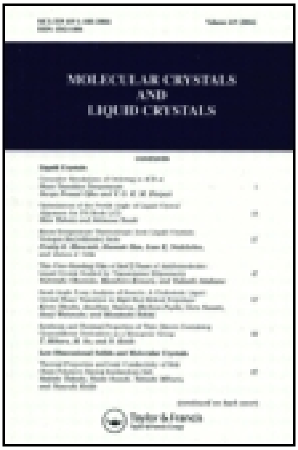

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Ultraviolet Photoelectron Spectra of Potassium Dosed Higher Fullerenes

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Ultraviolet photoelectron spectra of potassium dosed higher fullerenes are measured with a synchrotron radiation light source. Potassium dosing to higher fullerenes brings a new structure between the spectral onset of pristine fullerenes and the Fermi level. As the spectral edge of the new structure does not cross the Fermi level, potassium dosed higher fullerenes are not metallic but semiconductive. When the potassium is excessively dosed to the fullerenes, the lower binding energy structures above 5 eV become faint. In contrast to this phenomenon, four distinct structures appear between 5 and 14 eV.

Keywords: higher fullerene; electronic structure; photoelectron spectra; UPS; potassium doping

INTRODUCTION

In carbon soot, there are so-called higher fullerenes in addition to C_{60}. Alkali metal dosing to higher fullerenes is an issue to be considered, since the dosing may make the originally semi-conductive fullerenes metallic or possibly superconductive. This can be clarified by observing change of their electronic structure, particularly in the vicinity of the Fermi level (E_F) before and after the dosing [1]. The electronic state around the E_F level plays an important role in the nature of the material whether it is conductive or not. Ultraviolet photoelectron spectroscopy is a powerful tool to observe the electronic structure. We present ultraviolet photoelectron spectra (UPS) of potassium dosed higher fullerenes C_{76} and C_{82}, and discuss their electric structure with conjunction of the results of other higher fullerenes.

EXPERIMENTAL

Details of experimental procedure were basically the same as reported in ref. 2. Schematic illustration of the experimental setup is shown in Fig. 1. Specimens for the photoelectron measurement were prepared by the vacuum sublimation of fullerenes onto gold-deposited molybdenum disks. Sublimation was carried out from a resistive heating quartz crucible. The temperature of the sample disk was not controlled during sublimation. Potassium was provided from a pre-degassed SAES alkali-metal dispenser. The concentration of potassium to fullerene was estimated with an aid of a quartz-thickness monitor set beside the sample disk. There may be a systematic error in the potassium concentration, but the relative potassium ratio to fullerene was precise in a series of successive dosing. The K 3*p* spectra were also used to estimate the potassium concentration [3, 4] when it could be clearly observed. The spectra were measured by a photoelectron spectrometer at BL8B2 of UVSOR in Institute for Molecular Science. An energy calibration of the spectra was carried out using the Fermi edge of a gold-deposited sample disk before and after the measurement.

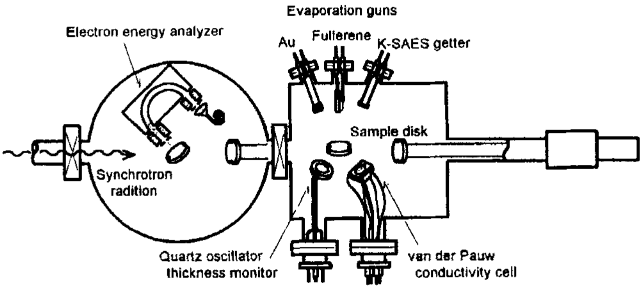

FIGURE 1. Schematic illustration of experimental setup.

RESULTS and DISCUSSION

Potassium dosing

Fig. 2 shows spectral change of the upper valence region of C_{76} and C_{82} induced by successive potassium dosing. Numeric beside the spectra indicates potassium concentration, x, in the formula of either K_xC_{76} or K_xC_{82}. At the early stage of potassium dosing, a new structure (N) appears between the spectral onset of pristine fullerenes and the E_F. This phenomenon was also observed in other fullerenes such as C_{78} [5], C_{96} [6], C_{102} [7], and C_{110} [8]. This is due to electron transfer from K 4s level to the LUMO of fullerenes. The spectral onset of higher fullerenes does not cross the E_F during the whole stage of potassium dosing except for C_{110} whose onset locates just at the E_F. This means that after potassium dosing higher fullerenes except for C_{110} are still semiconductive and C_{110} might be semi-metallic.

