Electronic Structure of Yttrium and Carbon Atoms Encapsulated Metallofullerenes, $Y_2C_2@C_{82}$: Ultraviolet Photoelectron Spectroscopy and Theoretical Calculation

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Ultraviolet photoelectron spectra (UPS) of two yttrium atoms and two carbon atoms encapsulated metallofullerenes, $Y_2C_2@C_{82}$ were measured using a synchrotron radiation light source. Their upper valence band UPS differ significantly from each other, while the lower valence band ones are almost the same. The UPS of $Y_2C_2@C_{82}$ (II) could be well reproduced by simulated spectra obtained with a Gaussian 03 program module assuming a distorted Y_2C_2 tetragonal form in C_{2v} C_{82} cage structure.

Multiple atoms, such as metal clusters,[1,2] metal nitrides,[3] and metal–carbon clusters[4,5] can be incorporated into the fullerene cage. These endohedral fullerenes are considered a different class from mono-metal atom encapsulated metallofullerenes ($M@C_{82}$), since the inner space of the cage seems to be too narrow to accommodate multiple atoms so that an interaction between the cage and entrapped atoms might be much larger than that in $M@C_{82}$.

Recently, three metallofullerenes in which yttrium and carbon atoms were encapsulated $Y_2C_2@C_{82}$ have been isolated[5] as well as $Y_2@C_{82}$ isomers.[4] NMR spectra of the three $Y_2C_2@C_{82}$ isomers revealed the symmetry of the cage structures of $Y_2C_2@C_{82}$ (I) to be C_s (82:6), $Y_2C_2@C_{82}$ (II) to C_{2v} (82:9) and $Y_2C_2@C_{82}$ (III) to C_{3v} (82:8) (Numbers in parenthesis corresponds to the Fowler and Manolopoulos nomenclature[6]). Absorption spectra of the three isomers differed significantly; the visible and near IR absorption edge of isomers I and III was respectively ca. 1400 and 1100 nm, while that of isomer II was much longer than 2000 nm. An NMR spectrum of $Y_2@C_{82}$ (III) revealed that its cage structure was exactly the same as that of $Y_2C_2@C_{82}$ (III).[4] Further, their absorption spectra resembled each other, suggesting their analogous electronic structures. Ultraviolet photoelectron spectra (UPS) of $Y_2C_2@C_{82}$ (III) and $Y_2@C_{82}$ (III) have been measured and it was found that their UPS were analogous but their difference spectrum revealed that additional two electrons were transferred from the entrapped atoms to the cage of $Y_2@C_{82}$ (III).[7]

Extensive UPS study of metallofullerenes established an empirical rule that the cage structure is principally responsible for the electronic structure of mono-metal atom encapsulated metallofullerenes.[8–10] That is, metallofullerenes of the same cage symmetry with an incorporated metal atom of the same oxidation state give essentially the same UPS. This empirical rule also holds in $Y_2C_2@C_{82}$ (III) and $Y_2@C_{82}$ (III), both of which have the same C_{2v} cage structure. However, it does not hold in $Ti_2C_2@C_{78}$ and $La_2@C_{78}$ although these endohedral fullerenes have the same D_{3h} (78:5) structure.[11] The case of $Ti_2C_2@C_{78}$ and $La_2@C_{78}$ is considered rather exceptional, since Ti atoms are fond of forming carbide and hybridization of orbitals derived from entrapped Ti and caged C atoms deforms the electronic structure of the fullerene cage so much. It is worthwhile to examine whether the empirical rule holds in three $Y_2C_2@C_{82}$ isomers.

In the current work, ultraviolet photoelectron spectra of $Y_2C_2@C_{82}$ (I) and $Y_2C_2@C_{82}$ (II) are presented, and the UPS of three yttrium carbide encapsulated fullerenes are compared. Molecular orbital calculation of $Y_2C_2@C_{82}$ (II) is also presented to consider the electronic structure and possible geometry of entrapped atoms.

