Ultraviolet photoelectron spectra of $(YC)_2@C_{82}$ and $Y_2@C_{82}$

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Ultraviolet photoelectron spectra (UPS) of metallofullerenes, $(YC)_2@C_{82}$ (III) and $Y_2@C_{82}$ (III) were measured using a synchrotron radiation light source. The spectral onset energy of $(YC)_2@C_{82}$ (III) was determined to be 0.8 eV below the Fermi level, and that of $Y_2@C_{82}$ (III) was 0.45 eV, indicating the semiconductive nature of these metallofullerenes. The UPS consisted of numerous crests and troughs. Further, a change in intensity upon tuning the excitation energy was observed; however, the intensity of the change was not as large as those observed for other fullerenes. The UPS of two metallofullerenes basically resemble each other, although there are minute differences between them. The UPS of $(YC)_2@C_{82}$ (III) was easily reproduced by a simulated spectrum obtained by molecular orbital calculations assuming a C_{3v} (8) cage structure with four additional electrons on the cage. A difference spectrum between the UPS of $(YC)_2@C_{82}$ (III) and $Y_2@C_{82}$ (III) indicates the existence of additional electrons on the cage of $Y_2@C_{82}$.

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INTRODUCTION

The synthesis and isolation of numerous metallofullerenes have been reported,[1] and it has been established that encapsulated metal atoms donate electrons to the fullerene cage. Recently, encapsulation of multiple atoms, such as metal clusters,[2,3] metal nitrides,[4] and metal-carbon clusters,[5,6] inside the cage has been reported. These metallofullerenes are considered a different class from monometal-atom-encapsulated metallofullerenes from the viewpoint of electron transfer from the encapsulated atoms to the fullerene cage. This is thought to be because encapsulated atoms may form chemical bonds among them as well as they may form bonds to the carbon atoms that constitute the cage.

Recently, numerous yttrium- and carbon-atom-encapsulated metallofullerenes $[(YC)_2@C_{82}]$ have been reported, and three isomers were isolated.[6] NMR spectra of the isomers were obtained, and the symmetry was able to be identified due to the diamagnetic properties of the $(YC)_2@C_{82}$ isomers.[6] The symmetries of the cage structures of isomers II and III were conclusively determined as C_{2v} (9) and C_{3v} (8), respectively (numbers in parentheses correspond to the Fowler-Manolopoulos nomenclature[7]). Yttrium atoms have also been reported to be encapsulated into the fullerene cage, and three $Y_2@C_{82}$ isomers were identified.[5] An NMR spectrum of $Y_2@C_{82}$ (III) revealed that its cage structure is exactly the same as that of $(YC)_2@C_{82}$ (III). Further, their absorption spectra resemble each other, suggesting their analogous electronic structures.

Ultraviolet photoelectron spectroscopy has been a powerful tool used to determine the electronic structure of numerous compounds under investigation. Thus, the electronic structure of these two metallofullerenes $(YC)_2@C_{82}$ (III) and $Y_2@C_{82}$ (III) was investigated in order to determine

their electronic properties. The amount of electrons transferred from the encapsulated species to the cage is also of interest. If the oxidation state of encapsulated yttrium atoms in both metallofullerenes is the same, the effect of encapsulated carbon atoms should also be considered. If not, the number of electrons transferred in each metallofullerene should be clarified.

In the current work, ultraviolet photoelectron spectra (UPS) of $(YC)_2@C_{82}$ (III) and $Y_2@C_{82}$ (III) are presented and the electronic structures are examined in order to determine the effect of encapsulation of two additional carbon atoms in the C_{82} cage. The amount of electrons transferred from the encapsulated atoms to the cage with an aid of molecular orbital (MO) calculation is deduced. The effect of encapsulated carbon atoms is also discussed.

