

Supporting information

High Rate Sodium Ion Insertion in Core–Shell Nanoparticles of Prussian Blue Analogues

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Experimental Section

The syntheses of the core particles (CuFe-PBA) and core@shell particles (CuFe-PBA@NiFe-PBA) were performed using procedures that have been previously described (D. Asakura *et al.*, *J. Am. Chem. Soc.*, 2013, **135**, 2793–2799.).

Powder X-ray diffraction patterns were recorded on a Rigaku SmartLab instrument using Cu K α radiation in steps of 0.01° over the 2 θ range of 10–80°. Transmission electron microscopy (TEM) was performed on a JEOL-2010F HRTEM at 200 kV. Energy dispersive X-ray spectroscopy (EDX) was performed with an Oxford Instruments EDS X-ray Microanalysis System coupled to the HRTEM microscope. Combustion analysis to determine carbon, hydrogen, and nitrogen (CHN) percentages was performed by the University of Florida Spectroscopic Service Laboratory.

Electrochemical experiments were performed by using a three-electrode glass cell, in which sodium metal was employed as counter and reference electrodes. Each sample (50 mg) was ground with acetylene black (13.3 mg) and polytetrafluoroethylene (PTFE) into a paste and used as the working electrode. 1 M NaClO₄ propylene carbonate (PC) solution was used for the electrolyte. The cutoff voltages were 2.2 V (vs. Na/Na⁺) for Na-ion insertion and 4.0 V for Na-ion extraction. The galvanostatic intermittent titration technique (GITT) was conducted with repeating application of low specific current for 10 min followed by an interruption of 30 min. Electrochemical impedance spectroscopy (EIS) was carried out at a frequency ranging from 5 mHz to 50 kHz with an amplitude of 10 mV (VMP3, BioLogic).

X-ray absorption near-edge structure (XANES) measurements were performed using synchrotron radiation on beamline BL-7C of the Photon factory. The quantitatively

sodiated/desodiated samples were prepared by GITT, washed with ethanol, and then dried in vacuum. The spectra were recorded in the transmission mode at room temperature under an ambient atmosphere. The X-ray energy for each edge was calibrated by using the corresponding metal foil. Experimental data were analyzed using Rigaku REX2000 software.

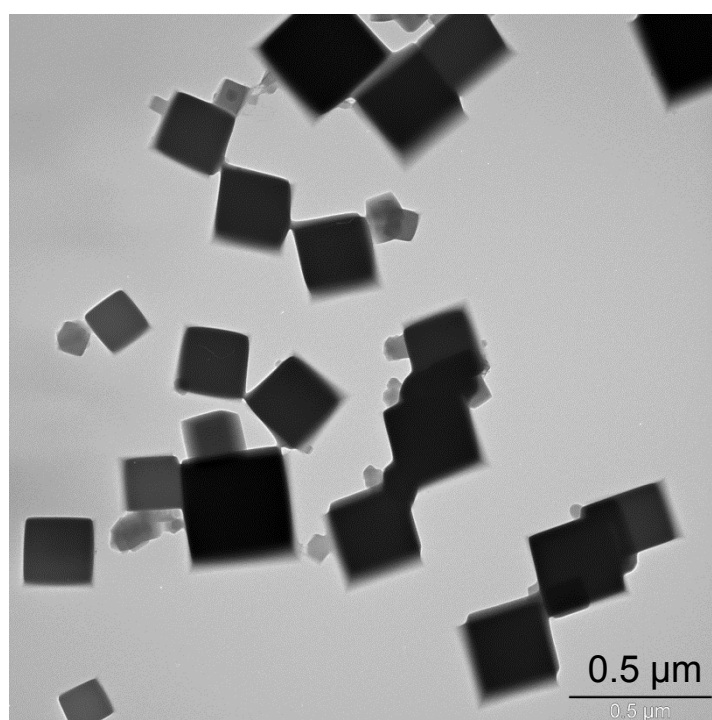


Fig. S1. TEM image for CuFe-PBA.

