

Supporting Information

Polyaniline Nanotube Arrays as High-Performance Flexible Electrodes for Electrochemical Energy Storage Devices

Zi-Long Wang,^a Rui Guo,^a Gao-Ren Li,^{*a} Han-Lun Lu,^a Zhao-Qing Liu,^a Fang-Ming Xiao,^b Mingqiu Zhang,^{*a} and Ye-Xiang Tong^{*a}

^a*KLGHEI of Environment and Energy Chemistry/MOE Laboratory of Bioinorganic and Synthetic Chemistry/MOE Laboratory for Polymeric Composite and Functional Materials, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China. Fax: 86-20-84112245; Tel: 86-20-84110071, E-mail: ligaoren@mail.sysu.edu.cn; ceszmq@mail.sysu.edu.cn; chedhx@mial.sysu.edu.cn*

^b*Guangzhou Research Institute of Non-ferrous Metals, Guangzhou 510651, China.*

Experimental Section

The electrochemical experiments were carried out in a simple three-electrode glass cell. 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. Ti plate (99.99 wt%, 1.5 cm²) were used as the substrate 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. All electrodeposition experiments were performed with a HDV-7C transistor potentiostatic apparatus connected with a simple three-electrode cell. ZnO nanorod arrays were firstly electrodeposited on Ti substrate in solution of 0.01 M Zn(NO₃)₂+0.05 M NH₄NO₃ by galvanostatic electrolysis with 1.0 mA/cm² for 90 min at 70 °C. Then the electrochemical polymerization of PANI was further carried out on the surfaces of ZnO nanorods in solution of 0.1 M aniline+0.05 M Na₂SO₄ at 70 °C by galvanostatic electrolysis with current density of 2 mA/cm² for 5.0 min. Finally the flexible PANI nanotube arrays were obtained by

etching ZnO nanorod arrays in ammonia solution (25%).

The surface morphologies of PANI nanotube arrays were characterized by field emission scanning electron microscopy (SEM, FEI, Quanta 400). The products were also characterized by X-ray diffraction (XRD, PIGAKU, D/MAX 2200 VPC) to determine the deposit structures. The optical properties of PANI nanotube arrays were tested with UV-Vis-NIR spectrophotometer (UV-3150) and infrared ray spectrometer (FT-IR, Nicolet 330). Raman scattering spectra were recorded with a Renishaw System 2000 spectrometer using the 514 nm line of Ar⁺ for excitation. A CHI 660D electrochemical workstation was utilized for electrochemical measurements. PPy nanotube arrays on Ti substrate as electrodes were studied for supercapacitor applications in 1.0 M H₂SO₄ solution. The loading of PANI film was 0.5 mg. The Pt sheet was used as a counter electrode and the SCE was used as the reference electrode. The cyclic voltammetry experiments were performed between 0.23 and 0.73 V vs SCE at a scan rate of 1.0~200 mV/s.

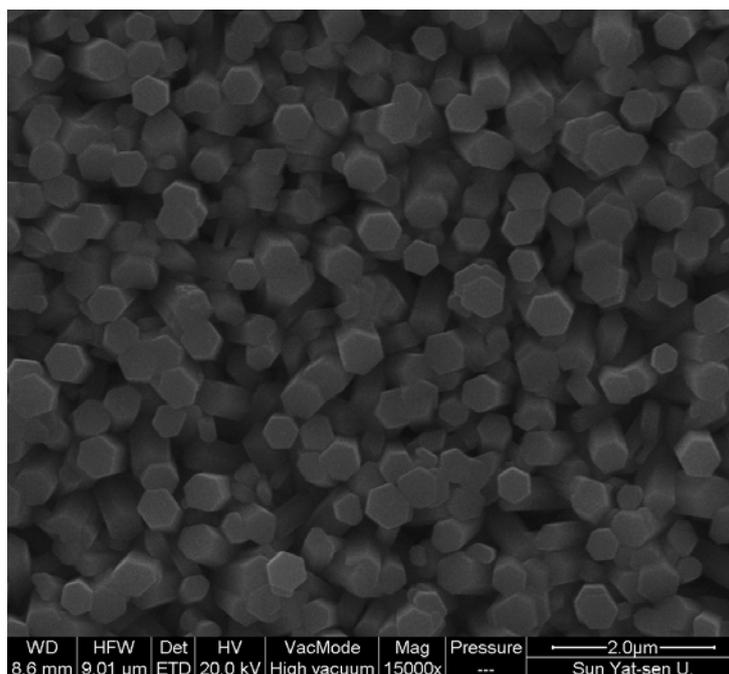


Figure S1. SEM image of the synthesized ZnO nanorod arrays.

