Ultraviolet photoelectron spectra of $Sc_3C_2@C_{80}$

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ABSTRACT

$Sc_3C_2@C_{80}$ is one of the well studied endohedral fullerenes. Recent band calculation suggests the possibility of its semimetallic behavior due to the small band gap (0.07 eV). We measured the Ultraviolet Photoelectron Spectra (UPS) of $Sc_3C_2@C_{80}$ and estimated the lower limit of the band gap to be 0.2 eV. A simulated spectrum obtained by averaging the results of DFT calculations on two stable Sc_3C_2 geometries reproduces the UPS well. In conclusion, $Sc_3C_2@C_{80}$ thin film is not a semimetal but a semiconductor. The discrepancy between the experimental and previously calculated results might be attributed to the coexistence of two Sc_3C_2 geometries.

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1. Introduction

Since the first macroscopic production of $La@C_{82}$ in 1991 [1], endohedral metallofullerenes have attracted much attention in both fundamental and applied research. Intramolecular charge transfer from encapsulated species to the carbon cage gives them unique and different characteristics from empty fullerenes. A fullerene cage encapsulates not only pure metals but also metal clusters such as metal nitride, metal carbide, metal sulfide, and so on [2]. $Sc_3C_2@C_{80}$ is one of such endohedral cluster fullerenes [3] and well studied because its highly symmetric I_h cage structure is expected to result in unique properties. Recently, Sato et al. reported considerably high carrier mobility (the highest among the polycrystalline endohedral fullerene films) and high electrical conductivity of polycrystalline $Sc_3C_2@C_{80}$ film compared to those of $La_2@C_{80}$ and $Sc_3N@C_{80}$ [4]. Their DFT calculation suggests that high conductivity of $Sc_3C_2@C_{80}$ is attributed not only to the high carrier mobility but also to its small band gap (0.07 eV), and that $Sc_3C_2@C_{80}$ can be considered as a semimetal at room temperature. To examine whether $Sc_3C_2@C_{80}$ really has such a small band gap, we measured the Ultraviolet Photoelectron Spectra (UPS). This letter presents the experimental information on the band gap of $Sc_3C_2@C_{80}$, and discusses the difference between the measured UPS and the results of DFT calculations.

2. Experimental and calculation method

$Sc_3C_2@C_{80}$ was synthesized according to the literature procedures [5]. The UPS were measured by the photoelectron spectrometer at the beamline 8B2 at the Ultraviolet Synchrotron Orbital Radiation Facility (UVSOR), and by our laboratory equipment which consists of He-Iα ($h\nu$ = 21.218 eV) discharge lamp (combination of MB Scientific L-1 and M-1) and a SCIENTA SES-100 electron energy analyzer. All the spectra are referenced to the Fermi level of the substrate, which was determined by measuring the Fermi edge of the gold deposited on a molybdenum disk. The $Sc_3C_2@C_{80}$ specimen for the UPS measurements were deposited in situ onto this gold-deposited molybdenum disk by sublimation from a resistively heated quartz crucible.

The simulated spectra were obtained from the DFT calculation on a single molecule using Gaussian 03 [6]. The unrestricted B3LYP functional with the CEP-31G basis set was used for the structural optimization. The Kohn–Sham energy levels were calculated on the optimized structure by using the unrestricted B3LYP functional with the TK/NOSeC-V-TZP basis set [7] for scandium atoms and the 6-31G(d) basis set for carbon atoms.

3. Results and discussion

Figure 1 shows the UPS of $Sc_3C_2@C_{80}$ measured at various incident photon energies. The spectra exhibit seven peaks denoted as

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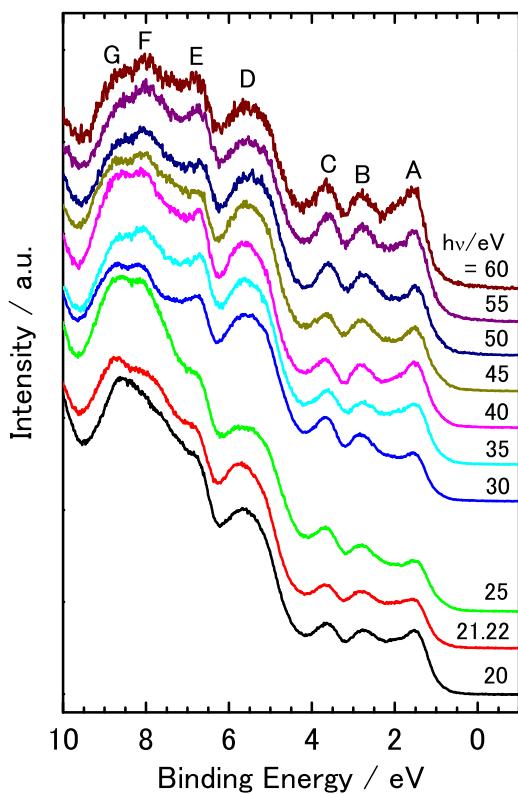
Figure 1. The incident photon energy dependence of the UPS of $Sc_3C_2@C_{80}$.

