Chemical state analysis of oxidizing graphene on porous alumina

Kota Takaoka[1], Shiro Entani[2], Seiji Sakai[2], Kei Mitsuhara[1], and Masaru Takizawa[1]
1) *Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, Nojihigashi 1-1-1, Kusatsu, Shiga 525-8577, Japan*
2) *National Institutes for Quantum and Radiological Science and Technology, Takasaki, Gunma 370-1292, Japan*

Graphene oxide (GO), which can be produced at low cost, has attracted attention as adsorption material in recent years, especially an efficient adsorbent for radioactive materials [1]. GO was reported as a better adsorption material than usual adsorbent material, since the oxygenated functional groups are considered to be the adsorption sites [1]. Control of oxidation state would lead to a selective adsorption performance. So far, the chemical states have been much studied and revealed that the existence of the functional groups such as epoxy, carboxyl, hydroxyl, and carbonyl groups [2]. X-ray absorption fine structure (XAFS) measurements have revealed a various type of oxygenated functional groups [3]. However, oxidizing process and the formation of the functional groups were not understood. In order to investigate the process of oxidizing graphene, the chemical states have been measured by XAFS.

GO was formed on a porous alumina substrate in this study. A porous alumina film was grown on a Si(100) substrate with a 300 nm thick oxide layer (SiO_2). Liquid alumisol (ALOOH; Kawaken Fine Chemicals) was used as precursor. A several-micrometer-thick alumisol film was deposited on the SiO_2 surface by spin coating. After prebaking at 170 °C in the atmosphere, the alumisol film was introduced into a custom-designed vacuum furnace. The base pressure of the furnace was evacuated up to 6×10^{-6} Pa. After the evacuation, the alumisol film was heated at 1000 °C for 1 h in order to convert the alumisol into porous alumina. Subsequently, the chemical vapor deposition growth of graphene was performed in the furnace at the same temperature by introducing 200 Pa methanol vapor for 30 min. After the graphene growth, the graphene in the graphene/porous alumina film was oxidized based on the modified Hummers method for 30-40 sec.

XAFS measurements were performed at the BL-8 of SR Center at Ritsumeikan University, equipped with a grazing incidence monochromator with a varied-line-spacing plane grating. Oxygen *K*-edge XAFS spectra of the samples were measured in partial electron yield by a micro-channel plate detector with retarding grids. The retarding voltage was set to -300 V. The incident angle of SR with respect to the surface normal was varied. The measurements were performed at room temperature under ultrahigh vacuum of $\sim 1 \times 10^{-7}$ Pa. No surface treatment was performed.

Figure 1 shows the O *K*-edge XAFS spectra of the porous GO (PGO). The prominent structures around ~536 eV and ~540 eV are σ^* states of mainly the porous alumina substrates. The structure around ~531 eV can be assigned to the π^* (O = C) states due to oxidation of graphene. The intensity of this structure decreases for 40 sec oxidation of graphene, indicating that the decrease of O = C functional group. This behavior is similar to that observed for GO on α-Al_2O_3 (0001) although the oxidation time to reduce the O = C functional group is different.

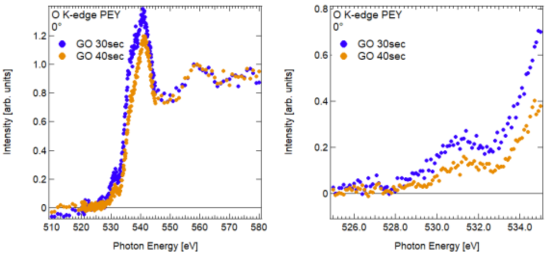

Fig. 1 O *K*-edge XAFS spectral change under oxidation process of PGO.

We have performed X-ray absorption fine structure measurements on oxidized single-layer graphene on a porous substrate. Even on the porous substrate, it is thought that the oxidation firstly introduces the oxygen functional group of C = O and excess oxidation reduces this oxygen functional group.

References

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