

Uniform Yolk-Shell Structured Si-C Nanoparticles as High Performance Anode Material for Li-Ion Battery

Xuequan Li^a, Yufeng Xing^a, Jun Xu^b, Qibo Deng^c and Li-Hua Shao^{*a}

Experimental section

Chemicals

All of the chemicals were used as received from Aladdin Co., Ltd., including the tetraethyl orthosilicate (TEOS), hexadecyl trimethyl ammonium bromide (CTAB), ammonium hydroxide (NH₃·H₂O, 28% by weight in water), hydrofluoric acid (40% solution) resorcinol, formaldehyde (37% solution), Mg powder, hydrochloric acid and the ethyl alcohol.

Synthesis of SiO₂@C core-shell nanoparticles: The synthesis method of SiO₂@C core-shell nanoparticles is modified from the one in literature. Here, SiO₂ nanospheres were prepared through a modified Stöber method. Firstly, 50 mL TEOS in 90 mL ethanol was added dropwise into 100 mL aqueous NH₃ (28%) and 300 mL ethanol. Keeping them reacting for 60 mins under vigorously stirring to form the silica nanospheres. In a typical coating process, the as-prepared SiO₂ (2 g) was dispersed in 90 ml D.I. water by sonication. The suspension was sequentially mixed with 1 mL ammonium hydroxide aqueous solution and an aqueous CTAB (10 mL, 0.01 M) solution, vigorously stirred for 60 mins to ensure that CTAB was completely adsorbed on the SiO₂ nanoparticles surface. Then the resorcinol (0.2 g) and formaldehyde solution (0.3 mL) were added. The reaction lasted for 12 hs by magnetic stirring. The SiO₂ coated with resorcinol formaldehyde resin (SiO₂@RF) core-shell composites were collected by centrifugation. Then the SiO₂ coated with carbon (SiO₂@C) core-shell nanoparticles were obtained by heating the SiO₂@RF composites at 650 °C under Ar atmosphere for 2 hs.

Synthesis of Si@void@C nanocomposites: SiO₂ in a hollow carbon sphere (SiO₂@void@C) nanocomposites were prepared by etching the as-prepared SiO₂@C core-shell nanoparticles with the hydrofluoric acid (HF). 7.5 mL HF acid (10%) was added dropwise into the suspension of SiO₂@C core-shell nanoparticles (150 mL, 5 mg mL⁻¹), and the solution was stirred for 60

mins. Then the SiO₂@void@C was obtained after washing with D.I. water for three times. Then the silica in the hollow carbon sphere was transformed to Si via the magnesiothermic reduction. MgO was removed using 1 M hydrochloric acid. Finally, the Si@void@C structure was obtained after washing with D.I. water for three times.

Structural Characterization: An X-ray diffractometer (X'pert3 powder, Netherlands) with a Cu-K α radiation source ($\lambda=1.54056$ Å) was used to measure the phases of the samples. A field-emission scanning electron microscope (SEM, HITACHI SU8200) was used to observe the microstructures of the samples. The transmission electron microscopy (TEM) was carried out with a FEI Tecnai G2 F20 instrument operated at an accelerating voltage of 200 kV. The pyrolysis of the sample was carried out by DSC/TG instrument (Mettler-Toledo STAR system, DSC/TG) with a heating rate of 10 °C min⁻¹ under oxygen flow at 50 mL min⁻¹.

Electrochemical characterization: The electrochemical measurements were carried out in 2032 coin cells. To fabricate the working electrodes, the slurry containing a mixture of active materials (SiO₂@void@C, Si@C and Si were used as control samples), carboxymethyl cellulose (CMC), and carbon black at a ratio of 80:10:10 (wt%) was bladed on a Cu foil (Shenzhen POXON Machinery Technology Co., Ltd). Then the foil was dehydrated at 120 °C for 12 hs under vacuum. The mass loading of the active material on each electrode disk was ca. 0.6 mg cm⁻². The electrolyte was 1 M LiPF₆ in a 1:1:1 (vol%) mixture of the dimethyl carbonate, ethylene carbonate, and diethyl carbonate. A polypropylene film (Celgard 2400) was employed as a separator, and the lithium foil was used as the counter electrode. All of the cells were assembled in an argon-filled glove box with both the contents of water and oxygen below 0.5 ppm. Galvanostatic charge-discharge tests were carried out on a Land CT2001A system (Wuhan, China). The operating voltage window was 0.01~1.00 V (vs Li/Li⁺). The cyclic voltammetry (CV) was conducted on a potentiostat (Autolab, PGSTAT100N, Switzerland) at different scanning rates to characterize the redox reactions of the electrodes during charging/discharging. Electrochemical impedance spectroscopy (EIS) was carried out using the

same potentiostat with the frequency range from 0.01 Hz to 100 kHz and at the AC amplitude of 5.0 mV. The current densities were calculated versus the mass of the active materials of the electrodes. All of the electrochemical measurements were performed at room temperature.

