

Designed Synthesis of SnO₂@C Yolk–Shell Spheres for High-Performance Lithium Storage

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Experimental Section

Synthesis of SnO₂@C Yolk–Shell Spheres. All the chemicals were analytical grade without further purification. First, Sn spheres were prepared by a simple polyol method according to the previous report.²⁶ Second, SiO₂ layer was coated on Sn sphere templates through a modified Stöber method.³³ Third, the Sn@SiO₂ spheres were oxidized in a tubular furnace at 600 °C for 12 h under flowing oxygen. Fourth, the SnO₂@SiO₂ spheres were coated with carbon layers through the pyrolysis of PVDF. Briefly, 0.1 g SnO₂@SiO₂ spheres and 0.1 g polyvinylidene fluoride (PVDF) were mixed and added into 2 mL N-methyl-2-pyrrolidone (NMP), and the mixture was stirred for 24 h and then dried at 120 °C under vacuum. Subsequently, the dried sample was pyrolyzed at 500 °C for 3 h under N₂. Finally, the obtained SnO₂@SiO₂@C spheres were treated with 10 % HF aqueous solution for 12 h to

remove SiO₂ layer, resulting in SnO₂@C yolk–shell spheres. For comparison, bare SnO₂ spheres was prepared by thermal oxidation of Sn spheres at 600 °C for 12 h under flowing oxygen, whereas pure PVDF-derived carbon was obtained through pyrolysis of PVDF at 500 °C for 3 h under N₂.

Characterization. The morphology, structure, and composition of the samples were characterized by transmission electron microscopy (TEM, JEOL H-7650, 120 kV), scanning electron microscopy (SEM, JEOL JSM-7600F), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, 200 kV) equipped with energy-dispersive X-ray spectrometer (EDX, Thermo Fisher Scientific, NORAN System 7). X-ray powder diffraction (XRD) measurements were performed with Model D/max-rC diffractometer using Cu-K α radiation ($\lambda=0.15406$ nm) and operating at 45 kV and 100 mA. The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution were measured at 77 K using a Micromeritics ASAP 2050 system. The differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) was performed on a Petkin Elmer Diamond instrument in air at a ramping rate of 5 °C min⁻¹.

Electrochemical Measurements of SnO₂@C Yolk–Shell Spheres.

Electrochemical measurements were performed by coin-type half cells which were assembled in an IL-2GB glove box (Innovative Technology) filled with ultra-pure argon. For the preparation of working electrodes, a mixture of SnO₂@C yolk–shell spheres, Super P, and PVDF in NMP at a weight ratio of 80 : 10 : 10 were mixed, then the slurry was coated on the surface of Cu foam substrates at room temperature and

dried at 120 °C under vacuum overnight. The counter electrode was lithium metal foil, and the electrolyte solution was 1 M solution of LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). Finally, the cells were aged for 12 h before measurements. A galvanostatic cycling test of the assembled cells was carried out on a Land CT2001A system in the potential range of 0.01-2 V. Cyclic voltammetry (CV) measurements were recorded on a CHI 660C electrochemical workstation in the potential range of 0.0-2.0 V at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) tests were performed on a CHI 760D electrochemical workstation with the frequency ranging from 100 kHz to 0.01 Hz and an ac signal of 5 mV in amplitude. The voltages mentioned herein were referred to Li⁺/Li redox couple.