Experimental and Calculation Method

Soot containing $Y_2C_2@C_{82}$ was produced by direct-current arc heating of an Y_2O_3/graphite composite rod. $Y_2C_2@C_{82}$ and $Y_2@C_{82}$ were extracted from the soot using *o*-xylene, 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.[4,5] Samples for the photoelectron measurements were

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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 $Y_2C_2@C_{82}$ (I) sublimation was at about 950 K and that of $Y_2C_2@C_{82}$ (II) was 985 K. The pressure of the chamber during the deposition went up to 4.5×10^{-6} Pa for isomer I (base pressure before the deposition was less than 1.0×10^{-7} Pa) and 1.5×10^{-5} Pa for isomer II (base pressure before the deposition was less than 7.5×10^{-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 around 0.4 nm, the thickness of the film was thought to be more than several nm, since the gold Fermi edge was not observed after the sample deposition.

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 were referenced against the Fermi level. The base pressure of the measurement chamber was $\leq 2.1 \times 10^{-8}$ Pa, and the pressure during the measurement was about 4×10^{-8} Pa.

Molecular orbital was calculated with a Gaussian 03 program module. Geometry of C_{2v}-$Y_2C_2@C_{82}$ was optimized at the Hartree–Fock level using the STO-3g basis set. The initial positions of Y atoms were arranged to keep C_{2v} cage symmetry with their separation distance of 0.33 nm. The DFT calculation was performed on the optimized C_{2v}-$Y_2C_2@C_{82}$ structure using the B3LYP hybrid functional to obtain the Eigen values (ionization potentials). Basis sets for C atoms were 6-31G(d) and those for Y atom were the TK/NOSeC-V-TZP function.[12,13] Simulation spectra were obtained by broadening the Eigen values with Gaussian functions of 0.2 eV full width at half maximum.

Results and Discussion

Figures 1 and 2 show the valence band UPS of $Y_2C_2@C_{82}$ (I) and $Y_2C_2@C_{82}$ (II) obtained with $h\nu = 20$–55 eV photon energy. Their spectral onsets were 0.88 and 0.67 eV, respectively, and the previously reported value of $Y_2C_2@C_{82}$ (III) was 0.8 eV.[7] The absorption spectral edge of these three isomers is 1400 nm (0.89 eV), longer than 2000 nm (0.62 eV) and 1100 nm (1.13 eV), respectively. The absorption edge corresponds to the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The UPS spectral onset relates to the HOMO that is to form the valence band and the conduction band derived from the LUMO. It is considered that the Fermi level situates at the middle of the HOMO–LUMO gap. Thus, there is a correlation between the absorption spectral edge (HOMO–LUMO gap) and the UPS spectral onset. $Y_2C_2@C_{82}$ (II) has the smallest onset energy and the smallest spectral absorption edge among the three isomers. This finding suggests that these two physical quantities have a correlation. However, the relation between absorption spectral edge and UPS spectral onset of $Y_2C_2@C_{82}$ (I) and $Y_2C_2@C_{82}$ (III) is opposite to the expectation; the former has a smaller absorption edge by about 0.25 eV but has slightly greater UPS onset energy than the latter. This finding might relate to the positioning of the Fermi level in fullerenes: UPS and inverse photoemission experiments[14] indicated that the Fermi level did not necessarily locate at the middle of conduction and valence bands.

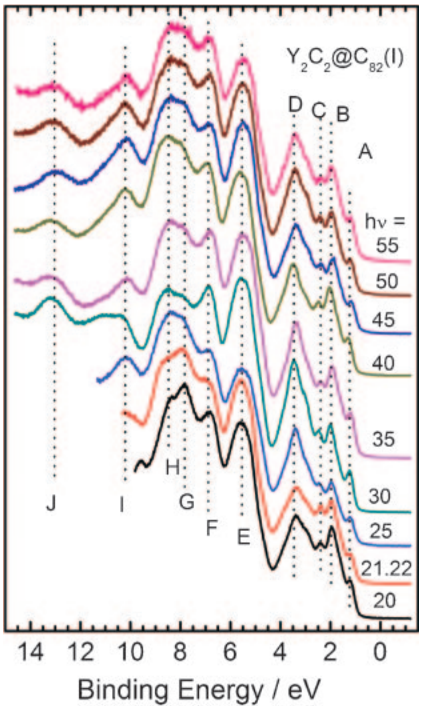

Figure 1. Ultraviolet photoelectron spectra of C_s symmetry $Y_2C_2@C_{82}$ (I) obtained with synchrotron light source. Numeric beside each spectrum indicates the photon energy.

