Rational Design of yolk-shell Silicon dioxide@ hollow carbon spheres as advanced Li–S Cathode Hosts

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Fig. S1 The nitrogen adsorption/desorption curves (a) and pore diameter distributions (b) of the SiO$_2$@C, SiO$_2$@HC and HC composites.

Fig. S2 SEM images of SiO$_2$@C/S.
Calculation of the volume expansion of the active materials: Because of the density differences, the reduction of elemental sulfur from $S_8 \ (\rho_s = 2.03 \text{ g cm}^{-3})$ to $\text{Li}_2\text{S} \ (\rho_{\text{Li}_2\text{S}} = 1.66 \text{ g cm}^{-3})$ accompanied by a large volumetric expansion of about 80%. To simplify the calculation, here we select one sphere as the example, assume $\rho_{\text{SiO}_2} \ (2.13 \text{ g cm}^{-3}) \approx \rho_{\text{sulfur}} \ (2.03 \text{ g cm}^{-3})$ and take the volume of $\text{SiO}_2$ sphere ($V_{\text{SiO}_2}$) as a reference.

According to the $\text{SiO}_2$ and sulfur content in $\text{SiO}_2@\text{HC/S}$ as we have shown in the manuscript, the mass of sulfur in one ball is calculate to be ten times of $\text{SiO}_2$, thus the total volume of sulfur in one sphere is $V_{\text{Sulfur}} = 10 \ V_{\text{SiO}_2}$ and when fully lithiation to $\text{Li}_2\text{S}$ the volume of $\text{Li}_2\text{S} \ (V_{\text{Li}_2\text{S}}) = 18 \ V_{\text{SiO}_2}$.

In our work, the designed large void space in yolk-shell structure not only allows a high loading of sulfur but also accommodates the volume expansion of sulfur during lithiation. The total volume that is available for accommodating volume expansion in the structure $V_{\text{total}} = V_{\text{void}} + V_{\text{pore}}$. The $V_{\text{void}}$ and $V_{\text{pore}}$ represent the void volume in hollow
structure and the pore volume of carbon shell, respectively. As is shown in Fig. S4, $R_{SiO2} = 50$ nm, $R_{HC} = 130$ nm, then $R_{HC}/R_{SiO2} = 2.6$. The void volume in hollow structure ($V_{void}$) can be calculated as follow: $V_{void} = V_{HC} - V_{SiO2} = 4/3\pi (2.5R_{SiO2})^3 - 4/3\pi R_{SiO2}^3 \approx 17V_{SiO2}$. The $V_{HC}$ and $V_{SiO2}$ represent the volume of whole sphere and SiO$_2$ core, respectively. As the pore volume of SiO$_2$@HC is 0.33 cm$^3$ g$^{-1}$ (Table S1), the pore volume of carbon shell ($V_{pore}$) in one sphere can be calculated as follow: the mass of sulfur in carbon shell ($M_{sulfur}$) = sulfur density * pore volume of SiO$_2$@HC = 0.67 $M_{SiO2@HC} = 2.2M_{SiO2}$, then $V_{pore} \approx 2V_{SiO2}$. Thus, $V_{total} = V_{void} + V_{pore} = 17V_{SiO2} + 2V_{SiO2} = 19V_{SiO2}$. This value is larger than that of volume expansion during lithiation ($18V_{SiO2}$).

From the calculation above, we can conclude that the void space in SiO$_2$@HC is of great importance for accommodating the huge volume change during cycling. The relative descriptions have been added in the revised manuscript which are highlighted in yellow.

Fig. S4 Schematic diagram of SiO$_2$@HC
Fig S5 Characterization of electrode films after 400 cycles, a-b SiO$_2$@HC/S and c-d HC/S.

The illustration of the fitting unit of the equivalent circuits for EIS fitting: The EIS spectra are composed of a depressed semicircle in the high frequency region and a long inclined line in the low frequency before cycling, corresponding to the charge-transfer process ($R_{ct}$) and a semi-infinite Warburg diffusion process, respectively. The intercept at high frequency is associated with the combination resistances (Rs) constituted by ionic resistance of electrolyte, the intrinsic resistance of active materials, and some contact resistances between active materials and current collectors. After the first few cycles, a new semicircle in the medium frequency appeared, which is related to the formation of an insulating layer of lithium sulfide (Li$_2$S) on the host matrix in the cathode and probably the gradual build-up of solid-electrolyte interphase (SEI) resistance ($R_e$).
Fig. S6 The equivalent circuits for EIS fitting before (a) and after (c) cycling test

![Equivalent circuits](image)

Fig S7. Electrochemical performances for the HC/S (a) and SiO$_2$@HC/S (b) cathode before and after rest for 24h at 10$^{\text{th}}$ cycles, the electrolyte without the LiNO$_3$ additive is adopted during electrochemical test.

**Preparation of Li$_2$S$_6$ and SiO$_2$-Li$_2$S$_6$ for XPS measurements:** The Li$_2$S$_6$ was prepared by dissolving lithium sulfide (Li$_2$S) and elemental sulfur according to the stoichiometric ratio (1:5) in DOL/DME (1 : 1, v/v) at 80°C with stirring for 12 h. The SiO$_2$-Li$_2$S$_6$ sample is prepared as follow: 50mg of SiO$_2$ powder was added to 30 mL of 0.05M Li$_2$S$_6$ solution with stirring for 10min, after settling and drying, the SiO$_2$-Li$_2$S$_6$ sample for XPS analysis was obtained. All procedures were completed in an Ar-filled glovebox.
Fig S8. XPS study of the interaction between Li$_2$S$_6$ and SiO$_2$. S 2p XPS spectra of (a) Li$_2$S$_6$ and (b) Li$_2$S$_6$/SiO$_2$. Si 2p XPS spectra of (c) Li$_2$S$_6$ and (d) Li$_2$S$_6$/SiO$_2$.

Fig S9. (a) The cycle performance of the SiO$_2$@HC/S electrode with 2.6 mg cm$^{-2}$ sulfur loading at 0.2 C and (b) the corresponding areal capacity.

Table S1. BET surface area and pore volume of the HC, SiO$_2$@HC, and SiO$_2$@C.

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<tr>
<th></th>
<th>HC</th>
<th>SiO$_2$@HC</th>
<th>SiO$_2$@C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m$^2$ g$^{-1}$)</td>
<td>373</td>
<td>282</td>
<td>67</td>
</tr>
<tr>
<td>Pore volume (cm$^3$ g$^{-1}$)</td>
<td>0.52</td>
<td>0.33</td>
<td>0.1</td>
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