

Supporting Information

TiO₂ and SnO₂@TiO₂ Hollow Spheres Assembled from Anatase TiO₂

Nanosheets with Enhanced Lithium Storage Properties

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Experimental Section

Materials Synthesis

Synthesis of anatase TiO₂-NS hollow spheres. 0.04 g of ~400 nm SiO₂ spheres synthesized by the Stöber method was dispersed in 41.7 ml of isopropanol (IPA) before 0.03 ml of diethylenetriamine (DETA) was added. After stirring gently by hand, 1.8 ml of titanium (IV) isopropoxide (TIP) was added into the solution. The reaction mixture was transferred into a 60 ml Teflon-lined stainless steel autoclave and kept at 200 °C for 24 h. After the reaction was completed, the white product was collected through centrifugation and washed thoroughly with ethanol before drying at 60 °C overnight. After that, the powder was calcined at 400 °C in air for 2 h with a ramping rate of 1 °C min⁻¹ to obtain highly crystalline anatase phase. For removal of silica, several milligrams of calcined SiO₂@TiO₂-NS core-shell spheres were dispersed into

0.6 wt% hydrofluoric acid (HF) solution and shaken under room temperature for 1 h before washing with water.

Synthesis of SnO₂@TiO₂-NS double-shelled hollow spheres. The synthesis is similar to the steps for synthesizing TiO₂-NS hollow spheres, except that 0.05 g of SiO₂@SnO₂ core-shell nano-template was dispersed in 41.5 ml of IPA with the addition of 0.03 ml of DETA and 2 ml of TIP. The subsequent calcination and removal of SiO₂ are the same as described above. The SiO₂@SnO₂ core-shell spheres are synthesized following our previously reported method (Small 2007, 3, 261).

Materials Characterizations.

The morphology of products was examined by transmission electron microscope (TEM; JEOL, JEM-2100F, 200 kV), field-emission scanning electron microscope (FESEM; JEOL, JSM-6700F, 5 kV). The elemental compositions of the samples were analyzed with energy-dispersive X-ray spectroscopy (EDX) attached to FESEM. Crystallographic information of the samples was investigated with X-ray powder diffraction (XRD; Bruker, D8 - Advance X-Ray Diffractometer, Cu K α , $\lambda = 1.5406 \text{ \AA}$). The surface area of the sample was measured using Quantachrome Instruments, Autosorb AS-6B. For the uncalcined sample, the thermogravimetric analysis (TGA) was carried out in a flow of air with a temperature ramp of $5 \text{ }^\circ\text{C min}^{-1}$.

Electrochemical Measurements.

The electrochemical measurements were carried out using two-electrode Swagelok cells (X2 Labwares) with pure lithium metal as the counter and also the reference electrodes at room temperature. The working electrode consists of active material

(e.g., TiO₂-NS hollow spheres), a conductive agent (carbon black, Super-P-Li), and a polymer binder (polyvinylidene difluoride, PVDF, Aldrich) in a weight ratio of 70:20:10. The electrolyte used was 1.0 M LiPF₆ in a 50:50 (w/w) mixture of ethylene carbonate and diethyl carbonate. Cell assembly was carried out in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. The charge/discharge tests were performed using a NEWARE battery tester at different current rates (1 C = 170 mA g⁻¹) with a voltage window of 1 V – 3 V.

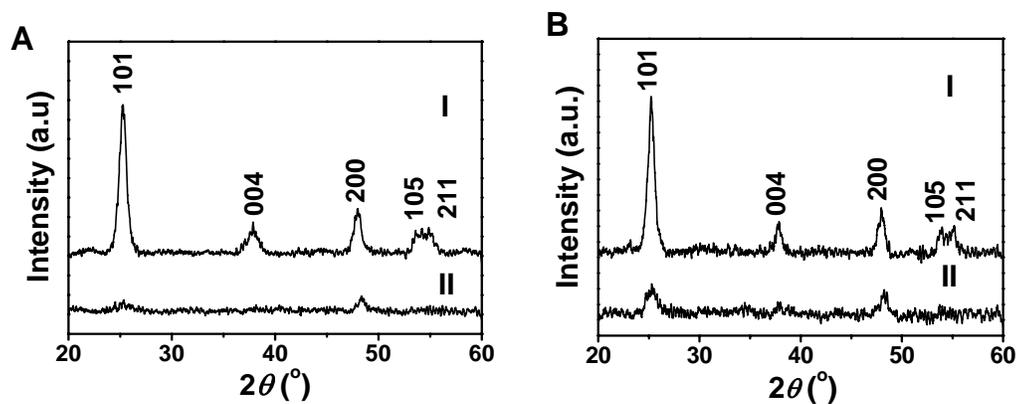


Figure S1. XRD patterns of the sample shown in Fig. 1A (A), Fig. 2A (B) after (I) and before (II) calcination at 400 °C. The absence of diffraction peaks due to SnO₂ in B is probably because that the SnO₂ shell deposited on the SiO₂ nanospheres is generally amorphous even after calcination.

