Electronic Supplementary Material (ESI) for Materials Advances.

# Supplementary Information

# Citric acid-assisted synthesis of $FeFe(CN)_6$ with reduced defects and high specific surface area for aqueous zinc-sodium hybrid batteries

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## Experimental

### 1. Materials and reagents

$K_3Fe(CN)_6$ (99.5%) was purchased from Shanghai No.1 Reagent Factory. $FeCl_3 \cdot 6H_2O$ (99%) was purchased from Macklin. Citric acid ($C_6H_8O_7 \cdot H_2O$, 99.5%) was purchased from National Group Chemical Reagent Co., LTD. $Na_2SO_4$ (99%) and $ZnSO_4 \cdot 7H_2O$ (99.5%) were purchased from Chengdu Jinshan Chemical Reagent Company. Zinc foil (99.99%, 0.02 mm) was purchased from Alfa Aesar.

### 2. Material synthesis

C-$FeFe(CN)_6$ was synthesized using a controlled crystallization method assisted by citric acid. Usually, 0.01 mol $FeCl_3 \cdot 6H_2O$ and 0.01 mol $C_6H_8O_7 \cdot H_2O$ are dissolved in 50 ml deionized water to form 0.2 mol $L^{-1}$ citrate$^{3-}$–$Fe^{3+}$ chelating solution. This solution (50 mL) and 0.2 mol $L^{-1}$ $K_3Fe(CN)_6$ solution (50 mL) were then added dropwise into 100 mL deionized water for co-precipitation. Thereafter the water bath was stirred at 60 °C for 6 hours. The precipitate was centrifuged, washed several times with deionized water, and finally dried at 80 °C for 12 h.

### 3. Material characterization

The crystal structure of the synthesized material was analyzed by X-ray diffraction (XRD) using Shimadzu 7000S X-ray diffractometer. The scanning speed was 5 ° $min^{-1}$ from 10° to 80°. Fourier transform infrared spectroscopy (FTIR) was recorded in transmission mode on an infrared spectrometer (FTIR, Nicolet iS5 type). The water content of the sample was determined by a thermogravimetric analyzer (TG, Netzsch TG/209 F3 Tarsus). The test was carried out under nitrogen protection, the heating rate was 10 °C $min^{-1}$, and the heating range was 30-500 °C. Raman spectroscopy was performed on the LabRAM HR Evolution Raman spectrometer using a laser with a wavelength of 532 nm. The morphology and structure were characterized by scanning electron microscopy (SEM, TESCAN MIRA LMS) and transmission electron microscopy (TEM, libra 200). X-ray photoelectron spectroscopy (XPS) measurements were performed on a single Al Kα radiation (Thermo Scientific K-Alphat), and all binding energies were adjusted using the standard signal of carbon at 284.80 eV. The K and Fe elements of the sample were measured by inductively coupled plasma emission spectrometry (ICP-OES, Agilent 5110, USA), and the sample was dissolved in hydrochloric acid. The C and N elements of the sample were measured by elemental analyzer (EA, Elementar UNICUBE, Germany).

**4. Electrochemical test**

The positive electrode was prepared by mixing the active material, acetylene black and polytetrafluoroethylene at a mass ratio of 7:2:1. The uniformly mixed slurry was coated on the carbon foil current collector and dried at 80 °C for 12 h. After drying, it was cut into 14 mm small discs for subsequent use, and the mass loading of the active material was 1.05 mg $cm^{-2}$. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were performed at the VersaSTAT 3 electrochemical workstation. The CV tests were carried out using a three-electrode system, in which C-$FeFe(CN)_6$ was used as the working electrode, and a zinc flake was employed as the counter and reference electrode. The test was performed in the range of 0.5-1.8 V. The EIS test was carried out in the frequency range of 100 kHz to 0.01

Hz with a potential amplitude of 5 mV. The coin-type cell (CR2025) was prepared by using C-FeFe(CN)$_6$ as the positive electrode, Zn metal as the negative electrode and glass fiber membrane as the separator. For zinc-sodium hybrid cells, the as-used electrolyte is a mixed solution containing 0.1 M $ZnSO_4$ and 1 M $Na_2SO_4$. The rate performance, cycling performance and galvanostatic current charge-discharge performance of the battery were tested in the voltage range of 0.1-1.8 V on the Land 3002A battery test system. In the galvanostatic charge-discharge (GCD) process, cells were initially discharged to 0.1 V, then were charged to 1.8 V, followed by the cycling process.

