

SUPPORTING INFORMATION

Hollow amorphous NaFePO₄ nanospheres as a high capacity and high rate cathode for sodium-ion batteries

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Summary: 17 Pages; 1 Table; 17 Figures;

Experimental

Synthesis of hollow amorphous NaFePO₄ nanospheres

All the reagents were analytical grade and without further purification before utilization. The molten salt reactor (Chanzheng AMS-70, China) was run using a personal computer through reaction conditions (time and temperature, etc.) control software. In a typical synthesis, a mixture of NaH₂PO₄ and sodium oleate (weight ratio: 1 : 4) (weight ratio of NaH₂PO₄ : sodium oleate =1:4) was firstly heated to 380 °C to form the molten salt in the reactor in a 5% H₂/95% Ar mixture.

Into it Iron-(II) stearate was added under stirring (the weight percentage of Iron-(II) stearate in the reaction system was about 10.1%). After the reaction was conducted for 30 min, and then cooling to room temperature, the product was obtained by washing the fusion with deionized water to remove the salts for several times, and dried in 100 °C for 12 h.

For comparison, conventional amorphous NaFePO₄ sample were prepared via the same method using anhydrous FeCl₂ instead of Iron-(II) stearate.

Characterization of hollow amorphous NaFePO₄ nanospheres

X-ray diffraction (XRD) patterns were obtained using an X'Pert X-ray powder diffractometer equipped with a CuK α radiation source ($\lambda = 0.15406$ nm). For compositional analyses, the dry samples were dissolved in boiling aqua fortis using a microwave digestion system. The Brunauer–Emmett–Teller (BET) specific surface areas of the samples were determined using a N₂ adsorption–desorption technique, in which the samples were degassed at 200 °C for 180 min before the measurements. Scanning transmission electron microscopy (STEM) images and selected-area electron diffraction

patterns (SAED) of the samples were taken using a FEI Tecnai G2 F20 S-Twin microscope. Samples for STEM analysis were prepared by depositing a single drop of diluted nanoparticle dispersion in ethanol on an amorphous, carbon-coated, copper grid. The energy dispersive X-ray spectroscopy (EDAX) data were acquired using an Oxford Instrument EDAX detector. The measured compositions were typically averaged from 5–10 spots, with an estimated systematic error of less than ± 2 at.%. The surface electronic states of the samples were investigated using X-ray photoelectron spectroscopy (XPS; Perkin–Elmer PHI 5000C ESCA, using $\text{AlK}\alpha$ radiation). The binding energies were referenced to the C1s peak (binding energy of 284.6 eV) of the surface adventitious carbon. The ^{57}Fe Mössbauer spectra of the samples were performed on an OXFORD MS-500 (Oxfordshire, UK) constant acceleration Mössbauer spectrometer with a 1024 multichannel analyzer. The velocity and isomer shifts were calibrated using iron (Fe) foil. The radiation source was $^{57}\text{Co}/\text{Pd}$.

Electrochemical performances were evaluated using a CR2032 coin cell composed of the cathode, sodium anode, Celgrade polypropylene separator, and NaPF_6 in 1:1 ethylene carbonate and diethyl carbonate as the electrolyte. The cathode was prepared by a slurry coating procedure. The slurry consisted of 65 wt.% active material, 20 wt.% acetylene black and 15 wt.% polytetrafluoroethylene (PTFE) binder and was coated on aluminum foil. After drying under vacuum at 90 °C for 24 h, the sample was pressed under a pressure of 15 MPa. The cells were galvanostatically cycled at different current rates ($C=155 \text{ mA g}^{-1}$) in the range 1.5–4.0 V using an Arbin Instruments testing system (Arbin BT-2000). Cyclic voltammetric measurements were performed at a scan rate of 0.1 mV s^{-1} on a CHI 660a electrochemical workstation (ChenHua Instruments Co., China). The

electrochemical impedance spectrum tests were performed on a Chenhua CHI660C electrochemical workstation. The AC perturbation signal was 5 mV, and the frequency range was from 0.01 Hz to 100 kHz. The EIS parameters were fitted using ZView2 software. All tests were performed at room temperature (25 °C).

Table S1 Fitted value of the Nyquist plot for amorphous NaFePO₄.

	Conventional	Hollow nanospheres
R _{sf} / Ohm	91.4	34.6
R _{ct} / Ohm	117.2	69.5
Warburg coefficient / s ^{1/2} cm ⁻¹	1×10 ⁸	4.86×10 ⁷

R_{sf} represents for the diffusion impedance of Na⁺ on the surface membrane, and R_{ct} for the charge transfer impedance.

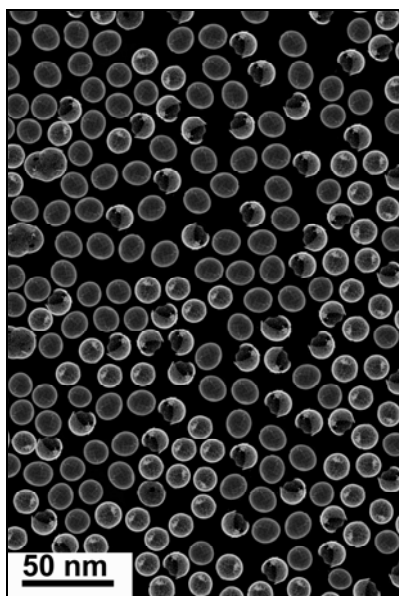


Fig.S1 The typical high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of hollow amorphous NaFePO_4 nanospheres dispersed in aqueous phase.

