

An XANES study on the modification of single-walled carbon nanotubes by nitric acid

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X-ray absorption near-edge structure (XANES) spectroscopy has been applied to identify the modification process of single-walled carbon nanotubes (SWCNTs) treated by nitric acid. The carboxyl groups created by the nitric acid treatment have been found to be formed on both the carbonaceous fragments and the side walls of SWCNTs. The carbonaceous fragments could be removed by a following washing treatment with sodium hydroxide. XANES spectra indicate that carbonaceous fragments are the result of the synthesis process and/or of the nitric acid treatment. Tube walls of SWCNTs are weakly oxidized by the nitric acid treatment although, after removing carbonaceous fragments, a direct oxidation process of SWCNTs is observed. Experimental data address the removal of carbonaceous fragments on SWCNTs as an efficient method for side-wall modification of a SWCNT.

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1. Introduction

Owing to their unique physical, electronic, chemical and mechanical properties (Satio *et al.*, 1998; Dresselhaus *et al.*, 2001; Baughman *et al.*, 2002), since their discovery in 1991 (Iijima, 1991) carbon nanotubes (CNTs) have attracted great interest and still now stimulate new theoretical and experimental research and applications. However, CNTs applications are seriously limited because as-produced CNTs generally contain impurities and cannot be dissolved in water or other organic solvents. Actually, to improve the properties of CNTs, considerable efforts have been spent to improve the purification and solubility of CNTs by chemical processes (Rinzler *et al.*, 1998; Wang, Gao *et al.*, 2006; Wang, Iqbal *et al.*, 2006; Pompeo & Resasco, 2002).

Among the numerous chemical modification methods, the most common way to introduce carboxylic groups is by treating CNTs with nitric acid or with a mixture of nitric and sulfuric acid (Hu *et al.*, 2003; Liu *et al.*, 1998). This method has been widely used and recognized as an effective way to modify CNT walls. However, recent reports showed that the modification of CNTs is a complex process in which the contribution of carbonaceous fragments is very important. They showed that carboxyl groups created by the nitric acid treatment were mainly present on the 'oxidation debris' (Verdejo *et al.*, 2007) or on 'carboxylated carbonaceous fragments' (Salzmann *et al.*,

2007), which are absorbed onto CNTs rather than directly on the side walls of a CNT. A recent work (Shao *et al.*, 2007) also suggested that oxidation debris is formed by the functionalization of amorphous carbon. Indeed, when a single-walled CNTs (SWCNTs) sample free of amorphous carbon is treated by nitric acid, oxidation debris formation is dramatically reduced and most of the functional groups are present on the CNTs. It is then fundamental to investigate the modification process of CNTs for different hosts of functional groups, which may affect further applications. In this work, by using XANES we investigated the electronic structure changes of SWCNTs samples treated with nitric acid giving evidence of the oxidation on both the carbonaceous fragments and the side walls of the SWCNTs. However, experimental data suggest that carbonaceous fragments originate from the synthesis process or from the nitric acid treatment which will break some parts of the SWCNTs. XANES spectra confirm that washing with sodium hydroxide removes the carboxylated carbonaceous fragments and a further acid treatment modifies directly the SWCNTs tube walls.

XANES spectroscopy is a technique that involves the excitation of electrons from a core level to local and partial empty states (Stöhr, 1992; Wu *et al.*, 1996). Recently, XANES spectroscopy has been used to investigate both structural changes and surface chemical functionalities of CNTs (Hemraj-Benny *et al.*, 2006; Tang *et al.*, 2001). It is an impor-

tant element-specific characterization tool capable of obtaining electronic, structural and bond information in carbon-based systems. Here we apply XANES spectroscopy to investigate electronic structure changes of SWCNTs in two processes: (i) refluxing the as-produced SWCNTs in nitric acid followed by washing thoroughly with NaOH; (ii) the same treatments on the washed SWCNTs obtained by the first process.

