

Supplementary Information

Surface Modification of Zinc Oxide Nanorods with Zn-Porphyrin via Metal-Ligand Coordination for Photovoltaic Applications

Jaehong Koo, Jin-Ju Cho, Pil J. Yoo,[†] Kyung Wha Oh,^{‡,*} and Juhyun Park^{*}*School of Chemical Engineering and Materials Science, Chung-Ang University, Seoul 156-756, Korea. *E-mail: jpark@cau.ac.kr**[†]School of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea**[‡]Department of Home Economics Education, Chung-Ang University, Seoul 156-756, Korea. *E-mail: kwhaoh@cau.ac.kr**Received November 22, 2011, Accepted January 13, 2012***ZnO Nanorod Synthesis**

In our ZnO nanorod synthesis, we used a two step procedure in which ZnO nanoparticle seeds were first synthesized in alcohols and then used as nucleating agents for nano-rod growth in aqueous medium. For ZnO nanoparticle synthesis, 0.04 g of NaOH was first dissolved in 8 mL of methanol at 70 °C. 0.219 g of zinc acetate dihydrate was also separately dissolved in 2 mL of methanol at 70 °C and added dropwise into the NaOH solution with refluxing under stirring at 70 °C for 1 hr, which results in a transparent ZnO seeds solution. To synthesize ZnO nanorods, 30 mL of an aqueous solution of zinc nitrate hexahydrate (2.975 g) and hexamethylenetetramine (1.402 g) were prepared in a reinforced one-neck glass flask. After directly adding 1 mL of the cooled ZnO seed solution into the aqueous solution, the flask was sealed with a Teflon cap and heated at 90 °C for 1 hr in an oil bath. The length of the ZnO nanorods was easily controlled by the reaction time; the heating for one hour at 90 °C was sufficient for growing the nanorods to about 150 nm in length while maintaining their diameter to be constant. After cooling the solution, ZnO nanorods were centrifuged,

washed with deionized water and methanol, and dried in a vacuum oven.

Measurements

UV-vis absorption spectra and photoluminescence spectra were obtained using spectrophotometer (JASCO V-670). The crystallinity and crystal structures were investigated by X-ray Diffractometer and a high-resolution transmission electron microscope (HRTEM; TECNAI, G2 F30 S-Twin, operated at an acceleration voltage of 300 kV), for which samples are prepared by drop casting a diluted solution on a

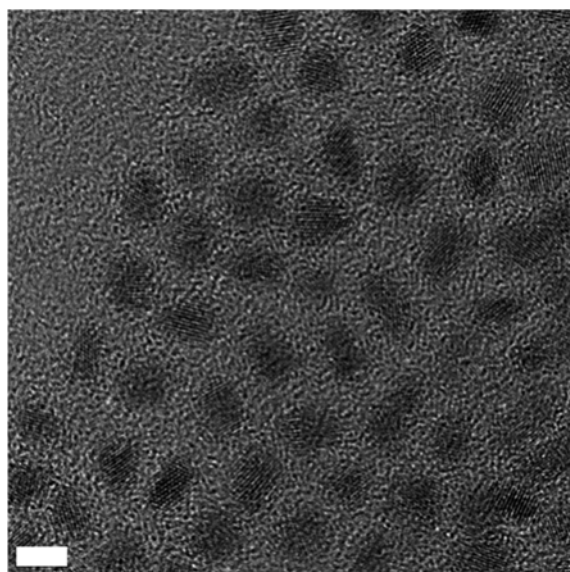


Figure S1. The HRTEM image of the ZnO seeds in which the scale bar is 5 nm.

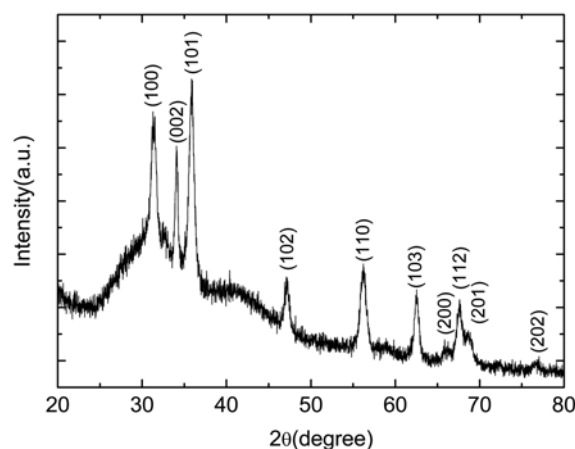


Figure S2. The X-ray diffraction spectrum of the ZnO nanorods.

