



# Truncated cobalt hexacyanoferrate nanocubes threaded by carbon nanotubes as a high-capacity and high-rate cathode material for dual-ion rechargeable aqueous batteries



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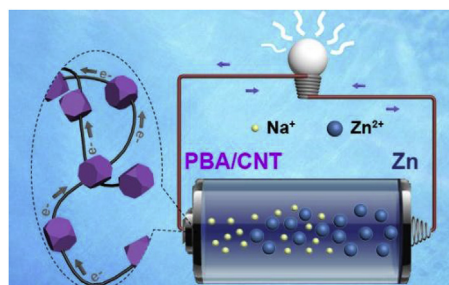
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## HIGHLIGHTS

- Truncated cobalt hexacyanoferrate nanocubes are threaded by carbon nanotubes.
- This composite shows reduced structure vacancies and enhanced conductivity.
- The specific capacity reaches  $107.2 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  and  $95 \text{ mAh g}^{-1}$  at  $5 \text{ A g}^{-1}$ .
- This composite is paired with Zn for dual-ion aqueous batteries.
- Full cells deliver an energy density of  $107.1 \text{ Wh kg}^{-1}$  at  $7.87 \text{ kW kg}^{-1}$ .

## GRAPHICAL ABSTRACT



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## ABSTRACT

Prussian blue (PB) and its analogues (PBAs) have been regarded as one of promising electrode candidates in aqueous batteries, due to its open framework, robust skeleton, and simple preparation protocol. However, intrinsic structure vacancies and poor electron conductivity lower their electrochemical performances, particularly in terms of reversible capacity, rate capability, and cycling stability. Here, truncated cobalt hexacyano-ferrate nanocubes threaded by carbon nanotubes are synthesized with the assistances of citrate and glycerol. The low content of structure vacancies in cobalt hexacyanoferrate, and the intimate contact between it and carbon nanotubes, well address the above issues, resulting in excellent performances in rechargeable aqueous batteries. The reversible capacity reaches  $107.2 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$ , 87.3% of which is kept at  $5 \text{ A g}^{-1}$ . After paired with Zn foil as a dual-ion full cell, it delivers a high energy of  $107.1 \text{ Wh kg}_{\text{cathode}}^{-1}$  at  $7.87 \text{ kW kg}_{\text{cathode}}^{-1}$ , exhibiting the high energy and high power simultaneously. All these results indicate the promising potential of this composite in rechargeable aqueous batteries.

## 1. Introduction

Rechargeable aqueous batteries have been receiving extensive attention in the past years, due to the usage of aqueous electrolytes that

could effectively lower the cost, increase ionic conductivity of salts, reduce the electrolyte flammability, and assemble easily in air as compared to organic electrolyte. All these features make rechargeable aqueous batteries (RABs) promising as the next-generation energy

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storage devices [1–4]. However, these RABs face the challenges from electrode materials and electrolytes. Firstly, aqueous electrolytes only work within a narrow potential window (1–2 V) dependent on electrode overpotential and electrolyte salts [3–5]. Otherwise, either hydrogen or oxygen would be generated, thereby reducing the coulombic efficiency of RABs [6]. Secondly, electrode materials fitted within this potential window are quite limited [3,4]. The ideal anode/cathode materials are supposed to make the best use of this potential window and achieve the large specific capacity.

