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Photoemission spectroscopy of single-walled carbon nanotube bundles

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Abstract

The electronic structures and the work functions of pristine and Cs-intercalated single-walled carbon nanotube bundles were investigated by C 1s and valence band photoemission spectroscopy. The C 1s spectrum of the pristine material showed a Doniach–Sunjic type asymmetry, indicating the existence of metallic tubes. The work function of the pristine bundles was found to be 4.8 eV, which is about 0.2 eV larger than that of graphite. A drastic decrease of the work function to about 2.0 eV was observed in the Cs-intercalated sample. The Cs intercalation also caused a nearly two-order increase in the spectral intensity at the Fermi level. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The electronic structure of single-walled carbon nanotubes (SWNTs) and their intercalation compounds has attracted much attention over the last several years because of their nanometer-scale highly one-dimensional structure. Moreover, the investigation of the electronic properties of SWNTs is becoming more important in view of their potential applications in areas such as electron field emission [1–3]. Although various experimental techniques have been used to investigate the electronic structure of SWNTs, few studies have used photoemission spec-

troscopy, which can provide information about the electronic structure over a wide energy range. Furthermore, photoemission spectroscopy has the advantage that it directly provides the work function, which is crucially important to understanding the field emission properties. We studied the work functions, valence band structures, and C 1s spectra of SWNT bundles by photoemission spectroscopy. Changes in the work function and valence band structures caused by Cs-intercalation were also studied.

2. Experimental

The SWNT bundles were synthesized by the laser ablation method [4]. The raw material was purified

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by ultrasonic-assisted filtration and was then deposited on metal substrates by a spray method [5]. The thickness of the SWNT film was estimated to be 0.5 μm . The average diameter of the nanotubes and the bundles were evaluated to be 1.4 and 20 nm, respectively, by X-ray diffraction intensity simulation [6].

Photoemission measurements were carried out at BL-1C [7] of the Photon Factory, High Energy Accelerator Research Institute, using an angle-integrated-type electron energy analyzer. Synchrotron radiation light of 340 eV (second-order light) was used as a light source for C 1s measurement, and an He discharge lamp ($h\nu=21.2$ eV) for work function and valence band measurements. The measurements were performed at room temperature. The overall energy resolutions, which are mostly determined by the Fermi–Dirac distribution function, were about 0.2 eV for the C 1s measurement and 0.1 eV for the work function and valence band measurements. Before the measurements, the pristine sample was annealed at 500°C in a vacuum to remove adsorbates on the surface. The Cs-intercalated sample was prepared by depositing Cs atoms on the pristine sample at room temperature using an alkali–metal dispenser. Our previous studies [4,8], which used an analytical electron microscope, revealed that alkali–metal atoms deposited on SWNT bundles intercalate into the bundles.

3. Results

Fig. 1 shows the C 1s spectra of the pristine SWNTs and graphite. Recently, Ago et al. [9] concluded from a curve-fitting analysis of C 1s spectra obtained by conventional X-ray photoelectron spectroscopy that multi-walled nanotubes (MWNTs) are considerably oxidized. However, no prominent oxidized component was observed in the spectrum, although the spectrum was obtained at much higher energy resolution. Thus, we conclude that there are almost no C–O bonds in the SWNTs. Although the spectra of both graphite and SWNTs are well fitted by a single Doniach–Sunjic type line shape convoluted by a Gaussian curve, the asymmetry is much larger than for SWNTs, as shown in the figure. The large Doniach–Sunjic type

