Electronic Supplementary Information

Mesocrystalline coordination polymer as promising cathode for sodium ion battery

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Experimental

$Na_4[Fe(CN)_6]\cdot 3H_2O$, NaCl, hydrochloric acid (HCl) and polyallylamine hydrochloride (PAH) were purchased from Sinopharm Chemical Reagent Co. and J&K Scientific Ltd. and used without further purification.

PB mesocrystals: The fabrication of PB mesocrystals was simply achieved by the Hydrothermal reaction of the $Na_4[Fe(CN)_6]$ solution. In a typical synthesis, PAH (400 mg) were dissolved in 10 mL 0.1 M of HCl to form a clear solution in bottle A. In the meantime, $Na_4[Fe(CN)_6]\cdot 10H_2O$ (96.8 mg) and NaCl (937 mg) were dissolved in 10 mL 0.1 M of HCl to form a clear solution in bottle B. The solution in bottles A and B was then mixed under magnetic stirring until the mixture became clear. The obtained solution was then placed into an electric oven and heated at 80 ^oC for 8 h. After that, the precipitates were collected by centrifugation and washed in distilled water and ethanol several times. After drying at 100 ^oC for 15 h, the PB mesocrystals were obtained.

PB single-crystals: According to Guo's paper,[1] 2 mmol of $Na_4[Fe(CN)_6]\cdot 10H_2O$ and 1 mL of HCl (37%) were dissolved in 100 mL of deionized water to form a clear solution. The mixture was maintained at 60 °C for 4 h under vigorous stirring. After that, the precipitates were collected by centrifugation and washed in distilled water and ethanol several times. After drying at 100 ^oC for 24 h, the PB single-crystals were obtained.

Structural Characterization: The structural characteristic of the prepared samples was monitored by XRD using a Rigaku RINT 2500X diffractometer with Cu-Kα

radiation and conventional θ-2θ geometry. SEM (Hitachi S - 4800), and TEM (JEOL JEM – 2100F) were used to characterise the morphology and size of the PB particles. Zeta potential measurements were performed with a Malvern Zetasizer Nano ZS.

Electrochemical Characterization: For a typical coin cell, electrochemical performances were evaluated with standard CR2032 coin cells. The cathodes were composed of 70 wt.% active material, 10 wt.% ketjen black, 10 wt.% acetylene black and 10 wt.% poly(vinyl difluoride) (PVDF) in N-methyl-2-pyrrolidone (NMP). The electrolyte comprised 1M $NaClO_4$ in ethylene carbonate (EC) and propylene carbonate (PC) (1:1 in volume) with 5% fluorinated ethylene carbonate. Sodium was used as anode material. All cells were assembled in an argon-filled glove box with moisture and oxygen levels below 0.1 ppm. The galvanostatic charge-discharge tests were conducted using a battery test system (Land CT2001A model, Wuhan，China). Cyclic voltammetry measurements were performed on CHI electrochemical workstation (CHI, 660E).

[1] Y. You, X.-L. Wu, Y.-X. Yin and Y.-G. Guo, Energy Environ. Sci., 2014, 7, 1643.

