



# Controllable synthesis of coaxial nickel hexacyanoferrate/carbon nanotube nanocables as advanced supercapacitors materials



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## ABSTRACT

The transition metal hexacyanoferrate (MHCF, M represents as Fe, Co, Ni, et al), has been studied and applied intensively in biosensor, catalysts, ion exchanger, molecular magnets and gas storage, but as yet remains largely unexplored for electrochemical energy storage device. This study shows that NiHCF can be uniformly deposited into the matrix of poly(4-vinylpyridine) grafted onto multiwalled carbon nanotubes (MWCNTs), and forms coaxial NiHCF/MWCNT nanocables with MWCNTs as core and NiHCF as shell. A different NiHCF content was loaded onto MWCNTs, and their electrochemical behavior and capacitive performance were determined. The as-prepared NiHCF/P4VP-g-MWCNT hybrids can possess a huge specific capacitance up to 1035 F·g<sup>-1</sup> at a discharge density of 0.05 A·g<sup>-1</sup>. These capacitance will decay by 10% at 25.6 A·g<sup>-1</sup>. They remain 92.7% of its initial capacitance at 2 A·g<sup>-1</sup> after 10000 discharge/charge cycles. Their energy density is nearly 56.2 Wh·kg<sup>-1</sup> at a power density of 10 W·kg<sup>-1</sup>. Their good electrochemical reversibility, high cyclic stability and excellent capacitive performance suggest a promising use as an advanced material for supercapacitors.

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## 1. Introduction

The past three decades have been witness to the fast-growing demand for sustainable and environmentally-friendly energy [1]. As a promising alternative for portable electronics, back-up power storage and hybrid electric vehicles, supercapacitors have gained an increasing attention due to their higher power density and longer cycle life compared with rechargeable batteries, and larger energy density compared with conventional solid-state and electrolytic capacitors [2,3]. According to the energy storage mechanism, supercapacitors can be divided into the electrical double layer capacitors (EDLCs) and pseudocapacitors. The EDLC performance depends on the available surface area of the electrodes and the finite charge separation between the electrode materials and the electrolyte [4]. Generally, EDLCs are constructed on the basis of

the pure graphitic nanostructures including graphene [5–8], carbon onions [9], nanoporous/mesoporous carbon [10], especially, carbon nanotubes (CNTs) [12–14]. CNTs are widely used in EDLCs due to their unique properties, such as high accessible surface area, excellent electrical conductivity and chemical stability [15,16]. However, the low capacitance of pure CNTs can not reach the standard of the commercial requirement for supercapacitors [17]. For pseudocapacitors, their energy storage capability is associated with the fast and reversible faradic reaction near the surface of pseudocapacitive materials [18]. Metal oxide or hydroxide [2,3,19] and conductive polymer [4,8,18] are studied extensively as supercapacitors due to their huge faradaic capacitance. But these pseudocapacitive materials are poor in conductivity and cycling stability [20]. Therefore, a combination of CNT and pseudocapacitive materials will be a solution to the bottleneck of supercapacitors in practical use.

Recently, transition metal hexacyanoferrates (MHCF, M represents as Fe, Co, Ni, et al) is of much interest and importance in energy storage and conversion because of their low cost, high ionic conductivity, excellent redox reversibility as well as superior environmental benignancy [21,22]. In addition, most of MHCF remains insoluble upon oxidation or reduction, which makes them very promising to be used in supercapacitors [23].

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Herein, we demonstrate a facile strategy to combine NiHCF with CNT to construct a novel supercapacitor. In this work, CNT was grafted with poly(4-vinylpyridine) (P4VP) via an in-situ polymerization [24,25]. This CNT modification can decrease damage to CNTs relative to oxidation by strong acid such as HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, and thus make CNTs stable and dispersible in aqueous solution for deposition of NiHCF [26]. In addition, the grafted P4VP can act as a linker to anchor NiHCF and control the growth of NiHCF on the surface of CNTs. As a result, NiHCF can be uniformly dispersed on CNTs to form a tunable core shell structure. The as-prepared NiHCF/CNT hybrids exhibit huge specific capacitance, excellent rate capacity and superior cycling stability, and hold promise as a solution to bottleneck of commercial utility for supercapacitor.

## 2. Experimental Section

### 2.1. Chemicals and materials

MWCNTs were obtained from Chengdu organic Chemicals Co., Ltd (purity > 95% out diameter 10–20 nm, length ~30 μm) and purified according to the reference [27]. NaCl, NaNO<sub>3</sub>, KMnO<sub>4</sub>, K<sub>3</sub>[Fe(CN)<sub>6</sub>], Ni(NO<sub>3</sub>)<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> (98%) and H<sub>2</sub>O<sub>2</sub> (30%), 4-ethenylpyridine and P4VP (Mw. 20000) was purchased from ACROS. The other chemicals were obtained from Shanghai Jingchun Co., Ltd. Water was purified by a Milli-Q system.

