Fe_{1-x}S@S-Doped Carbon Core-Shell Heterostructured Hollow Spheres as Highly Reversible Anode Materials for Sodium Ion Batteries

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Figure S1 XRD patterns of Fe$_2$O$_3$ hollow spheres (Fe$_2$O$_3$ HSs) and Fe$_2$O$_3$ polyhedral nanoparticles (Fe$_2$O$_3$ PPs).
Figure S2 XRD patterns of Fe$_3$O$_4$@C HSs and Fe$_3$O$_4$@C PPs.

Figure S3 SEM images of (A, B) Fe$_3$O$_4$@C HSs and (C, D) Fe$_3$O$_4$@C PPs,
respectively.

**Figure S4** XRD patterns of (A) Fe$_{1-x}$S@SC HSs and (B) Fe$_{1-x}$S@SC PPs.
**Figure S5** SEM images of pure S-Fe$_{1-x}$S (A, B), and P-Fe$_{1-x}$S (C, D) composite, respectively.
Figure S6 Raman spectra of Fe$_{1-x}$S@SC HSs and Fe$_{1-x}$S@SC PPs.
Figure S7 TGA curves of Fe$_{1-x}$S@SC HSs and Fe$_{1-x}$S@SC PPs.
Figure S8 Nitrogen adsorption-desorption isotherm curves of (A) Fe$_{1-x}$S@SC HSs and (B) Fe$_{1-x}$S@SC PPs.
Figure S9 Survey XPS spectra of Fe$_{1-x}$S@SC HSs.

Figure S10 (A) Charge and discharge profiles and (B) CV curves of Fe$_{1-x}$S@SC PPs electrode.
Figure S11 Charge and discharge profiles of pure S-Fe$_{1-x}$S (A) and P-Fe$_{1-x}$S (B) electrode.
Figure S12  Cycle performance of pure S-Fe$_{1-x}$S and P-Fe$_{1-x}$S electrode at 1.0 A g$^{-1}$. 
Figure S13 Cycle performance of Fe$_{1-x}$S@SC HSs and Fe$_{1-x}$S@SC PPs at 5.0 A g$^{-1}$. 

![Graph showing cycle performance of Fe$_{1-x}$S@SC HSs and Fe$_{1-x}$S@SC PPs at 5.0 A g$^{-1}$]
Table S1. Comparison of the electrochemical performance of Fe$_{1-x}$S@SC HSs and Fe$_{1-x}$S@SC PPs with that of reported iron sulfides-based anode materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Capacity, mA h g$^{-1}$</th>
<th>Cycle number, n</th>
<th>Current density, mA g$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS@Fe$_3$C@GC</td>
<td>219.8</td>
<td>200</td>
<td>1.0</td>
<td>15</td>
</tr>
<tr>
<td>3DG/FeS@C</td>
<td>358</td>
<td>300</td>
<td>1.0</td>
<td>17</td>
</tr>
<tr>
<td>FeS/CA</td>
<td>280</td>
<td>200</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>Fe$_{1-x}$S@CNTs</td>
<td>449.2</td>
<td>200</td>
<td>0.5</td>
<td>21</td>
</tr>
<tr>
<td>porous FeS nanofibers</td>
<td>592</td>
<td>150</td>
<td>0.5</td>
<td>27</td>
</tr>
<tr>
<td>Fe$_{1-x}$S@NC@G</td>
<td>385</td>
<td>500</td>
<td>0.2</td>
<td>36</td>
</tr>
<tr>
<td>CL-C/FeS</td>
<td>265</td>
<td>200</td>
<td>1.0</td>
<td>37</td>
</tr>
<tr>
<td>FeS$_x$@CS</td>
<td>638.9</td>
<td>100</td>
<td>0.1</td>
<td>38</td>
</tr>
<tr>
<td>FeS-rGO</td>
<td>547</td>
<td>50</td>
<td>0.1</td>
<td>S1</td>
</tr>
<tr>
<td>FeS@C-N</td>
<td>354.5</td>
<td>500</td>
<td>0.1</td>
<td>S2</td>
</tr>
<tr>
<td>FeS/CFs</td>
<td>283</td>
<td>400</td>
<td>1.0</td>
<td>S3</td>
</tr>
<tr>
<td>Fe$_{1-x}$S@SC PPs</td>
<td>286</td>
<td>500</td>
<td>1.0</td>
<td>This work</td>
</tr>
<tr>
<td>Fe$_{1-x}$S@SC HSs</td>
<td>454.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure S14 CV curves at various scan rates from 0.2 to 1.0 mV s$^{-1}$ (A), capacitive contribution at 0.8 mV s$^{-1}$ (B), and normalized contribution ratio of capacitive (blue) and diffusion (red) capacities at different scan rates (C) of Fe$_{1-x}$S@SC HSs electrode; comparison of the rate capability of this work with previously reported iron sulfides anodes for SIBs (D).
Figure S15 CV curves at various scan rate from 0.2 to 1.0 mV s$^{-1}$ for Fe$_{1-x}$S@SC PPs electrode (A), normalized contribution ratio of capacitive (blue) and diffusion (red) capacities at different scan rates for Fe$_{1-x}$S@SC PPs (B).