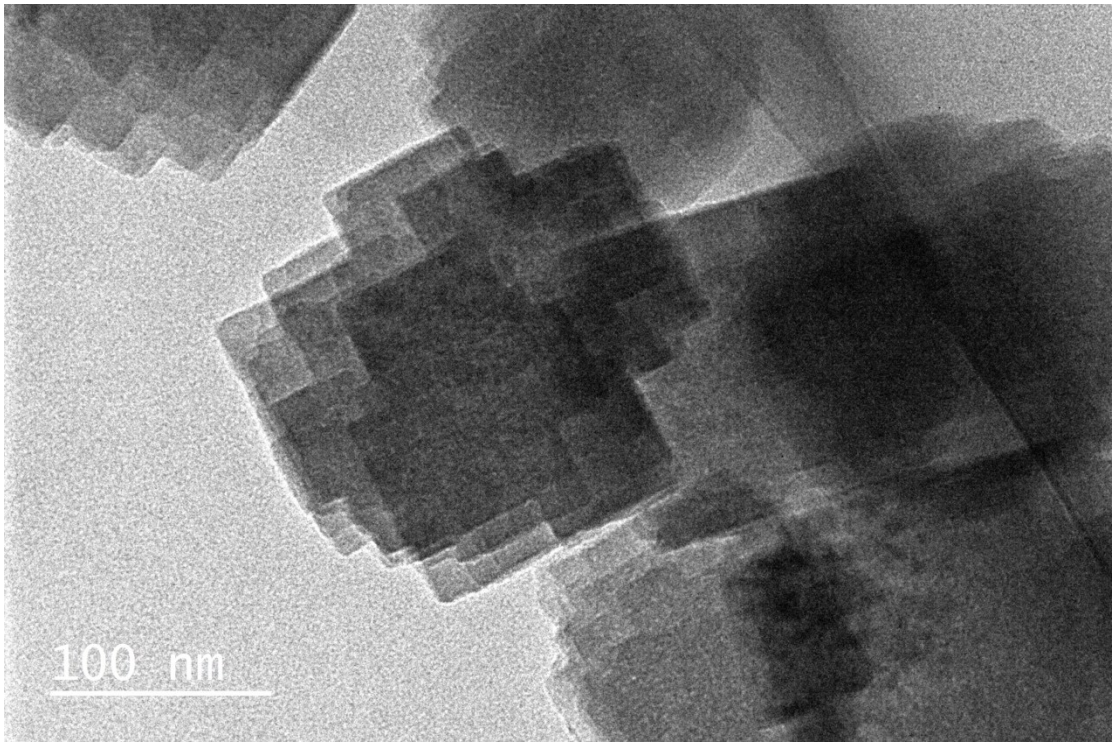

Fig. S1 Higher magnified TEM image of PB mesocrystals. Nanocubic subunits can be observed in each particle.

