High-quality prussian blue crystals as superior cathode materials for room-temperature sodium-ion batteries

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Experimental Section

Synthesis of HQ-NaFe: In a typical synthesis, 2 m mol Na₄Fe(CN)₆·10H₂O and 1 mL hydrochloric acid (37%) were dissolved in 100 mL deionized water to obtain a homogenous solution. The mixture was maintained at 60 °C for 4 h under vigorous stirring to obtain HQ-NaFe nanocubes. The composite was collected by filtration, washed by water and ethanol for three times and dried at 100 °C in a vacuum oven for 24 h.

Synthesis of LQ-NaFe: In a typical synthesis, 2 m mol Na₄Fe(CN)₆·10H₂O was dissolved in 80 mL deionized water to obtain solution A. 4 m mol FeCl₃·9H₂O was dissolved in 20 mL deionized water to form solution B. Solution B was slowly added to solution A and a blue precipitate formed immediately. The mixture was maintained at 60 °C for 4 h under vigorous stirring to obtain LQ-NaFe nanoparticles. The composite was collected by filtration, washed by water and ethanol for three times and dried at 100 °C in a vacuum oven for 24 h.

Structural Characterization: SEM (JEOL 6701F, operating at 10 kV) was used to investigate the morphology and size of the as-prepared composites. XRD measurements were carried out using a Philips PW3710 with filtered Cu Kα radiation (Rigaku D/max-2500, λ = 1.5405 Å). Raman spectra were obtained using a Digilab FTS3500 (Bio-Rad) with a laser wavelength of 532 nm. The chemical composition was examined by the elemental analysis (Flash EA 1112)
for C and N elements, and by ICP–AES (Shimazu ICPE-9000) for Fe and Na elements. TG and DTA were conducted on a TG/DTA6300 instrument at 2 °C min$^{-1}$ heating rate of under N$_2$ environment.

**Electrochemical Characterization:** A slurry of HQ-NaFe (LQ-NaFe), ketjen black, and poly(vinyl difluoride) (PVDF, Aldrich) at a weight ratio of 7:2:1 was coated onto aluminum foil (99.6%, Goodfellow) to prepare the working electrode. The electrochemical experiment was performed in two-electrode Swaglok-type cells assembled in an argon-filled glove box. The Na-ion battery configuration is consisted of a Na metal anode (10 mm in diameter), a porous separator (glass fiber (GF/D) from Whatman), and the prepared working electrode. 1 M NaPF$_6$ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) at 1:1 volume ratio was used as electrolyte. Galvanostatic tests were carried out using an Arbin BT2000 system. The voltage range was between 2.0 and 4.2 V vs. Na$^+$/Na. Cyclic voltammetry measurements were performed on an Autolab PG302N at a scan rate of 0.1 mV s$^{-1}$ within the potential range of 2.0 V–4.2 V (vs. Na$^+$/Na).

**Calculation of the apparent diffusion coefficient of Na$^+$:** The apparent diffusion coefficient $D$ of Na$^+$ is calculated from the inclined line in the Warburg region using the following equation:

$$D = \frac{RT^2}{2A^2n^4F^4C^2\sigma^2} \quad (1)$$

where $R$ is the gas constant, $T$ is the absolute temperature, $A$ is the surface area of the cathode electrode, $n$ is the number of electrons per molecule during oxidization, $F$ is the Faraday constant, $C$ is the Na$^+$ concentration (1.81 $\times$ 10$^{-3}$ mol cm$^{-3}$ for HQ-NaFe; 8.12$\times$ 10$^{-4}$ mol cm$^{-3}$ for LQ-NaFe), and $\sigma$ is the Warburg factor associated with $Z_{re}$. Due to $Z_{re} \propto \sigma \omega^{-1/2}$, the value of $\sigma$ can be obtained by linear fitting of the relationship plot $Z_{re}$ and reciprocal square root of the angular frequency $\omega$ (Fig. S2b). The value of $\sigma$ for HQ-NaFe and LQ-NaFe are 36.99 and 258.76, respectively. According to equation (1), the apparent diffusion coefficient $D$ of Na$^+$ can be calculated.
**Fig. S1** Schematic illustration of synthetic processes of HQ-NaFe nanocubes by single iron-source method. (a: Na$_4$Fe(CN)$_6$ and hydrochloric acid mixture; b: decomposition of [Fe(CN)$_6$]$^{4-}$ to Fe$^{2+}$; c: oxidation of Fe$^{2+}$ to Fe$^{3+}$; d: reaction of Fe$^{3+}$ or Fe$^{2+}$ with [Fe(CN)$_6$]$^{4-}$ to form HQ-NaFe nanocube nuclei; e: growing process of HQ-NaFe cubes.)

**Fig. S2** SEM images of HQ-NaFe nanocubes obtained at a reaction time of (a) 30 minutes; (b) 90 minutes and (c) 180 minutes.
Table S1 Element contents of HQ-NaFe and LQ-NaFe

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Fe</th>
<th>C</th>
<th>N</th>
</tr>
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<tbody>
<tr>
<td>HQ-NaFe</td>
<td>4%</td>
<td>34.2%</td>
<td>20.7%</td>
<td>24.2%</td>
</tr>
<tr>
<td>LQ-NaFe</td>
<td>1.3%</td>
<td>32.1%</td>
<td>18.2%</td>
<td>21.2%</td>
</tr>
</tbody>
</table>

Fig. S3 Cycling voltammograms of (a) HQ-NaFe and (b) LQ-NaFe at 0.1 mV s⁻¹ between the voltage limits of 2.0 V–4.2 V.
**Fig. S4** Typical galvanostatic discharge/charge voltage profiles of HQ-NaFe and LQ-NaFe. The voltage polarizations are 60 mV and 200 mV for HQ-NaFe and LQ-NaFe, respectively.

**Fig. S5** (a) The typical Nyquist plots of HQ-NaFe and LQ-NaFe electrodes. (b) Variations and fittings between $Z_{re}$ and reciprocal square root of the angular frequency $\omega$ in the low frequency region of HQ-NaFe and LQ-NaFe.
**Fig. S6** Cycling performances of HQ-NaFe and LQ-NaFe after stored in ambient condition for 4 months.

**Fig. S7** XRD characterizations of HQ-NaFe electrode before and after 150 cycles.
**Fig. S8** SEM images of HQ-NaFe electrodes after 150 cycles under a current density of 25 mA g⁻¹.