Relationship between Width and Height of π^* Peak in CK-XANES of Graphitic Carbons

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Abstract

The relationship between the width and height of the π^* peak on X-ray absorption near edge structure (XANES) in the C K region of graphitic carbons is investigated from XANES measurements and theoretical analysis. This relationship is herein named the "characteristic diagram of π^* peak profile". Mechanically ground (MG) graphite experimentally exhibits a linear correlation on the diagram. To understand the linear correlation, C K-XANES of the graphitic hexagonal carbon layers are calculated using first-principles calculations by focusing on the edge carbon atoms. The linear correlation is well explained by the ratio of the edge carbon atoms of the graphitic hexagonal carbon layers. The characteristic diagram of π^* peak profile is applied to industrial carbon black (CB) for identification. CBs exhibit identical distributions on the diagram, which depend on their uses. It is therefore confirmed that the proposed characteristic diagram of π^* peak profile can be a useful tool to identify graphitic carbons from the edge carbon atoms.

Keywords: Graphitic carbon, edge carbon, C K-XANES, π^* peak, local structure.

Introduction

Characterization of carbon materials is usually performed using laboratory-based methods.¹ X-ray diffraction (XRD) for crystal structure analysis reflects the lattice structure and crystallinity. Scanning electron microscopy (SEM) observes the surface structure, while transmission electron microscopy (TEM) reflects the local atomic order. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) provide surface atomic structure observations of the surface atomic order. Raman spectroscopy reflects the chemical-bonding structure. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) for surface electronic/chemical-state analysis reflect the electronic structure in the core and valence levels, respectively. Electron energy-loss spectroscopy (EELS) for the electronic/chemical state analysis reflects the electronic structure in the conduction bands and/or unoccupied orbitals. Additionally, X-ray absorption spectroscopy (XAS) using synchrotron radiation (SR) has been utilized for electronic/chemical-state analysis of carbon materials. In XAS, X-ray absorption near-edge structure (XANES), which can provide similar information as EELS, is a powerful tool for local structure analysis reflecting the electronic structure in the conduction bands and/or unoccupied orbitals.

Advantages of XANES measurements to characterize carbon materials are briefly summarized as follows. (1) Element/orbital-selective information of the electronic structure can be obtained. (2) High energy-resolution spectroscopy can be performed due to the highly resolved monochromatized SR beams. (3) The orientation of the carbon structure can be evaluated using the polarized SR beams. Additionally, theoretical XANES analysis has recently been performed using first-principles calculations. Hence, a combination of XANES measurements and theoretical analysis provides an advanced characterization method for carbon materials. For example, battery carbon-electrodes,^{2,3} catalysts,^{4,5} carbon alloys,^{6,7} nano-carbon (CNT),^{8,9} polymer/bio-carbons,^{10,11} and amorphous carbon^{12–15} have been analyzed by XANES with

theoretical analysis.

In the characterization of graphitic carbons composed of sp^2 -carbon (C) atoms, identification of the edge-C atoms in graphitic hexagonal carbon layers is important, because chemical/physical properties of graphitic carbons usually depend on the chemical/electronic states of the edge-C atoms.^{16–20} The edge-C atoms in hexagonal carbon layers have been directly observed by TEM/EELS.²¹ The EELS spectra in the C K region of the edge-C atoms exhibit different profiles than those of the inner-C atoms, which are well simulated by first-principles calculations. This suggests that C K-XANES can clearly identify the edge-C atoms from the inner-C atoms. On the other hand, we previously measured C K-XANES of various carbon black (CB) samples, and found that the π^* peak width and height depend on the CB crystalline size.²² From the theoretical analysis using the discrete variational (DV) $-X\alpha$ method,²³ which is a first-principles molecular orbital calculation, broadening of the π^* peak width can be explained by the hydrogenated edge-C atoms or non-benzenoid carbon rings.²⁴ This finding suggests that we can extract the information of the edge-C atoms from the π^* peak profile in C K-XANES. From further XANES analyses using density functional theory (DFT) calculations, broadening of the π^* peak width is well explained by the π^* peak splitting in the edge-C atoms. To experimentally prove the π^* peak splitting due to the edge-C structure, we measured C K-XANES of mechanically-ground (MG) graphite, which can be regarded as nano-graphite. The width and height of the π^* peak exhibit a linear correlation, which depends on the crystalline size of the MG-graphite.²⁵ This finding clearly means that the π^* peak profile provides local structure information on the edge-C atoms, and the relationship between the width and height of the π^* peak, which is herein named as "characteristic diagram of π^* peak profile", can be utilized to evaluate the local structure of the edge-C atoms in graphitic carbons.²⁶