Recently, Prussian blue (PB) and its analogues (PBAs) are successfully developed as cathode materials in Li/Na-ion RABs. Compared to other cathode candidates, PB and PBAs have the advantages like easy preparation, high electrochemical activity, and open frameworks to facilitate  $\text{Li}^+$ / $\text{Na}^+$  diffusion. However, intrinsic crystal defects and low electric conductivity become obstacles for high-performance cathodes [7,8]. Thus, various chemical synthesis were attempted to address the issues [8–12], and achieved remarkable progresses. Another important issue of PB and PBAs is how to increase the available capacity for RABs. Although there are several PBAs with a capacity to accommodate two  $\text{Li}^+$ / $\text{Na}^+$  ions per formula, only CoHCF and FeHCF have the redox reactions within the electrochemical window stable to water. In FeHCF, the two redox couples,  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  bonding to C in  $\text{C}\equiv\text{N}$  and  $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$  bonding to N in  $\text{C}\equiv\text{N}$ , are well separated by 0.7–0.8 V, which makes it inappropriate as a cathode material [13]. CoHCF reduced the potential gap of two redox couples to 0.4–0.5 V, by uplifting the low redox potential to 0.4 V (Vs. Ag/AgCl). This result would effectively improve the energy density and power density of full cells, as compared to FeHCF. Up to date, the works on CoHCF are quite limited [14–24]. Cui et al. investigated the electrochemical properties of CoHCF, and reported a poor rate performance about  $65 \text{ mAh g}^{-1}$  at 2C ( $\sim 0.36 \text{ A g}^{-1}$ ) [14]. As the current density increased to 10C, only  $\sim 24\%$  of the initial capacity was kept. Qian and Yang synthesized almost vacancy-free  $\text{Na}_2\text{CoHCF}$  nanocubes by a slow reaction [15]. These nanocubes could deliver a specific capacity of  $125 \text{ mAh g}^{-1}$  at  $0.13 \text{ A g}^{-1}$  47.6% ( $\sim 61 \text{ mAh g}^{-1}$ ) of the initial capacity was remained at  $2.6 \text{ A g}^{-1}$  in rate test.  $\text{Na}_2\text{CoHCF}$  was assembled with  $\text{NaTi}_2(\text{PO}_4)_3$  to build a full cell, which delivered an energy density of  $67 \text{ Wh kg}^{-1}$  at most. This is the first and only full cell developed on CoHCF. Zhao et al. explored the performances of CoHCF as a cathode material in supercapacitors (SCs) [16], where only one redox peak at  $\sim 0.4 \text{ V}$  was observed. To our knowledge, there is no report about CoHCF/C composite yet.

Here, truncated CoHCF nanocubes threaded by carbon nanotubes, denoted as CoHCF-Cit/CNT were synthesized by a simple process. Citrate and glycerol in the recipe effectively reduce the reaction rate and the growth rate, producing high-quality truncated nanocubes. The low content of crystal vacancies, and the intimate contact with CNTs endow CoHCF a high capacity and a fast sodiation/desodiation kinetics. This composite exhibit a specific capacity  $107.2 \text{ mAh g}^{-1}$  at  $0.1 \text{ A g}^{-1}$  87.3% of this data,  $\sim 95 \text{ mAh g}^{-1}$ , could be kept at  $5 \text{ A g}^{-1}$ , much higher than those of CoHCF, CoHCF-Cit, CoHCF-Cit + CNTs. After coupled with Zn foil to give a dual-ion full cell, it could deliver a high energy of  $107.1 \text{ Wh kg}^{-1}$  at  $7.87 \text{ kW kg}^{-1}$ , thus achieving the high energy and power simultaneously.

## 2. Material and methods

**Chemical Synthesis.** All the chemicals were purchased from Sinopharm Chem. Reagent Co. Ltd. and used without any purification, except multiwalled carbon nanotubes (MWCNTs) from Shanghai Aladdin Bio-Chem Technology Co., LTD. First, multiwall carbon nanotubes with diameters of 40–60 nm were treated by concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  with a volume ratio of 3:1 for 12 h at room temperature to remove impurities and make them well dispersible in water. Then, 1 mmol of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  and 2 mmol of trisodium citrate dihydrate were dissolved in a mixed solvent of 40 mL deionized water and 25 mL glycerol. After 25 mg of pre-treated CNTs was added, the solution was

sonicated for 30 min to generate a good suspension. 10 mL of  $0.1 \text{ M K}_3\text{Fe}(\text{CN})_6$  was added with vigorous stirring for 12 h. The as-obtained precipitate was filtered, washed by deionized water and absolute ethanol, and dried in air at  $60^\circ\text{C}$  overnight. The obtained product was denoted as CoHCF-Cit/CNT in the text. Meanwhile, several controls were also prepared to understand the effects of CNT and Cit(Citrate) on the performances. When CNTs were removed from the protocol, the product was named as CoHCF-Cit. If both CNTs and trisodium citrate were removed, the product was marked as CoHCF. The mixture of CoHCF-Cit and CNTs, obtained by ball-milling, was denoted as CoHCF-Cit + CNTs.