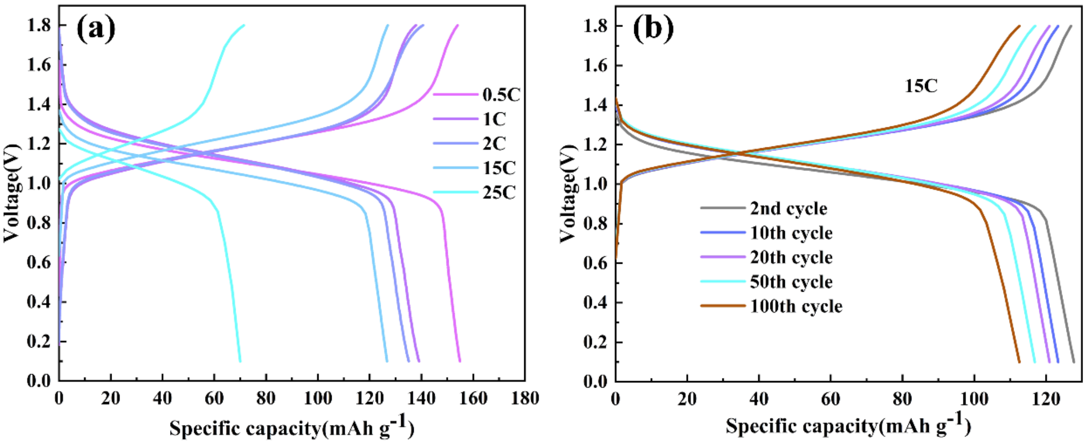

**Fig. S1** (a) Charge-discharge curves at different current densities from 0.5C, 1C, 2C, 15C to 25C; (b) GCD curves of different cycle times.

