

Electronic structure of single-walled carbon nanotubes encapsulating potassium

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Electronic structural change of single-walled carbon nanotubes induced by potassium encapsulation was studied by photoemission spectroscopy. The potassium encapsulation caused a shift of the overall valence-band spectrum toward the higher binding-energy side by about 0.5 eV, which is basically understood by the simple rigid band shift model. However, the spectral intensity increase observed near the Fermi level was much larger than that expected by assuming the simple π^* band filling, indicating that, in addition to the π^* band, a part of the density of states initially located in the unoccupied states dips below the Fermi level by the potassium encapsulation. The result is qualitatively consistent with a recent band-structure calculation, which predicted that the nearly free-electron state hybridized with the $K 4s$ state crosses the Fermi level. The potassium encapsulation also decreased the work function by 1.4 eV.

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I. INTRODUCTION

It has been well demonstrated that the physical properties of carbon nanotubes, such as their conductivity¹⁻⁵ and electron field emission⁶ can be widely controlled by intercalation by guest species. Nanotube intercalation compounds can be classified according to their structures. In an intercalated multiwalled nanotube (MWNT), the guest species are inserted between the adjacent graphene sheets as in graphite intercalation compounds.⁷ For a single-walled nanotube (SWNT) bundle, it has been known that the intercalants are inserted into the interstitial space between the adjacent SWNT's.⁸⁻¹⁰ More recently, some molecules and elements, such as fullerenes¹¹⁻¹⁴ and iodine,¹⁵ have been found to be inserted into the interior space inside the individual SWNT's. In this case, the intercalants are confined in a one-dimensional space, and novel physical and chemical properties are thus expected.

Previous experiments on alkali-metal-intercalated nanotubes have clearly revealed electron transfer from the alkali metal to carbon.^{1-5,16-19} In general, the transferred electrons have been considered to simply fill the π^* band of the nanotubes. That is, the electronic structural change has been explained based on the simple rigid band shift model. However, most previous studies dealt with intercalated MWNT's or intercalated SWNT bundles; only a few experimental reports on SWNT's encapsulating alkali-metals have been reported.

Shimoda *et al.*²⁰ synthesized SWNT's encapsulating lithium by electrochemical reaction (In this case, lithium was also intercalated into the interstitial sites between the SWNT's, and observed an increased density of states at the Fermi level in nuclear-magnetic-resonance measurements. Jeong *et al.*²¹ accomplished cesium encapsulation inside SWNT's by cesium plasma-ion irradiation. Their transmission electron microscopy (TEM) observation revealed several structural forms of encapsulated cesium, such as linear and spiral chains and a crystallized form. The electronic structure of SWNT's encapsulating alkali metals has been theoretically studied more extensively.²²⁻²⁶ Other than the simple electron transfer, some authors have paid attention to the alkali-metal-induced modification of the nearly free-

electron (NFE) state, which is located 3~4 eV above the Fermi level in a pristine SWNT and has a large charge density at the center of the interior space of a SWNT. Miyamoto *et al.*²² and Miyake and Saito²⁶ calculated the band structure of SWNT's encapsulating potassium. They showed that the NFE state is considerably affected by hybridization with the $4s$ state of the encapsulated potassium.

In this paper, we study valence band and work function change induced by potassium encapsulation by means of photoemission spectroscopy. Attention will mainly be paid to the valence-band spectra near the Fermi level, where a distinct deviation from the simple rigid band shift model was observed. The electronic structure deduced from the spectral change is discussed, and the results are compared to some of the recent band-structure calculations.

II. EXPERIMENT

Purified SWNT's grown by the high-pressure CO disproportionation (HiPco) method²⁷ were commercially obtained from Carbon Nanotechnology Inc. The average diameter of the SWNT's is ~ 1 nm. We prepared two types of samples for comparison: open-ended SWNT's, whose caps were removed by annealing the sample in air at 693 K (in accordance with a previous report¹⁴ on SWNT's encapsulating metallofullerenes) and close-ended SWNT's without the treatment. Potassium was inserted into the SWNT's by means of the two-zone vapor method. The SWNT flakes and potassium were heated in an evacuated and sealed quartz tube at 573 K for 25 h. This is essentially the same as the method that is often used to synthesize potassium-intercalated (close-ended) SWNT bundles,^{1-5,16} except for the removal of the caps for one sample before the reaction and for higher reaction temperature. For the open-ended SWNT's, the potassium atoms seemed to occupy the interior spaces of the SWNT's in addition to the interstitial space between the SWNT's as discussed below. After the reaction, the samples were removed from the quartz tube in air for photoemission measurements.