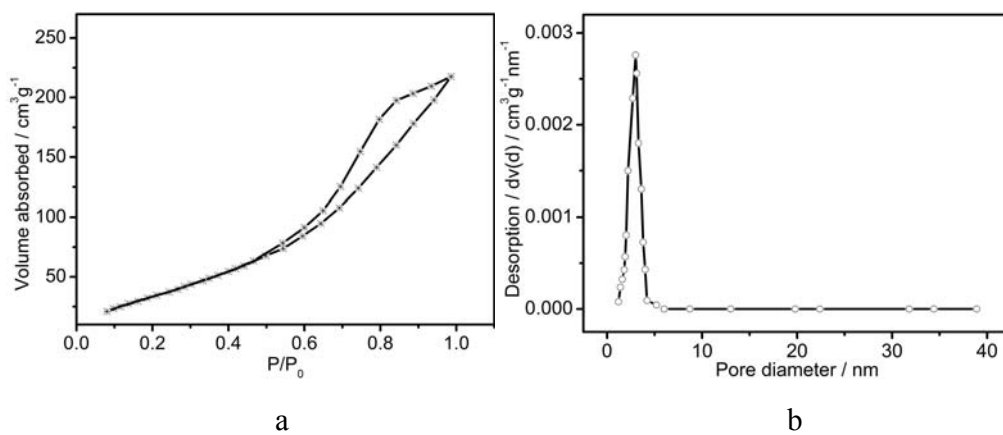


Fig.S2 (a) N_2 adsorption–desorption plots and (b) pore size distribution of hollow amorphous NaFePO_4 nanospheres.

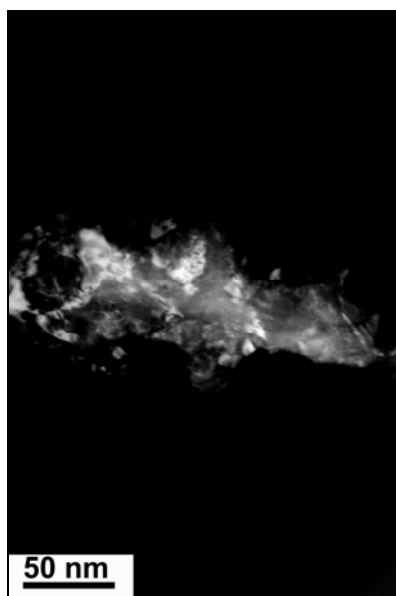


Fig.S3 The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of conventional amorphous NaFePO₄.

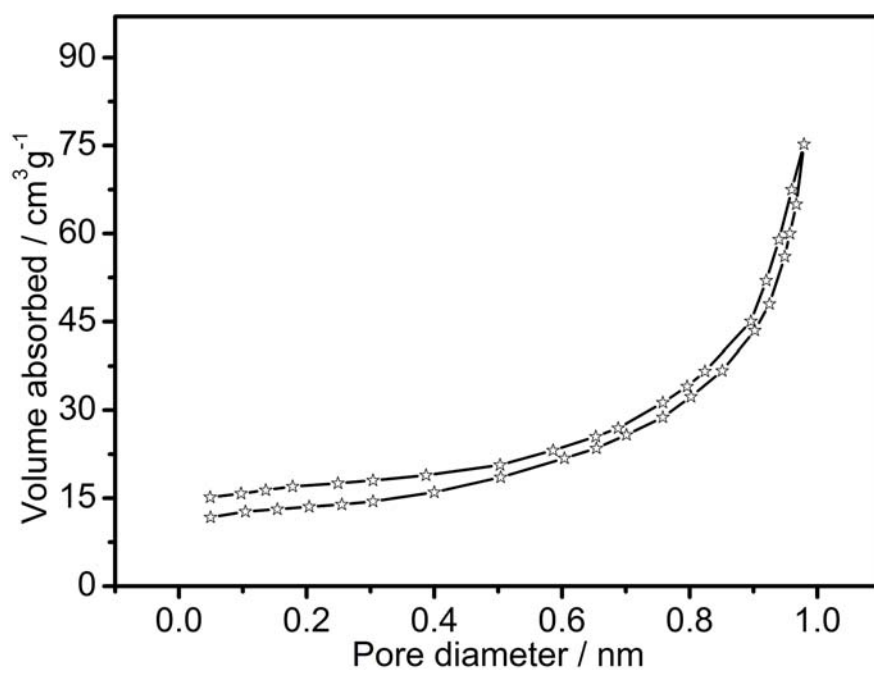


Fig.S4 N₂ adsorption-desorption plots of conventional amorphous NaFePO₄.

