Electronic Supplementary Information for Energy & Environmental Science

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

Ya You, Xing-Long Wu, Ya-Xia Yin, and Yu-Guo Guo*

CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, P.R. China. E-mail: ygguo@iccas.ac.cn;

Experimental Section

Synthesis of HQ-NaFe: In a typical synthesis, 2 m mol $Na_4Fe(CN)_6{\cdot}10H_2O$ 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 $Na_4Fe(CN)_6{\cdot}10H_2O$ was dissolved in 80 mL deionized water to obtain solution A. 4 m mol $FeCl_3{\cdot}9H_2O$ 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, $\lambda = 1.5405$ 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:

$$D=R^2T^2/2A^2n^4F^4C^2\sigma^2 \qquad (1)$$

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 (1.81×10^{-3} mol cm^{-3} for HQ-NaFe; 8.12×10^{-4} mol cm^{-3} for LQ-NaFe), and σ is the Warburg factor associated with Z_{re}. Due to $Z_{re} \infty \sigma\omega^{-1/2}$, the value of σ can be obtained by linear fitting of the relationship plot Z_{re} and reciprocal square root of the angular frequency ω (Fig. S2b). The value of σ 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.

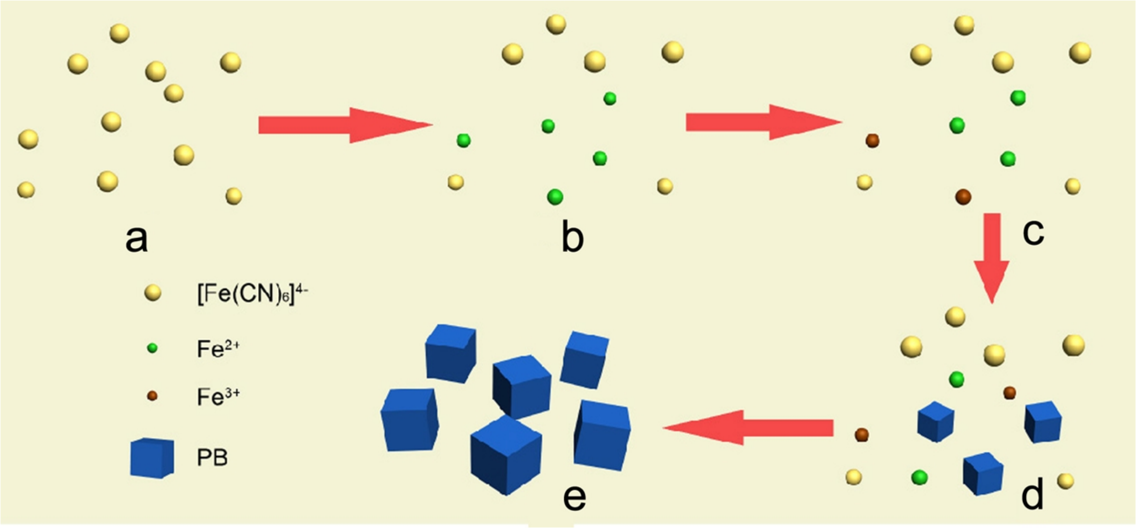

Fig. S1 Schematic illustration of synthetic processes of HQ-NaFe nanocubes by single iron-source method. (a: $Na_4Fe(CN)_6$ and hydrochloric acid mixture; b: decomposition of $[Fe(CN)_6]^{4-}$ to Fe^{2+} ; c: oxidation of Fe^{2+} to Fe^{3+}; d: reaction of Fe^{3+} or Fe^{2+} with $[Fe(CN)_6]^{4-}$ to form HQ-NaFe nanocube nuclei; e: growing process of HQ-NaFe cubes .)

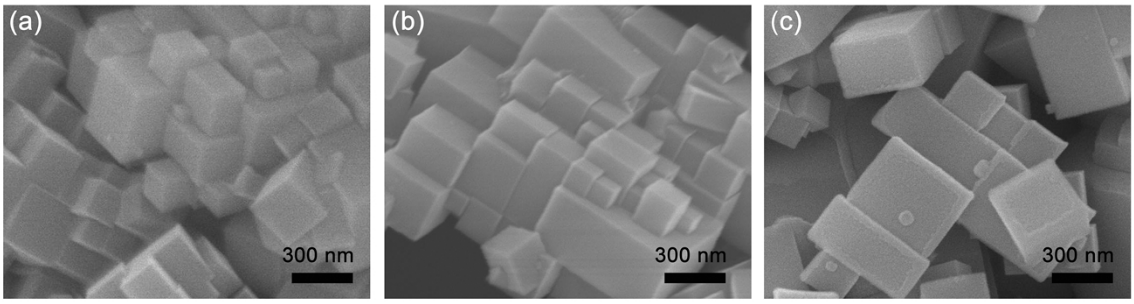

Fig. S2 SEM images of HQ-NaFe nanocubes obtained at a reaction time of (a) 30 minutes; (b) 90 minutes and (c) 180 minutes.