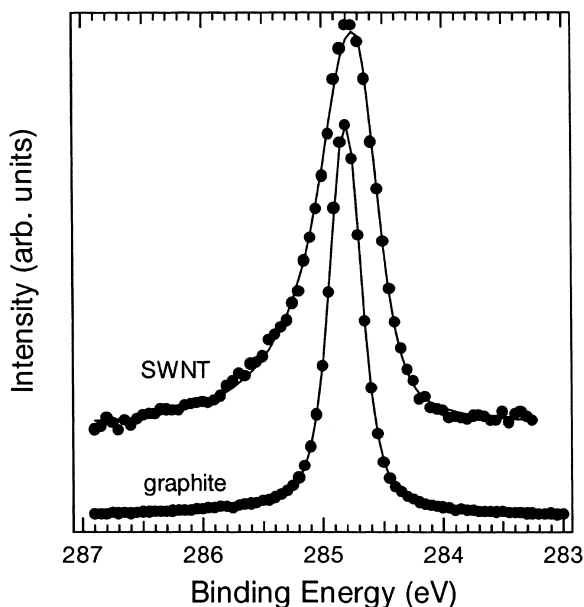


Fig. 1. C 1s photoemission spectra of the pristine SWNT bundles and graphite. The solid lines are curve-fitting results.

asymmetry indicates that the SWNT sample included metallic tubes, as expected from our nuclear magnetic resonance (NMR) result [10]. The peak width of the SWNTs (FWHM: 0.58 eV) is considerably larger than that of graphite (0.32 eV). We think that this is at least partly due to the larger Doniach–Sunjic type asymmetry, although there should be a small amount of contribution from carbon impurities (the sample contained 10–15% impurities such as amorphous carbon, graphitic particles, and Ni/Co catalyst).

Fig. 2 shows the spectra around the secondary electron threshold regions of graphite, the pristine SWNTs and Cs-intercalated SWNTs. The prominent peak of graphite at the nominal binding energy of about 13.6 eV is due to a large density of states in the unoccupied states and was attributed to the interlayer band which has large charge densities between carbon planes [11]. The corresponding peak almost disappears in the SWNT spectrum. This is considered to be due to the lack of the two-dimensional interlayers in a SWNT bundle.

As clearly seen in the figure, the threshold energy of the SWNT sample is shifted by 0.1–0.2 eV to the lower binding energy side. This means that the

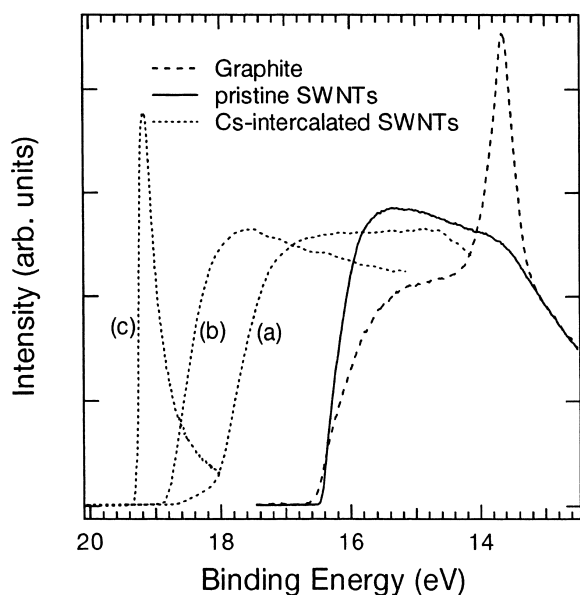


Fig. 2. Photoemission spectra around the secondary electron threshold regions of graphite and the pristine and Cs-intercalated SWNT bundles. (a), (b), and (c) correspond to different Cs concentrations.

SWNTs have a slightly larger work function than graphite. The work functions of the SWNT sample and graphite were determined to be about 4.8 and 4.6 eV, respectively, from the spectra in Fig. 2.

The work function of the SWNT sample drastically decreased when Cs was deposited on the sample (also shown in Fig. 2). The threshold energies after Cs deposition were shifted to the higher binding energy side by 1.7 (a), 2.4 (b) and 2.8 eV (c), resulting in work functions of 3.1, 2.4 and 2.0 eV, respectively. From the relative intensity of Cs $5p_{3/2}$ peak, the Cs/C compositional ratio of the sample (c) was estimated to be of the order of 0.1, by referring to a previous photoemission report [12] on Cs-intercalated graphite. The reduction may be partly due to Cs atoms remaining on the bundle surface, which will induce an electric dipole moment at the surface due to the electron transfer. However, half a day after the Cs deposition, the degraded surface also showed a relatively small work function of 2.55 eV. This suggests that the reduction is mainly associated with the bulk property of the Cs-intercalated SWNTs.