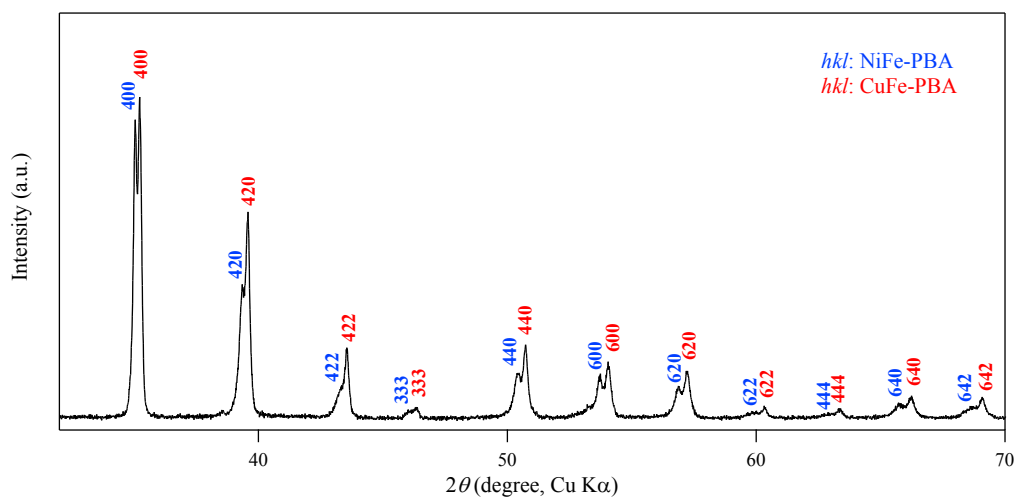


Fig. S2. Powder X-ray diffraction patterns for CuFe-PBA@NiFe-PBA.

(a)

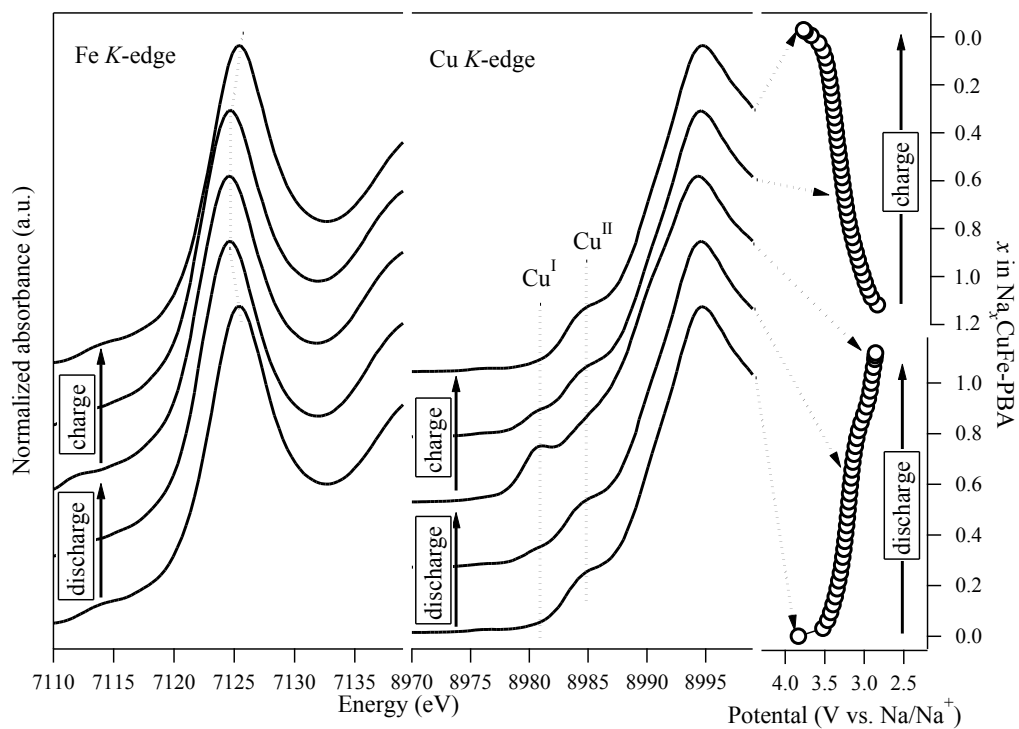


Fig. S3. *Ex situ* XANES spectra for Fe and Cu K-edges on discharge/charge of (a) CuFe-PBA and (b) CuFe-PBA@NiFe-PBA.

(b)

