



Manganese hexacyanoferrate/multi-walled carbon nanotubes nanocomposite: Facile synthesis, characterization and application to high performance supercapacitors

Xiaojuan Zhang^a, Ping He^{a, b, *}, Xingquan Zhang^c, Caixia Li^a, Huanhuan Liu^a, Shuai Wang^a, Faqin Dong^{d, **}

^a School of Materials Science and Engineering, State Key Laboratory for Environment-friendly Energy Materials, Southwest University of Science and Technology, Mianyang 621010, PR China

^b Mianyang Kingtiger New Energy Technology Co. Ltd., Mianyang 621000, PR China

^c Center of Analysis and Test, Southwest University of Science and Technology, Mianyang 621010, PR China

^d Key Laboratory of Solid Waste Treatment and Resource Recycle of Ministry of Education, Southwest University of Science and Technology, Mianyang 621010, PR China



ARTICLE INFO

Article history:

Received 3 February 2018

Received in revised form

14 April 2018

Accepted 18 April 2018

Available online 25 April 2018

Keywords:

Manganese hexacyanoferrate
Multi-walled carbon nanotubes
Nanocomposite
Supercapacitors

ABSTRACT

A novel manganese hexacyanoferrate/multi-walled carbon nanotubes (MnHCF/MWCNTs) nanocomposite was fabricated by mild chemical precipitation method at room temperature and further investigated as electrode materials for supercapacitors. The physical properties of as-fabricated materials were characterized by XRD, FTIR and FE-SEM techniques. Integrating these nanostructures resulted in a strong synergistic effect between the two materials, consequently leading to robust and superior composite materials with higher capacity compared with pure MnHCF and MWCNTs. Specific capacities of 370.4, 200.1 and 45.8 C g⁻¹ were acquired for MnHCF/MWCNTs nanocomposite, MnHCF and MWCNTs, respectively. Most importantly, as-fabricated MnHCF/MWCNTs nanocomposite exhibited favorable rate capability (370.4 C g⁻¹ and 270.6 C g⁻¹ at 1.0 A g⁻¹ and 6.0 A g⁻¹, respectively) and excellent cycling stability (87.4% capacitance retention after 2000 cycles at 1.0 A g⁻¹). The simple synthesis and excellent electrochemical properties made as-fabricated nanocomposite an attractive candidate in the fields of supercapacitors and new emerging areas.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

In order to solve the challenges of global warming and the non-renewable nature of fossil fuels, it is now very important to develop new, low-cost and eco-friendly energy conversion and storage systems [1]. As the intermediate devices between conventional batteries and dielectric capacitors, supercapacitors have attracted significant attention because of its advantages, such as high power density, fast charging/discharging, long cycle life and superior reversibility, etc [2,3]. According to the charge storage mechanism, supercapacitors can be classified into two categories, including electrochemical double layer capacitors (EDLCs) and Faraday

pseudocapacitor pseudo-capacitors [4,5]. The commonly used electrode materials in EDLCs are carbon-based materials, including activated carbon, carbon nanotubes, porous carbon and graphene oxide, etc [6–9]. However, the relatively low specific capacity of carbon-based materials limits their extensive applications, whereas Faraday pseudo-capacitive materials, such as conducting polymers (polyaniline, polypyrrole and polythiophene, etc.) [10,11] and transition metal compounds (metal oxide, metal hydroxide and metal sulfide, etc.) [12,13], exhibit much higher specific capacities, but suffer from the limited cycle stability and conductivity [14]. Yu et al. [15] reviewed electrode materials for supercapacitors from 0 to 3 dimensions, including carbon-based materials, metal oxide, metal hydroxide, metal sulfide and conducting polymers. It is pointed out that the vital factor determining the electrochemical performance of supercapacitors is electrode materials. Nowadays, exploiting an electrode material with excellent electrochemical properties and high conductivity is very important for the

* Corresponding author. School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, PR China.

** Corresponding author.

E-mail address: heping@swust.edu.cn (P. He).

development of supercapacitors.

Prussian blue (PB), namely iron hexacyanoferrate with FCC crystal structure [16], is an important kind of mixed-valence compounds and considered as one of the oldest synthetic coordination compounds [17–19]. The common chemical formula of PB can be expressed as $A_hFe[Fe(CN)_6]_k \cdot nH_2O$ (where A = alkali metal cation, $0 < h < 2$, $0 < k < 1$) [20–22]. In the structure of PB, one Fe^{2+} or Fe^{3+} is connected by six cyano ligands, forming octahedral geometry in crystal structure and open channels along the crystal orientation [23]. The open channels provide enough space for intercalation/deintercalation of electrolyte ions, along with slight distortion of the crystal structure when the valence state of iron ions is changed during the multiple electrochemical cycles [24]. Compared with PB, Prussian blue analogues (PBAs) show similar crystal structure with partial or entire iron positions replaced by other transition metal ions (such as Ni, Co, Fe, Cu and Mn, etc.), exhibiting different electrochemical properties [25,26]. As one kind of PBAs, transition metal hexacyanoferrate have attracted numerous attentions in the electrochemical field due to the unique characteristics, such as tunnel structure, lower cost and higher specific area, etc [27,28].

Among the transition metal hexacyanoferrate, manganese hexacyanoferrate (MnHCF) has attracted attention in some field due to the abundant raw materials, unique tunnel structure, low cost and higher specific area, etc [29,30]. Up to now, MnHCF are prepared and further widely applied in electrochemical sensors, sodium-ion batteries, supercapacitors, optical switching and other fields [29,31–34]. However, bulk MnHCF exhibits the defects of poor electrical conductivity and stability during the electrochemical measurements [29,33]. To solve the key issue, combining MnHCF with conductive materials (such as carbonaceous materials) is likely to be a feasible approach.

