

Supporting Information

Introducing a Cell Moisturizer: Organogel Nano-Beads with Rapid Response to Electrolytes for Prussian White Analogues Based Non-Aqueous Potassium Ion Battery

Fang Chen^a, Jiaying Liao^a, Junru Wang^a, Xiaodong He^a, Xiang Ding^a, Qiao Hu^a, Fei Chen^a, Shuo Wang^a, Jiemin Dong^a, Zhaoyin Wen^b and Chunhua Chen^{*a}

^aCAS Key Laboratory of Materials for Energy Conversions, Department of Materials Science and Engineering, Collaborative Innovation Center of Suzhou Nano Scienceand Technology, University of Science and Technology of China, Hefei 230026, Anhui, China. E-mail: cchchen@ustc.edu.cn; Fax: +86-551-63601592; Tel: +86-551-63606971

^bShanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Experimental section

Preparation of KFeHCF with PP bead

Synthesis of PBMA nano-bead: The suspension of PBMA nano-bead was synthesized with template of micelles of sodium dodecyl sulfate (SDS). To obtain a uniform dispersion of monomer butyl methacrylate (BMA), in 3.5 mL water, SDS (220 mg) was added in excess, then ammonium persulfate (APS, 10 mg) as the initiator, ethylene glycol dimethyl acrylate (20 μ L) the cross-linker and BMA (1.5 g) the monomer was added. Then the suspension was purged with air, stirred with a magneton and heated to 70 °C for an hour and a half in the fluid of N₂. Then the synthesis of suspension of PBMA was completed. The PBMA powders was collected via precipitation from the suspension with the aid of non-solvent, like ethanol, then it was washed with water while sonicated repeatedly to remove SDS.

Synthesis of KFeHCF with polypyrrole-PBMA nano-bead: The product was synthesized, in general, by means of KFeHCF precipitation in the suspension of PP nano-bead in a three-necked flask in the fluid of N₂. 200 μ L of as-prepared PBMA suspension was added into 100 mL water to get a clear, diluted suspension. Then excessive pyrrole (1 mL) was added and stirred until fully dissolved. 4 mmol potassium ferricyanide (K₃Fe(CN)₆) was dissolved in 5 mL water, then added into the above solution and the bottle was sealed. The polymerization of polypyrrole took place for 1 h. Then 5 mmol FeSO₄·7H₂O, 5 g potassium citrate and 0.5 g ascorbic acid were dissolved in 100 mL water and added drop by drop into the three-necked flask while stirring. The final product was collected after 10 h and washed with mixture of water and ethanol. The barely KFeHCF sample was synthesized exactly the same route except the synthesis of PP bead. The sample with PPy were prepared exactly the process except the addition of PBMA suspension. The sample with PBMA was prepared without adding pyrrole and K₃Fe(CN)₆ was replaced with K₄Fe(CN)₆.

Characterization

The structure and functional groups of synthesized materials were characterized via fourier transform infrared spectra (FTIR, Magna-IR 750 spectrometer) in the range of 500-3500 cm⁻¹ and X-ray diffractometer (XRD, Philips X'Pert Pro Super, Cu Ka radiation) in the range of 10-70° with scanning rates of 10°/min. The morphology was observed by scanning electron microscopes (SEM, JSM-6390 LA) and transmission electron microscopy (TEM, JEM-2100F). The glass transition temperature was determined by DSC-TGA analysis.

The determination of electrolytes swelling and retention capability: Maximum swelling ratio of PBMA nano-bead powders was evaluated by weighing the weight before and after fully swelling with four different electrolytes. The retention tests were tested by adding 150 μ L electrolytes into 0.1 g PBMA dried powders, heated to 80 °C and test the weight change every 30 min. The swelling ratio was determined as followed:

$$\epsilon_{\text{Swelling ration}} = \frac{m_{\text{swollen gel}}}{m_{\text{dried powder}}} = \frac{m_{\text{electrolytes}} + m_{\text{dried powder}}}{m_{\text{dried powder}}} \quad (1)$$

Electrochemical measurements: The obtained product was blended with carbon black and PVDF with the ratio of 7:2:1, then coated on Al foil with a mass loading of 1.2-1.5 mg cm⁻². Electrochemical performance of the prepared cathode was tested by assembling CR2032 coin-cell with 0.5 M LiPF₆ in PC/FEC (1:1) as the electrolytes, K foil as the counter electrode. The galvanostatic charge–discharge tests were carried out in the range of 2-4.5 V by NEWWARE BTS-610 multichannel battery test system. The cyclic voltammetry (CV) tests were conducted on a CHI 660E workstation. The electrochemical impedance spectroscopy (EIS) for a symmetric cell was operated in the range from 10⁻² Hz to 10⁵ Hz with an amplitude of 5 mV.