Photoemission measurements on the pristine and potassium-doped open-ended SWNT's were carried out at a

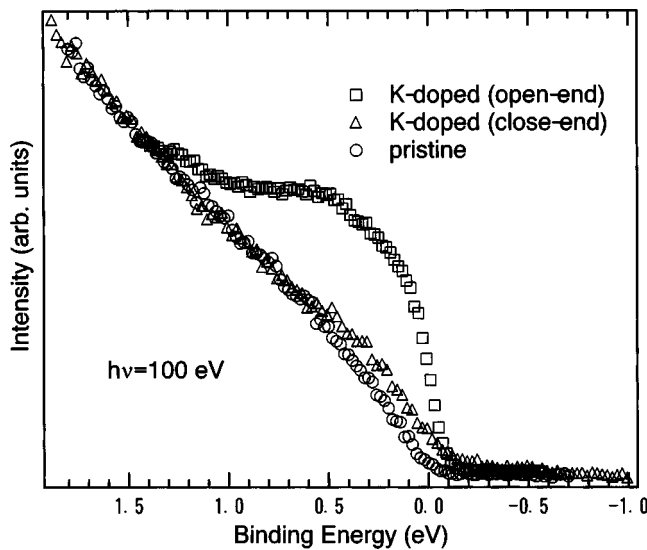


FIG. 1. Valence-band photoemission spectra near the Fermi level of the potassium-intercalated open- and close-ended SWNT's. Note that the measurements were done after exposing the samples to air and water and annealing in a vacuum at 873 K. The spectrum of the pristine SWNT's is also shown for comparison. The spectra were normalized by the spectral intensity of the valence band at higher binding energies, which showed similar spectral features after appropriate binding-energy shifts. The energy region used for the normalization is 2.5–10 eV for pristine SWNT's.

beam line BL-IC of the Photon Factory, High Energy Accelerator Research Institute, Tsukuba, Japan. The photon energy $h\nu$ and the energy resolution were 100 eV and 50 meV, respectively, for valence-band photoemission measurements. A helium discharge lamp (He I: $h\nu=21.2$ eV) was also used as a light source for work-function measurements. The base pressure of the analysis chamber was 1×10^{-9} Torr. The potassium-doped close-ended SWNT's were measured at the beam line ABL-3B of the normal-conducting accelerating ring, Atsugi R&D Center, NTT Corp., Japan. The photon energy and the energy resolution were 100 eV and 0.25 eV, respectively. The base pressure of the analysis chamber was 8×10^{-10} Torr.

After exposure to air, the sample surface was covered with thick potassium compounds, probably due to deintercalation in air and excess potassium on the sample surface. To remove the potassium compounds on the sample surface and the potassium remaining between the SWNT's, the samples were rinsed in water for 1 min. Valence-band photoemission spectra showed that the sample surface was still covered by potassium compounds. They were finally eliminated by annealing at about 873 K in a vacuum for 30 min. All spectra shown below were measured at room temperature after this annealing.

III. RESULTS

The valence-band spectra near the Fermi level of the potassium-doped SWNT's after exposure to air and water were strongly dependent on the structure of the ends of the SWNT's. Figure 1 shows the spectra near the Fermi level of

the potassium-doped open- and close-ended SWNT's. The spectrum of the pristine SWNT's is also shown for comparison. The pristine SWNT's show a little spectral intensity at the Fermi level, as we previously observed for SWNT's synthesized by the laser ablation method.¹⁷ The potassium-doped open-ended SWNT's show a large density of states near the Fermi level and a distinct Fermi edge. This indicates a metallic character, which has been commonly observed for alkali-metal intercalated MWNT's (Ref. 19) and SWNT bundles.^{1–5,18} On the other hand, the spectrum of the potassium-doped close-ended SWNT's is very similar to that of the pristine SWNT's and shows a much smaller density of states near the Fermi level. This means that potassium initially intercalated into the interstitial sites between the SWNT's almost completely deintercalated when the sample was exposed to air and rinsed in water. It has been demonstrated by previous TEM,^{8,9} conductivity,¹ and Raman scattering⁹ measurements that alkali-metal atoms intercalated into SWNT bundles immediately deintercalate when the doped samples are exposed to air. A previous conductivity measurement⁴ also showed that annealing a potassium-doped SWNT bundle at 400 K in a vacuum leads to deintercalation. In all the previous reports, the experiments were performed on SWNT's without any treatment for removal of the caps and potassium was therefore considered to be located at the interstitial sites between the SWNT's.