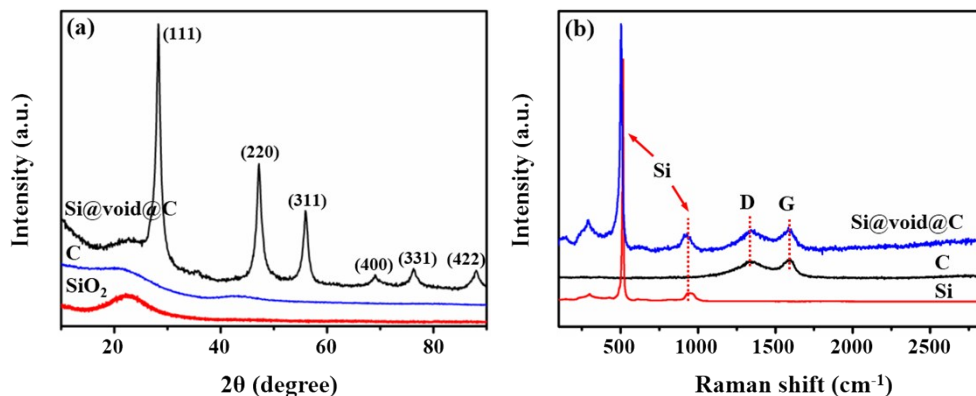


Figure S1. (a) XRD patterns and (b) Raman spectra of SiO₂, C and Si@void@C samples.

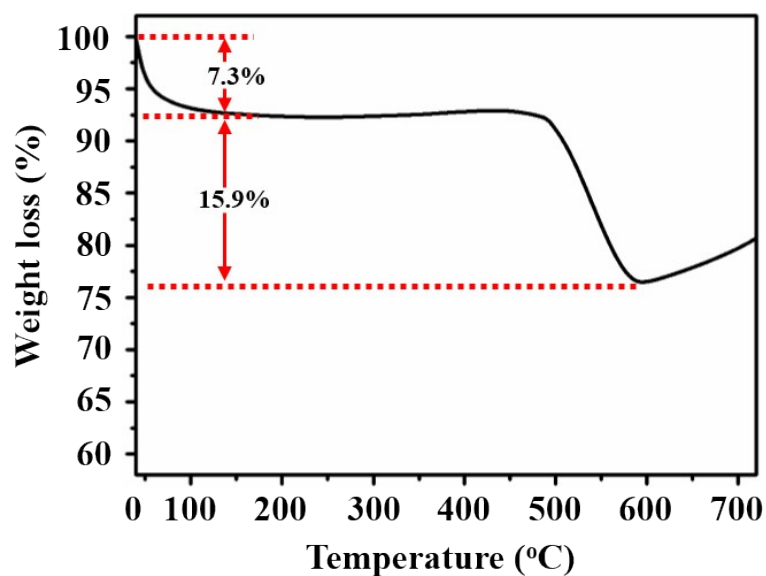


Figure S2 DSC-TGA curves of the Si@void@C composite.

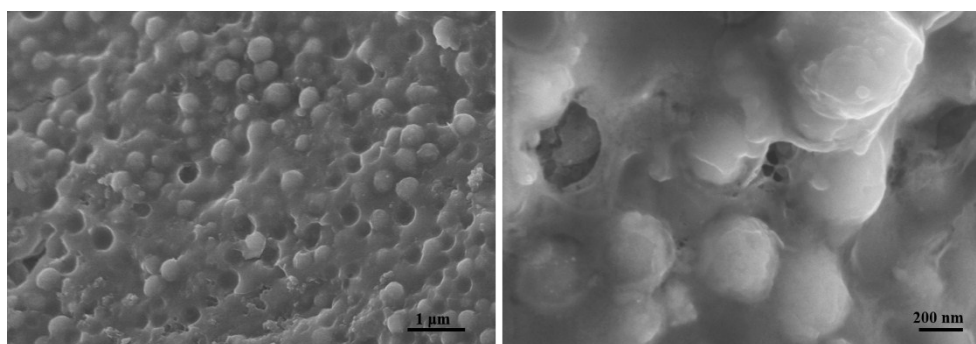


Figure S3 SEM images of Si@void@C electrode after 1500 cycles at a current density of 1.0

A g⁻¹

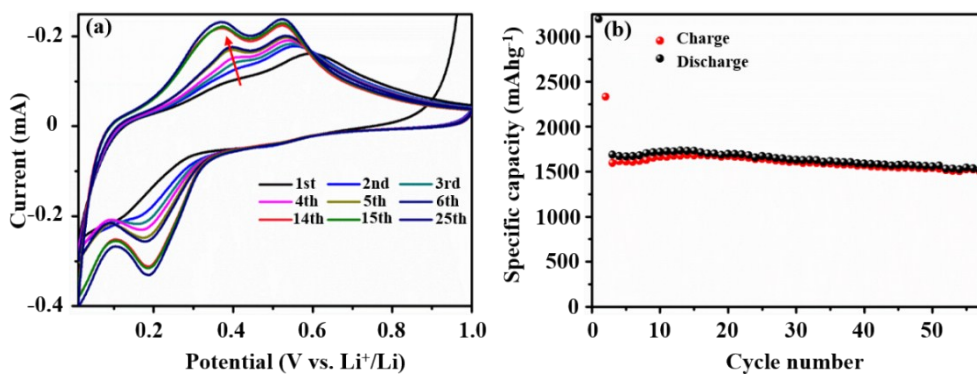


Figure S4. (a) Cyclic voltammogram for Si@void@C from 1.0 V to 0.01 V versus Li/Li⁺ at the scan rate of 0.01 mV s⁻¹. (b) Specific delithiation capacity and lithiation capacity of the first 57 galvanostatic cycles between 0.01~1 V.

