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Electronic structure study of Li⁺/OH⁻ modified single-walled carbon nanotubes by soft-x-ray absorption and resonant emission spectroscopy

Jun Zhong,^{1,2} Li Song,³ Jauwern Chiou,^{2,4} Chungli Dong,^{2,5} Xianqing Liang,¹ Dongliang Chen,¹ Sishen Xie,³ Way-Faung Pong,⁶ Chinglin Chang,⁶ Jinghua Guo,^{2,a)} and Ziyu Wu^{1,7,8,b)}

¹*Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

²*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

³*Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China*

⁴*Department of Applied Physics, National University of Kaohsiung, Kaohsiung 81148, Taiwan*

⁵*National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan*

⁶*Department of Physics, Tamkang University, Tamsui, Taiwan 251, Taiwan*

⁷*University of Science and Technology of China, Hefei 230026, People's Republic of China*

⁸*Theoretical Physics Center for Science Facilities, Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

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Li⁺ and OH⁻ modified single-walled carbon nanotubes (SWNTs) treated with the LiOH water solution have been investigated by soft-x-ray absorption and resonant emission spectroscopy. A reconstruction of the band structure after hydroxyl modification and intensity changes between π and σ states in the resonant emission spectra are presented and discussed. A charge transfer induced valence state near Fermi level has been detected at the resonant excitation energy of 285.5 eV, which indicates the tuning of electronic properties of SWNTs by Li⁺ adsorption. © 2010 American Institute of Physics. [doi:10.1063/1.3441027]

Carbon nanotubes (CNTs) are simple structure systems with unique properties and a large variety of possible applications.¹ To design CNTs with specific properties, different modifications represent an effective way that is capable to tailor the electronic properties.² The hydroxyl group modification has been reported to be a basic and important precursor for surface modification of CNTs.^{3–5} Pan *et al.*³ reported the modification of single-walled carbon nanotubes (SWNTs) with potassium hydroxide at room temperature producing single-walled carbon nanotubols (SWNTols). Recently MWNTs treated with H₂O₂ under neutral conditions have been synthesized with hydroxyl group modifications.⁵ Li⁺ modified CNTs have also been reported and aroused a lot of interests because of the great potential applications for Li ion battery.^{6,7} The adsorption of Li⁺ on SWNTs will help to understand the performance of carbon based anodes.⁶ The suitable Li⁺ adsorption environment could improve the discharge-charge process in Li ion battery and a better efficiency for the battery can be expected.⁷ In this work we have studied the structure changes of SWNTs by both Li⁺ adsorption and hydroxyl modification using soft x-ray absorption (XAS) and resonant soft x-ray emission spectroscopy (XES).

When tailoring the electronic properties of CNTs, it is important to characterize the electronic structure changes of CNTs induced by different processes. XAS probes the unoccupied local and partial density of states (DOS) while XES probes the occupied DOS.⁸ The resonant soft XES allows to select the specific element in a complex system or distinguish the contribution of same atomic element in different chemical environments, thus to be a suitable tool to charac-

terize the band structure of modified SWNTs.^{8–10} This method is widely used in different research fields ranging from the atomic and molecular physics to materials science.^{9,10}

XAS and XES experiments were performed on BL7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory.⁹ The energy resolution of monochromator was set to 0.2 eV for the C *K*-edge XAS and 0.3 eV for XES experiments, respectively. At the C *K*-edge the resolution of the x-ray emission spectrometer was set to 0.3 eV. To minimize the contribution of the self-absorption effect, the incident angle was 20° in respect to the sample surface. The XES spectrometer was installed perpendicular to the incoming photon beam.⁹ XAS spectra were recorded using the total electron yield mode with the energy scale calibrated to the π^* peak of the C *K*-edge of a highly oriented pyrolytic graphite (HOPG) sample at 285.5 eV.

