Supporting Information

Single-Crystal ZnO Nanorod/Amorphous and Nanoporous Metal Oxide Shell Composites: Controllable Electrochemical Synthesis and Enhanced Supercapacitor Performances

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Experimental Section

Electrochemical deposition of ZnO nanorods was carried out in solution of 0.01 M $Zn(NO_3)_2$ +0.05 M NH_4NO_3 via galvanostatic electrolysis at a current density of 1.0 mA/cm^2 at 70 ^{0}C for 90 min. The working electrode was titanium sheet (99.99 wt%) with surface area of 0.96 cm^2. Before electrodeposition, the titanium sheet was polished by successively finer grades of SiC paper, and then they were washed with acetone, 0.1M HCl, and distilled water, respectively. During electrodepositon, a graphite rod and a saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. All potential values determined in this study are the values versus SCE. Single-crystal ZnO nanorod/amorphous and nanoporous MnO_2 shell composites were prepared by the electrochemical deposition of Mn onto the surfaces of ZnO nanorods in soloution of 0.01 M $Mn(CH_3COO)_2$ at -0.58 V for 8 min and then heat treatment at 150 ^{0}C in

atmosphere for 180 min to compact MnO_2 shells on the surfaces of ZnO nanorods.

The morphologies of the prepared samples were characterized by thermal field emission environmental scanning electron microscopy (SEM; FEI Quanta 400F) and transmission electron microscopy (TEM, JOEL JEM-2010HR operated at 200 kV) equipped with energy dispersive X-ray spectroscopy (EDX, Oxford INCA300). The high-resolution transmission electron microscopy (HRTEM) images and the selected area electron diffraction (SAED) patterns were also recorded. The compositions and structures were analyzed using powder X-ray diffraction (XRD, Bruker D8 ADVAVCE), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCA Lab250) and EDX. The electrochemical measurements were accomplished by a Chi 750B electrochemical workstation. ZnO nanorod/MnO_2 shell composites and ZnO nanorod/NiO shell composites as electrodes were studied for supercapacitor applications in 1.0 M Na_2SO_4 electrolyte, respectively. The loading mass of ZnO nanorod/MnO_2 shell composites and ZnO nanorod/NiO shell composites is 0.10 mg and 0.21 mg, respectively. During electrochemical measurements, the graphite rod was used as a counter electrode and the SCE was used as the reference electrode.