2. Experimental

SWCNTs used in this work were manufactured by the Chengdu Organic Institute of the Chinese Academy of Sciences. Their content of impurities [metal catalyst, amorphous carbon and multi-walled CNTs (MWCNTs)] is less than 10 wt%. The sequence of treatments follows a procedure adapted in the literature (Salzmann *et al.*, 2007). For process (i), the as-produced SWCNTs were refluxed in 3 M nitric acid at 413 K for 48 h, followed by filtration and washing with deionized water. SWCNTs treated by the nitric acid were stirred in an 8 M sodium hydroxide solution at 373 K for 48 h, then filtered. To neutralize the remaining solid, they were rinsed by a diluted hydrochloric acid solution, filtered again, and then washed with an excess of deionized water on the filter membrane. The final NaOH solution treatment was repeated several times. During washing, the filtrate is red for the first washing, then becomes light yellow and finally colourless after several washings, when the separation is completed. Regarding the process (ii), washed SWCNTs as obtained by the process (i) were refluxed in the nitric acid and subsequently washed with a NaOH solution again.

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 of the Chinese Academy of Sciences. Samples were loaded in an ultrahigh-vacuum chamber and maintained at a background pressure of $\sim 8 \times 10^{-10}$ torr, reaching a pressure up to $\sim 1 \times 10^{-9}$ torr during data acquisition. All spectra were recorded in the energy range from 280 to 325 eV with an experimental resolution of 0.2 eV at room temperature, using the total electron yield mode, a surface-sensitive detection method with a typical probing depth of a few nanometres.

3. Results and discussion

In Fig. 1 we compare C *K*-edge XANES spectra of SWCNTs without chemical treatment (a), treated by nitric acid (b) and subsequently washed with sodium hydroxide (c). All spectra have been processed using the pre- and post-edge normalization routines (Hemraj-Benny *et al.*, 2006). The spectrum (a) refers to the SWCNTs without any chemical treatments in good agreement with previous published data of carbon nanotube systems (Banerjee *et al.*, 2004; Zhong *et al.*, 2006; Kuznetsova *et al.*, 2001). The spectrum is characterized by three main features: the edge, the atomic contribution of the C–C π^* transition at about 285.5 eV, a shoulder owing to the C–C σ^* transition at about 292.5 eV and a feature in the region

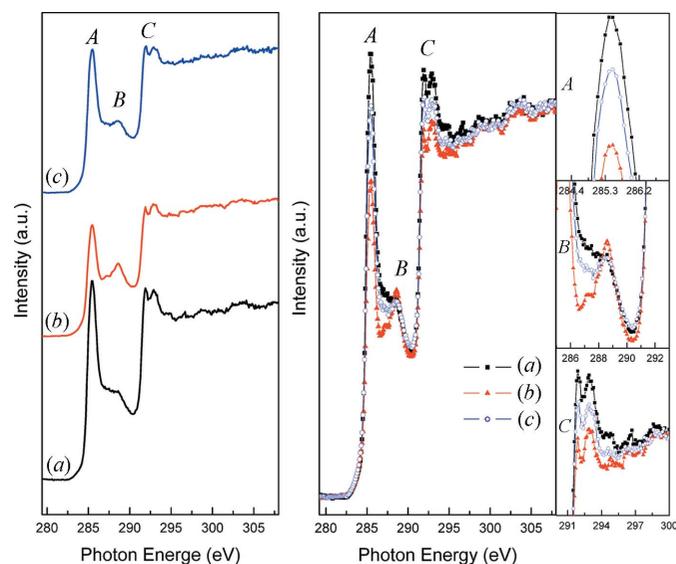


Figure 1
Left panel: C *K*-edge XANES spectra of the SWCNTs, without chemical treatments (a), after the nitric acid treatment (b) and following a thorough washing with NaOH (c). Right panel: a detailed comparison with magnified views of the XANES features.

between 286.6 and 291.6 eV, features labelled A, C and B in all spectra, respectively. The feature B has been recently recognized as a transition to sp^3 hybridized states owing to the interaction between SWNTs and oxygenated surface groups or owing to a surface contamination (Banerjee *et al.*, 2004; Kuznetsova *et al.*, 2001; Abbas *et al.*, 2005). However, we have to underline that, because our SWCNT samples contain randomly oriented nanotubes, features in the C *K*-edge XANES spectra are averaged or integrated results over all orientations of the graphitic planes.