Scratch and tearing test: To evaluate the adhesion of the electrodes on the Al foil, a few lines were created by a knife on the surface of the electrode material side, and a tripe of tape was employed to tear the surface. Then the state of the tape-torn electrode surface was recorded.

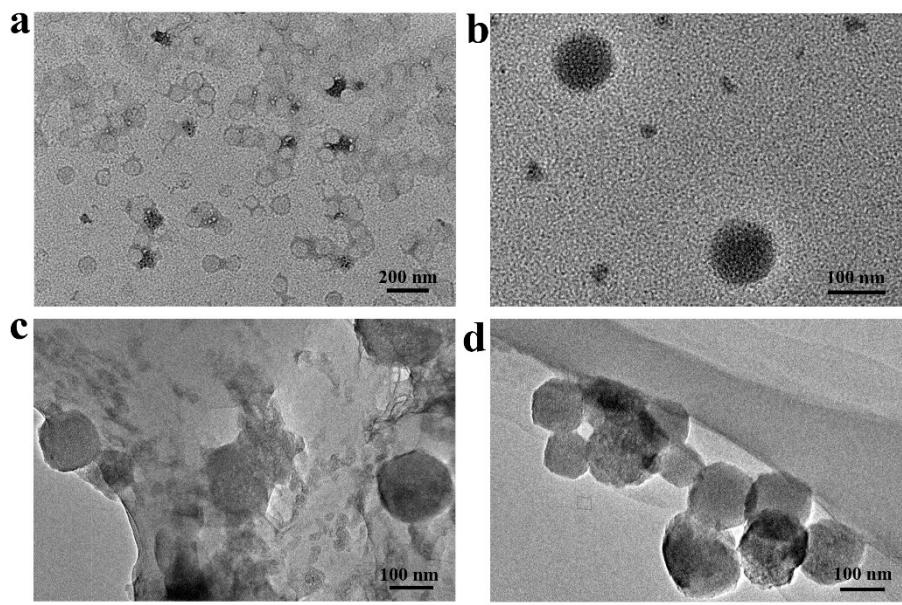


Fig. S1. TEM images of (a) Templates formed by SDS and (b) (c) (d) scattered PBMA nano-bead.

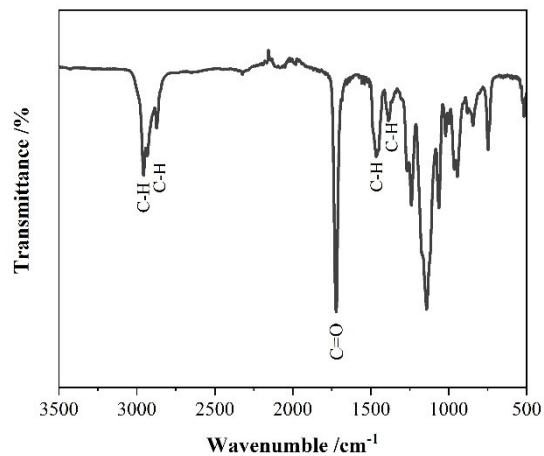


Fig. S2. FTIR spectrum of synthesized PBMA nano-beads

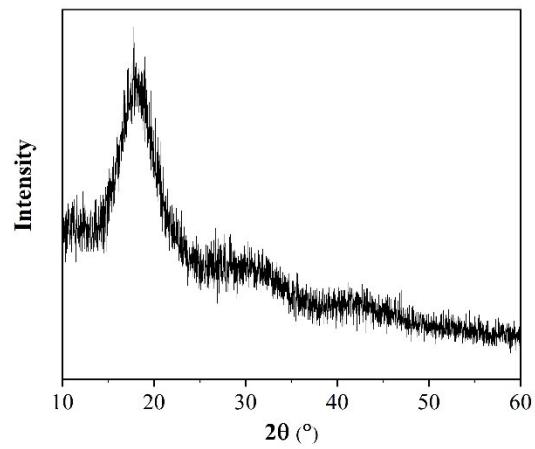


Fig. S3. XRD pattern of PBMA nano-beads.