The result for the potassium-doped open-ended SWNT's indicates that a considerable amount of potassium remains even after exposure to air and water and annealing at 873 K. It is very unlikely that potassium atoms occupy the interstitial sites because they are unstable in air and water and at the high-annealing temperature, as mentioned above. Actually, the result for the potassium-doped close-ended SWNT's is quite consistent with the previous results. We thus conclude that potassium is encapsulated inside individual SWNT's in this case. The result also means that the encapsulated potassium is remarkably stable in air and water and at a high temperature of 873 K, as has been found in the previous studies for encapsulated lithium²⁸ and cesium.²¹ We think that both the interior space of each SWNT and the interstitial sites between the SWNT's were once occupied by potassium atoms during the reaction with potassium at 573 K. After exposure to air and water and annealing at 873 K, potassium atoms inside the SWNT's seem to remain. The spectral intensity near the Fermi level of the potassium-doped close-ended SWNT's is slightly larger than that of the pristine SWNT's. This is probably because the SWNT's are slightly filled by potassium due to defects formed during the synthesis or purification procedure. Hereafter, we will focus on the potassium-doped open-ended SWNT's. The K/C ratio of the SWNT's encapsulating potassium was roughly estimated to be ~ 0.14 from K 2*p* and C 1*s* x-ray photoelectron spectroscopy (XPS).

Figure 2 shows valence-band photoemission spectra of the pristine SWNT's and the SWNT's encapsulating potassium in a wide energy range. The peaks of the pristine SWNT's observed at binding energy of about 3 and 8 eV are assigned to van Hove singularities of the π and σ bands, respectively. Although the overall spectral shapes are quite

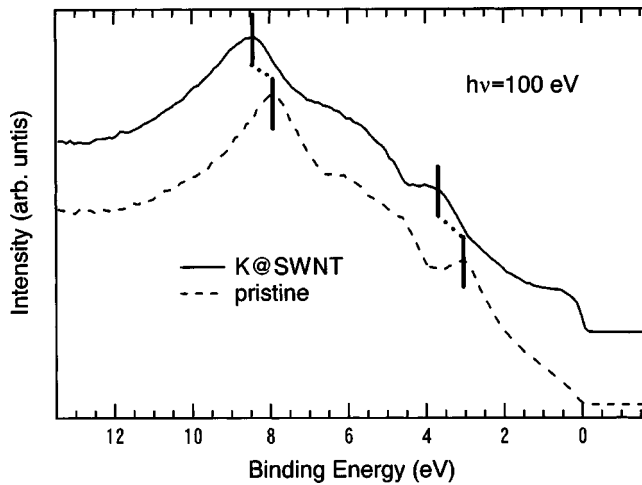


FIG. 2. Valence-band photoemission spectra of the pristine SWNT's and the SWNT's encapsulating potassium (K@SWNT).

similar to each other, the spectra of the SWNT's encapsulating potassium shifted to the higher binding-energy side by about 0.5 eV. This indicates an upward Fermi-level shift caused by electron transfer from potassium to carbon.

The spectral similarity of the overall valence-band spectra shown in Fig. 2 can basically be understood in terms of the rigid band shift model. However, a distinct deviation from the rigid band shift model was clearly observed near the Fermi level. Figure 3 shows magnification of the spectra near the Fermi level in Fig. 2. The spectrum expected from the rigid band shift model is also shown in the figure. Here, the density of states of the π^* bands was obtained from the experimentally obtained density of states of the π bands assuming that the Fermi level of the pristine SWNT's is located at the center between the π and π^* bands and that the

