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Decoration of nickel hydroxide nanoparticles onto polypyrrole nanotubes with enhanced electrochemical performance for supercapacitors

Jun Zhang, Yang Liu, Huijuan Guan, Yafei Zhao*, Bing Zhang

School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, PR China

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ABSTRACT

A facile and novel method of growing nickel hydroxide nanoparticles on polypyrrole nanotubes ($Ni(OH)_2$/PNTs) is presented using methyl orange and ferric chloride formed fibrillar complex as self-degrading tubular template coupled with hydrothermal synthesis. The $Ni(OH)_2$/PNTs samples were characterized by SEM, TEM, FTIR, XRD and XPS. As pseudocapacitors, the obtained $Ni(OH)_2$/PNTs in three-electrode configuration display a significantly enhanced specific capacitance (864 F/g at 1 A/g), better rate performance, lower charge-transfer resistance and higher cycling performance (91.1% of the initial capacitance retention at 5 A/g over 2000 cycles) compared to the individual $Ni(OH)_2$ and PNTs, and previously reported composite electrodes based on $Ni(OH)_2$ or PNTs. Besides, the symmetric supercapacitors of $Ni(OH)_2$/PNTs in two-electrode configuration show a maximum energy density of 18.8 Wh/Kg at the power density of 414.6 W/Kg and a maximum power density of 3.4 kW/kg at the energy density of 8.4 Wh/Kg. The high electrochemical performance of $Ni(OH)_2$/PNTs can be attributed to the synergistic effect of both components and the unique nanostructure. These encouraging results reveal that the $Ni(OH)_2$/PNTs can be used as promising electrode materials for supercapacitors in energy storage. In addition, the method described in this paper provides a generalized route for the construction of transition metal oxides (hydroxides)/PNTs-based composite nanostructures with improved electrochemical performance.

1. Introduction

Electrochemical capacitor is a potential energy storage device with the advantages of high power density, long cycle life and comparable energy density and environmental friendliness [1–3]. In order to meet the requirements of green and renewable energy resources, the exploration of high performance for supercapacitors is still a great challenge [4,5]. Supercapacitors can be divided into electric double-layer capacitors (EDLCs) and pseudocapacitors on the basis of the charge storage mechanisms [6]. EDLCs have high electrical power and high stability but they store charge by reversibly adsorbing electrolyte ions at the interface of electrode, leading to a low capacitance [7–9]. Differently, pseudocapacitors store charge according to rapid redox reactions at or near the surface of electrode and reveal better capacitance and energy density compared to EDLCs [10,11].

Transition metal oxides/hydroxides such as MnO_2, NiO, Co_3O_4, $Ni(OH)_2$ and etc. are the main pseudocapacitive materials, which have been widely investigated as supercapacitors in consideration of their multiple oxidation states, low cost, and low toxicity [8,12–14]. Among various pseudocapacitive materials, nickel hydroxide ($Ni(OH)_2$) is an attractive candidate for high performance supercapacitors on accounts of its high specific capacitance, excellent chemical stability, easy preparation, and various morphologies [15,16]. However, the poor conductivity of pseudocapacitive $Ni(OH)_2$ hinders the rate of electron transfer, leading to a huge loss of capacitance and restricting their practical applications. In order to address these problems, an effective way to enhance the electrochemical performance of $Ni(OH)_2$ is incorporating conducting additives (graphene, carbon nanotubes, or carbonaceous species) to form pseudocapacitive nanocomposites [17]. These conductive materials can efficiently improve the conductivity of the

* Corresponding author.
E-mail address: zhaoyafei007@126.com (Y. Zhao).

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samples and short the electron and ion diffusion pathways. Polypyrrole (PPy) is one of the most important conductive polymers which are widely used in lots of fields, such as electrochemical sensor, advanced batteries, electrochemical capacitors, and etc. [18–20]. Due to its excellent energy storage ability, high degree of flexibility, high conductivity and strong hydrophobicity, PPy is considered as one of the most prospective functional materials for supercapacitors [18,21]. Researchers find that the morphology of PPy, such as nanospheres, nanowires and nanotubes, plays a vital impact on the electrochemical properties [21–23]. The one-dimensional polypyrrole nanotubes (PNTs) are famous for their faster electron transportation, relatively larger surface area and easier accessibility of electroactive species through their porous network than nanorods or nanowires [20]. However, as conductive polymer, PNTs have poor cycle-life compared with $Ni(OH)_2$ since they swell and contract substantially on charge and discharge respectively, which leads to premature attenuation and decrease of specific capacitance [24]. Modification or treatment of PNTs with inorganic materials is one possible approach to address the above problem [25]. Taking into account the characteristics of $Ni(OH)_2$ and PNTs, it will be significant to decorate $Ni(OH)_2$ particles onto the outer surface of PNTs, in which $Ni(OH)_2$ protects PNTs from intense swelling and contracting to some extend during charge and discharge and PNTs offers the efficient path for electron transport. We expect that excellent electrochemical performance can be achieved.

