

# Soft X-Ray Absorption Spectroscopy of High-Abrasion-Furnace Carbon Black

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**Abstract.** The soft x-ray absorption spectra of high-abrasion-furnace carbon black were measured to obtain local-structure/chemical-states information of the primary particles and/or crystallites. The soft x-ray absorption spectral features of carbon black represent broader  $\pi^*$  and  $\sigma^*$  peak structures compared to highly oriented pyrolytic graphite (HOPG). The subtracted spectra between the carbon black and HOPG, (carbon black) – (HOPG), show double-peak structures on both sides of the  $\pi^*$  peak. The lower-energy peak, denoted as the “pre-peak”, in the subtracted spectra and the  $\pi^*/\sigma^*$  peak intensity ratio in the absorption spectra clearly depend on the specific surface area by nitrogen adsorption (NSA). Therefore, it is concluded that the pre-peak intensity and the  $\pi^*/\sigma^*$  ratio reflect the local graphitic structure of carbon black.

**Keywords:** Soft X-ray spectroscopy, X-ray absorption, Synchrotron radiation, Carbon

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## INTRODUCTION

The fundamental properties of carbon black depend on the primary particle size, microstructure, and physical/chemical properties of the particle surfaces. Carbon black has been actively investigated and since the 1940s, some structural models of crystallites in the primary particles have been proposed [1-2]. These models are typically illustrated as aggregates of the graphitic crystallites from structure analysis using XRD, TEM, and STM etc. However, these models provide little information on the chemical states. Thus, we have investigated typical carbon black using soft x-ray spectroscopy in order to conduct an in-depth study on the structure of the primary particles from a chemical state viewpoint.

Recently, a technique, which uses soft x-ray emission and absorption spectroscopy with highly brilliant synchrotron radiation has been utilized to characterize various carbon materials[3-7]. This technique reveals the electronic-structure of both occupied and unoccupied orbitals, which directly reflect the local structure and chemical states. To extract useful information on the local-structure/chemical-states of carbon black, we measured the soft x-ray absorption spectra of various high-abrasion-furnace carbon black samples, which are categorized using the American Standard Testing Material (ASTN) code. In this paper, we describe the

soft x-ray absorption spectra of the carbon black, and the differences in spectral features are discussed relative to the local-graphitic-structure and chemical states.

## EXPERIMENTS

The measured samples were high-abrasion-furnace carbon black, which are categorized as N110, N220, N326, N330, N347, N550, and N660 in the ASTN code, and the reference compounds of the highly oriented pyrolytic graphite (HOPG) and *p*-terphenyl. Table 1 lists the ASTM grade and the specific surface area by nitrogen adsorption (NSA) of the carbon black samples.

**TABLE 1.** ASTM grade and NSA of the measured carbon black samples.

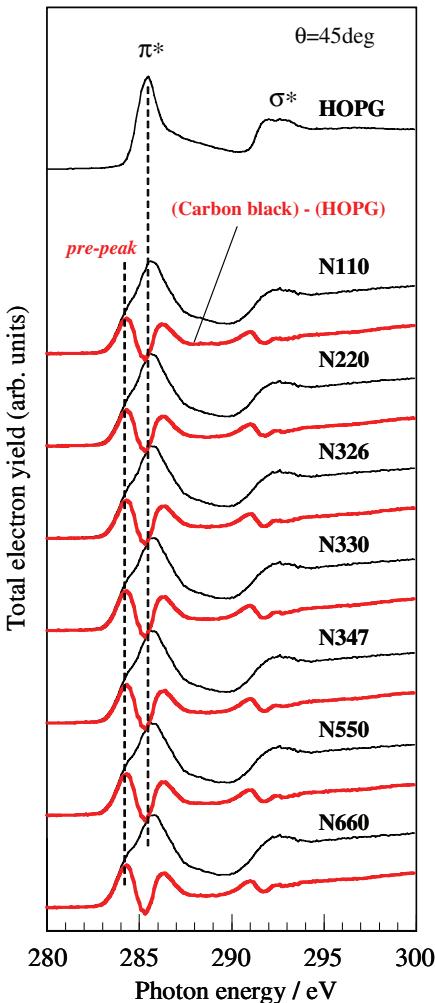
ASTM grade	NSA / m <sup>2</sup> g <sup>-1</sup>
N110 (SAF)	142
N220 (ISAF)	119
N326 (HAF-LS)	83
N330 (HAF)	79
N347 (HAF-HS)	81
N550 (FEF)	42
N660 (GPF)	27

Powder samples of the carbon black and *p*-terphenyl were pressed and held on indium-sheet substrates. Soft x-ray absorption spectra (XAS) of the samples were measured with the total-electron-yield

(TEY) in beamline BL-6.3.2 [8] at the Advanced Light Source (ALS).

