Electrochimica Acta 178 (2015) 439–446

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

In situ growth of nickel-cobalt oxyhydroxide/oxide on carbon nanotubes for high performance supercapacitors

Min Li, J.P. Cheng*, F. Liu, X.B. Zhang

State Key Laboratory of Silicon Materials, School of Materials Science & Engineering, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Zhejiang University, Hangzhou 310027, PR China

ARTICLE INFO

Article history:
Received 2 June 2015
Received in revised form 4 August 2015
Accepted 10 August 2015
Available online 12 August 2015

Keywords:
Nickel-cobalt oxyhydroxide
Nickel-cobalt oxide
Carbon nanotubes
Supercapacitor
Asymmetric capacitor

ABSTRACT

A carbon nanotubes (CNTs)-nickel-cobalt oxyhydroxide nanoflake core-shell structure is designed and fabricated by a facile one-step chemical bath deposition method at 80 °C. After its annealing at 300 °C, a CNTs/Ni-Co oxide core-shell heterostructure is thus achieved. Phase characterization proves that Ni-Co oxyhydroxide and Ni-Co oxide as shells are (Ni,Co)OOH and $NiCo_2O_4$, respectively. Structural analysis confirms that the as-synthesized oxyhydroxide and oxide shells are conformally coated on the external surface of CNTs. Electrochemical data demonstrate that (Ni,Co)OOH/CNTs composite exhibits a high specific capacitance of 853 F g^{-1} at 5 mV s^{-1} and an excellent high rate capability, with 75% retention after a 10-fold increase in current density. Meanwhile, the hybrid of $NiCo_2O_4$/CNTs has an enhanced performance of 940 F g^{-1} at 5 mV s^{-1}. Its rate capability is much better than the oxyhydroxide precursor because of its high conductivity. Both of these heterostructures have an excellent cycling performance of 100% capacitance retention after 10,000 cycles and Coulombic efficiency. An asymmetric capacitor is also fabricated with (Ni,Co)OOH/CNTs as positive electrode and activated carbon as negative electrode. It possesses a high specific capacitance of 164 F g^{-1} and a high energy density of 73.8 Wh Kg^{-1} within 1.8 V.

1. Introduction

With the issue of the severe environment pollution, developing clean energy systems and synthesizing high-efficient, sustainable materials for energy storage become two urgent requirements [1,2]. Electrochemical capacitor/supercapacitor is one of the most effective and practical devices for energy storage. Recently, considerable efforts have been devoted to the exploration of high-performance electrode materials for supercapaitor. Carbon-based materials, [3–6] transition metal oxides/hydroxides [1,7–10] and conductive polymers [11] are three common electrode materials for supercapacitor. With fast and reversible chemical reactions (redox reactions) during the charge and discharge processes, transition metal oxides/hydroxides are the most widely investigated.

Cobalt based compounds including cobalt oxide, hydroxide and oxyhydroxide have been fabricated and studied for high capacitance derived from Co^{4+}/Co^{3+} and Co^{3+}/Co^{2+} redox processes in an aqueous solution [12–16]. Those cobalt-based materials have been considered as promising candidates for electrode materials due to their low-cost and easy-fabrication. It was reported that the aggregated cobalt oxyhydroxide could only have a low capacitance less than 200 F g^{-1} due to its low surface area-resulted poor electroactivity [17]. Subsequently, numerous efforts have been dedicated to increase surface of cobalt oxyhydroxide through the building of various nanostructures to promote the electrode reactions. Recently, a core-shell nanostructure has shown promise as a means to enhance the electrochemical properties in these heterostructure [18]. This unique structure can make use of the synergistic effects from individual constituents and improve the surface area. Carbon nanotube (CNT) has been well investigated since 1991[19]. It can not only be used as an electrode material for electrical double-layer capacitors, but also serve as the backbone of guest electrode materials to form a hybrid with enhanced electrochemical performances due to its highly electrical conductivity. *In situ* growth of cobalt oxyhydroxide on the surface of CNTs is a good choice to form a core-shell structure. However, there are very limited reports on the fabrication of CoOOH/CNTs as electrode materials for supercapacitor. Zhu et al. found that a hybrid of CoOOH nanorods with CNTs had a specific capacity of 312 F g^{-1}, much higher than

