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Ultraviolet Photoelectron Spectra of Mono Metal Atom Encapsulated Fullerenes

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Ultraviolet photoelectron spectra of mono metal atom encapsulated fullerenes, M@C_{82} (M = La, Gd and Sc), are measured with a synchrotron radiation light source. When the excitation energy is tuned, spectral intensity oscillation is observed in these mono metal atom encapsulated fullerenes as was in empty fullerene, C_{82}. Their incident photon energy dependence is essentially the same. Their spectra deeper than 5 eV are almost identical and are similar to those of empty fullerene. The noticeable difference among the spectra is in the energy region between the Fermi level and 4 eV, which reveals the degree of electron transfer from the metal atom to the fullerene cage.

Keywords: metallofullerene; electronic structure; UPS; fullerenes; photoelectron spectra

INTRODUCTION

Isolation and purification of mono metal atom encapsulated fullerenes (metallofullerenes) in macroscopic quantities have made it possible to investigate their properties, such as their molecular structure and electronic structure. The interpretation of ultraviolet photoelectron spectra (UPS) of metallofullerenes, M@C_{82} (M = La, Gd and Sc) has helped to clarify their electronic structure and indicates the amount of electrons transferred from the metal atom to the cage [1-5]. In this

paper, we compare the electronic structure of these fullerenes.

EXPERIMENTAL

Details of preparation and separation of La@C_{82} and Gd@C_{82} were described in Ref. [6]. A method adopted for the preparation and separation of Sc@C_{82} [7] is slightly different from the one used for La@C_{82} and Gd@C_{82}. The UPS were measured by a photoelectron spectrometer at BL8B2 of UVSOR in the Institute for Molecular Science [2-5].

RESULTS and DISCUSSION

Fig. 1 shows the UPS of the M@C_{82} (M = La, Gd and Sc) together with that of C_{82}. The spectra of metallofullerenes exhibit several distinct structures between the Fermi level and 7 eV. These structures are also observed in empty fullerene C_{82} except for the existence of structure indicated by ***N***. Appearance of structure ***N*** is obviously induced by an introduction of the metal atom into the cage. Among these fullerenes, structure ***B***, ***C***, and ***D*** are almost same in their position and intensity.

The intensity of these structures oscillates with the incident photon energy. The intensity of structures ***A*** - ***C*** is plotted in Fig. 2 as a function of the incident photon energy. The intensity of each structure is normalized by the sum of ***A*** - ***C***. It seems that the spectral dependence on the incident photon energy is essentially the same in these fullerenes. The intensity of structure ***A*** exhibits a maximum at 20 eV and a minimum at 30 eV. The intensity of structure ***B*** is low at 40 or 45 eV. The intensity ratio of ***A*** to ***B*** is almost unity at 20 or 40 eV, but it is 0.5 at 30 eV. Intensity of structure ***A*** and ***C*** exhibit opposite behavior on the incident photon energy dependence.

The intensity of structure ***N*** also oscillates upon the incident photon energy change, which is evidence of charge transfer from the metal atom to the cage. Interference among outgoing wave functions of

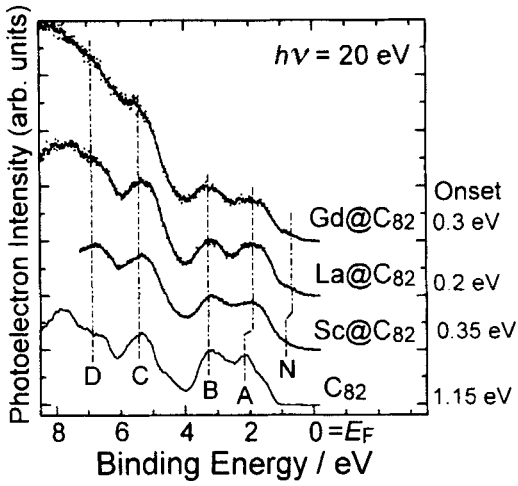

FIGURE 1. UPS of the mono metal atom encapsulated fullerenes. Excitation energy is 20 eV.