Table S1 Element contents of HQ-NaFe and LQ-NaFe

	Na	Fe	C	N
HQ-NaFe	4%	34.2%	20.7%	24.2%
LQ-NaFe	1.3%	32.1%	18.2%	21.2%

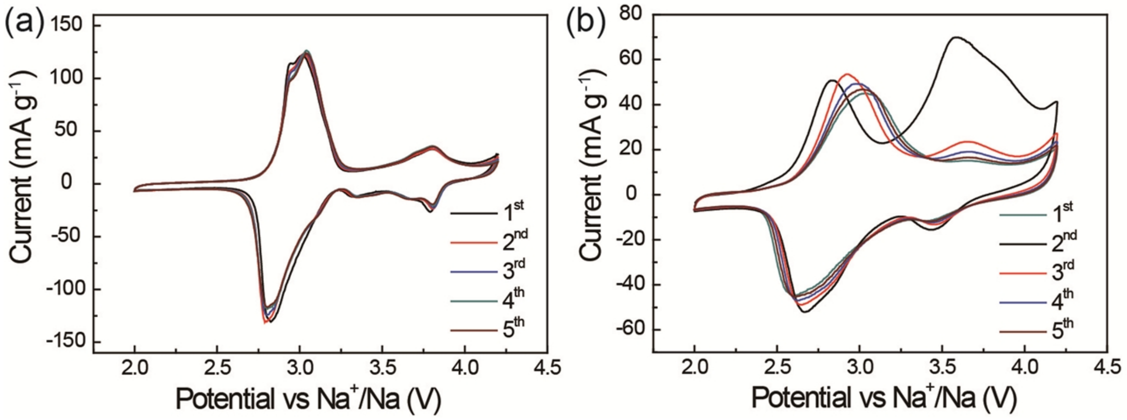

Fig. S3 Cycling voltammograms of (a) HQ-NaFe and (b) LQ-NaFe at 0.1 mV s^{-1} between the voltage limits of 2.0 V–4.2 V.

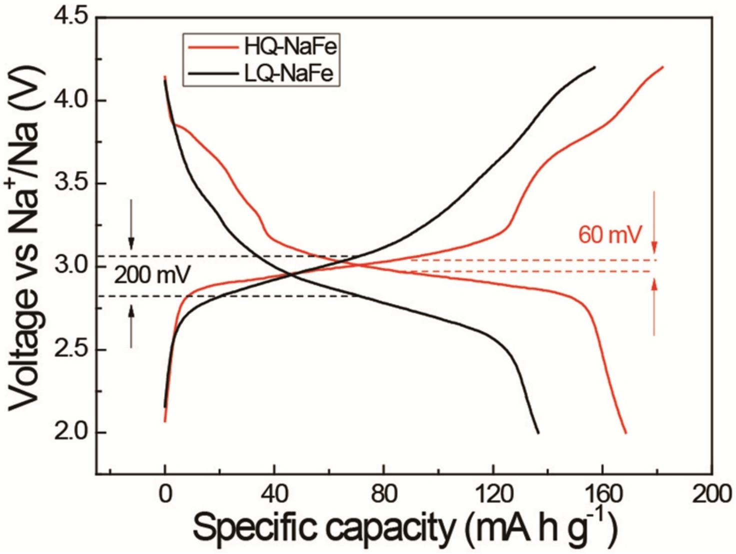

Fig. S4 Typical galvanostatic discharge/charge voltage profiles of HQ-NaFe and LQ-NaFe. The voltage polarizations are 60 mV and 200 mV for HQ-NaFe and LQ-NaFe, respectively.

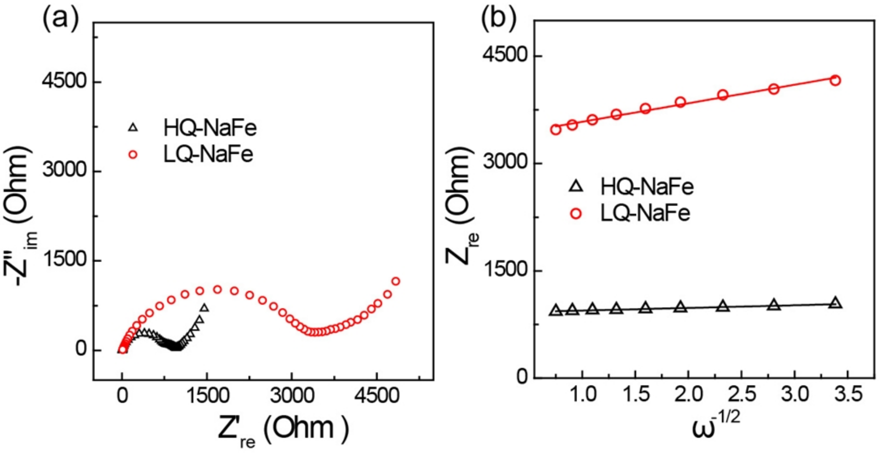

Fig. S5 (a) The typical Nyquist plots of HQ-NaFe and LQ-NaFe electrodes. (b) Variations and fittings between Z_{re} and reciprocal square root of the angular frequency ω in the low frequency region of HQ-NaFe and LQ-NaFe.