Figure 2. (a) The secondary electron cut off and (b) the onset of the UPS of $Sc_3C_2@C_{80}$.

Figure 3. Top and side view of the uB3LYP/CEP-31G optimized structures of $Sc_3C_2@C_{80}$.

A–G in the figure. The intensity ratios of those peaks oscillate with the incident photon energy, which is due to the spherical shape of the molecule and is the characteristics of the UPS of fullerenes [8–11]. Figure 2 shows the secondary electron cut-off and the onset of the UPS of $Sc_3C_2@C_{80}$. From the secondary electron cut-off, the work function of the $Sc_3C_2@C_{80}$ thin film is estimated to be 4.7 eV. The onset energy of the UPS (E_{onset}), which is the energy separation between the Fermi level and the valence band maximum, is 0.2 eV for $Sc_3C_2@C_{80}$. This value is much smaller than the E_{onset} of $La_2@C_{80}$ (0.77 eV) [12] and $Sc_3N@C_{80}$ (1.1 eV) [13]. The Fermi level of the n-type semiconducting fullerene thin film usually does not situate at the midgap but closer to the conduction band minimum [13,14], so the band gap of $Sc_3C_2@C_{80}$, $La_2@C_{80}$ and $Sc_3N@C_{80}$ is probably between E_{onset} and twice of the E_{onset}. The small onset energy of $Sc_3C_2@C_{80}$ is qualitatively consistent with the previous DFT calculation by Sato et al. [4] in which the band gap of $Sc_3C_2@C_{80}$, $La_2@C_{80}$ and $Sc_3N@C_{80}$ is estimated to be 0.07, 0.41 and 1.23 eV, respectively.