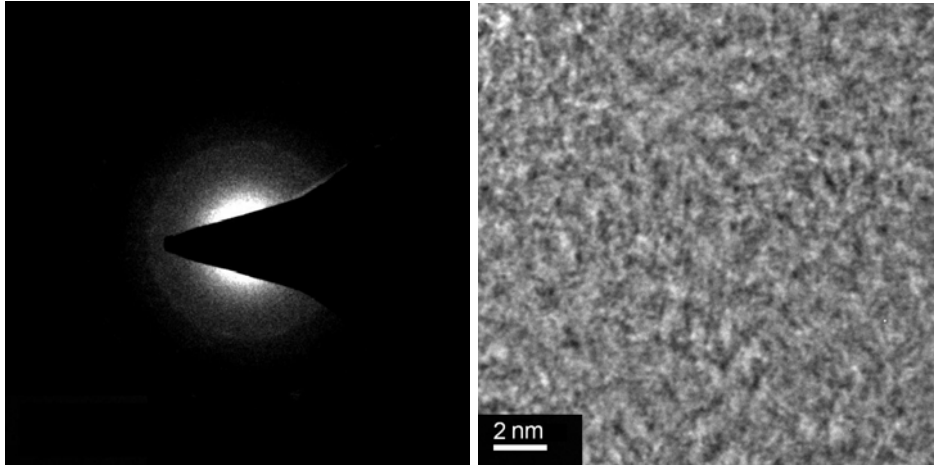


Fig.S5 (a) SEAD pattern and (b) HR-STEM of hollow amorphous NaFePO_4 nanospheres.

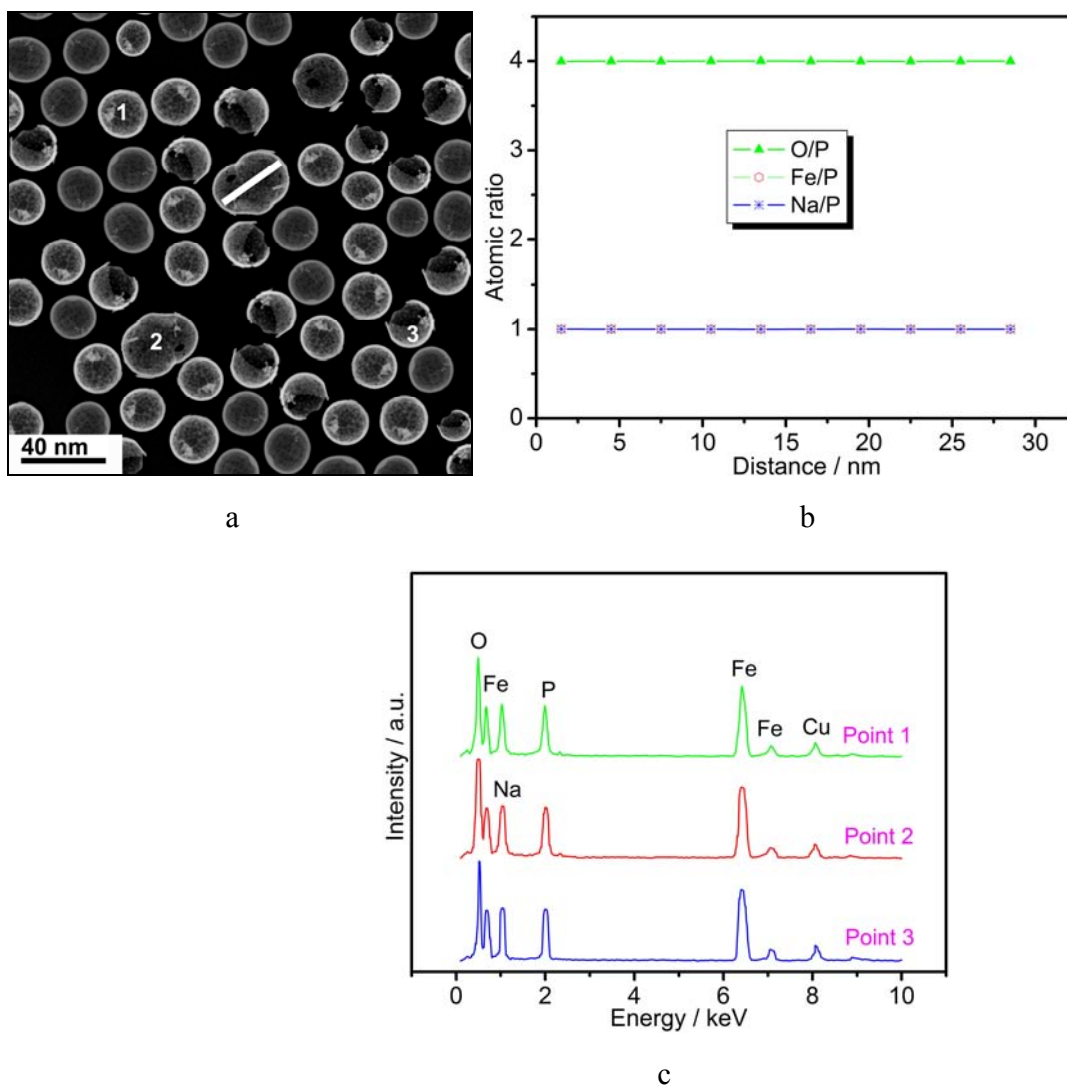


Fig.S6 (a) The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM); (b) O/P, Na/P, and Fe/P atomic ratios recorded along the white cross-sectional compositional line shown in (a); (c) the Energy-dispersive X-ray spectroscopy (EDS) at points 1-3 in (a) of the as-prepared hollow amorphous NaFePO_4 nanospheres.

