

Nickel hydroxide-impregnated and -coated carbon nanotubes using an easily manipulated solvothermal route for supercapacitors



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ABSTRACT

Coaxial β -Ni(OH)₂ nanoparticle-impregnated and -coated CNT composites were fabricated via a facile and controllable solvothermal strategy. By reacting Ni(NO₃)₂ with NaOH before ethanothermal treatment the β -Ni(OH)₂ nanoparticles with diameters of several nanometers are densely packed on the surfaces of CNTs. Using ammonia hydroxide as precipitator and water/ethanol mixture as solvent the cavity of CNTs can be fully filled with the β -Ni(OH)₂ nanoparticles with diameters of \sim 3 nm. The key mechanism for the formation of the two different Ni(OH)₂/CNT composite structures lies in the different solvents and precipitation sequences. Both types of Ni(OH)₂/CNT composites exhibit enhanced specific capacitances compared with blank Ni(OH)₂ and the acidic CNTs. By loading 5 wt% of CNTs, the capacitance of Ni(OH)₂-impregnated composite is 65% higher than that of pure Ni(OH)₂ nanoparticles due to the enhanced electrical conductivity and unique cavity confined structure. These results imply that the CNT-confined structures are promising candidates for high performance supercapacitor.

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1. Introduction

With growing concern about the shortage of natural resources and the environmental deterioration, more and more studies have been focused on searching for renewable energy storage solutions [1–4]. Supercapacitor, one of the most promising types of energy storage devices, shows many unique advantages including high power performance, long cycle life and low maintenance cost [3,5,6]. Metal hydroxide materials, such as nickel hydroxide (Ni(OH)₂), arouse a lot of interests as cost-effective pseudocapacitive materials for fabricating supercapacitors because of their well-defined electrochemical redox activity, high specific capacitance, mild synthetic conditions and lower thermal budget than metal oxides [7–10]. In addition, it is easy to tune the morphologies and microstructures of Ni(OH)₂, such as crystallinity, crystal size, specific surface area, and so on, due to its low crystallization temperature. However, the poor electrical conductivity of metal hydroxide electrodes limits their power density for practical applications [8]. Considerable efforts have been made to improve the electrochemical performance of Ni(OH)₂ by tuning morphology at nanoscale and forming composite materials [11–13].

Carbon nanotubes (CNTs) are unique one-dimensional nanomaterials. Their hollow interior space and high specific surface

area can provide large amounts of electrochemical reactive sites for many applications such as supercapacitor, catalysis, etc. [7,14]. Attaching or filling various inorganic nanomaterial, such as metal, oxide, sulfide and halide, to or into CNTs have been widely studied to obtain the superior composites with heterostructures [15–17]. Previous studies have shown the benefits of using carbon nanotubes (CNTs) as conducting supports to confine the size of inorganic particles and thus to improve the specific capacitance [14]. The first problem encountered in such process is that CNTs have a strong tendency to agglomerate due to their inert surface and high length-to-diameter ratio. Moreover, a strong interfacial interaction between hydroxide and CNTs is highly desired to facilitate the charge transfer between the two components, which can enhance the electrochemical performance of the composites.

Recently, several attempts have been reported to combine the advantages of Ni(OH)₂ and carbon nanotubes. Kim et al. [7] synthesized oxidized carbon nanotube/Ni(OH)₂ composite by a chemical co-precipitation method, whereas a thin Ni(OH)₂ layer was uniformly formed on the CNT surface. Such composite showed higher energy and power densities than its single component. By embedding the Ni(OH)₂ nanoparticles inside the 3D matrix of CNTs/reduced graphene oxide using chemical vapor deposition method, more intimate contact was realized between the matrix and the active material, further boosting the electrocapacitive characteristics [8]. The distinguished example can be found for MnO₂: the MnO₂ nanoparticles confined in the CNT channels produced more than 50% higher specific capacitance compared to

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MnO₂ nanoparticles coated on the outer surface of CNTs [14]. So far, there still remains lacking controllable and reliable methods to fabricate hydroxide-in-carbon nanotubes composites.

In this paper, a facile solvothermal method was introduced to fabricate different types of Ni(OH)₂/CNT composites with easy control. We obtained Ni(OH)₂ nanoparticles-coated CNT composite, which exhibits an enhanced electrochemical properties relative to both pure Ni(OH)₂ and CNTs electrodes. By changing the solvent and the precipitator, the CNT composite with Ni(OH)₂ nanoparticles impregnated into their cavities was firstly fabricated in this work. The resulting coaxial composite exhibits an even greater specific capacitance than that of Ni(OH)₂-coated CNTs.

2. Experimental procedure

Pristine CNTs were oxidized by refluxing in concentrated nitric acid for 6 h at 140 °C. After the product was washed with distilled water, the acidic CNTs were obtained by further centrifugation and drying. Chemical modification of CNTs is necessary for: (1) introducing the functional groups onto the nanotubes and opening the nanotube tip; (2) dispersing the functionalized hydrophilic nanotubes in the solvents; (3) obtaining a good interfacial contact between the nanotubes and other materials.

For the preparation of Ni(OH)₂ nanoparticles-coated CNT composites (denoted as Ni-co-CNT), 0.05 g acidic CNTs were dispersed in 20 ml H₂O by ultrasonication, and then mixed with 60 ml of 0.167 M Ni(NO₃)₂·6H₂O aqueous solution. 20 ml of 2 M NaOH aqueous solution was dropwise added into the above mixture. The suspension was filtered and washed with ethanol repeatedly. The washed precipitate was re-dispersed in 60 ml of ethanol, which was transferred into a Teflon-lined autoclave and heated at 160 °C for 34 h. The product was finally obtained by further washing and drying. The blank Ni(OH)₂ samples without CNTs were produced using the same methods for comparison.

