

VUV-induced reduction of graphene oxide in two-dimensional pattern arrays with sub- μm resolution

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Graphene oxide (GO), which is a derivative of graphene decorated with polar functional groups such as hydroxyl, carbonyl, carboxyl and epoxy groups [1]. Chemical processing, in which graphite is oxidized to some extent, has been applied to produce GO [2, 3] and accepted as a promising method as the mass-scale production of graphene-based materials, among all known approaches like micromechanical exfoliation of graphite, chemical vapor deposition, epitaxial growth, etc.[4]. Due to the hydrophilic nature of GO, it can be dispersed in a polar solvent, even in water, consequently, GO thin films can be readily formed on any types of solid substrates by simply casting from an aqueous solution of GO nanosheets. However, GO is distorted in electronic properties compared with graphene, since oxidized parts in GO are much less conductive than the sp^2 network in graphene. The elimination of oxygen functionalities and recovering of the π -conjugated network are, thus, very important in order to restore the graphene characteristics. The reduction of GO is an approach to increase conductivity of GO. Reduced GO (rGO), which is a reduced form of GO at least partially, show resemble characteristics to graphene. Actually, electronic conductivities were reported to be recovered when GO was reduced to rGO [5]. The rGO can be prepared via thermal annealing or chemical reduction using strong reducing agents like hydrazine hydrate [5]. Although these processes are certainly effective, there have been some disadvantages, that is, large energy consumption or the use of toxic reagent, unfavorable for industrial applications. In order to overcome such problems, a variety of approaches based on photochemical, -catalytical or -thermal reduction, which are performable around room temperature have been reported so far [6-8]. However, further studies to develop a new reduction process are still necessary to fulfill requirements to adopt rGO to microelectronic devices.

Here we propose another approach to reduce GO to rGO by the use of vacuum ultra-violet (VUV) light. This idea is based on VUV-decomposition of poly(methyl methacrylate) (PMMA) resin. In our previous research, we found that oxygen-containing parts of PMMA was decomposed when irradiated with a VUV light at 172 nm wavelength [9]. We have expected that oxidized parts of GO could be trimmed similarly.

GO nanosheets with a size of 20-50 μm were prepared by a modified Hummers' method [3]. The aqueous GO solution was spin-casted onto a highly-doped Si substrate covered with a surface oxide layer of 90 nm in thickness. The GO-based substrate was located in a vacuum chamber. After evacuated below 10^{-3} Pa, VUV light was irradiated to the sample surface for 15 min. A Xe excimer lamp (Ushio Inc., radiating wavelength and intensity: 172 nm and 10 mWcm^{-2}) was used for the VUV light source. Figure 1 shows C1s-XPS profiles of GO and VUV-irradiated GO. Due to VUV-irradiation, the peak intensity around 287-288 eV corresponding to photoelectrons from C atoms bonded with O with a form of C-O, C=O, or COO decreased. On the contrary, the peak intensity around 285 eV corresponding to those from the sp^2 graphene network increased with the VUV-irradiation. This result means that GO is certainly reduced to rGO and the π -conjugated network is recovered by the VUV-irradiation in vacuum. Figure 2 shows topographic and surface potential images of GO and rGO-VUV acquired by Kelvin-probe force microscopy (KFM). Both GO and rGO sheets show a topographic height about 1 nm. However, the surface potential of GO is 50 mV higher than that of the SiO_2/Si substrate, while the potential of rGO-VUV is 30 mV lower than the substrate. Although the origin of these surface potential contrasts are still under investigation, KFM is proved to be a powerful means to probe a state of GO (oxidized or reduced) locally.

Next, another GO-casted sample in vacuum was irradiated with VUV light for 2 min with the same procedure except that a photomask (Cr patterns formed on a quartz plate) was placed on the sample. Figure 3 shows optical, topographic and surface potential images of GO sheets with the patterned VUV-irradiation through the photomask. As clearly indicated in the optical micrographs, the VUV-irradiated regions (rGO-VUV) are seen as dark compared with the un-irradiated regions (GO). In the surface potential images, the VUV-irradiated regions (rGO) show lower surface potentials in accordance with the results shown in Fig. 3. In addition, from the close inspection of the topographic images, the rGO-VUV regions are confirmed to be depressed about 0.2 μm in depth.

In conclusion, the VUV-irradiation to GO in vacuum has been found effective to reduce GO to rGO probably through the selective trimming of oxygen containing parts in GO. This chemical change could be visible by KFM. Moreover, we have succeeded in fabricating rGO patterns with a spatial resolution of

0.5 μm on GO. This method is useful for GO/rGO based microelectronics and its extension to a wafer-scale production will be possible.