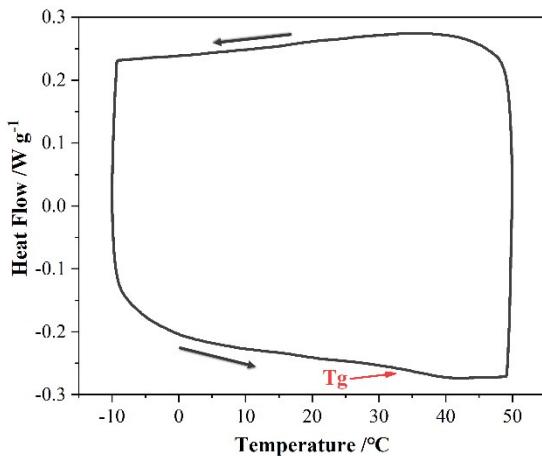


Fig. S4. DSC curve of PBMA nano-beads.

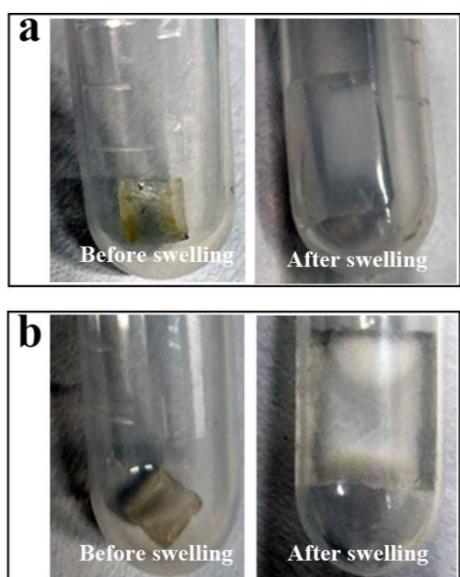


Fig. S5. PBMA bulk swells with electrolytes (a) DEC and (b) DME.

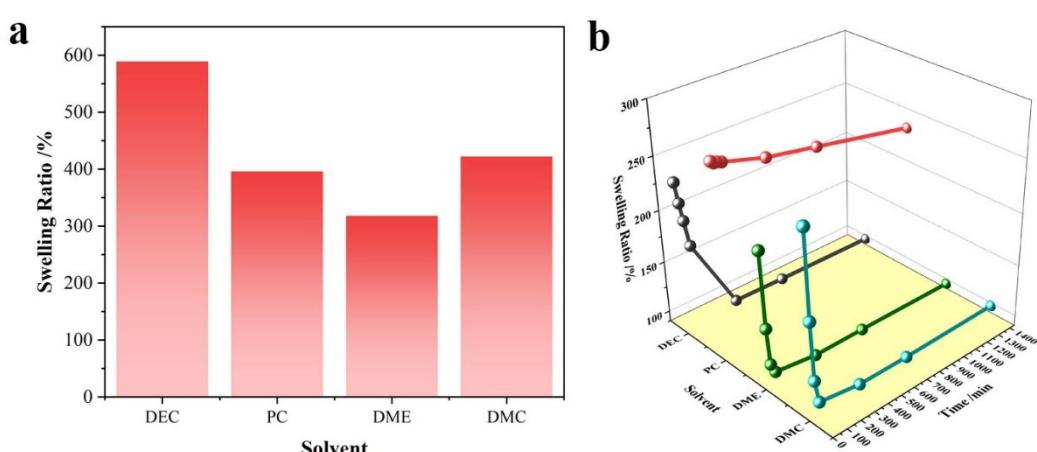


Fig. S6. (a) Maximum swelling ratio of PBMA nano-bead powders. (b) Solvent retention ability of PBMA nano-beads at 80 °C.

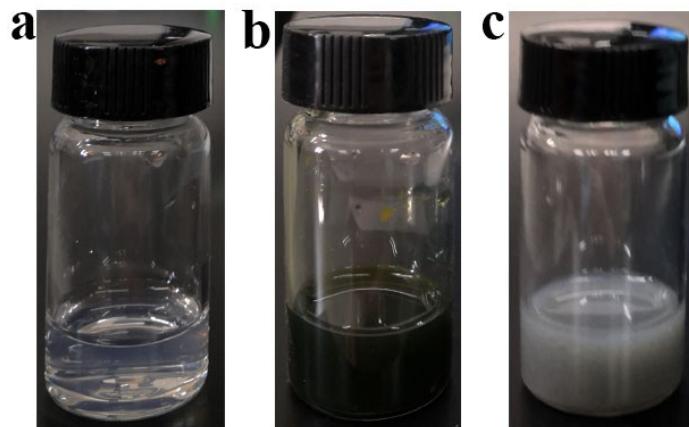


Fig. S7. Pictures of solutions during synthesis of KFeHCF with PP bead. (a) PBMA diluted in water. (b) Suspension of PP bead. (c) KFeHCF precipitation with PP bead.

