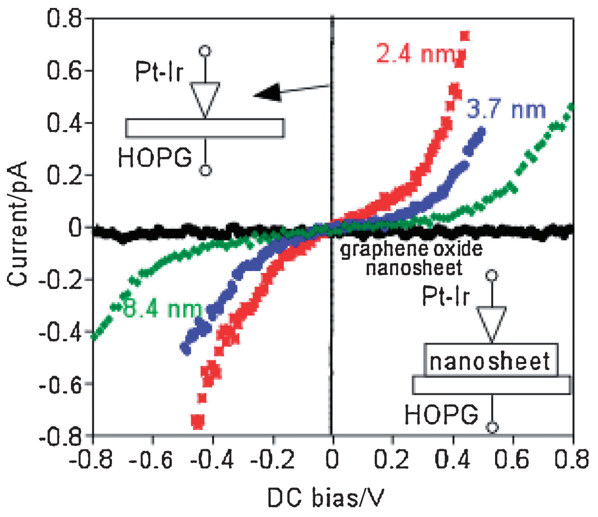

Figure 5. *I–V* curves of the aggregated photoreduced graphene oxide nanosheets with various thicknesses. The UV photoreduction was carried out under N_2. The conductivities of the aggregated nanosheets are very high compared with the graphene oxide nanosheet before the photoreduction. The conductivity of the graphene oxide nanosheet was about zero.

graphene oxide nanosheet (in the same applied voltage region current was about zero), indicating that the photoreduction occurs even in solution. In fact, the C(1s) peak intensities (in the XPS spectra) arising from oxygenated groups of the aggregated nanosheet were lower than those of the starting oxidized graphite powder.

In conclusion, the photoreduction of graphene oxide nanosheet easily proceeded under UV-light illumination increasing conductivity, although the reduction was not complete. In particular, UV-light illumination under H_2 was the most effective for the photoreduction. Probably, more complete reduction will occur if the intensity of the UV light and/or the illumination time increase. This process will be very useful for photopatterning conductive areas on graphene oxide nanosheet. Flash photopattering of graphite oxide reported recently is quite different from our UV photoreduction in principle, because it relies on photothermal effects.[32] Our photoreduction process will be more useful, because the process avoids increasing temperature of the substrate. In fact, the present process was facile even in solution as stated above.

Refrences and Notes

1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
2 P. Blake, E. W. Hill, A. H. Castro Neto, K. S. Novoselov, D. Jiang, R. Yang, T. J. Booth, A. K. Geim, *Appl. Phys. Lett.* **2007**, *91*, 063124.
3 G. M. Rutter, J. N. Crain, N. P. Guisinger, T. Li, P. N. First, J. A. Stroscio, *Science* **2007**, *317*, 219.
4 C. Berger, Z. M. Song, X. B. Li, X. S. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, W. A. de Heer, *Science* **2006**, *312*, 1191.
5 T. Ohta, A. Bostwick, T. Seyller, K. Horn, E. Rotenberg, *Science* **2006**, *313*, 951.
6 A. N. Sidorov, M. M. Yazdanpanah, R. Jalilian, P. J. Ouseph, R. W. Cohn, G. U. Sumanasekera, *Nanotechnology* **2007**, *18*, 135301.
7 K. A. Ritter, J. W. Lyding, *Nanotechnology* **2008**, *19*, 015704.
8 K. V. Emtsev, A. Bostwick, K. Horn, J. Jobst, G. L. Kellogg, L. Ley, J. L. McChesney, T. Ohta, S. A. Reshanov, J. Röhrl, E. Rotenberg, A. K. Schmid, D. Waldmann, H. B. Weber, T. Seyller, *Nat. Mater.* **2009**, *8*, 203.
9 S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, *Nature* **2006**, *442*, 282.
10 U. Unal, Y. Matsumoto, N. Tanaka, Y. Kimura, N. Tamoto, *J. Phys. Chem. B* **2003**, *107*, 12680.
11 S. Park, R. S. Ruoff, *Nat. Nanotechnol.* **2009**, *4*, 217.
12 S. Gilje, S. Han, M. Wang, K. L. Wang, R. B. Kaner, *Nano Lett.* **2007**, *7*, 3394.
13 G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.* **2008**, *3*, 270.
14 X. Wang, L. Zhi, K. Müllen, *Nano Lett.* **2008**, *8*, 323.
15 J. T. Robinson, F. K. Perkins, E. S. Snow, Z. Wei, P. E. Sheehan, *Nano Lett.* **2008**, *8*, 3137.
16 H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, Y. Chen, *ACS Nano* **2008**, *2*, 463.
17 Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 5856.
18 S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, R. S. Ruoff, *Carbon* **2007**, *45*, 1558.
19 D. Li, M. B. Müller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.* **2008**, *3*, 101.
20 C. Gómez-Navarro, R. T. Weitz, A. M. Bittner, M. Scolari, A. Mews, M. Burghard, K. Kern, *Nano Lett.* **2007**, *7*, 3499.
21 M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z. Wang, I. T. McGovern, G. S. Duesberg, J. N. Coleman, *J. Am. Chem. Soc.* **2009**, *131*, 3611.
22 G. Wang, J. Yang, J. Park, X. Gou, B. Wang, H. Liu, J. Yao, *J. Phys. Chem. C* **2008**, *112*, 8192.
23 Y. Si, E. T. Samulski, *Nano Lett.* **2008**, *8*, 1679.
24 S. Park, J. An, R. D. Piner, I. Jung, D. Yang, A. Velamakanni, S. T. Nguyen, R. S. Ruoff, *Chem. Mater.* **2008**, *20*, 6592.
25 G. Williams, B. Seger, P. V. Kamat, *ACS Nano* **2008**, *2*, 1487.
26 O. Akhavan, E. Ghaderi, *J. Phys. Chem. C* **2009**, *113*, 20214.
27 B. C. Brodie, *Ann. Chim. Phys* **1860**, *59*, 466.
28 M. Muramatsu, K. Akatsuka, Y. Ebina, K. Wang, T. Sasaki, T. Ishida, K. Miyake, M. Haga, *Langmuir* **2005**, *21*, 6590.
29 O. Akhavan, *Carbon* **2010**, *48*, 509.
30 Supporting Information is avaiable electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
31 X. Li, G. Zhang, X. Bai, X. Sun, X. Wang, E. Wang, H. Dai, *Nat. Nanotechnol.* **2008**, *3*, 538.
32 L. J. Cote, R. Cruz-Silva, J. Huang, *J. Am. Chem. Soc.* **2009**, *131*, 11027.