In the present paper, to explain the linear relationship between the π^* peak width and height of MG-graphite, C K-XANES of various graphitic carbon models are simulated using the DFT

calculation method, and the calculated characteristic diagram of π^* peak profile is obtained by considering the edge-C atom structures in graphitic carbons. Additionally, to demonstrate the utility of the diagram for characterization of graphitic carbons, the characteristic diagram of π^* peak profile is applied to identify industrial CB.

Experimental

Samples and XANES Measurements

We previously measured C K-XANES of MG-graphite samples.^{25,26} Experiments of the sample preparation and XANES measurements are described herein briefly. Commercially available graphite powder was finely powdered by a MG method using agate balls and a vessel under an Ar atmosphere. MG time was varied up to 80 h. The MG-graphite samples are denoted by MG t , where t is the MG time ($t = 0, 1, 2, 4, 8, 20, 80$ h). The MG-graphite powders were washed with dilute hydrochloric acid (HCl) solution to remove oxidized portions, and then washed with water. The crystal structure of the MG t was monitored by X-ray diffraction (XRD), and their particle sizes were estimated from the full width half maximum (FWHM) of the 002 reflection peak using Scherrer's equation, as shown in Figure 1. The width of the 002 reflection peak becomes wider as the MG time increases, suggesting that graphite powder can be fine by MG to the particle size of several nm orders in MG4 – MG80. The 002 reflection peak width reflects particle size on c -axis (*i.e.*, layered graphitic thickness) of graphite. Graphitic layer size in a , b -axes may change corresponding to the layered graphitic thickness. It is therefore estimated that graphitic layer size is also several nm orders in MG4 – MG80.

The MG t powders were pressed and held on indium substrates for XANES measurements. Commercially available highly oriented pyrolytic graphite (HOPG) was used as a reference compound. Some industrial carbon black (CB) samples, which were supplied from Tokai Carbon, were also measured. XANES spectra in the C K region were measured in BL-6.3.2²⁷ at the

Advanced Light Source (ALS) using a total-electron-yield (TEY) method. The incident angle of SR beams to the sample plane was tuned at the magic angle of 54.5° . Some CB samples were also measured in BL10²⁸ at NewSUBARU under the same conditions as BL-6.3.2/ALS.

XANES Calculations

C K-XANES spectra were theoretically calculated by the DFT calculation code of CASTEP²⁹ on the Material Studio platform. Calculation models were hydrogen (H)-terminated hexagonal carbon layers with *zigzag* edges ($C_{96}H_{24}$) and *armchair* edges ($C_{60}H_{24}$). Details of the models will be explained later. Each individual model was placed in a sufficiently larger super cell to suppress the intermolecular effects. In the super cell, distance between cell walls and calculation model edge was set longer than 0.5 nm which is sufficiently longer than usual chemical bonds. Hence, such the super cell condition can perform the calculations for isolated models without intermolecular effects. After structure optimization by the Material Studio, DFT calculations in the ground state (initial state) were achieved in CASTEP. Then calculations in an excited state (final state) with a $C1s^{-1}$ core hole were performed for each carbon atom to determine the transition probability, because XANES can mainly reflect the electronic structure in the final state. The transition energy of the calculated XANES was corrected by considering the energy differences at the valence and core levels in the ground (initial) and excited (final) states.³⁰ The calculated XANES spectra were finally obtained from the transition probability as a function of the transition energy.

Results and Discussion

C K-XANES of MG-Graphite and the Characteristic Diagram of π^* Peak Profile

Figure 2 shows the measured C K-XANES of MGt ($t = 0 - 80$ h) and reference HOPG normalized by the 285.5 eV peak (π^*) height. The subtracted spectra between MGt and HOPG,