Although the underestimate of the band gap is one of the well-known problems of DFT calculation itself, the difference of the experimental and calculated band gap of $Sc_3C_2@C_{80}$ may be partly attributed to another factor; the motion of the encapsulated cluster. The thermal motion of the Sc_3C_2 cluster was implied by the ESR experiment [3]. Tan and Lu suggested theoretically that the geometry of the Sc_3C_2 cluster may fluctuate between trifoliate and planar structure [15], in which the C_2 unit is either perpendicular to or in the Sc_3 plane, whereas Sato et al. adopted only a planar-like structure [4]. In our DFT calculation, we obtained two optimized structures, isomer 1 (planar) and isomer 2 (trifoliate), and their total energy difference is only 0.84 kcal/mol (Figure 3). Simulated spectra of isomer 1 and 2 were obtained by broadening their Kohn–Sham energy levels with a Gaussian function (σ = 0.3 eV), and they are shown in Figure 4 with the UPS. The simulated spectra for both structures do not reproduce the UPS well, but a spectrum obtained by adding the simulated spectra of isomer 1 and 2 reproduces the UPS very well, especially for the width and the position of the
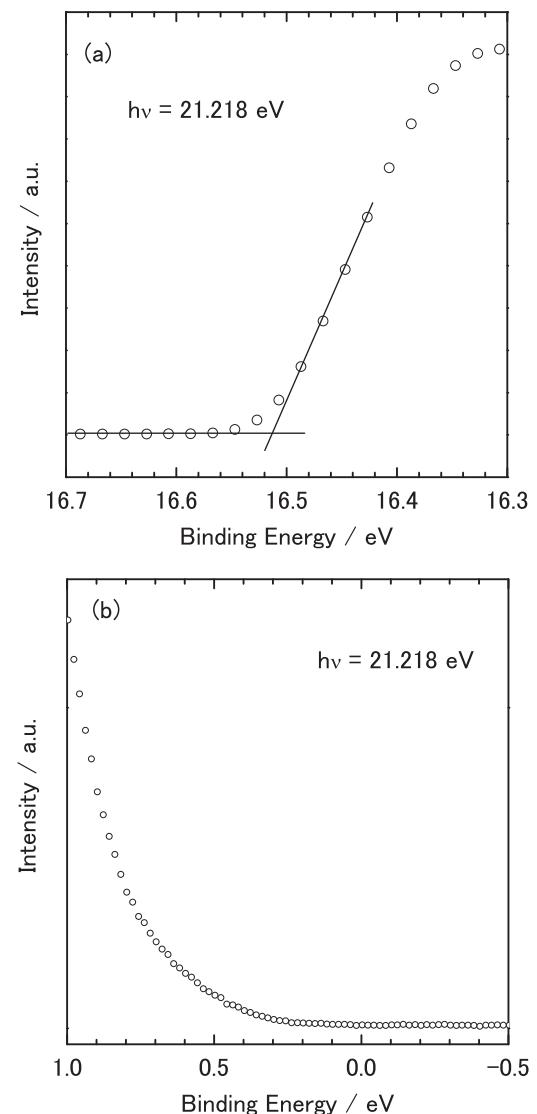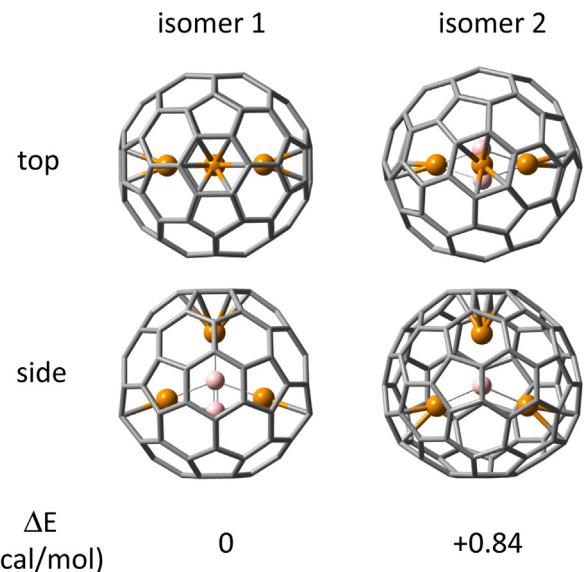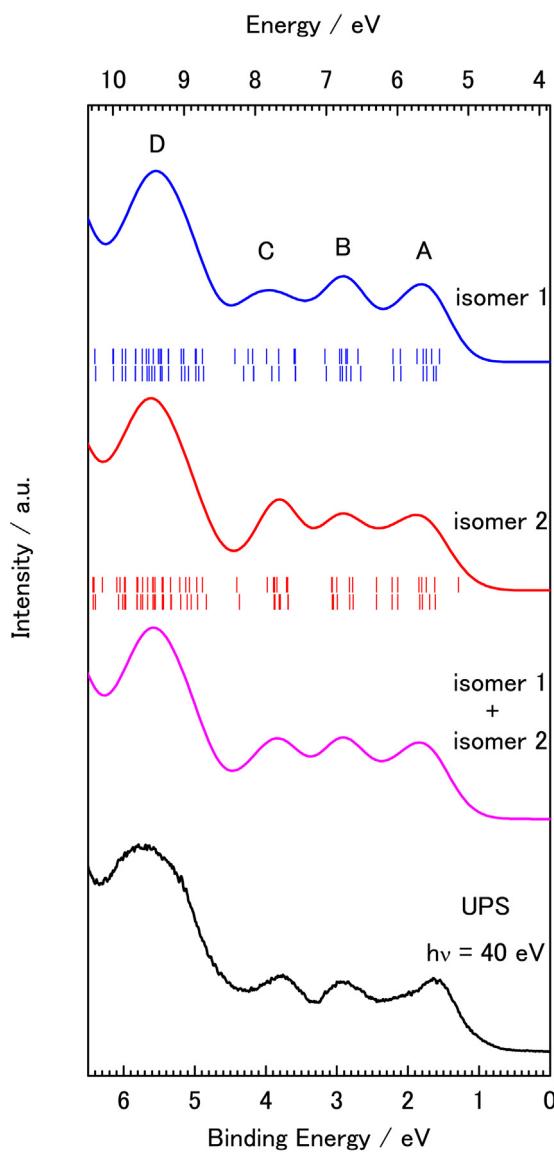
Figure 4. Comparison between the UPS and the simulated spectra. Vertical bars represent the Kohn–Sham energy levels of alpha and beta spin orbitals. The abscissa of the simulated spectra is shifted by 3.85 eV so that they can be easily compared with the UPS.

peak C. These findings indicate that the coexistence of these two structures should be adopted to consider the electronic structure of $Sc_3C_2@C_{80}$. Finally, comparison of the calculated wave functions of $Sc_3C_2@C_{80}$ and empty C_{80} (I_h symmetry) revealed that the

oxidation state of both isomers was $(Sc_3C_2)^{6+}@C_{80}^{6-}$. That is, entrapped cluster donates 6 electrons to the C_{80} cage.

4. Summary

$Sc_3C_2@C_{80}$ thin film is not a semimetal as predicted by the previous band calculation, but a semiconductor with a small band gap (more than 0.2 eV). Considering the coexistence of two different structures of $Sc_3C_2@C_{80}$ reduces the discrepancy between the measured UPS and the theoretical spectra calculated on a single molecule. It seems important for the band calculation of $Sc_3C_2@C_{80}$ to consider that it could take two stable structures.

Acknowledgements

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