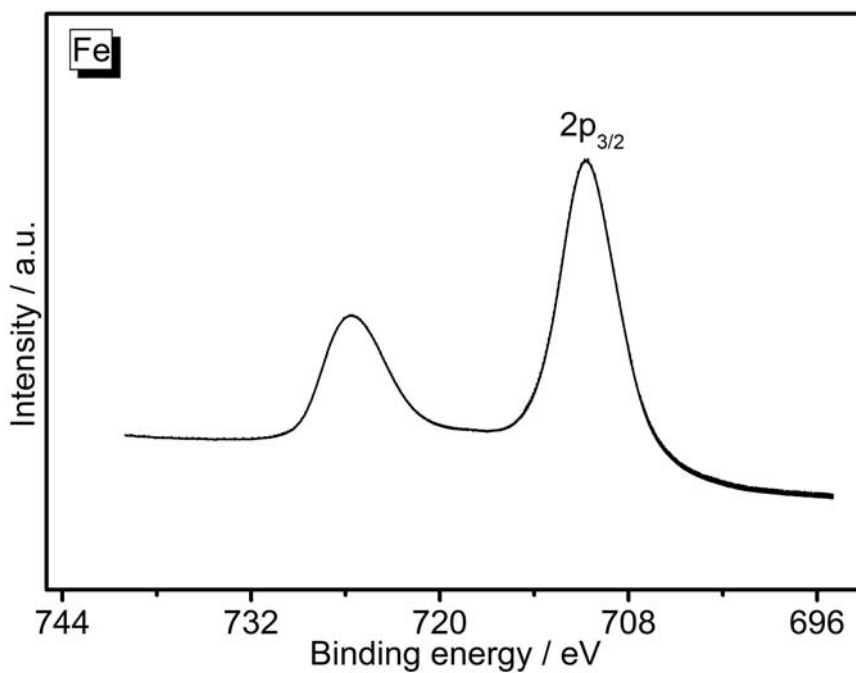


Fig.S7 Fe 2p_{3/2} XPS spectrum of the as-prepared hollow amorphous NaFePO₄ nanospheres.

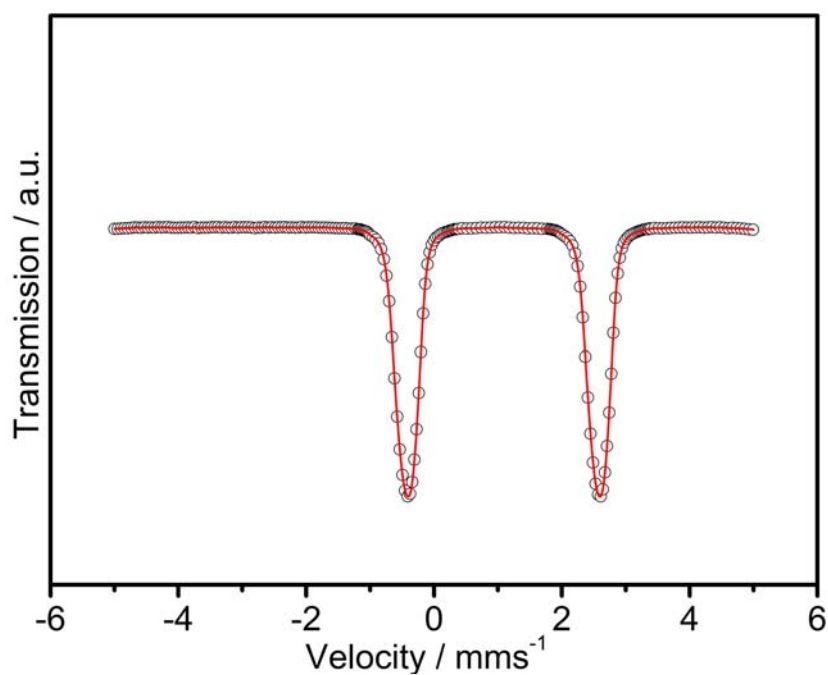


Fig.S8 Mössbauer spectrum of the as-prepared hollow amorphous NaFePO₄ nanospheres.

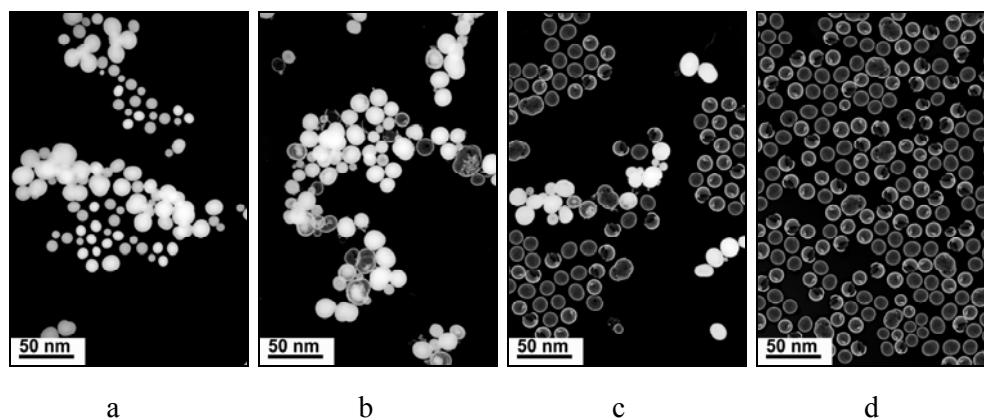


Fig.S9 STEM images of the as-prepared hollow amorphous NaFePO_4 nanospheres with different reaction times: (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min.