To further understand the high rate capability of the Fe$_{1-x}$S@SC HSs, the capacitive behaviors of the sample was investigated. Figure S15A exhibits the CV curves of Fe$_{1-x}$S@SC HSs electrode at various scan rates range from 0.2 to 1.0 mV s$^{-1}$. To analyzed the degree of capacitive effect, the following relationship were carried out: $i = av^b$, where $i$ is the peak current corresponding to a particular scan rate ($v$), $a$ and $b$ are both constants.[S4,S5] Subsequently, the percentage of capacitive and diffusion contributions were determined based on the following equation: $i (V) = k_1v^{1/2} + k_2v$.

And the equation can be further transformed to the following equation: $i (V)/v^{1/2} = k_1 + k_2v^{1/2}$. $k_1$ and $k_2$ can be facilely achieved by plotting $i(V)/v^{1/2}$ vs $v^{1/2}$, and thus the
capacitive current $i_c (V) = k_2v$ could be extracted from the total one with the value of $k_2$. [S6] As a result, at a given 0.6 mV s$^{-1}$ sweep rate, the CV profile for the capacitive current compared with that of the total measured current is shown in Figure S15B, in which 74.3% is quantified as capacitive. Therefore, the capacitive contributions at 0.2, 0.4, 0.8 and 1.0 mV s$^{-1}$ were also can be measured, and we summarizes the capacitive contributions at various scan rates, the results as shown in Figure S15C. The capacitive contributions are 65.1%, 68.9%, 74.3%, 76.7%, and 78.1% at scan rates of 0.2, 0.4, 0.6, 0.8, and 1.0 mV s$^{-1}$, respectively. On the other hand, the capacitive contributions at different scan rates for Fe$_{1-x}$S@SC PPs electrode were also investigated based on the same method. Figure S16A shows the CV curves at various scan rates from 0.2 to 1.0 mV s$^{-1}$ for Fe$_{1-x}$S@SC PPs electrode, respectively. And all of the curves at different scan rates exhibit similar shapes, which match well with the Fe$_{1-x}$S@SC HSs electrode. The capacitive contributions at different scan rates for P-Fe$_{1-x}$S@SC electrode were also determined, and the result as shown in Figure S16B. It is worth noting that the Fe$_{1-x}$S@SC HSs electrode exhibits higher capacitive contribution than the Fe$_{1-x}$S@SC PPs electrode, which indicate that the Fe$_{1-x}$S@SC HSs electrode shows more outstanding rate capability compare to Fe$_{1-x}$S@SC PPs electrode, and match well with the rate test results. [S7] Finally, the rate capability of Fe$_{1-x}$S@SC HSs electrode compare to the previously reported iron sulfides anodes for SIBs were summarized (Figure S15D), and suggested that Fe$_{1-x}$S@SC PPs electrode exhibits better rate performance compare to most of previously reported iron sulfides anodes.
Figure S16 Nyquist plots of as-prepared S-Fe$_{1-x}$S@SC and P-Fe$_{1-x}$S@SC electrode (A), and the equivalent circuit model used for fitting the experimental EIS data (B).

