Chemical and Electronic State Analyses of Oxidizing Graphene*

Kota Takaoka,† Kei Mitsuhara, and Masaru Takizawa
Department of Physical Science Faculty of Science and Engineering, Ritsumeikan University,
Nijo-higashi 1-1-1, Kusatsu, Shiga 525-8577, Japan

Shiro Entani and Seiji Sakai
National Institutes for Quantum and Radiological Science and Technology, Tokai, Ibaraki 319-1195, Japan
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In order to investigate the process of oxidizing graphene, the chemical and electronic states have been studied by X-ray absorption fine structure (XAFS) and photoelectron spectroscopy (PES) measurements. Single layer graphene oxide was formed on α-Al₂O₃(0001). After oxidation until 30 s, XAFS results showed a decrease of C 1s intensity and an appearance of O 1s intensity and PES results showed a similar electronic state. However, 45 s oxidation led to a different electronic state, and the O 1s intensity decreased for 60 s oxidation. The oxidation is thought to firstly introduce the oxygen functional groups, then to modify the graphene.

I. INTRODUCTION

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 [1–5]. 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 [6]. X-ray absorption fine structure (XAFS) measurements have revealed a various type of oxygenated functional groups [7]. The electronic structures have been also studied and found that the band gap opening and the appearance of the O 2p states [8]. However, oxidizing process and the formation of the functional groups are not understood. In order to investigate the process of oxidizing graphene, the chemical and electronic states have been measured by XAFS and photoelectron spectroscopy (PES).

II. EXPERIMENTAL

A. Preparation of single-layer GO (SLGO)

SLGO was formed on α-Al₂O₃(0001) [sapphire(0001)]. Before synthesizing SLGO, single-layer graphene (SLG) was grown on a sapphire(0001) substrate. The substrate was annealed at 900°C in open air in order to obtain atomically flat surface. Then, the substrate was introduced into a vacuum furnace. The base pressure of the furnace was 6 × 10⁻⁶ Pa. After evacuating, the substrate was annealed up to 1000°C for 1 h. For the graphene growth, a methanol vapour was used as a precursor. SLG was grown by introducing 200 Pa methanol vapor for 30 min [9]. After the SLG growth, the SLG was oxidized as follows: The mixture of H₂SO₄ and KMnO₄ was prepared by slowly adding KMnO₄ (1.8 g) into concentrated H₂SO₄ (20 mL) and stirring in the beaker. SLG/sapphire(0001) was dipped in the mixture for 5–60 s. The oxidized specimens were washed with purified water and dried under nitrogen gas blow.

B. Chemical state analysis

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 −150 V and −350 V, respectively. In order to see orientation of functional groups, the in-plane and mainly out-of-plane polarization of SR was selected by varying the incident angles of 0° and 60°.

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† Corresponding author: rp0041rr@ed.ritsumei.ac.jp

FIG. 1. O K-edge XAFS spectra of oxidized single-layer graphene.
FIG. 2. Polarization-dependent O K-edge XAFS spectra of oxidized single-layer graphene: (a) 5 s. (b) 30 s. (c) 45 s. (d) 60 s.

FIG. 3. Spectral analysis of O K-edge XAFS spectra of oxidized single-layer graphene: (a) 5 s. (b) 30 s. (c) 45 s. (d) 60 s.

respectively. The measurements were performed at room temperature under ultrahigh vacuum of $\sim 1 \times 10^{-7}$ Pa. No surface treatment was performed.

### C. Electronic state analysis

The PES was performed at the linearly polarized soft x-ray beamline BL-7 of SR center, Ritsumeikan University, using a hemispherical electron energy analyzer, Scienta SES2002. Utilizing the analyzer, we can obtain the position-resolved electronic structures. The measurements were performed at room temperature under ultrahigh vacuum of $\sim 1 \times 10^{-7}$ Pa. Photon energy was set to 60 eV. No surface treatment was performed.

FIG. 4. Intensity changes of peak A and peak B as a function of the oxidation time.