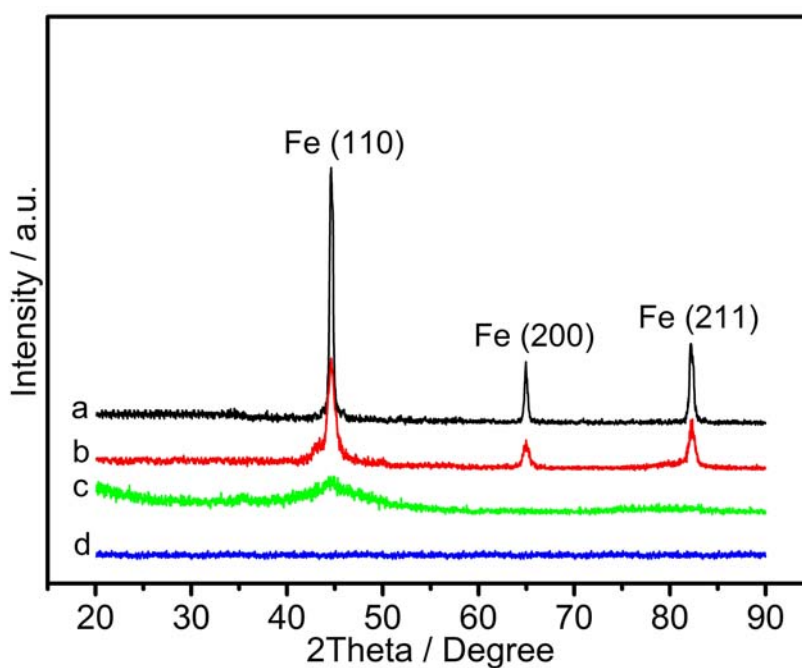


Fig.S10 XRD patterns of the as-prepared hollow amorphous NaFePO_4 nanospheres with different reaction times: (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min.

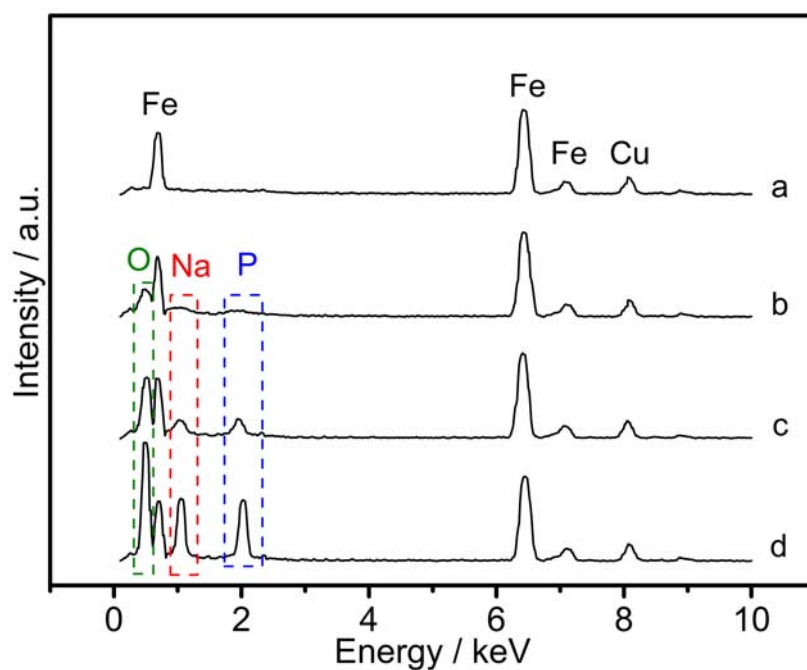


Fig.S11 EDAX patterns of the as-prepared hollow amorphous NaFePO₄ nanospheres with different reaction times: (a) 5 min, (b) 10 min, (c) 20 min, and (d) 30 min.

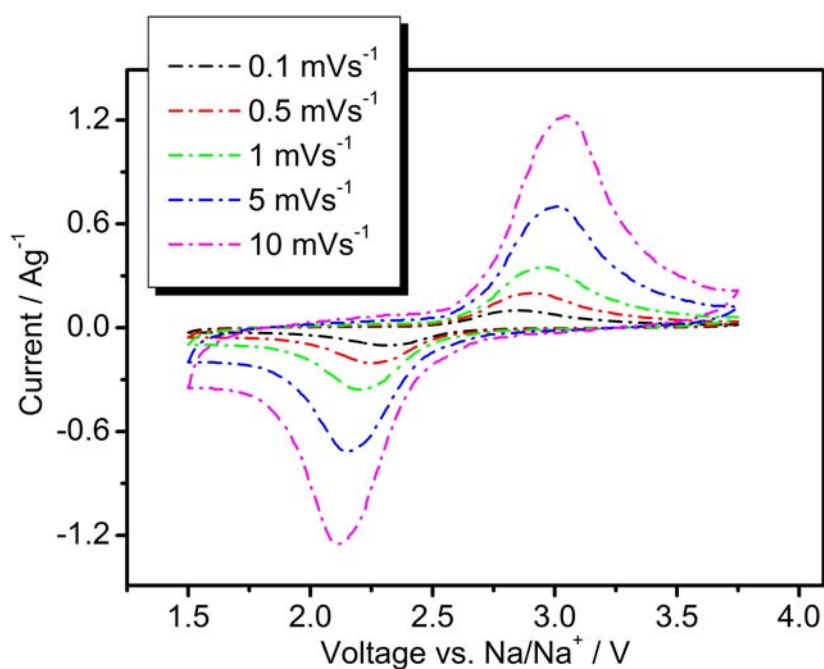


Fig.S12 CV tests for the as-prepared hollow amorphous NaFePO₄ nanospheres under different scan rates (voltage window 1.5–3.75V).