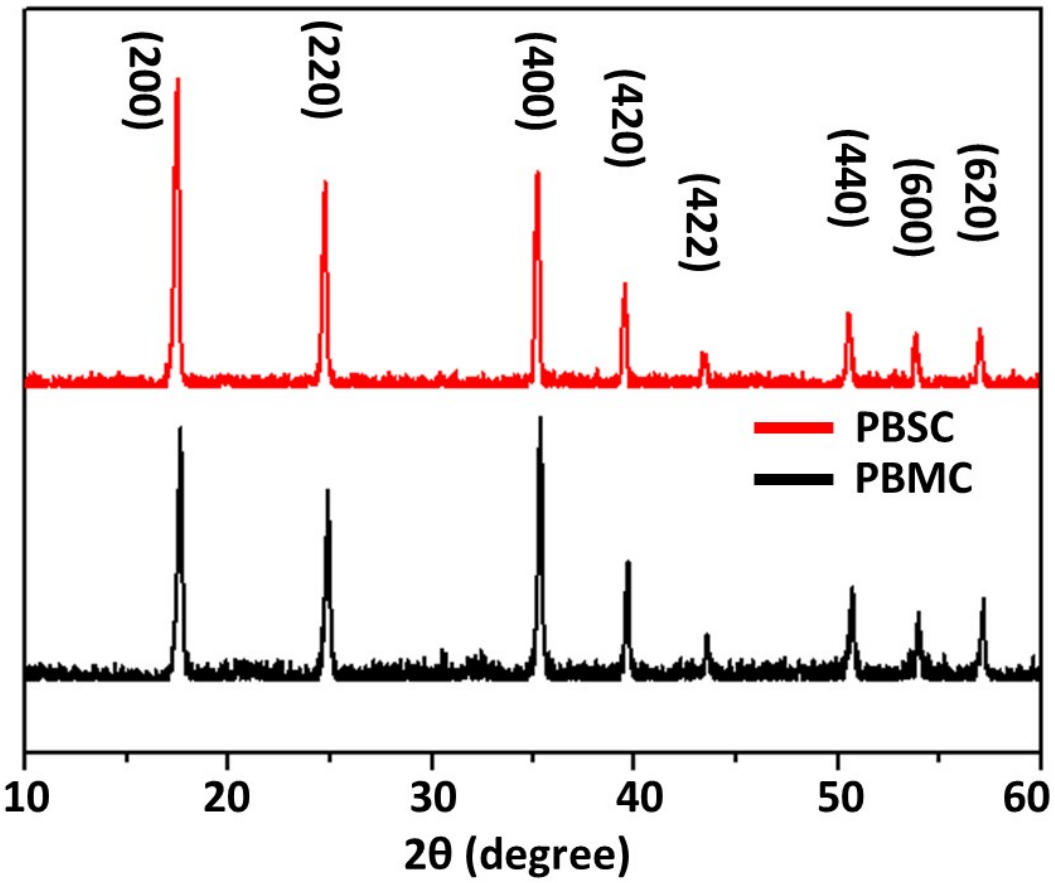

Fig. S2 PXRD patterns of PB mesocrystals and single-crystals. PBSC represents PB single-crystals, and PBMC represents PB mesocrystals.

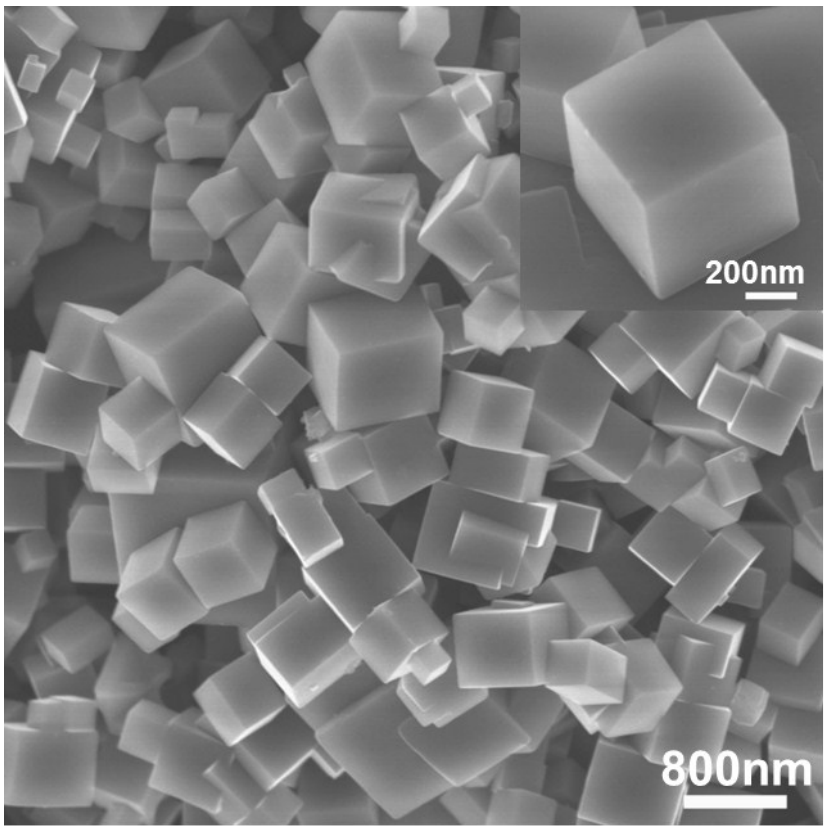

Fig. S3 SEM image of PB single-crystals. The inset is an enlarged image.