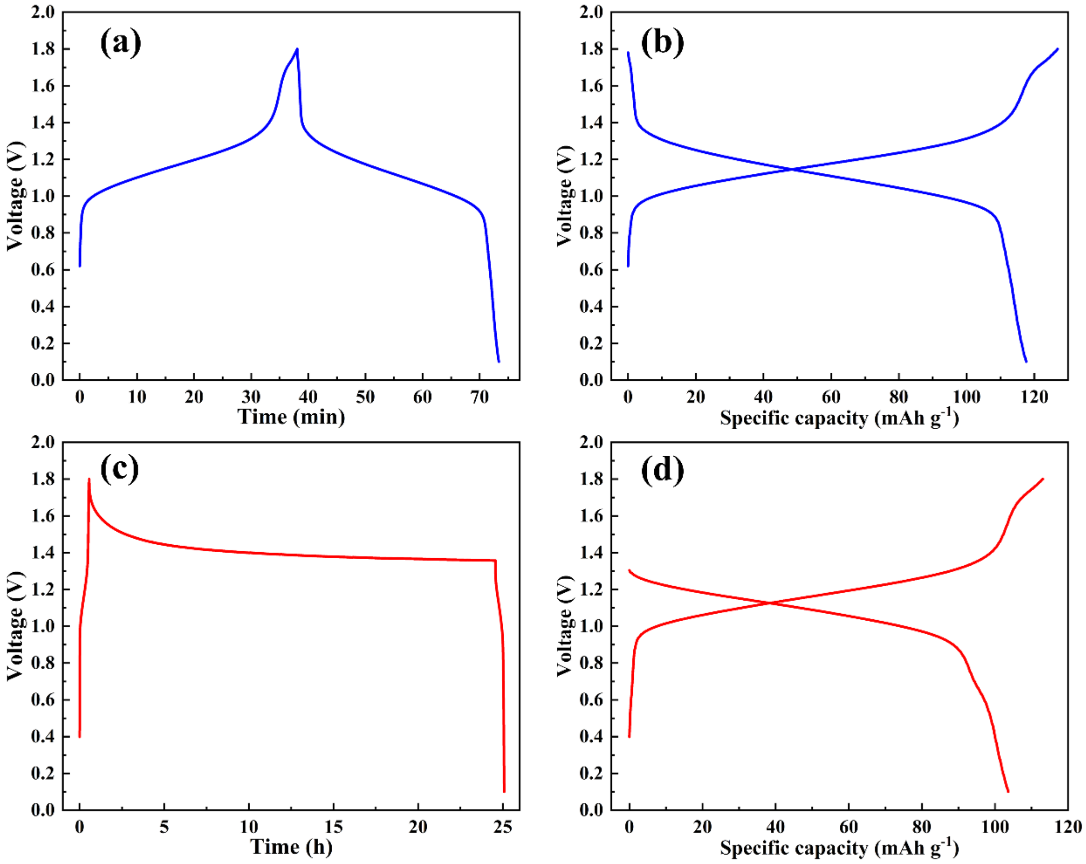

**Fig. S2** Self-discharge performance evaluations of the C-FeFe(CN)$_6$. (a) Voltage-time and (b) voltage-specific capacity without resting; (c) voltage-time and (d) voltage-specific capacity for resting 24 h.