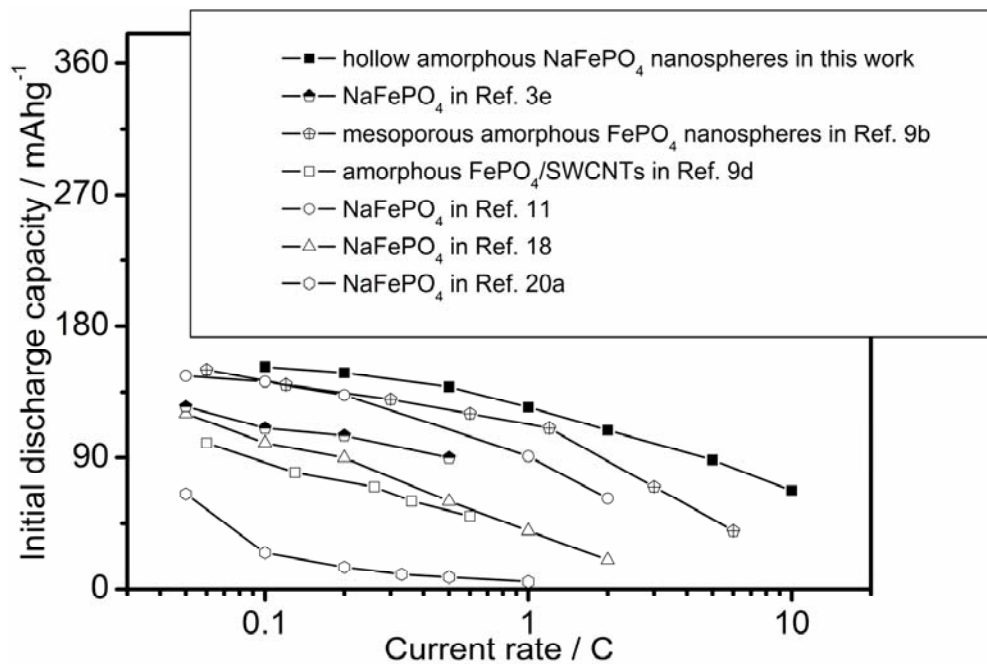


Fig.S13 Rate performance comparison of the as-prepared hollow amorphous NaFePO₄ nanospheres with those previously reported for similar materials. 1 C = 155 mA g⁻¹.

