Achieving high-performance room-temperature sodium–sulfur batteries with S@interconnected mesoporous carbon hollow nanospheres

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Abstract
Despite the high theoretical capacity of the sodium-sulfur battery, its application is seriously restrained by the challenges due to its low sulfur electroactivity and accelerated shuttle effect, which lead to low accessible capacity and fast decay. Herein, an elaborate carbon framework, interconnected mesoporous hollow carbon nanospheres, is reported as an effective sulfur host to achieve excellent electrochemical performance. Based on in-situ synchrotron X-ray diffraction, the mechanism of the room temperature Na/S battery is proposed to be reversible reactions between S8 and Na2S4, corresponding to a theoretical capacity of 418 mAh g⁻¹. The cell is capable of achieving high capacity retention of ~ 88.8% over 200 cycles, and superior rate capability with reversible capacity of ~ 390 and 127 mAh g⁻¹ at 0.1 and 5 A g⁻¹, respectively.

Keywords
carbon, mesoporous, S@interconnected, batteries, hollow, nanospheres, room-temperature, achieving, high-performance, sodium−sulfur

Disciplines
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Achieving High-Performance Room-Temperature Sodium-Sulfur Batteries With S@Interconnected Mesoporous Carbon Hollow Nanospheres


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Supporting Information Placeholder
Experimental section

Figure S1. Schematic illustration of the fabrication of the interconnected mesoporous carbon hollow nanosphere (iMCHS) frameworks.

As shown in Figure S1, the specific synthetic procedures for the interlaced hollow mesoporous carbon nanospheres are as follows:

**Synthesis of core-shell Si@SiO$_2$ nanoparticles:** Via the Stöber sol-gel method, 0.15 g of commercial Si nanoparticles (80-100 nm) was dispersed in a mixed solution containing deionized water (70 mL), ethanol (280 mL), and ammonia (5 mL, 28 wt %) under ultrasound for 20 min. Afterwards, 1.0 mL of tetraethyl orthosilicate (TEOS) was added dropwise every 30 min (4.0 mL in total), and the reaction continued at 25 °C for 10 h under mechanical stirring (220 rpm). The core-shell Si@SiO$_2$ nanoparticles were obtained after centrifugation and washing with ethanol for several times.

**Synthesis of core-shell Si@SiO$_2@m$SiO$_2$ nanoparticles:** Mesoporous silica ($m$SiO$_2$) with a thickness of ~ 15 nm was deposited on the surface of the Si@SiO$_2$ nanoparticles through a well-established surfactant-templating sol-gel route by using cetyltrimethylammonium bromide (CTAB) as the template. Typically, 0.15 g of the Si@SiO$_2$ nanoparticles obtained above and 0.225 g of CTAB were added into a solution of deionized water (75 mL), ethanol (45 mL), and ammonia (0.825 mL, 28 wt %). The mixture became a homogeneously dispersed solution after treatment with ultrasound and stirring, for 30 min each, and then 0.12 mL of TEOS was injected. The reaction was allowed to proceed for 6 h at 25 °C under gentle stirring. The products were collected by centrifugation, washed with ethanol, and re-dispersed into 60 mL of NH$_4$NO$_3$/ethanol (6 g L$^{-1}$) solution to remove the CTAB surfactant. This
extraction process proceeded at 60 °C for 10 h to yield core-shell Si@SiO$_2@m$SiO$_2$ nanoparticles.

**Synthesis of core-shell Si@SiO$_2@m$SiO$_2$-Resol nanoparticles:** Firstly, low-molecular-weight resol precursors were prepared as the carbon source. Briefly, 8.0 g of phenol was melted at 45 °C and mixed with NaOH aqueous solution (1.36 g, 20 wt. %). This was followed by the dropwise addition of formalin solution (14.2 g, 37 wt. %) under magnetic stirring. Upon further reaction for 1 h at 70 °C, the resol solution was cooled to room temperature and adjusted to neutral pH (pH ≈ 7) with HCl (0.6 M). The resol could then be fabricated by vacuum-evaporating water in the solution at 50 °C. A nano-casting route was followed: 0.20 g of the core-shell Si@SiO$_2@m$SiO$_2$ nanoparticles was dispersed in 5.0 mL of ethanol, followed by the addition of 1.0 g of the above-prepared resol. The mixture was stirred at room temperature while open to air to evaporate the ethanol solvent. Finally, the dry Si@SiO$_2@m$SiO$_2$-Resol powder was obtained.