References

- [1] D. R. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, *Chem. Soc. Rev.* **39** (2010) 228.
- [2] W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.* **80** (1958) 1339.
- [3] M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara and M. Ohba, *Carbon*, **42** (2004) 2929.
- [4] M. J. Allen, V. C. Tung and R. B. Kaner, *Chem. Rev.* **110** (2010) 132.
- [5] C. K. Chua, M. Puram, *Chem. Soc. Rev.* **43** (2014) 291.
- [6] Y. Zhou, Q. Bao, B. Varghese, L. A. L. Tang, C. K. Tan, C.-H. Sow and K. P. Loh, *Adv. Mater.* **22** (2010) 67.
- [7] Y. Matsumoto, M. Koinuma, S. Y. Kim, Y. Watanabe, T. Taniguchi, K. Hatakeyama, H. Tateishi and S. Ida, *ACS Appl. Mater. Interf.* **2** (2010) 3461.
- [8] S. Prezioso, F. Perrozzi, M. Donarelli, F. Bisti, S. Santucci, L. Palladino, M. Nardone, E. Treossi, V. Palermo, and L. Ottaviano, *Langmuir* **28** (2012) 5489.
- [9] A. Hozumi, T. Masuda, K. Hayashi, H. Sugimura, O. Takai, and T. Kameyama, *Langmuir* **18** (2001) 9022.

Figures

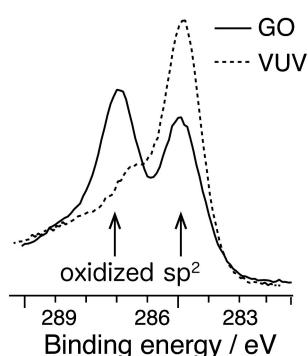


Fig. 1 C1s-XPS profiles of GO and VUV-irradiated GO.

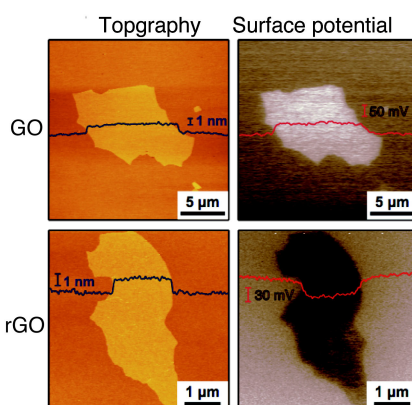


Fig. 2 Topography and surface potential images of GO and rGO .

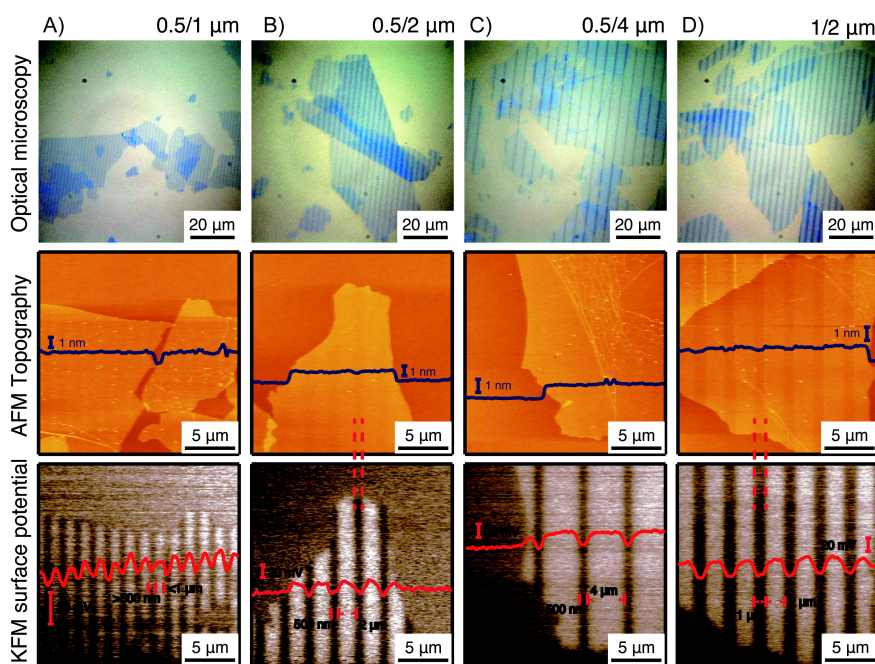


Fig. 3 VUV-micropatterning of GO. The widths of VUV-irradiated and masked areas are A) 0.5 and 1 μm , B) 0.5 and 2 μm , C) 0.5 and 4 μm and D) 1 and 2 μm .