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EXAMINE THE GAS ABSORPTION PROPERTIES OF SINGLE WALL CARBON NANOTUBE BUNDLES BY X-RAY ABSORPTION TECHNIQUES

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Abstract. The absorption mechanism and electrical properties of Single Wall Carbon Nanotube bundles (SWCNTs) are examined with high-resolution C K-edge X-ray absorption near-edge structures (XANES) using the synchrotron radiation facility at NSRRC, Taiwan. The X-ray absorption experiments show that an effective desorption of oxygen and hydrocarbon from the surface of SWCNTs can be achieved by evacuating to high vacuum at 500K for several hours. The n-type behavior of SWCNTs exists in pure CO gas and will become the p-type behavior when SWCNTs has preadsorbed the oxygen. The experiments also show that the amphoteric property in electrical behavior of SWCNTs is determined by the oxygen absorption.

1. INTRODUCTION

A single wall carbon nanotube (SWCNT) [1,2] is a nano scale tube of a monolayer graphene sheet rolled up into a long seamless cylinder. Nanotubes have diameter of a few nm and length up to 100 μm so that they form extremely thin wires. Experimental and theoretical studies have found that SWCNTs have a large specific surface area and a nano-scale structure that provides plenty sites at which gases can react. They therefore exhibit very good adsorption properties that lead to many applications. For example, a carbon nanotube (CNT) gas sensor [3] can alter the electric properties of the CNTs by adsorbing the gaseous molecule on the surface of the CNTs. The use of CNTs to store hydrogen [4], given their capacity for adsorption, has also been widely investigated. These properties have led to applications of nanotubes as gas sensor, scanning probes [5], and nanoelectronic devices [6].

X-ray Absorption Near-Edge Structure (XANES) usually exists in the energy level of 50 eV above the absorption edge. It includes the unoccupied part of band structure just above the Fermi level. Thus, certain aspects of the electronic structure of detected element can be revealed. With this in mind, we have recorded the high-resolution C K-edge XANES spectra of CNTs. These measurements will directly probe the band structure in terms of density of states above the Fermi level. In this study, CO gas absorbed on the SWCNTs is examined by XANES techniques with Synchrotron Radiation sources in Taiwan. The C and O K-edges of x-ray absorption are used to examine the absorption properties of CO gas. Gas molecules adsorb weakly on SWCNTs and act as donors or acceptors. Charge transfer and gas-induced charge fluctuation might significantly alter the transport properties of SWCNTs. The results indicate that the amphoteric property of SWCNTs is determined by the oxygen absorption. The vacant orbital and electronics properties of the CO absorption on the surface of the SWCNTs can be measured from XANES spectrums and will help to understand the gas sensing mechanisms of SWCNTs.

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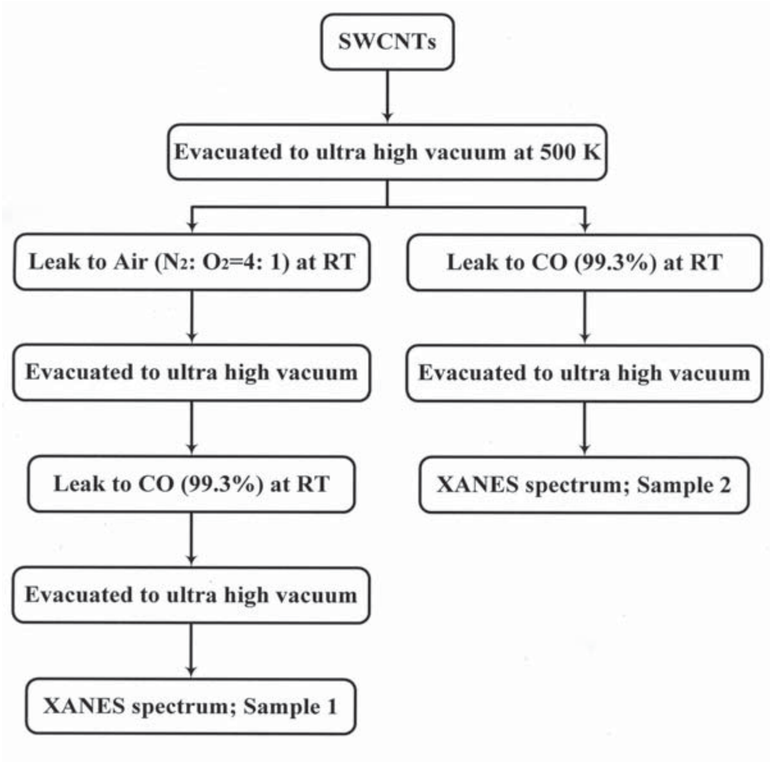

Fig. 1. The experimental processes of X-ray absorption measurements for samples 1 and 2.

