Photoemission and inverse photoemission study of the electronic structure of C\textsubscript{60} fullerenes encapsulated in single-walled carbon nanotubes

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We have measured the valence-band photoemission and inverse photoemission spectra of single-walled carbon nanotubes (SWNTs) with mean radii of 0.7 and 0.64 nm encapsulating C\textsubscript{60} fullerenes (peas), so-called “peapods.” The photoemission spectrum of the C\textsubscript{60} peas in the SWNTs is obtained by subtracting the spectrum of empty SWNTs from the spectrum of the peapod. The structures in the C\textsubscript{60} pea spectra correspond well to those in the spectrum of a C\textsubscript{60} face-centered-cubic solid. No structure is observed at binding energies ranging from the Fermi level ($E_F$) to the onset of the highest occupied molecular orbital (HOMO) peak; the $t_{1u}$ level of the C\textsubscript{60} peas inside the SWNT stays above $E_F$.

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I. INTRODUCTION

Hybrid carbon material consisting of single-walled carbon nanotubes (SWNTs) and C\textsubscript{60} fullerenes, known as peapods,\textsuperscript{1,2} has attracted much attention because of its nanoscale structure, which has the potential to drastically change the electronic properties of SWNTs and C\textsubscript{60} fullerenes. The electronic structures of C\textsubscript{60} peapods (C\textsubscript{60} PPDs) have been intensively studied both theoretically\textsuperscript{3−11} and experimentally.\textsuperscript{12−15} For example, using a density functional theory (DFT) calculation taking into account hybridization between the C\textsubscript{60} molecular $\pi$ states and nearly free-electron (NFE) states of SWNTs, Okada et al.\textsuperscript{3,4} and Otani et al.\textsuperscript{5} pointed out that the intersection of the $t_{1u}$ band of C\textsubscript{60} Peas with the Fermi level ($E_F$) leads to the appearance of a multicarrier state in metallic C\textsubscript{60} PPDs. However, using a DFT calculation taking into account hybridization between C\textsubscript{60} and the SWNT unoccupied $\pi$ states, Dubay and Kresse concluded that the $t_{1u}$ band stays above $E_F$.\textsuperscript{9} Moreover, on the basis of the extended H"{u}kel method, Rochefort stated that the band gap between the highest occupied molecular orbital (HOMO) level and $t_{1u}$ level is decreased compared with the band gap in a C\textsubscript{60} face-centered-cubic (fcc) solid.\textsuperscript{10}

Spectroscopic studies have also been performed by several groups.\textsuperscript{12−14} For example, Pichler et al. reported from an investigation of the intercalation properties of C\textsubscript{60} PPDs with Raman spectroscopy that the $t_{1u}$ level of the C\textsubscript{60} does not lie close to $E_F$.\textsuperscript{12} Using C L$_2$ core-level excitation electron-energy-loss spectroscopy (EELS), Liu et al. demonstrated that the electronic and optical properties of C\textsubscript{60} peas are very similar to those of C\textsubscript{60} fcc solids.\textsuperscript{13} The authors concluded that the C\textsubscript{60} $\pi$ states weakly hybridize with the SWNT $\pi$ states.\textsuperscript{12,13} In contrast, Hornbaker et al. detected periodic spatial modification of the unoccupied $\pi$ states of SWNTs corresponding to the C\textsubscript{60} array above $E_F$ using scanning tunneling microscopy (STM), and concluded that the C\textsubscript{60} $\pi$ states strongly hybridize with the SWNT $\pi$ states.\textsuperscript{14} As mentioned above, many investigations have been performed; however, the electronic structures of C\textsubscript{60} PPDs remain a subject of controversy. It is, therefore, necessary to verify these electronic features through reliable experiments using high-purity samples.

Recent successes in the production of high-purity SWNT samples have enabled us to detect prominent peak structures in optical absorption and photoemission spectra due to one-dimensional van Hove singularities (VHSs), the features of which depend on the chiral angle and radius of the SWNTs.\textsuperscript{18} The purpose of this study is to investigate the electronic structure of C\textsubscript{60} PPDs by photoemission and inverse photoemission spectroscopy, which allows direct observation of the occupied and unoccupied density of states, respectively.