For the preparation of Ni(OH)₂ nanoparticles-impregnated-CNT composites (denoted as Ni-im-CNT), 0.05 g acidic CNTs were dispersed in 20 ml ethanol by ultrasonication, and then mixed with 50 ml of 0.1 M Ni(NO₃)₂·6H₂O aqueous solution. 5 ml concentrated ammonia hydroxide (NH₃·H₂O, 28 wt%) was dropwise added into the mixture. The obtained suspension was transferred into a Teflon-lined autoclave and heated at 180 °C for 24 h. The product was washed with ethanol and dried in vacuum at 80 °C for 24 h. The bare Ni(OH)₂ samples without CNTs were fabricated using the same methods as the control samples for comparison.

X-ray diffraction (XRD) was used to identify the phase of the samples with a D/MAX 2550 V (Rigaku, Japan) diffractometer using Cu K α radiation ($\lambda=1.5406$ Å). Transmission electron microscopy (TEM, JEM 2010, JEOL, Japan) and High resolution transmission electron microscopy (HRTEM, JEM 2010, JEOL, Japan) were used to characterize the microstructure of the composites. Electrochemical properties tests were carried out as follows. To measure the electrochemical properties, 0.05 g of sample was mixed with the binder composed of polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidinone (NMP) and pressed into a pellet. The pellet was mounted onto a foam nickel as a working electrode and dried at 80 °C for 24 h in vacuum. A standard three electrode electrochemical cell includes a Pt foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. 7.5 M KOH aqueous solution was used as the electrolyte. Cyclic voltammetric (CV) experiments were controlled by a ZF-3 potentiostat and ZF-4 potential scanner (Zhengfang Electronic Factory, Shanghai).

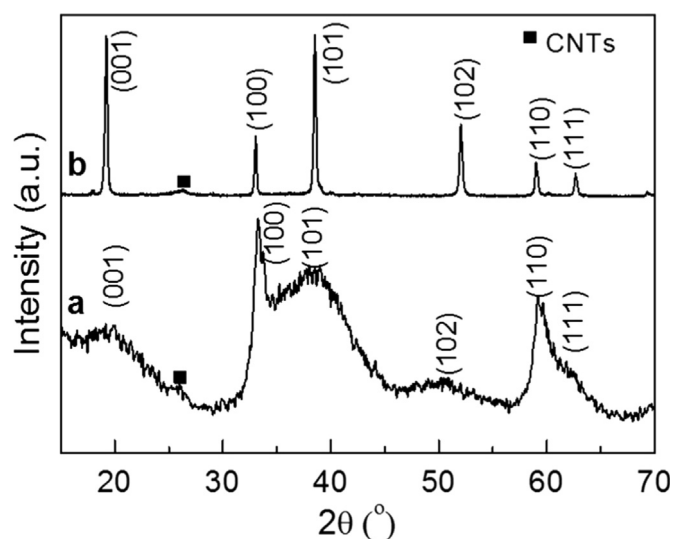


Fig. 1. XRD Patterns of (a) Ni-co-CNTs and (b) Ni-im-CNT composites.

3. Results and discussion

The XRD patterns of the obtained Ni(OH)₂/CNT composites are illustrated in Fig.1. All the diffraction peaks can be indexed to the hexagonal β -Ni(OH)₂ (JCPDS no. 14-0117). The small peak at 26.06° is attributed to the characteristic peak of CNTs. In curve (a), the diffraction peaks of Ni-co-CNT composite are remarkably broadened, which is due to the isoaxial nature of the Ni(OH)₂ nanoparticles coated on the outer surfaces of CNTs. While in curve (b), the diffraction peaks of Ni-im-CNT composite are much sharper. More interesting, the relative intensity of the (100) and (110) peaks in curve (a) are unusually stronger than those from the standard powder diffraction (JCPDS no. 14-0117). The difference in the relative intensity of the diffraction peaks between these two composites indicates their difference in microstructure and morphology [18].

The microstructure of the pristine CNTs used in this work is shown in Fig. 2. They are multi-walled carbon nanotubes (MWNTs) with closed tips and clean and smooth surfaces. The inner diameters of the nanotubes are about 10 nm. Fig. 3 shows the

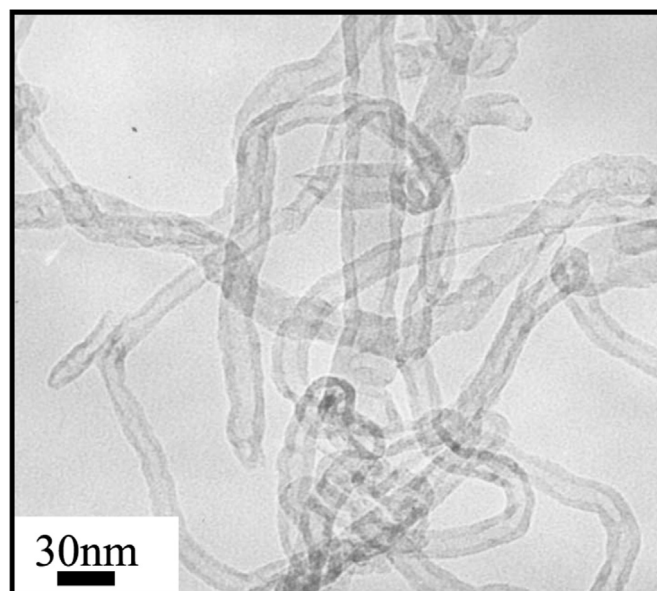


Fig. 2. TEM image of pristine MWNTs.

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