Spectral changes are outlined in Fig. 1 for SWCNTs after the nitric acid treatment [curve (b)] and compared with the as-produced SWCNTs [curve (a)]. The feature B shows an enhanced intensity while the feature A decreases. An obvious decrease of feature C can also be observed. The increase of feature B can be attributed to sp^3 hybridized states resulting from oxygenated groups (Banerjee *et al.*, 2004; Kuznetsova *et al.*, 2001), while the decrease of the feature A indicates a weakening of the C–C π^* network. The C–C σ^* transition is also a useful feature for characterizing the structural information of CNTs (Hemraj-Benny *et al.*, 2006; Tang *et al.*, 2001). When side walls of CNTs are destroyed or shortened to small pieces, the spectral feature C should change owing to the different contributions of carbonaceous fragments and defect sites. The decrease of the feature C after treatment can be associated with a shortening of long SWCNTs from defect sites. We observed that when as-produced SWCNTs are treated with nitric acid the metal catalyst is dissolved into the nitric acid solution and has no effect on the XANES. The amorphous carbon might be functionalized forming carboxylated carbonaceous fragments as we will discuss below. Actually, MWCNTs remain after the nitric acid treatment but the amount of them is negligible and does not affect XANES results. Therefore, the spectral changes of features A and B

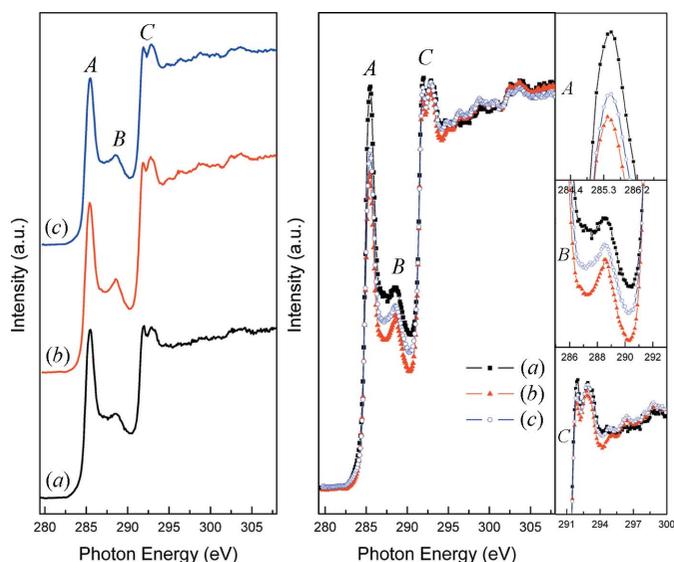


Figure 2 Left panel: C K-edge XANES spectra of washed SWCNTs (a), after nitric acid treatment (b) and following a thorough washing with NaOH (c). Right panel: a detailed comparison with magnified views of the XANES features.

can be assigned to the introduction of oxygen-containing functional groups by nitric acid oxidation in agreement with a previous report (Kuznetsova *et al.*, 2001). Moreover, the decrease of the feature C indicates that some parts of SWCNTs side walls may be damaged and/or reduced to carbonaceous fragments after the nitric acid treatment.

After thoroughly washing with NaOH, SWCNTs show an obvious decrease and a broadening of the feature B with a contemporary increase of feature A in spectrum (c). According to previous reports (Abbas *et al.*, 2005; Kuznetsova *et al.*, 2001), the spectral features ('B' region) are mainly due to a chemical oxidation while additional smaller contributions may be due to C–H at some defective sites and to oxygen adsorption. The broadening of the feature B after the NaOH washing is probably due to an enhanced affinity of washed SWCNTs to the gas molecules. It is also well known that oxygenated functionalities hinder absorption by blocking entry ports to gas molecules. Therefore, the decrease and the broadening of the feature B indicates that most of the oxygen-containing functional groups along with their hosts are removed by NaOH washing, a procedure consistent with

previous reports (Verdejo *et al.*, 2007; Salzmann *et al.*, 2007). The NaOH will react with the carboxyl groups forming conjugate salts that can be washed out of the SWCNT sample. After washing, the remaining sample mainly consists of carbon nanotubes plus the weak feature B indicating that the side walls of SWCNTs have been weakly oxidized by the nitric acid treatment. Therefore, the XANES results clearly show that the carboxyl groups created by nitric acid treatment are formed on both the carbonaceous fragments and the side walls of SWCNTs. The enhanced feature C in the spectrum (c) compared with the spectrum (b) also indicates the removal of carbonaceous fragments and the occurrence of a long-range order of the SWCNTs. Actually, carbonaceous fragments may come from the synthesis process or from the smaller parts of SWCNTs which can be easily modified and broken during the nitric acid treatment.