EXPERIMENT AND THEORY

Soot containing $(YC)_2@C_{82}$ and $Y_2@C_{82}$ was produced by direct-current arc heating of a Y_2O_3/graphite composite rod. $(YC)_2@C_{82}$ and $Y_2@C_{82}$ were extracted using o-xylene from the soot, and each isomer was isolated using multiple-stage high-performance liquid chromatography with toluene as an eluent. Details of the isolation of yttrium containing metallofullerenes have been described elsewhere.[5,6] Samples for the photoelectron measurements were prepared by the vacuum sublimation of metallofullerenes onto a gold-deposited molybdenum disk. Sublimation was conducted using a resistive heating quartz crucible in a preparation vacuum chamber directly attached to a photoelectron measurement chamber. The temperature of the crucible during sublimation of $Y_2@C_{82}$ was about 650 C, and that of $(YC)_2@C_{82}$ was about 700 C. The pressure of the chamber during the deposition went up to 2.0×10^{-5} Pa (base pressure
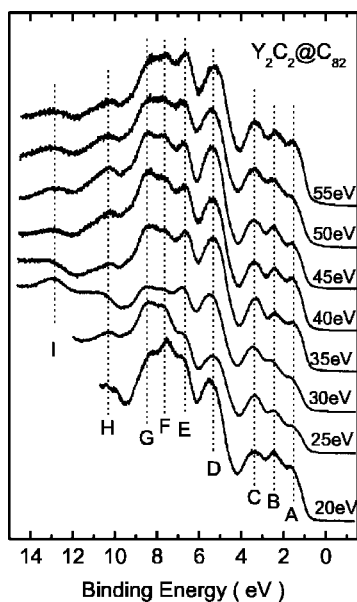
FIG. 1. Incident photon energy dependence of the ultraviolet photoelectron spectra of $(YC)_2@C_{82}$. Nine structures are observed and their intensity changes upon the tuning of the incident photon energy. Their peak position also shifts.
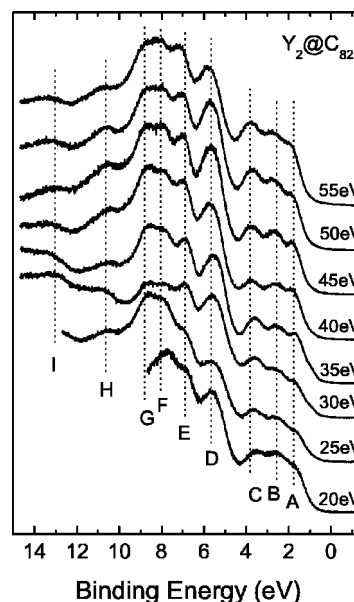

FIG. 2. Incident photon energy dependence of the ultraviolet photoelectron spectra of $Y_2@C_{82}$. Nine structures are observed and their intensity changes upon the tuning of the incident photon energy. Their peak position also shifts.

less than 1.0×10^{-7} Pa). The thickness of sublimed metallofullerenes deposited on the disk measured by the quartz thickness monitor located beside the disk did not reflect the actual thickness of the deposited film because the crucible was so collimated. Thus, although the reading from the thickness monitor was 0.3 nm, the thickness of the film was thought to be more than several nm, which was thick enough to prevent the penetration of photoelectrons from the substrate.

The spectra were measured using a photoelectron spectrometer at BL8B2 of UVSOR (Ultraviolet Synchrotron Orbital Radiation Facility) at the Institute for Molecular Science. The resolution of the spectrometer was 110 meV. Energy calibration of the spectra was carried out using the Fermi edge of a gold-deposited sample disk before each measurement. The spectra referenced against the Fermi level. The base pressure of the measurement chamber was $\leqslant 2.0 \times 10^{-8}$ Pa, and the pressure during the measurement was about 4×10^{-8} Pa. Semiempirical MO calculations were carried out using the program module Fijitsu WINMOPAC version 3. PM3 parametrization was adopted. The WINMOPAC program module could not handle encapsulated metal atoms; therefore, the calculation was carried out on both C_{3v} cages with an additional four or six electrons. Eigenvalues (EV's) were obtained after geometry optimization of the fullerene cage. Calculated EV's were broadened with Gaussian functions in order ot obtain simulated spectra.