2. EXPERIMENTAL

The purified SWCNTs [7] produced using the HiPco process [8,9] and prepared on lightly compacted mats of tangled SWCNTs bundles are supplied by Carbon Nanotechnologies Inc. Fig. 1 shows the experimental processes of X-ray absorption measurements. Samples 1 and 2 denote samples with and without the preadsorbed oxygen on the surface of the SWCNTs before CO treatment, respectively. The measurements of XANES spectra of the SWCNTs are conducted at the 6-meter spherical grating monochromator (6 m SGM) beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. Gas adsorption is studied using 99.3% CO gas.

3. RESULTS AND DISCUSSION

The transport measurements indicate that, once SWCNTs have been exposed to oxygen or air, it is not possible to fully be deoxygenated at room temperature even under high vacuum conditions. Fig. 2 shows that after degassing at T = 500K for about 12 hours in a vacuum of 10^{-8} Torr to remove moisture and oxygen, the C-H σ^* peak is not found. It indicates that hydrocarbons have been desorbed. Also, most of the oxygen has been desorbed from SWCNTs surface in terms of reducing the unoccupied electron density of nanotubes O-2p states. The O-K edge peak of 534.6 eV in Fig. 2a A has shifted to a low energy of about 0.5 eV. This indicates that the oxidation number of oxygen has decreased. We find that the samples must be evacuated to ultra high vacuum of 10^{-8} Torr and heated to 500K for several hours for removing the oxygen and hydrocarbon. Tang *et al.* [10] proves that the C-H peak σ^* is associated with the surface of the nanotubes. Sumanasekera *et al.* [11] presents the result of the quasi-one-dimensional nature of the conduction in a SWCNTs bundle and the fact that most of the C atoms are accessible to the gas. Therefore, SWCNTs could be sensitive to gas molecules at 500K under ultra high vacuum.

CO gas molecules have a lone electron pair that can be donated to other species and is known as a strong deoxidizer. For evaluating the suitability of nanotubes as a CO detecting material, the reaction between nanotubes and CO by synchrotron radia-

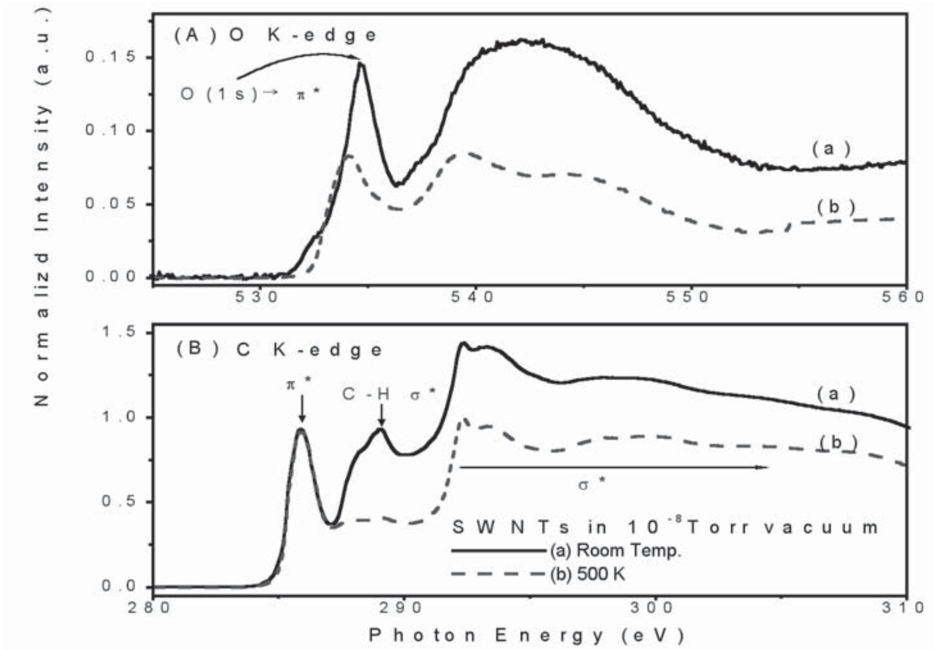

Fig. 2. (a) O K-edge; (b) C K-edge XANES spectra of SWCNTs in ultra high vacuum at RT and 500K.

