Supporting Information

Controllable synthesis of ZnO-based core/shell nanorods and core/shell nanotubes

Zi-Long Wang, Gao-Ren Li,* Yan-Nan Ou, Liang-Xin Ding, Rui Guo, and Ye-Xiang Tong

MOE of Key Laboratory of Bioinorganic and Synthetic Chemistry/School of Chemistry and Chemical Engineering/Institute of Optoelectronic and Functional Composite Materials, Sun Yat-sen University, Guangzhou 510275, P. R. China
E-mail: ligaoren@mail.sysu.edu.cn

Experimental Section

A simple three-electrode cell was used in our experiments. The graphite electrode was used as a counter electrode (spectral grade, 1.8 cm²). The saturated calomel electrode (SCE) was used as the reference electrode that was connected to the cell with a double salt bridge system. The metal (Ti and Cu) plates (99.99 wt%, 1.5 cm²) were used as the substrates for electrodeposition, and they are prepared complying the following steps before each experiment: firstly polished by SiC abrasive paper from 300 to 800 grits, then dipped in HCl solution (5%) for 5 min and rinsed with acetone in ultrasonic bath for 5 min, and finally washed by distilled water. ZnO nanorods were firstly electrodeposited in solution of 0.01 M Zn(NO₃)₂+0.1M NH₄NO₃ by galvanostatic electrolysis for 60 min at 70 °C. ZnO/Bi₂O₃ core/shell nanorods were synthesized on Ti substrate by the electrodeposition of Bi₂O₃ on the surfaces of ZnO nanorods in solution of 0.01 M Bi(NO₃)₃+0.02M...
NH$_4$NO$_3$ (pH=6.5) by galvanostatic electrolysis with current density of 1.5 mA/cm$^2$ for 60 min at room temperature. ZnO/PANI core/shell hybrid nanotubes were prepared on Cu substrate by the electrochemical polymerization of PANI on the surfaces of ZnO nanorods in solution of 0.1 M aniline+0.1 M NH$_4$NO$_3$ (pH=1) with current density of 0.5 mA/cm$^2$ for 60 min and synchronously etching of ZnO nanorods under the role of acid.

The synthesized ZnO/Bi$_2$O$_3$ core/shell nanorods and ZnO/PANI core/shell nanotubes were characterized by thermal field emission environment scanning electron microscope (TFE-SEM, FEI, Quanta 400), transmission electron microscope (TEM, JEM-2010HR), X-ray diffraction (XRD, PIGAKU, D/MAX 2200 VPC), and X-ray photoelectron spectroscopy (XPS, ESCALAB 250). The electrochemical measurements were carried out in a Chi 660C electrochemical workstation. ZnO/Bi$_2$O$_3$ core/shell nanorods were deposited on Ti substrate with a surface area of 1.0 cm$^2$, and they were studied as electrodes for supercapacitor applications in 1.0 M Na$_2$SO$_4$ electrolyte. The graphite sheet was used as a counter electrode and the SCE was used as the reference electrode. The cyclic voltammetry experiments were performed between -0.20 and -1.0 V vs SCE at a scan rate of 5 mV/s. ZnO/PANI core/shell hybrid nanotubes were synthesized on Cu substrate by electrochemical polymerization/etching process. The photoluminescence (PL) measurements of ZnO/PANI core/shell nanotubes were carried out on a fluorescence spectrophotometer at room temperature, and the excited wavelength was 325 nm.
Fig. S1 (a) TEM image, (b) HRTEM image and SAED pattern (inset), (c) XRD pattern of ZnO nanorods deposited in solution of 0.01 M Zn(NO₃)₂ with current density of 2.5 mA/cm² at 70 °C for 60 min.
Fig. S2 XPS spectra of ZnO/Bi$_2$O$_3$ core/shell nanorods. (a) O1s; (b) Zn 2p; (c) Bi 4f.
Fig. S3 IR spectrum of ZnO/PANI core/shell nanotubes.