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To evaluate nitrogen in graphitic carbon materials, we propose a simple quantitative and fingerprint analysis method, which measures the total electron yield X-ray absorption spectra (TEY-XAS) of aromatic compounds possessing typical nitrogenated functional groups as standard samples, and nitrogen analysis is performed using the X-ray absorption near edge structure (XANES) in the N K and C K regions. The relationship between the atomic ratio of nitrogen to carbon (N/C) and the X-ray absorption intensity ratio of N K edge to C K edge (N Kα/C Kα) of standard samples yields a working curve to quantitatively analyze nitrogen. The successful application to carbon nitride films demonstrates that the proposed method is capable of quantitative and fingerprint analysis.

1. Introduction

Nitrogen-containing graphitic carbon materials have been extensively investigated as new electrode materials.¹⁻⁶ To control the electrical, chemical, and physical properties of the carbon materials, quantitative and chemical state analyses of nitrogen in carbon matrices are important. Although the carbon materials have been analyzed using spectroscopic methods such as X-ray diffraction (XRD), Raman spectroscopy, infrared (IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS), XPS is typically employed for quantitative and chemical state analyses. However, carbon and/or oxygen contamination on the sample surface often interferes with quantitative and chemical state analyses in surface sensitive XPS.

X-ray absorption spectroscopy (XAS) using synchrotron radiation (SR) is an advantageous tool for electronic/chemical state analyses of carbon materials.⁷⁻¹⁴ Firstly, elemental/orbital information of target atoms can be selectively extracted from XAS via the selection rule of the electric dipole transition. Secondly, X-ray absorption near edge structure (XANES), which can be measured by highly resolved SR beams, can provide chemical state information. In the soft X-ray region, the total electron yield (TEY) method is often used in XAS measurements instead of the transmission method because TEY can be easily obtained by measuring the sample photocurrent. Thirdly, the electrons’ mean free path in a solid determines the TEY-XAS observation depth; the estimated depth for electrons excited by soft X-rays is a few dozen nm, which can provide deeper bulk information compared to XPS. Therefore, TEY-XAS in the soft X-ray region can be regarded as a quasi-surface analysis method with less surface contamination compared to XPS. Fourthly, TEY-XAS is a non-destructive analytical method.

As mentioned above, TEY-XAS (XANES) has been used as an electronic/chemical state analysis method in carbon materials. However, characterization of carbon materials should be further improved if TEY-XAS can simultaneously achieve quantitative analysis. To this end, we have proposed a method for quantitative and fingerprint analyses of oxygen in oxidized carbon materials using TEY-XAS in the soft X-ray region.¹⁵⁻¹⁸ To draw a working curve to quantitatively analyze oxygen in carbon materials, standard samples mixed with carbon and oxygen compounds are necessary. However, such O/C-mixed samples are difficult to prepare. Hence, we focused on organic compounds possessing oxygenated functional groups. A working curve can be drawn from the relationship between the atomic ratio of oxygen to carbon (O/C) and their X-ray absorption intensity ratio of O K edge to C K edge (O Kα/C Kα). In this method, organic compounds are selected according to the target carbon matrix; aromatic compounds are suitable for graphitic sp²-carbon materials, while aliphatic compounds are suitable for diamond-based or polymer sp³-carbon materials. Then chemical state analysis is performed by a fingerprint method in the C K- and O K-XANES of these standard samples. We have successfully demonstrated that this method is applicable to the quantitative and fingerprint analyses of oxidized graphite¹⁶ and food.¹⁹

To establish a quantitative and fingerprint analysis method for nitrogen in graphitic carbon materials using TEY-XAS, the aforementioned idea is applied, but using aromatic compounds with various nitrogenated functional groups as the standard samples. In this study, we demonstrate the working curve for quantitative analysis of nitrogen and fingerprint analysis of carbon and nitrogen from TEY-XANES in the N K and C K regions of the standard samples. The present method is applied to carbon nitride films.

2. Experimental Procedure

Standard samples were commercially available powders (>95% purity) used without further purification. Figure 1 and Table I show the 25 standard aromatic compounds possessing various nitrogenated functional groups. These compounds were labeled according to the functional group; A, I, AI, and AN denote amine (–NH₂, –NH–, –N<), imine (–N=), complex of amine/imine, and complex of amine/nitro (–NO₂), respectively. The atomic ratio of nitrogen to carbon (N/C) in the standard samples ranged from 0.06 to 0.80. Highly oriented pyrolytic graphite (HOPG) was used as a reference carbon sample.