RESULTS AND DISCUSSION

Figures 1 and 2 show the valence band UPS of $(YC)_2@C_{82}$ (III) and $Y_2@C_{82}$ (III) obtained with $h\nu = 20-55$ eV photon energy. Their spectral onsets were 0.8 eV and 0.45 eV, respectively. These values imply that

the energy level of the highest occupied molecular orbital (HOMO) of $Y_2@C_{82}$ (III) lies above that of $(YC)_2@C_{82}$ (III). Nine structures labeled $A-I$ were observed in the UPS of each metallofullerenes. The intensity of these structures oscillates when the incident photon energy is tuned, as was observed in the incident photon-energy-dependent photoelectron spectra of other fullerenes.[8–11] However, the change in the first three structures was not as significant as that observed in other fullerenes. The intensity ratio of structure A to structure C in $(YC)_2@C_{82}$ (III) changed from 1:2 ($h\nu = 25$ eV) to 4:5 ($h\nu = 40$ eV). In $Y_2@C_{82}$ (III), the intensity ratio of structure A to C ranged from 2:3 ($h\nu = 25$ eV) to almost unity ($h\nu = 40$ eV). The intensity oscillation observed in empty fullerenes and other metallofullerenes is significantly larger; in C_{60} the intensity ratio of the first band (derived from the highest occupied molecular orbital) to the second, ranges from 1:4 to 5:4,[12] and in $La@C_{82}$ the ratio of the second to the third band ranges from 1:2 to slightly larger than unity.[10] The origin of the intensity oscillation is believed to be derived from interference of ejected photoelectrons from a large molecular cage, about 1 nm diameter.[12] Molecular orbitals that contribute to form structure A or C of the UPS of $(YC)_2@C_{82}$ (III) and $Y_2@C_{82}$ may have slightly different character compared with those of other fullerenes. A possible explanation for this observation follows. Electrons that are observed as structure A may be localized primarily between metal atoms and the carbon atoms that form the fullerene cage; that is, bond formation is implied. In this situation, photoelectrons responsible for structure A are ejected from much narrower region than the cage itself.

Peak positions of structures $A-I$ of the UPS of both metallofullerenes deviate when the incident photon energy is tuned. This corresponds to the intensity oscillation, as each structure consists of several electronic levels that may have

TABLE I. Position and range of structures of the UPS of $(YC)_2@C_{82}$ and $Y_2@C_{82}$ in eV.

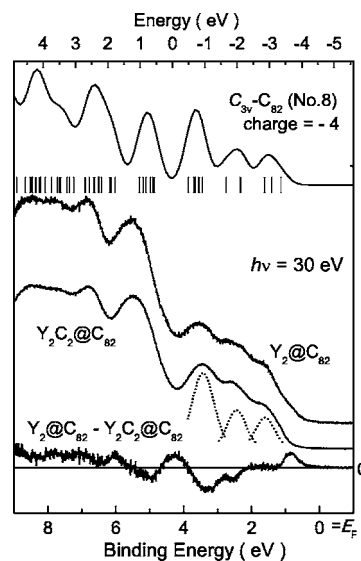| Structure	$(YC)_2@C_{82}$ Peak top (nominal)	Peak range	$Y_2@C_{82}$ Peak top (nominal)	Peak range
A	1.55	1.55–1.75	1.75	1.65–1.85
B	2.45	2.35–2.60	2.50	2.50–2.75
C	3.35	3.25–3.50	3.75	3.55–3.80
D	5.30	5.20–5.50	5.65	5.55–5.80
E	6.65	6.60–6.80	6.90	6.75–7.15
F	7.60	7.50–7.75	8.05	7.90–8.10
G	8.50	8.25–8.50	8.85	8.60–8.85
H	10.30	10.20–10.50	10.70	10.45–10.70
I	12.80	12.80–13.05	13.05	13.05–13.30

FIG. 3. Normalized spectra of $(YC)_2@C_{82}$ and $Y_2@C_{82}$ obtained with 30 eV photon energy (middle) and their difference spectrum (bottom). The first three structures of the spectrum of $(YC)_2@C_{82}$ are deconvoluted by dotted lines. The difference spectrum indicates that $Y_2@C_{82}$ possesses excess electrons in the vicinity of the Fermi level compared with $(YC)_2@C_{82}$. A simulated spectrum calculated by MO calculation assuming C_{3v}-C_{82} (8) cage structure with four additional electrons on the cage and bars indicating the position of calculated eigenvalues (upper). The scale of the simulated spectrum is shifted to have easy comparison with the UPS.