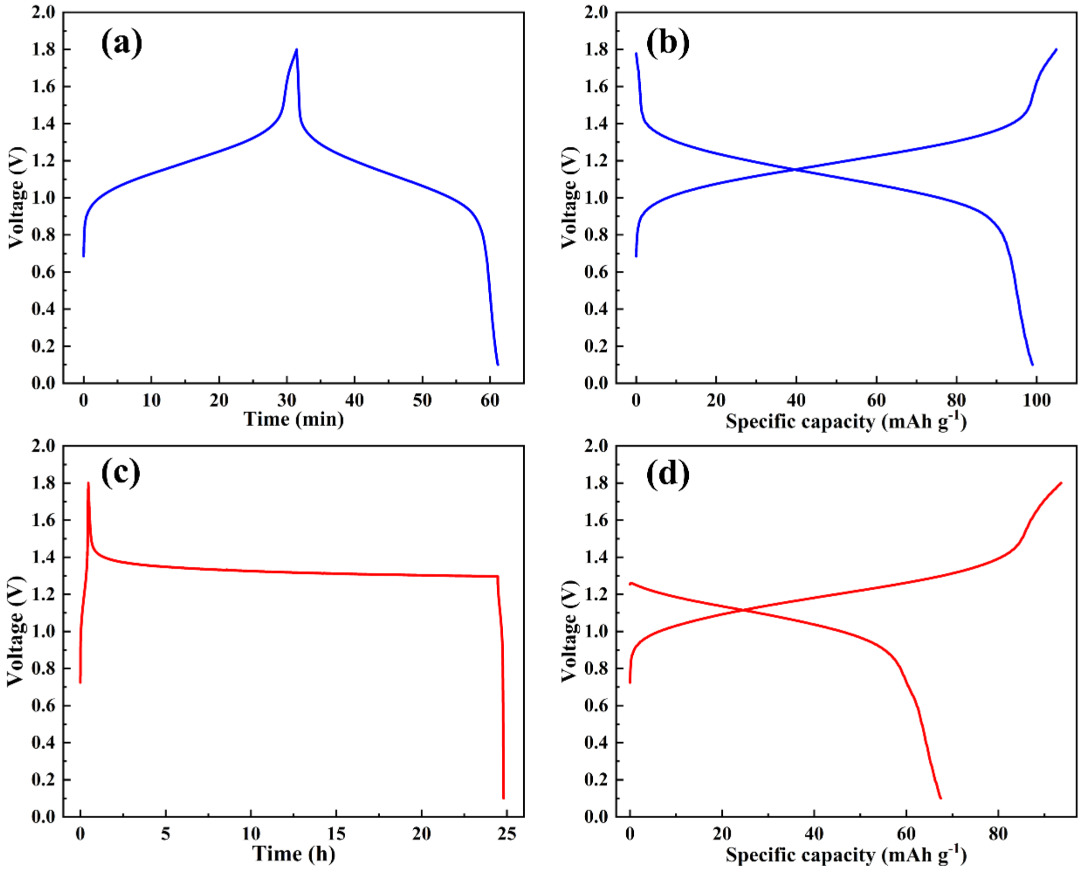

**Fig. S3** Self-discharge performance evaluations of the FeFe(CN)$_6$ electrode. (a) Voltage-time and (b) voltage-specific capacity without resting; (c) voltage-time and (d) voltage-specific capacity resting for 24 h.