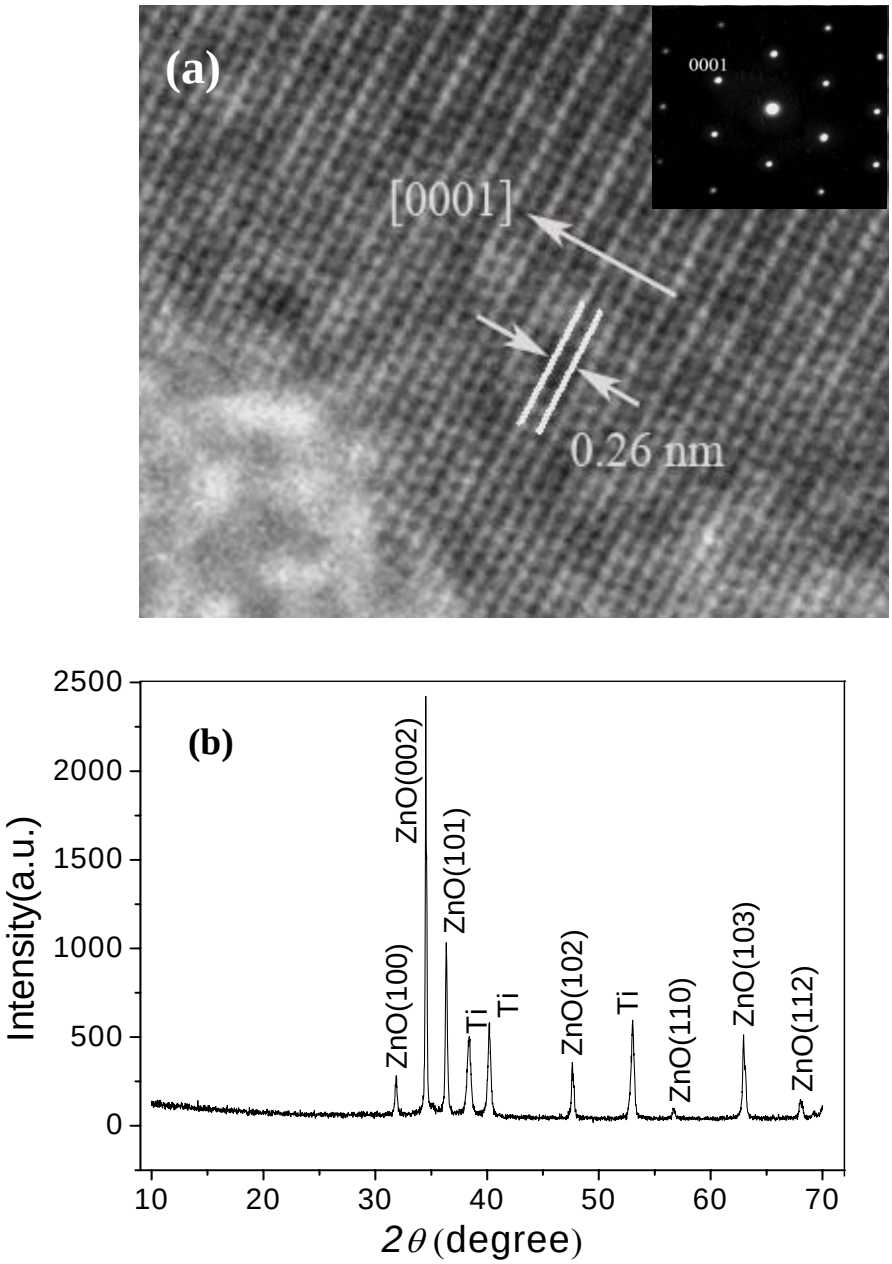


Figure S1 (a) HRTEM image and SAED (inset) of ZnO nanorods; (b) XRD pattern of ZnO nanorods.

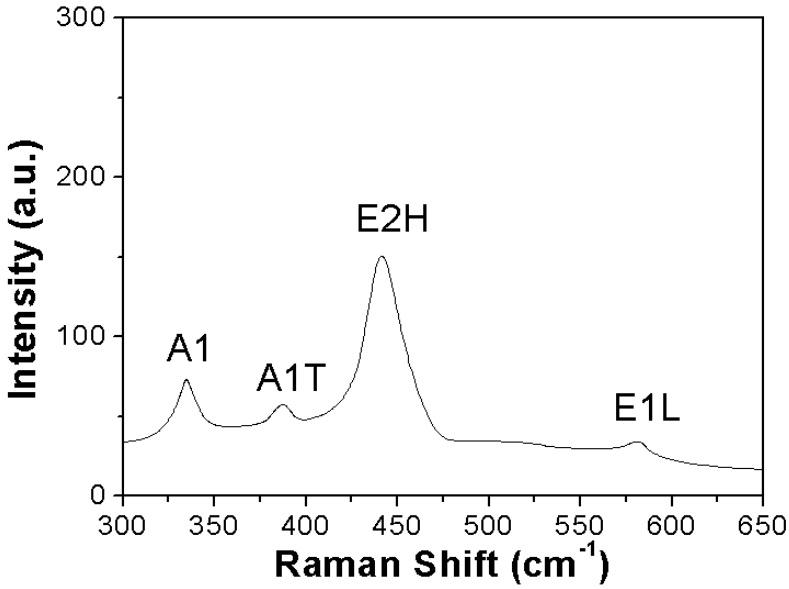


Figure S2. Raman spectrum of single crystal ZnO nanorod/amorphous and nanoporous metal oxide shell composites.

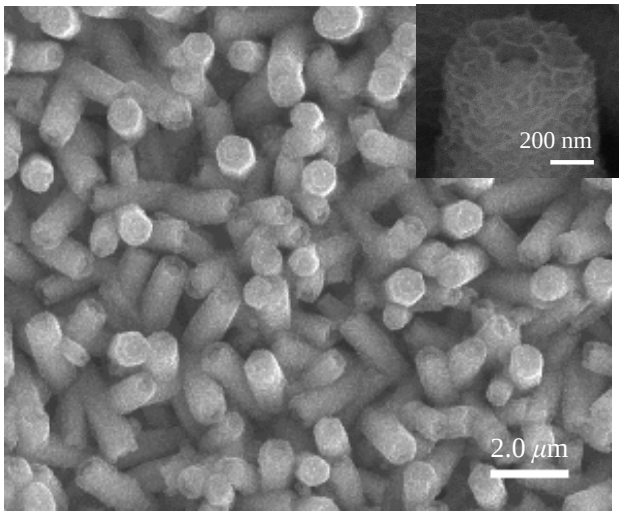


Figure S3. SEM image of ZnO nanorod/amorphous and nanoporous MnO_2 shell composites after 500 cycles. (Inset is the magnified SEM image of single ZnO/MnO_2 nanocable)

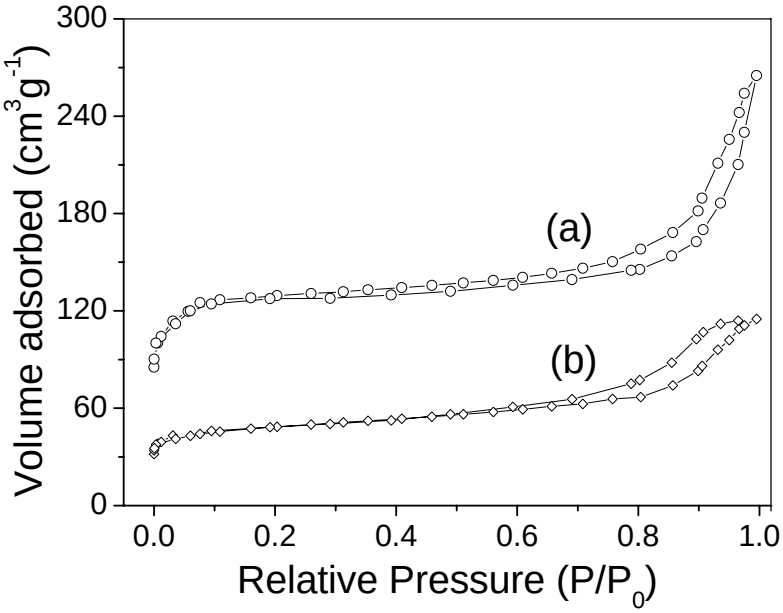


Figure S4. Adsorption-desorption isotherms of (a) ZnO nanorod/amorphous and nanoporous MnO_2 composite and (b) ZnO nanorods.