TEY-XAS measurements in the C K and N K regions were performed in beamline BL-6.3.2 at the Advanced Light
Fig. 1. Twenty-five aromatic compounds with various nitrogenated functional groups as standard samples. Asterisks indicate the selected 10 samples described in Fig. 6.

Table I. Standard aromatic compounds possessing various nitrogenated functional groups.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Label</th>
<th>Compound</th>
<th>N/C (Relative Intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{-}\text{NH}_2)</td>
<td>A1</td>
<td>4-amino-o-terphenyl</td>
<td>1/6 (0.167)</td>
</tr>
<tr>
<td>(\text{NH}^-)</td>
<td>A2</td>
<td>1-pyrenamine</td>
<td>1/16 (0.063)</td>
</tr>
<tr>
<td>(\text{N}^-)</td>
<td>A3</td>
<td>4-(4-amino-3,5-dimethylphenyl)-2,6-dimethylaniline</td>
<td>2/16 (0.125)</td>
</tr>
<tr>
<td></td>
<td>A4</td>
<td>4-[3,4-diaminophenyl]benzene-1,2-diamine</td>
<td>4/12 (0.333)</td>
</tr>
<tr>
<td></td>
<td>A5</td>
<td>9H-carbazole</td>
<td>1/12 (0.083)</td>
</tr>
<tr>
<td></td>
<td>A6</td>
<td>3,3'-methylenebis(1H-indole)</td>
<td>2/17 (0.118)</td>
</tr>
<tr>
<td></td>
<td>A7</td>
<td>(N,N)-diphenylbenzidine</td>
<td>2/24 (0.083)</td>
</tr>
<tr>
<td></td>
<td>A8</td>
<td>2-phenyl-1H-indole</td>
<td>1/14 (0.071)</td>
</tr>
<tr>
<td></td>
<td>A9</td>
<td>4-methyl-N-(4-methylphenyl)-N-phenylaniline</td>
<td>1/20 (0.050)</td>
</tr>
<tr>
<td></td>
<td>A10</td>
<td>(N,N)-di(phenyl)-4-[4-(N-phenylanilino)phenyl]aniline</td>
<td>2/36 (0.056)</td>
</tr>
<tr>
<td></td>
<td>A11</td>
<td>4-[4-(dimethylamino)phenyl]-N,N-dimethylaniline</td>
<td>2/16 (0.125)</td>
</tr>
<tr>
<td></td>
<td>A12</td>
<td>1-methyl-2-phenylindole</td>
<td>1/15 (0.067)</td>
</tr>
<tr>
<td>(\text{N}=)</td>
<td>I1</td>
<td>9-phenylacridine</td>
<td>1/19 (0.053)</td>
</tr>
<tr>
<td></td>
<td>I2</td>
<td>phenazine</td>
<td>2/12 (0.167)</td>
</tr>
<tr>
<td></td>
<td>I3</td>
<td>4,7-dimethyl-1,10-phenanthroline</td>
<td>2/14 (0.143)</td>
</tr>
<tr>
<td></td>
<td>I4</td>
<td>4,7-diphenyl-1,10-phenanthroline</td>
<td>2/24 (0.083)</td>
</tr>
<tr>
<td></td>
<td>I5</td>
<td>benzof[e]cinnoline</td>
<td>2/12 (0.167)</td>
</tr>
<tr>
<td>(\text{NH}_2/\text{NH}^-/\text{N}&lt;=)</td>
<td>A11</td>
<td>quinolin-6-amine</td>
<td>2/9 (0.222)</td>
</tr>
<tr>
<td>and</td>
<td>A12</td>
<td>4-[4-(dimethylaminostyryl)quinoline</td>
<td>2/19 (0.105)</td>
</tr>
<tr>
<td>(\text{N}=)</td>
<td>A13</td>
<td>9H-pyrido[3,4-b]indole</td>
<td>2/11 (0.182)</td>
</tr>
<tr>
<td></td>
<td>A14</td>
<td>7H-purine</td>
<td>4/5 (0.800)</td>
</tr>
<tr>
<td></td>
<td>A15</td>
<td>5,10,15,20-tetraphenylporphyrin</td>
<td>4/44 (0.091)</td>
</tr>
<tr>
<td>(\text{NO}_2)</td>
<td>AN1</td>
<td>4-nitronaphthalen-1-amine</td>
<td>2/10 (0.200)</td>
</tr>
<tr>
<td>and</td>
<td>AN2</td>
<td>4-[4-nitrophenyl]aniline</td>
<td>2/12 (0.167)</td>
</tr>
<tr>
<td>(\text{NO}_2)</td>
<td>AN3</td>
<td>4-nitrobenzene-1,2-diamine</td>
<td>3/6 (0.500)</td>
</tr>
</tbody>
</table>
Source (ALS). A 1200 lines/mm varied line spacing (VLS) grating was used in a beamline monochromator, and the exit slit width was 40 μm. The theoretical energy resolution ($E/\Delta E$) of the XAS measurements was approximately 3000 to 3000 for the C K to N K regions. Each powder sample was pressed onto an indium substrate and mounted in the measurement chamber. Then the sample was irradiated with a monochromatized SR beam, and the sample photocurrent ($I$) was monitored. Photocurrent of a gold plate ($I_0$) cleaned with sodium hypochlorite solution was also monitored as an incident beam monitor. Then the TEY was obtained by $I/I_0$. The incident angles of the SR beam were tuned to normal (90°) for powder samples and the magic angle (∼54.5°) for HOPG. The scanning time for each XAS spectrum was 1 to 2 min, and sample decomposition was ignored while scanning.

