

Supplementary Information

Synthesis of hierarchically mesoporous anatase spheres and their application in lithium batteries

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A. Experimental details

Preparation of mesoporous TiO₂ spheres: In a typical synthesis, one solution containing 0.46 g cadmium acetate dihydrate (Merck), 0.19 g thiourea (Merck), and 0.19 g 1-thioglycerol (Sigma) in 20 mL of N,N-dimethylformamide/water (3:1, in volume) solvent was added into 40 mL of continuously stirred butanol solution with 1.5 mL Ti(OBu)₄ (Aldrich) and 0.3 mL acetylacetone (Aldrich) at room temperature. Then the mixture was stirred for 20 min and refluxed at 140 °C for about 3 h. The as-produced white precipitates were collected by using centrifuge and repeatedly washed with ethanol and distilled water. The Ti-Cd precursor was calcined at 500 °C under air for 5 h to obtain crystalline TiO₂/CdSO₄ composites. To form the mesoporous TiO₂ spheres CdSO₄ was completely removed in dilute HNO₃ (10 wt-%) aqueous solution, followed by thorough rinsing with distilled water.

Characterization of materials: XRD measurements were carried out with a PHILIPS PW3710 using filtered Cu K α radiation. A JEOL 6300F scanning electron microscope (SEM) was used to investigate the morphology of the spheres. TEM and HRTEM images were collected by using a JEOL 4000EX transmission electron microscope (operating at 400 kV), respectively. The nitrogen adsorption and desorption isotherms at 77.4 K were obtained with an Autosorb-1 system (Quanta Chrome) after the sample was degassed in vacuum at 120 °C overnight.

Electrochemical Characterization: Electrochemical experiment was performed using two-electrode Swagelok-typeTM cells. For preparing working electrodes, a mixture of mesoporous TiO₂ spheres, carbon black, and poly (vinyl difluoride) (PVDF) at a weight ratio of 60:20:20, was pasted on pure Cu foil (99.6 %, Goodfellow). Similar experiment was also conducted on commercial TiO₂ (anatase, Aldrich). Glass fiber (GF/D) from Whatman[®] was used as a separator. The electrolyte consists of a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, in volume) obtained from Ube Industries Ltd. Pure lithium foil (Aldrich) was used as counter electrode. Discharge and charge cycling was carried out on an Arbin MSTAT system. The cells were assembled in an argon-filled glove box.

B. Fig. S1. Galvanostatic discharge (Li-insertion)/charge (Li-extraction) curves of a commercial TiO₂ electrode (anatase, particle size ~ 300 nm) cycled at C/5 between voltage limits of 1 and 3 V.