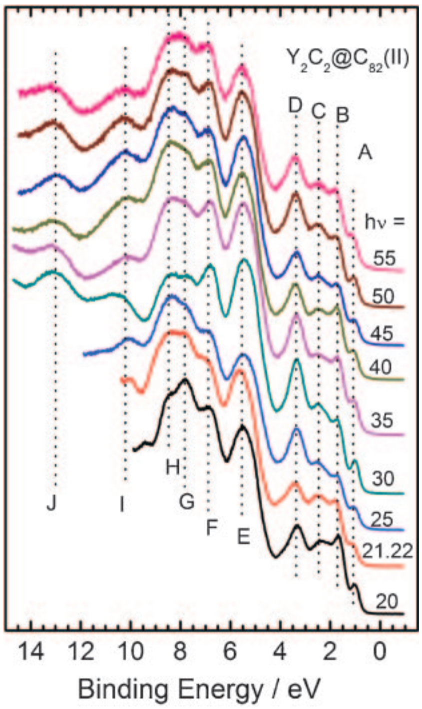

Figure 2. Ultraviolet photoelectron spectra of C_{2v} symmetry $Y_2C_2@C_{82}$ (II) obtained with synchrotron light source. Numeric beside each spectrum indicates the photon energy.

Table 1. Peak Position of Structures, ×1/eV

Structure	Peak top (nominal)			
	$Y_2C_2@C_{82}$ (I)	$Y_2C_2@C_{82}$ (II)	$Y_2C_2@C_{82}$ (III)$^{a)}$	$Y_2@C_{82}$ (III)$^{a)}$
A	1.26	1.10	1.55	1.75
B	1.98	1.74		
C	2.41	2.48	2.45$^{b)}$	2.50$^{b)}$
D	3.42	3.38	3.35$^{b)}$	3.75$^{b)}$
E	5.56	5.54	5.30$^{b)}$	5.65$^{b)}$
F	6.90	6.84	6.65$^{b)}$	6.90$^{b)}$
G	7.81	7.83	7.60$^{b)}$	8.05$^{b)}$
H	8.47	8.50	8.50$^{b)}$	8.85$^{b)}$
I	10.23	10.23	10.30$^{b)}$	10.70$^{b)}$
J	13.03	13.02	12.80$^{b)}$	13.05$^{b)}$

a) Data of $Y_2C_2@C_{82}$ (III) and $Y_2@C_{82}$ (III) were taken from Ref. 7. b) Labeling of higher binding energy structures of these two endohedral fullerenes were changed so that structures of nearly the same energy have the same labeling.

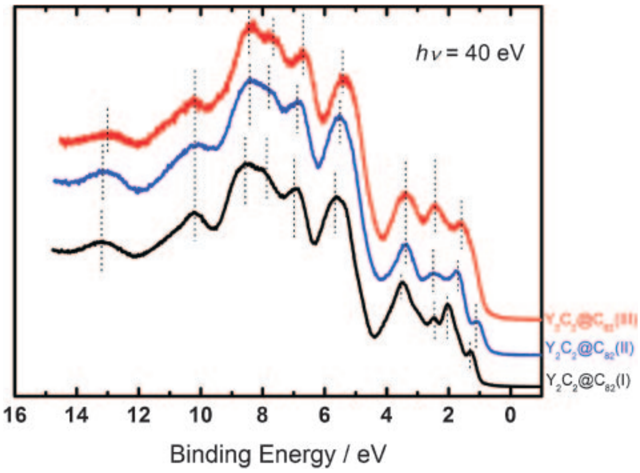

Figure 3. Ultraviolet photoelectron spectra of three $Y_2C_2@C_{82}$ (III) isomers obtained with 40 eV photon.

