Extremely Small Pyrrhotite Fe$_7$S$_8$ Nanocrystals with Simultaneous Carbon-Encapsulation for High-Performance Na–Ion Batteries

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Na/FeS$_x$ batteries have remarkable potential applicability due to their high theoretical capacity and cost-effectiveness. However, realization of high power-capability and long-term cyclability remains a major challenge. Herein, ultrafine Fe$_7$S$_8$@C nanocrystals (NCs) as a promising anode material for a Na–ion battery that addresses the above two issues simultaneously is reported. An Fe$_7$S$_8$ core with quantum size (≈10 nm) overcomes the kinetic and thermodynamic constraints of the Na–S conversion reaction. In addition, the high degree of interconnection through carbon shells improves the electronic transport along the structure. As a result, the Fe$_7$S$_8$@C NCs electrode achieves excellent power capability of 550 mA h g$^{-1}$ (≈79% retention of its theoretical capacity) at a current rate of 2700 mA g$^{-1}$. Furthermore, a conformal carbon shell acts as a buffer layer to prevent severe volume change, which provides outstanding cyclability of ≈447 mA h g$^{-1}$ after 1000 cycles (≈71% retention of the initial charge capacity).

Over the past several years, significant efforts have been focused on developing large-scale applications such as electric vehicles (EVs) and plug-in hybrid EVs. Li–ion batteries (LIBs), which have been successfully applied as the energy storage system (ESS) for mobile devices such as cell phones and laptops, are one of the possible candidates for large-scale ESSs.

However, increasing concerns over the limited resources of Li and their high price have motivated researchers to investigate other battery technologies that can overcome the above issues of LIBs. In this context, Na–ion batteries (NIBs) have been recognized as one of the potential alternatives to LIBs because of earth-abundant Na sources and their similar reaction mechanism to LIBs.

However, research on NIBs is still at an early stage, mainly due to relatively low energy density and insufficient cyclability. Designing suitable electrode materials that satisfy high energy density and long cycling life is one of the most important issues in current NIB technology.

Iron sulfide (FeS$_x$, $x \leq 2$) has received a great deal of attention as a promising anode material for NIBs because of its high theoretical capacity, low cost, and abundance in nature.

However, several challenges to the use of Na/FeS$_x$ batteries have arisen, including low electric conductivity, sluggish Na diffusion kinetics, and severe volume expansion during the reaction, which have prevented the practical application of FeS$_x$ as a anode material for NIBs.

To overcome these issues, following strategies should be required. First, the particle size of FeS$_x$ should be small enough for it to offer highly reversible and efficient conversion reaction. Because of the sluggish kinetics of the conversion reaction between Na and FeS$_x$, the surface-limited charge/discharge reaction occurs when the particle size is bigger than the kinetic limits.

Considering the short diffusion lengths of Fe in FeS$_x$ ($\approx 10^{-18}$ cm$^2$ s$^{-1}$ at room temperature), the ideal size of FeS$_x$ particles would be within only few tens of nm to assure a full conversion reaction. Second, introducing of carbon-based materials could enhance the electrical conductivity of the active materials and act as a buffer layer to prevent large volume changes.

Several approaches have been reported to solve above issues on Na/FeS$_x$ batteries by preparing nanosized particles or introducing of carbon-coating on particles. However, there has been no report that achieves both strategies simultaneously, which can further boost the performance of Na/FeS$_x$ batteries.

Herein we demonstrate pyrrhotite Fe$_7$S$_8$ nanocrystals (NCs) as a promising anode material for NIB. Unique Fe$_7$S$_8$@C NCs have been successfully explored via one-pot colloidal synthesis, which consist of Fe$_7$S$_8$ cores with a size of ≈10 nm and homogeneous carbon shells with a thickness of ≈2 nm. The Fe$_7$S$_8$@C NCs exhibit highly reversible conversion reaction,
owing to the quantum size of NCs and highly interconnected carbon shells. As a result, Na/Fe\(_7\)S\(_8\)@C NC battery achieves a remarkable power capability of 550 mAh g\(^{-1}\) (=79% retention of its theoretical capacity) at a current rate of 2700 mA h g\(^{-1}\). Furthermore, conformal carbon shell accommodates large volume expansion during charge/discharge, leading to outstanding cycle performance of Fe\(_7\)S\(_8\)@C NCs (=447 mAh h g\(^{-1}\) after 1000 cycles, ≈71% retention of the initial charge capacity), while commercial Fe\(_2\)S\(_2\) particles deliver poor cyclability with severe capacity degradation. These novel Fe\(_7\)S\(_8\)@C NCs exhibiting extraordinary power-capability and excellent cyclability are a potential anode material for practical NIBs.

