



# Iron oxyhydroxide@cobalt hexacyanoferrate coaxial nanostructure: Synthesis, characterization and pseudocapacitive behavior



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## ABSTRACT

Iron oxyhydroxide@cobalt hexacyanoferrate coaxial nanostructure is synthesized by a simple precipitation method and characterized by scanning electron microscopy, transmission electron microscopy, FT-IR spectroscopy and an X-ray diffraction pattern. The coaxial nanostructure is then applied in a carbon paste and the electrochemical behavior of the resultant modified electrode is studied. Voltammograms of the modified electrode recorded in phosphate buffer solution, pH 7.4, show one quasi-reversible redox transition with a mid-peak potential of 366 mV, related to the Fe(II)/Fe(III) transition. The diffusion of the counter cation into the active material and the charge transfer kinetics across the electrode/electrolyte interface are studied. The modified electrode shows an excellent pseudocapacitive behavior and displays a specific capacitance as high as  $932.2 \text{ F g}^{-1}$  at  $5.3 \text{ A g}^{-1}$  which is greater than the summation of the capacities of iron oxyhydroxide nanorods and cobalt hexacyanoferrate particles. The specific energy and power of the electrode material are  $82.9 \text{ W h kg}^{-1}$  and  $0.53 \text{ W kg}^{-1}$ , respectively. The electrode retains more than 99% of the initial capacitance after 1000 charge/discharge cycles.

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## 1. Introduction

One-dimensional nanostructured materials, such as nanotubes, nanorods and nanowires, have unique properties which strongly depend on their size and shape [1], and have potential applications in optics, electronics, magnetics, catalysis, sensors, biotechnology and as building blocks for nanoscale devices [1]. These materials have been synthesized using various wet chemical methods of sol-gel processes, microemulsions, chemical co-precipitation, solvo- or hydro-thermal synthesis and forced hydrolysis of precursors [1]. In particular, hydrothermal synthesis offers effective control over the size and shape of nanostructures at relatively low reaction temperatures and short reaction times, providing well-crystallized reaction products with high homogeneity and definite composition [2].

Mixed-valence hexacyanoferrates, as inorganic redox polymers, have raised renewed and growing interest in various fields such as ion exchange, electrochromism, electrocatalysis, sensors and

biosensors, and, in magnetic, charge storage and bioselective devices [3–7]. These compounds represent well-defined electrochemical responses during their reversible redox processes due to their unique structural characteristics such as three dimensional network and tunnel structure, as well as the low cost and environmental toxicity [3–7]. Among the metal hexacyanometallates, cobalt hexacyanoferrate (CoHCF) is especially interested due to unique structure and redox properties. Both the cobalt and iron entities can be electroreactive and participate in the redox behavior of CoHCF. This compound and its composites represent quasi-reversible electron transfer kinetics and have applications in the design of batteries, pseudocapacitors, and electrocatalysts [6–12].

Energy storage devices are key elements for alternative environmentally clean energy. The forefronts of these devices are batteries and electrochemical supercapacitors. Electrochemical supercapacitors can operate at high charge/discharge rates over an almost unlimited numbers of cycles. In supercapacitors, energy stores through specific adsorption of ions (electrical double layer capacitors) or both double layer capacity and reversible Faradic reactions (pseudocapacitors). In order to identify new materials to be used in pseudocapacitor electrodes, various composite materials have been evaluated. In this regard, composites of metal

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oxides [13], conducting polymers [14] and metal hexacyanoferrates [8] have been fabricated.

In the present work, a novel coaxial nanostructure of iron oxyhydroxide@CoHCF was synthesized, characterized and employed as a pseudocapacitor electrode material. Based on our knowledge, this matter has been never attained.

## 2. Experimental

### 2.1. Materials

All chemicals used were analytical grade from Merck or Scharlau and used without further purification. Graphite fine powder with an average size of  $<50\ \mu\text{m}$  was received from Merck. All solutions were prepared with distilled water.

### 2.2. Synthesis of $\alpha$ -iron oxyhydroxide ( $\alpha$ -FeOOH) nanorods

$\alpha$ -FeOOH nanorods were synthesized by a solution chemical route involving two steps of a room-temperature chemical reaction followed by a hydrothermal treatment procedure. In the first step, a mixture of iron (II) sulfate (0.5 mmol) and sodium acetate (1 mmol) was added into a 100 mL beaker. Then, 20 mL water was added, and the above solution was stirred vigorously in air. A yellowish suspension appeared in the solution after several seconds, and the amount of suspension increased with continuous stirring. The mixture was further stirred for 20 min, and a yellow suspension was finally obtained. In the second step (the hydrothermal treatment), the obtained yellow suspension was transferred into a 20 mL Teflon-lined autoclave up to 80% of the total volume. The autoclave was sealed and heated at  $100\ ^\circ\text{C}$  for 8 h. The autoclave was then cooled to room temperature naturally. The

final yellow solid product was centrifuged and washed with distilled water and absolute ethanol several times, and then dried under vacuum for 4 h.