tion techniques is performed. The near edge absorption results, however, show some unsaturated carbon π* bonds as evidenced by a 1s→π* feature. Results show unoccupied π*-bonds in such SWCNT mats react with CO molecules. The peaked intensity of C 1s→π* transition in Fig. 3b B indicates that the CO gas molecules will reduce the unoccupied electron density of nanotubes C-2p_z state. Charge transfer and gas-induced charge fluctuation significantly change the transport properties of SWCNTs. Here the SWCNTs mats exhibit n-type transistor characteristics upon exposure to CO gas molecules. On the other hand, as shown in Fig. 3a, the unoccupied electron density increases after CO has reacted with preadsorbed oxygen nanotubes. It is found that CO can interact with SWCNTs. Charge transfer from the CO to SWCNTs should be the mechanism of increasing electron carriers of SWCNTs and enhancing conductance in SWCNTs. But it is not true for the preadsorbed oxygen on the surface of the SWCNTs. Preadsorbed oxygen on the surface of the SWCNTs could interact with CO and affect the electrical properties of the SWCNTs. The possible reason is that the CO decreases hole carriers in SWCNTs and lowers conductance. Here the preadsorbed oxygen of SWCNTs exhibits p-type transistor characteristics under CO gas. This suggests that oxygen dominates the electrical properties of SWCNTs and directly affects the CO sensing behavior in different environment. The results

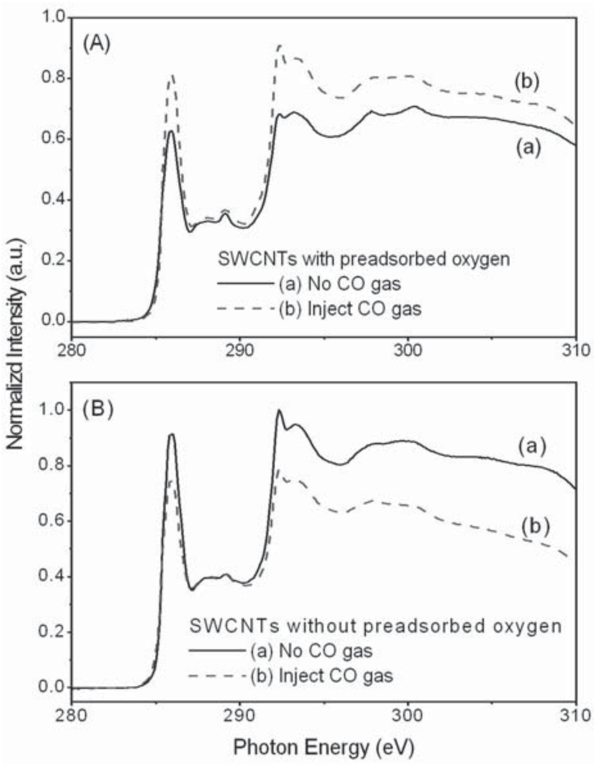

Fig. 3. Effects of CO gas molecules on C K-edge XANES spectra of SWCNTs (a) with preadsorbed oxygen (sample 1) and (b) without preadsorbed oxygen (sample 2).

indicate the amphoteric property in electrical behavior of SWCNT mats is determined by the oxygen absorption.

4. CONCLUSION

X-ray absorption experiments show that an effective desorption of oxygen and hydrocarbon from the surface of SWCNTs can be achieved by evacuating to high vacuum at 500K for several hours. The SWCNTs in pure CO gas shows the properties of n-type semiconductor and will become the p-type behavior when SWCNTs have preadsorbed the oxygen. Oxygen or vacuum environment play an important role in the electrical properties of SWCNTs. The amphoteric property in electrical behavior of SWCNT mats is determined by the oxygen absorption.

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