Fig. 3 shows the photoemission spectra in the

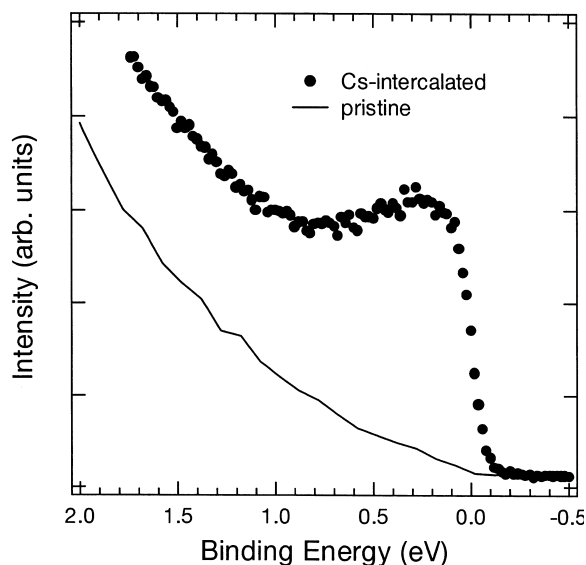


Fig. 3. Photoemission spectra in the vicinity of the Fermi level of the pristine and Cs-intercalated SWNT bundles.

vicinity of the Fermi levels of the pristine and the Cs-intercalated SWNT bundles [(c) in Fig. 2]. The spectral intensity at the Fermi level of the pristine SWNTs is very small. On the other hand, a distinct Fermi edge is observed for the Cs-intercalated sample. From the spectral intensity at the Fermi level, we can conclude that the density of states at the Fermi level of the Cs-intercalated sample is roughly two orders larger than that of the pristine material. This is consistent with a previous report [13] in which a resistance reduction of about 1/100 was observed by Cs intercalation. An upward shift of the Fermi level was also observed in the overall valence band spectrum of Cs-intercalated SWNTs, as reported elsewhere [14]. These spectral features are similar to those of alkali-metal intercalated graphite and indicate the electron transfer from Cs to C.

4. Discussion

As shown in the previous section, the work function of the SWNTs was found to be slightly larger than that of graphite. The increase in the work function of the SWNTs is completely opposite from the recent results of Ago et al. [9] and Chen et al.

[15] on MWNTs, in which the work function decrease by 0.1 to 0.2 eV relative to graphite were observed. Furthermore, the actual values of the work functions obtained in this study and the previous reports are different from each other. The value for graphite determined in this study is fairly consistent with previous studies on graphite (4.6 eV) [11]. On the other hand, Chen et al. (estimated from the spectra in Ref. [15]) and Ago et al. gave values of about 5.7 and 4.3 eV for MWNTs and 5.8 and 4.4 eV for graphite. The exact reason for the discrepancies is not clear at present. However, we would like to stress that our experiment gives the actual value of the work function of graphite.

It is unlikely that the relatively large work function value of the SWNTs is due to oxidation of the nanotubes [9] because we did not observe any prominent oxidized component in the high-energy resolution C 1s spectrum (Fig. 1). The effect of surface contamination can also be excluded because the sample was annealed before the measurement, as previously stated. Although the reason for the large work function is not clear at present, we think that it is intrinsic to a nanotube having a nm-scale diameter. Interestingly, the work function of C₆₀ (diameter: 0.7 nm) was evaluated to be 4.7 eV [16], which is also a slightly larger value than that of graphite.

5. Conclusion

The electronic structures of pristine and Cs-intercalated SWNT bundles were investigated using photoemission spectroscopy. The C 1s spectrum of the pristine material showed a Doniach–Sunjic type asymmetry, which is indicative of the existence of metallic tubes. The work function of the pristine SWNTs was determined to be about 0.2 eV larger than that of graphite, and it drastically decreased to 2.0 eV with the Cs deposition. The Cs intercalation also caused a two-order increase in the spectral intensity at the Fermi level. These results indicate that it would be interesting to measure the field emission properties of Cs-deposited carbon nanotubes.

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