X-ray Absorption Spectroscopic Studies of Eu-treated ZnO Nanowires

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Eu L_3-edge XANES spectra were obtained at the wiggler-17C beamline; O *K*- and Zn L_3-edge XANES spectra were obtained at the Dragon-11A beamline in fluorescence mode, at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. Pure ZnO-NWs were grown by chemical vapor deposition, Eu-treated ZnO-NWs were obtained by thermal diffusion of Eu atoms into ZnO nanowires. Commercial-grade Eu oxide (Eu_2O_3) powder was compared with the samples. The diameter of ZnO-NWs was approximately 200 nm; they were approximately 1 μm long. Details of the preparation of Eu-treated ZnO-NWs and ZnO-NWs can be found elsewhere [1].

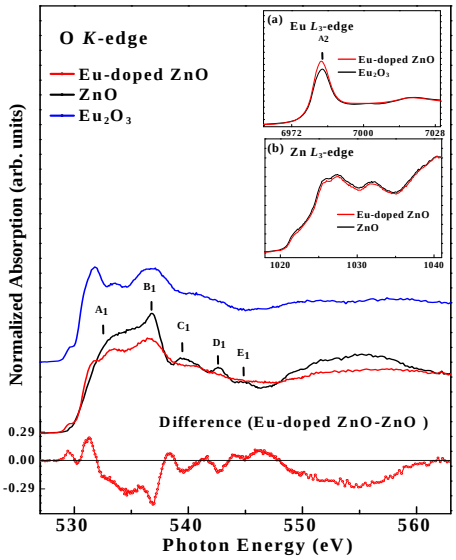

Fig. 1: Normalized O *K*-edge XANES spectra of Eu-treated ZnO-NWs, ZnO-NWs and Eu_2O_3 powder. Lower inset plots difference XANES spectrum between Eu-treated ZnO-NWs and ZnO-NWs. Insets (a)(b) present, respectively, Eu L_3-edge XANES of Eu-treated ZnO-NWs and Eu_2O_3, and Zn $L_{3,2}$-edge XANES of Eu-treated ZnO-NWs and ZnO-NWs.

The Fig. 1 presents normalized O *K*-edge XANES spectra of Eu-treated, untreated ZnO-NWs, and reference Eu_2O_3. The characteristic features A_1-E_1 in the O *K*-edge spectrum of ZnO-NWs corresponds primarily to O 1*s* transitions to the O $2p_{ab}$ (along the ***bi***-layer) and O $2p_c$ (along the ***c***-axis) unoccupied states[2,3]. The lower panel in Fig. 1 presents difference spectrum between Eu-treated and untreated ZnO-NWs. The overall spectral intensity of Eu-treated ZnO-NWs is reduced and the near-edge feature is broadened relative to those of ZnO-NWs, which indicates that the number of O 2*p* unoccupied states decreases following the Eu-diffusion process and suggests an increase in the occupation of the O 2*p* orbitals and the negative effective charge of the O ion. The increase of the effective charge of the O ions can be understood by the fact that the Pauling's electronegativity of Eu (1.2) is much smaller than that of Zn (1.65).

The inset (a) in Fig. 1 displays XANES spectra at the Eu L_3-edge of the Eu-treated ZnO-NWs and Eu_2O_3. The Eu-treated ZnO-NWs and Eu_2O_3 yield almost identical spectral line-shapes with a strong feature (**A_2**), clearly suggesting that the trivalent Eu ions form an Eu_2O_3-like layer on the surface, instead of the substitution of Zn ions in the interior of the nanowires. Feature **A_2** of Eu-treated ZnO-NWs corresponds to the transition of Eu 2*p* to 5*d* unoccupied states and is considerably more intense than that of reference Eu_2O_3. The relatively high intensity of feature **A_2** may be caused by enhanced localization of Eu 5*d* states in Eu-treated ZnO-NWs due to the reduced size of narowires. The enhanced feature **A_2** is also consistent with the fact that the overall intensity of spectral features in Zn L_3-edge XANES, which corresponds to Zn 2*p* to 4*s*/3*d* transitions in Eu-treated ZnO-NWs, is slightly lower than the intensity of that of ZnO-NWs, as presented in the inset (b) in Fig. 1. Again, the lowering of the intensity and broadening of the near-edge feature in the O *K*-edge of Eu-treated ZnO-NWs can be understood as being caused by hybridization of O 2*p* and Eu 5*d* orbitals, which promotes transfer of electrons from Eu to neighboring O atoms in Eu-treated ZnO-NWs.

The results of O *K*- and Eu L_3-edge XANES confirmed formation of Eu_2O_3-like layer on the surface of ZnO-NWs.

References

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