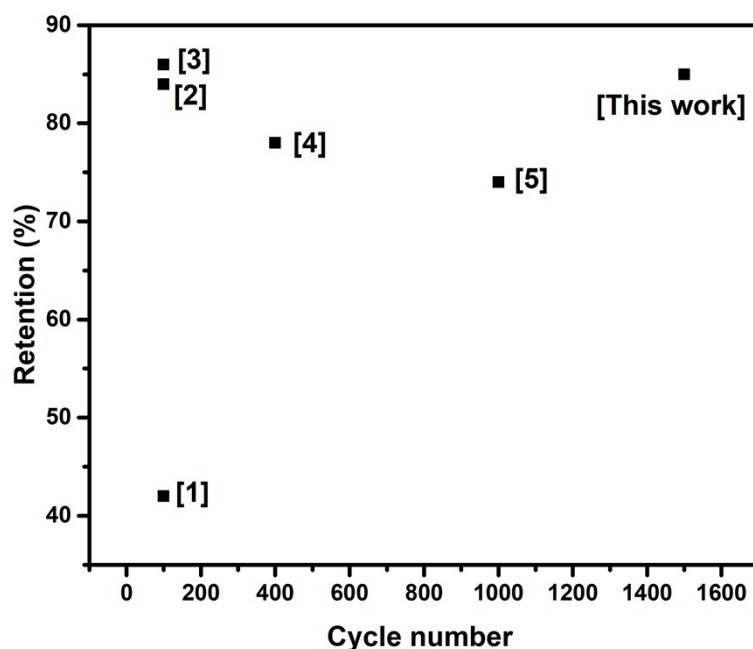


Fig. S5 Performance comparison of this work versus the previous reports.

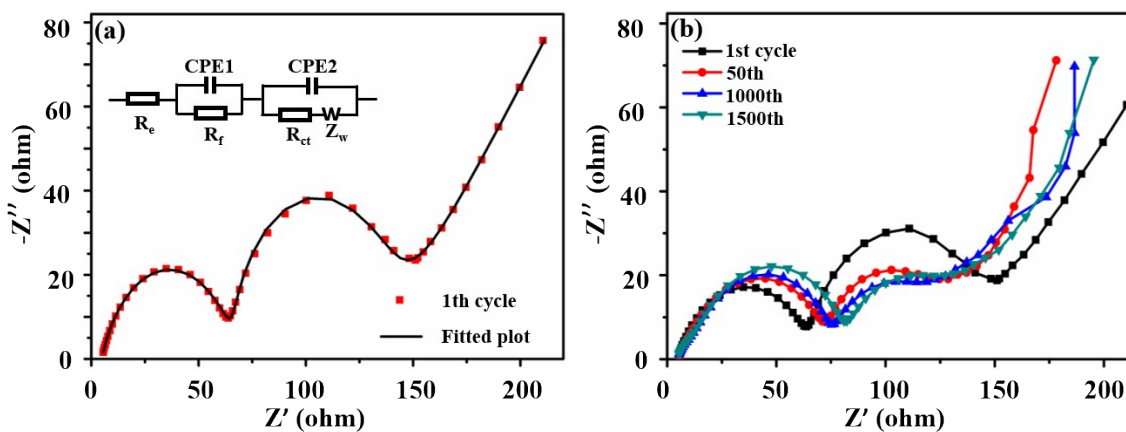


Figure S6. The electrochemical impedance spectra results. (a) The first cycle and the corresponding fitting curve, and (b) the evolution of the real and imaginary impedance at various stages.

1. L. W. Su, J. Xie, Y. W. Xu, L. B. Wang, Y. H. Wang and M. M. Ren, *PCCP*, 2015, **17**, 17562-17565.
2. X. L. Li, P. Meduri, X. L. Chen, W. Qi, M. H. Engelhard, W. Xu, F. Ding, J. Xiao, W. Wang, C. M. Wang, J. G. Zhang and J. Liu, *J. Mater. Chem.*, 2012, **22**, 11014-11017.
3. B. Li, R. Qi, J. Zai, F. Du, C. Xue, Y. Jin, C. Jin, Z. Ma and X. Qian, *Small*, 2016, **12**, 5281-5287.
4. J. P. Yang, Y. X. Wang, S. L. Chou, R. Y. Zhang, Y. F. Xu, J. W. Fan, W. X. Zhang, H. K. Liu, D. Y. Zhao and S. X. Dou, *Nano Energy*, 2015, **18**, 133-142.
5. N. Liu, H. Wu, M. T. McDowell, Y. Yao, C. M. Wang and Y. Cui, *Nano Lett.*, 2012, **12**, 3315-3321.