### III. RESULTS AND DISCUSSION

Figure 1 shows O K-edge XAFS spectral changes under oxidation process. After the oxidation of SLG, shoulder structures appear around $\sim$531 eV, where only the tail of the $\alpha$-Al$_2$O$_3$ structure located around 540 eV [10] is seen for SLG on sapphire (0 s). The intensities of this structures do not change significantly for 5–30 s oxidized SLG. For 45 s oxidation of SLG, the intensity of this structure increases. However, further oxidization of SLG (60 s) makes the intensity of this structure decreased. According to [11], this structure can be attributed to O=C $\pi^*$ (carbonyl group).

Figure 2 shows the polarization-dependent O K-edge XAFS spectra under oxidation process. The polarization dependence is slightly observed for initial oxidation of SLG [5–30 s, Fig. 2(a, b)], meaning that the O=C bond is roughly parallel to the substrate surface. Further oxidation of SLG (45 s, Fig. 2(c, d)) decreases the polarization dependence, indicating that the O=C bond becomes randomly orientated.

In order to clarify the oxygenated functional groups, the spectral analysis of this structure is performed as shown in Fig. 3. Besides O=C $\pi^*$ around 531.3 eV (peak A), another peak around 530 eV (peak B) is needed to fit the spectral line shape. This peak B may be assigned

FIG. 5. C K-edge XAFS spectra of oxidized single-layer graphene.
around the binding energy of 322 J-Stage: https://www.jstage.jst.go.jp/browse/ejssnt/

also make an anisotropy measurement [oriented in the substrate plane, i.e., the graphene sheet

to C–O–C π* [11] or a contamination. The spectrum of SLG is also used as a background (BG). Figure 4 shows thus obtained peak intensities. The intensities of peak A (O=C) change during oxidation, while that of peak B does not change so much.

Figure 5 shows C K-edge XAFS spectra of the samples. After the oxidation of SLG, the intensity around ~285 eV significantly decreases while the intensity around ~288 eV does not change (Fig. 5). According to the previous X-ray absorption study of graphene oxide [12], these two peaks are assigned to C=C π* and C=O π*, respectively. Note that the transitions to continuum and σ* states appear above ~293 eV [12].

The polarization-dependent C K-edge XAFS spectra (Fig. 6) indicate that the C=C bond in SLGO is mainly oriented in the substrate plane, i.e., the graphene sheet is parallel to the substrate surface. X-ray Raman scattering experiment with varying the scattering vector can also make an anisotropy measurement [13].

Figure 7 shows the position-dependent valence band of each sample. As shown in Fig. 7(a), the SLG (0 s) has the characteristic features of graphene, that is, the structure around the binding energy of ~3 eV comes from C 2p π states, while the structure around ~6 eV comes from C 2p σ states [8]. There is no difference between regions A and B, indicating that the uniform SLG is grown in the entire regions of the sample. For 5 s oxidation of SLG [Fig. 7(b)], the characteristic features of graphene become smeared out in some regions (region A). For 10 s oxidation of SLG [Fig. 7(c)], the characteristic features of graphene near the Fermi level still exist in some regions (region A). For 20 s and 30 s oxidation of SLG

FIG. 6. Polarization-dependent C K-edge XAFS spectra for each oxidation of single-layer graphene: (a) 0 s. (b) 5 s. (c) 10 s. (d) 20 s. (e) 30 s. (f) 45 s. (g) 60 s.

FIG. 7. Position-dependent valence band for each oxidation of single-layer graphene: (a) 0 s. (b) 5 s. (c) 10 s. (d) 20 s. (e) 30 s. (f) 45 s. (g) 60 s.

FIG. 8. Valence band spectral changes under oxidization process of single-layer graphene.
[Fig. 7(d, e)], the characteristic features of GO appears in the entire regions of the sample. The band gap is opened. The broad structure of O 2p appears around ~8 eV [8]. For 45 s oxidization of SLG [Fig. 7(f)], the characteristic features of GO changes in some regions (region A). For 60 s oxidization of SLG [Fig. 7(g)], a new electronic state other than GO appears in some regions (region A).

Figure 8 summarizes the characteristic electronic structure changes with oxidization of SLG. The oxidizing graphene firstly leads to the decrease of C 2p π states, then to the increase of O 2p states, and finally to the formation of the other electronic states, maybe due to the destruction of the aromatic rings.

IV. CONCLUSION

We have performed X-ray absorption fine structure measurements and photoelectron spectroscopy on oxidized single-layer graphene. It is thought that the oxidation firstly introduces the oxygen functional groups and then destroys the aromatic rings in the graphene.