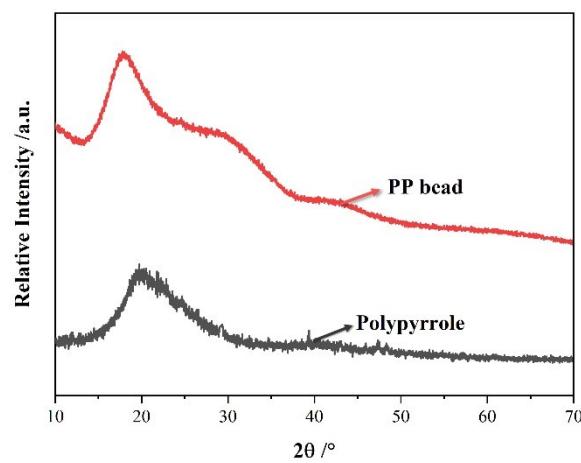


Fig. S8. XRD patterns of polypyrrole and PP bead.

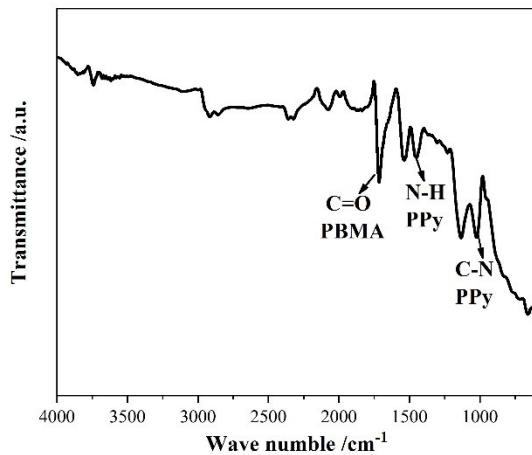


Fig. S9. FTIR spectrum of PP bead.

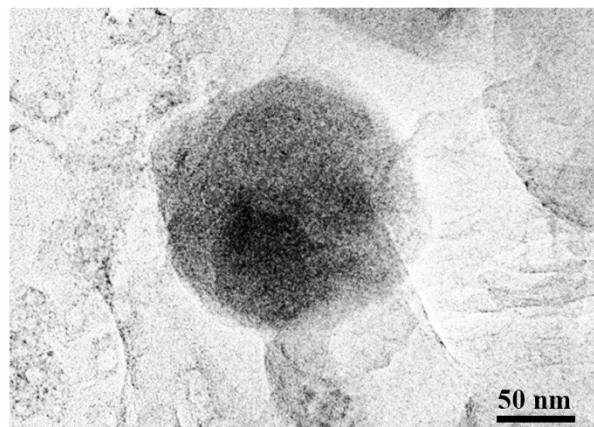


Fig. S10. TEM image of PP bead.

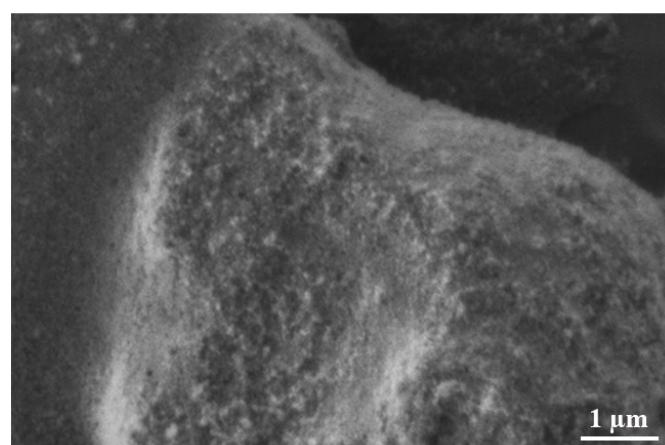


Fig. S11. SEM image of synthesized KFeHCF with PP bead.

