



Soft X-ray emission and absorption spectra in the O K region of oxygen incorporated in microporous carbon

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Abstract

Soft X-ray emission and absorption spectra in the O K region of oxygen incorporated in microporous carbon were measured using synchrotron radiation, in order to directly observe the oxygen and identify its chemical bonding states on the graphitic surface in microporous carbon. The O K X-ray emission spectrum exhibits a peak at 526 eV with a low-energy tail, and the absorption spectrum at the O K threshold exhibits a sharp peak at 531.5 eV and then rises from 535 eV. Spectral feature analysis using DV-X α molecular orbital calculations show that the measured X-ray spectra are not sufficiently explained by H₂O or typical substituents, such as –OH, –CHO, and –COOH, on the graphitic surfaces. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Microporous carbon has been widely used for adsorbents and catalysts in many industrial fields. In particular, its high adsorption capacity for many organic compounds has led to one of its most important uses being in environmental treatment, such as in water treatment to remove organic pollutants from water and in air pollution sensors to concentrate organic pollutants [1]. Its adsorption properties were thought likely to depend on the surface structure and chemical states of the graphitic surface in the micropores. One of the most important surface-structure/chemical-states is the oxidation state of the graphitic surface. The oxidized surface structure in microporous carbon was estimated from thermally desorbed gaseous fractions such as CO₂, CO, and H₂O by the gas-phase chemical modification method [2], which can be regarded

as an indirect method of detecting oxygen. On the other hand, studies of the oxidation states in microporous carbon using direct detection methods, such as Raman spectroscopy and X-ray photoelectron spectroscopy (XPS), have recently been conducted, and these spectroscopic methods were shown to be useful for oxidation state analysis [3,4].

Soft X-ray emission and absorption (SXE) spectroscopy using synchrotron radiation has recently been utilized to characterize various carbon films [5–9]. SXE spectroscopy, which can provide significant information about the occupied and unoccupied molecular orbitals, has high resolution and high efficiency due to the highly-resolved and highly brilliant synchrotron radiation, and bulk-sensitivity due to the longer transmission length of soft X-rays in solid matter. These advantages enable SXE spectroscopy to analyze the chemical bonding states of the bulk matrix. Recently, we have shown unprecedented examples of in situ direct observations of adsorbate benzene and pyridine molecules in microporous carbon by SXE, and demonstrated that SXE is a powerful method for chemical bonding state analysis of the graphitic surface in bulk

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microporous carbon [10,11]. However, there have been no studies using SXEA for oxidation analysis of microporous carbon.

The aim of this work is therefore to directly observe oxygen in microporous carbon by SXEA and determine its chemical bonding states. In this paper, we describe high-resolution soft X-ray emission and absorption spectra of microporous carbon in the O K region, and discuss their spectral features to obtain information about the chemical bonding states of oxygen on the graphitic surface in micropores, referring to some molecular orbital calculations.

2. Experiment

Commercially obtained microporous carbon powder (average particle size: 250 μm) and graphite powder (45 μm) were used as references for the spectroscopic measurements. Before the spectroscopic measurements, the untreated powder samples were held for several hours in a vacuum of 10^{-8} Torr at room temperature. Spectroscopic measurements of X-ray emission in the O K region were performed at both the Advanced Light Source (ALS) and the Photon Factory (PF). The O K X-ray emission spectra of the samples were measured using a grating X-ray spectrometer installed in beamline BL-8.0 [12] at ALS and using a similar spectrometer in BL-2C [13] at PF. Photon energy of the monochromatized incident beam was tuned to about 550 eV to effectively excite the O1s-electrons and prevent multiple ionization. The resolving power ($E/\Delta E$)

of the spectrometer in BL-8.0 at ALS was estimated to be ~ 300 in the O K region, using a 50- μm entrance slit and a 600-lines/mm spherical grating, which had a 10-m radius. The resolving power of the spectrometer using a 20- μm entrance slit and a 1200-lines/mm spherical grating, which had a 5-m radius, in BL-2C at PF was estimated to be ~ 750 . Measurement time for one spectral scanning was 20 min at ALS and 2 h at PF. Fluorescence yield (FY) X-ray absorption spectra of the porous carbon at the O K threshold were measured using the above-mentioned X-ray spectrometer in BL-8.0 at ALS. The resolving power of the beamline monochromator for this absorption measurement was estimated to be several thousand using 100- μm entrance/exit slits and a 380-lines/mm grating. It took 1 h to perform this absorption spectral scanning.