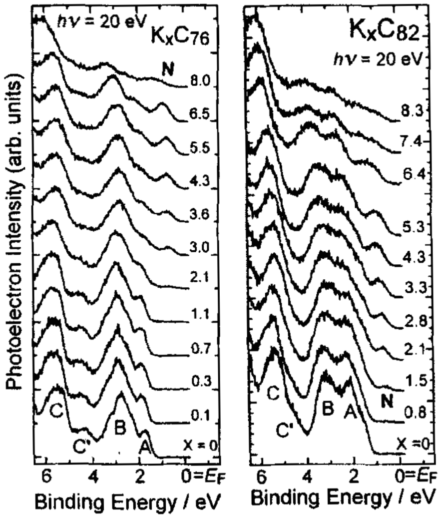

FIGURE 2. Spectral change of upper valence region of C_{76} and C_{82} films upon successive potassium dosing.

Excessive potassium dosing ($x > 4$)

Fig. 3 shows the spectral change of the whole valence band region of the fullerenes and K 3*p*. With increases in potassium dosage ($x > 4$), structure *N* grows in intensity and its position seems to shift toward the large binding energy side; at the same time, structure ***A*** shifts, and structures ***A*** and ***B*** diminish. Furthermore, structures indicated by α, β, and γ are appeared between 6 eV and 12 eV, the appearance of which is in contrast with the intensity loss of the structures above 4 eV. The structures α, β, and γ can be considered to be the result of the shift of structures ***C***, ***E***, and ***F***. However, the degree of the shift of the individual pairs is not the same, and the intensities of the structures α – γ are much larger than their counter parts. The origin of the shift of the structures is not clear but the structures α - γ have few correspondences with structures ***C*** - ***F***. It is plausible that structures α - γ are due to heavily potassium dosed fullerene complex (HPDF). When dosing proceeds, islands of HPDF form in the fullerene film so that the spectra are to reflect the specimen, a mixture of fullerene and HPDF. When the dosage is very large, the film primarily consists of

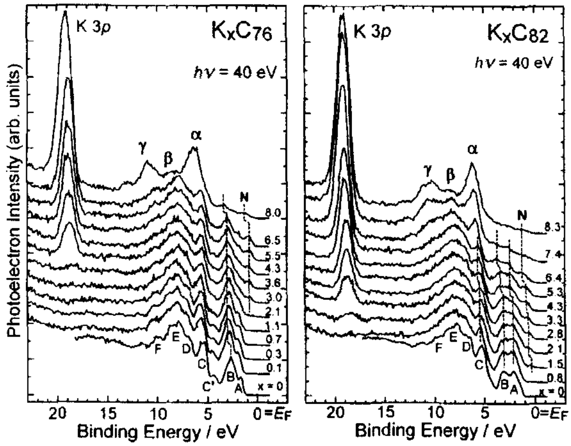

FIGURE 3. Spectral change of the C_{76} and C_{82} films upon successive potassium dosing obtained with $h\nu = 40$ eV.

HPDF. At this stage the intensity of the spectra above 4 eV derived from π-electrons [9, 10] is small and that below 5 eV from mainly σ-electrons is large, which means that HPDF has more σ-bonding electrons than pristine fullerene. A possible explanation for this spectral change is a bond rearrangement or bond breakage of fullerenes.

Re-deposition of fullerene on to the excessive potassium dosed fullerene

Fig. 4 shows the spectra of (a) pristine C_{82}, (b) potassium dosed C_{82}, (c) excessively potassium dosed C_{82}, and (d) C_{82} deposited on to the excessively potassium dosed C_{82}. There are some similarities between the spectra (b) and (d). It means that the spectral shape depends on the potassium concentration in K_xC_{82}. In the case of K_xC_{102} [7], on the other hand, there is no similarity between the spectra of having close potassium concentration with different preparation history. This means that the reaction between potassium and small carbon number fullerene is reversible

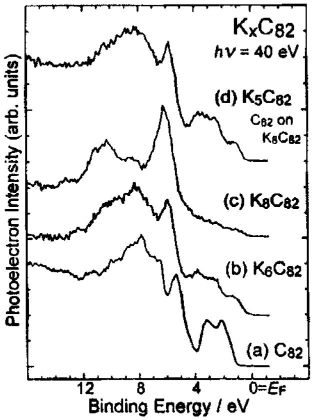

FIGURE 4. Comparison of the spectra of (a) pristine C_{82}, (b) potassium dosed C_{82}, (c) excessively dosed C_{82}, and (d) C_{82} re-deposited on to the excessively potassium dosed C_{82}. Potassium contents are shown beside the spectra respectively, in the chemical formula.

but that between potassium and large carbon number fullerene is irreversible. The molecular structure of large fullerene such as C_{102} is more distorted than that of smaller fullerenes so that the bonds between the carbon atoms of the former is not able to bear steric stress less than that of the later. Probably the cage structure of the large fullerene is vulnerable to dosing, electron acceptance from the potassium atoms.

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