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Formation of SnO_2 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)@SiO_2 core-shell composite particles (*Chem. Mater.* **2010**, *22*, 2693 – 2695), where CTAB was used as the porogen agent to generate the mesopores in the SiO_2 shell. The SnO_2 hollow spheres were formed inside silica nanoreactors. In a typical experiment, a certain amount of Tin (II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$, 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 ^oC and kept for 24 hours for complete diffusion of $SnCl_2{\cdot}2H_2O$. After that, the excess $SnCl_2{\cdot}2H_2O$ 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 ^oC 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 ^oC overnight. SnO_2 solid nanoparticles were obtained by directly calcining $SnCl_2{\cdot}2H_2O$ in air at 700 ^oC for 2 hours. SnO_2 solid nanospheres were produced via a modified hydrothermal method. Briefly, 16 mM of K_2SnO_3 was dissolved in a aqueous solution containing 37.5 vol% ethanol and 0.5 M urea. The mixture was then hydrothermally treated at 140 ^oC for 2 hours.

Materials Characterizations. The products were characterized by X-ray powder diffraction (Bruker, D8 Advance X-ray Diffractometer, Cu Kα, 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 SnO_2 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 (polyvinylidenedifluoride, PVDF, Aldrich). The electrolyte used was 1 M $LiPF_6$ 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).

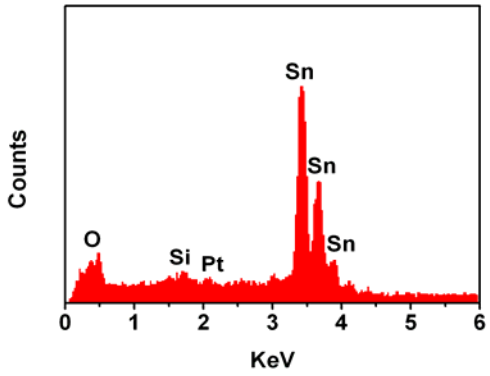

Figure S1. EDX analysis of SnO_2 hollow spheres with diameter ~ 400 nm.

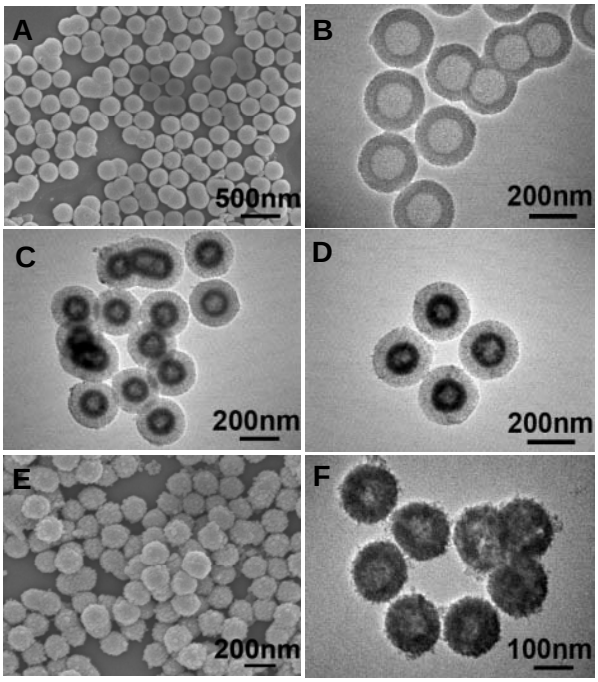

Figure S2. FESEM (A) and TEM (B) images of mesoporous hollow silica spheres with diameter around 250 nm. TEM images (C, D) of SnO_2@silica double-shelled spheres. FESEM (E) and TEM (F) images of ~140 nm SnO_2 hollow spheres.

