XANES Study of Carbon Based Nanotubes*

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Abstract Single-walled carbon nanotubes (SWNTs), double-walled carbon nanotubes (DWNTs) and multi-walled carbon nanotubes (MWNTs) have been investigated using X-ray Absorption Near Edge Spectroscopy (XANES) after different thermal annealing procedures performed in ultra high vacuum. Carbon K-edge spectra show that the contaminants present on the surface of MWNTs are more sensitive to thermal treatments than those for DWNTs and SWNTs. In addition, multiple-scattering features in the XANES region shift towards low energies going from single to multi-walled nanotubes, addressing a different interaction between layers in these different nanotube systems.

Key words carbon nanotubes, XANES, thermal treatment

1 Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima[1] in 1991, the synthesis of these materials have been continuously growing due to their unique properties and potential applications[2]. CNTs exhibit remarkable mechanical[3], thermal[4] and electrical properties[5, 6] and can be used as very hard fibers[7], electron field emitters[8], scanning probes[9, 10], nanoelectronic devices[11], gas absorbent[12], etc.

Three specific kinds of CNTs, i.e., single-walled carbon nanotubes (SWNTs), double-walled carbon nanotubes (DWNTs) and multi-walled carbon nanotubes (MWNTs) can be identified. Theoretical[13] and experimental[14] investigations shown that a SWNT can be metallic, semiconducting or semimetalic, depending on its chiral angle and diameter, while for a DWNT[15] that consists of two concentric cylindrical graphitic layers, the chirality pairs of the inner and outer layers can be: metallic-metallic, metallic-semiconducting, or semiconducting-semiconducting[16]. A MWNT[17] has several layers and the understanding of its properties is more complicated because of the more complex interaction between the constituent layers. However, the intrinsic properties of CNTs, such as curvature induced effects[15, 18, 19] and interlayer interaction[17, 20], have been mainly investigated using these three typical systems.

X-ray Absorption Near Edge Spectroscopy (XANES) is a spectroscopy that provides electronic and structural information about atoms, molecules and local chemical functionalities[21]. In a XANES experiment, an intense tunable monochromatic flux of X-rays excites an electron from an atomic core

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level to empty or partially occupied valence electron states. At photon energies in resonance with these transitions, a large increase in the excitation cross section is observed and from the analysis of the shape and the structures of the absorption cross section is possible to reconstruct the electronic structure at the surface, as well as bonding formation of a variety of amorphous and ordered solid-state materials[22].

In this work, we collect XANES spectra to investigate the stability of the contaminants on the surface of the three typical carbon nanotube systems performing in situ thermal treatment. We find that contaminants on the surface of different CNTs exhibit a different sensitivity to thermal treatment, which we assigned to the curvature effect of their different outer layer diameters. This effect may have a critical role in their application as gas sensors[23—25], one of interesting research areas of CNTs. We also find that, going from single to multi-walled nanotubes, the multiple-scattering features in the XANES region shifts towards low energies, a behavior which may be attributed to a different interaction between layers.

2 Experimental details

SWNT materials were synthesized by a hydrogen arc discharge method[26] under H_2 atmosphere using Fe, Ni, and Co as co-catalysts. The obtained products contain 70% SWNTs in volume percentage and have a mean diameter of 1.85nm. Both DWNTs and MWNTs were synthesized by the catalytic decomposition of hydrocarbons at 1373—1473K using Fe particles as catalyst and methane (for DWNT) or benzene (for MWNT) as the carbon source[27, 28]. The percentage in volume of these two products is higher than 70%. The DWNTs have outer diameter[27] ranging from 1.6 to 2.8nm, with a Gaussian mean diameter of 2.26nm, and inner diameter ranging from 1.0 to 2.0nm, with a Gaussian mean diameter of 1.52nm, while the MWNTs have outer diameter[28] ranging from 10 to 100nm. For comparison we use highly oriented pyrolitic graphite commercially available.

The C K-edge XANES experiments were performed at the Photoelectron Spectroscopy station of the Beijing Synchrotron Radiation Facility of the Institute of High Energy Physics, Chinese Academy of Sciences. Samples, cleaned with ultrasonic cleaner in acetone, were loaded in a ultrahigh vacuum chamber and maintained in a background pressure of $\sim 8\times10^{-10}$ torr, reaching a pressure up to $\sim 1\times10^{-9}$ torr during data acquisition. All spectra were recorded using the total electron yield (TEY) mode, a surface-sensitive detection method with a typical probing depth of a few nm, in the energy range from 275 to 337eV and with an experimental resolution of 0.2eV. The annealing treatments have been performed on all systems in the XAS sample compartment, under ultrahigh vacuum at the temperatures of 603K and 673K for one hour.

