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Photoelectron spectroscopy and local structure of the Se chain confined in single carbon nanotube

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Trigonal selenium (t-Se) is the stable crystalline form in which Se atoms form three-turn helical chains with twofold covalent bonds, and these chains are stacked through interchain interactions. This hierarchical structure—where the helical chains constitute the primary structure and the stacked chains constitute the secondary one—is a characteristic feature of chalcogen elements, including Se. This unique characteristic arises from the four 4p valence electrons: two form covalent bonds, while the others form lone-pair (LP) bonds. The LP bonds are located at the top of the valence band, with a gap between the LP bands and the anti-bonding (σ*) bands, making t-Se a semiconductor. The physical properties are strongly correlated with its structure. Therefore, it is crucial to study both the electronic state and local structure. In this report, we present the electronic structure and the local structure of selenium chains confined within single-walled carbon nanotubes (Se@SWCNT), as determined by extended X-ray absorption fine structure (EXAFS) and photoelectron spectroscopy (PES) measurements.

Se@SWCNT was synthesized by heat treatment of a glass tube sealing Se and SWCNT. PES experiments were perfomed at BL-7 in HiSOR using 120 eV excitation photon energy at both room temperature (RT) and 20 K (LT). EXAFS measurements for the Se K-edge (12.7 keV) were conducted at BL12C in KEK-PF using transmission mode over a temperature range of 20–300 K.

Figure 1 shows the PES spectra of SWCNTs with and without Se, where the backgrounds were subtracted using the Shirley method [1]. Since the Se atoms are confined within the SWCNTs, their contribution is relatively small. The PES spectra of Se@SWCNT were obtained by subtracting the spectra of SWCNTs without Se from those with Se. A key observation is the spectral weight near the Fermi energy (E_F); nearly zero at RT while finite at LT. This suggests that Se@SWCNT could exhibit metallic behavior at LT, while at RT it behaves like a semiconductor similar to t-Se.

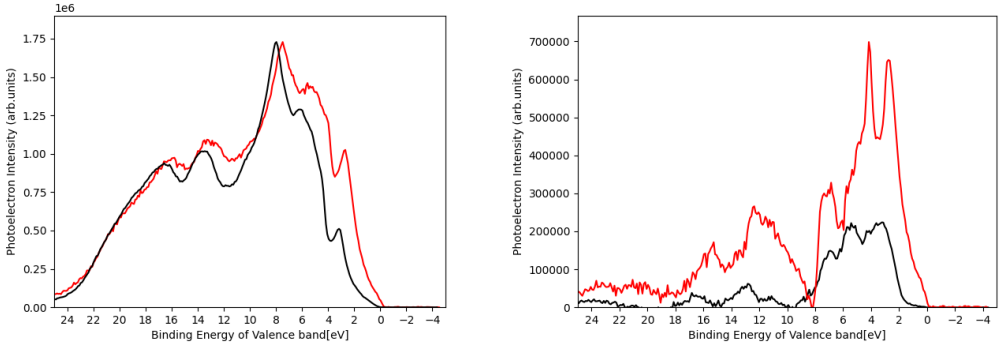

FIGURE 1. (a) The PES spectra of SWCNTs with and without Se at LT, (b)The PES spectra of Se@SWCNT at RT and LT.

The most interesting result from the EXAFS analysis is the temperature-dependent variation of the coordination number (N) of Se covalent bonds. At RT, the value of N is close to two, indicating that the two-fold covalent bonds remain intact even in Se@SWCNT. However, the value decreases to about 1.8 at LT. If we simply consider it, this suggests that the covalent bonds partially break as the temperature decreases.

We will discuss these interesting results in conjunction with the PES and EXAFS studies with other consideration.

REFERENCES

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