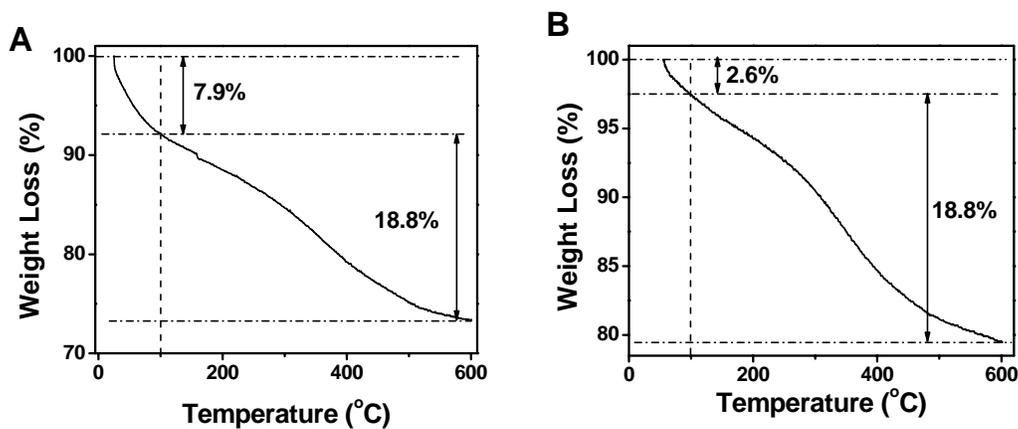


Figure S2. TGA data of the samples shown in Fig. 1A (A), Fig. 2A (B) before calcination.

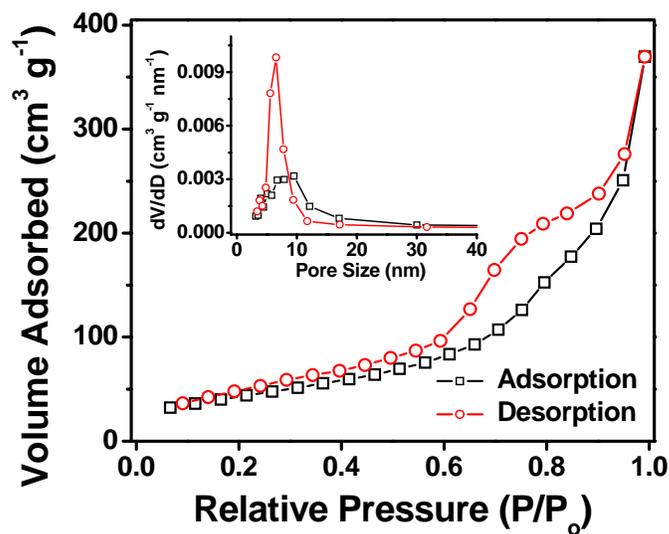


Figure S3. Typical N₂ adsorption-desorption isotherm of the TiO₂-NS hollow nanospheres. The hysteresis loop indicates a mesoporous structure. The inset shows the pore size distribution by Barrett-Joyner-Halenda (BJH) method from both branches of the isotherm.

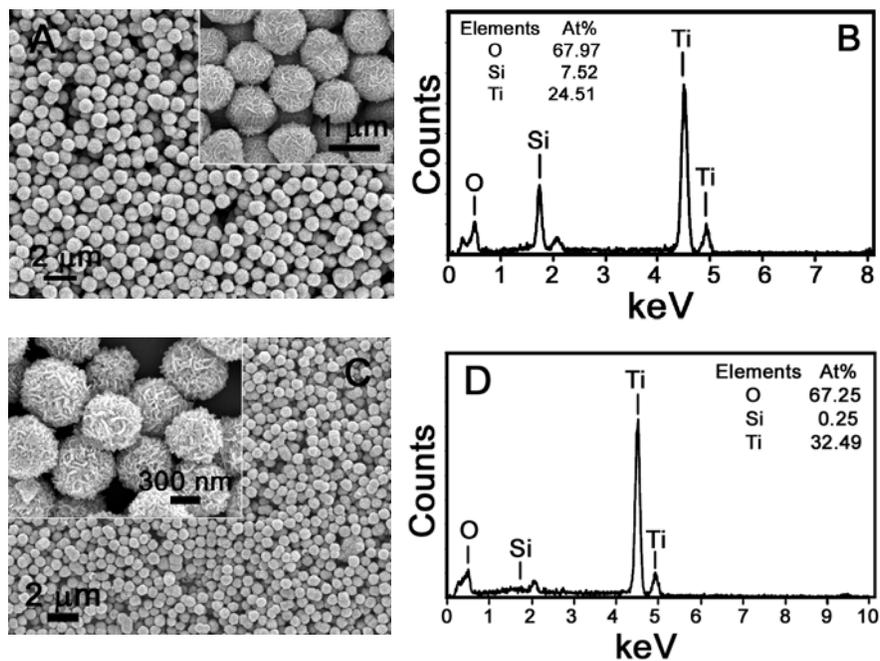


Figure S4. (A) FESEM image of SiO₂@TiO₂-NS core-shell nanostructure; (B) EDX analysis of the sample shown in A; (C) FESEM image and (D) EDX analysis of TiO₂-NS hollow spheres after removing the SiO₂ cores (see structure A1 in Figure 1).