3. Results and discussion

The left panel of Fig. 1 shows the O K X-ray emission spectra, measured at ALS (closed-circle lines) and at PF (solid lines), of the microporous carbon and graphite powders. Their spectral features and the relative peak intensity between the microporous carbon and graphite, measured at ALS, are in good agreement with those measured at PF, which confirms the reliability of these spectral measurements. The spectral features of the microporous carbon consisted of a main peak at 526 eV and a low-energy tail. The spectral features of the graphite powder were almost the same, which shows that the chemical bonding state of oxygen in graphite is similar to

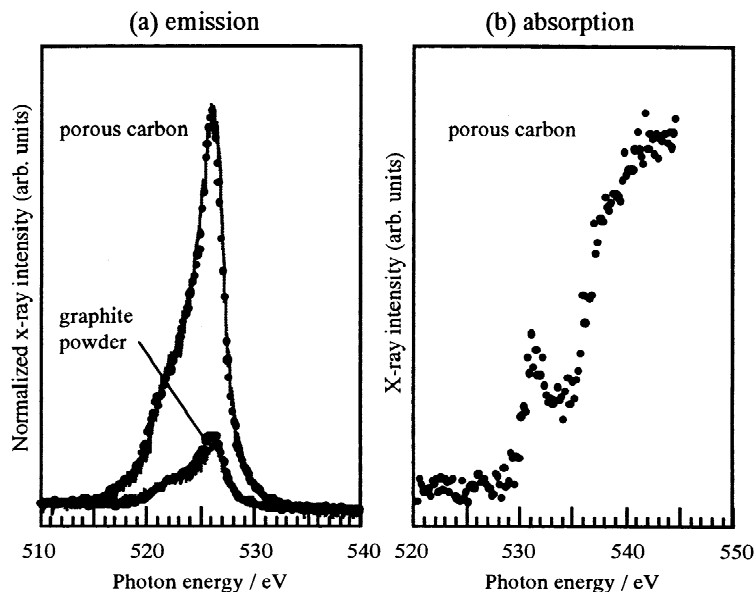


Fig. 1. The left panel (a) shows soft X-ray emission spectra in the O K region of microporous carbon and graphite powder, measured at ALS (closed-circle lines) and PF (solid lines). Excitation energy was tuned to 550 eV. The right panel (b) shows the FY absorption spectrum of microporous carbon at the O K threshold, measured at ALS.

that in microporous carbon. However, the peak intensity of the microporous carbon was about six times higher than that of graphite powder. This may be explained by the larger graphitic surface area in microporous carbon than in graphite powder. If we make quantitative calibration lines using standard carbon powder samples whose oxygen concentration is known, then O K X-ray emission measurements can be utilized for quantitative analysis of oxygen in microporous carbon. The right panel of Fig. 1 shows the FY absorption spectrum of the microporous carbon at the O K threshold. A sharp peak was clearly observed near 531.5 eV, and then the spectrum rose from 535 eV.

From spectral simulation of the measured X-ray emission and absorption spectra by discrete variational (DV)

X α molecular orbital calculations [14], the chemical bonding states of the target element/molecules can generally be well analyzed [15]. Thus, we calculated the O2p density of states (DOS) of the simple cluster models of (C₂₄H₁₁)–R, where R is –OH, –CHO, or –COOH, which are typical substituents incorporating oxygen atoms. The units of C₂₄H₁₁, which consists of seven benzene rings terminated by hydrogen atoms, simply expresses the graphitic surface. The molecular structures of the cluster models were optimized by the MM2 methods [16], and the DV-X α molecular orbital calculations were performed using a commercially obtained SCAT program [17]. Fig. 2 shows the occupied (left panel) and unoccupied (right panel) O2p-DOS spectra, broadened with 0.5-eV-FWHM (full width at half maximum) Lorentzian functions, of the

