# Supporting Information

# **Copper hexacyanoferrate nanoparticles as cathode material for aqueous aluminum ion batteries**

### **Experimental details**

## Preparation and characterization of CuHCF

Nanoparticle CuHCF was synthesized by a coprecipitation method as reported previously.<sup>1</sup> Brifely, equal volumes (120 mL) of 0.1 M Cu(NO<sub>3</sub>)<sub>2</sub> and 0.05 M K<sub>3</sub>Fe(CN)<sub>6</sub> aqueous solution were dropwise added into water (60 mL) under vigorous stirring simultaneously. A tawny brown precipitate formed immediately. After sonication for 20 min, the suspension was allowed to sit for six hours. The precipitate was filtered, washed with water, and dried in vacuum at room temperature.

Phase identification of the as-prepared CuHCF sample, pristine CuHCF electrode and Al inserted CuHCF electrode were determined by X-ray diffraction (XRD, Rigaku MiniFlex II) with a range of 20 from 8 to 80° at a rate of 5° min<sup>-1</sup>. The Al inserted CuHCF electrode was prepared by polarizing the CuHCF electrode at 0.2 V (vs. SCE) for 5 min in 0.5 M aqueous  $Al_2(SO_4)_3$ , followed by washing with deionized water and drying at 50 °C. The morphology and microstructure of the sample powders were characterized by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai F20). The specific zeolitic water water content in the moleculefomula of CuHCF was determined by using a thermogravimetric analyzer (TG, Mettler Toledo, TGA/DSC1) under Ar atmosphere.

#### **Electrochemical measurements**

The working electrode was prepared by mixing the powders of CuHCF, acetylene black and polytetrafluoroethylene (PTFE) with a weight ratio of 80:15:5 in ethanol. After the ethanol was evaporated, the mixture was rolled into a sheet and cut into a circular strip of 8 mm in diameter. After dried at 50 °C, the strip (ca. 2 mg) was pressed onto a Ti mesh under 30 MPa as the working electrode.

Electrochemical measurements were performed in three-electrode flooded cell, in which CuHCF electrode was used as the working electrode, graphite electrode and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. 0.5 M aqueous  $Al_2(SO_4)_3$  was used as electrolyte. To compare the cation effects on Al insertion The CuHCF electrodes were tested with cyclic voltammetry (CV, IM6ex electrochemical workstation, Zahner) and galvanostatic electrochemical charge-discharge test (Land, Wuhan). In the galvanostatic charge/discharge test, the potential ranged from 0.2 to 1.1 V (vs. SCE). A prototype of aqueous Al-ion battery is fabricated by using electrochemical Al inserted (discharge state) CuHCF as cathode, the TiO<sub>2</sub> nanotube arrays as anode,<sup>2</sup> and 0.5 M  $Al_2(SO_4)_3$  as electrolyte. The mass ratio of cathode and anode active materials is 4:5. The voltage ranged from 0.5 to 2.1 V. The specific capacity of the cell was calculated based on the mass of CuHCF. All the electrochemical tests were performed at ambient temperature.

#### **Supplementary Reference**

1. C. D. Wessells, R. A. Huggins and Y. Cui, Nat. Commun., 2011, 2, 550.

2. S. Liu, J. J. Hu, N. F. Yan, G. L. Pan, G. R. Li and X. P. Gao, *Energy Environ. Sci.*, 2012, 5, 9743.



Fig. S1 CV curves of CuHCF electrode in 0.5 M Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 1 M AlCl<sub>3</sub> and 1 M Al(NO<sub>3</sub>)<sub>3</sub> aqueous solutions at the scan rate of 1 mV s<sup>-1</sup>.



Fig. S2 XRD patterns of the pristine CuHCF electrode and Al inserted CuHCF electrode.



Fig. S3 The typical charge/discharge curves of the prototype of aqueous Al-ion battery. The specific capacity of the cell was calculated based on the mass of CuHCF.