As one kind of carbonaceous materials, multi-walled carbon nanotubes (MWCNTs) are considered as very attractive active materials because of super mechanical strength, high surface area, environmental compatibility and unique electrical properties, etc [35–38]. Based on these advantages, combining MWCNTs with MnHCF is a meaningful idea to improve the electrochemical performance of MnHCF. It is expected that MnHCF/MWCNTs nanocomposite will give strong synergistic effects on enhancing the cycle stability and improving the electrochemical performance of MnHCF nanoparticles.

In this work, we reported a simple and effective method to synthesize MnHCF/MWCNTs nanocomposite. MWCNTs acted as conducting network and supporting backbone, thereby enhancing not only electrochemical stability but also the electrochemical specific capacity of MnHCF. Compared with MnHCF nanoparticles, MnHCF/MWCNTs nanocomposite exhibited larger specific capacity, excellent cycle stability and higher rate capability. The enhanced electrochemical performances of MnHCF/MWCNTs nanocomposite benefited from the strong synergistic effect between MnHCF nanoparticles and MWCNTs, showing that transition metal hexacyanoferrate compositing carbonaceous materials are promising electroactive materials for high performance supercapacitors.

2. Experimental

2.1. Reagents and materials

Potassium hexacyanoferrate ($K_3[Fe(CN)_6]$), sodium sulphate (Na_2SO_4), manganese acetate ($Mn(CH_3COO)_2 \cdot 4H_2O$) and ethanol (C_2H_5OH) were analytical grade and purchased from Chengdu Chemical Reagent Factory (Chengdu, China). Polytetrafluoroethylene (PTFE) and carbon black were purchased from Tianjin Chenhua Chemical Reagent Factory (Tianjin, China).

Commercial MWCNTs (outer diameter \times inner diameter \times length: 20–40 nm \times 10–15 nm \times 5–15 μ m, purity: >95%) were purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Science (Chengdu, China). MWCNTs were acidized in 8.0 M HNO_3 solution for 4 h under ultrasonication to remove the impurities and endow the surface with hydrophilic groups such as $-OH$ and $-COOH$.

Ni foam was purchased from Jinan Henghua Chemical Reagent Factory (Jinan, China). Ni foam substrates were treated under ultrasonication by sequentially immersing in acetone, deionized water and ethanol each for 20 min, respectively, and dried at 60 °C before use.

Distilled water was used throughout the experiments. High purity nitrogen (99.999%) was used for deaeration before electrochemical test.

2.2. Synthesis of MnHCF/MWCNTs nanocomposite

In a typical synthesis procedure of MnHCF/MWCNTs nanocomposite, 20 mL $Mn(CH_3COO)_2$ solution (0.030 M) was added into 1.00 mg mL⁻¹ MWCNTs suspension with different contents (10, 20, 30 and 40 mL) under ultrasonic treatment for 30 min. Subsequently, 20 mL $K_3[Fe(CN)_6]$ solution (0.020 M) was dropwise added into the above mixture under magnetic stirring at room temperature for 2 h. Finally, the as-obtained brownish yellow suspension were sealed and aged at room temperature for 24 h and then were collected by filtering and washing with deionized water and absolute ethanol. The as-obtained precipitates were dried at 80 °C for 12 h for further characterization.

Shown in Fig. 1 was schematic illustration of the synthetic procedure of MnHCF/MWCNTs nanocomposite.

As-prepared materials with different mass fraction of MWCNTs (0.00, 7.80, 14.50, 20.30 and 25.30 wt%) were marked as MnHCF, MFC-1, MFC-2, MFC-3 and MFC-4, respectively.

2.3. Characterization of as-prepared materials

The crystallographic structures of as-prepared materials were investigated by X-ray diffractometer (XRD, X' Pert PRO, Philips) with $Cu K_\alpha$ radiations ($\lambda = 0.15406$ nm) recorded from 10° to 80° at a speed of 2° min⁻¹. Fourier transform infrared (FTIR) spectroscopy of as-prepared materials was obtained from Nicolet 5700 (Nicolet Instrument Co., USA) in the wavenumber range of 4000–400 cm⁻¹ with KBr pellet. Field emission scanning electron microscopy (FE-SEM) images of as-prepared materials were acquired by Ultra 55 microscope (Carl Zeiss SMT Pte Ltd., Germany).

2.4. Electrode fabrication and electrochemical measurements

2.4.1. Fabrication of MnHCF/MWCNTs based electrode

MnHCF/MWCNTs based electrode was fabricated as follows. Briefly, as-prepared electroactive materials (MnHCF/MWCNTs nanocomposite), conductive carbon black and 10% PTFE emulsion were mixed with a mass ratio of 6: 2: 2 and dispersed in ethanol. The resulting mixture was ultrasonically treated for 30 min to form sticky slurry and then pasted onto nickel foam with size of 1.0 cm \times 2.0 cm (coated active area = 1.0 cm²), followed by drying at 80 °C under vacuum for 24 h. And then coated nickel foam was pressed to a thin foil under a pressure of 5.0 MPa. The mass loading of electroactive materials on nickel foam was about 10 mg cm⁻².

For comparison, pure MnHCF or MWCNTs based electrode was fabricated under the similar conditions while MnHCF or MWCNTs replaced MnHCF/MWCNTs nanocomposite, respectively.

Download English Version:

<https://daneshyari.com/en/article/6602810>

Download Persian Version:

<https://daneshyari.com/article/6602810>

[Daneshyari.com](https://daneshyari.com)