

# Oxidation states of graphite studied by near edge x-ray absorption fine structure measurements

Masaru Takizawa, Kensaku Kondo, and Hidetoshi Namba

Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

## 1. Introduction

Graphene oxide has attracted much attention as a precursor of graphene production. Understanding of bonding nature between oxygen and carbon is important to control the reduction of oxidized graphite. Near edge x-ray absorption fine structure (NEXAFS) is a promising tool for such an electronic structure study. In this report, we have studied the electronic states of various oxidized graphites.

## 2. Experimental

Three samples of oxidized graphite were prepared; graphene oxide paper (ALLIANCE), atomic-oxygen exposed highly ordered pyrolytic graphite (HOPG), and oxygen sputtered HOPG. Atomic-oxygen exposure was achieved by dosing the oxygen gas to the high vacuum chamber with W filament facing the HOPG. For a reference, we also measured the samples with carbonyl (JSR) and epoxy (SIGMA-ARDRICH) groups.

NEXAFS 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 [1]. NEXAFS spectra of the samples were measured in partial electron yield by a micro-channel plate detector with retarding grids. The incident angle of SR with respect to the surface normal was set to  $60^\circ$  in order to see changes of the  $\pi^*$  peaks of the C K-edge spectra.

## 3. Results and Discussion

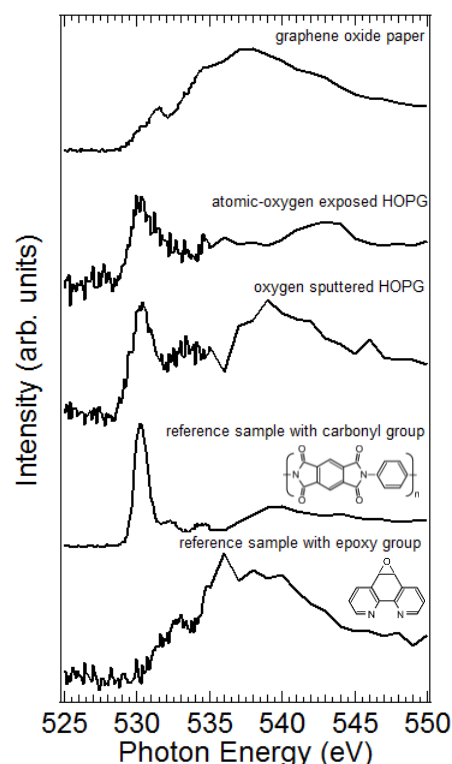


Fig. 1 O K-edge spectra of oxidized graphites.

Figure 1 shows the O K-edge spectra of the samples. The spectral line shapes are different each other, meaning that the oxidation states are different among the samples.

For the graphene oxide paper, the nitrogen signal is observed as shown in Fig. 2. This is because the chemical treatment using nitric acid and this result indicates the existence of NO<sub>2</sub> groups. Therefore, interpreting the oxidation states of the graphene oxide paper from O K-edge (Fig.1) and C K-edge (Fig. 3) spectra is very difficult, though the significant decreasing of the  $\pi^*$  peak around 285 eV of the C K-edge spectrum indicates the destruction of  $sp^2$  bonding of graphite.

On the other hand, for the atomic-oxygen exposed surface of HOPG, the nitrogen signal is not detected (Fig. 2). The peak around 530 eV of the O K-edge spectrum (Fig. 1) indicates the formation of C=O groups as seen in the reference sample. However, the broader peak suggests the formation of other functional groups, such as an epoxy group located around 533 eV for the reference sample. No significant changes of the C K-edge spectrum may be due to the small amount of the oxidized graphite.

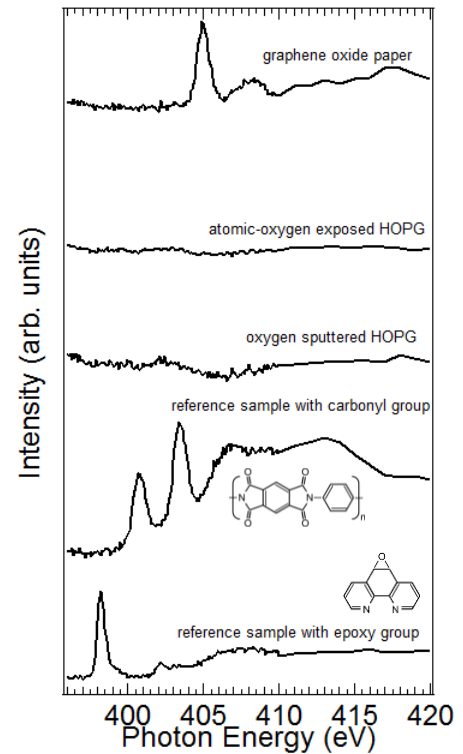
Similarly, for the oxygen sputtered HOPG, the nitrogen signal is not detected (Fig. 2) and the formation of carbonyl groups and other functional groups are indicated from the O K-edge spectrum (Fig. 3). Furthermore, there is a significant change in the C K-edge spectrum (Fig. 3), indicating the amorphisation of graphite.

#### 4. Conclusions

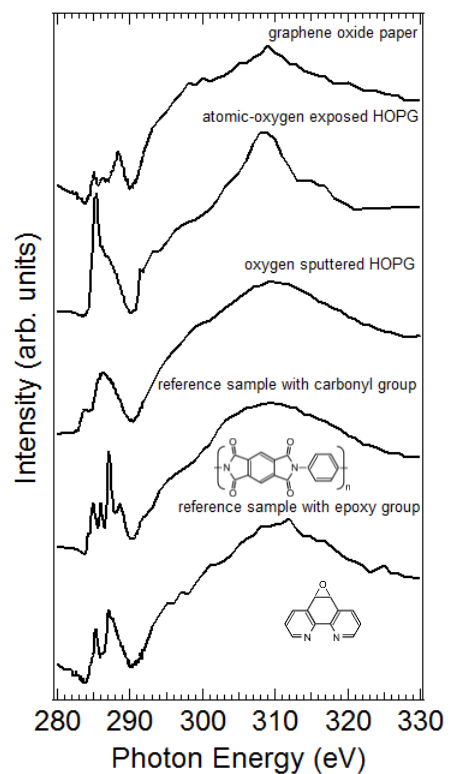
We have studied the electronic states of oxidized graphite by near edge x-ray absorption fine structure measurements. Oxidation of graphite leads to the formation of epoxide and/or carbonyl groups.

#### References

- [1] H. Namba *et al.*, J. Synchrotron Rad. **5**, 557 (1998).



**Fig. 2** N K-edge spectra of oxidized graphite.



**Fig. 3** C K-edge spectra of oxidized graphite.