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Photoemission Spectroscopy of MetalloFullerene Peapods

Hiroyoshi ISHII*[1], Yuji NAKAYAMA[1], Shinichiro FUJIKI[1], Yasuharu HIRADO[1], Hidetsugu SHIOZAWA[1], Tsuneaki MIYAHARA[1], Yutaka MANIWA[1], Takeshi KODAMA[1], Yohji ACHIBA[1], Hiromichi KATAURA[2], Masashi NAKATAKE[3] and Tomohiko SAITOH[4]
[1]Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan
[2]National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8562, Japan
[3]HiSOR, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan
[4]Tokyo University of Science, Shinjuku, Tokyo 162-8601, Japan

Introduction

Metallofullerene peapods (PPDs), which are single-wall carbon nanotubes (SWCNTs) encapsulating metallofullerenes, have attracted much attention from the viewpoint of their application to new nano-devices. Many studies of PPDs have been performed. However, only a few experimental studies concerning the electronic structures of PPDs have been performed so far [1]. In this study, we have measured the electronic structures of M@C_{82} PPDs (M= La, Gd, Dy) using photoemission spectroscopy [2].

Experimental

The photoemission experiments were performed using synchrotron radiation at the beam line BL-11D of the Photon Factory, High Energy Accelerator Research Organization (KEK). The instrumental resolutions were 50 meV and 150 meV at photon energies of 65 eV and 160 eV, respectively. SWCNT samples were prepared by the laser vaporization method.

Results and Discussion

Figure 1 shows the photoemission spectra of the Dy@C_{82} PPD sample measured at photon energies ranging from 65 eV to 161 eV. The Dy 4*f* emission appears around *hν*= 161 eV, as indicated by the arrow in Fig. 1.

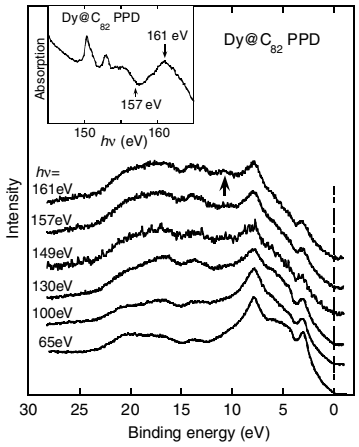

Figure 1 Photoemission spectra of the Dy@C_{82} PPD sample measured at photon energies ranging from 65 eV to 161 eV. The inset shows the absorption spectrum near the Dy 4*d*-4*f* excitation region.

To obtain the Dy 4*f* spectrum, we subtracted the spectrum taken at $h\nu$ = 157 eV from the spectrum at $h\nu$ = 161 eV. The obtained Dy 4*f* spectrum is shown in Fig. 2. To investigate the origin of these complicated structures, we calculated the multiplet structures of the $4f^9$ (Dy^{3+}) and $4f^{10}$ (Dy^{2+}) final state configurations by the Cowan's code, where the Slater integral F^k (4*f*, 4*f*) was reduced by 30 %. The calculated multiplet components are indicated by vertical bars in Fig. 2. The structures located at binding energies ranging from 7 eV to 15 eV are due to the Dy^{3+} state; the Dy^{2+} state is observed at 3-6 eV. The intensity ratio of the Dy^{2+} to Dy^{3+} states was estimated to be about 0.12. The effective Dy valence was estimated to be about +2.9. Taking into account the fact that the Dy valence in Dy@C_{82} is +3 [3], it is considered that 0.1 electrons move back to Dy following encapsulation of Dy@C_{82} in SWCNTs. Such a charge transfer is consistent with the prediction of the theoretical calculation [4].

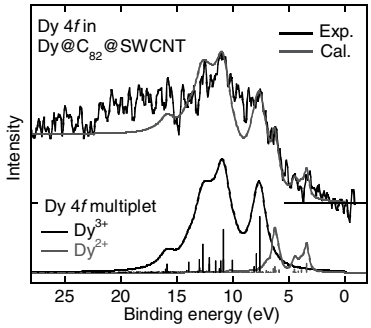

Figure 2 Comparison between the Dy 4*f* spectrum of Dy@C_{82} PPD and the spectrum calculated taking into account the multiplet structures of the $4f^8$ (Dy^{3+}) and $4f^9$ (Dy^{2+}) final state configurations. The multiplet components are represented by vertical bars.

References

[1] H. Shiozawa et al., Phys. Rev. B 73, 075406 (2006).
[2] Y. Nakayama et al., submitted to Physica Status Solidi (b).
[3] S. Iida et al., Chem. Phys. Lett. 338, 21 (2001).
[4] Y. Cho et al., Phys. Rev. Lett. 90, 106402 (2003).

* h_ishii@tmu.ac.jp