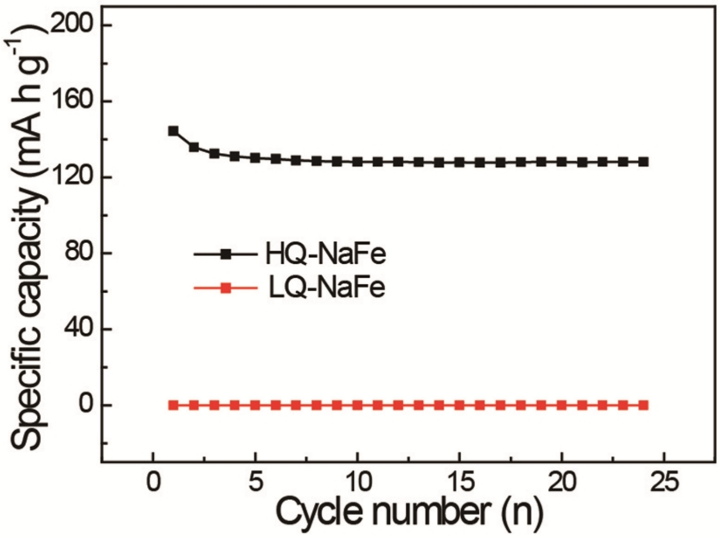

Fig. S6 Cycling performances of HQ-NaFe and LQ-NaFe after stored in ambient condition for 4 months.

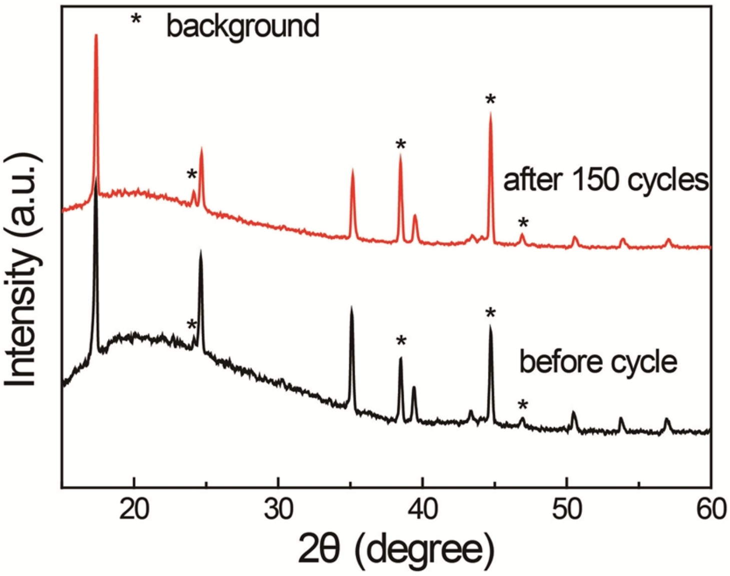

Fig. S7 XRD characterizations of HQ-NaFe electrode before and after 150 cycles.

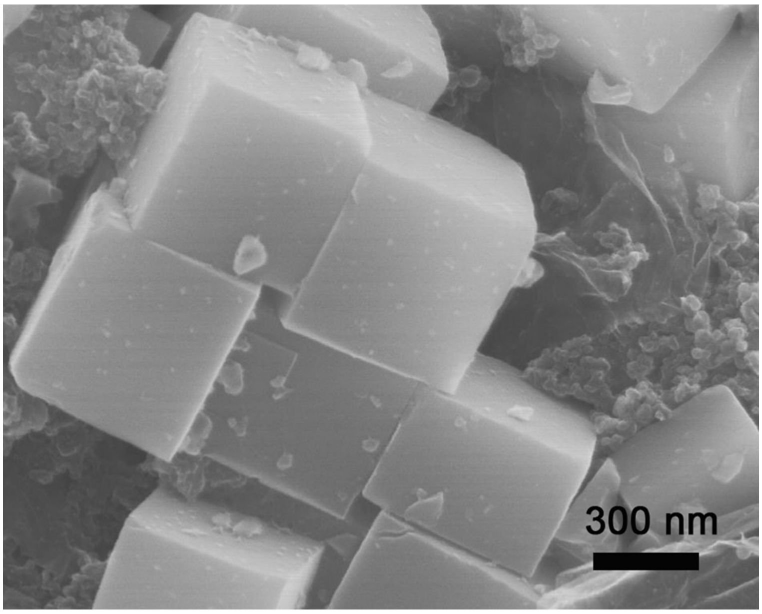

Fig. S8 SEM images of HQ-NaFe electrodes after 150 cycles under a current density of 25 mA g^{-1}.