Electronic Structure of WO_2 Nanorods by X-ray-absorption Spectroscopy and Scanning Photoelectron Microscopy

H. M. Tsai (蔡煌銘)[1], C. W. Pao (包志文)[1], J. W. Chiou (邱昭文)[1], P. D. Babu (巴布)[1], S. C. Ray[1], W. F. Pong (彭維鋒)[1], and Y. R. Ma (馬遠榮)[2]

[1]Department of Physics, Tamkang University, Tamsui, Taiwan
[2]Institute of Applied Physics and Department of Physics, Dong Hwa University, Hualien, Taiwan

We report the results of x-ray absorption near edge spectra (XANES) and scanning photoelectron microscopy (SPEM) studies of WO_2 nanorod and its powder using the high-energy spherical grating monochromator (HSGM), W20-C Wiggler and U5-SGM undulator beamlines. The WO_2 nanorod exhibits vertically aligned rod-like crystals having rod length of ~300 nm and diameter ~50nm.

Figure 1 shows the O *K*-edge spectra of the WO_2 nanorod and its powder. The first two peaks in the π* region are due to excitation of core electron to O 2*p* and metal *d* hybridized states. They are split into t_{2g}(a peak) and e_g(b peak) due to crystal field effects. σ* features (c peak) is attributed to the transition of O 2*p* and W 6*sp* hybridized states. No edge shift between the rod and powder was observed, but the peak intensity is larger in case of powder than rod indicates that the rod has lower unoccupied *d*-orbital state.

The W L_3-edge spectra shown in the Fig. 2, is the 2*p* → 5*d* transition of WO_2 materials. The W powder spectrum is also included in the plot for comparison. In W L_3-edge, it is observed that the white line intensity of WO_2 nanorod and its powder are larger than the W powder. There is no energy shift between the WO_2-rod and powder, but the peak intensity is larger in case of rod than the powder which indicates that the rod has more unoccupied *d*-orbital state. From O *K*- and W L_3-edge XANES data, it shows the intensity differences between the WO_2-rod and powder, which indicates that the two materials have different electronic structure.

Fig. 3 shows valence-band photoemission spectra originated from the tip and sidewall regions of nanorod. WO_2 powder spectra also included for comparison. Fermi level is identified with Binding Energy =0 eV. The SPEM cross-sectional image of WO_2 nanorods is shown in inset fig.3. The bright area denoted by black circle is the sidewall of the nanorod and white circle is the tip of the rod. The structure I was identified as the signature of the σand π type molecular orbitals, resulting the formation of metal-oxygen band from the combination of O2*p* and W *d* electrons. The XPS spectra shows that nanorod tip and sidewall have a similar valence-band DOS but are different with powder, especially close to the Fermi-level. This enhanced DOS in rod-type could be due to the defects and/or dangling bonds of the rod surface.