The synthetic procedure for preparing ultrathin core–shell Fe\(_7\)S\(_8\)@C NCs is illustrated in Figure 1. We adapted the colloidal synthesis method to achieve both of extremely small size of NCs and simultaneous carbon-encapsulation, which is the key point of our strategy. First, the Fe\(_7\)S\(_8\) NCs were nucleated by injecting the sulfur dissolved in oleylamine (OLA) into the solution containing iron-oleate complexes. The oleic acid (OA) and OLA acted as surface capping ligands, which lead to homogeneous growth of NCs and prevent agglomeration of NCs. After successful synthesis of colloidal Fe\(_7\)S\(_8\) NCs (see the Experimental Section for more details), the OA and OLA were converted to homogeneous carbon shell through short annealing treatment under inert condition. It should be emphasized that the organic capping ligands enable both of the ultrafine colloidal NCs and direct carbon-encapsulation of NCs by acting as carbon source. Therefore, no additional treatment is needed for carbon-coating, which is distinct property of our approach. Finally, the uniform core–shell Fe\(_7\)S\(_8\)@C NCs were fabricated because excess sulfur (\(x\)) was removed in the form of vapor during the annealing treatment.\(^{[32]}\) Our synthetic strategy significantly simplifies the overall process for the preparation of carbon-coated metal sulfide, that can be readily applicable on industry as well.

The success of this strategy could be confirmed by the X-ray diffraction (XRD) patterns of as-prepared core–shell Fe\(_7\)S\(_8\)@C NCs shown in Figure 2. All diffraction peaks are fully consistent with hexagonal P31 space group of pyrrhotite Fe\(_7\)S\(_8\) (PDF: 24-0220). The XRD patterns centered at 30.02°, 33.99°, 44.03°, 53.32°, and 71.55° correspond to the (200), (203), (206), (220), and (406) crystal planes of the pyrrhotite Fe\(_7\)S\(_8\), respectively. Few minor peaks that are not matched with pyrrhotite can be ascribed by the Fe\(_2\)S\(_8\)\(_{1+x}\) NCs (Figure S1, Supporting Information). Fe\(_2\)S\(_8\) can store 16 Na ions through the following conversion reaction (Fe\(_2\)S\(_8\) + 16Na \(\rightarrow\) 7Fe + 8Na\(_2\)S) and its theoretical capacity is ≈700 mAh h g\(^{-1}\).