The UPS of $Y_2C_2@C_{82}$ (I) and $Y_2C_2@C_{82}$ (II) in 0–15 eV energy region show 10 explicit structures labeled by A–J in the figure. Their positions deviate slightly and their intensity changes when the incident photon energy is tuned, as has been observed in the UPS of other fullerenes.[7–11,14] Their approximate positions are summarized in Table 1. The peak positions of the UPS of $Y_2C_2@C_{82}$ (III) and $Y_2@C_{82}$ (III)[7] are also listed in Table 1. Peak labels of lower valence band structures of $Y_2C_2@C_{82}$ (III) and $Y_2@C_{82}$ (III) are changed from original labeling in Ref. 7, so that the structures of almost the same energy region have the same label. Most structures of the three $Y_2C_2@C_{82}$ isomers appear more or less at very close energy region, which will be discussed later.

As for the incident photon energy dependent intensity change, the change is very drastic. In the UPS of $Y_2C_2@C_{82}$ (I) the intensity of structure C is almost the same as that of structure B in the UPS obtained with 21.22, 25, 45, or 50 eV photons while it is clearly small in other UPS. Further, a shoulder structure is observed at around 3 eV. The intensity ratio of this shoulder to structure D varies from 84% ($h\nu = 20$ eV) to less than 70% ($h\nu = 50$ eV). Reversion of the intensity of structures is also found in the UPS of $Y_2C_2@C_{82}$ (II). Structure B is larger than structure C in the UPS obtained with 20 and 40 eV photons, but the relation is reversed in the UPS obtained with other incident photon energy.

Among the UPS obtained with various incident photon energy, the UPS obtained with 40 eV incident energy shows the upper valence band structures due to π-electrons (0–5 eV binding energy region) clearly as well as the deeper valence band structure due to σ-electrons. Thus 40 eV UPS of three $Y_2C_2@C_{82}$ isomers are shown in Figure 3 for comparison. The approximate peak energy regions are indicated with dot lines. As for the structures located at larger binding energy region than 4.5 eV, all spectra are almost identical and the peaks appear more or less at the same position although some of them deviate slightly as was described above and in Table 1. This spectral resemblance indicates that there is hardly any difference in the electronic structure of C–C bonding backbone (σ-electron bonding) of these three $Y_2C_2@C_{82}$ isomers. On the other hand, drastic difference is observed in the upper valence band region. While three large structures are observed in the upper valence UPS of $Y_2C_2@C_{82}$ (III), four or more structures are observed in those of isomers I and II. This finding is another example that the UPS of this energy region are characteristic to each fullerenes and it can be used as a fingerprint region to identify fullerenes. It should be noted that the first band (structure A) of $Y_2C_2@C_{82}$ (II) appeared at the smallest binding energy among the isomers, which seemed to correspond to its longest IR absorption edge.

Since a semiempirical calculation on a C_{3v}-C_{82} cage (82:8) assuming additional 4 electrons on the cage well reproduced the UPS of $Y_2C_2@C_{82}$ (III),[7] simulation spectra of $Y_2C_2@C_{82}$ (I) and (II) have been calculated using a Fujitsu Win MOPAC program module. However, simulation spectra obtained from the semiempirical calculation on cage structures assuming C_s (82:6) and C_{2v} (82:9) with four or six electrons on the cage show very poor correspondence to respective UPS. This was partly because of adding excess electrons to the cage. In this calculation there are no positive ions to concentrate electrons in the center of the cage, hence molecular orbitals to which excess electrons were to be seated became energetically unstable and split energy levels. Calculation on the whole metallofullerene molecule could avoid this disadvantage so ab initio calculation on C_{2v}-$Y_2C_2@C_{82}$ was performed. A C_{2v}-C_{82} isolated pentagon rule (IPR) satisfying structure was adapted as a starting geometry and geometry of entrapped atoms was varied. The initial geometry of entrapped atoms was chosen either square or tetragonal arrangement, but both geometries turned into a tetragonal form after geometry optimization. Although geometry optimization failed when the distance between entrapped carbon atoms was chosen as a single bond distance, it was successful when a double bond length was adopted. Using the optimized tetragonal structure of entrapped atoms and cage geometry, orbital energy was calculated and simulation spectra were obtained. Thus obtained the most stable structure is that Y atoms made bonds with three carbon atoms that constituted a hexagon ring (Figure 4a). The next most stable structure was