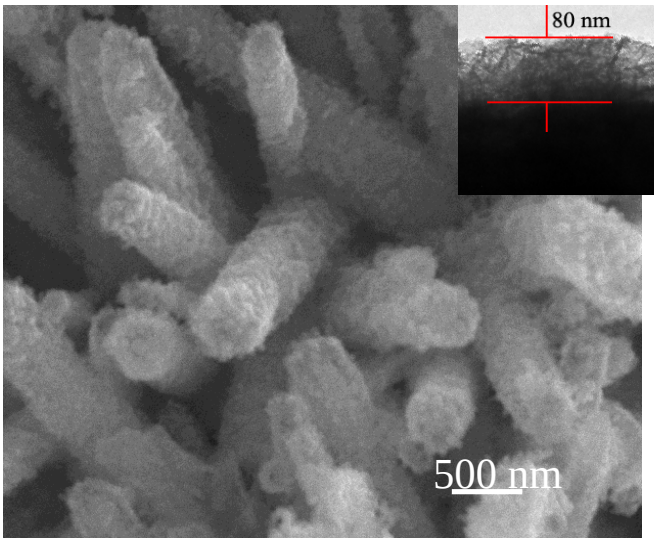


Figure S5. (a) SEM and (b) TEM images of ZnO nanorod/NiO shell composites. (The thickness of NiO shell is about 80 nm)

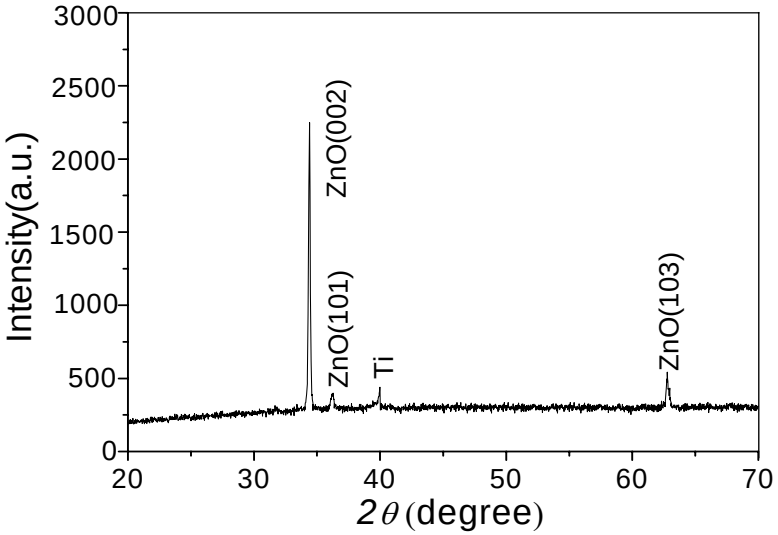
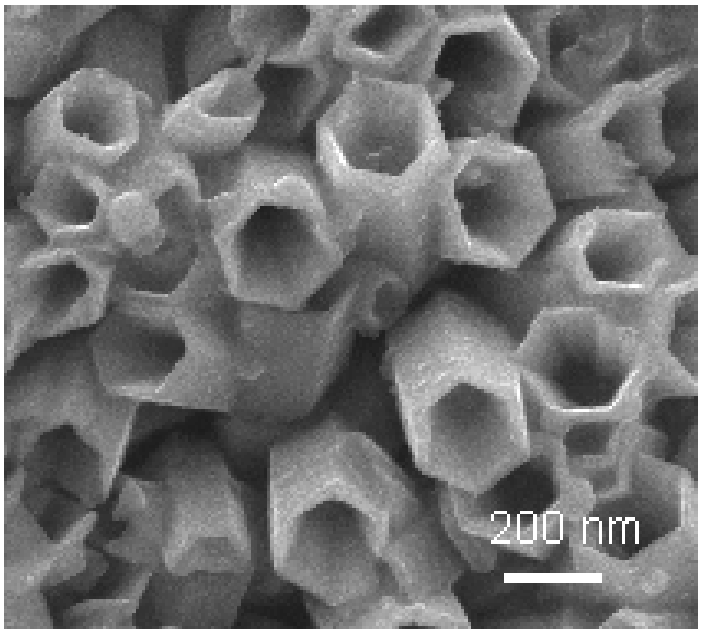


Figure S6. XRD of ZnO nanorod/NiO shell composites (Ti peaks come from substrate).



Figrue S7. SEM image of NiO nanotubes.