SWNT samples before and after the treatment were investigated and labeled as SWNT1 and SWNT2, respectively. The samples were prepared by the optimal floating chemical vapor deposition (CVD) method and the purified samples contained more than 70 wt % of carbon nanotubes as measured by the thermogravimetry analysis method.¹¹ Based on TEM images the mean length of SWNT1 was several microns. The original materials (SWNT1) were then treated by immersion in a 1 M LiOH water solution (pH=12) for 5 days and labeled as the SWNT2 sample.

Figure 1 (left panel) shows the C *K*-edge XAS spectra of SWNTs before (a) and after (b) the treatment in a LiOH water solution. The spectra have been normalized to the pre- and postedges.¹² The two XAS spectra of SWNTs showed in Fig. 1 are characterized by four main features: A, B, C, and D at about 285.5 eV, 287.8 eV, 292.5 eV, and 305.4 eV, respectively. Based on previous XAS studies of both HOPG

^{a)} Author to whom correspondence should be addressed. Electronic mail: jguo@lbl.gov.

^{b)} Electronic mail: wuzy@ustc.edu.cn.

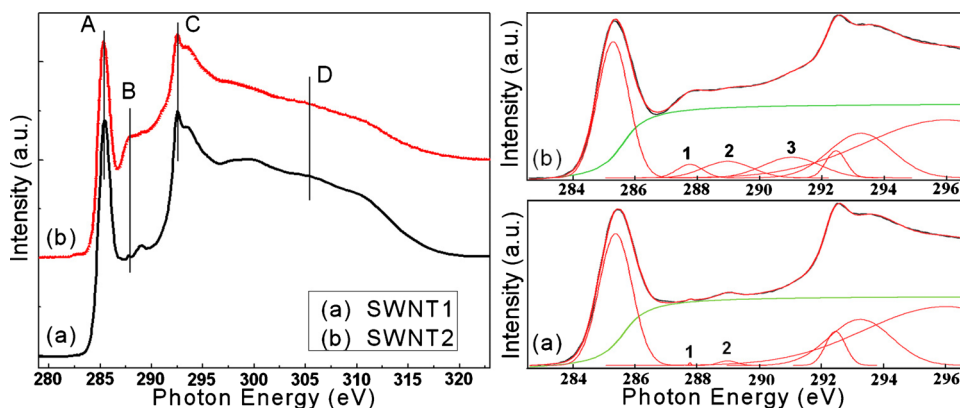


FIG. 1. (Color online) Left panel: Comparison of C K-edge XAS spectra of: (a) SWNT1 and (b) SWNT2; right panel: The fit of the C K-edge XAS spectra of both (a) SWNT1 and (b) SWNT2.

and SWNTs, the feature A was assigned to the π^* excitation of C—C bonds while the feature C to σ^* excitation of C—C bonds, respectively.^{12,13} The large feature D has been assigned to the superposition of multiple-scattering resonances. Recently, the feature B has been recognized as hybridized states due to the interaction between SWNTs and oxygenated surface groups or surface contaminations.^{12,13} SWNT1 (spectrum a) shows a weak feature B addressing a weak contamination. On the contrary, the treated sample (SWNT2) shows a broad and prominent feature B suggesting the structure modification of SWNTs as the result of LiOH treatment.

Previous reports showed that chemical modifications easily affected the atomic and electronic structures of SWNTs.^{3-5,13} To introduce hydroxyl modified SWNTs a solid-phase reaction with potassium hydroxide or an alkaline-mediated hydrothermal treatment have been used.^{3,4} The SWNT2 sample has been treated with a LiOH water solution for five days and the mild LiOH solution may slowly etch the tube wall with hydroxyl groups. A previous report also showed the immersion effect of a HBr solution with the modification of Br on SWNTs and an enhanced feature B in XANES spectrum.¹³ Here the prominent feature B may also suggest the modifications of SWNTs in a LiOH solution. Since ions in a LiOH water solution with a pH value of 12 are mainly OH^- and Li^+ , the functionalization of hydroxyl groups on the surface of SWNTs may significantly modify the atomic and electronic structures of SWNTs so that an enhanced feature B can be observed, as in Fig. 1(b).