3. Results and Discussion

3.1 TEY-XAS spectra in the C K and N K regions

The background spectrum must be subtracted to measure the XANES spectra and X-ray absorption intensity. As an example, Fig. 2 compares the TEY-XAS spectrum between 250 and 450 eV of A1 (4-amino-p-terphenyl) to HOPG. Because the XAS profile between 270 and 285 eV is below the C K threshold, it is almost flat for A1 and HOPG. Consequently, an approximated linear line between 270 and 285 eV can be used to subtract the background in the C K region. On the other hand, a polynomial approximation is necessary to profile the background in the N K region because the XAS profile below the N K threshold cannot be regarded as flat due to the weaker N K absorption intensity compared to the background level. Therefore, Eq. (1), the Victoreen formula, which is a polynomial function representing the X-ray absorption scattering components ($\mu$), is applied to treat the background in the N K region:

$$\mu = CA^3 - DX^4 + \text{const.} \tag{1}$$

Here $C$ and $D$ are the cubic and quartic coefficients of the wavelength ($A$), respectively. The TEY-XAS profile in the N K region of HOPG, which lacks nitrogen, is considered to be the scattering component. Thus, a polynomial formula fitted to the HOPG profile can be used as the background function in the N K region.

Figure 3 shows the XANES in the C K and N K regions of the standard samples after background subtractions.

In the N K region, characteristic peak structures occur in the 398–405 eV region. Because peak $a$ occurs around 399 eV in all the amine compounds (I1 to 5, A1 to 5), it is attributed to an amine. Peak $b$, which is around 402 eV, is attributed to an amine because it appears in the amine compounds (A1 to 12). Amine compounds can be classified as primary (A1–A4), secondary (A5–A8), or tertiary (A9–A12). Due to the structural differences in nitrogen, characteristic profiles can be observed around peak $b$ in N K-XANES of amine compounds. Primary amines exhibit...
a broad peak structure in the 401–408 eV range, while secondary and tertiary amines have sharper peaks in the 401–404 eV range. Although amine nitrogens exhibit complicated peak b structures, peak b implies the presence of amine nitrogens. Peak c at 404 eV is attributed to a nitro group because it occurs only in the nitro samples (AN1 to 3). Peak d at 408 eV is assigned to the σ+ peak because it is present in all compounds. Hence, fingerprint analysis of nitrogen can be performed from the N K-XANES of these standard samples.

For detailed chemical state analysis using standard compounds, the peaks in the C K- and N K-XANES must be theoretically assigned. Spectral analysis using molecular orbital (MO) calculations has progressed.