The transmission electron microscope (TEM) image and high-resolution TEM image in Figure 3a shows the size of as-prepared colloidal Fe\(_7\)S\(_8\) NCs is 9.0 ± 1.3 nm with high uniformity. After carbonization process using rapid thermal annealing system for 5 min at 600 °C under Ar atmosphere, the core–shell Fe\(_7\)S\(_8\)@C NCs were fabricated as shown in Figure 3b. The structure of Fe\(_7\)S\(_8\)@C NCs were composed of the Fe\(_7\)S\(_8\) cores with a size of 12.3 ± 1.9 nm and the carbon shell with a thickness of ≈2 nm. The average size of cores slightly increased, which may result from the agglomeration during the annealing process. However, the size of the cores is small enough to overcome the kinetic barriers of the conversion reaction between Na and Fe\(_7\)S\(_8\). The selected-area electron diffraction (SAED) pattern of the multiple Fe\(_7\)S\(_8\)@C NCs in Figure 3c shows several ring patterns with d-spacings of 0.17, 0.20, 0.26, and 0.30, respectively, which correspond to the (220), (206), (203), and (200) planes of the pyrrhotite Fe\(_7\)S\(_8\) structure. Furthermore, the high-resolution TEM (HRTEM) image in the inset of Figure 3b displays parallel fringes with a d-spacing of 0.26 nm of the core, corresponding to the (203) plane of the pyrrhotite Fe\(_7\)S\(_8\) structure. The thickness of carbon shell is well-matched with the length of oleic acid and oleylamine (18-carbon-chain). In addition, the structure of core–shell Fe\(_2\)S\(_8\)@C NCs shows an extensively interconnected morphology, which can improve the electronic and ionic conductivities compared to a structure with individually separated Fe\(_2\)S\(_8\)@C NCs. The scanning electron microscope (SEM) image of the Fe\(_2\)S\(_8\)@C NCs confirms their long-range interconnected structure and homogeneous morphology (Figure S2, Supporting Information).
Fe7S8@C NCs (Figure S3, Supporting Information). The Fe 2p used to determine the surface chemistry composition of the material. The average calculated values of crystalline size were determined by using the Scherrer equation (Tables S1 and S2, Supporting Information). To obtain more in-depth information about the size of NCs statistically, we calculated the crystalline size of NCs from XRD data by using the Scherrer equation (Tables S1 and S2, Supporting Information). The average calculated values of crystalline size for the Fe7S8@C NCs are 10.52 nm, according to an elemental analysis result. The carbon content of the core–shell Fe7S8@C NCs was estimated to be 80.76 wt%, according to an elemental analysis result. The carbon content of the core–shell Fe7S8@C NCs was further characterized by Raman spectra (Figure 3e). After the carbonization process, strong peaks at 710.9 and 724.3 eV were attributed to the Fe2+ state, and the peaks at 713.6 and 726.7 eV originated from the Fe3+ state. These results are in good agreement with the composition of Fe7S8, which is composed of Fe2+ and Fe3+ states. In addition, the strong signal at 284.8 eV in the C 1s spectrum corresponds to the carbon shell of the Fe7S8@C NCs.

To obtain more information about the size of NCs statistically, we calculated the crystalline size of NCs from XRD data by using the Scherrer equation (Tables S1 and S2, Supporting Information). The average calculated values of crystalline size for the Fe7S8@C NCs are 10.5 and 13.2 nm, respectively, which is consistent with the result obtained from the TEM images. This result supports that the core–shell Fe7S8@C NCs can provide very short diffusion paths for the conversion reaction between Na and Fe7S8.

The electrochemical performance of the core–shell Fe7S8@C NCs is displayed in Figure 4, presenting excellent electrochemical characteristics, which is in agreement with our expectations. Figure 4a shows cyclic voltammograms of Fe7S8@C NCs at the scan rate of 0.5 mV s⁻¹ for 3 cycles. During initial discharge, a large peak is detected at ~0.6 V (vs Na+/Na), which may indicate the conversion reaction from Fe7S8 to the mixture of Fe and Na2S with the formation of solid electrolyte interphase (SEI) layers. The broad peaks at 1.0–2.0 V observed during the charge process are associated with the formation of Na2FeS3, which is similar to previous reports on various iron sulfides.[17,33] As shown in Figure 4b, the core–shell Fe7S8@C NCs exhibited a respectable power capability at fast charging and discharging current (90, 180, 270, 450, 900, 1800, and 2700 mA g⁻¹) in the 0.08–3.0 V window. It should be noted that even at 2700 mA g⁻¹, its discharge capacity was maintained up to ~550 mA h g⁻¹, which is ~79% of the theoretical capacity of Fe7S8. This remarkable capability is achieved by the structural synergy between the homogeneous carbon shells and the ultrafine size of cores, which improves the electrical conductivity and minimizes the Na–ion diffusion paths, thus overcoming the slow kinetics of the conversion reaction. The carbon shell can contribute the capacity of 10.5–15.8 mA h g⁻¹ considering the carbon content of the Fe7S8@C NCs.[34,35]

To demonstrate the effect of the ultrafine size and homogeneous carbon shell, we investigated the electrochemical properties of relatively large Fe7S8@C NCs (~50 nm) and Fe7S8@C NCs without a carbon shell. The size and composition of the larger Fe7S8@C NCs were confirmed by the SEM and XRD measurement results, as shown in Figure S4 in the Supporting Information. As demonstrated in Figure 4c, the large Fe7S8@C NCs exhibited a lower discharge capacity compared to those of the smaller Fe7S8@C NCs, likely due to the longer diffusion paths for electron and ions. In addition, severe capacity degradation with a much lower capacity was observed for the Fe7S8@C NCs as compared to the Fe7S8@C NCs. These results suggest that the extremely small size and homogeneous carbon coating are the main reasons for the excellent electrochemical properties of the Fe7S8@C NCs.