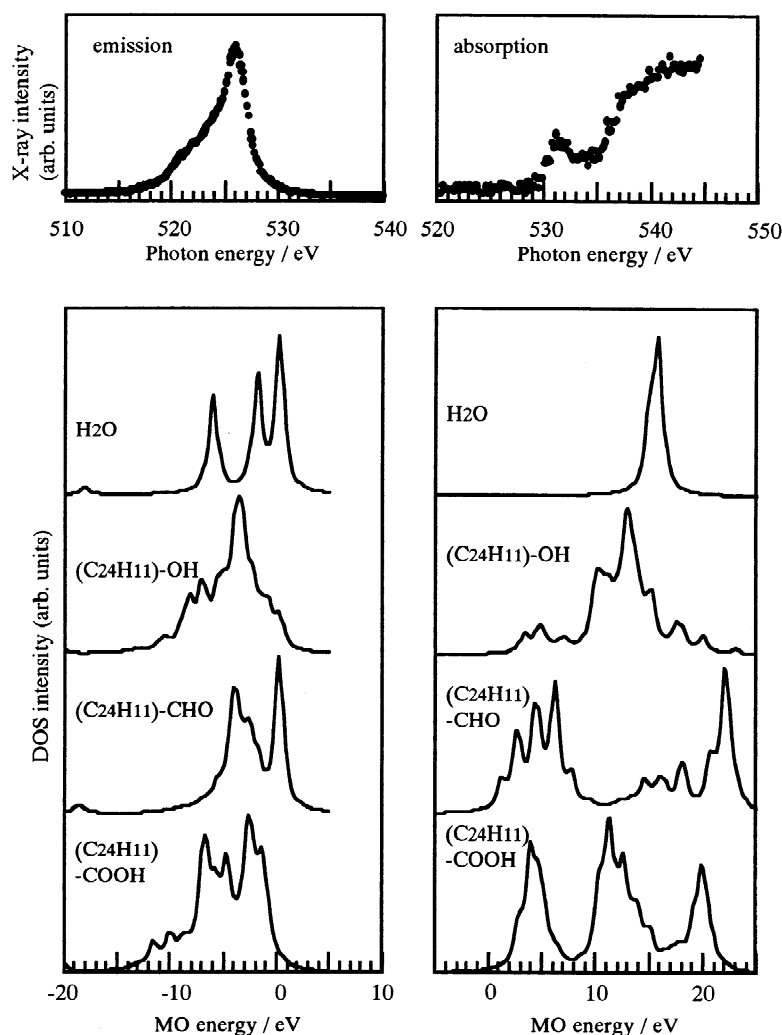


Fig. 2. The lower panels show the occupied (left panel) and unoccupied (right) O2p-DOS spectra of H₂O, (C₂₄H₁₁)–OH, (C₂₄H₁₁)–CHO, and (C₂₄H₁₁)–COOH broadened with 0.5-eV-FWHM Lorentzian functions. The upper panels show the measured X-ray emission (left panel) and FY absorption (right) spectra of microporous carbon, measured at ALS.

oxygen atoms in the $(C_{2.4}H_{1.1})-R$ and H_2O cluster models. Measured X-ray emission and absorption spectra of the microporous carbon are also shown in the upper panels in the figure. Comparing the calculated O2p-DOS spectra with the measured X-ray spectra, we found that spectral features in the occupied/unoccupied O2p-DOS of $(C_{2.4}H_{1.1})-OH$ were slightly similar to the measured X-ray emission/absorption spectral features, and that those of the other cluster models apparently differed from the measured X-ray spectra. However, the measured X-ray spectral features could not be sufficiently reproduced by the O2p-DOS spectra of $(C_{2.4}H_{1.1})-OH$. This therefore indicates that the major chemical bonding states of oxygen in the measured microporous carbon were not due either to the typical substituents of $-OH$, $-CHO$, and $-COOH$ on the graphitic surface or to the adsorbed H_2O .

4. Conclusion

In conclusion, we measured synchrotron-radiation-excited O K X-ray emission and absorption spectra of oxygen incorporated in microporous carbon in order to directly observe the oxygen and identify its chemical bonding states on the graphitic surface in microporous carbon. The O K X-ray emission spectrum exhibited a peak at 526 eV with a low-energy tail, and the absorption spectrum at the O K threshold exhibited a sharp peak at 531.5 eV and then rose from 535 eV. Spectral feature analysis using DV-X α molecular orbital calculations showed that the measured X-ray spectra were not sufficiently explained by typical substituents such as $-OH$, $-CHO$, and $-COOH$ on the graphitic surface, nor by adsorbed H_2O . This demonstrates that SXEA spectroscopy will be a powerful method for direct observation and chemical bonding state analysis of the graphitic surface in microporous carbon. Further theoretical analysis, using more complicated cluster models having other substituents and backbone structures, of these X-ray spectra is in progress to determine the chemical bonding states of oxygen on the graphitic surface in microporous carbon. In addition, further spectroscopic measurements using SXEA and XPS of the microporous carbon and reference compounds are in progress to analyze the chemical composition of the surface species.

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