(MGt) - (HOPG), are also plotted. As the MG time increases, the π^* peak width of MGt becomes broader and its height becomes smaller compared to the σ^* peak. Such a broadening of the π^* peak width is clearly shown in the subtracted spectra. The subtracted spectra show peaks at 284.6 eV (denoted by *a*) and 286.4 eV (*b*), which mean broader portions of the π^* peak. Both peak heights become higher as the MG time increases. As the MG time increases, a small peak gradually appears near 289 eV. This 289-eV peak can be assigned to the oxygenated carbon structure slightly formed on the graphitic carbon layers, because O K-XANES shows gradual oxidation. Such an oxygenated 289-eV peak profile may slightly overlap the higher energy side (peak *b* region) of the π^* peak. Figure 3 shows the peak *a* and *b* heights, and peak height ratio of π^*/σ^* as functions of the estimated average particle size. Plots of peak *a* and *b* heights exhibit similar behaviors, where their peak heights rapidly increase as the particle size become smaller in several nm orders. On the other hand, the peak height ratio of π^*/σ^* gradually decreases as the particle size become smaller. This suggests that the π^* peak splits into peaks *a* and *b* in nm-size graphitic particles. In general, the ratio of the edge-C atoms in graphitic hexagonal carbon layers increases as the primary particle size decreases. Therefore, the relationship between the peak heights of peaks *a* and *b* and the relative peak height of π^*/σ^* reflect the local structure of the edge-C atoms in graphitic carbons.

The height of peak *a* is a better index to quantitatively evaluate the π^* peak width broadening than peak *b*, because peak *a* exhibits a single peak profile, while peak *b* continues to the higher-energy broadening portion, including the above mentioned oxidation effects. Figure 4 shows the relationship between the peak *a* height and peak height ratio of π^*/σ^* (*i.e.*, characteristic diagram of π^* peak profile) of MG-graphite. The distribution is well approximated with a linear function. This linear correlation between the width and height of the π^* peak strongly reflects the local structure of the edge-C in graphitic carbons.

Calculated C K-XANES of Graphitic Carbon Atoms

To understand the linear correlation in the characteristic diagram of π^* peak profile of MG-graphite, C K-XANES spectra of graphitic models were calculated using CASTEP. Considering the *zigzag* and *armchair* edges of graphitic hexagonal carbon layers, two models such as the *zigzag* edge model of $C_{96}H_{24}$ and the *armchair* edge model of $C_{60}H_{24}$ were used for the calculations. Their model structures and the calculated XANES are shown in Figure 5.

In the *zigzag* edge model (Fig. 5 (a)), carbon atoms are labeled 1C - 8C from the inside to outside, in which 1C - 5C can be identified as inner atoms, 6C as the conjugated edge-C atom, and 7C - 8C as hydrogen (H) terminated edge-C atoms. The calculated C K-XANES of 1C - 8C are compared to the measured XANES of HOPG and MG20. The transition energy of the lower-energy peak of 1C is tuned to 0 eV, and the measured π^* peak of HOPG is aligned to it. The calculated XANES of 1C - 5C exhibit two peaks at 0 eV and near 6.6 eV relative to the transition energy, which correspond to the measured π^* and σ^* peaks, respectively. On the other hand, the edge-C atoms of 6C - 8C show split π^* peak profiles. The conjugated edge-C atom (6C) displays π^* peak splitting with a lower-energy shift (−0.14 eV) and a higher-energy shift (+1.03 eV). The H-terminated edge-C atoms (7C, 8C) exhibit π^* peak splitting with a lower-energy shift (−0.90, −0.67 eV) and a higher-energy shift (+1.68, +1.88 eV). Comparing the π^* peak splits of 6C – 8C to the measured subtracted spectra of (MG20) - (HOPG), peak *a* corresponds to the lower-energy shifted π^* peak of the H-terminated edge-C atoms (7C, 8C), and the peak *b* tailing in the higher-energy region corresponds to the higher-energy shifted π^* peaks of the conjugated and H-terminated edge-C atoms (6C – 8C). Therefore, it is confirmed that the π^* peak of the edge-C atoms is split into the lower- and higher-energy sides. These calculation results agree with the previously reported DFT calculations²¹ and the DOS (density of state) calculations.³¹ Such a π^* peak splitting of the edge-C atoms gives rise to broadening of the π^* peak width in C K-XANES.