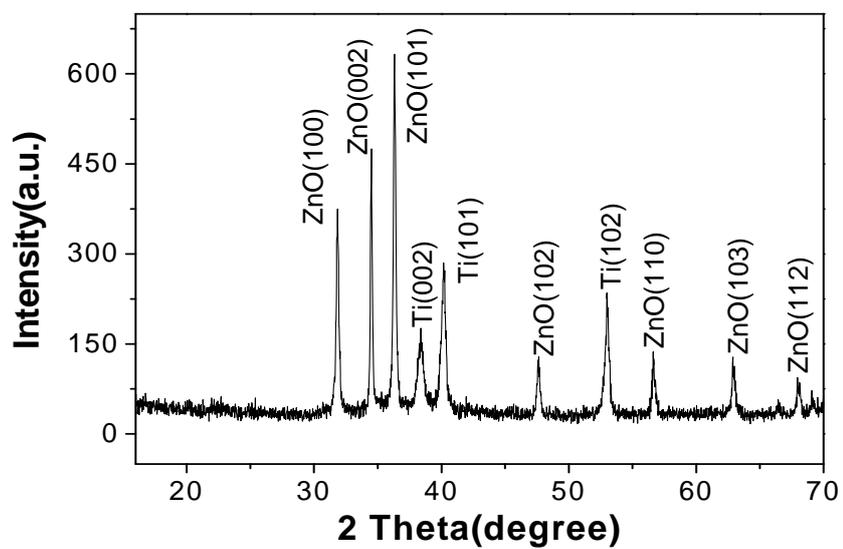


Figure S2. XRD pattern of ZnO nanorod arrays.

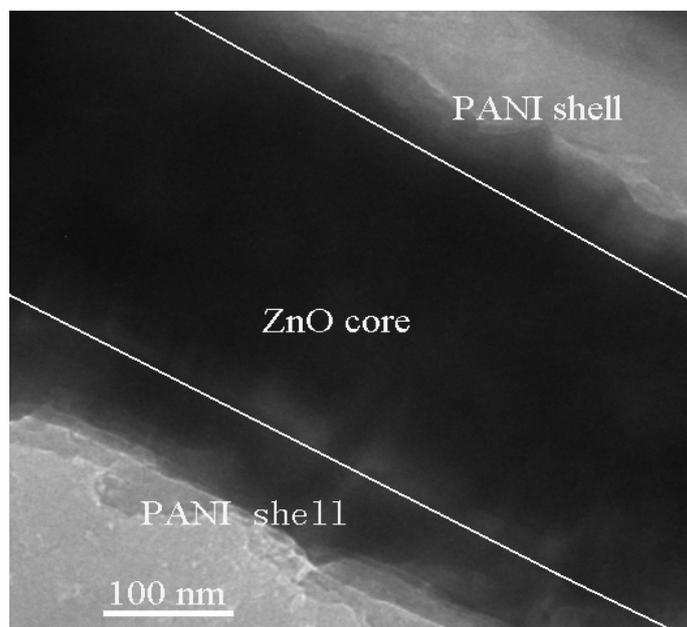


Figure S3 TEM image of ZnO-PANI core-shell nanorod.