II. EXPERIMENTAL

The SWNT samples SWNT-A and SWNT-B were prepared using the laser ablation method and purified with H$_2$O$_2$ treatment.\textsuperscript{16} The mean radii of the SWNTs in the empty SWNT-A and SWNT-B samples were estimated to be 0.7 and 0.64 nm, respectively, through Raman spectroscopy. These values are large enough to encapsulate C\textsubscript{60} peas with a radius of 0.34 nm.\textsuperscript{3,6,10} The C\textsubscript{60} PPD samples C\textsubscript{60} PPD-A and C\textsubscript{60} PPD-B were synthesized by exposing the SWNT-A and the SWNT-B, respectively, to vapor phase C\textsubscript{60} in a sealed quartz tube. From x-ray diffraction analysis, we estimated the filling factor of C\textsubscript{60} peas above, many investigations have been performed; however, the electronic structures of C\textsubscript{60} PPDs remain a subject of controversy. It is, therefore, necessary to verify these electronic features through reliable experiments using high-purity samples.

Photoemission experiments were performed using an angle-integrated hemispherical electron energy analyzer at beamline BL-1 of the Hiroshima synchrotron radiation research center (HiSOR), Hiroshima University, and at beam-
line BL-11D of the Photon Factory (PF), High Energy Accelerator Research Organization. Photoemission spectra were recorded at room temperature with experimental resolutions of 35 meV at HiSOR and 50 meV at the PF. The inverse photoemission spectra were measured using a spectrometer consisting of a varied-line-spaced spherical grating and a two-dimensional position sensitive detector in Tokyo Metropolitan University.20 In general, the inverse photoemission spectrum is measured with bremsstrahlung isochromat spectroscopy (BIS) mode detecting the constant photon energy ($E_p$) or tunable photon energy (TPE) mode using the incident electron beam with the constant energy ($E_i$). In this study, the spectra were measured with TPE mode using the incident electron beam of $E_i=76$ eV. The experimental resolution was 0.5 eV. Zero of the binding energy scale and the experimental resolution were calibrated with the Fermi edge of an evaporated Au film. We heated the samples at about 200 °C under an ultrahigh vacuum for several hours before each series of measurements to ensure a clean surface. Cleanliness was confirmed through the disappearance of the O 2p peak located at a binding energy of 6 eV.

### III. RESULTS AND DISCUSSION

Figure 2 shows the photoemission spectra of the SWNT and C$_{60}$ PPD samples measured at $h\nu=65$ eV. The photoemission spectra of the C$_{60}$ PPD are, as a whole, similar to those of the SWNT, except for some additional peaks or shoulders in the C$_{60}$ PPD spectra, and essentially composed of $sp^2$ hybrid $\sigma$ and $\pi$ states. The inverse photoemission spectra of the SWNT-A and C$_{60}$ PPD-A samples are shown in the negative binding energy region in Fig. 2. The spectral shape of the SWNT-A is, as a whole, similar to that of graphite.21 A broad peak around $-9.3$ eV is mostly due to transition into the unoccupied $\sigma^*$ states of the SWNTs. A prominent peak at $-2.5$ eV is mostly due to transition into the unoccupied $\pi^*$ states of the SWNTs. The $\pi^*$ and $\sigma^*$ peaks in the C$_{60}$ PPD spectrum are broader than those in the SWNT spectrum. This is due to the spectral weight coming from the C$_{60}$ PPD molecular states.

Figure 3 shows the detailed spectra of the C$_{60}$ PPD and SWNT samples at binding energies below 1.5 eV. Three peak structures originating from the one-dimensional VHSs can be seen in all spectra. Previously, Ishii et al. successfully reproduced the photoemission spectrum using a tight-binding calculation taking into account the Gaussian distribution of the SWNTs radius.17 Using their procedure, we calculated the photoemission spectra of the samples. The standard de-
The C$_{60}$ filling factor of 85% in the present C$_{60}$ PPD-A composed of a SWNT with a radius of 0.7 nm and C$_{60}$ peas, the ratio of the number of carbon atoms included in a unit length in the C$_{60}$ peas to that in the SWNT is about 0.39. The ratio of the number of carbon atoms included in a SWNT was estimated to be 0.66 nm.