In the *armchair* edge model (Fig. 5 (b)), the carbon atoms are labeled 1C – 10C from the

inside to outside, in which 1C – 3C can be identified as inner atoms, 4C – 6C as conjugated edge-C atoms, and 7C – 10C as H-terminated edge-C atoms. The calculated C K-XANES of 1C – 10C are compared to the measured XANES of HOPG and MG20. Similar to the *zigzag* edge model, the transition energy of the lower-energy peak of 1C is tuned to 0 eV, and the measured π^* peak of HOPG is aligned to it. The calculated XANES of the inner 1C – 3C exhibits two peaks at 0 eV and near 6.6 eV relative to the transition energy, which correspond to the measured π^* and σ^* peaks, respectively. The conjugated edge-C atoms of 4C – 6C have similar π^* and σ^* peak profiles as the inner C atoms. The π^* peak shows lower-energy shifts with $-0.27 \sim -0.42$ eV compared to the inner C atoms, but do not display π^* peak splitting. The conjugated edge-C atom in the *zigzag* edge model bonds to two H-terminated edge-C atoms. On the other hand, the conjugated edge-C atom in the *armchair* edge model bonds to one H-terminated edge-C atom. The conjugated edge-C atom in the *armchair* edge model has less hybridization with the H-terminated edge C atoms but has more hybridization with the inner C atoms. The bonding structure difference of the conjugated-C atoms between the *zigzag* and *armchair* models causes their π^* peak profile difference. The H-terminated edge-C atoms (7C – 10C) exhibit π^* peak splitting with a lower-energy shift ($-0.106 \sim -0.69$ eV) and a higher-energy shift ($+1.50 \sim +1.75$ eV), which is the same as the H-terminated edge-C atoms in the *zigzag* model. Comparing the π^* peak splits of 7C – 10C to the measured subtracted spectra of (MG20) - (HOPG), peak *a* corresponds to the lower-energy shifted π^* peak and peak *b* tailing in the higher-energy region corresponds to the higher-energy shifted π^* peaks of the H-terminated edge-C atoms.

Consequently, the measured broadening of the π^* peak width can be assigned mainly to the H-terminated edge-C atoms both in the *zigzag* and *armchair* edge structures and partially to the conjugated edge-C atoms in *zigzag* edge structures.

Calculated Characteristic Diagram of π^* Peak Profile

To explain the linear correlation of MG-graphite in the characteristic diagram of π^* peak profile (Fig. 4) from the edge-C atom structure, the diagram was simulated from the calculated C K-XANES of the *zigzag* and *armchair* edge models. Figure 6 shows the geometrical shapes of the *zigzag* and *armchair* edge models with the numbers of total C, H-terminated edge-C, conjugated edge-C, inner-C atoms, diameter d of the models, and fraction of edge-C atoms. The models are based on polycyclic hexagonal carbon layers enlarged with the parameter n . Hence, the chemical formula of the *zigzag* model can be described as $C_{6n}^2H_{6n}^2$ while the *armchair* model can be described as $C_{3(n+n)}H_{6n}$. Figure 7 shows the fraction of the edge-C atoms in the *zigzag* and *armchair* models as functions of diameter d . The fraction of the edge-C atoms rapidly decreases to 0.1 as the diameter increases to 10 nm for the *zigzag* edge model and to 20 nm for the *armchair* edge model. This means that the effect of the edge-C atom on C K-XANES appears in small d models less than 10 nm for the *zigzag* edge model and 20 nm for the *armchair* edge model.

Figure 8 shows the calculated C K-XANES of the *zigzag* and *armchair* edge models as functions of model size. The calculated XANES spectra were synthesized by summing the calculated XANES spectra of the H-terminated edge-C atoms (7C – 8C in the *zigzag* model, 7C – 10C in the *armchair* model), conjugated edge-C atoms (6C in the *zigzag* model, 4C – 6C in the *armchair* model), and inner-C atom (1C in both the *zigzag* and *armchair* models), considering their numbers shown in Figure 6. The calculated XANES spectra are drawn with the summed-up inner-C atoms, summed-up edge-C atoms, and their total, and compared to the measured C K-XANES of HOPG. In the *zigzag* edge model, a small model with $n = 4$ ($C_{96}H_{24}$, $d = 1.72$ nm) exhibits π^* peak width broadening due to the edge-C atoms, which corresponds to peak *a*. On the other hand, larger models with $n \geq 10$ ($C_{600}H_{60}$, $d = 4.68$ nm) hardly exhibit the peak *a* profile. In the *armchair* models, the peak *a* profile can be strongly observed in the smallest model with $n = 6$ ($C_{126}H_{36}$, $d = 2.09$ nm). Even in the models with $n = 14$ ($C_{630}H_{84}$, $d = 5.05$ nm) and 27 ($C_{2268}H_{162}$, $d = 9.84$ nm), the peak *a* profile can be identified in the broadened π^* peak. On the other hand,

larger models with $n \geq 55$ ($C_{9240}H_{330}$, $d = 20.2$ nm) hardly show the peak a profile. This tendency, which is dependent n or d , agrees with the result shown in Figure 7.