Herein, we developed a facile and novel approach to grow $Ni(OH)_2$ on the pre-synthesized PNTs coupled with hydrothermal synthesis. The one-dimensional, hollow, and tubular PNTs were synthesized by using fibrillar complex formed by self-assembly of methyl orange and ferric chloride and then polymerization of pyrrole. The as-synthesized $Ni(OH)_2$/PNTs exhibit high specific capacitance, good rate performance, low charge-transfer resistance and excellent cycling performance when working as electrodes for supercapacitors, attributing to the synergistic effects of both of the individual component. The $Ni(OH)_2$ provides high capacitance to a large extent, and the PNTs not only offers the efficient path for electron transport resulting in enhanced reaction kinetics between electroactive center and current collector but also supplies additional pseudocapacitance. The results reveal the great potential of $Ni(OH)_2$/PNTs as high-performance electrode materials for supercapacitors. Besides, the simple and scalable method described in this work may be feasible to prepare other transition metal oxides (hydroxides)/PNTs-based composite nanostructures with good electrochemical performance, which extends their potential applications in many fields.

2. Experimental section

2.1. Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were purchased from Tianjin Fengchuan Chemical Reagent Co. Ltd. China. Pyrrole, methyl orange (MO) and the other reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. China. All the reagents were used as received without purification. Deionized water was used throughout all the experiments.

2.2. Synthesis of PNTs

In a typical synthesis of PNTs, methyl orange (0.784 g) and $FeCl_3$ (4.5 g) were dissolved in deionized water (480 mL) with magnetically stirring for 30 min. Then a certain amount of pyrrole (0.7 mL) was added into the above solution and continuously stirred for 24 h at room temperature. After that, the formed precipitate was filtered and washed with deionized water and ethanol alternatively until the filtrate was colorless. Finally, the product was freeze-dried for 24 h, followed by vacuum drying at 70 °C for another 6 h.

2.3. Synthesis of $Ni(OH)_2$

The $Ni(OH)_2$ was obtained by hydrothermal method according to the following procedures: nickel nitrate (86.6 mg) was dissolved in deionized water (25 mL) under stirring for 0.5 h. Then ammonium hydroxide (NH_4OH) (0.4 mL, 28%) was added into the above suspension, followed with ultrasonication for 5 min. Then the reaction mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 180 °C for 2 h. The precipitate formed was collected by filtration, washed with deionized water and ethanol for several times and finally dried for 12 h under vacuum at 70 °C.

2.4. Synthesis of $Ni(OH)_2$/PNTs

First, the pre-weighted PNTs (5 mg) was dissolved in 25 mL deionized water, and treated with ultrasonication for 1 h. Then, 25 mL $Ni(OH)_2$ (2 mg/mL) precursor solution was added to the above suspension. The mixture was sonicated for 30 min and stirred for 1 h in order to obtain a uniform dispersion. Then the whole suspension was transferred to a Teflon-lined stainless steel autoclave and heated at 90 °C for 7 h. Finally, the resulting solution was filtered and washed with deionized water and ethanol for several times and then dried in vacuum oven at 70 °C for 12 h.

2.5. Material characterization

The morphologies and structures of the samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM, JEOL JEM-2100). The Brunauer-Emmett-Teller (BET) surface area was measured by a specific surface area analyzer (Quantachrone NOVA 2000e). Powder X-ray diffraction (XRD) patterns of the samples were carried out on an x-ray diffractometer (XRD, X'Pert PRO, PANalytical) with filtered Cu Kα radiation ($\lambda = 0.15406$ nm). Elemental composition analysis was performed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) using focused monochromatized Al Kα radiation.

2.6. Electrochemical measurements

Electrochemical analyses were carried out by using a three-electrode system equipped with a $Hg/Hg_2Cl_2/KCl$ reference electrode and a platinum counter electrode on a Princeton Applied Research VersaSTRAT electrochemical workstation. Working electrodes were prepared by the traditional slurry coating method. Specifically, the activated materials, acetylene black and binding material (PTFE) were mixed in the mass ratio of 80:10:10. Then, the mixture was pasted onto Ni foams (1 cm × 1 cm) with a mass of *ca.* 3 mg. All the electrochemical measurements include cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS).

The specific capacitances (Cs, F/g) can be calculated from the CV curves based on the following equation:

$$Cs = \int I \cdot \frac{dV}{v \cdot m \cdot \Delta V} \quad (1)$$

where I is the response current (A), v is the scan rate (V/s), m is the mass of electroactive materials in the electrodes (g), V is the potential (V).

It can also be obtained from the discharging progress according