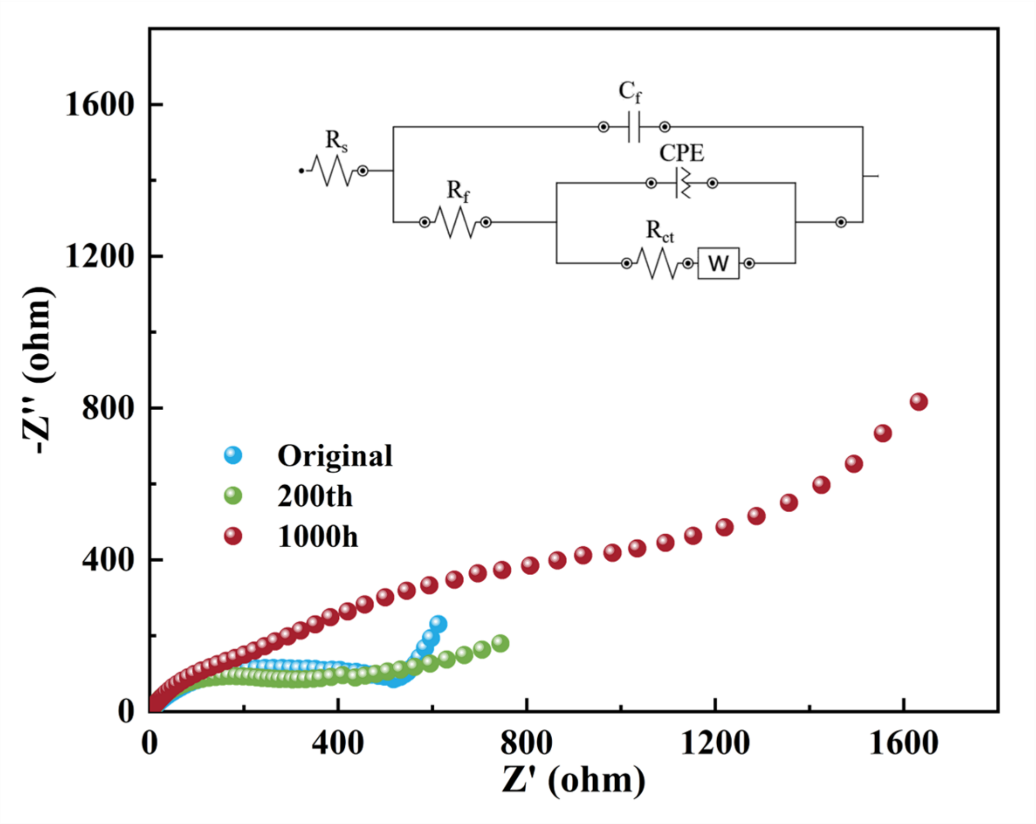

**Fig. S4** EIS curves under different cycles of the $FeFe(CN)_6$.

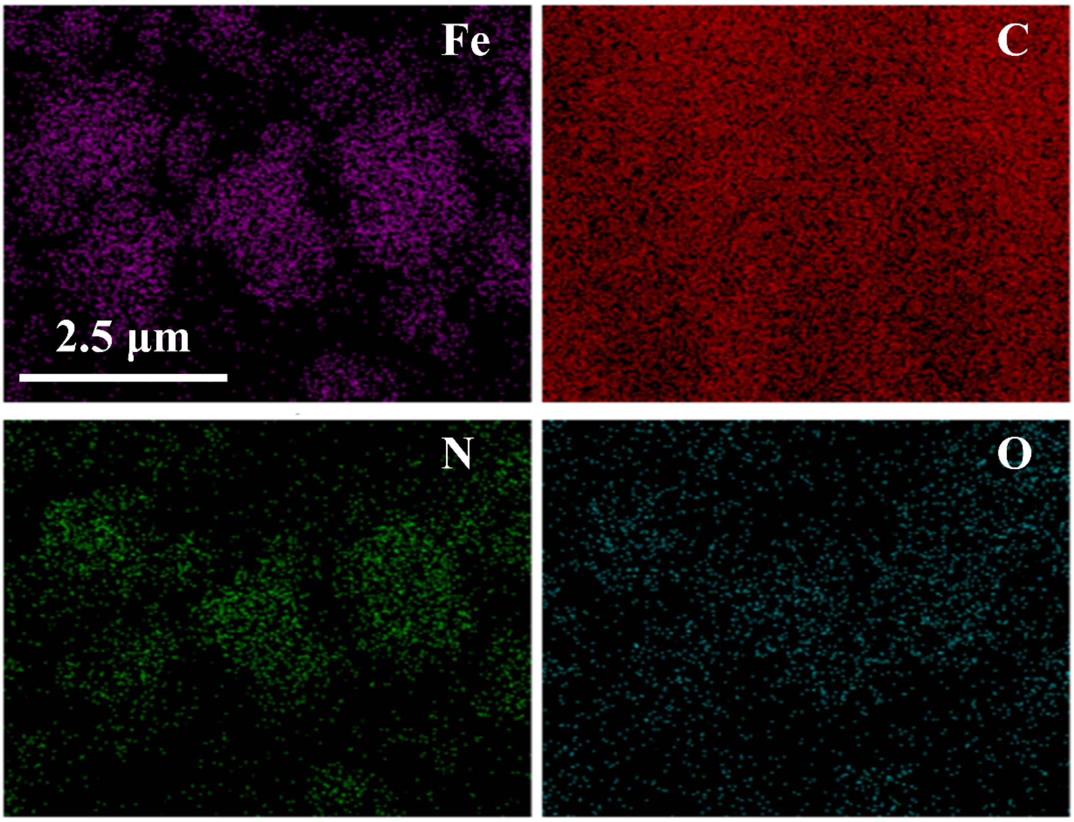

**Fig. S5** EDS elemental mappings of the $FeFe(CN)_6$.

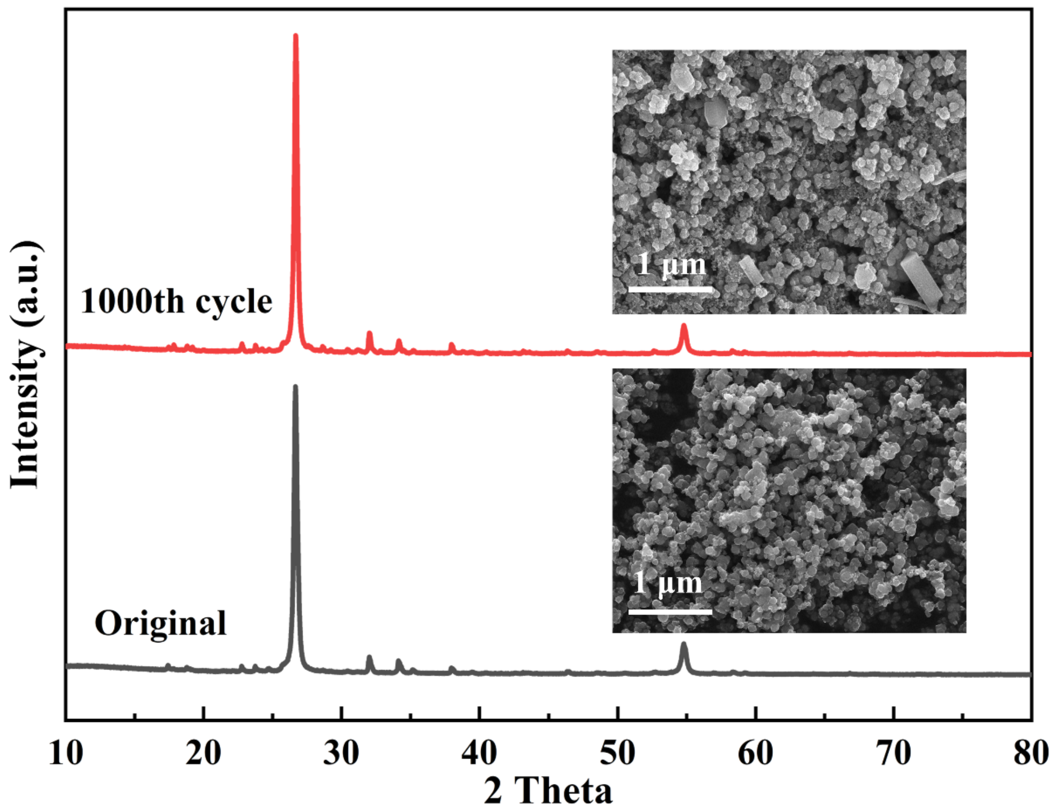

**Fig. S6** XRD patterns and SEM images of $FeFe(CN)_6$ electrode before and after cycling.

**Table S1** Comparison of BET data of C-$FeFe(CN)_6$ and $FeFe(CN)_6$.

| **Materials** | **$S_{BET}$ ($m^2$ $g^{-1}$)** | **Pore volume ($cm^3$ $g^{-1}$)** | **Average pore size (nm)** | **Maximum pore volume ($cm^3$ $g^{-1}$)** |
|---|---|---|---|---|
| **C-$FeFe(CN)_6$** | 406.625 | 0.251 | 2.472 | 0.207 |
| **$FeFe(CN)_6$** | 28.143 | 0.036 | 5.056 | 0.012 |

**Table S2** Elemental contents of C-$FeFe(CN)_6$ and $FeFe(CN)_6$ samples.

| **Methods** | **ICP-OES** | | **Elemental analysis** | | **TG** |