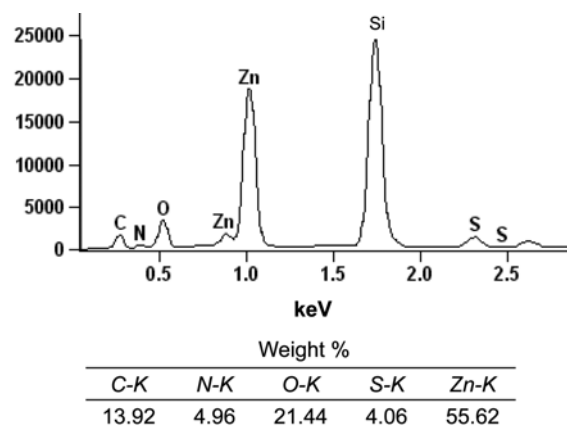


Figure S3. The EDS spectrum of the ZnO nanorods modified by BT and PTT, and Zn-porphyrin.

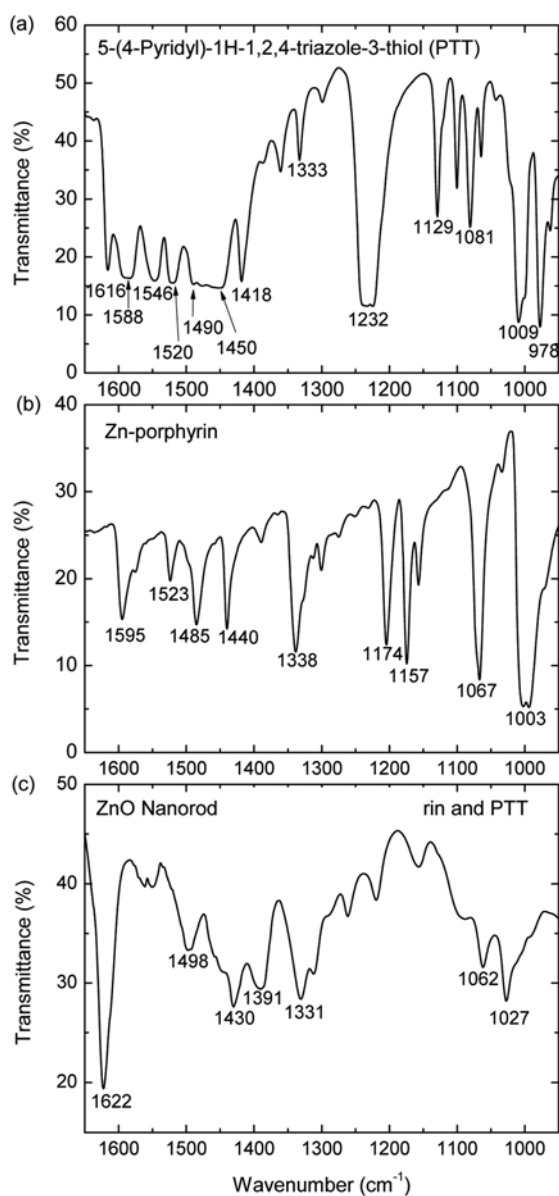


Figure S4. The FT-IR spectra of 5-(4-Pyridyl)-1H-1,2,4-triazole-3-thiol (PTT), Zn-porphyrin, and ZnO nanorods modified by butanethiol, PTT and Zn-porphyrin.

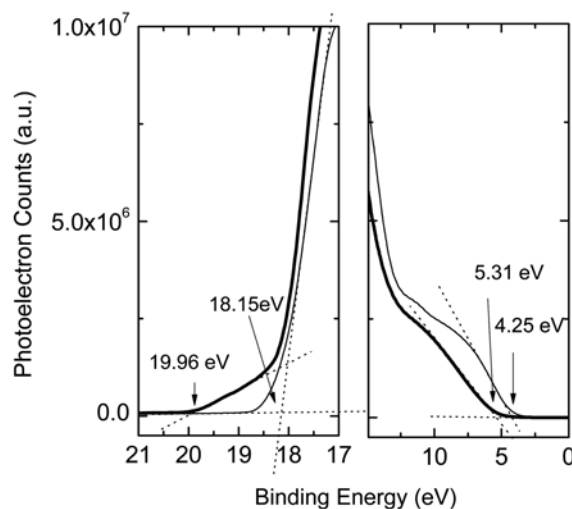


Figure S5. Enlarged UPS spectra of the ZnO nanorods modified with Zn-porphyrin (thick solid line) and the pristine ZnO nanorods (thin solid line). The HOMO edge of the ZnO nanorods modified by Zn-porphyrin = 21.23 eV – 19.96 eV + 5.31 eV = 6.58 eV. The valence band edge of the pristine ZnO nanorods = 21.23 eV – 18.15 eV + 4.25 eV = 7.33 eV.

carbon coated copper grid. X-rays photoelectron spectroscopy (XPS, $h\nu = 1486.6$ eV AlK α) and ultraviolet photoelectron spectroscopy (UPS, $h\nu = 21.23$ eV He(I)) experiments were carried out on a ULVAC-PHI 5000 Versaprobe.