

## Supplementary Information

# Ultra-Stable Cu-Ion-Exchanged Cobalt Hexacyanoferrate (II) in Aqueous Copper-Ion Storage

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## Experimental section

*Material synthesis:*  $\text{CuCoFe(CN)}_6$  is synthesized by coprecipitating and ion-exchanging as schematically illustrated in **Figure 1a**. Briefly, solution A was prepared by dissolving 7.97 g of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  in 120 mL of deionized water. Solution B was obtained by adding 3.3576 g of  $\text{Na}_4\text{Fe(CN)}_6 \cdot 7\text{H}_2\text{O}$  into 50 mL of deionized water. After these two solutions were completely dissolved, solution A and solution B were carefully mixed with magnetic stirring at room temperature for 12 h and subsequently aged for another 12 h. Then, the blackish green suspension was centrifuged and washed with deionized water until the supernatant became colorless. The obtained precipitate was dried in vacuum at 60 °C for 36 h to obtain  $\text{Co}_2\text{Fe(CN)}_6 \cdot 10.5\text{H}_2\text{O}$ . Afterwards,  $\text{Co}_2\text{Fe(CN)}_6 \cdot 10.5\text{H}_2\text{O}$  was soaking in  $\text{CuSO}_4$  solution for about 5 hours. After the aforementioned precipitate centrifuged, washed, and dried, the brown powder  $\text{CuCoFe(CN)}_6$  was finally yielded.

*Characterization:* The chemical compositions of samples were performed by Fourier transform infrared instrument (60-SXB infrared-ray spectrometer). The crystal structure and morphology of samples were characterized by X-ray diffraction (Bruker D8 advanced diffractometer with Cu  $K\alpha$  radiation) and scanning electron microscope (Hitachi SU-70). Thermogravimetric (TG) analysis was conducted on TG/DTA 6300 instrument in the temperature range from 30 to 700 °C.

*Electrochemical measurements:* The electrochemical performance of the samples is evaluated in the three-electrode battery system including working electrode, counter electrode (carbon paper), and the AgCl/Ag reference electrode. The working electrode

was fabricated by coating a mixture of active material ( $\text{CuCoFe}(\text{CN})_6$ , 70 wt %), acetylene black (20 wt %), and polytetrafluoroethylene (10 wt %) onto a carbon paper. The electrolyte is 0.5 M  $\text{CuCl}_2$  in deionized water. Galvanostatic charge-discharge tests and cyclic voltammetry (CV) were gained by a Bio-Logic VSP electrochemical workstation and LANHE CT2001A battery test system, respectively. Furthermore, all the capacities of electrodes are calculated based on the mass of active materials on the electrode.

**The detailed calculation of the Cu<sup>2+</sup> concentration in the lattice of CuCoFe(CN)<sub>6</sub>,**

**C.**

For better understanding, we assume our material after CV test is an ideal CuCoFe(CN)<sub>6</sub> cell, it contains 4 Cu<sup>2+</sup>, the molar amount of Cu<sup>2+</sup> is:

$$n = \frac{4}{6.023 \times 10^{23}} = 6.64 \times 10^{-24} \text{ mol}$$

The lattice volume of ideal CuCoFe(CN)<sub>6</sub> cell is 1001.5 Å<sup>3</sup>.

Therefore, the Cu<sup>2+</sup> concentration in the lattice of CuCoFe(CN)<sub>6</sub> is 6.63 × 10<sup>-3</sup> mol cm<sup>-3</sup>.

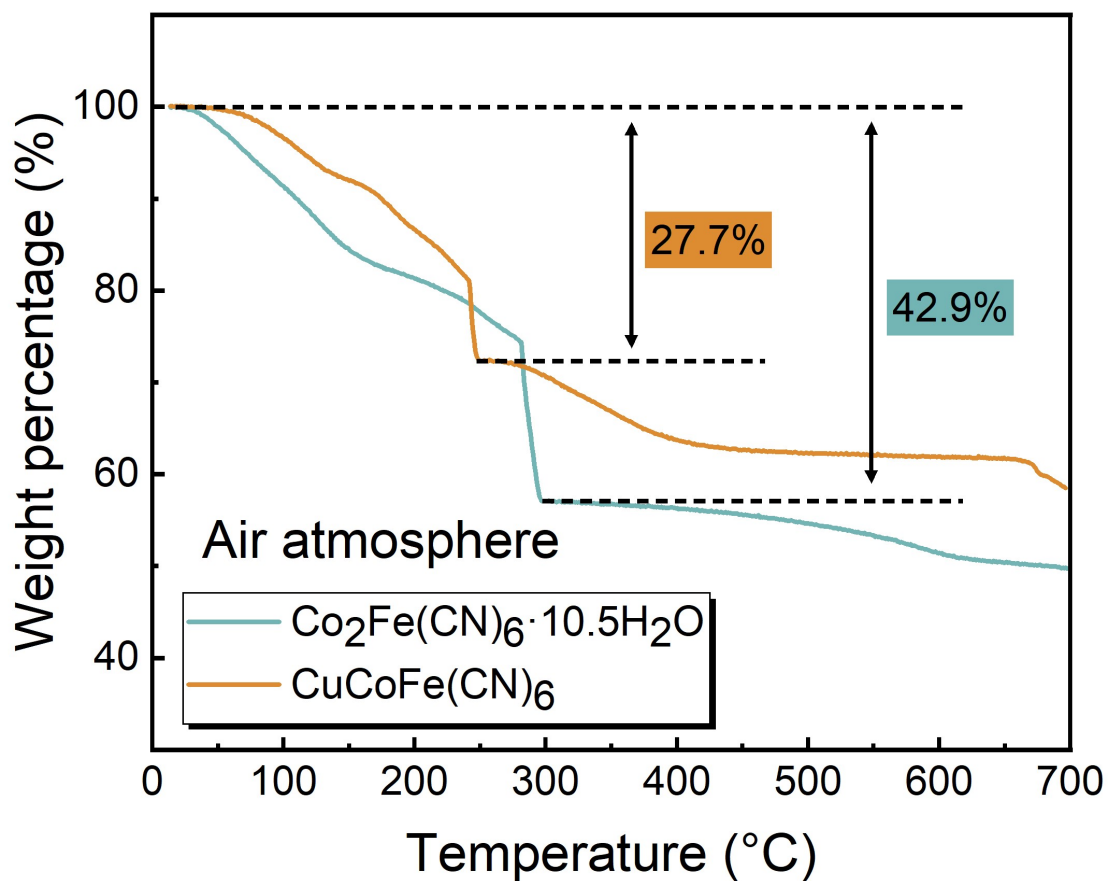


Figure S1 TG curves of  $\text{Co}_2\text{Fe}(\text{CN})_6 \cdot 10.5\text{H}_2\text{O}$  and  $\text{CuCoFe}(\text{CN})_6$ .