|---|---|---|---|---|---|
| **Materials** | **K** | **Fe** | **C** | **N** | **$H_2O$** |
| **C-$FeFe(CN)_6$** | 2.60 | 37.08 | 20.65 | 24.78 | 14.89 |
| **$FeFe(CN)_6$** | 0 | 39.64 | 20.31 | 24.21 | 15.84 |

**Table S3** The measurement results of C-$FeFe(CN)_6$ EIS data.

| Components | Original | 200th | 1000th |
|---|---|---|---|
| **$R_s$ (Ω)** | 1.14 | 1.07 | 0.83 |
| **$C_f$ (F)** | $4.49*10^{-4}$ | $2.95*10^{-5}$ | $7.39*10^{-6}$ |
| **$R_f$ (Ω)** | 7.53 | 3.56 | 7.71 |
| **Q-$Y_o$** | $4.35*10^{-4}$ | $1.53*10^{-4}$ | $3.49*10^{-4}$ |
| **Q-n** | 0.58 | 0.74 | 0.57 |
| **$R_{ct}$ (Ω)** | 804.5 | 548.6 | 244.0 |
| **W** | $4.44*10^{-3}$ | $2.30*10^{-3}$ | $2.93*10^{-3}$ |

**Table S4** The fitting results of C-$FeFe(CN)_6$ EIS data according to the equivalent circuit of [R(C[R(Q[RW])])], fitted by Zsimpwin software.