* Corresponding author. Tel./fax: +86 571 87951411.
E-mail address: chengjp@zju.edu.cn (J.P. Cheng).

http://dx.doi.org/10.1016/j.electacta.2015.08.041
0013-4686/

that of pristine CoOOH (136 F g^{-1}) [20]. CNTs were used to form nanostructured composites with CoOOH through electrodeposition as reported by Zheng et al. The as-formed CoOOH/CNTs multilayer structure facilitated the transportation of electrolyte ions, resulting in the specific capacitance promotion of CoOOH to be 389 F g^{-1} [21,22]. Zhu and co-workers reported a two-step hydrothermal-oxidation method to fabricate a composite of CoOOH nanoplates/CNTs and it could be as a cathode material for supercapacitor to achieve 270 F g^{-1} at a current density of 1 A g^{-1}. Here, we report a facile one-step route to synthesize core-shell structured CoOOH/CNTs composite by chemical bath deposition. Meanwhile, we can change the composition of CoOOH to be Ni-Co oxyhydroxide by the same method.

On the other hand, the relatively low electrochemical capacitance and poor cycling performance limit the possible usage of cobalt-based materials in energy storage. It is well-known that nickel-based materials usually have higher capacitances as well as lower cost than cobalt-based materials. A practical strategy is to incorporate nickel element into cobalt-based materials [23–25]. Nickel-cobalt binary oxides, hydroxides and sulfides have been thus widely investigated in the past decade [26–33]. They could exhibit enhanced performance and outstanding advantages over single metal system. However, to the best knowledge of ours, Ni-Co oxyhydroxide as electrode material for supercapacitor has not been reported yet. In this work, we will synthesize Ni-Co oxyhydroxide/CNTs composites by a chemical deposition method under a low temperature, where Ni-Co oxyhydroxide is conformally and homogeneously coated on the surface of CNTs. Both the unique heterostructure containing CNTs as core and the introduction of Ni can benefit its specific capacitance and cycling stability. Combination with an annealing under a reasonable temperature, a CNTs/Ni-Co oxide core-shell structure similar to its Ni-Co oxyhydroxide/CNTs precursor is thus synthesized. These two Ni-Co heterostructures are well characterized and their electrochemical properties are compared in detail.

2. Experimental

2.1. Preparation of materials

To oxidize the surface of CNTs, 100 mg pristine CNTs and 3 g potassium persulfate ($K_2S_2O_8$) were dispersed into 150 mL distilled water for 1 h by sonication. This process introduced functional groups (*e.g.* hydroxyl, carbonyl, and carboxyl, **Fig. S1** in Supplementary materials) onto the surface of CNTs. Then, a chemical bath deposition (CBD) method was carried out to prepare CoOOH and (Ni,Co)OOH onto CNTs. Total 0.0045 mol metal sulphate (0.0045 mol cobalt sulphate for CoOOH, 0.003 mol cobalt sulphate and 0.0015 mol nickel sulphate for (Ni,Co)OOH) and 350 mL water were added into above solution. With strong stirring, 15 mL 1 wt% ammonia was added dropwise into the metal-cations containing solution. After 2 hrs reaction at 80 °C, CoOOH and (Ni,Co)OOH nanoflakes were then *in situ* grown onto the surface of CNTs. In the obtained Ni-Co oxyhydroxide/CNTs composite, the mass content of CNTs was evaluated to be 10 wt% by carefully weighing their final product. Meanwhile, the XPS result demonstrates that the ratio of Co to Ni is 1: 0.58. So, to be precise, the (Ni,Co)OOH composite stoichiometry is $Ni_{0.37}Co_{0.63}OOH$. The resultant Ni-Co oxyhydroxide/CNTs was then heated at 300 °C for 2 h with a heating rate of 2 °C min^{-1} in air to obtain nickel-cobalt oxides/CNTs.

