TiO₂ Hollow Spheres Composed of Highly Crystalline Nanocrystals Exhibit Superior Lithium Storage Properties**

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Experimental Section

Materials synthesis: In a typical synthesis, carbonaceous (C) spheres were first synthesized by a previously reported hydrothermal method (X. M. Sun, Y. D. Li, Angew. Chem. Int. Ed. 2004, 43, 597-601). Then, 20 mg of C spheres was added into 50 mL of anhydrous ethanol solution followed by sonication to reach a uniform dispersion. After this, 1.5 mL of titanium tetrabutoxide (TTB) solution was added into the above mixture upon stirring. Next, some ammonium solution is then added into the solution to initiate hydrolysis of TTB. The obtained mixture was then transferred into a round bottom flask and kept refluxing at 50 °C for 24 h with an oil bath. The mixture was then naturally cooled down to room temperature, and the product was collected by centrifugation and washed with ethanol for several times. In order to obtain TiO₂ hollow spheres, the product was further annealed at 500 °C in air for 2 h with a slow heating rate of 1 °C min⁻¹.

Materials characterization: X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advanced X-Ray Diffractometer. Field-emission scanning electron microscope (FESEM) images were obtained on a JEOL JSM 6700F microscope. Transmission electron microscope (TEM) images were taken on a JEOL JEM 2010 microscope. High resolution TEM (HRTEM) analysis was performed on a JEOL JEM 2100F microscope.

Electrochemical measurements: The electrochemical measurements were carried out using CR2032 coin-type half-cells. The working electrode consisted of active material (i.e., TiO₂ hollow spheres), carbon black (Super-P-Li), and polymer binder (polyvinylidene fluoride, PVDF) in a weight ratio of 70:20:10. Lithium foil was used as both the counter electrode and the reference electrode. 1M LiPF₆ in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte. Cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. Cyclic voltammetry measurements were performed on a CHI660C electrochemical workstation. The galvanostatic charge-discharge tests were performed on a NEWARE battery test system.
Figure S1. Typical TEM image (A) and corresponding SAED pattern of C@TiO$_2$ core/shell particles.

Figure S2. Typical XRD pattern of TiO$_2$ hollow spheres after thermal annealing treatment in air at 500 °C for 2 h.
Figure S3. Typical TEM images of TiO\textsubscript{2} hollow spheres after sonication for 2 h dispersed in ethanol.

Figure S4. Nitrogen adsorption-desorption isotherm of TiO\textsubscript{2} hollow spheres.
**Figure S5.** Cyclic voltammetry (CV) curves of TiO$_2$ hollow spheres.

**Figure S6.** (A) FESEM and (B) TEM images of TiO$_2$ hollow spheres after cycling at 5 C for 100 cycles. The small nanoparticles observed in the images are carbon black.