3 Results and discussions

Fig. 1(a) (solid line) shows the comparison of the C K-edge XANES spectra of SWNTs (1), DWNTs (2), MWNTs (3) and HOPG (Highly Oriented Pyrolitic Graphite) (4) at room temperature of all spectra normalized in the region around 317eV. The spectrum of HOPG is in very good agreement with previous XANES data collected with synchrotron radiation[29, 30]. To interpret the XANES features we present in Fig. 1(b) a polarized XANES calculation of graphite using a very simplified atomic cluster in the framework of the multiple-scattering (MS) theory[31, 32]. It is quite clear looking at Fig. 1(b) (curve (1)) that the π^* unoccupied states (at about 285.2eV) are well reproduced by the z-polarized component which corresponds to C $2p_x$ and $2p_y$ orbitals. This resonance has to be intense at grazing X-ray incidence, when the X-ray electric field vector has a large projection along the direction of the p orbital, while is very weak at normal X-ray incidence, when the electric field vector is perpendicular to the p orbital[33]. The corresponding $1s$ to σ^* transitions at 292.1eV appear in the xy-polarized calculation (Fig. 1(b) curve(2)) which contains the C $2p_z$ orbital and exhibits the opposite trend as expected since σ^* is orthogonal to a π^* state. It is worth to notice that the best-fit spectra (Fig. 1(b) curve(3))

of this calculation based on a very simplified cluster made by only 3 nearest atoms does not show multiple-scattering contributions.

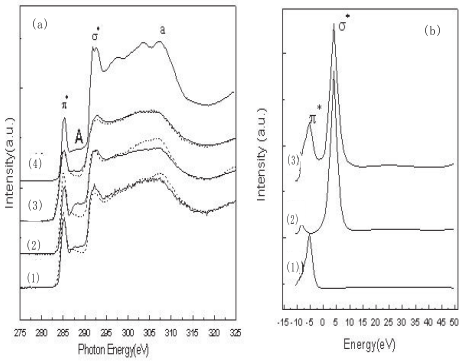

Fig. 1. (a) Comparison of C 1*s* XANES spectra of fresh CNTs and HOPG. From bottom to top: (1) SWNTs, (2) DWNTs, (3) MWNTs and (4) HOPG. The dash lines show the spectra of the same samples after 673K annealing treatment as the background; (b) MS calculation of C *K*-edge XANES in graphite by using a simplified atomic cluster composed by a central carbon plus the nearest 3 carbon atoms: (1) the polarized *z*-component, (2) the polarized *xy*-components and (3) the best-fit of the calculation.

As labeled in Fig. 1(a), we assigned the common features at about 285.2eV and 292.1eV to transition from C 1*s* to π* and σ* unoccupied states, respectively. A feature labeled A (at about 288eV) between π* and σ* bands detected in previous XANES works on graphite[34] and present also in more recent papers on carbon nanotubes[35, 36] is clearly detected using the TEY mode. To clarify feature A, we show the spectra with dash line of the same samples after 673K annealing treatemt as the background. Such a feature has been previously assigned to the so-called free electron like interlayer states[34—36] but recent investigations[37, 38] questioned this assignment because feature A disappears after in situ annealing treatment. They suggest that this signal is the result of a surface contamination, especially by oxygen contamination following chemical processes or gas adsorption. Actually the spectral feature A may be a precise marker of surface contamination. In Fig. 1(a) a broad feature A is detected in all spectra at room temperature, including HOPG. However, feature A is weaker in MWNTs than that of SWNTs and DWNTs suggesting that MWNTs may adsorb gas with more difficulty and in general seems to exhibit a weaker chemical reactivity. Smaller diameter tubes have larger surface curvature and the graphite-like carbon sp^2 bonds of CNTs may easily gain more sp^3 character[39], as a consequence CNTs with smaller outer diameter are more active in term of chemical bonding. The outer diameter of a MWNT is greater than 10nm, while in SWNT and DWNT they are about 1.85nm and 2.26nm, respectively. Thus MWNTs are not favoured to form chemical bonds. Moreover, Fig. 1(a) shows the C *K*-edge XANES of HOPG, which have flat planes, has a very weak feature A, similarly to MWNTs, supporting the hypothesis of a correlation between curvature and contaminations.

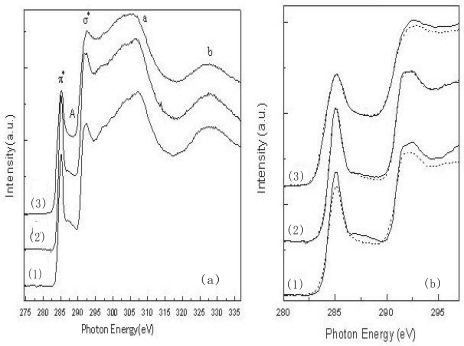

Fig. 2. (a) C 1*s* XANES spectra of CNTs after the thermal treatment at 603K for one hour: (1) SWNTs, (2) DWNTs and (3) MWNTs; (b) the magnified spectra of Fig. 3(a) with a background (dash line) after 673K annealing treatment for DWNTs and MWNTs and after 773K annealing treatment for SWNTs.