For a detailed analysis, we performed a peak fitting of the data using the Igor package. Results are summarized in Fig. 1 (right panel). For the original sample SWNT1, in the region of the feature B we identify two weak contributions labeled peak1 and peak2. On the contrary, the treated sample SWNT2 shows the two prominent peak1 and peak2 with an additional one (peak3). The intense peak1 around 287.8 eV can be assigned to π^* (C—OH) according to reported XANES data.^{14,15} The peak2 around 288.9 eV has been widely reported and assigned to π^* (C=O) state of COOH,^{12,13} which can be attributed to the possible oxidation. The peak3 around 291.0 eV can be attributed to σ^* (C—O) from either C—OH or COOH. The prominent peak1 for C—OH clearly demonstrates the hydroxyl modification of SWNTs.

To further investigate the structural changes of SWNTs treated by a LiOH solution, we also measured the C 1s x-ray photoelectron spectroscopy (XPS) spectra showed in Fig. 2. In particular, in Fig. 2(a) we show the spectrum of SWNT1 with a dominant peak around 284.6 eV assigned to C—C

bonds. Two small peaks around 286.2 and 288.2 eV are also observed and assigned to C—O and C=O bonds.^{3,14} The dotted lines (blue) in both Figs. 2(a) and 2(b) represent the subtracted background. The comparison between the normalized curves in Figs. 2(a) and 2(b) shows a significant increase of the intensity of the C—O component.^{3,14} The observed changes are attributed to the modification of hydroxyl groups on SWNTs, a mechanism in good agreement with previous XPS data of hydroxyl modified SWNTs.³⁻⁵ The enhancement of C=O peak indicates the possible oxidation which is also consistent with the XAS result. Both XAS and XPS experiments indeed confirm the occurrence of hydroxyl modification of SWNT2.

Resonant XES analysis has also been used to study the electronic structure changes of the modified SWNTs. Figure 3 (left panel) shows the C K-edge emission spectra of both SWNT1 and SWNT2 at different excitation energies: 285.5 eV (a), 287.8 eV (b), 292.5 eV (c), and 305.4 eV (d). In good agreement with previous reports, six main bands (labeled 1 to 6) are identified.^{10,16,17} A clear enhancement of the band 3 in the spectrum of the SWNT2 sample is observed in the

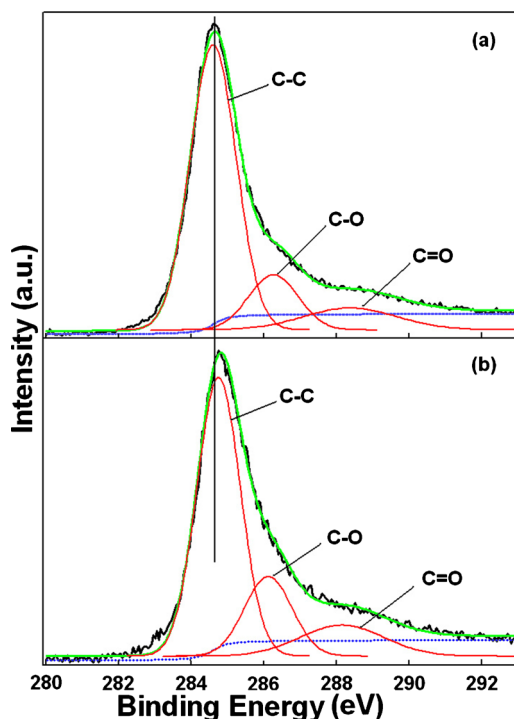


FIG. 2. (Color online) Comparison between the C 1s XPS spectra of (a) SWNT1 and (b) SWNT2.