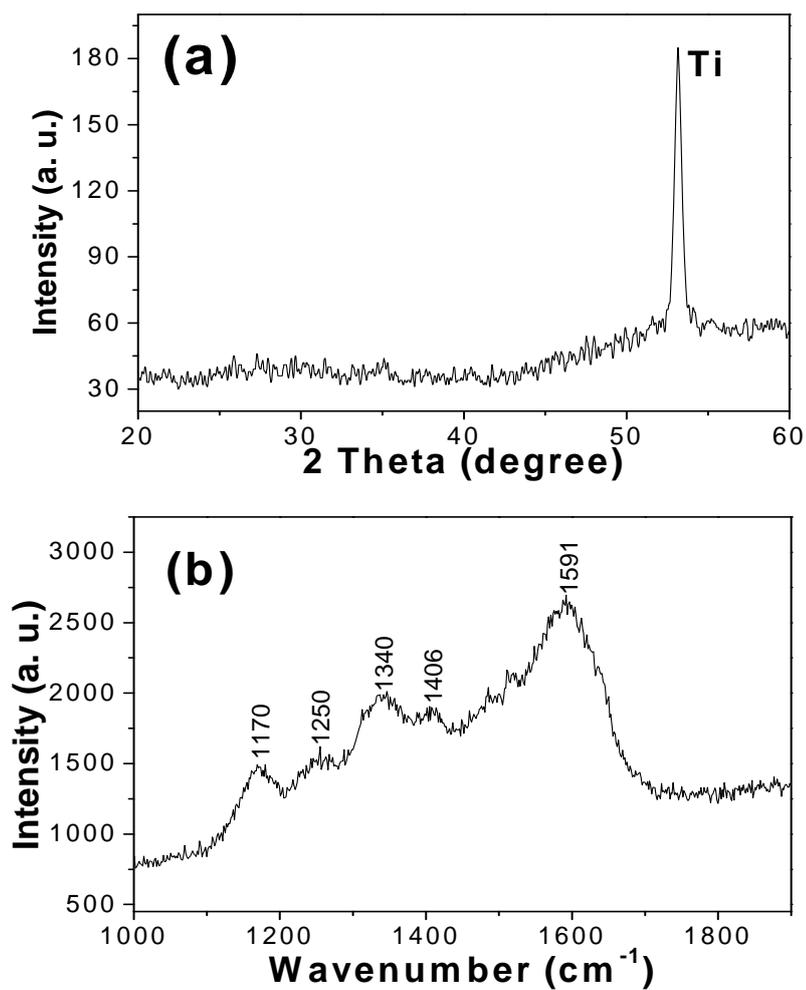


Figure S4 (a) XRD pattern and (b) Raman spectrum of PANI nanotube arrays.

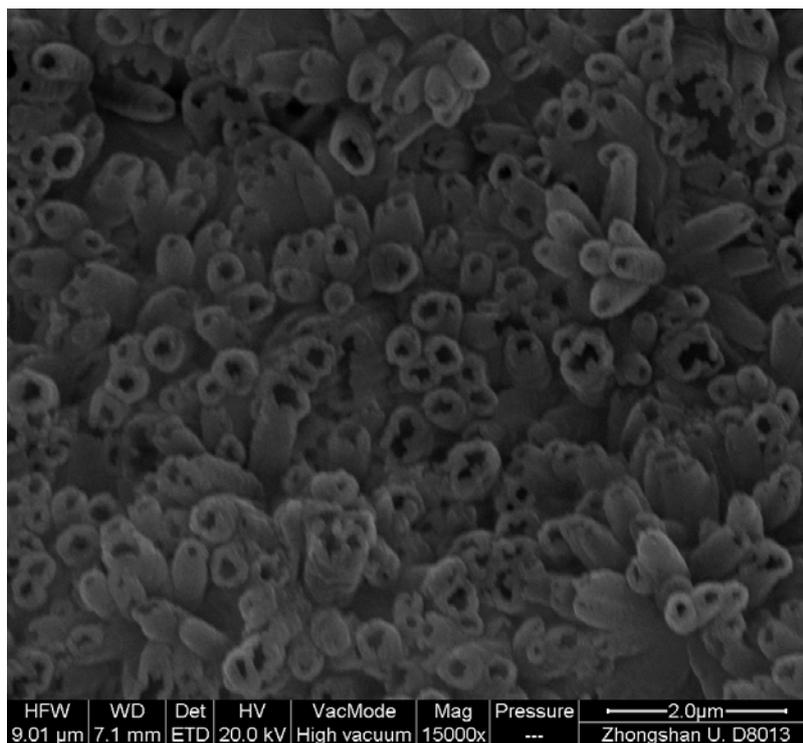


Figure S5 SEM image of PANI nanotube arrays after 400 cycles.