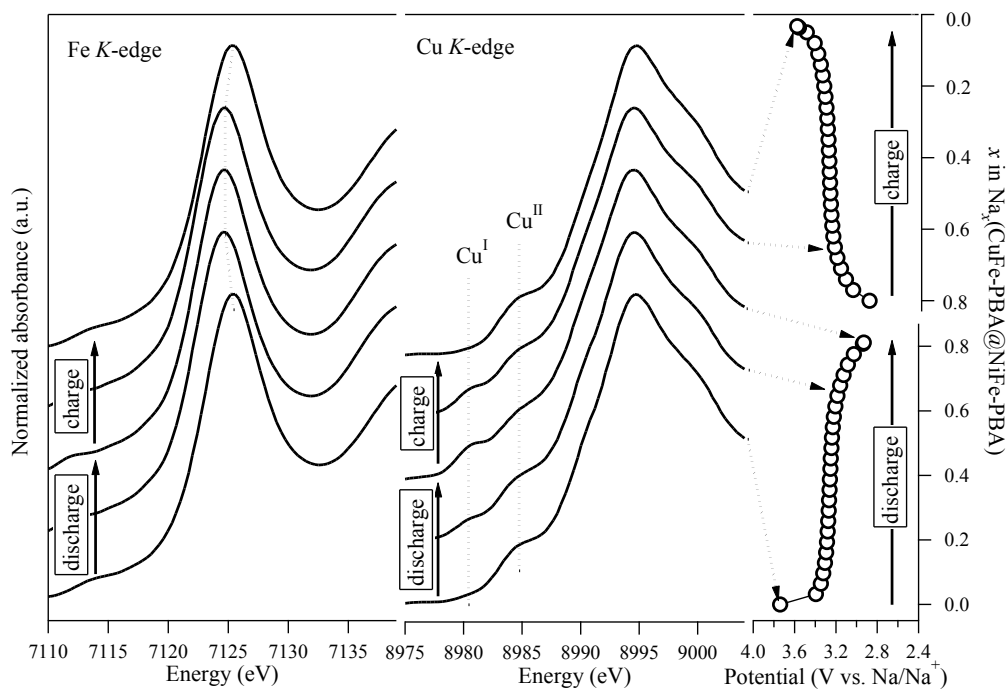


Fig. S3. *Ex situ* XANES spectra for Fe and Cu K-edges on discharge/charge of (a) CuFe-PBA and (b) CuFe-PBA@NiFe-PBA.

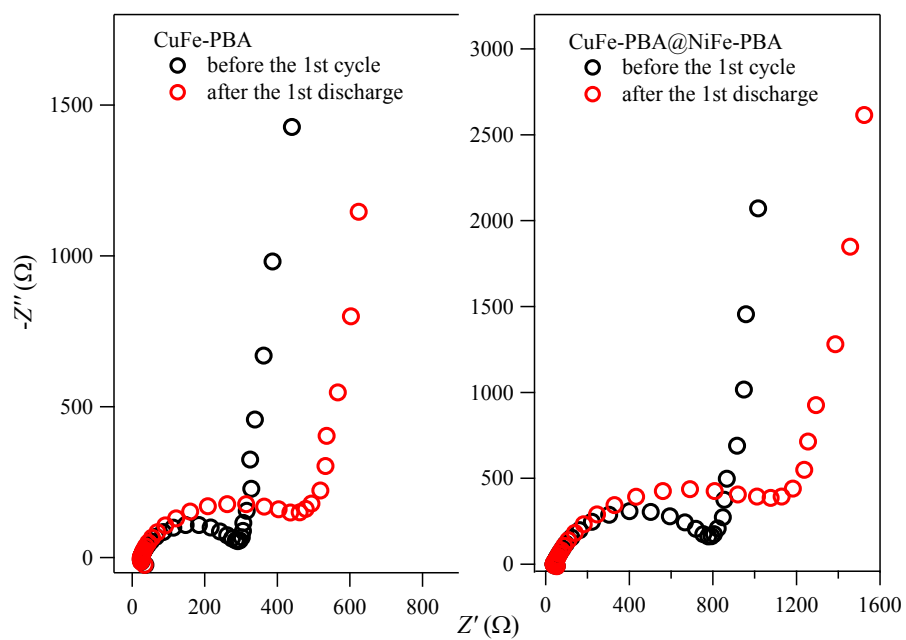


Fig. S4. Nyquist plots for CuFe-PBA and CuFe-PBA@NiFe-PBA.

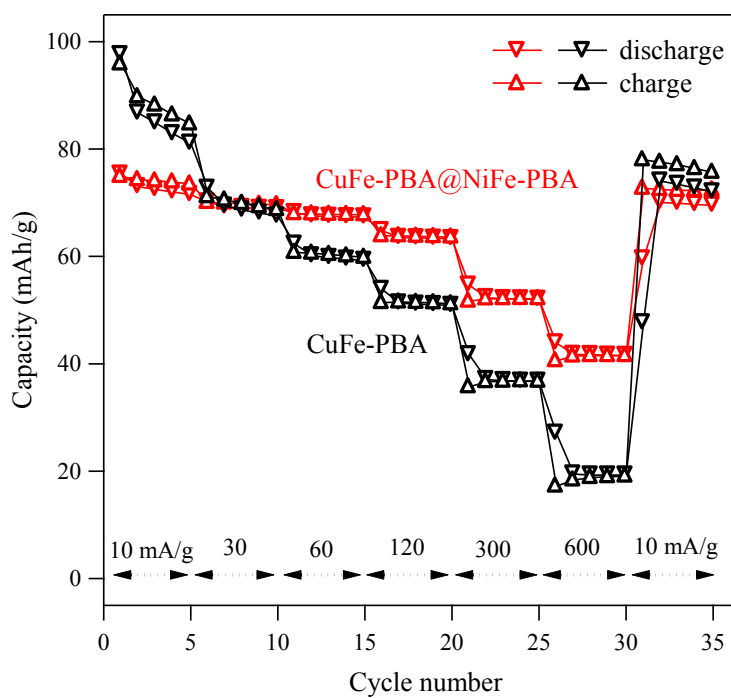


Fig. S5. Cycle stability of CuFe-PBA and CuFe-PBA@NiFe-PBA during the high charge/discharge rate experiment.