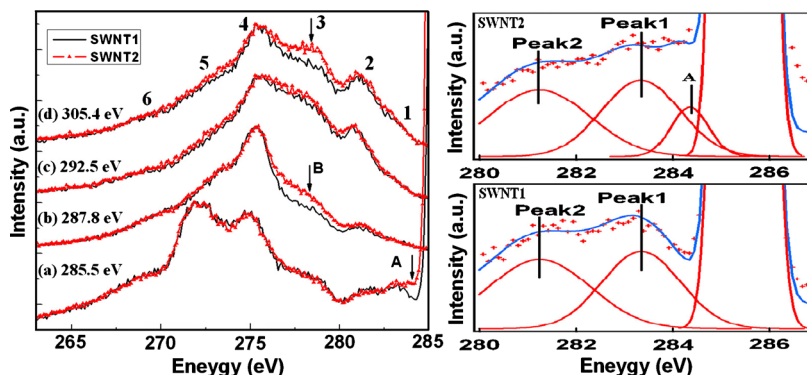


FIG. 3. (Color online) Left panel: Comparison of the K -edge emission spectra of SWNT1 (solid line) and SWNT2 (triangles) at different excitation energies: 285.5 eV (a), 287.8 eV (b), 292.5 eV (c), and 305.4 eV (d); right panel: The peak fitting results of the emission spectra near Fermi level excited at 285.5 eV.

normal emission (curves d) which shows the electronic changes induced by the LiOH treatment. Using resonant excitation, we could then identify which adsorbed group is related to the change of electronic structure. When using excitation energy at 287.8 eV, which is related to the occurring hydroxyl modification (C—OH) in the XAS spectrum, may reveal the direct band structure changes induced by hydroxyl modification. Clearly, an enhancement of the band 3 in curve b for the treated SWNTs is observed and recognized as the effect of hydroxyl modification. Actually, with a different excitation energy such as the σ^* excitation energy at 292.5 eV, the resonant emission spectra in curve c do not show differences between the two samples. The resonant soft x-ray emission spectra reveal that the hydroxyl modification of SWNTs with a LiOH water solution mainly affects the band structure between the π and σ bands. This represents a direct evidence of the band structure changes of hydroxyl modified SWNTs.

In Fig. 3(a) (left panel) the resonant XES spectra at the π^* excitation energy have also been shown. By a comparison of the spectra of both SWNT1 and SWNT2, an additional feature labeled A (see arrow) near Fermi level is detected for the modified SWNTs. For clarify, we also plot the peak fitting in Fig. 3 (right panel) which clearly shows the additional feature A for treated SWNTs. Previous UPS study of hydroxyl or carboxyl modified MWNTs showed almost no increase of the DOS near Fermi level.¹⁸ The additional feature should be related to different effects. The ions in LiOH water solution are mainly OH^- and Li^+ , thus Li^+ in solution may also contribute to the modification with Li^+ adsorption on SWNTs. Actually, both experimental and theoretical studies for the electronic structure of Li intercalated graphite reported a Li-doped state in the emission spectrum near Fermi level.^{19,20} The tuning of the electronic properties of SWNTs by Li^+ adsorption in LiOH solution can thus be identified by resonant XES spectrum at the π^* excitation energy. The excitation energy of 285.5 eV is just above Fermi level and the corresponding emission spectrum is extremely sensitive to the charge density near Fermi level.^{16,17} The additional feature A can be assigned to the doped state due to Li^+ adsorbed on SWNTs, which is hard to be detected in normal emission spectra and may help to understand the performance of carbon based anodes in Li ion battery.

In conclusion we have used XAS and XES methods to investigate the electronic structure of SWNTs under Li^+ adsorption and hydroxyl modification. XAS and XPS data collected after the treatment indicate that SWNTs have been modified by hydroxyl groups. The resonant XES emission spectra represent a direct evidence of band structure changes

of hydroxyl modification with an increased emission feature between π and σ bands (peak3). A Li^+ -doped state near Fermi level in the resonant XES spectrum can be also detected in the modified SWNTs at the excitation energy of π^* peak.

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