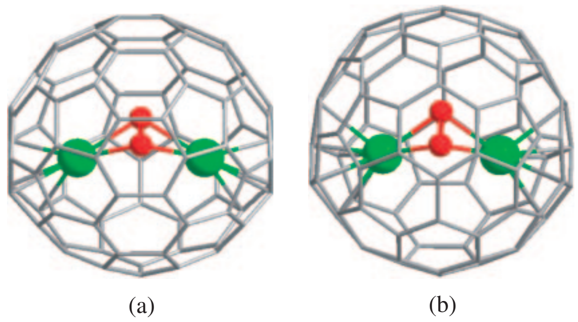

Figure 4. Optimized structure of C_{2v}-$Y_2C_2@C_{82}$. Green and red balls indicate entrapped yttrium and carbon atoms, respectively. Figure 4a is the most energetically stable structure and Y atoms situate on the hexagon rings (On 6). Figure 4b is the next stable structure and Y atoms situate on the pentagon rings (On 5).

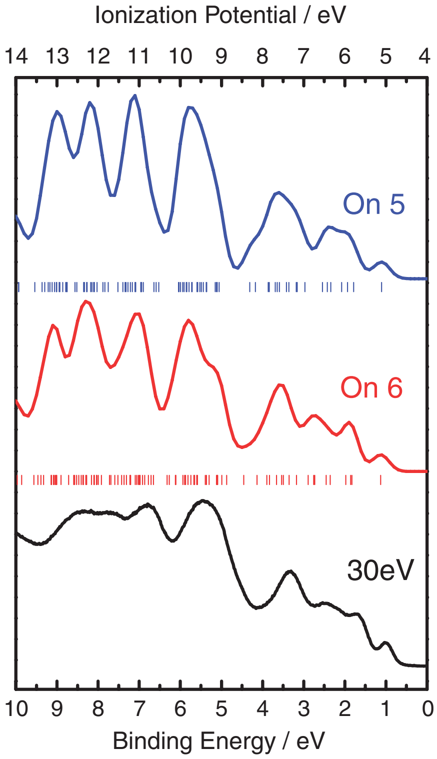

Figure 5. Ultraviolet photoelectron spectrum of C_{2v}-$Y_2C_2@C_{82}$ obtained with 30 eV photon and simulation spectra calculated from optimized geometry shown in Figure 4a (On 6) and Figure 4b (On 5).

characterized by Y atoms forming bonds with four carbon atoms that constituted a pentagon ring (Figure 4b). The formation energy difference between these two models was 8.3 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). In either structure the entrapped C–C distance was 0.127 nm, which was an intermediate bond length between C–C double and triple bonds.

Figure 5 shows simulation spectra obtained from the geometry shown in Figures 4a and 4b and the UPS obtained with 30 eV photon energy. The UPS was plotted as a function of binding energy (bottom axis) and the simulation spectra was plotted as a function of ionization potential obtained by using Koopmans' theorem. The simulation spectra were shifted so that both the UPS and the simulated ones had the best correspondence. These simulation spectra showed four distinct structures at the upper valence region and reproduce the UPS very well. This indicates that the entrapped Y_2C_2 cluster in C_{2v}-$Y_2C_2@C_{82}$ have tetragonal (bend) form as was predicted by theoretical calculation on $Sc_2C_2@C_{82}$.[15] It is hard to conclude the molecular structure of C_{2v}-$Y_2C_2@C_{82}$ from the comparison between the UPS and theoretical calculation, since the calculation did not reproduce the UPS completely. However, the Y atoms situated on the hexagon ring structure (On 6 model shown in Figure 4a) might be a more favorable structure because (a) it is more energetically stable, (b) the simulated spectrum (On 6 in Figure 5) reproduces the UPS much better, and (c) X-ray Rietveld analysis combined with maximum entropy method on $Y_2C_2@C_{82}$ (III) favors the Y atomic position on hexagon rings.[16]

Conclusion

The upper valence band UPS of three $Y_2C_2@C_{82}$ are completely different, which suggests that the cage structure dominates the π-electronic structure of endohedral fullerenes. On the other hand, their lower lying valence band UPS are analogous, which suggests cage structure is not a decisive factor to the σ-electronic structure. The simulation spectrum on C_{2v}-$Y_2C_2@C_{82}$ assuming tetrahedral structure of entrapped elements well reproduced the UPS, which suggests that entrapped atoms are not coplanar but in a tetragonal form.

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