## RESULTS AND DISCUSSION

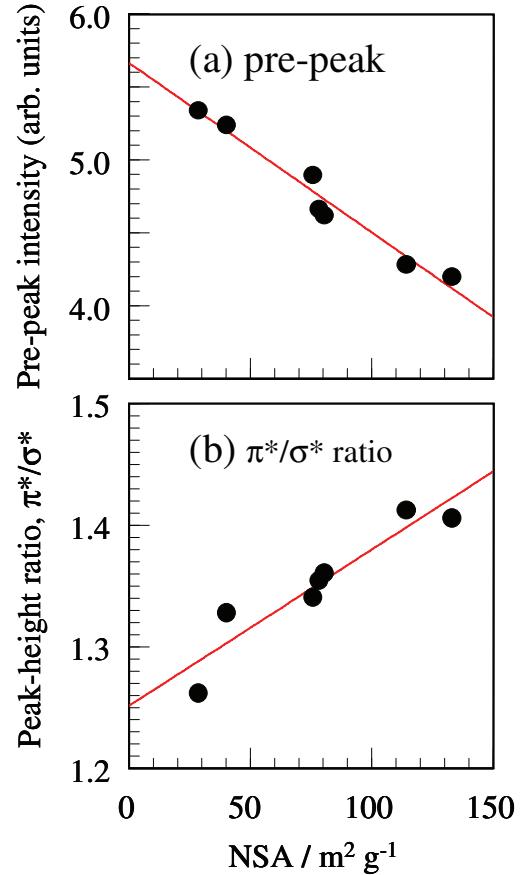
Figure 1 shows the XAS in the CK region of carbon black and HOPG. Compared to HOPG, carbon black shows broad spectral features, especially the  $\pi^*$  peak. In order to quantify the broadness of the spectral features, Fig 1 also shows the subtracted spectra, (carbon black) – (HOPG). The subtracted spectra of the carbon black clearly show the broad portion of the  $\pi^*$  peak; the peak structures are observed at 284.2 eV (denoted as the *pre-peak*) and 286.2 eV. Therefore, the spectral feature, which results in the broad  $\pi^*$  peak, is a characteristic index of carbon black.



**FIGURE 1.** Soft x-ray absorption spectra in the CK region of carbon black and HOPG. Subtracted spectra, (carbon black) – (HOPG), are shown on the absorption spectra.

To determine the relationships between the spectral features of the XAS and the NSA in carbon black, the pre-peak intensity in the subtracted XAS and the

