



# Facile synthesis of cobalt hexacyanoferrate/graphene nanocomposites for high-performance supercapacitor



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## ABSTRACT

Prussian blue and its analogues are promising for energy storage devices owing to the rigid open framework, yet suffer from poor conductivity and relatively low energy density. Herein, we report a facile preparation of cobalt hexacyanoferrate/reduced graphene oxide nanocomposites (CoHCF/rGO) for supercapacitors with enhanced performance. The CoHCF nanoparticles with a size of around 50 nm are adhered onto the rGO nanosheets, which, in turn, not only prevent the agglomeration of the CoHCF nanoparticles but also provide conductive network for fast electron transport. The CoHCF/rGO nanocomposite delivers a maximum specific capacitance of 361 F g<sup>-1</sup> in Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte. Asymmetric supercapacitor cells are assembled by pairing up an optimized nanocomposite electrode with an activated carbon negative electrode, which exhibits a wide reversible operating voltage of 2.0 V and a high energy density of 39.6 Wh kg<sup>-1</sup>. The enhanced electrochemical performance of CoHCF/rGO benefits from the strong synergistic utilization of CoHCF nanoparticles and rGO nanosheets, rendering the nanocomposites a great promise for high-performance supercapacitors.

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## 1. Introduction

Supercapacitors have attracted extensive attention owing to their fascinating characteristics of high power density, high energy density and long cycle life in recent years [1]. The advantages of supercapacitors make them suitable in the fields of consumer electronics, electric vehicles and intermittent renewable energy sources [2]. According to the energy-storage mechanism, supercapacitors can be divided into two types: (1) electrical double-layer capacitors (EDLCs) that accumulate charges at the electrode-electrolyte interface through electrostatic interaction and (2) pseudocapacitors that store energy on basis of rapid Faradaic reactions [3,4]. Electrode material is a vital factor for determining the performance of supercapacitors. The widely-used electrode materials in EDLCs are carbonaceous materials [5–8], including carbon xerogel [6], carbon nanotubes [7] and graphene [8]. However, the relatively low specific capacitance of carbonaceous materials limits their practical applications. In sharp contrast, pseudocapacitive materials, such as conductive polymers and

transition-metal oxides, exhibit much higher specific capacitances, but they suffer from the limited cycling stability [1,9].

Prussian blue (PB), namely iron hexacyanoferrate with FCC crystal structure [10–12], can be considered as one of the oldest synthetic coordination compound [13]. The chemical formula of the PB can be generally expressed as A<sub>x</sub>Fe[Fe(CN)<sub>6</sub>]<sub>y</sub>·mH<sub>2</sub>O (A, alkaline metal; 0 < x < 2, y < 1). In the structure of PB, one Fe<sup>2+</sup> or Fe<sup>3+</sup> was connected by six cyano ligands, forming octahedral geometry in crystal structure and open channels along the crystal orientation of (100). The open channels in PB structure offer enough space for insertion/extraction of various ions, accompanying slight distortion of the crystal structure and the valence change of iron ions [14]. Compared to PB, prussian blue analogues (PBAs) show similar crystal structure with partial or entire iron positions substituting by other transition metal ions, but possess totally different electrochemical properties [15–18].

Recently, PBAs have attracted tremendous interest in energy storage community as they can exhibit good specific capacitance and excellent cycling stability. Among the different PBA species (e.g. NiHCF and CuHCF), it is demonstrated that cobalt hexacyanoferrate (CoHCF) manifests the best electrochemical performance in Na<sub>2</sub>SO<sub>4</sub> aqueous solution [19]. To improve the electrochemical properties of bulk CoHCF, nanoscaled CoHCF particles was purposely prepared for high-rate and ultra-stable supercapacitor

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electrode material [20]. However, the pure PBAs still suffer from poor electrical conductivity, which results in low electrochemical utilization [21]. One feasible approach to address the critical issue is combining PBAs with conducting materials, such as nanocarbons. In this regard, graphene is believed to be an excellent candidate due to its distinct merits of large specific surface area and high electrical conductivity [22]. It is anticipated that a hybrid of CoHCF and graphene will give rise to a strong synergistic effect of inhibiting the restacking of graphene nanosheets and improving the electronic conductivity of CoHCF nanoparticles. Therefore, a rational synthesis method is necessary to be explored to develop CoHCF/graphene nanocomposites with enhanced electrochemical performance.

In this work, we reported a simple yet effective method to synthesize a series of CoHCF/reduced graphene oxide (CoHCF/rGO) nanocomposites. The rGO not only serves as a mechanical support for CoHCF nanoparticles, but also improve the electrochemical kinetics of CoHCF nanoparticles. A maximum specific capacitance of  $361 \text{ F g}^{-1}$  is obtained for the nanocomposites. Furthermore, the optimal CoHCF/rGO nanocomposites electrode is coupled with activated carbon (AC) to construct an asymmetric supercapacitor cell, which exhibits a high energy density of  $39.6 \text{ Wh kg}^{-1}$ .