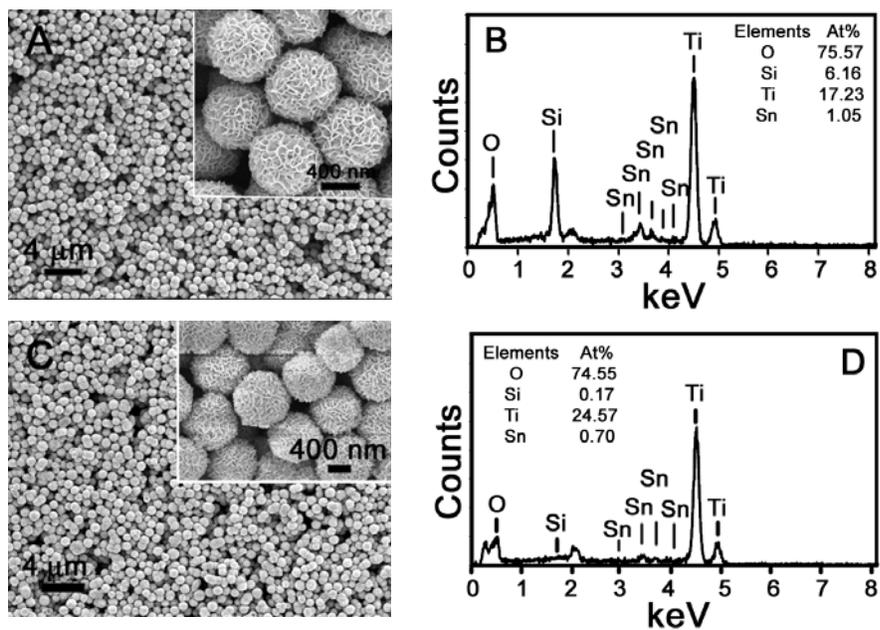


Figure S5. (A) FESEM image of SiO₂@SnO₂@TiO₂-NS nanostructures, and (B) its corresponding EDX analysis. (C) FESEM image of SnO₂@TiO₂-NS double-shelled hollow spheres (see structure A2 in Figure 1), and (D) its EDX analysis.

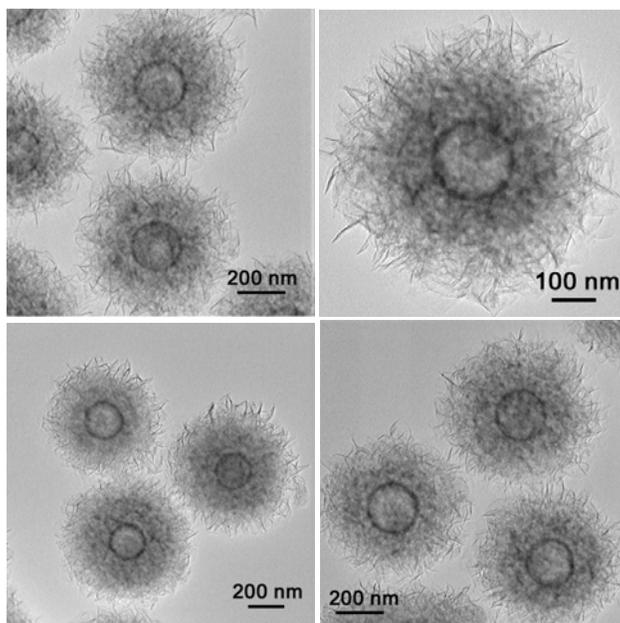


Figure S6. TEM images of TiO_2 -NS nanostructure assembled on ~ 200 nm $\text{SiO}_2@ \text{SnO}_2$.

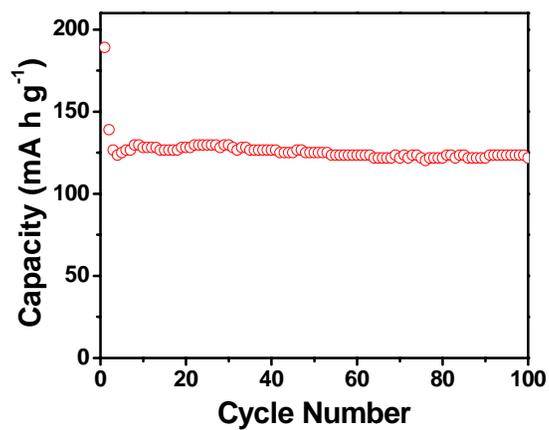


Figure S7. Cyclic performance of $\text{SnO}_2@ \text{TiO}_2$ -NS hollow nanospheres at the current rate of 10 C between 1 V to 3 V.