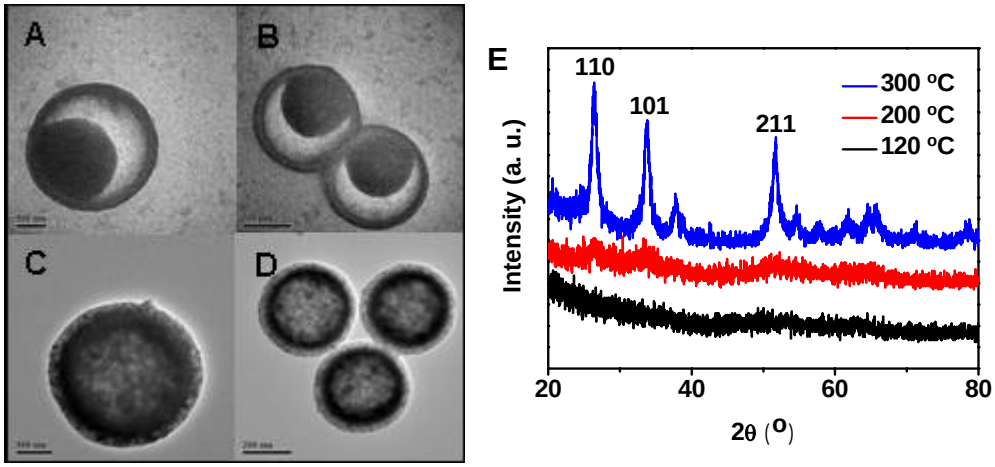

Figure S3. TEM images of precursor-loaded silica nanoreactors after annealed at 120 °C (A & B) and 400 °C (C & D). E) XRD patterns of precursor-loaded silica nanoreactors after annealed at 120 °C, 200 °C, and 300 °C.

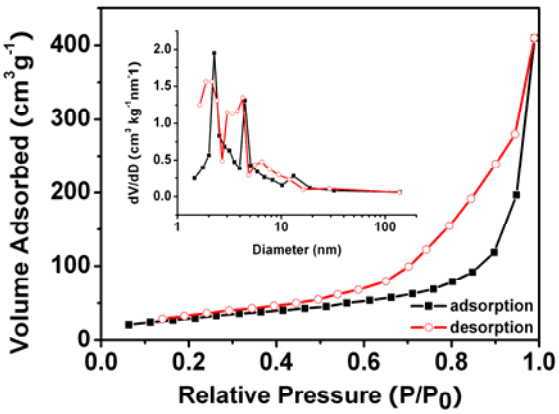

Figure S4. N_2 adsorption/desorption isotherm of the SnO_2 hollow spheres with diameter around 400 nm. Inset is the pore size distributions calculated using the BJH method from both adsorption and desorption branches.

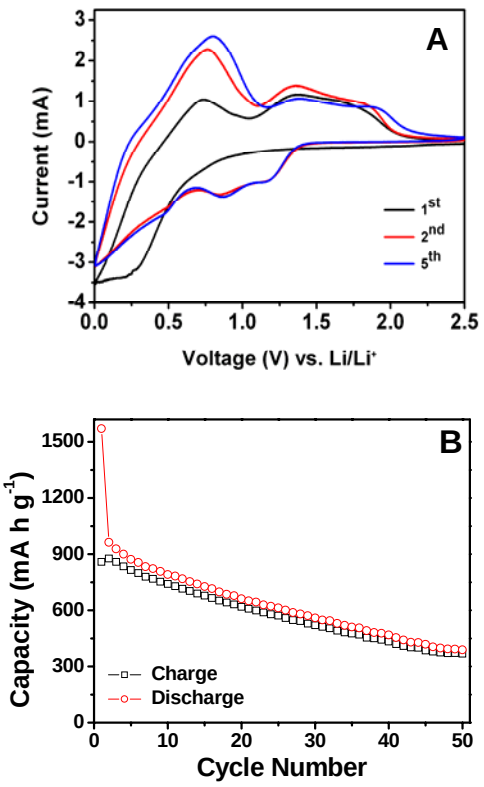

Figure S5. (A) Representative CVs for the first, second and fifth cycles at a scan rate of 0.2 mV s^{-1} with a voltage window o f 0.005-2.5 V. (B) cycling performance of the as-prepared SnO_2 hollow nanospheres for 50 cycles at a current rate of 160 mA g^{-1} between 0.01 V and 2 V.

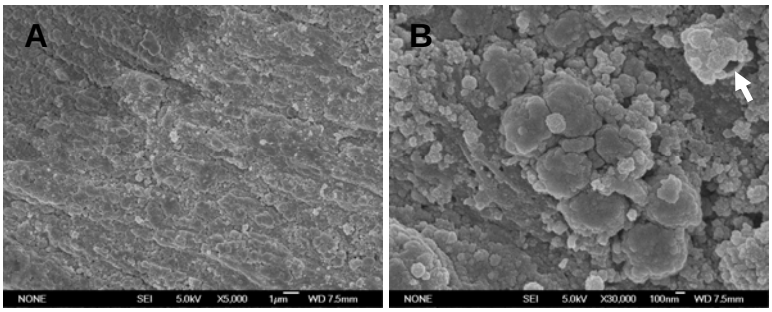

Figure S6. Low (A) and high (B) magnification FESEM images showing the morphology of the as-prepared SnO_2 hollow nanospheres after 20 charge-discharge cycles at a current rate of 160 mA g^{-1} between 0.01 V and 2 V. B shows a cluster of 8 spherical particles, and the hollow structure is somewhat retained (indicated by the white arrow).