3.2 Working curve for quantitative analysis of nitrogen in carbon materials

The N/C and the X-ray absorption intensity ratio between the N K and C K edges of the standard samples can be used to draw a working curve to quantitatively analyze nitrogen in a carbon matrix. As an example, the upper panel of Fig. 4 shows the TEY-XAS spectrum of A1, which exhibits π∗ and σ+ peaks in both the C K and N K regions. The σ+ peak is a better index of the X-ray absorption intensity than the π∗ peak because the σ+ peak profile is generally less sensitive to changes in the chemical state than the π∗ peak.15,16 The figure displays two patterns to measure the absorption intensity of an indicative σ+ peak: absorption peak height and area. Although the peak area is usually more accurate than the peak height, the peak height is easier to measure. To measure the peak area in XAS spectra, the σ+ region must be determined because the σ+ peak continues into the lower-energy π∗ region and the higher-energy ionization region. According to molecular orbital calculations of all the standard samples using the discrete variational (DV)-Xα method as described later, energy regions above 291 and above 405 cover the σ+ regions (gray areas in Fig. 4) of the C K and N K edges, respectively. To experimentally determine adequate σ+ regions, the energy ranges are divided into four 5-eV wide parts: region I (291–296 eV for C K, 405–410 eV for N K), II (296–301 eV, 410–415 eV), III (301–306 eV, 415–20 eV), and IV (306–311 eV, 420–425 eV). Then the relationships between the N/C and the peak intensity ratio of N K/σ to C K/σ of the standard samples. The ratios of N K/σ/C K/σ were measured by peak heights and peak areas with 5 eV widths (I, II, III, IV), 10 eV width (I–II), 15 eV width (I–III), and 20 eV width (I–IV).

Figure 4 (lower panel) shows the relationships between the N/C and the X-ray absorption intensity ratio (N K/σ/C K/σ) of the standard samples. The ratios of N K/σ/C K/σ were measured by peak heights and peak areas with 5 eV widths (I, II, III, IV), 10 eV width (I–II), 15 eV width (I–III), and 20 eV width (I–IV).

Fig. 4. (Color online) Upper panel shows TEY-XAS in the C K and N K regions of 4-aminophenyl (A1). Lower panels show the relationships between the N/C and the X-ray absorption intensity ratio (N K/σ/C K/σ) of the standard samples. The ratios of N K/σ/C K/σ were measured by peak heights and peak areas with 5 eV widths (I, II, III, IV), 10 eV width (I–II), 15 eV width (I–III), and 20 eV width (I–IV).

The approximated lines measured from the σ+ peak areas with 15 eV width can provide a highly accurate working curve. Additionally, the relationship obtained from the σ+ peak height exhibits a fairly high R2 (0.94). Hence, the σ+ peak height can easily provide a rough working curve. This result is similar to that for a working curve to quantitatively analyze nitrogen in a carbon matrix obtained from the O Kσ/C Kσ of oxygenated standard samples.15,16 In the working curve obtained from the peak area with a 15 eV width, the standard deviation (σ) of the working curve is 0.0278. Thus, limit of detection (LOD) of N/C can be obtained as 0.10 (= 3 × 0.0278/0.82) from the 3σ of N K/σ/C K/σ.
To prove theoretically the relationships between the N/C and N Kσ+/C Kσ+, the relationships were simulated using the DV-Xα method, which employs the first principle MO calculations. The DV-Xα method can easily calculate the density of states (DOSs) and analyze X-ray spectral profiles. Although the core-hole effect should be considered to exactly simulate the XANES profiles, the ground-state DOSs can roughly reproduce the spectral profiles as approximations. Prior to the DV-Xα calculations, cluster models of the compounds were formed with structural optimization using the molecular mechanics (MM2) method. The DV-Xα calculations were performed on the ground states with a basis set of 1s, 2s, and 2p orbitals of the carbon and nitrogen atoms using commercially available DV-Xα software. As an example, the upper panel in Fig. 5 shows the unoccupied DOSs of all the carbon and nitrogen atoms in A1; the σ region formed from hybridization with 2s and 2p orbitals is within the MO energy range of 6 to 24 eV. The highest peak in the σ region and the total area (gray area in the figure), respectively. The lower panel in Fig. 5 depicts the relationships between the N/C and the calculated DOS intensity ratios (Nσ+/Cσ+) obtained from (a) the peak height and (b) peak area with a 15 eV width for all the standard compounds. Both theoretical relationships show a positive correlation, and the plot position of each compound approximately reproduces the measured result shown in Fig. 4. Additionally, $R^2$ for the peak area is above 0.99, while that for the peak height is 0.91. This trend also reproduces the measured result. Hence, the measured working curves drawn in Fig. 4 are theoretically confirmed.