The partial density of states of the C$_{60}$ peas inside the SWNT was obtained by subtracting the empty SWNT spectrum from the C$_{60}$ PPD spectrum as follows: In a C$_{60}$ PPD-A sample, the minimal SWNT radius which can encapsulate C$_{60}$ fullerenes was estimated to be 0.66 nm. This value is in good agreement with the theoretical value of 0.64 nm predicted by Okada et al.$^3$ Taking into account the minimal radius of 0.66 nm, the filling factor for the C$_{60}$ PPD-B sample was estimated to be 40%.

The overall spectral shapes are similar to those of the C$_{60}$ solid spectra.$^{22–27}$ The peaks in a binding energy region between 5 and −5 eV are due to the π bands.$^{23}$ The peaks at binding energies ranging from $E_F$ to −5 eV are due to the π$^*$ band structures.

The C$_{60}$ pea spectra near $E_F$ obtained for the present PPD samples are shown in Fig. 5, together with the spectra of a C$_{60}$ fcc solid obtained by Takahashi et al.$^{25}$ and Weaver.$^{26}$ The peak at 2.3 eV is derived from a HOMO with $h_u$ symmetry with fivefold degeneracy. The peak at 3.6 eV is derived from the next HOMO (NHOMO) with $g_u$ and $h_u$ symmetry with ninefold degeneracy. The NHOMO and HOMO peak positions are nearly equal to the respective corresponding peak positions of the C$_{60}$ solid spectra.$^{25,26}$ The peak located at a binding energy of −1.1 eV can be assigned to a highest occupied molecular orbital (LUMO) level with $t_{1u}$ symmetry with threelfold degeneracy of the C$_{60}$ pea, although the LUMO peaks showed different spectral shapes depending upon the conditions of measurement.$^{25,26}$ According to the DFT calculation of Okada et al.$^{3,4}$ and Otani et al.$^5$ the photoemission spectra of the C$_{60}$ PPD and SWNT, respectively, which were normalized so as to have the same integrated intensity after subtraction of respective inelastic backgrounds. In this study, the inverse photoemission spectra were measured with TPE mode using $E_i=76$ eV. The inverse photoemission spectrum in Ref. 25 was measured with BIS mode detecting $E_p=9.5$ eV and in Ref. 26 with TPE mode using $E_i=19.25$ eV.
The $t_{1u}$ level of the C$_{60}$ pea intersects with $E_F$ when the SWNT radius is larger than 0.64 nm. However, as shown in Fig. 5, there is no structure in binding energies ranging from the onset of the HOMO peaks to $E_F$ with the present PPD-A sample, which has a SWNT mean radius of 0.7 nm; the $t_{1u}$ peak of the C$_{60}$ peas stays above $E_F$. These results are consistent with the experimental results of the potassium and electrochemical doping effect and EELS, and with the prediction made by Dubay and Kresse using the DFT calculation.

As mentioned above, the present photoemission and inverse photoemission data indicate that the $t_{1u}$ level of the C$_{60}$ peas stays above $E_F$ even when the SWNT mean radius is larger than 0.7 nm. If electrons transfer from the SWNT to the C$_{60}$ peas under encapsulating C$_{60}$ fullerenes, the unoccupied $t_{1u}$ level of the C$_{60}$ peas can shift toward $E_F$. We must, therefore, consider the effect of charge transfer on the $t_{1u}$ level of the C$_{60}$ peas. The doping effect on the electronic structure of C$_{60}$ fullerenes has been investigated on A$_x$C$_{60}$ (A=alkali metal) solids, which exhibit a variety of interesting electronic properties ranging from insulators to high-$T_C$ superconductors. Regarding doped A$_x$C$_{60}$ solids, when a triply degenerated $t_{1u}$ level of C$_{60}$ fullerenes is partially filled with doped carriers, it is well known that the Jahn-Teller effect is consequently induced. Also, as for C$_{60}$ PPDs, the degeneracy of the $t_{1u}$ level of the C$_{60}$ peas is expected to be removed, because the symmetry of the doped C$_{60}$ cage in SWNT is lowered from the icosahedral $I_h$ symmetry. As a result, static lattice distortion of the C$_{60}$ cage will occur, which might lead to structural deformation of the SWNT, such as undulation of the SWNT wall. However, taking into account the fact that Peierls instability due to a lattice distortion does not occur in SWNTs, such a structural transformation is likely to be blocked because of the high energy cost of changing the SWNT geometry. Thus, it is probable that electron doping to the $t_{1u}$ level of the C$_{60}$ peas does not occur in C$_{60}$ PPDs.