Figure 9 compares the calculated characteristic diagram of π^* peak profile of the *zigzag* and *armchair* models obtained from Figure 8 to the measured distribution of the MG-graphite shown in Figure 4. The calculated distribution of the *zigzag* and *armchair* edge models on the diagram are well approximated with linear functions. The slopes of the approximated lines for the *zigzag* and *armchair* edge models slightly differ. Hence, the graphitic carbons may exhibit slightly wider distributions on the diagram. The calculated lines normalized at the measured π^* peak height clearly exhibit a wider distribution in the higher peak a height region. The calculated lines normalized at the measured π^* peak height and adjusted to the measured peak a height are also shown in the figure. Such a linear correlation on the calculated diagram reproduces the measured linear correlation of MG-graphite. Therefore, the measured characteristic diagram of π^* peak profile of MG-graphite can be explained from the fraction of the edge-C atoms in the graphitic hexagonal carbon layers.

Application of the Characteristic Diagram of π^* Peak Profile to Industrial CB

The characteristic diagram of π^* peak profile was applied to various industrial CB samples. Figure 10 shows the diagram of furnace black (a), CB for rubber (b), CB for pigment (c), and CB for electric conductor (d), which were obtained from the C K-XANES measurements in BL-6.3.2/ALS (solid marks) and in BL10/NewSUBARU (open marks). Although slight differences are observed in the plots measured in BL-6.3.2 and BL10, they have almost the same distribution profiles. This confirms the reproducibility of the XANES measurements. These CBs are distributed around the measured MG-graphite line. This means that these CBs essentially adopt a graphitic carbon structure. Furnace black has a narrow distribution in the peak a height around 0.4, which suggests a fairly uniform particle size and structure. CB for rubber assumes a wider

distribution in the peak a height around 0.35 – 0.5. This suggests the wider particle size distribution than furnace black. CB for pigment has an even wider distribution in the peak a height around 0.25 – 0.5, and a higher distribution in the π^* peak height. This suggests that a wider particle size distribution, which includes small aromatic molecules such as polycyclic aromatic hydrocarbon (PAH). Because small aromatic molecules generally exhibit a higher π^* peak than HOPG. CB for the electric conductor takes a wider and lower distribution in the peak a height around 0.1 – 0.4. The lower peak a height suggests that CB has a larger graphitic structure similar to graphite. Because graphite is a high-electric conductive material, it is rational that the CB for an electric conductor is the graphite-like particle.

These results demonstrate that the characteristic diagram of π^* peak profile can identify CB from the viewpoint of the average particle size and local structure dependence on the edge-C.

Conclusion

C K-XANES spectra of MG graphite particles were measured. The width and height of π^* peak in C K-XANES exhibited a linear correlation, which depended on the particle size of the MG-graphite. The relationship between the π^* peak width and height is named as the "characteristic diagram of π^* peak profile". To clarify the linear correlation of the MG-graphite on the diagram, C K-XANES spectra of graphitic hexagonal carbon layer models with *zigzag* and *armchair* edges were calculated by DFT calculations. The calculated XANES exhibited π^* peak splitting in the edge-C atoms. This π^* peak splitting broadened the π^* peak profile. From the calculated C K-XANES of the graphitic hexagonal carbon models whose diameter varied from several nm to 100 nm, the calculated diagram was obtained. The calculated diagram exhibited a linear correlation, corresponding to the measured diagram of the MG-graphite. Consequently, the relationship between the π^* peak width and height provides the information of graphitic particle size and edge-C structure in graphitic carbons. The diagram was applied to various industrial

carbon black (CB). The distribution of CBs on the diagram can be identified for their industrial uses.

TEM/EELS can provide similar information as XANES on the atomic level. On the other hand, XANES using SR provides average information within the SR beam size in sub mm^2 – several mm^2 . Hence, the characteristic diagram of π^* peak profile measured by SR will especially be useful to identify bulk graphitic carbons having complicated local structures.

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Figure Captions

Fig. 1 XRD patterns of MG-graphite. Inset shows FWHM of the 002 peak and estimated average particle size as functions of MG time.