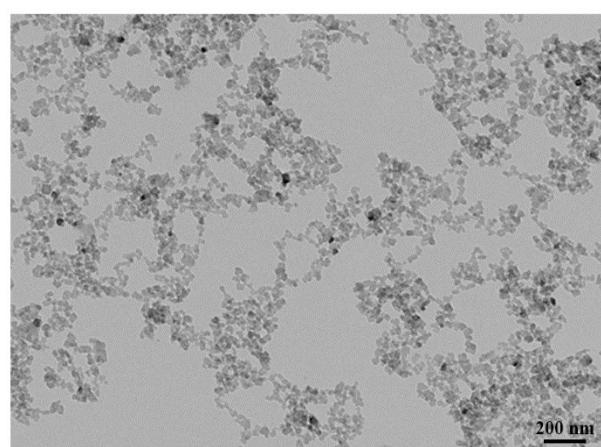


Fig. S12. TEM image of bare KFeHCF.

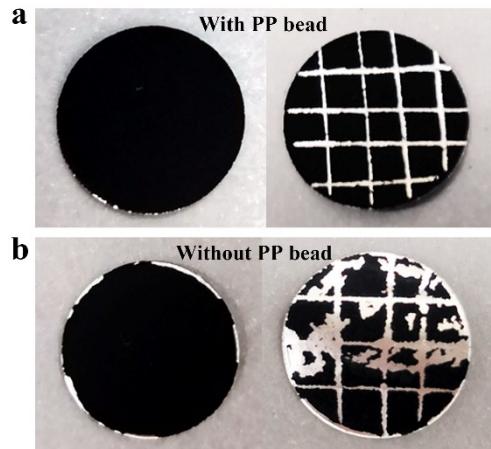


Fig. S13. Scratch-tearing tests of electrodes (a) with and (b) without PP nano-bead.

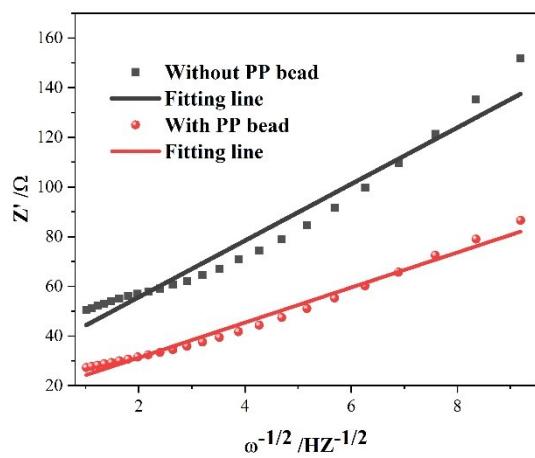


Fig. S14. Relationship between Z' and $\omega^{-1/2}$ in the low-frequency region corresponding to Figure 3e.

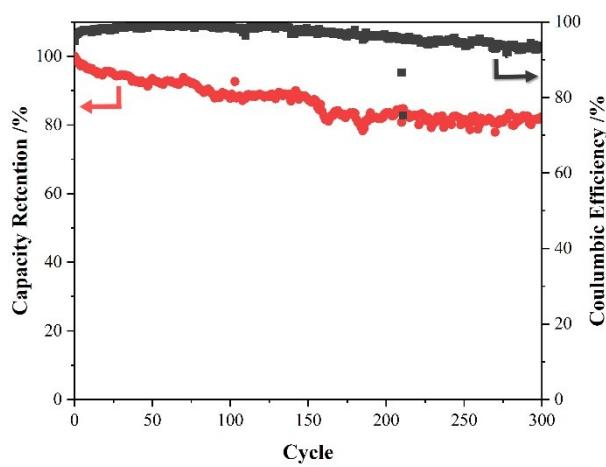


Fig. S15. Discharge capacity with 300 charge-discharge cycles at 1C.

