Supporting Information

Si/SiO₂ Hollow Nanospheres/Nitrogen-Doped Carbon Superstructure with Double Shell and Void for High-Rate and Long-Life Lithium-Ion Storage

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Figures

Fig. S1 SEM image of SiO₂ hollow nanospheres with an average diameter of ~450 nm.
**Fig. S2** SEM image of Si/SiO$_2$-DSHSs.

**Fig. S3** TEM image of Si/SiO$_2$ and its corresponding EDS elemental mapping.
**Fig. S4** Low magnification TEM image of Si/SiO$_x$-DSHSs.

**Fig. S5** XRD patterns of Si hollow nanospheres, SiO$_2$ hollow nanospheres and Si/SiO$_x$-DSHSs.
Fig. S6 Raman spectra of the bare Si and Si/SiO$_x$-DSHSs.

Fig. S7 Thermogravimetric analysis curve of the Si/SiO$_x$-DSHSs.
Fig. S8 Nitrogen adsorption and desorption isotherm of the Si/SiO$_x$-DSHSs alongside its porosity information.

Fig. S9 N$_2$ adsorption–desorption isotherm of commercial Si nanoparticles.
**Fig. S10** The SEM images of commercial Si nanoparticles with an average size of ~70 nm.

**Fig. S11** Survey XPS spectra of as-prepared Si/SiO₂-DSHSs.
Fig. S12 XPS spectra of the Si/SiO\textsubscript{x}-DSHSs (a) Si 2p signal and (b) N 1s signal.

Fig. S13 The cycling performance of bare Si and Si/SiO\textsubscript{x}-DSHSs electrodes for 100 cycles at 0.1 C.

Fig. S14 Charging/discharging profiles of bare Si and carbon coated hollow Si nanosphere (HSi/C) electrodes at different cycles at a high current rate of 5 C.
Fig. S15 The cycling performance of Si/SiOx-DSHSs electrodes for 500 cycles at 3 C with a reversible capacity of around 750 mAh g\(^{-1}\) and an excellent cycle retention of 94.5% after 500 cycles.

Table S1 Comparison of electrochemical properties of Si/SiOx-DSHSs with previously reported Si-based anode materials. Electrode compositions are listed using mass ratios of active material : conductive carbon : binder.

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrode composition</th>
<th>Loading density (mg cm(^{-2}))</th>
<th>Rate capability</th>
<th>Cycling performance</th>
<th>Initial CE</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/SiOx-DSHSs</td>
<td>70 : 20 : 10</td>
<td>1.5</td>
<td>1290, 1203, 1160, 1005, 750, 562 and 360 mA h g(^{-1}) at 0.1, 0.2, 0.5, 1, 3, 5 and 10 C, respectively</td>
<td>1231 mA h g(^{-1}) after 100 cycles 0.1 C 709 mA h g(^{-1}) after 500 cycles 3 C 323 mA h g(^{-1}) after 1000 cycles at 10 C</td>
<td>71.7%</td>
<td>this work</td>
</tr>
<tr>
<td>Carbon-Coated Silicon/Graphite Spherical Composites</td>
<td>65 : 25 : 10</td>
<td>1.4</td>
<td>700 mA h g(^{-1}) at 2 C;</td>
<td>568 mA h g(^{-1}) after 100 cycles 0.2 C 500 mA h g(^{-1}) after 100 cycles 1 C</td>
<td>–</td>
<td>S1</td>
</tr>
</tbody>
</table>
Yolk-shell silicon-mesoporous carbon 80 : 15 : 5 – – 999.8 mA h g⁻¹ after 400 cycles 0.42 A g⁻¹ – S2
Porous Si Nanowires 70 : 20 : 10 1.0 548 mA h g⁻¹; 282 mA h g⁻¹ at 7.2 A g⁻¹ 1503 mA h g⁻¹ after 560 cycles 0.6 A g⁻¹ 43% S3
3D microfibers constructed from silicon–carbon 75 : 15 : 10 – 500 mA h g⁻¹ at 2 C 860 mA h g⁻¹ after 200 cycles 0.3 C – S4
Si/N-doped carbon/CNT spheres 70 : 20 : 10 1.1–1.4 978 mA h g⁻¹ at 1 A g⁻¹ 1031 mA h g⁻¹ after 100 cycles 0.5 A g⁻¹ 72% S5
Silicon-Reduced Graphene Oxide 70 : 20 : 10 0.2 – 778 mA h g⁻¹ after 100 cycles 50 mA g⁻¹ – S6
Crystalline Amorphous Core-Shell Silicon Nanowires 70 : 20 : 10 – – 1060 mA h g⁻¹ after 100 cycles 0.85 A g⁻¹ – S7
Si/Reduced Graphene Oxide Bilayer Nanomembranes 70 : 20 : 10 – – 636, 325, 111 mA h g⁻¹ at 3, 7, and 15 A g⁻¹, respectively 821 mA h g⁻¹ after 700 cycles 1 A g⁻¹ 59%1 A g⁻¹ S8
Silicon embedded in porous carbon matrix 70 : 20 : 10 – – ~1000, 750 mA h g⁻¹ at 5 and 10 A g⁻¹, respectively 736 mA h g⁻¹ after 800 cycles 2 A g⁻¹ – S9

Table S2 Impedance parameters and Li⁺-ion diffusion coefficients of Bare Si, cycled cell of bare Si and Si/SiOₓ-DSHSs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_b$ (Ω)</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ (Ω)</th>
<th>$σ$ (Ω s⁻⁰.⁵)</th>
<th>$D$ (cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh of bare Si</td>
<td>2.24</td>
<td>-</td>
<td>150.3</td>
<td>64.9</td>
<td>4.57×10⁻¹²</td>
</tr>
<tr>
<td>Cycled cell of bare Si</td>
<td>3.79</td>
<td>-</td>
<td>231.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si/SiOₓ-DSHSs</td>
<td>2.33</td>
<td>35.6</td>
<td>30.7</td>
<td>6.83</td>
<td>8.69×10⁻¹¹</td>
</tr>
</tbody>
</table>

The calculation of Li⁺-ion diffusion coefficient

The Li⁺-ion diffusion coefficients of Si/SiOₓ-DSHSs and bare Si can be calculated according to the following equations:[S10]
\[ Z = R_b + R_1 + R_2 + \omega^{-1/2} \]  
\[ D = \frac{R^2T^2}{(2S^2\pi^2\sigma^2)} \]

where \( R_b, Z, \omega, R, T, S, F \) and \( C \) refer to the Ohmic resistance of the half cell, the real part of the impedance, the angular frequency in the low-frequency region, the gas constant, the absolute temperature, the real surface area, the Faraday constant and the molar Li\(^+\) ion concentration, respectively; \( R_1 \) and \( \text{CPE}_1 \) in the equivalent electrode circuit model (the \textit{inset} of Fig. 3a) refer to the Li\(^+\) ion desolvation/adsorption and electron transfer; \( R_2 \) and \( \text{CPE}_2 \) are associated with Li\(^+\) ion insertion in the particle surface; \( \sigma \) represents the Warburg factor, which is relative to \( Z - \omega^{-1/2} \) (Equation (S1)) and can be obtained by measuring the slope of the oblique line in the low-frequency region (Fig. 3b).

References