Fig. 2 C K-XANES of MG-graphite (MGt) and reference HOPG. Subtracted spectra between MGt and HOPG, (MGt) - (HOPG), are also plotted.

Fig. 3 Peak *a* and *b* heights, and peak height ratio of π^*/σ^* of MG-graphite as functions of the average particle size.

Fig. 4 Characteristic diagram of π^* peak profile of MG-graphite.

Fig. 5 Comparison of the calculated C K-XANES of the *zigzag* (a) and *armchair* (b) edge models to the measured C K-XANES of HOPG and MG20.

Fig. 6 Geometrical shape of the *zigzag* (a) and *armchair* (b) edge models. Lower table shows the numbers of total C, H-terminated edge-C, conjugated edge-C, and inner-C, diameter, and fraction of edge-C.

Fig. 7 Relationship between the fraction of edge-C atoms and diameter of graphitic hexagonal carbon layers with the *zigzag* and *armchair* edges.

Fig. 8 Comparison of the calculated CK-XANES of H-terminated hexagonal carbon layers based on the calculated C K-XANES of edge- and inner-C atoms in the *zigzag* (a) and *armchair* edge model (b) to the measured C K-XANES of HOPG. Size parameter n is varied between 4–201 for the *zigzag* model and 6–271 for the *armchair* model.

Fig. 9 Comparison of the calculated characteristic diagram of π^* peak profile of the *zigzag* and *armchair* edge models (bold solid lines) with the measured diagram of MG-graphite (solid line). Calculated diagram corrected for the π^* peak intensity (dotted lines) and for π^* and peak a intensities (dashed lines) are also plotted.

Fig. 10 Measured characteristic diagram of π^* peak profile of various industrial CBs: furnace black (a), rubber (b), pigment (c), and an electric conductor (d). Closed marks are measured in BL-6.3.2/ALS and open marks are in BL10/NewSUBARU.

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Fig. 4 Characteristic diagram of π^* peak profile of MG-graphite.

(a) *Zigzag* edge model

$C_{96}H_{24}$

(b) *Armchair* edge model

$C_{60}H_{24}$

Fig. 5 Comparison of the calculated C K-XANES of the *zigzag* (a) and *armchair* (b) edge models to the measured C K-XANES of HOPG and MG20.

(a) Zigzag edge model

(b) Armchair edge model

model	<i>Zigzag</i> edge model	<i>Armchair</i> edge model
Total C	$6n^2$	$3(n^2+n)$
H-Term. edge-C	$6n$	$6n$
Conj. edge-C	$6(n-1)$	$6(n-1)$
Inner-C	$6n^2-12n+6$	$3(n^2-3n+2)$
d/nm	$0.25x(2n-1)$	$0.14x(3n-1)x3^{1/2}/2$
*Fraction of edge-C	$(2n-1)/n^2$	$2(2n-1)/(n^2+n)$

*Fraction of edge-C: $\{(H\text{-Term. edge-C}) + (Conj. Edge-C)\} / (Total\ C)$

Fig. 6 Geometrical shape of the *zigzag* (a) and *armchair* (b) edge models. Lower table shows the numbers of total C, H-terminated edge-C, conjugated edge-C, and inner-C, diameter, and fraction of edge-C.

Fig. 7 Relationship between the fraction of edge-C atoms and diameter of graphitic hexagonal carbon layers with the *zigzag* and *armchair* edges.

Fig. 8 Comparison of the calculated CK-XANES of H-terminated hexagonal carbon layers based on the calculated C K-XANES of edge- and inner-C atoms in the *zigzag* (a) and *armchair* edge model (b) to the measured C K-XANES of HOPG. Size parameter n is varied between 4–201 for the *zigzag* model and 6–271 for the *armchair* model.

Fig. 9 Comparison of the calculated characteristic diagram of π^* peak profile of the *zigzag* and *armchair* edge models (bold solid lines) with the measured diagram of MG-graphite (solid line). Calculated diagram corrected for the π^* peak intensity (dotted lines) and for π^* and peak *a* intensities (dashed lines) are also plotted.

Fig. 10 Measured characteristic diagrams of π^* peak profile of various industrial CBs: furnace black (a), rubber (b), pigment (c), and an electric conductor (d). Closed marks are measured in BL-6.3.2/ALS and open marks are in BL10/NewSUBARU.

Characteristic diagram of π^* peak profile

Zigzag edge model,
 $C_{96}H_{24}$

Armchair edge model,
 $C_{60}H_{24}$