To further investigate the modification of SWCNTs *via* the nitric acid treatment, we treated the washed SWCNTs sample, which mainly consisted of pure carbon nanotubes, with a nitric acid and the NaOH solution. The treatment is described in process (ii). C K-edge XANES spectra of treated SWCNT samples are showed in Fig. 2. After refluxing with nitric acid, SWCNTs also show an increased feature B with a correlated reduction of the spectral feature A (b). It addresses the introduction of carboxyl groups by the nitric acid treatment. The modifications directly affect SWCNTs because of the removal of carbonaceous fragments. The almost unchanged feature C also indicates the existing long-range order in SWCNTs. Experimental results suggest that after removing the carbonaceous fragments the modification with carboxyl groups may directly occur only on SWCNTs tube walls, although it is weaker than for fragments. The spectrum of a SWCNTs sample after washing is shown in the spectrum (c). SWCNTs remain after NaOH washing; therefore, the intensity of features A and B shows only small changes compared with spectrum (b), indicating the lack of small pieces left on the sample and the occurrence of direct modification on SWCNTs tube walls. After washing, the surface of SWCNTs become a sodium carboxylate and remains, showing an enhanced peak B compared with spectrum (a). Thus, XANES results suggest that side-wall modifications of SWCNTs can be obtained by nitric acid oxidation after removal of the oxidized carbonaceous fragments. For the sake of clarity, the scheme adopted is showed in Fig. 3.

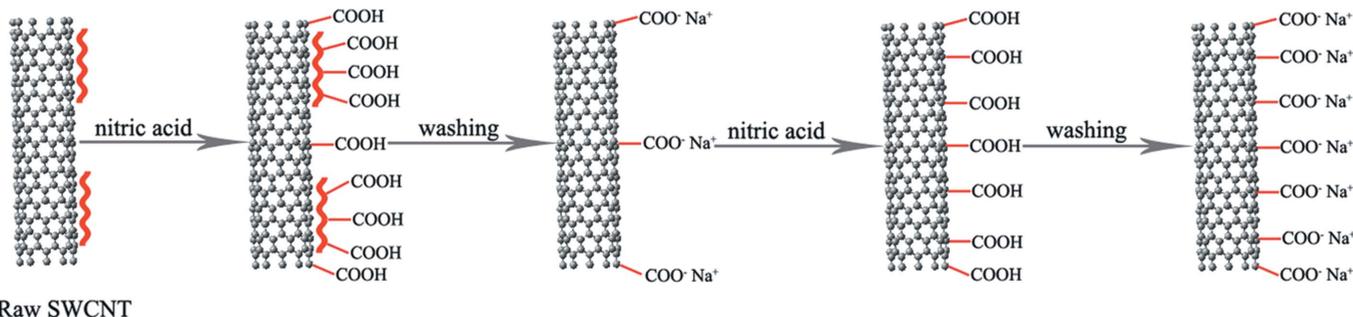


Figure 3 The modification process of SWCNTs by nitric acid treatment and NaOH washing. Carbonaceous fragments are represented by red wavy lines.

Side-wall modifications of SWCNTs have been accurately investigated by XANES. This study presents an effective way to modify SWCNTs. According to previous reports (Yang *et al.*, 2002; Zhang *et al.*, 2003, 2004), SWCNTs with small diameters and many defect sites can be oxidized and broken to form small carbonaceous fragments much more easily than SWCNTs with a large diameter. After removal of the oxidized carbonaceous fragments, the remaining SWCNTs are relatively stable so that, under proper oxidation conditions, side walls of SWCNTs can be efficiently modified avoiding the formation of oxidized carbonaceous fragments.

4. Conclusions

We applied XANES spectroscopy to perform a systematic investigation of the modification of SWCNT materials by nitric acid treatment. Experimental results suggest that carboxyl groups created by a nitric acid treatment can be formed on both carbonaceous fragments and side walls of SWCNTs. Carbonaceous fragments which may be removed by washing with sodium hydroxide may originate from a synthesis process or from the nitric acid treatment which will damage sections of SWCNTs. Nevertheless, after removal of carbonaceous fragments, a direct modification of SWCNTs, which can never be removed by washing, can be identified by XANES. The experimental data suggest that removal of carbonaceous fragments is an essential probe for direct covalent modification of SWCNTs. In addition, we also showed that XANES spectroscopy is a useful tool for investigating chemical bondings and structural information of carbon-based systems.

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