Chemical state analysis of oxidizing graphene on porous alumina

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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 [1,2]. GO was reported as a better adsorption material than usual adsorbent material, since the oxygenated functional groups are considered to be the adsorption sites [3,4]. Control of oxidation state would lead to a selective adsorption performance. The chemical states have been much studied and revealed that the existence of the functional groups such as epoxy, carboxyl, hydroxyl, and carbonyl groups [5].

In practical application to adsorbent material, porous substrates are often used due to an effective adsorption and collection of adsorbed materials [4]. In order to investigate the process of oxidizing graphene on porous alumina substrate, the chemical states have been measured by X-ray absorption fine structure (XAFS).

GO was formed on a porous alumina substrate in this study. The details are described in refs [4, 6]. 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. Carbon and 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 -100 V, -300 V, respectively. The incident angle of SR with respect to the surface normal was varied. The measurements were performed at room temperature under the ultrahigh vacuum of ~1×10⁻⁷ Pa. No surface treatment was performed.

Figure 1 shows C K-edge XAFS spectra of the samples. The C=C π* bond around 285 eV [7,8] appears even for 0° incidence [Fig. 1(a)], indicating that the graphene domain covers the porous substrate surface. This intensity decreases with the oxidation [Fig. 1(b)], meaning that the amount of C = C bond decreases by oxidation.

Figure 2 shows O K-edge XAFS spectral changes under oxidation process. The structure around 532 eV is seen even for the graphene on the porous alumina [Fig. 2(a)]. This structure is associated with oxygen vacancy of the γ-Al₂O₃. After the oxidation of the graphene (30 sec), a structure around 531 eV grows, indicating the introduction of the oxygen functional groups. Further oxidation of the graphene (40 sec) does not increase the intensity of this structure. This behavior is similar to that observed for the oxidation of the graphene on the sapphire substrate [Fig. 2(b)]. Spectral analysis of these structures indicated that the ratio of the dominant carboxyl group to the carbonyl group is different depending on the substrate, suggesting that the edge of graphene affects the formation of the oxygen functional group.

Figure 1 C K-edge XAFS spectra for each oxidation of GO on porous alumina. (a) 0 sec (graphene). (b) 240 sec.

Figure 2 O K-edge XAFS spectra spectral changes under oxidation process. GO on the porous alumina (a) and the sapphire (0001) (b) substrates.

References