different incident photon energy dependence. This could be the reason of the peak position deviation. The observed peak positions and deviation ranges are summarized in Table I. The UPS of both $(YC)_2@C_{82}$ (III) and $Y_2@C_{82}$ resemble each other, and structures denoted with the same label correspond to each other. This finding suggests that the electronic structures of these metallofullerenes are analogous. However, the peak positions of the structures of $(YC)_2@C_{82}$ (III) lie at the lower-binding-energy side by around 0.2 eV compared with those of the corresponding positions for $Y_2@C_{82}$ (III). This finding together with the difference in the spectral onset energy is thought to be due to amount of electrons transferred from the encapsulated atoms to the fullerene cage. The carbon cage of $Y_2@C_{82}$ (III) appears to bear more electrons than that of $(YC)_2@C_{82}$ (III). This finding will be discussed in further detail.

UPS of multiple scandium encapsulated fullerenes, having a chemical composition of Sc_2C_{84} [$Sc_2@C_{84}$ (III) was assumed], have been reported.[13] NMR measurement of this metallofullerene suggested D_{2d} symmetry.[14] This was later confirmed by a combination of the maximum entropy method (MEM) and the Rietveld refinement of x-ray diffraction pattern.[15] However, the UPS of $Sc_2@C_{84}$ (Ref. 13) is almost identical to the present results for $(YC)_2@C_{82}$ (III). The UPS is a direct reflection of the electronic structure of the material investigated. The electronic structure of fullerenes is thought to strongly depend on the cage structure and the amount of additional electrons on the cage of metallofullerenes. Therefore, resemblance of these spectra implies that the metallofullerenes have identical cage structures, C_{3v}-$(MC)_2@C_{82}$ (M denotes metal atom), and that the structure of $Sc_2@C_{84}$ deduced from NMR analysis and the MEM-Rietveld analysis may be erroneous. The NMR spectral window adopted for $Sc_2@C_{84}$ may not have been sufficiently wide to detect all signals for the carbon-atom-constructed fullerene cage, and the starting model for MEM analysis in order to deduce the cage structure was not sufficient. Reexamination of NMR measurement and/or MEM-Rietveld analysis of $Sc_2@C_{84}$ seems to be required in order to clarify its cage structure.

In an effort to estimate the amount of transferred electrons, MO's of C_{3v}-C_{82} were calculated. There are two C_{3v} geometries for C_{82} cages that satisfy the so-called isolated pentagon rule: No. 7 and No. 8 by the Fowler-Manolopoulos nomenclature.[7] The 30-eV UPS of $(YC)_2@C_{82}$ shows the best agreement with a simulated spectrum assuming C_{3v}-C_{82}^{4-} (8) (Fig. 3). In Fig. 3 the simulated spectrum was shifted so that the peak positions of both the UPS and the simulated one show the best fit. The bars in Fig. 3 indicate the calculated eigenvalues. There are four EV's that constitute the first band, five EV's for the second, and nine EV's for the third band. The abscissa of the simulated spectrum is shifted in order to compare the spectra easily. The first three structures of $(YC)_2@C_{82}$ (III), $A-C$, derived mainly from π electrons, can be deconvoluted, as is shown in Fig. 3 by dotted lines. The ratio of the three deconvoluted areas is nearly 4:5:9, which is good agreement with the first three structures of the simulated spectrum. The UPS of the region with higher binding energy than 5 eV, which corresponds to σ electrons, cannot be reproduced precisely by the simulated spectra in terms of energy; however, both spectra show good one-to-one correspondence. This indicates that (a) the cage structure of $(YC)_2@C_{82}$ (III) is actually C_{3v} (8) as was proposed by the NMR measurement,[5,6] and (b) four electrons are transferred from the encapsulated atoms to the cage.

