



# Copper and nickel hexacyanoferrate nanostructures with graphene-coated stainless steel sheets for electrochemical supercapacitors



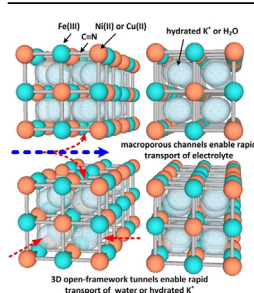
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## HIGHLIGHTS

- Cu and Ni hexacyanoferrates are prepared by coprecipitation for supercapacitors.
- 3D open tunnels enable fast transport of  $K^+$  ions to enhance the rate performance.
- Formation of a protective carbon layer mitigates the loss of electroactivity.
- Graphene layer can suppress the corrosion of stainless steel effectively.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Copper and nickel hexacyanoferrate (CuHCF and NiHCF) nanostructures featuring three-dimensional open-framework tunnels are prepared using a solution-based coprecipitation process. CuHCF shows superior supercapacitive behavior than the NiHCF, due to the presence of numerous macropores in CuHCF particles for facilitating the transport of electrolyte. Both CuHCF and NiHCF electrodes with stainless steel (SS) substrate tend to lose their electroactivity towards intercalation/deintercalation of hydrated potassium ions owing to the partial corrosion of SS. Formation of a protective and conductive carbon layer in between SS and CuHCF (NiHCF) film is of paramount importance for improving the irreversible loss of electroactivity. Thin and compact graphene (GN) layer without observable holes in its normal plane is the most effective way to suppress the corrosion of SS compared with porous carbon nanotube and activated carbon layers. Specific capacitance of CuHCF electrode with GN layer (CuHCF/GN/SS) reaches  $570 \text{ F g}^{-1}$ , which is even better than that of CuHCF with Pt substrate ( $500 \text{ F g}^{-1}$ ) at  $1 \text{ A g}^{-1}$ . The CuHCF/GN/SS exhibits high stability with 96% capacitance retention over 1000 cycles, greater than the CuHCF with Pt (75%).

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## 1. Introduction

Metal hexacyanoferrates (MHCs), known as the Prussian blue analogues, are very promising materials for charge-storage and sensor applications due to their unique structural characteristics

such as three-dimensional (3D) network with a distinct tunnel and pore structures [1–7]. In aqueous electrolyte containing alkali salts, the MHCs with 3D open-framework tunnel structures can reversibly accommodate water or hydrated alkali cations, facilitating the transport of hydrated alkali cations through the materials without significant disturbance of the framework [8–10]. Prussian blue analogues exhibit reversible redox reactions (such as  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) accompanied with reversible intercalation and deintercalation of hydrated alkali cations, low cost, and low

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environmental toxicity. Several reports have been devoted to studying the supercapacitive behavior of MHCs. Insoluble iron, cobalt, and nickel hexacyanoferrates prepared by a simple coprecipitation method are reported to have suitable capacitive behavior for electrochemical supercapacitors [11,12]. To further improve the capacitive behavior of MHCs, hybrid MHCs have been explored. The nanostructures of hybrid nickel-cobalt hexacyanoferrate showed a much higher capacitance than those obtained with nickel hexacyanoferrate (NiHCF) or cobalt hexacyanoferrate (CoHCF) [13]. In addition, introduction of metal oxides or polymers to form hybrid MHCs also received positive effect on the capacitive behavior of the electrodes due to the enhanced structural stability [14–18].

Current collector materials, which play an important role in determining the utilization efficiency of the active materials, are electrochemically stable materials when in contact with electrolyte in the potential window of the electrodes. Several conductive materials such as carbon, noble metal, stainless steel (SS), and nickel have been considered as the electrode substrates (current collector materials) for supporting the MHCs [4,11–15,19–22]. Among these materials, SS sheet and mesh (grid) have the potential to serve as a current collector material because of their low cost and high electrical conductivity. Nano-sized CoHCF and NiHCF materials have been prepared by a simple co-precipitation method as the supercapacitor materials. However, a significant loss of specific capacitance can be observed for the CoHCF and NiHCF electrodes using SS grid substrate after 1000 galvanostatic charge and discharge cycles [11,12]. Previous report indicated that when NiHCF films are coated on nickel substrate, the stoichiometrically excessive nickel ions originating from the partial corrosion of the nickel substrate are likely to be immobile, sit on potassium counteraction sites, and influence the system potential in a similar way as the nitrogen-coordinated (lattice) nickel ions [19]. At the interface formed by a composite film (polyaniline composite film containing Prussian blue and hexacyanoferrate anions) with SS, the interaction of hexacyanoferrate with iron (II, III) and some chromium (III) originating from the partial corrosion of SS may lead to the formation of a thin insoluble MHC layer [22]. In practice, the corrosion of current collectors may result in a gradual increase in the internal resistance of electrodes, leading to a serious capacitance fading. Thus, the formation of thin and compact protective film on the surface of current collectors is highly important to ensure the capacitive performance of the MHC electrodes.