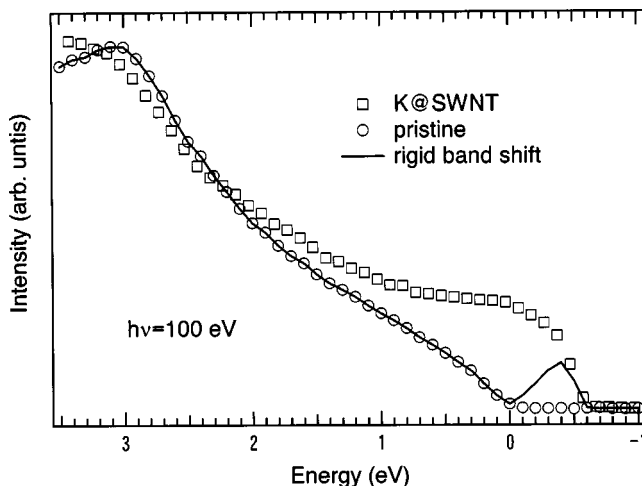


FIG. 3. Magnification of the spectra near the Fermi level in Fig. 2. The spectrum expected from the rigid band shift model is also shown. The spectrum of the SWNT's encapsulating potassium (K@SWNT) and that expected from the rigid band shift model shifted toward lower-energy side by 0.5 eV, for comparison. The origin of the energy was set to the Fermi energy of the pristine SWNT's.

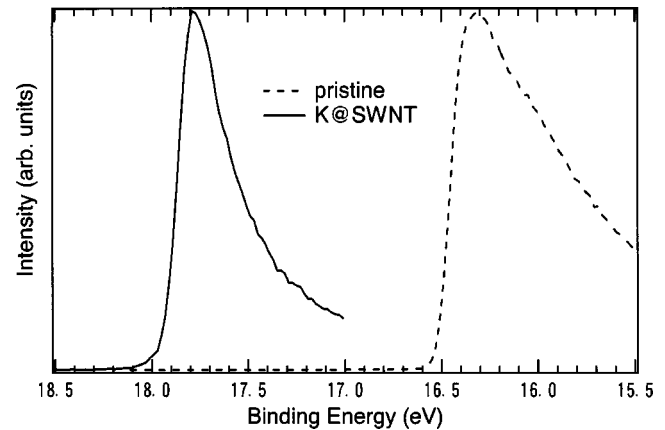


FIG. 4. Secondary electron threshold spectra of the pristine SWNT's and the SWNT's encapsulating potassium (K@SWNT). The work-function value can be determined by the difference between the photon energy (21.2 eV) and the nominal binding energy of the secondary electron threshold.

density of states of the π and π^* bands is symmetric near the Fermi level. The obtained density of states was multiplied by the Fermi-Dirac distribution function at room temperature and then convoluted by the experimental energy resolution. The spectrum of the SWNT's encapsulating potassium and the spectrum calculated by assuming the rigid band shift model were shifted toward the lower binding-energy side by 0.5 eV (the origin of the energy was set to the Fermi level of the pristine SWNT's in order to clarify the spectral intensity differences. At a glance, it is very clear that the spectra of the SWNT's encapsulating potassium cannot be explained by the rigid band shift model. The spectral intensity increase caused by the potassium encapsulation is much larger than that expected by the rigid band shift model. Moreover, the potassium encapsulation seems to also increase the density of states in a range of 0–1 eV or more, which would be unchanged in the simple rigid band shift picture. Note that the conclusions described above are essentially unchanged regardless of the exact Fermi-level position of the SWNT's because the spectral shape and intensity change induced by the potassium encapsulation is significantly large. If we assume that the Fermi level is located at the top of the valence band, as usually observed in transport property measurements, the deviation of the rigid band shift model from the experimental result will be larger. In the following section, we will discuss the electronic structural change deduced from the spectra in detail.

The potassium encapsulation also considerably changes the work function of the SWNT's, which is crucial for controlling the field-emission properties of SWNT's.⁶ Here, the work function is defined as the energy difference between the vacuum level and the Fermi level. Figure 4 shows secondary electron threshold spectra of the pristine SWNT's and the SWNT's encapsulating potassium. The work functions of the pristine and the SWNT's encapsulating potassium were determined to be about 4.7 eV and 3.3 eV, respectively. That is, the potassium encapsulation decreased the work function by 1.4 eV. The value for the SWNT's encapsulating potassium is

rather close to the calculated work-function value (about 3.6 eV, Ref. 25) of a potassium-doped (10,10) tube bundle KC_{10} (in the calculation, potassium is inserted both between and inside SWNT's). The work-function decrease is partly explained by the Fermi-level shift toward the vacuum level. However, it should be noted that the work-function decrease is considerably larger than the observed spectral shift (0.5 eV). Thus, the large work-function decrease cannot be simply understood in terms of the rigid band shift picture, either.