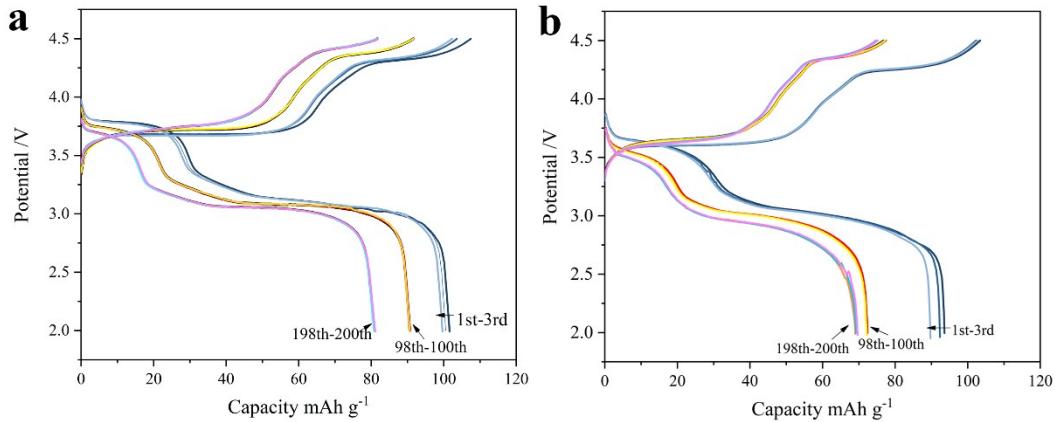


Fig. S16. Charge-discharge curves of samples (a) with and (b) without PP bead.

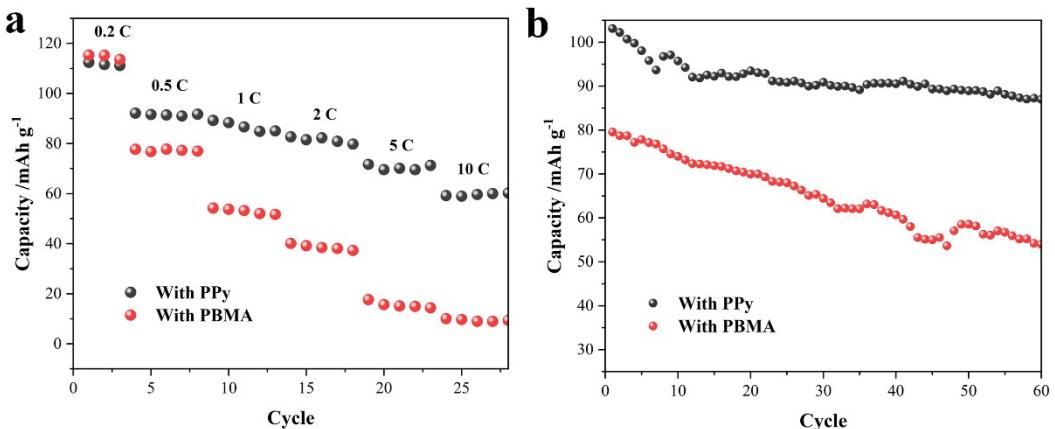


Fig. S17. (a) Rate performance and (b) cycling performance of KFeHCF with only PPy or PBMA as additive.

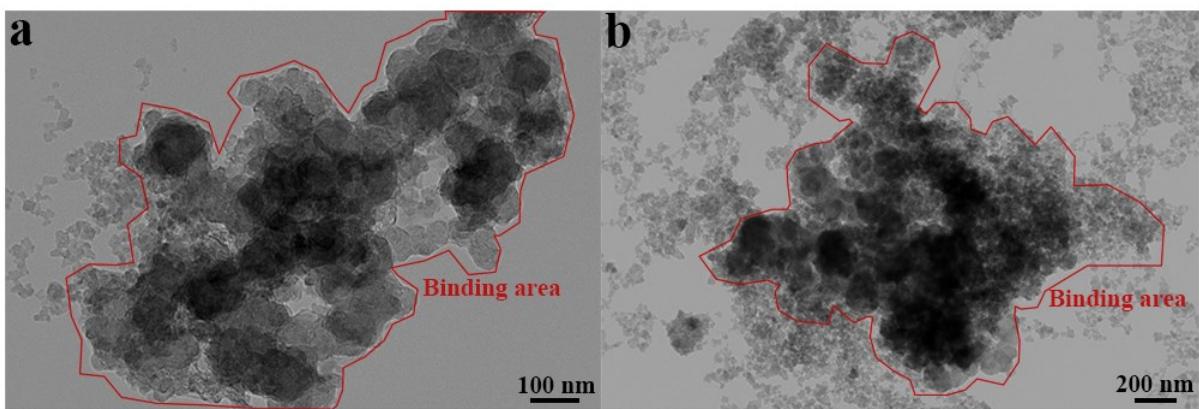


Fig. S18. TEM images of electrode materials (a) before and (b) after cycling.