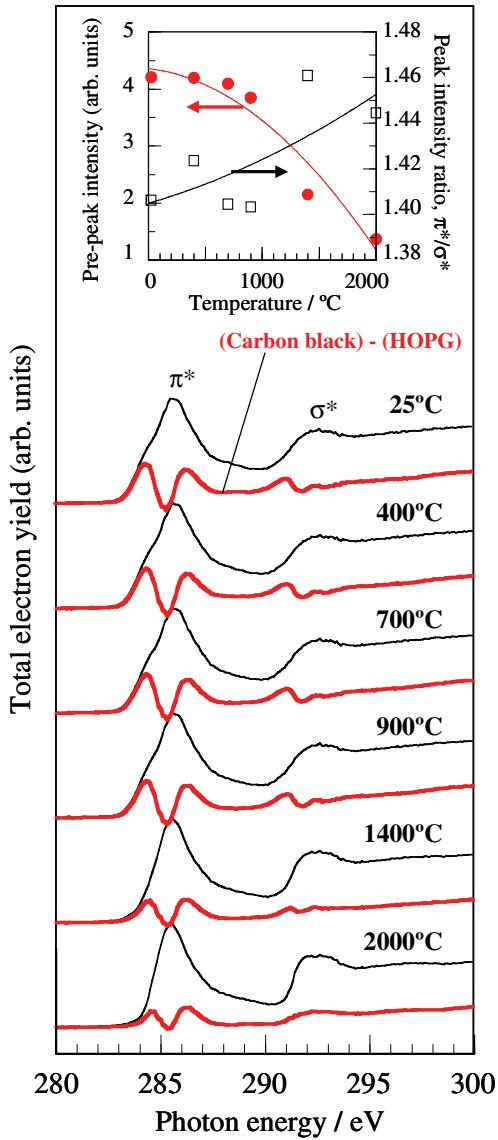
$\pi^*/\sigma^*$  peak intensity ratio in the XAS (Fig. 1) are plotted as functions of the NSA in Fig. 2. Figure 2 shows that the pre-peak intensity proportionally decreases and the  $\pi^*/\sigma^*$  ratio increases as the NSA increases, suggesting that the graphitic structure is degraded as the primary particle size of carbon black becomes larger (i.e. NSA decreases). Therefore, XAS may be useful for extracting local-graphitic-structure information.



**FIGURE 2.** The NSA dependences on (a) the pre-peak intensity in the subtracted spectra and on (b) the  $\pi^*/\sigma^*$  ratio in the absorption spectra of carbon black.

Figure 3 shows the temperature dependence of the XAS and the subtracted spectra of the N110 carbon black heated up to 2000 °C. The temperature dependences on the pre-peak intensity and on the  $\pi^*/\sigma^*$  ratio are also shown in the inset. The  $\pi^*$  peak feature in the XAS becomes sharper as the heating temperature increases, which corresponds to a decreased pre-peak intensity and an increased  $\pi^*/\sigma^*$  ratio. It is well known that the graphitic structure of carbon black increases as the heat temperature increases. Consequently, the pre-peak intensity and the  $\pi^*/\sigma^*$  ratio of carbon black are indices for the degree of the local-graphitic-structure in crystallites; the pre-

peak intensity decreases and  $\pi^*/\sigma^*$  ratio increases as the graphitic structure increases.



**FIGURE 3.** Soft x-ray absorption spectra in the CK region of carbon black heated up to 2000 °C and the subtracted spectra, (carbon black) – (HOPG). The inset describes the heating temperature dependences on the pre-peak intensity and  $\pi^*/\sigma^*$  ratio.

From this analogy, the NSA dependences in the carbon black of the pre-peak intensity and the  $\pi^*/\sigma^*$  ratio, which are shown in Fig. 2, show that carbon black with a larger NSA may have a higher graphitic structure. In general, the NSA increases as the primary particle size decreases. Therefore, the pre-peak intensity and  $\pi^*/\sigma^*$  ratio of carbon black contain graphitic structure information of the primary particles and/or crystallites. To understand this experimental finding, a study investigating the density of states

(DOS) of various cluster models is currently under way using discrete variational (DV)-X $\alpha$  molecular orbital calculations[9].

## CONCLUSION

Soft x-ray absorption spectra of high-abrasion-furnace carbon black samples where the NSA ranges from 27 to 142 m<sup>2</sup>g<sup>-1</sup> were measured using synchrotron radiation at the ALS to obtain local-structure/chemical-states information of the primary particles. The subtracted spectra between the carbon black and HOPG show a double-peak structure on both sides of the  $\pi^*$  peak at 285.5 eV. The peak intensity of the lower-energy portion (pre-peak) of the broader  $\pi^*$  peak and the  $\pi^*/\sigma^*$  peak intensity ratio clearly depend on the NSA values. The temperature dependences of the pre-peak intensity and  $\pi^*/\sigma^*$  ratio are also clearly observed in the heated carbon black. Therefore, it is concluded that the relationships in the pre-peak intensity and the  $\pi^*/\sigma^*$  ratio in the XAS between the NSA and the heating temperature of carbon black clearly reflect the graphitic structure of the primary carbon black particle and/or crystallites.

## ACKNOWLEDGMENTS

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