Although the work-function decrease is considerably large, the work-function value for the SWNT's encapsulating potassium is still quite larger than that of the Cs-intercalated (close-ended) SWNT's we previously obtained (2.0–2.4 eV).^{17,18} In the previous study, the Cs intercalation was achieved by depositing Cs onto the sample surface in vacuum at room temperature. We thus think that the work-function difference is mainly due to Cs ions on the sample surface in the latter case. It seems that the remaining Cs ions on the sample surface form an electric dipole moment at the surface, which would further reduce the work function [even in this case, the possibility that thick Cs layers were formed on the sample can be excluded because the Cs saturation coverage at room temperature is ~ 1 ML (Ref. 19), where ML is monolayer].

IV. DISCUSSION

In this section, we will analyze the valence-band spectra near the Fermi level in detail, and discuss a possible reason for the deviation from the rigid band shift model. We estimated the spectral intensity change near the Fermi level caused by the potassium encapsulation, relative to the total spectral intensity of the overall valence bands that spread up to a binding energy of about 25 eV. Before the analysis, the Shirley-type background was subtracted from the raw spectra, although the spectra near the Fermi level shown in Fig. 3 were almost unchanged by the background subtraction. The spectral intensity increase was estimated to be about 2.5% of the total valence-band intensity of the pristine SWNT's. On the other hand, that expected by assuming the rigid band shift of 0.5 eV was only about 0.24%. That is, the spectral intensity increase observed in the experiment is nearly one order of magnitude larger than that expected from the rigid band shift model.

Next, we estimated the amounts of electron transfer from the experimentally obtained and the calculated spectra assuming the rigid band shift model. The valence bands of SWNT's consist of four electrons of each carbon atom. One is a $2s$ electron and the other three are $2p$ electrons. We neglect the polarization dependence of the valence-band spectra because the SWNT's are considered to be randomly oriented in the sample, and assume that the ratio of $C\ 2s/2p$ excitation cross section per electron for $h\nu = 100$ eV is 2.1 according to the calculated photoionization cross section²⁹ (the difference in the cross section has only a minor effect and the discussion given below is qualitatively unchanged even if the $2s/2p$ cross-section ratio is assumed to be unity). Here, we also assume that the newly occupied states due to the potassium encapsulation are the π^* ($2p_z$) bands, or that

the cross section of the electronic states is the same as that of the π^* bands (the validity of the assumption is discussed later). Then, we can ascertain from the observed spectral intensity enhancement of 2.5% that 0.12 electrons per C atom are transferred from potassium. This value is close to the K/C ratio of the sample estimated from the XPS result, and thus indicates a highly ionic character of encapsulated potassium atoms. On the other hand, the amount of electron transfer estimated from the rigid band shift of 0.5 eV was evaluated to be only about 0.012 per carbon atom. Our estimation also showed that a rigid band shift of about 1.8 eV is necessary in order to explain the observed spectral intensity increase. Assuming the calculated density of states of graphite³⁰ instead of that shown in Fig. 3 (solid line), we also obtained qualitatively similar results.

Up to now, we have not considered the contribution of potassium-derived states to the spectrum. One may think that the large spectral intensity increase is mainly due to the formation of occupied $K\ 4s$ states. If we assume that the excitation cross section of a $K\ 4s$ electron is the same as that of a $C\ 2p$ electron, this idea leads to an almost neutral character in the encapsulated potassium. However, it is very unlikely that potassium having a low ionic potential is encapsulated in SWNT's in the neutral state. Moreover, according to the theoretical calculation,²⁹ the cross section of a $K\ 4s$ electron seems to be considerably smaller than that of a $C\ 2p$ electron for $h\nu$ of 100 eV (although the cross section of the $K\ 4s$ state is not apparently presented in the reference paper, we can roughly estimate it from the value of $Ca\ 4s$ state). Thus, even if the encapsulated potassium is in the neutral state, the observed spectral intensity increase cannot be explained at all. Therefore, we conclude that the $K\ 4s$ state does not largely contribute to the spectrum and that the spectral intensity near the Fermi level is dominated by electronic states that originate mainly in carbon.