**Structure Characterization.** Powder X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Bruker D8 Advance, Germany), using Cu  $\text{K}\alpha$  line ( $\lambda = 1.5418 \text{ \AA}$ ) as the radiation source. SEM and TEM images were recorded on scanning electron microscope (ZEISS Sigma 300, Germany) and transmission electron microscope (JEOL JEM-1101, Japan), respectively. The contents of C, H, and N were detected by elemental analyzer (Elementar Vario EL CUBE, Germany). The contents of K, Co, and Fe, were obtained by a Flame Atomic Adsorption Spectrometer (Flame AAS, Persee TAS-990, China). Thermogravimetric Analysis (TGA) was tested on a thermogravimetric analyzer (Mettler Toledo TGA/SDTA851, Germany) within a temperature range from 20 to  $600^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . Raman spectra were recorded by a micro-Raman spectrometer (LabRAM HR800, HORIBA Jobin Yvon, France) with an excitation wavelength at 514.5 nm.

**Electrochemical measurements.** Electrochemical properties of CoHCF-Cit/CNT, CoHCF-Cit, CoHCF and CoHCF-Cit + CNT, were evaluated in a typical three-electrode setup, using a platinum mesh as the counter electrode, a saturated Ag/AgCl electrode as the reference electrode and 1 M  $\text{Na}_2\text{SO}_4$  as the electrolyte. As to the working electrode, it was made of 70 wt% active materials, 20 wt% carbon powders and 10 wt% polytetra-fluoroethylene (PTFE). These materials were milled together in a trace of isopropanol and dried at  $60^\circ\text{C}$  in air, producing a thin film. Then, the thin film was punched in discs with diameter of 10 mm, corresponding to mass loading of  $\sim 3 \text{ mg cm}^{-2}$ , and pressed on titanium meshes by a static pressure of 10 MPa for 30 s. The full cell was tested with CoHCF-Cit/CNT as a cathode, Zn foil as an anode and an aqueous solution of  $\text{Na}_2\text{SO}_4$  (1 M) and  $\text{ZnSO}_4$  (0.5 M) as electrolyte. All the batteries were electrochemically activated for 10 cycles at  $100 \text{ mA g}^{-1}$  then used for cycling and rate performances. Galvanostatic charge-discharge profiles were measured by a battery test system (LAND CT2001A, China). Cyclic voltammograms (CV) were obtained on an electrochemical workstation (CHI760E, ChenHua Instruments Co., China). Electrochemical impedance spectra (EIS) were acquired from another electrochemical workstation (Autolab PGSTAT302 N, Switzerland).

## 3. DFT calculations

All geometries are optimized by DFT using the local density approximation (LDA) within the plane-wave-based Vienna Ab-initio Simulation Package (VASP) code [25]. The energy cutoff energy is at 400 eV for all the calculations. The  $\Gamma$ -centered Monkhorst-Pack grid of  $2 \times 2 \times 2$  is set in Brillouin zone for the unit cell. Geometries of the structures are optimized until the force on each atom is less than  $0.05 \text{ eV \AA}^{-1}$ . The lattice constant of  $\text{KCo}[\text{Fe}(\text{CN})_6]$  is  $9.648 \text{ \AA}$ . When one Co atom is removed and six  $\text{H}_2\text{O}$  molecular are added, the constant is changed to be  $9.697 \text{ \AA}$ , which is bigger than  $\text{KCo}[\text{Fe}(\text{CN})_6]$ .

## 4. Results and discussion

Fig. 1a shows the XRD patterns of CoHCF-Cit/CNT, CoHCF-Cit and CoHCF. All the diffraction peaks are similar to each other, consistent with the face-centered cubic structure of Prussian blue. The absence of peak splitting for (220), (420), and (440) diffractions excludes the

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