For comparison, the same procedure was also carried out using 200 mg and 50 mg of CNTs. When the mass of CNTs was 200 mg, the SEM image showed an uneven distribution of oxyhydroxide nanosheets on CNTs. On the other hand, for 50 mg CNTs, the oxyhydroxide nanosheets layer on CNTs was very thick. (**Fig. S2** in Supplementary materials)

2.2. Materials characterization

The phase structure and morphology of the samples were characterized by powder X-ray diffractometer (XRD, using Cu-Kα

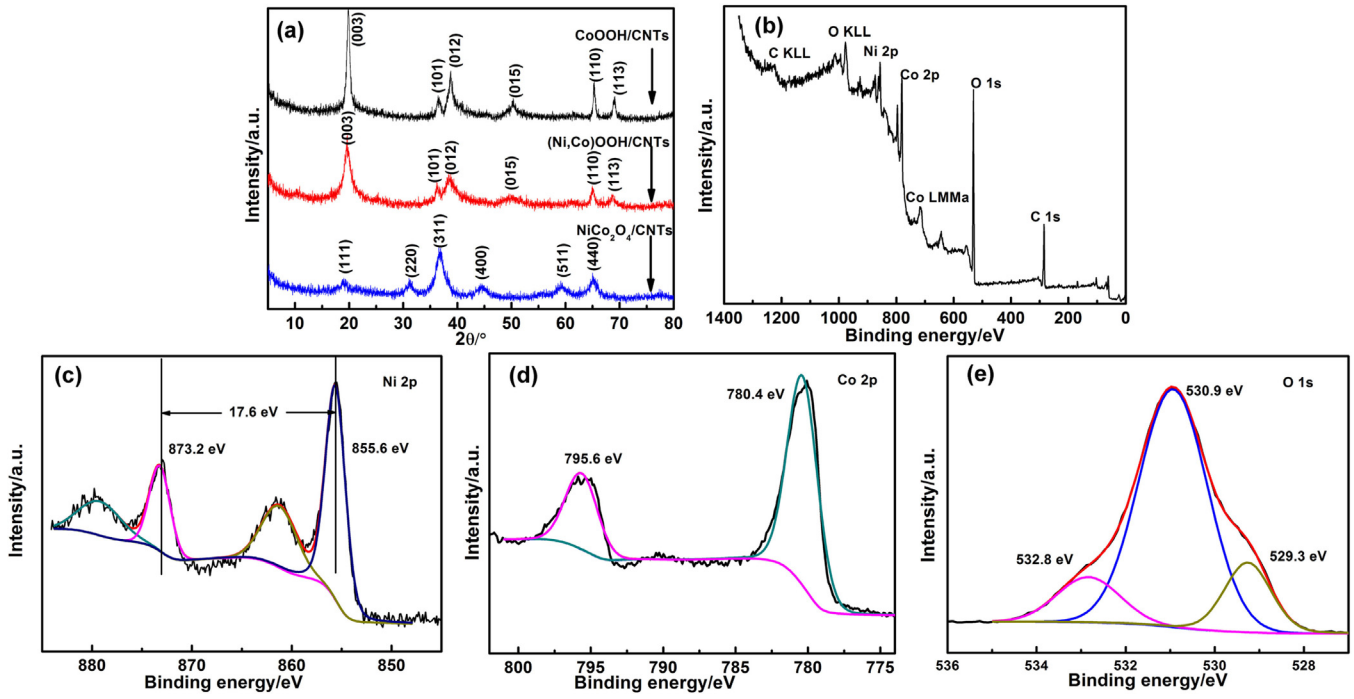

Fig. 1. **(a)** XRD patterns of samples CoOOH/CNTs, (Ni,Co)OOH/CNTs and $NiCo_2O_4$/CNTs, **(b)** XPS wide spectrum and **(c)** Ni 2p, **(d)** Co 2p and **(e)** O 1s spectra of (Ni,Co)OOH/CNTs composite.