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Supporting Information for

Formation of SnO₂ Hollow Nanospheres Inside Mesoporous Silica Nanoreactors
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Experimental Section

Materials Synthesis. The mesoporous silica nanoreactors were prepared by calcining corresponding polystyrene (PS)@SiO₂ core-shell composite particles (Chem. Mater. 2010, 22, 2693 – 2695), where CTAB was used as the porogen agent to generate the mesopores in the SiO₂ shell. The SnO₂ hollow spheres were formed inside silica nanoreactors. In a typical experiment, a certain amount of Tin (II) chloride dihydrate (SnCl₂·2H₂O, Aldrich, 99.9%) and silica hollow spheres were added to a 20 mL sealed glass bottle, that was then transferred into an oven at 80 °C and kept for 24 hours for complete diffusion of SnCl₂·2H₂O. After that, the excess SnCl₂·2H₂O was removed by washing with ethanol for 3 times, then a certain amount of water was added into the bottle and stirred for 1 hour. Afterwards the precursor-loaded silica nanoreactors were put into a furnace at 700 °C for 2 hours in air. The silica nanoreactors were finally removed by HF etching (2 wt%). The yellow product was harvested by centrifugation and washed with deionized water and ethanol before drying at 60 °C overnight. SnO₂ solid nanoparticles were obtained by directly calcining SnCl₂·2H₂O in air at 700 °C for 2 hours. SnO₂ solid nanospheres were produced via a modified hydrothermal method. Briefly, 16 mM of K₂SnO₃ was dissolved in an aqueous solution containing 37.5 vol% ethanol and 0.5 M urea. The mixture was then hydrothermally treated at 140 °C for 2 hours.

Materials Characterizations. The products were characterized by X-ray powder diffraction (Bruker, D8 Advance X-ray Diffractometer, Cu Ka, λ=1.5406 Å). Morphology and structure of the samples were examined with transmission electron microscope (JEOL, JEM-2100F, 200 kV) and field-emission scanning electron microscopy (FESEM; JEOL, JSM-6700F). The elemental composition of the samples was analyzed with energy-dispersive X-ray spectroscopy (EDX) attached to the FESEM instrument. The surface area of SnO₂ hollow nanospheres was measured using BET (Quantachrome Instruments, Autosorb AS-6B).

Electrochemical Measurements. The electrochemical measurements were performed using two-electrode Swagelok-type cells (X2 Labwares, Singapore) with lithium serving as both the counter and reference electrodes under ambient temperature. The working electrode was composed of 70 wt% of active material, 20 wt% of conductivity agent (carbon black, Super-P-Li), and 10 wt% of binder (polyvinyldenedifluoride, PVDF, Aldrich). The electrolyte used was 1 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an argon filled glove box with both moisture and oxygen contents below 1 ppm.
Cyclic voltammetry (CV, 5 mV to 2.5 V, 0.2 mV s⁻¹) was performed using an electrochemical workstation (CHI 660C). Galvanostatic charging/discharging was performed using a battery tester (NEWAER).

**Figure S1.** EDX analysis of SnO₂ hollow spheres with diameter ~ 400 nm.

**Figure S2.** FESEM (A) and TEM (B) images of mesoporous hollow silica spheres with diameter around 250 nm. TEM images (C, D) of SnO₂@silica double-shelled spheres. FESEM (E) and TEM (F) images of ~140 nm SnO₂ hollow spheres.
**Figure S3.** TEM images of precursor-loaded silica nanoreactors after annealed at 120 °C (A & B) and 400 °C (C & D). E) XRD patterns of precursor-loaded silica nanoreactors after annealed at 120 °C, 200 °C, and 300 °C.

**Figure S4.** \( \text{N}_2 \) adsorption/desorption isotherm of the \( \text{SnO}_2 \) hollow spheres with diameter around 400 nm. Inset is the pore size distributions calculated using the BJH method from both adsorption and desorption branches.
**Figure S5.** (A) Representative CVs for the first, second and fifth cycles at a scan rate of 0.2 mV s\(^{-1}\) with a voltage window of 0.005-2.5 V. (B) cycling performance of the as-prepared SnO\(_2\) hollow nanospheres for 50 cycles at a current rate of 160 mA g\(^{-1}\) between 0.01 V and 2 V.

**Figure S6.** Low (A) and high (B) magnification FESEM images showing the morphology of the as-prepared SnO\(_2\) hollow nanospheres after 20 charge-discharge cycles at a current rate of 160 mA g\(^{-1}\) between 0.01 V and 2 V. B shows a cluster of 8 spherical particles, and the hollow structure is somewhat retained (indicated by the white arrow).