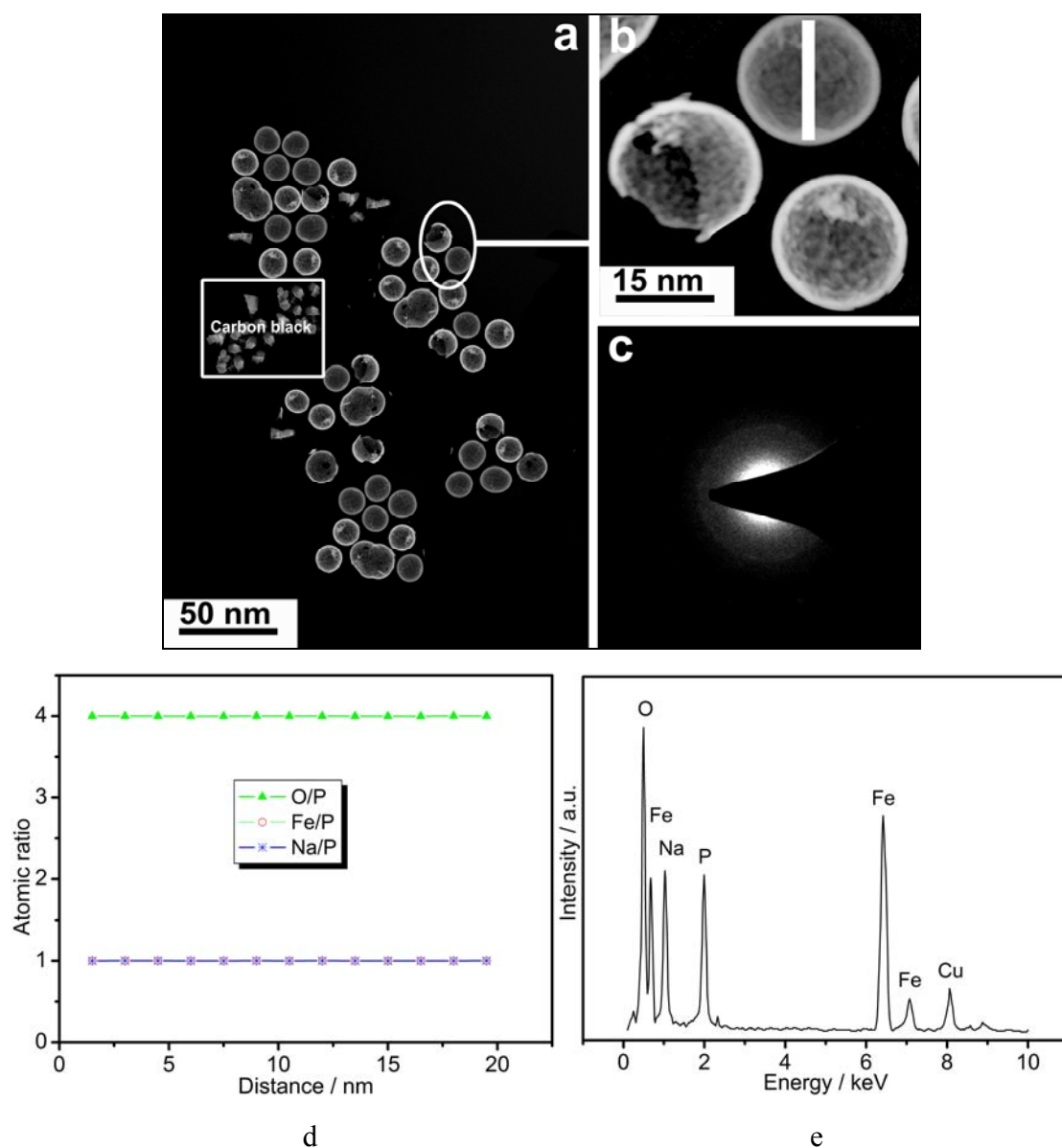


Fig.S14 (a) STEM images; (b) The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM); (c) SAED pattern; (d) O/P, Na/P, and Fe/P atomic ratios recorded along the white cross-sectional compositional line shown in (b); and (e) EDAX pattern of the as-prepared hollow amorphous NaFePO₄ nanospheres after cycling at 5 C for 100 cycles. The small nanoparticles observed in the image (a) are carbon black.

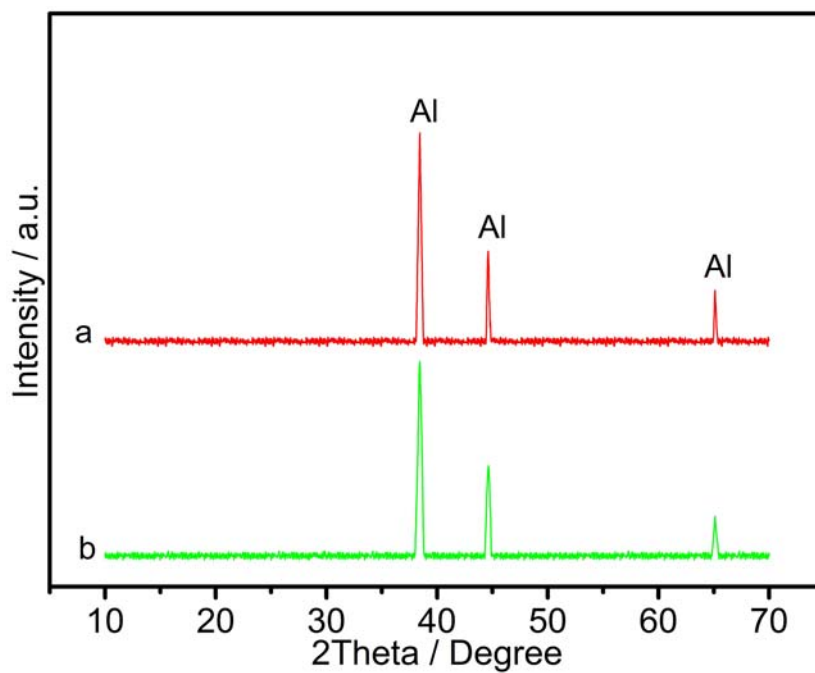


Fig.S15 The XRD patterns of the NaFePO_4 cathodes at full charging and discharging states after 100 cycles. No crystalline peak appears throughout the whole discharging/charging processes expect for the Al current collector.

