Electronic Supplementary Information (ESI)

Preparation and Lithium Storage Performance of Yolk-Shell Si@Void@C Nanocomposites

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Experimental

All the reagents were of analytic grade and used without any further purification. The yolk-shell Si@void@C nanocomposites were prepared by a two-step method: RF coating and LiOH etching. In a typical synthesis, Si nanoparticles (0.2 g), cetyltrimethylammonium bromide (CTAB, 8 mg), and ammonia (28%, 0.2 mL) were dispersed in the H_2O (40 mL) and ethanol (20 mL) mixture solution separately. After vigorously stirring for 30 min, 150 mg resorcinol and 0.2 mL formaldehyde solution (37-40 wt.%) were added into the above suspension and kept continual stirring for 12 h. The products were centrifuged and washed with ethanol for three times, and further carbonized under an Ar atmosphere at 800 °C for 2 h to obtain core-shell Si@C nanocomposites. Then, the Si@C precursors were immersed in a 1 M LiOH solution for 15 min at 70 °C, centrifuged and washed with water for three times. After drying at 80 °C for 12 h, yolk-shell Si@void@C nanocomposites were obtained. Moreover, other Si@void@C nanocomposites were prepared in the same conditions except the etching times (5, 10 and 20 min).

The samples were characterized by X-ray diffraction (XRD, PANalytical X'Pert

Pro diffraction system using Cu K_α radiation, $\lambda = 1.5418$ Å, 60 kV and 60 mA), scanning electron microscopy (SEM, Hitachi S-4700 operated at 15 kV), transmission electron microscopy (TEM, Tecnai G2F30 S-Twin operated at 300 kV), and thermogravimetric analysis (TGA, Perkin Elmer in air at 10 °C min^{-1}).

The electrochemical performances of the samples were tested in CR2032-type coin cells. The working electrodes consisted of active materials, acetylene black, and PVDF in an N-methyl-pyrrolidinone (NMP) solution with a weight ratio of 70: 15: 15. The mixture slurry was pasted onto a Cu foil using the doctor-blade method, dried at 120 °C overnight and finally punched into disks (12 mm in diameter). The average loading mass of the electrodes was about 0.8 mg cm^{-2}. Li disks were used as the counter and reference electrodes. The electrolyte was 1 M $LiPF_6$ dissolved in a 1: 1 : 1 mixture of ethylene carbonate (EC), ethylene methyl carbonate (EMC), and dimethyl carbonate (DMC). The cells were assembled in a glove box filled with high-purity argon (O_2 and H_2O < 1 ppm). Discharge–charge measurements were performed in the voltage range of 0.005–1.5 V on a Land-CT2001A instrument. Cyclic voltammetry (CV) testing was carried out on a CHI 604E electrochemical workstation at a scan rate of 0.1 mV s^{-1}, with a potential range of 0.005-1.5 V.
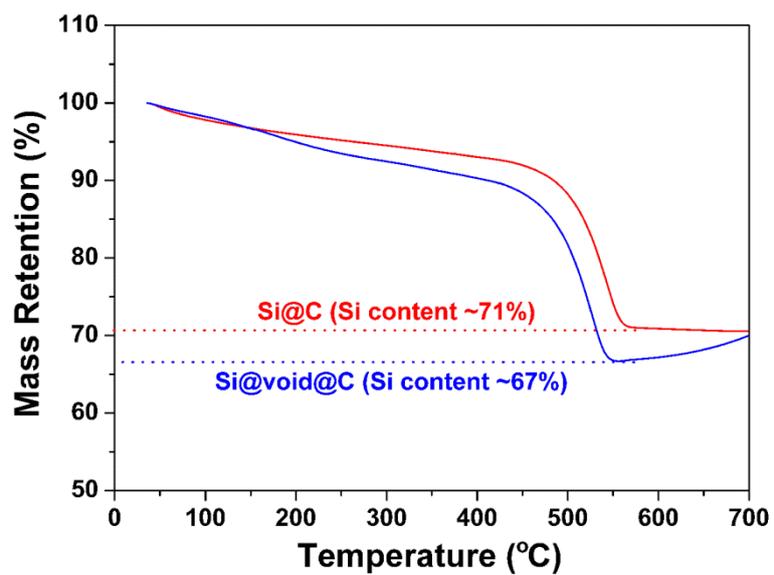
Figure S1. TGA curves for the Si@C and Si@void@C nanocomposites.
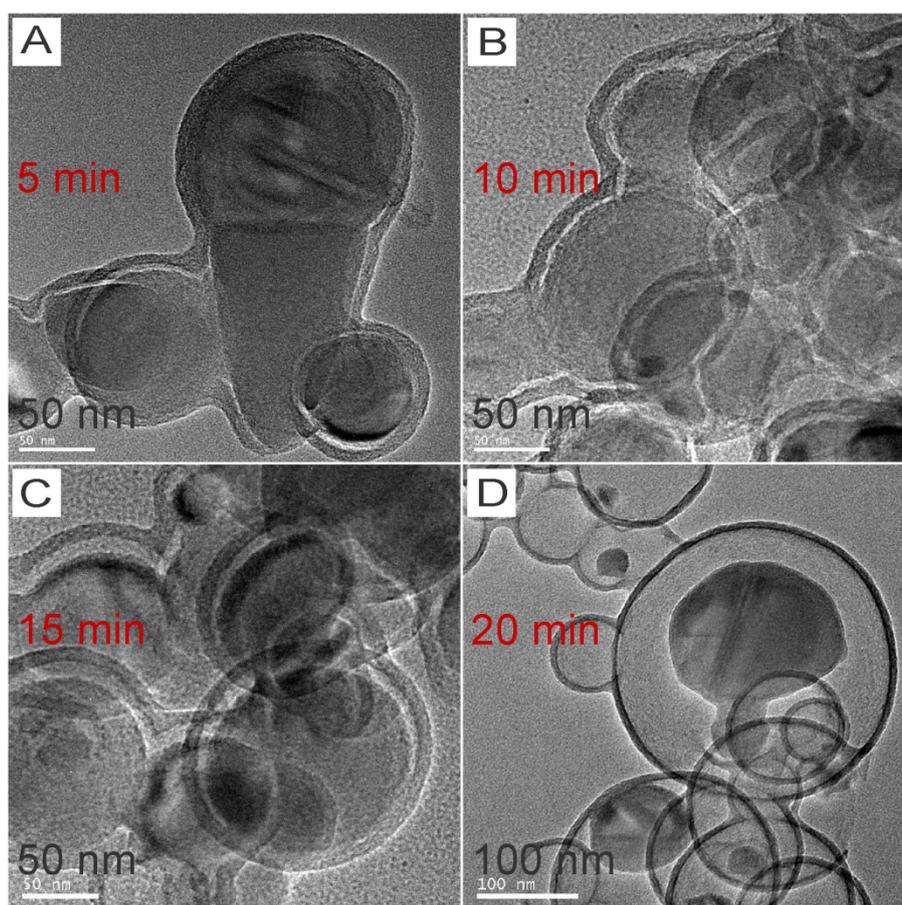