The oxidation state of scandium atoms in $Sc_2@C_{84}$ [as described above; however the actual structural formula of this metallofullerene must be $(ScC)_2@C_{82}$, hereafter described as $Sc_2@C_{84}$] was estimated by MEM-Rietveld

analysis[15] to be 2.2, and Raman spectroscopy[16] indicated more than two electrons were transferred from the scandium atoms. X-ray absorption measurements on $Sc_2@C_{84}$ (Ref. 13) indicated 2.6+ as the formal charge on each scandium atom. Both yttrium and scandium are group-3 elements. Yttrium is more easily ionized than scandium. It is highly plausible that the oxidation state of Y in $(YC)_2@C_{82}$ is higher than that of Sc in $Sc_2@C_{84}$. However, as described above, the UPS of $(YC)_2@C_{82}$ is well reproduced by the simulated spectrum assuming a C_{3v}-C_{82}^{4-} (8) cage structure. A reasonable explanation is that each yttrium atom donates about two electrons to the cage and another electron lies on the encapsulated carbon atom in order to form carbide or make chemical bonds with encapsulated carbon atoms. Thus, the resulting oxidation state of the encapsulated yttrium atom is around 3+.

Figure 3 shows a difference spectrum obtained by subtracting the UPS of $(YC)_2@C_{82}$ from that of $Y_2@C_{82}$. Subtraction was performed after normalizing the UPS by the intensity of structure D for each UPS (the UPS of both metallofullerenes shown in Fig. 3 are the thus obtained normalized spectra). The difference spectrum reveals a small structure between 0.4 and 1.2 eV, with an area of about a quarter of deconvoluted structure A. This suggests that $Y_2@C_{82}$ possesses more electrons than $(YC)_2@C_{82}$ in the vicinity of the Fermi level. Assuming that structure A of the UPS of $(YC)_2@C_{82}$ is derived from four MO's (eight electrons), it can be concluded that about two electrons produce the small structure in the difference spectrum. As described above, there are an additional four electrons on the cage—that is, $(YC)^{2+}_2@C_{82}^{4-}$. Therefore, the oxidation state of $Y_2@C_{82}$ is thought to be $Y^{3+}_2@C_{82}^{6-}$. A simulated spectrum obtained by MO calculations assuming a C_{3v}-C_{82}^{6-} (8) cage structure reproduces the UPS of $Y_2@C_{82}$ fairly well. The upper valence band (0–5 eV) UPS of $Y_2@C_{82}$ shows three distinct structures A–C, but MO calculations give four corresponding bands. Close inspection of the UPS of $Y_2@C_{82}$ shown in Fig. 3 reveals a faint shoulder at around 0.8 eV, which is

almost smeared out by structure A. The following explanation is offered in order to explain the reason that the MO calculations were not able to reproduce the UPS of $Y_2@C_{82}$ satisfactory: Calculation was performed only on the ionized state, not on the actual atom-encapsulated neutral state; therefore, the MO's of additional electrons were to spread out in the higher-energy region. Calculations including encapsulated atoms may reproduce the UPS much better.

CONCLUSION

The UPS of both $(YC)_2@C_{82}$ and $Y_2@C_{82}$ show intensity oscillations upon tuning of the incident photon energy; however, the change in the first few structures (due to π electrons) is not significant compared to that of other fullerenes. This implies that the nature of such structures may differ slightly from other structures; some of these electrons may be localized at a much narrower area than others on the fullerene cage. Bonds between yttrium atoms and both encapsulated and cage carbon atoms are thought to form. The UPS of $(YC)_2@C_{82}$ (III) is well reproduced by the simulated spectrum assuming a $C_{3v}(8)$-C_{82}^{4-} structure, confirming the cage structure deduced from NMR analysis. This indicates the transfer of four electrons to the cage—namely, a $(YC)^{2+}_2@C_{82}^{4-}$ electronic structure. The UPS of both $(YC)_2@C_{82}$ and $Y_2@C_{82}$ resemble each other; however, the difference spectrum indicates two additional electrons on the cage of $Y_2@C_{82}$. Thus, the oxidation state is thought to be $Y^{3+}_2@C_{82}^{6-}$.

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