Electronic Supplementary Information for

Enhanced Photoluminescence of Single Crystalline ZnO nanotubes in $ZnAl_2O_4$ Shell

By H. G. Cha,[a] D. I. Kang,[a] T. H. Kwon[b] and Y. S. Kang[a]

[a]*Korea Center for Artificial Photosynthesis, Department of Chemistry Sogang University #1, Shinsu-dong, Mapo-gu, Seoul, 121-742, South Korea.*

[b]*Department of Electronic Pukyong National University 599-1 Daeyeong 3-dong, Namgu, Busan, 608-737, South Korea.*

Experimental Details

Synthesis of vertically aligned ZnO nanorods: ZnO nanorods were synthesized in a conventional furnace with a horizontal quartz tube, as illustrated schematically in Figure 1(a). The silicon (100) substrate was placed downwards on a quartz boat loaded with Zn powder (purity: 99.999%; distance between the Zn source and the Si substrate 2-3 cm; vapor pressure of Zn: 1 torr at 487 ^oC), and then the quartz boat was transferred into the center of the tube furnace. Afterwards, the chamber was heated to 500 ^oC, a flow of a mixture of O_2 and Ar (5% O_2 in Ar) with a flow rate of 2-3 sccm was introduced into the chamber and maintained for 1 h. After cooling, a white layer was found to be deposited on the Si wafer.

Synthesis of vertically aligned ZnO nanorods coated with Al_2O_3. The substrate covered with as-synthesized ZnO nanowires was transferred to the ALD chamber, as illustrated in Figure 1(b) (GV-ALD, GV Tech Co., Korea), and prebaked at 200 ^oC for 60 min in vacuum (1.5×10^{-1} torr) with a steady Ar stream of 10 sccm. The reactants were dosed into the reactor through a custom-made, multiple-input flange that prevented the reactants from sharing plumbing until introduced into the reaction section. The deposition took place at 200 ^oC using trimethylaluminium [$Al(CH_3)_3$, 99.9999%, UPChem Co. Ltd., Korea] and water as the aluminium and oxygen sources, respectively. Each cycle consisted of a 1.3 s precursor pulse, 20 s exposition time and 60 s purging time with Ar. As two precursors were used, a total cycle lasted for 162.6 s. Our process is rather conservative. The deposition time was found not to play an essential role, and we can obtain identical results if the exposition and purging times are reduced by 50%. The thickness of the Al_2O_3 shell is controlled by the number of precursor/purge cycles. In our study, a total number of 65 cycles was used, which gives an alumina thickness of 10.0 ± 0.3 nm as measured from TEM images. This corresponds to an average growth rate for Al_2O_3 of 1.5 A per cycle. The sample of ZnO/Al_2O_3 (core/shell) nanowires was then annealed in an open quartz tube furnace at 700 ^oC for 4 h to activate the interfacial solid-state reaction.

Instrumentations. Scanning electron microscopy (SEM) images were obtained using a field-effect scanning electron microscope (Hitachi S-4300) operated at an acceleration voltage of 20 kV. A platinum/palladium alloy (in the ratio of 8 to 2) was deposited with a thickness of about 15 nm on top of the samples. Transmission electron microscope (TEM, JEM 2100F) images, selected area electron diffraction (SAED), and chemical composition were obtained from a JEOL transmission electron microscope (JEM 2100F) installed with an EDX operated at accelerating 200 keV. In these HRTEM experiments, the electron beam was incident along the direction perpendicular to the 1D nanostructure. The nanostructures were transferred onto TEM copper grids by sonication of the substrate in alcohol following dipping the grids into the solution. Energy dispersive X-ray (EDX) line scans were obtained using Oxford a Horiba EX-220 Energy Dispersive X-ray Micro Analyzer (model: 6853-H). Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX-2500/pc diffractometer. Raman spectra of the samples were recorded on a homemade setup equipped with an Ar^+ ion laser (Spectra-Physics Stabilite 2017) as an excitation beam source, a spectrometer (Horiba Jobin Yvon TRIAX 550), and a CCD detector (Horiba Jobin Yvon Symphony) cooled to -133 ℃. The wavelength of the excitation beam was 514.5 nm. PL studies of the samples were conducted at room temperature using 325 nm line of a He–Cd laser at 1.7mW as the excitation source. The luminescence signal was dispersed by a SPEX 0.55 ms spectrometer and detected with a liquid-nitrogen-cooled back-illuminated charge-coupled device (CCD).

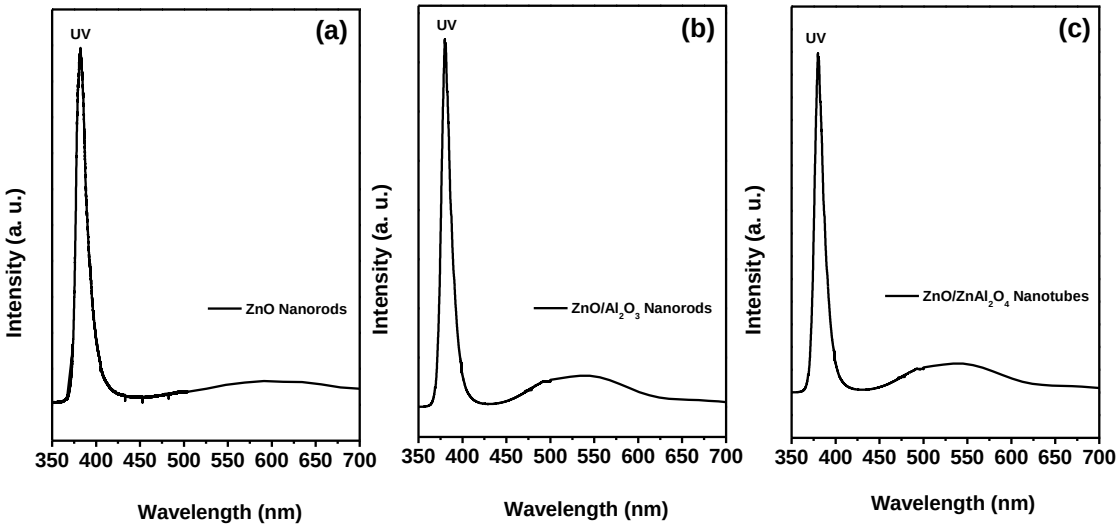

Fig. S1. Normalized PL spectra of ZnO nanorods (a), ZnO/Al_2O_3 nanorods (b), and $ZnO/ZnAl_2O_4$ nanotubes (c) by excitation wavelength at 325 nm (He-Cd laser).