

## Photoemission Spectroscopy of Metallofullerene and C<sub>70</sub> Fullerene Peapods

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### Introduction

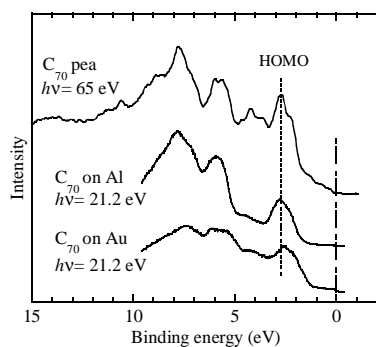
The electronic structures of metallofullerene or fullerene peapods (PPDs), which are single-wall carbon nanotubes (SWCNTs) encapsulating metallofullerenes or fullerene, respectively, have been intensively studied both theoretically and experimentally. However, only a few photoemission studies have been performed so far [1, 2]. In this study, we have measured the electronic structures of M@C<sub>82</sub> PPDs (M= La, Gd, Dy) and C<sub>70</sub> PPD using photoemission spectroscopy [2].

### Experimental

The photoemission experiments were performed using synchrotron radiation at the beam lines BL-11D and BL-28A of the Photon Factory, High Energy Accelerator Research Organization (KEK). The instrumental resolution was 50 meV at  $h\nu = 65$  eV. SWCNT samples were prepared by the laser vaporization method.

### Results and Discussion

Figure 1 shows the photoemission spectra of the C<sub>70</sub> peas and C<sub>70</sub> film. The spectrum of C<sub>70</sub> peas was obtained by subtracting the pristine SWCNT spectrum from the C<sub>70</sub> PPD one. The peaks were obtained at binding energies of 2.5, 6 and 8 eV. The peak at 2.5 eV is due to the highest occupied molecular orbital (HOMO) level. The energy positions of these peaks are nearly equal to respective corresponding peak positions of the C<sub>70</sub> film spectra. From the theoretical calculation, Otani et al. predicted the downward shift of the HOMO level by about 2 eV,



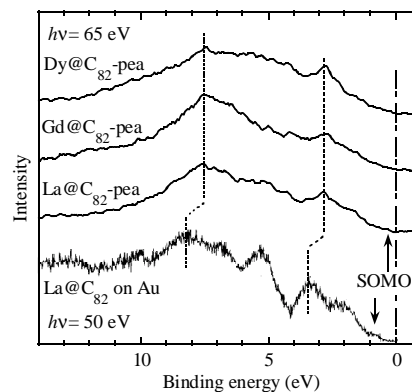
**Figure 1** Photoemission spectra of the obtained C<sub>70</sub> pea and C<sub>70</sub> films. The C<sub>70</sub> films were prepared by evaporating onto clean Au and Al substrates.

caused by the hybridization between the C<sub>70</sub>  $\pi$  states and the nearly free-electron (NFE) states of SWCNTs [3]. However, such a large shift cannot be observed, indicating that the hybridization is negligibly weak. This result is consistent with the photoemission results for C<sub>60</sub> PPD [1].

Figure 2 shows the photoemission spectra of the M@C<sub>82</sub> peas and La@C<sub>82</sub> film [4]. The peak structures were observed at 3 and 7.5 eV. These structures shift toward  $E_F$  by about 0.7 eV, compared with the corresponding structures in the La@C<sub>82</sub> film spectrum. In the spectrum of La@C<sub>82</sub> peas, the singly occupied molecular orbital (SOMO) peak was observed near  $E_F$ . From the comparison between the pristine SWCNT and La@C<sub>82</sub> PPD spectra, it can be seen that the structures originating from the SWCNT in La@C<sub>82</sub> PPD shift toward  $E_F$  by 0.1 eV. These facts indicate that charge transfer occurs from the SWCNTs to the La@C<sub>82</sub> peas, which is consistent with the prediction of the theoretical calculation [5].

### References

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**Figure 2** Photoemission spectra of the obtained M@C<sub>82</sub> peas (M= La, Gd, Dy) and La@C<sub>82</sub> film.

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