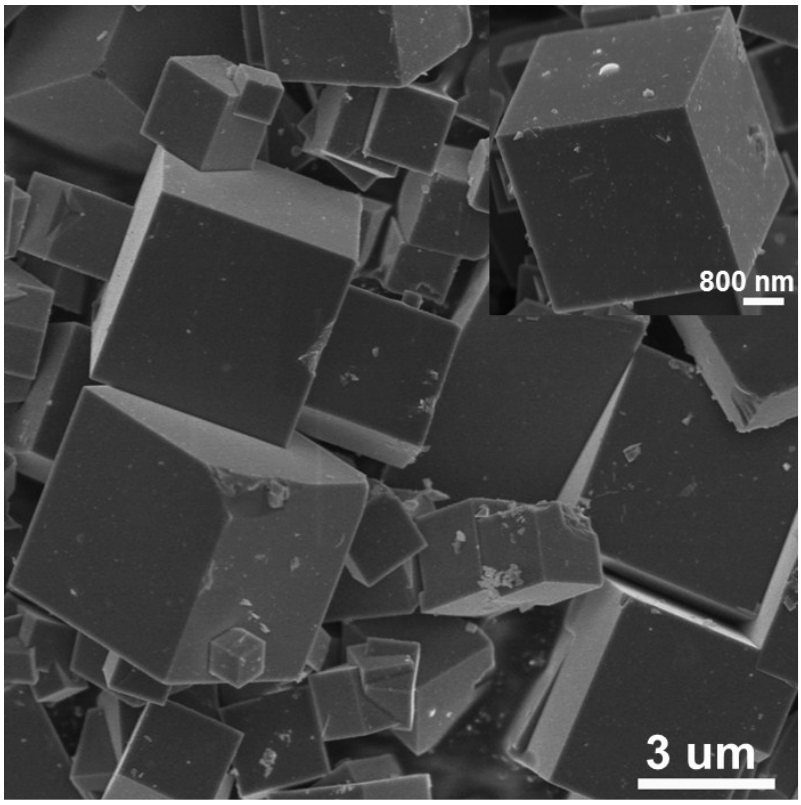

Fig. S4 SEM image of PB obtained without using PAH. The inset is a single particle.