Furthermore, as illustrated in Figure 4d and Figure S5 (Supporting Information), the core–shell Fe7S8@C NCs have excellent cyclability over 1000 cycles. The core–shell Fe7S8@C NCs retain a capacity of ~447 mA h g⁻¹, which is ~71% of the initial charge capacity after 1000 cycles at a current rate of 180 mA g⁻¹. To understand the long-term cyclability, we observed the morphological changes of the Na/Fe7S8@C NCs cells. As shown in the SEM and TEM images, the anode retains...
its ultrafine particle structure after sodiation/desodiation processes (Figures S6 and S7, Supporting Information). This is ascribed to the homogeneous carbon shell of the NCs, which act as a buffer layer to prevent severe volume changes during the charge/discharge process. Additionally, it is difficult to find a crystalline structure in the TEM image when the anode is discharged to 0.1 V, which can be ascribed to the intermediate Na-rich phases. On the other hand, the corresponding SAED patterns could be indexed to the (111), (220), and (422) planes of the crystalline Na2S and (110) planes of crystalline Fe, which supports the contention that the conversion reaction between Na and Fe7S8 produces the Na2S and Fe phases (Fe7S8 + 16Na → 7Fe + 8Na2S). Moreover, the results of the XPS analyses support the conversion-based reaction mechanism of Fe7S8 for Na storage (Figure S8, Supporting Information). In the Fe 2P spectra of the sample discharged to 0.08 V, broad peaks for Fe0 were observed at 704.8 and 719.7 eV, despite their weak intensity levels. It was assumed that other peaks (≈710 and ≈715 eV) may correspond to the intermediate Na-rich phases. During the subsequent charge process, Fe was fully reoxidized.

To evaluate the performance of the Fe7S8@C NCs, we compared the electrochemical properties of other representative iron sulfides for NIBs, as shown in Table 1. It is noteworthy that our core–shell Fe7S8@C NCs exhibit superior specific
capacity levels due to the structural synergy between the conformal carbon shells and the ultrafine size of the cores. This result suggests a path forward in the design of structures for iron sulfide anodes for NIBs.

In summary, we have successfully designed and experimentally confirmed a new strategy to synthesize extremely small core–shell Fe$_7$S$_8$@C NCs for NIB battery. These ultrafine core–shell NCs enable highly reversible conversion reaction between Na and Fe$_7$S$_8$, resulting in excellent power capability (≈79% of the theoretical capacity at a current rate of 2700 mA g$^{-1}$) and outstanding cyclability. In addition, the core–shell Fe$_7$S$_8$@C NCs deliver a stable discharge capacity of ≈447 mA h g$^{-1}$ after 1000 cycles. This remarkable performance proves that the core–shell Fe$_7$S$_8$@C NCs are promising anode materials for NIB. Furthermore, our approach to fabricate carbon-coated core–shell structure is very simple and can be applicable in various types of materials. We believe that this synthetic approach can provide important insights for research on high-energy NIBs and new potential applications.

**Experimental Section**

**Synthesis of Core–Shell Fe$_7$S$_8$@C NCs:** First, 189 mg of FeCl$_2$, 384 mg of 1,2-hexadecanethiol, 30 mL of octadecene, and 12 mL of oleic acid were mixed in a three-neck flask and heated to 100 °C under an N$_2$ atmosphere for 1 h to form iron-oleate complexes. Separately, the sulfur precursor was prepared in an N$_2$-filled glovebox by dissolving sulfur (576 mg) in oleylamine (15 mL) and then rapidly injected into the flask. The solution was subsequently heated to 240 °C and kept for 1 h. After the solution was cooled to room temperature, the Fe$_7$S$_8$ NCs