Figure S2. TEM images of Si@void@C nanocomposites obtained with different

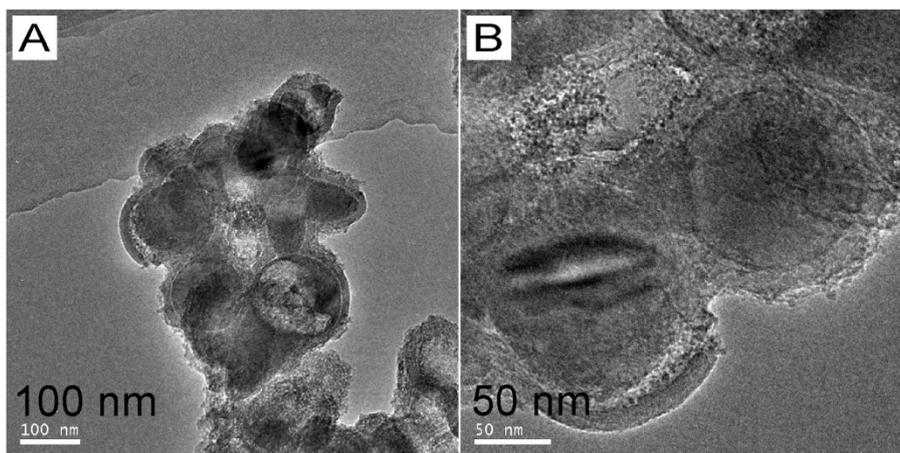LiOH etching times of: (A) 5 min, (B) 10 min, (C) 15 min, and (D) 20 min.

Figure S3. TEM images of the Si@void@C electrodes after 30 cycles at 500 mA g^{-1}.
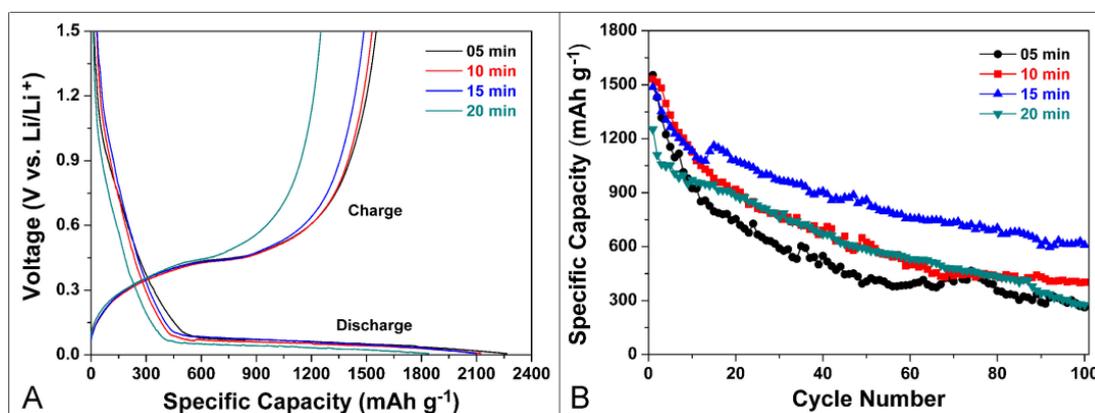

Figure S4. (A) Initial discharge–charge profiles and (B) cycling performances of Si-C composites with different etching times of 5, 10, 15, and 20 min (denoted as Si-5 to Si-20, respectively), in the voltage range of 0.005-1.5 V at 50 mA g^{-1}.