**Synthesis of interconnected mesoporous carbon hollow nanospheres:** The dried Si@SiO$_2@m$SiO$_2$-Resol powder was calcined at 900 °C for 3 h under a nitrogen atmosphere to obtain a carbon-coated composite (designated as Si@SiO$_2@m$SiO$_2$-C). The mesoporous SiO$_2$ hard templates and the Si nanospheres were etched away with 2 M NaOH solution, thereby creating the mesoporous carbon shells and the void spaces. The etching process was conducted over 3 days at room temperature, followed by a washing with excess deionized water. The resultant interconnected mesoporous carbon hollow nanospheres (iMCHS) were dried at 60 °C in vacuum for further characterization.

**Synthesis of S incorporated iMCHS nanocomposite (S@iMCHS):** The final S@iMCHS composite was prepared via a facile melt-diffusion strategy at 155 °C for 24 h with a fixed weight ratio of S/C at 60/40 in a sealed Teflon container. For comparison, the S incorporated mesoporous carbon nanocomposite (S@mesoporous C) and the S incorporated reduced
graphene oxides nanocomposite (S@RGO) were fabricated with the same conditions.

**Characterization.** The morphologies of the samples were investigated by field-emission scanning electron microscopy (FESEM; JEOL JSM-7500FA) and transmission electron microscopy (TEM, JEOL 2011, 200 kV). The XRD patterns were collected by powder X-ray diffraction (XRD; GBC MMA diffractometer) with Cu Kα radiation at a scan rate of 2 and 0.5 ° min⁻¹. The porosity was measured by nitrogen sorption isotherms at 77 K with a Micromeritics Tristar 3020 analyzer (USA). Before measurements, the samples were degassed in vacuum at 180 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area (S_{BET}), using adsorption data in a relative pressure (P/P₀) range from 0.04 to 0.2. The pore volume and pore size distributions were derived from the adsorption branches of isotherms by using the Barrett-Joyner-Halenda (BJH) model. The total pore volume, V_t, was estimated from the amount adsorbed at a relative pressure P/P₀ of 0.995. Raman spectra were collected using a 10 mW helium/neon laser at 632.8 nm excitation, which was filtered by a neutral density filter to reduce the laser intensity, and a charge-coupled detector (CCD). The thermal decomposition behavior of the products was monitored by using a Mettler Toledo TGA/SDTA851 analyzer from 30 to 450 °C in Ar with a heating rate of 5 °C min⁻¹.

**Electrochemical measurements.** The electrochemical tests were conducted by assembling coin-type 2023 cells in an argon-filled glove box. The slurry was prepared by fully mixing 70 wt. % active materials (S@iMCHS, S@mesoporous C, S@RGO), 10 wt. % carbon black, and 20 wt. % carboxymethyl cellulose (CMC) in an appropriate amount of water with a planetary mixer (KK-250S). In order to estimate the capacity contribution of the iMCHS, we tested an electrode consisting of 42 wt. % iMCHS, 10 wt. % carbon black, and 20 wt. % CMC, which is the same as the proportion of iMCHS in S@iMCHS. Then, the obtained slurry was pasted on copper foil using a doctor blade with a thickness of 100 μm, which was
followed by drying at 50 °C in a vacuum oven overnight. The cathode electrode was prepared by punching the electrode film into discs 0.97 cm in diameter. The sodium foil was cut using a surgical blade from sodium bulk stored in mineral oil. The sodium foil was employed as anode electrode. The electrodes were separated by a glass fiber separator. Electrolyte consisting of 1.0 M NaClO₄ in propylene carbonate/ethylene carbonate, in a volume ratio of 1:1, and 5 wt. % fluoroethylene carbonate additive (PC/EC + 5 wt. % FEC), was prepared and utilized in this work. The electrochemical performance of the cells was tested by a Land Battery Test System with a cut-off voltage range from 0.8 to 2.8 V (vs. Na/Na⁺). Cyclic voltammetry and impedance testing were performed using a Biologic VMP-3 electrochemical workstation from 0.8 to 2.8 V at a sweep rate of 0.1 mV s⁻¹.