### 2.3. Synthesis of iron oxyhydroxide@cobalt hexacyanoferrate coaxial nanostructure (FeOOH@CoHCF)

$\alpha$ -FeOOH nanorods were suspended in 10 mL solution of 0.10 M  $\text{K}_3[\text{Fe}(\text{CN})_6]$  containing 10 mM HCl and stirred for about 30 min. Then, 10 mL 0.10 M  $\text{CoCl}_2$  solution containing 10 mM HCl was added, and the resultant mixture was stirred for further 30 min. CoHCF precipitated as a layer on the surface of  $\alpha$ -FeOOH nanorods, as the nucleation centers, and produced cobalt hexacyanoferrate coated iron oxyhydroxide nanorods. The obtained coaxial nanostructure was then collected and removed from the solution by filtration and washed with 10 mM HCl until the washing solution became colorless. Then, it was washed with redistilled water to neutralize. The FeOOH@CoHCF nanostructure was kept in vacuum at room temperature.

### 2.4. Synthesis of CoHCF particles

CoHCF particles were synthesized similarly to the method employed for the synthesis of the FeOOH@CoHCF nanostructure without using the  $\alpha$ -FeOOH nanorods.

### 2.5. Apparatus

Electrochemical measurements were carried out in a conventional three-electrode cell containing 100 mM Na-phosphate buffer solution, pH 7.4 (PBS) or a symmetrical two-electrode cell powered by a  $\mu$ -Autolab potentiostat/galvanostat, type III, FRA2

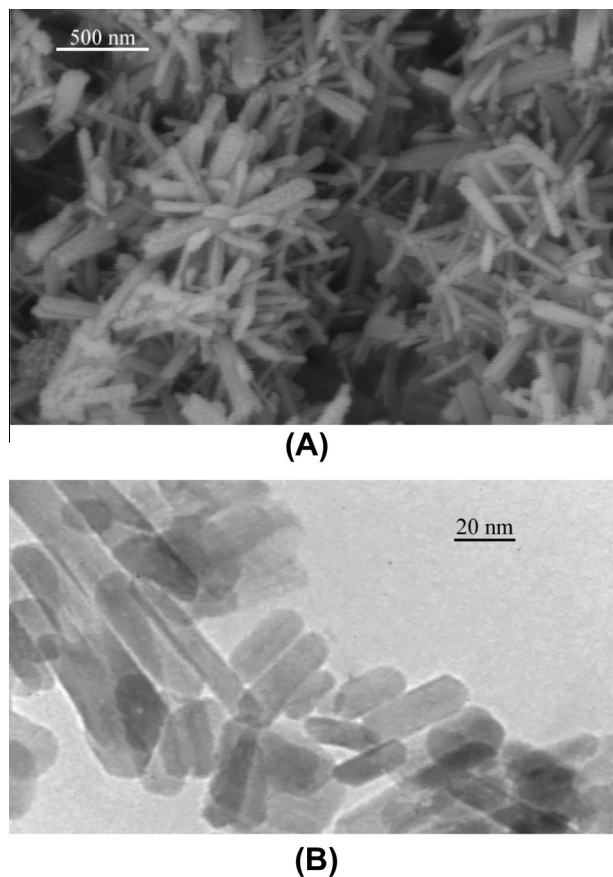


Fig. 1. SEM (A) and TEM (B) images of  $\alpha$ -FeOOH sample.

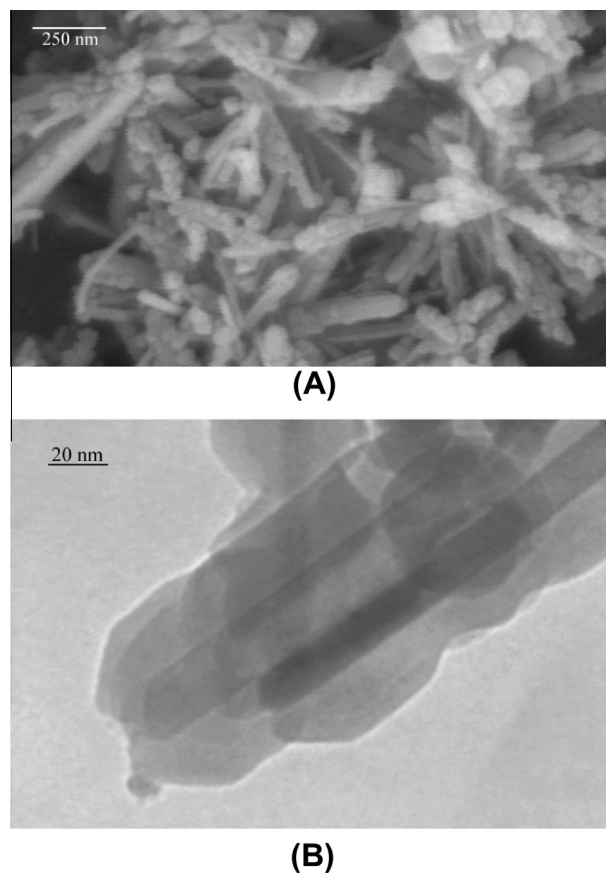


Fig. 2. SEM (A) and TEM (B) images of the FeOOH@CoHCF nanostructure.

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