To explain why the large spectral intensity increase was observed in spite of the rather small spectral shift, we have to assume that in addition to the simple π^* bands filling, a large amount of initially unoccupied states of a SWNT dips below the Fermi level due to potassium encapsulation. This means that the electronic structure in the unoccupied states and near the Fermi level cannot be described by the rigid band shift model. The band-structure calculation by Miyamoto *et al.*²² on a SWNT encapsulating potassium predicted that hybridization between the NFE state of the SWNT and $K\ 4s$ state produces two well-separated bands. This indicates a considerable deviation from the rigid band shift model. However, their calculation does not explain the observed spectral intensity increase near the Fermi level because both bands are completely located in the unoccupied states. It seems that the band-structure calculation by Miyake and Saito²⁶ is at least qualitatively consistent with our experimental results. Their calculation predicts that one of the bands produced by the hybridization between the NFE state and $K\ 4s$ state crosses the Fermi level. It also shows that the dispersion of the state is quite small below the Fermi level, and this will lead to a large density of states. Therefore, if the value of the excitation cross section of the NFE state is comparable to that of the π^* bands, as assumed above, we can

qualitatively understand the spectral intensity increase and the small Fermi-level shift. It seems that the difference in the results of the two band-structure calculations mainly originates in the difference in tube diameters.²⁶ Miyamoto *et al.*²² dealt with SWNT's having a diameter of 0.56 nm, while Miyake and Saito²⁶ found the Fermi-level crossing for SWNT's having diameters of 0.78 and 0.94 nm. Thus, the latter calculation is much closer to the situation in our experiments.

Unfortunately, further detailed comparison of the experimental and the calculated results seems to be difficult because the K/C ratio assumed in the calculation²⁶ (0.025 or less) is much smaller than that of this study. Considering that the ionic radius of potassium is 0.13 nm, the encapsulated potassium may often form plural chains or a crystal inside the SWNT's, as observed by a previous scanning-transmission electron microscopy study on SWNT's encapsulating iodine¹⁵ and cesium,²¹ although the calculation²⁶ dealt with a single chain of potassium.

The NFE state in a SWNT corresponds to the interlayer state in graphite, which has a large charge density between the adjacent sheets.^{31,32} The interlayer state in graphite has been intensively observed by vacuum-ultraviolet inverse photoemission spectroscopy.³³⁻³⁵ These results strongly suggest that the cross section of the interlayer state, and thus that of the NFE state is comparable to those of the π (π^*) and σ (σ^*) bands for a photon energy of vacuum-ultraviolet region. Therefore, it is likely that the state below the Fermi level induces a large spectral intensity increase as observed here.

The above discussion suggests that a considerable amount of the density of states near the Fermi level of the SWNT's encapsulating potassium originates in the band derived from the NFE state. Thus, the physical properties may be dominated by the NFE state rather than the π^* band, although, in a pristine SWNT, the NFE state should have little direct contribution to the physical properties because it is located far above the Fermi level.^{26,36}

Finally, we should mention that the spectral feature near the Fermi level observed in this study does not seem to be characteristic only of the SWNT's encapsulating potassium. Similar features were also observed in our previous studies on Cs-intercalated MWNT's (Ref. 19) and Cs-intercalated (close-ended) SWNT bundles,¹⁸ although we did not mention the deviation from the rigid band shift model in the previous reports. Previous calculations showed that a NFE (interlayer) state also exists at the intertube region in a SWNT bundle³⁶

and at the interwall region in an MWNT.³⁷ These results strongly suggest that the Fermi-level crossing of the hybridized state between the NFE (interlayer) state and alkali-metal s state commonly occurs in alkali-metal-intercalated SWNT's, regardless of the alkali-metal occupation sites (between the SWNT's and inside individual SWNT), and in alkali-metal-intercalated MWNT's (graphite). Actually, a recent band-structure calculation on potassium-intercalated graphite KC₈ resulted in a Fermi-level crossing of the interlayer state.³⁸ However, a calculation on a potassium-intercalated SWNT bundle by Saito, in which potassium was inserted between the SWNT's, did not result in a Fermi-level crossing of the NFE state, but in an almost rigid band shift behavior.³⁹ At this stage, the reason for the discrepancy is not clear.

V. CONCLUSION

We measured the valence-band photoemission spectra of both potassium-doped close- and open-ended SWNT's after deintercalation in air and water. The results indicated that potassium remained inside the open-ended SWNT's. The overall valence-band spectra of the SWNT's encapsulating potassium is well explained by the simple rigid band shift model. However, the spectra near the Fermi level showed a much larger spectral intensity increase than that expected by assuming the simple π^* bands filling, indicating that a part of the unoccupied states dips below the Fermi level by the potassium encapsulation. The band-structure calculation by Miyake and Saito,²⁶ which predicted that one of the hybridized states between the NFE and K $4s$ state comes downward and crosses the Fermi level, is qualitatively consistent with the experimental result. The potassium encapsulation also caused a large decrease of the work function of the SWNT's.

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