3.3 Selection of the standard samples for simplification
To apply this method for quantitative and fingerprint analyses of actual materials, the standard samples and target samples should be measured under identical conditions because the σ peak intensities in the C K and N K regions depend on the incident X-ray intensity distribution, which can be determined by the SR beamline conditions. To simplify the method, the number of standard samples is reduced from 25 to about 10. An asterisk in Fig. 1 denotes the 10 standard samples selected to maintain a wide range of N/C (0.06–0.80) as well as a variety of nitrogenated functional groups: A1, A3, A4, A12, I2, I1, A3, A4, AN1, and AN3. Neither the slope nor $R^2$ of the working curve changes upon decreasing the number of samples. Figure 6 shows (a) the working curve and (b) N K-XANES obtained from the selected 10 samples. The working curve maintains a high $R^2$ value (0.98), and the XANES exhibits the characteristic profiles of typical nitrogenated functional groups (–NH2, –NH, –N= –NH2, –N< –NH, –N=).
carbon atoms in the carbon hexagonal layers depends on the nitrogen concentration. Peak $\alpha$ for CN#2 in the N K-XANES is less intense than in CN#1, suggesting that the imine structure decreases as the nitrogen concentration increases. Compared to C K-XANES, the absorption intensity of N K-XANES for CN#1, which has a lower N concentration, is weaker than that of CN#2, which has a higher N concentration. The $\text{N} \sigma^+$/C$\pi^*$ peak area ratios of CN#1 and CN#2 are obtained from XANES, and their N/C atomic ratios from the working curve in Fig. 6(a) are 0.109 and 0.413, respectively. Figure 7(b) shows the relationship between the N/C measured by XANES and XPS. The slope of the approximated line is 1.07, indicating that the N/C measured by the proposed XANES method is consistent with the XPS method. The intercept of 0.027 confirms that the N/C atomic ratio by XANES is slightly larger than that by XPS, which may be due to the difference in the observation depths of TEY-XANES and XPS. The deeper observation depth of TEY-XANES may reflect the fact that nitrogen has a higher concentration in the bulk than on the surface. Consequently, the proposed method can be successfully applied to the quantitative and fingerprint analyses of nitrogen in ECR-CN films.

4. Conclusions

TEY-XAS is proposed as a quantitative and fingerprint analysis method for nitrogen in graphitic carbon materials. The initial method employs 25 standard samples, which are aromatic compounds with typical nitrogenated functional groups. We measured their TEY-XAS spectra in the C K and N K regions in BL-6.3.2/ALS, and subtracted the background of the weak N K-XANES using the polynomial formula. N K-XANES of the standard samples provides fingerprint analysis of nitrogen, while C K-XANES provides information about the carbon backbones. A working curve for quantitative analysis can be drawn from the relationships between the N/C and N K absorption intensities. The energy ranges of the $\sigma^*$ peak area are optimized between 291–306 and 405–420 eV for the C K and N K regions, respectively. The limit of detection in the working curve is N/C = 0.10. Because simulations using the DV-Xa molecular orbital method can reproduce the measured working curve, the validity of the working curve is theoretically demonstrated. Additionally, in the simplified method, we reduced the number of standard samples from 25 to 10. Our observations confirm that the simplified method can easily analyze the nitrogen in graphitic carbon materials. For example, the successful application of the simplified method to ECR-CN films demonstrates the capability of the quantitative and fingerprint analyses.

In actual nitrogen-containing graphitic carbon materials, nitrogen assumes various chemical states in addition to amine, imine, and nitro states. If the materials contain these other states, then the appropriate standard samples with these other nitrogenated functional groups are required to apply this method. Regardless, the concept described herein, which compares XANES and draws a working curve from the TEY-XAS of nitrogen-containing aromatic compounds, can be utilized for quantitative and fingerprint analyses of actual materials.
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