| Components | Original | 200th | 1000th |
|---|---|---|---|
| **$R_s$ (Ω)** | 1.14 | 1.07 | 0.83 |
| **$C_f$ (F)** | $4.49*10^{-6}$ | $2.95*10^{-6}$ | $7.39*10^{-6}$ |
| **$R_f$ (Ω)** | 7.52 | 3.56 | 7.71 |
| **Q-$Y_o$** | $4.35*10^{-4}$ | $1.53*10^{-4}$ | $3.49*10^{-4}$ |
| **Q-n** | 0.58 | 0.74 | 0.57 |
| **$R_{ct}$ (Ω)** | 804.5 | 548.7 | 244.0 |
| **W** | $4.44*10^{-3}$ | $2.30*10^{-3}$ | $2.93*10^{-3}$ |

**Table S5** The fitting results of $FeFe(CN)_6$ EIS data according to the equivalent circuit of [R(C[R(Q[RW])])], fitted by Zsimpwin software.

| Components | Original | 200th | 1000th |
|---|---|---|---|
| **$R_s$ (Ω)** | 3.74 | 0.66 | 0.74 |
| **$C_f$ (F)** | $4.43*10^{-6}$ | $7.46*10^{-6}$ | $5.93*10^{-6}$ |
| **$R_f$ (Ω)** | 4.93 | 5.99 | 6.98 |
| **Q-$Y_o$** | $3.70*10^{-4}$ | $3.17*10^{-4}$ | $1.97*10^{-4}$ |
| **Q-n** | 0.53 | 0.64 | 0.60 |
| **$R_{ct}$ (Ω)** | 500.7 | 356.7 | 1112 |
| **W** | $1.65*10^{-2}$ | $9.70*10^{-3}$ | $1.03*10^{-2}$ |

**Table S6** Comparison of the electrochemical performances of the Zn//C-FeFe(CN)$_6$ with other reported aqueous batteries.

| **Materials** | **Electrolyte** | **Specific capacity at *x* A g$^{-1}$** | **Capacity retention at *y* A g$^{-1}$ after *n* cycles** | **Ref.** |
|---|---|---|---|---|
| Na//Na$_2$CoFe(CN)$_6$ | 1 M Na$_2$SO$_4$ | 128 ($x$=0.13) | 90% ($n$=800, $y$=2.6) | 1 |
| Na//Na$_2$CoFe(CN)$_6$ | 1 M NaClO$_4$ | 153 ($x$=0.01) | 90% ($n$=200, $y$=0.1) | 2 |
| Na//Na$_{1.70}$FeFe(CN)$_6$ | 1 M NaClO$_4$ | 120.7 ($x$=0.2) | 75% ($n$=100, $y$=0.2) | 3 |
| Na//Na$_{1.87}$NiMnFe(CN)$_6$ | 1 M NaPF$_6$ | 120 ($x$=0.05) | 91% ($n$=400, $y$=0.1) | 4 |
| Zn//C-FeFe(CN)$_6$ | 0.1 M ZnSO$_4$+1 M Na$_2$SO$_4$ | 162.5 ($x$=0.02) | 88% ($n$=200, $y$=9) | This work |

**Table S7** Comparison of the electrochemical performances of the Zn//C-FeFe(CN)$_6$ with other reported Zinc-ion batteries.

| **Materials** | **Electrolyte** | **Specific capacity at *x* A g$^{-1}$** | **Capacity retention at *y* A g$^{-1}$ after *n* cycles** | **Ref.** |
|---|---|---|---|---|
| FeFe(CN)$_6$ | aqueous HCZLE electrolyte | 60 ($x$=1) | 73% ($n$=10000, $y$=3) | **5** |
| FeFe(CN)$_6$ | 1.0 M Zn(OAc)$_2$/([Ch]OAc+30 wt% water mixtures | 120 ($x$=0.01) | 94% ($n$=10, $y$=0.01) | **6** |
| FeFe(CN)$_6$ | K/Zn (3:3) hybrid electrolyte | 169.2 ($x$=0.1) | 57% ($n$=1000, $y$=1) | **7** |
| C-FeFe(CN)$_6$ | 0.1 M ZnSO$_4$+1 M Na$_2$SO$_4$ | 162.5 ($x$=0.02) | 66% ($n$=1000, $y$=9) | This work |

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