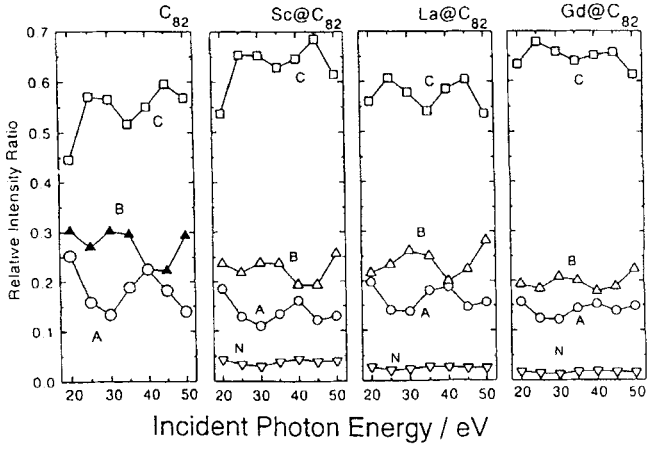

FIGURE 2. The relative intensity of the structures ***A*** - ***C*** of the fullerenes plotted as a function of the incident photon energy. The intensity of each structure is normalized by the sum of ***A*** - ***C***.

the emitted photoelectrons are able to explain the intensity oscillation [8, 9]. The basis for this explanation is that fullerene is spherical and photoelectrons are ejected from the carbon atoms constituting the cage of about 0.7 nm or more diameter. The fact that the intensity of N oscillates means that these electrons are not on the metal atom but actually on the cage. This is further evidence of electron transfer from the metal to the cage.

Scandium, lanthanum and gadolinium are group III elements and they are trivalent. It is probable that a trivalent atom gives three electrons to the cage. To understand the difference among the UPS of the upper valence band region, a comparison of the spectra of M@C_{82} (M = La, Sc) and C_{82} are useful. Analysis of the difference spectra reveals that there are two components just below the Fermi level (0.3 - 2.2 eV). In La@C_{82} the intensity ratio between the two components is 1 : 2, but it is unity in Sc@C_{82}. This finding implies that the amount of transferred electrons in La@C_{82} and Sc@C_{82} is 3 and 2, respectively.

There are theoretical calculations on the electronic structures of metallofullerenes. Fig. 3 shows the UPS of La@C_{82} and the calculated ionization potentials (I_Ps) of $La^{+3}@C_{82}^{-3}$ of four structures of different geometry [10]. In order to have better comparison of the UPS with the calculation, I_Ps are multiplied by 0.8, and broadened by a convolution with a 0.8 eV FWHM Gaussian. UPS of La@C_{82} gives the best fit with C_2 geometry among the 4 structures. Similar comparison was done on the spectrum of Sc@C_{82} and the calculated I_Ps of three $Sc^{+2}@C_{82}^{-2}$ structures of different geometry. It reveals that the C_{2v} geometry could be the precise structure of Sc@C_{82} (Fig. 4). This conclusion is supported by an X-ray powder study using the Rietveld analysis combined with maximum entropy method [11].

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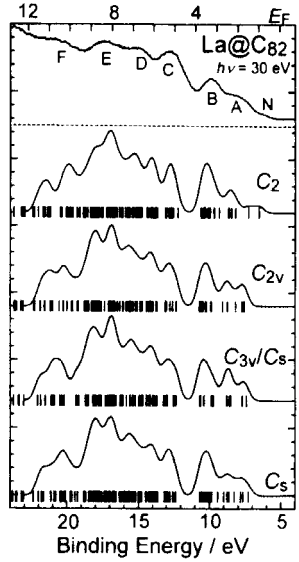

FIGURE 3. The UPS of La@C82 (upper part) and the calculated spectra obtained with four different structures (lower part). Note that energy scales for the UPS and calculated ones are different.

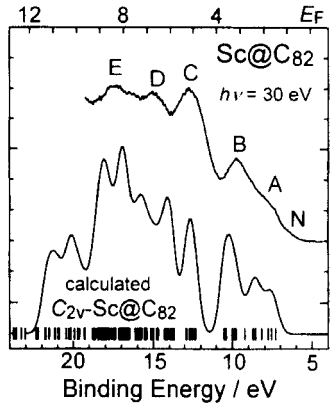

FIGURE 4. The UPS of Sc@C82 (upper part) and the calculated spectra of C_{2v} - $Sc^{+2}@C_{82}^{-2}$ (lower part). Note that energy scales for the UPS and calculated one are different.

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