Electronic Structure Determination for Composite Materials in Dye-Sensitized Solar Cells by Photoelectron Spectroscopy

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Electronic structures, energy level alignment and electronic interactions of the composites within a dye-sensitized solar cell as well as the charge transfer processes at the oxide/dye/electrolyte interface and the electron transport process through the nanostructure to the external circuit must be understood clearly for the optimum performance. At present, no detailed discussion has been done yet to depict a complete energy diagram for a DSSC. In this study, we plan to use synchrotron radiation photoelectron spectroscopy technique to investigate the electronic structures of oxide semiconductor/organic dyes/redox electrolyte (ZnO and TiO_2/Dye/I3) even more comprehensive.

We use a single crystal to determine the absolutely position of Fermi energy level as showed in Fig.1. (Fermi energy level = 21.213ev).

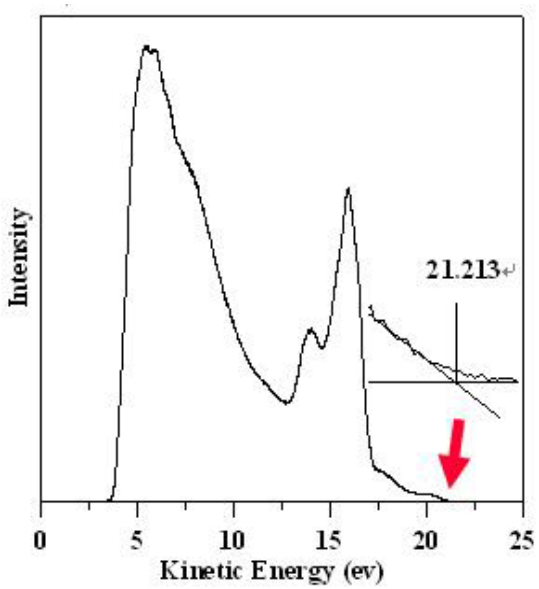

Figure 1. UPS spectrum of single crystal Ag was taken with -4 V bias.

All UPS spectra have been calibrated with a reference spectrum from a standard sample of gold. Fig. 2 (a) shows the UPS spectra of the ZnO films deposited on Si (100) and Si (111). The features at 11.35, 8.15, and 5.15 eV agree well with previous studies and correspond to Zn 3d, mixed Zn 4s–O 2p, and O 2p states, respectively [5]. While the spectra looks similar except higher ratio of the hybrid state for the ZnO on Si(111), the characteristics of the spectra for ZnO nanomaterials differs significantly as shown in Fig.2(b). The valence band structure is largely affected by the form of the nanomaterial including the shift and broadening of the O 2p orbital, which may be arisen from surface-related dangling bond states. By extrapolating the edge of the O 2p peak, the position of the valence band edge with respect to the Fermi level was determined and found to have little dependence on the surface preparation.

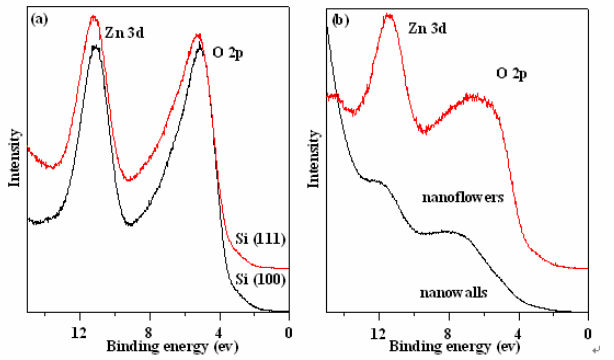

Figure 2. ZnO UPS spectra for (a) thin films deposited on different Si substrate (b) nanowalls and nanoflowers.

The relative energy levels of individual components in various cells were determined by ultra-violet photoemission spectroscopy (UPS) and plotted in Fig. 3, including TiO_2 nanoparticles, ZnO nanotubes, TiO_2/N3 dye and TiO_2/Chlorophyll dye (Green solar cells). From the results, the HOMO levels of N3 and Chlorophyll dye are located at 4.43 and 5.54 eV below the vacuum level, respectively, and the LUMO levels are located 2.74 and 3.69 eV below the vacuum level. The performance of solar cells is determined by the carrier transport behavior, which is related to the relative energy level positions of constituent components. From these results, we learn that the LUMO level of the N3 dye is higher than the conduction band of TiO_2 and ZnO, whereas the Chlorophyll dye is just opposite, responsible for the lower efficiency of 0.205% of the green solar cells.

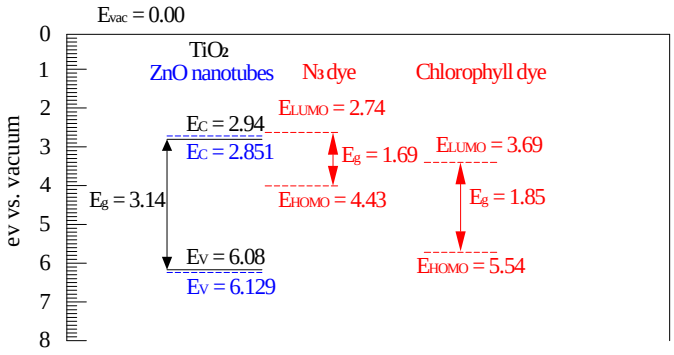

Figure 3. Energy band diagram for TiO_2 nanoparticle, ZnO nanotubes, TiO_2/N3 dye and TiO_2/Chlorophyll dye determined by UPS.