**In-situ synchrotron XRD measurements.** The cells for *in-situ* synchrotron XRD were similar to the above-mentioned coin-cells for electrochemical performance testing. In order to enhance the intensity of the diffraction peaks, a much thicker layer of cathode material was loaded on the Al foil, with loading up to 5 mg cm⁻². To collect the signals of the full cell, two holes with a diameter of 4 mm were punched on the negative and positive caps, respectively, guaranteeing that the X-ray beams could go through the whole cell and monitor the electrochemical reactions. Afterwards, the holes in the negative and positive caps were covered by Kapton film (only showing slight bumps in XRD measurements), followed by complete sealing with AB glue. Meanwhile, a battery test system (Neware) was connected to the cell to carry out the charge/discharge process.
Figure S2. Scanning electron microscope (SEM) images at (a) low and (b) high magnification; and TEM images at (c) low and (d) high magnification for the interconnected mesoporous hollow carbon nanospheres (iMHCS).
Figure S3. SEM images at (a) low and (b) high magnification, and (c) elemental mapping for the elements C and S in the S@iMCHS nanocomposite.
Figure S4. (a) XRD patterns and (b) Raman spectra of S-iMCHS mixture and the S@iMCHS nanocomposite.
Figure S5. Galvanostatic discharge/charge profiles of the RT-Na/S@iMCHS cell at various current rates.
Figure S6. (a) Cycling performance and (b) charge/discharge curves at selected cycles for S@mesoporous carbon cathode. (c) Cycling performance and (d) charge/discharge curves at selected cycles for S@reduced graphene oxide cathode.
Figure S7. (a) First cycle discharge/charge profiles and (b) cycling performance of the S@MCHS cells after different rest times.
Figure S8. SEM images of the S@MCHS cathodes: the fresh electrode at (a) low magnification and (b) high magnification; and the electrode after rate-capability testing at (c) low magnification and (d) high magnification.
Figure S9. (a) Elemental mapping of elemental C, O, F, Na, S, Cl, and Cu. (b) Phase mapping of Na$_2$S, Na$_2$O, and NaF for the S@iMCHS cathode after rate-capability testing.
Figure S10. Impedance spectra of the S@iMCHS cell at selected cycles.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>$R_c$</th>
<th>$R_{int}$</th>
<th>$R_{ct}$</th>
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<tbody>
<tr>
<td>1</td>
<td>5.15</td>
<td>176.3</td>
<td>$6.79 \times 10^{-7}$</td>
</tr>
<tr>
<td>2</td>
<td>6.06</td>
<td>217.6</td>
<td>$6.63 \times 10^{-6}$</td>
</tr>
<tr>
<td>5</td>
<td>7.06</td>
<td>691.4</td>
<td>2.28</td>
</tr>
<tr>
<td>50</td>
<td>5.26</td>
<td>768.9</td>
<td>43.71</td>
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</tbody>
</table>

$R_c$: combination resistance; $R_{int}$: interface resistance; $R_{ct}$: charge transfer resistance.
<table>
<thead>
<tr>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Current density (mA/g)</th>
<th>1st capacity (mA h/g)</th>
<th>Capacity (mA h/g) after (n) cycles</th>
<th>Capacity retention (%)</th>
<th>Capacity (mA h/g) at various current rate (A/g)</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>70 wt. % S@/MCHS (with 60 wt. % S) 10 wt. % carbon black 20 wt. % CMC</td>
<td>1M NaClO₄+EC/PC+FEC</td>
<td>100</td>
<td>328.4</td>
<td>292 (200)</td>
<td>88.8</td>
<td>386 (0.2) 352 (0.5) 305 (1) 174 (2) 127(5)</td>
<td>This work</td>
</tr>
<tr>
<td>60 wt. % S 20 wt. % C 20 wt. % PEO</td>
<td>1M NaClO₄SO₃ + TEGDME</td>
<td>No data</td>
<td>538</td>
<td>238 (10)</td>
<td>44.2</td>
<td>No data</td>
<td>5</td>
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<tr>
<td>80 wt. % S/C nanofibers (with 50 wt. % S) 10 wt. % Super P 10 wt. % PEO</td>
<td>1M NaPF₆ + tetruglyme</td>
<td>167</td>
<td>776</td>
<td>511 (20)</td>
<td>65.9</td>
<td>No data</td>
<td>7</td>
</tr>
<tr>
<td>60 wt. % S 30 wt. % Super P 10 wt. % PVDF</td>
<td>1.5 M NaClO₄ and 0.3 M NaNO₃ + TEGDME</td>
<td>No data</td>
<td>791</td>
<td>381 (20)</td>
<td>48.1</td>
<td>No data</td>
<td>9</td>
</tr>
<tr>
<td>90 wt. % S/Ketjenblack (with 50 wt. % S) 10 wt. % Super P 10 wt. % PVD 80 wt. % S/Cu-decorated mesoporous C (with 50 wt. % S) 10 wt. % acetylene black 10 wt. % CMC</td>
<td>1 M NaClO₄ +TEGDME</td>
<td>167</td>
<td>763</td>
<td>336 (70)</td>
<td>44</td>
<td>No data</td>
<td>11</td>
</tr>
<tr>
<td>80 wt. % S/microporous carbon polyhedron (with 47 wt. % S) 10 wt. % carbon black 10 wt. % PVDF</td>
<td>1M NaClO₄+EC/PC</td>
<td>84</td>
<td>689</td>
<td>354 (100)</td>
<td>51.3</td>
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<td>16</td>
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