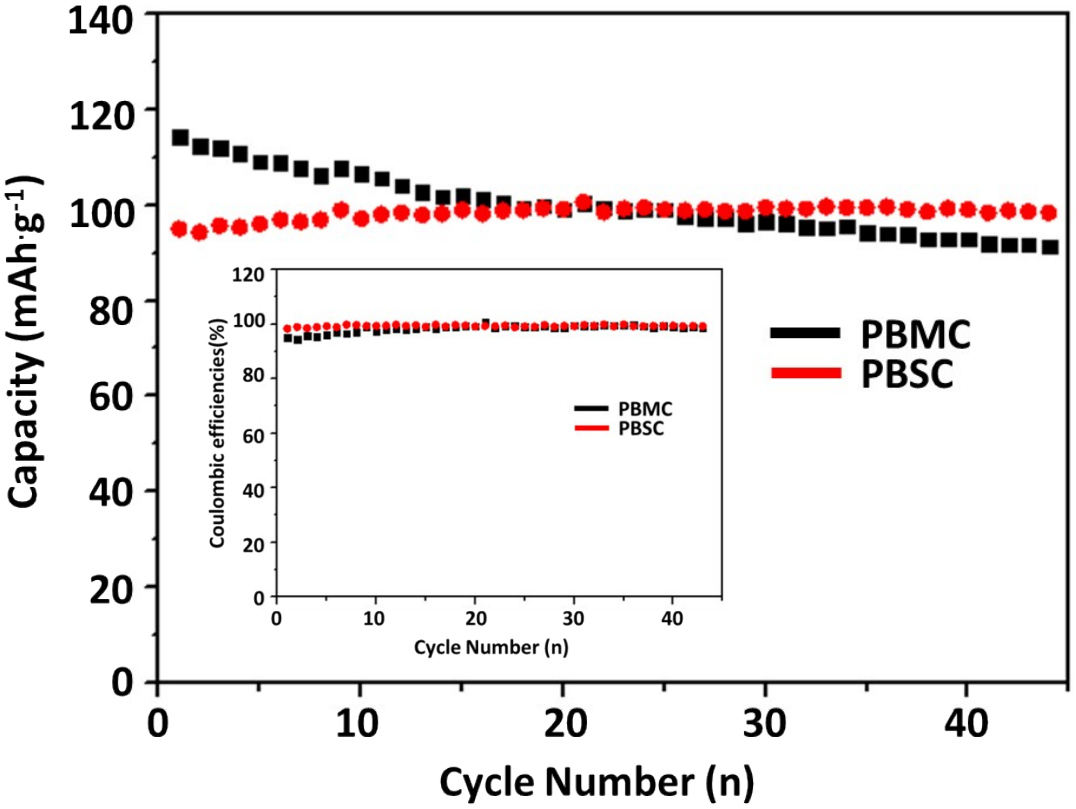

Fig. S5 Cycling performance of PB mesocrystals and single-crystals under a current density of 25 $mA \cdot g^{-1}$.

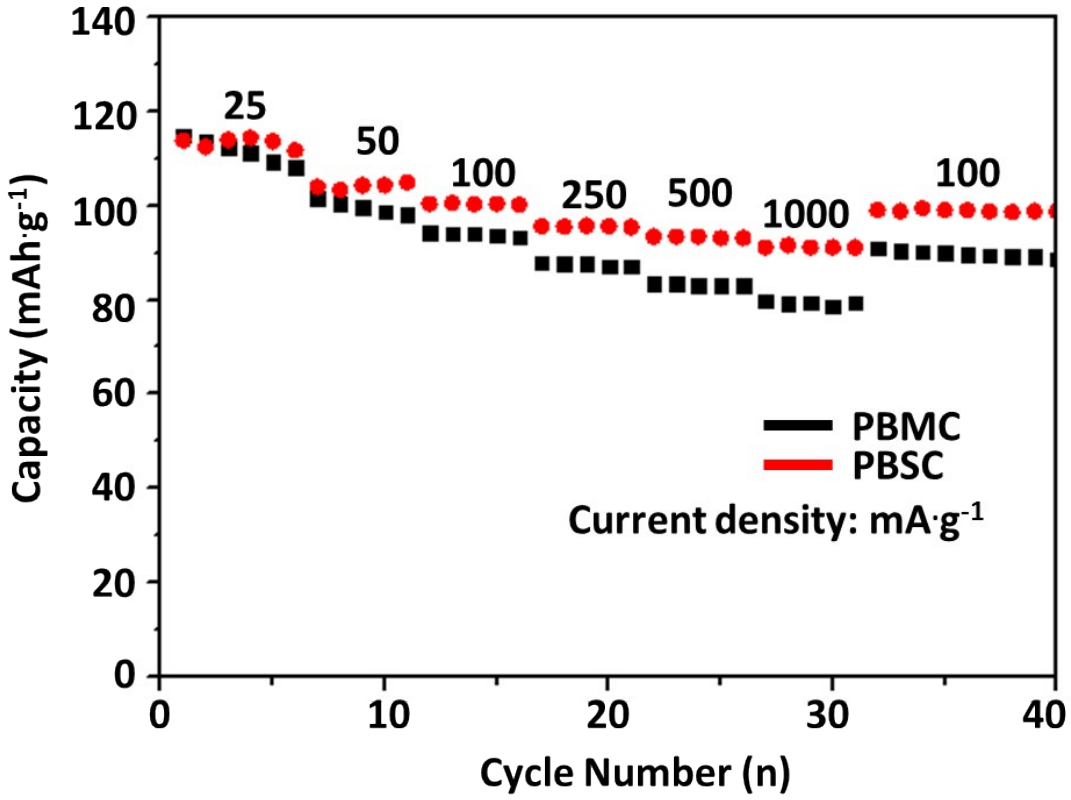

Fig. S6 Rate-performance of PB mesocrystals and PB single-crystals as cathodes for sodium ion battery.