Table S2 Impedance parameters obtained from equivalent circuit model (Figure S16) for Fe$_{1-x}$S@SC HS sand Fe$_{1-x}$S@SC PPs based electrode.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R$_{\Omega}$ (Ω)</th>
<th>R$_{ct}$ (Ω)</th>
<th>D$_{Na^+}$ (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{1-x}$S@SC HSs</td>
<td>4.8</td>
<td>158.5</td>
<td>6.51$\times$10$^{-12}$</td>
</tr>
<tr>
<td>Fe$_{1-x}$S@SC PPs</td>
<td>7.63</td>
<td>345.3</td>
<td>2.95$\times$10$^{-12}$</td>
</tr>
</tbody>
</table>
Figure S16 shows the electrochemical impedance spectroscopy (EIS) of Fe\(_{1-x}\)S@SC HSs and Fe\(_{1-x}\)S@SC PPs based electrode. The ohmic resistance \((R_{\Omega})\) and charge transfer resistance \((R_{ct})\) can be obtained by data fitting according to the equivalent circuit model in Figure S16B, the results are listed in Table S1. The Na\(^+\) diffusion coefficient \((D_{Na^+})\) could be calculated based on Eqs. (S1) and (S2):

\[
Z = R_{\Omega} + R_{ct} + \sigma \omega^{0.5} \quad \text{(S1)}
\]

\[
D_{Na^+} = \frac{(RT)^2}{2(A n^2 F^2 C_{Na^+} \sigma)^2} \quad \text{(S2)}
\]

where \(R\), \(T\), \(A\), \(n\), \(F\), \(C\) and \(\sigma\) are the gas constant, absolute temperature, contact area of the electrode, number of electrons per molecule during oxidation, Faraday constant, concentration of Na-ions, and Warburg coefficient, respectively.[S8, S9] As a result, the Na\(^+\) ions diffusion coefficient of Fe\(_{1-x}\)S@SC HSs and Fe\(_{1-x}\)S@SC PPs are \(6.51 \times 10^{-12}\) and \(2.95 \times 10^{-12}\), respectively (Table S1). The Fe\(_{1-x}\)S@SC HSs based electrode exhibits a much higher Na\(^+\) ions diffusion coefficient, and it confirms that the heterostructured hollow spheres can significantly facilitates Na\(^+\) ions diffusion.[S10]
Figure S17 SEM images of Fe$_{1-x}$S@SC HSs (A, B), and Fe$_{1-x}$S@SC PPs (C, D) after 500 cycles at 1.0 A g$^{-1}$, respectively.

The morphologies of Fe$_{1-x}$S@SC HSs and Fe$_{1-x}$S@SC HSs electrode after long cycles were studied for structural changes. Figure S16 revealed that the SEM images of Fe$_{1-x}$S@SC HSs and Fe$_{1-x}$S@SC PPs electrode after 500 cycles at 1.0 A g$^{-1}$. Figure S16A and S16B clearly show that the sphere-like structures are almost maintained in the Fe$_{1-x}$S@SC HSs electrode after 500 cycles. But for Fe$_{1-x}$S@SC PPs electrode, polyhedral particles cracked can be obtained after 500 cycles (Figure S16C and S16D). Therefore, these results further strongly indicated that the S-doped carbon shell and hollow structure can effectively accommodate the large volume change of Fe$_{1-x}$S and maintain the structural stability during the cycling process.
Figure S18 Schematic illustration of Fe_{1-x}S@S-doped carbon electrodes during cycling.
References