### 2.2. Preparation of P4VP-g-MWCNT hybrids

P4VP-g-MWCNT hybrids can be synthesized by in situ polymerization according to our previous reports [24,25]. In brief, 20 mg of MWCNTs was mixed with 1 mL 4-ethenylpyridine in 50 mL water by ultrasound dispersion. This mixture solution was purged with nitrogen for 15 minutes to remove oxygen in solution. Then an initiator K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (18 mg) was added. The polymerization started at 90 °C under continuous stirring, and stopped after 24 hours by cooling down to room temperature. P4VP-g-MWCNT hybrids were recovered by centrifugation and purified with 1 M HCl solution and alcohol under ultrasonication.

### 2.3. Preparation of NiHCF/P4VP-g-MWCNT hybrids

NiHCF/P4VP-g-MWCNT hybrids were prepared according to a co-precipitation strategy similar to our reports in acid aqueous solution [28]. A equivalent amount of Ni<sup>2+</sup> (20 mM) and [Fe(CN)<sub>6</sub>]<sup>3-</sup> (5 mM) were added in batches and stirred in 20 mL P4VP-g-MWCNT dispersion (0.5 mg·mL<sup>-1</sup>) containing 3 M acetic acid for 24 h. The NiHCF will form and grow in the matrix of P4VP chain grafted on MWCNT. The resulting NiHCF/P4VP-g-MWCNT hybrids were collected by centrifugation and washed with de-ionized water and ethanol.

For comparison, pure NiHCF was also prepared in the strategy similar to that of NiHCF/P4VP-g-MWCNT hybrids without P4VP-g-MWCNT hybrids.

### 2.4. Characterization

The composition of samples was analyzed by fourier transform infrared spectroscopy (FTIR) (Nicolet NEXUS670 spectrometer), thermogravimetric analysis (TGA) (Netzsch STA 449 C analyzer), X-ray photoelectron spectroscopy (XPS) (ESCALAB-MKII spectrometer) and the inductively coupled plasma-atom emission spectroscopy (ICP-AES) (Vista MPX). The structure and morphology of samples was investigated by X-ray powder diffraction (XRD) technique and transmission electron microscopy (TEM), respectively.

### 2.5. Electrochemical investigation

The as-prepared sample powders (50 mg, 90 wt.%) were mixed and ground with poly(tetrafluoroethylene) (PTFE) (5 wt.%) and alcohol (5 wt.%) to form homogeneous slurry. This sample slurry was filled and pressed into stainless steel grids as current collector. The electrochemical behaviors were carried out by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) tests in a conventional three electrode interfaced with a CHI 660C electrochemical workstation.

The total gravimetric specific capacitances C (F·g<sup>-1</sup>), energy density E (Wh·kg<sup>-1</sup>) and power density P (W·kg<sup>-1</sup>) were calculated from the GCD curves using the following equation [29]:

$$C = \frac{I\Delta t}{m\Delta V}$$

$$E = \frac{1}{2}C\Delta V^2$$

$$P = \frac{E}{\Delta t}$$

Where I (A) is the discharge current, Δt (s) is the discharge time, m (g) is the mass of the electroactive materials, and ΔV (V) is the voltage range of the discharge portion.

The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range from 100 kHz to 10 mHz at open circuit potential with an ac perturbation of 5 mV.

## 3. Results and discussion

### 3.1. Characterization of P4VP-g-MWCNT hybrids

As a proton acceptor, the dispersion of P4VP-g-MWCNT hybrids depends on the solution pH value. They can be easily dispersed in acid solution and will lose stability in neutral or alkaline solution [24,25]. TEM images show the aggregation of P4VP-g-MWCNT hybrids after deprotonation, and their high resolution TEM (HRTEM) reveals uneven distribution of P4VP on the surface of MWCNTs (Fig. S1, Supplementary material). The mass ratio of P4VP grafted to MWCNTs was estimated to be 25% according to TGA analysis investigated in nitrogen atmosphere (Fig. S2, Supplementary material). The P4VP modification on MWCNTs will benefit the co-precipitation of NiHCF on the surface of MWCNTs.

### 3.2. Characterization of NiHCF/P4VP-g-MWCNT hybrids

The composition of NiHCF/P4VP-g-MWCNT hybrids was investigated by FTIR and XPS as shown in Fig. 1. For P4VP-g-MWCNT hybrids, two sharp absorptions on the FTIR spectra at 1415 and 1597 cm<sup>-1</sup> can be assigned to the ring vibration of pyridine group in P4VP [30], indicative of the covalent bonding of P4VP on the surface of MWCNTs. For NiHCF/P4VP-g-MWCNT hybrids, another couple of absorption peaks at 2093 and 2180 cm<sup>-1</sup> is associated with the stretching vibration of CN group [31], suggesting NiHCF anchored with P4VP chains on MWCNTs. The XPS survey profile of P4VP-g-MWCNT hybrids exhibits an observable N 1s signal at ca. 400 eV [24,25], also confirming P4VP modification on the surface of MWCNTs. After NiHCF was deposited on MWCNTs, Ni 2p and Fe 2p signals appear at ca. 717 eV and 868 eV on the XPS spectrum of NiHCF/P4VP-g-MWCNT hybrids [28], respectively, further demonstrating NiHCF deposition on P4VP-g-MWCNT hybrids. The content of Ni, Fe and K can be determined by ICP-AES (Table S1, Supplementary

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