Hollow Core-Shell Structured Porous Si-C Nanocomposites for Li-Ion Battery Anodes

Xiaolin Li,*a Praveen Meduri,a Xilin Chen,a Wen Qi,a,b Mark H. Engelhard,a Wu Xu,a Fei Ding,a,c Jie Xiao,a Wei Wang,a Chongmin Wang,a Ji-Guang Zhang,*a Jun Liu*a

a Pacific Northwest National Laboratory, Richland, WA 99352, USA

b Department of Materials Science and Engineering, Tianjin University, Tianjin 300072, China
c National Key Lab of Power Sources, Tianjin Institute of Power Sources, Tianjin 300381, China

* Xiaolin.Li@pnnl.gov; Jiguang.Zhang@pnnl.gov; Jun.Liu@pnnl.gov

Carbon coating

A thin layer (<5 nm) of carbon was coated by CVD using a homemade vacuum tube furnace. (Unlike the CVD synthesis of active electrode materials (such as Si), which may be difficult to scale up, CVD carbon coating is cost effective and widely used in large scale production process). Si@SiO₂ composite or nano-Si powder was first loaded in a ceramic boat and placed at the center of the tube furnace. The furnace was evacuated at room temperature to a vacuum level of ≤ 1 mTorr. The furnace was then heated to 600°C at a rate of 10°C/min followed by the introduction of precursor gas (argon: acetylene = 9:1). The furnace temperature was increased to 690°C over a 10 min period and kept at 690°C for 30 min. At high temperatures, decomposition of acetylene led to carbon deposition on the surface of Si nanoparticles. The furnace was then cooled to room temperature in pure argon.
Supporting figures

**Figure S1.** XPS of Si@SiO$_2$ and Si@SiO$_2$@C showing the coating of SiO$_2$ and carbon.

**Figure S2.** TEM images of core-shell structured porous Si-C nanocomposites.
Figure S3. Isothermal curves of nano-Si, the core-shell structured porous Si-C nanocomposite and intermediate products.

Table S2. Summary of the BET surface area and pore volume of the core-shell structured porous composite at different synthesis stages.

<table>
<thead>
<tr>
<th></th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>123.7</td>
<td>0.81</td>
</tr>
<tr>
<td>Si@SiO₂</td>
<td>121.6</td>
<td>0.61</td>
</tr>
<tr>
<td>Si@SiO₂@C</td>
<td>74</td>
<td>0.55</td>
</tr>
<tr>
<td>Si@SiO₂@C@HF</td>
<td>256.4</td>
<td>1.13</td>
</tr>
</tbody>
</table>
**Figure S4.** Multiple test results on long cycle stability and rate performance using 1M LiPF$_6$ in EC: DMC (1:2) with 10% FEC as electrolyte additive. a) Cycling stability data of 4 more coin cells tested at a current density of 1 A/g. b) Rate performance of the core-shell structured porous composite under different current densities.

**Figure S5.** Long cycle stability data of the core-shell structured porous composite tested using 1M LiPF$_6$ in EC: DMC (1:2) with 10% VC as electrolyte additive.
Figure S6. XRD of the core-shell structured porous Si-C nanocomposite and nano-Si.

Figure S7. TEM image of the core-shell structured porous Si-C nanocomposite after cycling.