Okada et al. and Otani et al. proposed an energy shift of the $t_{1u}$ level of C$_{60}$ peas originating from hybridization between the C$_{60}$ $\pi$ states and NFE states of SWNTs; they indicated that electrons are transferred mainly from $\pi$ orbitals of the SWNT to the interstitial space between the SWNT and C$_{60}$ peas. According to their DFT calculation, a downward shift of the electronic levels of C$_{60}$ peas occurs, while on the other hand, the occupied $\pi$ band of the SWNT shifts toward $E_F$ by about 0.1 eV. As shown in Fig. 3, however, the VHS peaks in the C$_{60}$ PPD spectra are located at the same binding energies as their respective VHS peaks in the SWNT spectra within the experimental accuracy. This fact demonstrates that such charge transfer is negligibly small.

The NHOMO peak width in the C$_{60}$ pea spectrum seems to be slightly narrower than that in the C$_{60}$ solid spectrum obtained by Golden et al. under similar experimental conditions, while the HOMO peak width is similar. The full width at half maximum (FWHM) of the NHOMO peak in the C$_{60}$ pea spectrum was estimated to be 0.6–0.7 eV, which is slightly narrower than 0.8 eV in the C$_{60}$ solid spectrum. In fcc crystal geometry, inter-fullerene electron hopping results in band dispersion of the $\pi$ states, so that broad HOMO and NHOMO peaks are observed in the C$_{60}$ photoemission spectrum. According to the angle-resolved photoemission study by Gensterblum et al., dispersion of the HOMO bands in C$_{60}$ solids is of the order of 0.4 eV. Within a simple tight-binding model, the intrinsic band width depends, to the first order, only on intermolecular $\pi$ band overlap, and is proportional to $nt$, where $n$ is the number of nearest neighbor fullerenes, and $t$ is the nearest neighbor transfer energy integral, which depends on the molecular orbital and inter-fullerene distance $d$. In an ideal C$_{60}$ chain, $n$ is reduced from 12 in the C$_{60}$ fcc solid to 2. The distance $d$ between adjacent C$_{60}$ peas was estimated to be about 0.95 nm by electron and x-ray diffraction measurements, shrinking from $d=1.0$ nm for the C$_{60}$ fcc solid. Using the empirical relationship $t=0.27d^{2.7}$, the inherent $\pi$ band width of an ideal one-dimensional C$_{60}$ chain is reduced by a factor of 0.8 from that in the C$_{60}$ fcc solid; dispersion of the HOMO bands of the C$_{60}$ chain is expected to be of the order of 0.08 eV, which is much smaller than the observed width.

Hornbaker et al. discussed the degree of electron hopping between adjacent C$_{60}$ peas, and between a C$_{60}$ pea and SWNT. From a semiempirical calculation with a strong coupling energy of 1.25 eV between SWNT $\pi$ states and the $t_{1u}$ states of the C$_{60}$ pea, they concluded that electron hopping between adjacent C$_{60}$ peas is not as dominant as indirect electron hopping between C$_{60}$ peas through the SWNT. If their conclusion is applied to the whole $\pi$ bands of the C$_{60}$ peas, the HOMO and NHOMO peaks in the C$_{60}$ pea spectrum should be broader than those in the C$_{60}$ solid spectrum, which is contrary to our result. On the other hand, according to the DFT calculation by Lu et al., the electron transfer energy between the SWNT and C$_{60}$ $\pi$ states is much weaker, $\sim$0.1 eV. This implies that the $\pi$ derived peak width in the C$_{60}$ pea spectrum should be narrower than those in the C$_{60}$ solid spectrum. The observed narrowing of the NHOMO width is qualitatively consistent with the prediction of the DFT calculation.

In summary, we successfully observed C$_{60}$-derived structures in the valence-band photoemission and inverse photoemission spectra of C$_{60}$ PPDs. The C$_{60}$ pea spectra exhibited structures similar to those in the C$_{60}$ solid spectra. We did not find evidence showing a relative energy shift of the electronic levels between C$_{60}$ and SWNT in the C$_{60}$ PPD. This fact indicates that unusual electronic properties, such as the theoretically predicted multicarrier character, cannot be expected with encapsulation of C$_{60}$ fullerenes.

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