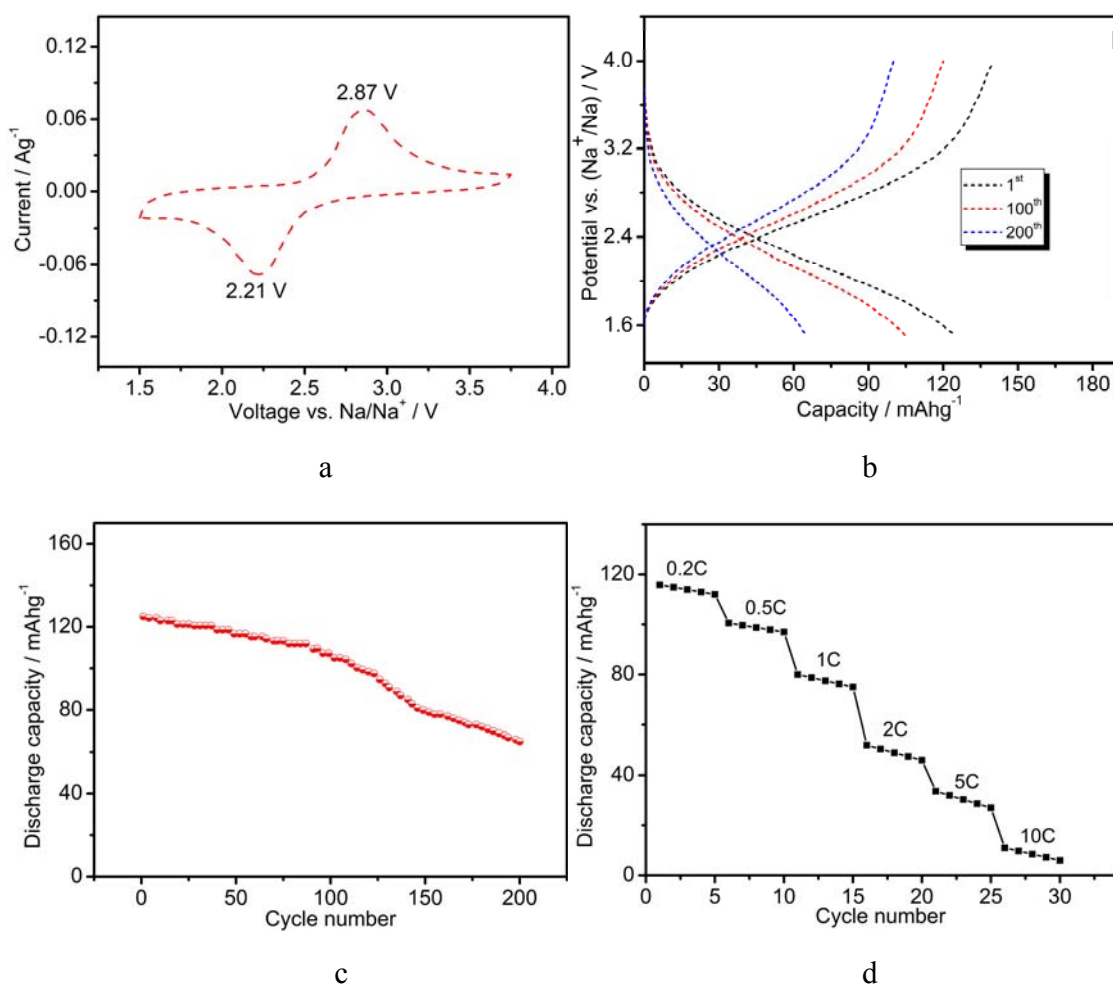


Fig.S16 Electrochemical characterization of the conventional amorphous NaFePO₄: (a) CV curve conducted at a scan rate of 0.1mVs⁻¹ (voltage window 1.5–3.75V); (b,c) galvanostatic discharging/charging profiles performed at a current density of 0.1C and the corresponding cycling performance; and (d) rate capability. The counter electrode was a Na disk and the electrolyte was 1.0 molL⁻¹ NaPF₆ dissolved in an EC/DEC solution (EC/DEC =1:1 by vol), voltage window was 1.5–4.0 V.

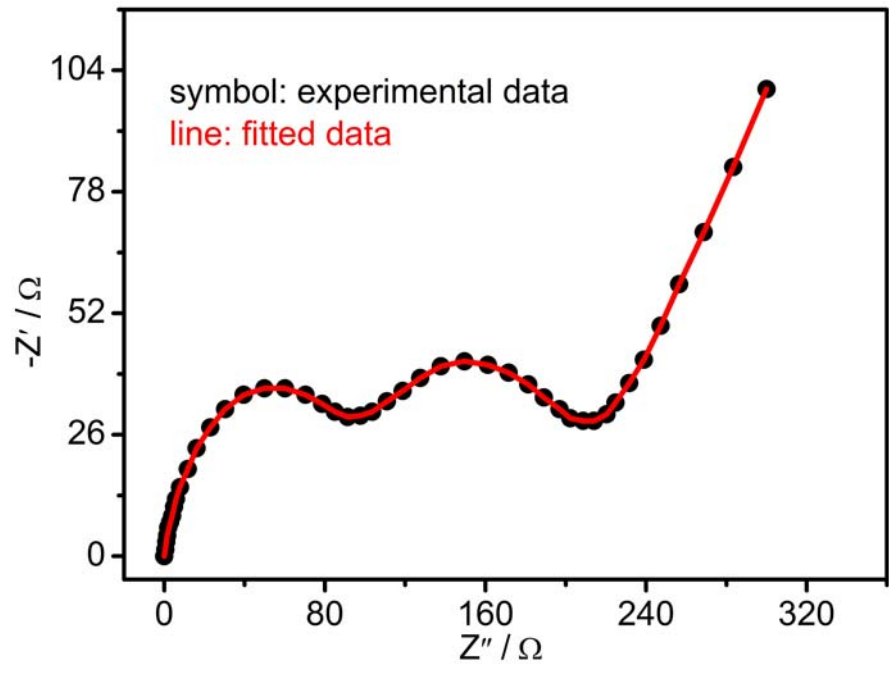


Fig.S17 Nyquist plots for the conventional amorphous NaFePO₄ obtained by electrochemical impedance spectroscopy (EIS) tests at fully charged states at the 20th charging process.