Supporting information

Encapsulation of core-satellites silicon in carbon for rational balance the void space and capacity

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## Experimental section

**Synthesis of Si@SiO$_2$ nanoparticles:** For a typical procedure, 150 mg commercial silicon nanoparticles (~ 50 nm, obtained from Nanostructured and Amorphous Materials, Inc.) was dispersed in a mixed solution containing 280 mL of absolute ethanol and 70 mL deionized water under ultrasonic treatment for 20 min. Afterwards, 3 mL of ammonia (28 wt %) was added in the dispersion and stirred for 10 min. Then, 1 mL TEOS was added dropwise every 30 min (2 mL in total). The mixture was reacted for 10 h at room temperature under continuous stirring. The Si@SiO$_2$ core-shell nanoparticles were isolated by centrifugation and washed with ethanol for three times, and dried at 60 °C overnight under vacuum.

**Synthesis of Si@SiO$_2$@C nanoparticles:** 300 mg of Si@SiO$_2$ nanoparticles and 920 mg of hexadecyltrimethylammonium bromide (CTAB) were added into a solution of deionized water (28.16 mL) and ethanol (11.28 mL), then ultrasonic treated for 30 min to form homogeneous mixture. Next, resorcinol (140 mg) and ammonia (0.1mL) were added to the mixed solution and stirred at 35 °C for 30 min. After that, 4 mL of formaldehyde was added into the mixed solution and reacted at 35 °C for 6 h. Then aged at room temperature for 12 h. The Si@SiO$_2$@RF nanoparticles were obtained after centrifugation and drying at 60 °C. Finally, the Si@SiO$_2$@C core-shell nanoparticles were collected after heated in Ar atmosphere at 750 °C for 3 h with a temperature ramping rate of 2 °C/min.

**Synthesis of Si@pSi@C nanoparticles:** A mixture of 200 mg Si@SiO$_2$@C nanoparticles and 200 mg of Mg powders were annealed at 750 °C for 4 h under 5 % H$_2$/Ar atmosphere to reduce the SiO$_2$ to Si. Finally, byproduct MgO was removed by immersing the product in 1 M HCl solution for 6h, and excess SiO$_2$ was removed by 5 % hydrofluoric acid.

**Synthesis of Si@void@C yolk-shell nanoparticles:** The SiO$_2$ middle layer of the as obtained Si@SiO$_2$@C were removed to create the Si@void@C yolk-shell structure by etching with 5 % hydrofluoric acid solution for 1 h.

**Synthesis of Si@C core-shell nanoparticles:** Synthetic method of Si@C is the same as Si@SiO$_2$@C, only need to adjust the amount of phenolic resin (120 mg).

### Characterization.

The nanostructure images of these samples were observed on a Field emission scanning electron microscopy (FESEM, Hitachi SU8010). The morphologies and elemental mappings were characterized by transmission electron microscopy (TEM, JEOL JEM-2100 F). The phase of sample was recorded on wide-angle X-ray diffraction (XRD, Rigaku D/Max-2550 PC). X-ray photoelectron spectroscopy (XPS) was used to further identify the chemical state of Si and C in the sample. Raman spectra were tested with a Dilor LabRam-1B microscopic Raman spectrometer (France), using a He-Nelaser with an excitation wavelength of 633 nm. The thermal gravimetric analysis (TGA) was performed using a TG 209F1 apparatus under air atmosphere in the temperature range of 50-900 °C with a heating rate of 10 °C min$^{-1}$. The pore structure was tested by measuring Nitrogen Nitrogen sorption isotherms using a Micro ASAP2046 machine according to the Brunauer- Emmett-Teller (BET) method.
Electrochemical Characterizations.

The electrochemical measurements were tested by using CR2032 coin-type half-cells with Li foil as the counter electrode. The electrode was obtained by mixing the active materials, super P, and carboxymethyl cellulose (CMC) in a weight ratio of 7:1.5:1.5. The obtained slurry was coated on Cu foil and dried at 80 °C in a vacuum oven overnight. The mass loading of the active material was 0.8-1.1 mg cm$^{-2}$. The prepared electrodes were assembled in an argon-filled glove box. The electrolyte was 1.0 M LiPF$_6$ in 3:4:3 (weight ratio) of ethylene carbonate/dimethyl carbonate/diethylene carbonate, with 5 wt % fluoroethylene carbonate additive.

Cyclic voltammograms (CV) was performed on an electrochemical workstation (CHI660E, Chenhua, CHN) at a scan rate of 0.1 mV s$^{-1}$ within a range from 0.01 to 3.0 V. The electrochemical impedance spectrum measurements (EIS) was recorded over the frequency range from 100 kHz to 0.01 Hz. Discharge-charge experiments measurements were performed on a New Battery Measurement System within a voltage range of 0.01-2 V (vs. Li/Li$^+$). All the electrochemical measurements were conducted at 25 °C.
Calculation process of the thickness of the pSi interlayer:

- \( r_1 \): radius of Si
- \( r_2 \): radius of Si@pSi
- \( V_1 \): volume of Si
- \( V_2 \): volume of Si@pSi
- \( V_{\text{SiO}_2} \): volume of SiO\(_2\) before reduction
- \( V_{\text{Si}} \): volume of porous silicon after reduction

According to the density and reaction molar ratio of SiO\(_2\) and Si, the volume ratio of SiO\(_2\) before reduction to the reduction product pSi can be calculated:

\[
2\text{Mg} + \text{SiO}_2 \rightarrow \text{Si} + 2\text{MgO}
\]

\[
2.24 \ V_{\text{Si}} = V_{\text{SiO}_2}
\]

Assuming that half of the SiO\(_2\) can be completely reduced, the volume ratio of SiO\(_2\) before reduction to the final product can be calculated:

\[
2.24 \ V_{\text{Si}} = 0.5 \ V_{\text{SiO}_2}
\]

Calculated by volume expansion of 300 % when silicon is completely lithiated:

\[
3V_{\text{Si}} + 3V_1 = V_2
\]

\( r_1 = 30 \ \text{nm} \)

\( \rightarrow r_2 = 56 \ \text{nm} \)

The thickness of the pSi is about 26 nm.
Fig. S1 SEM image of Si@pSi@C.
Fig. S2 (a)TEM image of Si@pSi@C.
Fig. S3 TEM image of (a) Si@C, (b) Si@void@C.
Fig. S4 (a) XPS survey spectra of Si@pSi@C. (b) Si 2p XPS spectra and (c) C 1s XPS spectra of Si@pSi@C.
Fig. S5 TEM image of the Si@pSi@C in lithiated state.
**Fig. S6** Rate capability at various current densities of three kinds of electrodes.
**Fig. S7** Cycling performance of Si@pSi@C at a current density of 100 mA g\(^{-1}\).
Fig. S8 SEM images of (a) Si@C, (b) Si@void@C, and (c) Si@pSi@C electrodes before cycling.