## 2. Experimental

### 2.1. Materials preparation

All chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. GO was prepared through a modified Hummers method [23,24]. In a typical synthesis procedure of the CoHCF/rGO nanocomposites, 20 ml of  $0.02 \text{ M K}_3\text{Fe}(\text{CN})_6$  aqueous solution was added into 30 ml of GO solution ( $1.0 \text{ mg ml}^{-1}$ ) under ultrasonic treatment for 0.5 h. Subsequently, 20 ml of  $0.03 \text{ M Co}(\text{NO}_3)_2$  aqueous solution was added by dropwise into the above mixture under vigorous magnetic stirring at room temperature for 1 h. Finally, 150 mg of thiourea was dissolved into the above suspension, and heated to  $95^\circ\text{C}$  with a duration of 8 h. The GO was reduced by thiourea at the mild temperature, which provides diamine and  $\text{C}=\text{S}$  bonds to remove the oxygen-containing functional groups in GO [24]. Black CoHCF/rGO nanocomposites were obtained and washed with deionized water and ethanol for several times, and dried at  $80^\circ\text{C}$  for 12 h. For comparison, pure CoHCF and CoHCF/rGO nanocomposites with different rGO content (0, 15, 30 and 45 mg) were synthesized without altering the experimental conditions.

### 2.2. Materials characterization

The crystallographic structure of the as-prepared samples was characterized by X-ray powder diffraction (XRD, X'Pert Pro MPD, Philips). Raman spectrum was collected on Renishaw Invia RM200 (England, laser wavelength:  $514 \text{ nm}$ ) at room temperature in the spectral range of  $200\text{--}2500 \text{ cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific) measurements were employed to investigate the surface chemistry of the nanocomposites. The morphology of the samples was observed on field emission scanning electron microscopy (FE-SEM, FEI NanoSEM 450) and transmission electron microscopy (TEM, FEI Tecnai F30G<sup>2</sup>). The surface characteristic was examined by  $\text{N}_2$  adsorption/desorption measurement (Mike ASAP 2020).

### 2.3. Electrochemical measurements

The electrochemical tests of CoHCF/rGO nanocomposites were performed on an electrochemical workstation (Solartron 1260+1287) in a three-electrode configuration system with

platinum foil, saturated calomel electrode (SCE), and  $0.5 \text{ M Na}_2\text{SO}_4$  aqueous solution as the counter electrode, reference electrode and electrolyte, respectively. The working electrodes were fabricated by mixing active materials, carbon black and polytetrafluoroethylene (PTFE) with a mass ratio of 7:2:1. The slurry was uniformly painted on the nickel foam followed by drying at  $90^\circ\text{C}$  for 12 h in an oven. The mass loading of active materials on the working electrode was about  $2.0 \text{ mg cm}^{-2}$ . To evaluate the electrochemical performance of the working electrodes, cyclic voltammetry (CV) and galvanostatic charge-discharge techniques were employed within a potential window ranging from  $-0.1$  to  $1.0 \text{ V}$ . The specific capacitance is calculated based on the mass of the active materials. Electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range of  $10 \text{ kHz}$  to  $0.01 \text{ Hz}$ .

Asymmetric supercapacitor cells were constructed by pairing CoHCF/rGO as the positive electrode with an activated carbon (AC) negative electrode in  $0.5 \text{ M Na}_2\text{SO}_4$  aqueous solution. Considering the different specific capacitances of AC and CoHCF/rGO electrodes, the mass ratio of the positive and negative electrodes is estimated to be 1:3. CV and galvanostatic charge-discharge techniques were employed to evaluate the electrochemical performance of the asymmetric cells. The energy density ( $E$ ) and the power density ( $P$ ) of the asymmetric cell were calculated by the equations of  $E = 1/2C(\Delta V)^2$  and  $P = E/\Delta t$ , respectively, where  $C$  is the specific capacitance of the asymmetric cell,  $\Delta V$  is the potential window, and  $\Delta t$  is the discharge time.

## 3. Results and discussion

The XRD patterns of CoHCF/rGO nanocomposites, pure CoHCF and rGO are shown in Fig. 1(a). The diffraction peaks with

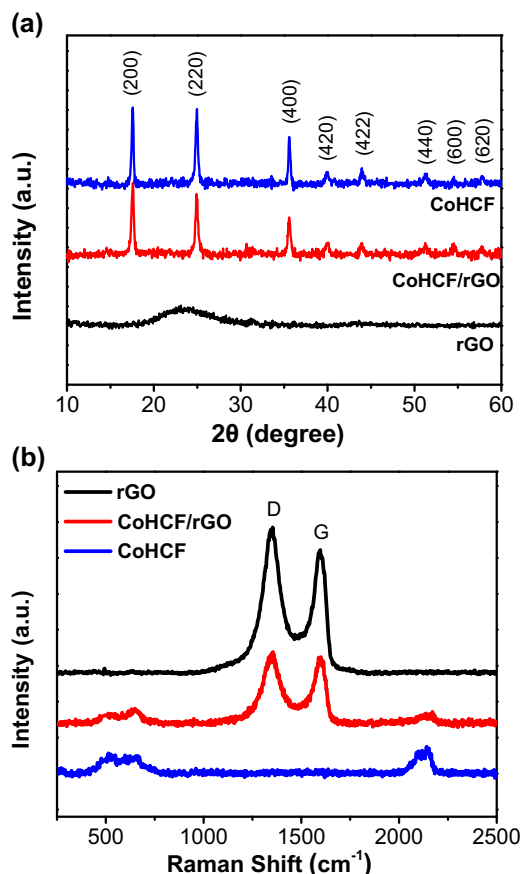


Fig. 1. (a) XRD patterns and (b) Raman spectra of CoHCF/rGO, CoHCF and rGO.

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