To check the existence of this unexpected correlation, we performed two slightly different thermal treatments in ultrahigh vacuum. In Fig. 2(a) we compare the spectra of different CNTs after a thermal treatment in situ at 603K for one hour. We also show the magnified spectra in Fig. 2(b) (right, solid) and use the spectra (dash line) after 673K annealing treatment for DWNTs and MWNTs but a spectrum (dash line) after 773K annealing treatment for SWNTs to get a smooth background between 286 and 290eV. In the spectrum of MWNTs feature A disappears, confirming that this structure is not an intrinsic feature of carbon nanotube sys-

tems. The intensity of feature A in DWNTs and SWNTs decrease rapidly, however this feature does not disappear completely and is more intense in the spectrum of SWNTs than DWNTs. From these data we confirm the sensitivity of CNTs to thermal treatment and the different amount of contaminants on the surface of different nanotube following the order: MWNTs>DWNTs>SWNTs. In other words, MWNTs have less available chemical bonds on the surface than DWNTs and SWNTs, supporting the existence of a correlation with the nanotube curvature.

In Fig. 3(a) we compare spectra after a further thermal treatment at 673K for one hour. The same background in Fig. 3(b) (dash line) as that in Fig. 3(b) for SWNTs is used. Feature A disappears also in DWNTs while the peak for SWNTs can still be distinguished, showing lower intensity. This behavior confirms the decreasing sensitivity to thermal treatment from multi-walled to single-walled carbon nanotubes.

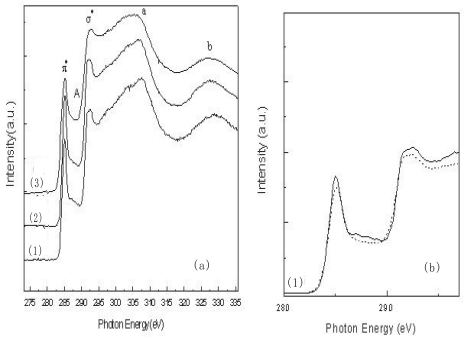

Fig. 3. (a) C 1*s* XANES spectra of CNTs after the thermal treatment at 673K for one hour: (1) SWNTs, (2) DWNTs and (3) MWNTs; (b) the magnified spectra of Fig. 4(a) for SWNTs with a bckground (dash line) after 773K annealing treatment.

Actually, when thermal treatments are performed, atomic contaminants are washed out and spectra show some intrinsic features of CNTs. To enhance these contributions, in Fig. 4 we compared spectra after normalization of the data at the σ* structure at about 292eV. It can be clearly seen from this figure that MS (multiple-scattering) features labeled a and b shift towards lower energies going from single to multi-walled nanotubes. Taking in consideration the different geometrical structures of these CNTs, e.g., the MWNT and the DWNT have multiple walls and double walls, respectively, we demonstrate that multiple-scattering paths which involve atoms in different layers as well as in the same layer are sensitive to these different geometries, in other words, we may attribute the observed energy shift to the different MS contributions within nanotube layers.

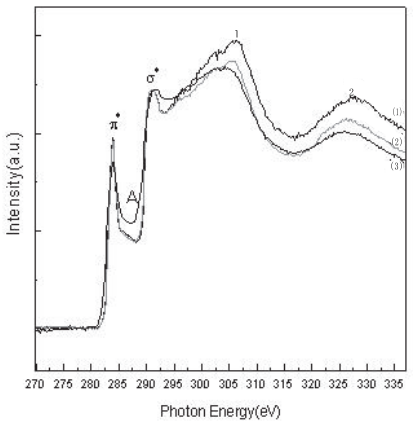

Fig. 4. C 1*s* XANES spectra as in Fig. 3(a) but after a normalization of the spectra at the σ* structure at about 292eV: (1) SWNTs, (2) DWNTs and (3) MWNTs.

4 Conclusions

To summarize, we performed XANES experiments to investigate the presence and the degree of atomic contamination in different carbon nanotubes. Our data give evidence for a correlation between contamination and curvature in a way that MWNTs are more sensitive to thermal treatment than DWNTs and SWNTs. Moreover, MS contributions from different layers (walls) affect the spectra of different CNTs and a small but clear shift towards lower energy going from single to multi-walled nanotubes has been detected in the multiple-scattering region. This result is extremely useful since it may support the relevance of further XANES investigations on CNTs devoted to the characterization of the intrinsic properties of these unique systems.

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碳纳米管的近边吸收谱研究*

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摘要 用X射线近边吸收谱研究了单壁, 双壁和多壁碳纳米管在超高真空系统中不同温度下退火处理后的行为. 碳的K边吸收谱表明, 多壁管上吸附的杂质将在热处理过程中最先被去除, 其次是双壁管, 最后是单壁管. 这种热处理下杂质去除的顺序说明了曲率越小杂质吸附得越牢靠, 即越容易吸附杂质. 另外, 结果中显示, 经退火处理后3种碳纳米管在多重散射区域的峰结构呈现规律性的移动, 由单壁管到多壁管, 谱峰向低能方向移动; 这是由于碳纳米管的层数不同造成的, 证明这部分谱峰结构直接受到碳纳米管层数的调制, 有利于鉴别3种碳纳米管.

关键词 碳纳米管 X射线近边吸收谱 热处理

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