Various types of thin MHC films can be readily formed on the electrode substrates by electrochemical deposition or electrostatic deposition [23–25]. MHC nanoparticles are generally prepared by means of chemical coprecipitation. Slurry coating technique enables the formation of thick MHC film on electrode substrate [26]. In this work, to mitigate the corrosion of electrode substrates, various types of protective carbon layers such as carbon black, carbon nanotube (CNT), and graphene nanosheet (GN) are directly formed on the SS substrates by electrophoretic deposition (EPD). MHC nanoparticles prepared by coprecipitation are homogeneously deposited on the carbon-protected SS substrates by EPD technique. EPD has the advantages of short formation time, simple apparatus, easy production, and suitable for deposition in various shapes of electrode substrate. We demonstrate that GN layer exhibits excellent protecting behavior due to the absence of observable holes in its normal plane that prevents the electrolyte to reach the substrate. Copper hexacyanoferrate (CuHCF) electrode with protective GN layer exhibits high specific capacitance, high rate capability, and stable cycle life. This configuration of electrode is low-cost, scalable and extendable to other MHC and hybrid nanostructures.

## 2. Experimental

### 2.1. Preparation of NiHCF and CuHCF nanoparticles

NiHCF and CuHCF samples were synthesized by a chemical coprecipitation method [8]. In a typical procedure, NiHCF nanoparticles were prepared by dropwise addition of 50 mL of nickel nitrate solution (0.04 M) to 50 mL of potassium hexacyanoferrate [ $K_3Fe(CN)_6$ ] solution (0.02 M). The solution was stirred with a Teflon-coated magnetic stir bar at 300 rpm (revolutions per minute) and kept at 70 °C by a hot-plate magnetic stirrer during reaction. After precipitation, the suspension was stirred (300 rpm) at room temperature for 6 h, then filtered and washed with de-ionized water several times. The preparation procedure of CuHCF nanoparticles was similar to that of NiHCF except that the copper nitrate solution (0.04 M) was used instead of nickel nitrate solution as a precursor and the reaction temperature was kept at room temperature.

### 2.2. EPD of protective carbon layers on SS substrate

Super P (SP, conductive carbon black) was purchased from Timcal Graphite & Carbon and used as received without further treatment. Multiwalled CNTs were purchased from ECHO Chemical (Taiwan) with an external diameter of 20–40 nm and a length of 0.5–200  $\mu\text{m}$ . The raw CNT powder was etched in 15 M boiling nitric acid solution under reflux for 1 h. The acid-treated CNTs were then washed several times with de-ionized water until the pH value of the solution became neutral. The synthesis of GNs was described in our previous report [27]. Carbon materials (SP, CNT, and GN) were coated on the SS substrates as a protective and conductive layer by EPD in an isopropyl alcohol (IPA) solution at room temperature. EPD was carried out in a suspension containing 20 mg of carbon powder (SP, CNT, or GN), hydrated manganese nitrate (0.1 mM) as a charging agent, and IPA (50 mL) by applying an electric field of  $-30 \text{ V cm}^{-1}$  between a working (SS, 2 cm  $\times$  2 cm) and counter (Pt, 2 cm  $\times$  2 cm) electrodes. After EPD, the carbon-coated SS electrodes were heat-treated at 300 °C in air for 1 h. The loading amount of carbon layer in each electrode was approximately the same (about 0.1 mg) by tuning the deposition time.

### 2.3. EPD of NiHCF and CuHCF films

NiHCF powder (0.5 g) was suspended in IPA solution (50 mL) under successive sonication for 30 min. CuHCF suspension was prepared in a similar way to the NiHCF suspension. The polarity of an applied electric field depended on the zeta potential of colloidal suspension. Zeta potentials of NiHCF and CuHCF suspensions were measured to be 20 and -39 mV, respectively. EPD of NiHCF nanoparticles was carried out by applying an electric field of  $-30 \text{ V cm}^{-1}$  between working and counter (Pt) electrodes at room temperature. The Pt, SS, carbon-coated SS sheets were used as the working electrode. EPD of CuHCF nanoparticles was similar to that of NiHCF except that the electric field of  $30 \text{ V cm}^{-1}$  was applied for deposition. After EPD, the electrodes were dried at 100 °C in air for 1 h.

### 2.4. Material characterization and electrochemical measurements

The crystal structure of NiHCF and CuHCF powder was characterized by an X-ray diffractometer (Bruker D8) with a Cu  $K\alpha$  target (wavelength = 1.54056 Å). The surface morphology of samples was observed by a field-emission scanning electron microscope (FE-SEM, Jeol JSM-6700F). The internal microstructure of samples was characterized by a transmission electron microscopy (TEM, Jeol JEM-1400). Specific surface area of samples was measured by the

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