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**Table 1.** Comparison of the electrochemical properties with other iron sulfide samples.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Current density [mA g$^{-1}$]</th>
<th>Specific capacity [mA h g$^{-1}$]</th>
<th>Cut-off voltage [V]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_7$S$_8$@C NCs</td>
<td>90</td>
<td>700</td>
<td>0.08–3.0</td>
<td>Our work</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>602</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>2700</td>
<td>552</td>
<td></td>
<td></td>
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<tr>
<td>Fe$_7$S$_8$ microspheres</td>
<td>200</td>
<td>250</td>
<td>0.5–3.0</td>
<td>[20]</td>
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<tr>
<td></td>
<td>1000</td>
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<tr>
<td>Fe$_7$S$_8$ nanospheres</td>
<td>50</td>
<td>300</td>
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<td></td>
<td>2000</td>
<td>190</td>
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<tr>
<td>Fe$_7$S$_8$ particles</td>
<td>20</td>
<td>640</td>
<td>0.5–3.0</td>
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<td></td>
<td>100</td>
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<td>200</td>
<td>290</td>
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<tr>
<td>Fe$_7$S$_8$ NCs</td>
<td>1000</td>
<td>900</td>
<td>0.02–2.5</td>
<td>[31]</td>
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<tr>
<td></td>
<td>5000</td>
<td>700</td>
<td></td>
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<tr>
<td>Yolk–shell Fe$_7$S@C</td>
<td>100</td>
<td>621</td>
<td>0.01–2.3</td>
<td>[17]</td>
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<td></td>
<td>500</td>
<td>537</td>
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<td>2500</td>
<td>452</td>
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<tr>
<td>Fe$_7$S$_8$ NCs</td>
<td>100</td>
<td>500</td>
<td>0.001–3.0</td>
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were isolated by the addition of methanol followed by centrifugation. The obtained FeS2 NCs were then annealed at 600 °C for 5 min by using a rapid thermal annealing system under a mild vacuum (1.5 Torr) under an Ar gas flow. The large Fe7S8@C NCs (~50 nm) were produced through the carbonization process of the FeS2 NCs by using the tube furnace at 600 °C for 2 h in Ar gas flow.

**Material Characterization:** The size and the surface morphology of the FeS2 NCs and Fe7S8@C NCs were observed using a transmission electron microscope (Titan cubed G2 60-300) and a field emission scanning electron microscope (Hitachi, S-4800). Investigation of the crystal structure was carried out using an XRD (Rigaku, D/MAX-RB diffractometer, Tokyo, Japan) equipped with Cu-Kα by step scanning (0.03° s⁻¹) in the 2θ range of 20°–80°. The samples were further characterized using a high-resolution dispersive Raman microscope (Lab-RAM HR UV/vis/NIR) with Raman shifts from 100 to 4000 cm⁻¹. The elemental analysis of FeS1.35@C NCs was carried out by an elemental analyzer (Thermo Scientific, Flash 2000 series).

**Electrochemical Characterization:** Electrochemical tests were performed in a CR2032-type coin cell assembled in an Ar-filled glovebox. Fe7S8@C NCs electrode was prepared as follows. 80 wt% of the active material and 20 wt% super P were homogeneously mixed using a ball-mill at 100 rpm for 10 h. 90 wt% of this mixture was then remixed with 10 wt% sodium carboxymethyl cellulose binder. Total weight percent of the active material is 3 g cm⁻³. 3 g cm⁻³ loading of the active material is 3 g cm⁻³ (0.03 g cm⁻³ range of 2θ). The size and the surface morphology of FeS2 NCs by using the tube furnace at 100 rpm for 10 h. 90 wt% of this mixture was then remixed with 20 wt% super P were homogeneously mixed using a ball-mill at 100 rpm for 10 h. 90 wt% of this mixture was then remixed with 3 g cm⁻³ loading of the active material is 3 g cm⁻³. 3 g cm⁻³ (0.03 g cm⁻³ range of 2θ).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

carbon shells, colloidal nanocrystals, one-pot synthesis, pyrhhotite, sodium–ion batteries

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