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$NiCoO_2$ flowers grown on the aligned-flakes coated Ni foam for application in hybrid energy storage

Xiaoyang Xu [a], Huilin Zhao [a], JingKuo Zhou [a], Ruinan Xue [a], Jianping Gao [a, b, *]

[a] Department of Chemistry, School of Science, Tianjin University, China
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

HIGHLIGHTS

- The $NiCoO_2$ flowers were grown in the $NiCoO_2$ flakes coated Ni foam.
- The $NiCoO_2$/Ni foam was directly used as the working electrode without any binders.
- The specific capacitance of $NiCoO_2$/Ni foam can reach 756 F/g at 0.75 A/g.
- The $NiCoO_2$/Ni foam//rGO hybrid supercapacitor show high energy density.

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ABSTRACT

Many $NiCoO_2$ flowers with an average diameter of about 4 μm were grown on the $NiCoO_2$ flakes coated Ni foam (denoted as $NiCoO_2$/Ni foam) through a simple hydrothermal method and confirmed by scanning and transmission electron microscopies, X-ray diffraction and X-ray photoelectron spectrum measurements. The $NiCoO_2$/Ni foam with high specific area and porosity was directly used as the working electrode without any binders. The measured specific capacitance of $NiCoO_2$ grown on Ni foam is 756 F/g at 0.75 A/g using a three-electrode setup in 1 M KOH. Considering the high capacity of $NiCoO_2$ and the good stability of rGO, the $NiCoO_2$/Ni foam//rGO hybrid supercapacitor combining $NiCoO_2$/Ni foam and rGO shows very good properties, such as high specific capacitance (82 F/g at 2 A/g based on the total mass of active materials), high energy density (25.7 Wh/kg at 1500 W/kg based on the total mass of active materials), good stability (about 90% capacitance retention after 2000-cycle at 100 mV/s), and low charge ion transfer resistance.

1. Introduction

The clean energy conversion and storage devices, such as supercapacitors, Li-ions batteries and fuel cells, have been vigorously exploited to reach the global excellent environment goal. Especially for supercapacitors, their research interest has been rising at alarming rates in the past several years, and predicted to be still growing at soon in the future, owing to their remarkable superiorities, including short charge time, high power density and long lifetime [1–4].

The properties for supercapacitors greatly depend on the inherent features of electrode materials [5,6]. Transition metal oxides can not only store charge like carbon materials, but also offer rich Faradic redox reactions due to the multiple valence states, which can generate high capacitance. Thus transition metal oxides can be described as alternative electrode materials. Especially, some oxides of inexpensive, abundant and environmentally benign transition metal elements, such as Mn, Co and Ni, have attracted enormous interest. Moreover, the mixed transition metal oxides, such as $MnCo_2O_4$, $NiCo_2O_4$, have been investigated to own higher electrical conductivity and capacitance than single components [7]. The mixed nickel cobaltite oxides have been widely studied on account of the co-existence of Ni and Co, that is, Ni^{2+} can replace Co^{2+} in the spinel Co_3O_4 and cubic crystal CoO to form $NiCo_2O_4$ and $NiCoO_2$ respectively [8].

Recently, many researches about the preparation and supercapacitive performances of $NiCo_2O_4$ have been reported, such as nanoflakes [9], nanoparticles [10], nanowires [11] and flowers [12].

* Corresponding author. Department of Chemistry, School of Science, Tianjin University, China.
E-mail address: tjujianpinggao@163.com (J. Gao).

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However, few studies on the synthesis and supercapacitor evaluation of $NiCoO_2$ have been investigated. Du et al. prepared $NiCoO_2$ single-crystalline nanoparticles with a specific capacitance of 184 F/g at 1 A/g [13]. Xu et al. synthesized $NiCoO_2$ nanotubes for supercapacitors based on the template of polymeric nanotubes [14]. Moreover, some $NiCoO_2$ based composites, like $CoNiO_2$/TiN–TiOxNy composites [15], branched $CoMoO_4$@$CoNiO_2$ core/shell nanowire arrays [16] and N-doped reduced graphene oxide (rGO)/$NiCoO_2$ [17], have been also determined to use in supercapacitors. In addition, $NiCoO_2$ with some other structures, including nanowires [18] and flowers [19], has been used for water oxidation and Li-ion batteries, rather than supercapacitors. Therefore, the supercapacitor performances of $NiCoO_2$ with the specific structure are worth being researched. It is reported that the hierarchical structures can not only inherit the merits of the single components but also provide novel properties form the synergistic interactions between the nano building blocks [20]. The Ni foam was used to be the template in the preparation procedure of $NiCoO_2$. It was surprised to find that the hierarchical $NiCoO_2$ flowers grown on the aligned-flakes coated Ni foam were formed (denoted as $NiCoO_2$/Ni foam) and then it was used for supercapacitors. Compared with the reported similar works [19,21], the novelties are as follows: (a) the good interconnectivity from flowers grown on the aligned-flakes can promote the charge ion transport; (b) it can be directly used as the electrode without binders, avoiding the contact limitation of active materials with electrolyte from binders; (c) the flower-like $NiCoO_2$ is the first time to be used in supercapacitors, to our knowledge.

In order to explore the practical value of $NiCoO_2$/Ni foam, the hybrid supercapacitor ($NiCoO_2$/Ni foam//rGO) was established with $NiCoO_2$/Ni foam as the positive material and rGO as the negative material. The 1 M KOH was selected as the electrolyte on account of low cost, safety and environmental friendliness [22]. In view of this design, this hybrid supercapacitor combines the high capacity of $NiCoO_2$ as well as the good stability of rGO.

2. Experimental

2.1. Materials

$NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, urea, ethanol, hydrazine hydrate, etc. were purchased from Tianjin Jiangtian Chemical Technology Company without any post-processing. Ni foam was from Kunshan dessco Electronics Company. Graphite was from Qingdao Graphite Factory.

2.2. Preparation of $NiCoO_2$/Ni foam

The Ni foam was sheared into the pieces (1.0 × 4.0 × 0.15 cm^3, 30 mg/cm^2) and then treated with acetone, ethanol and deionized water under ultrasonic processing to remove the surface oxidation layer. 0.3 mmol of $NiCl_2 \cdot 6H_2O$, 0.3 mmol of $CoCl_2 \cdot 6H_2O$ and 3 mmol urea were dissolved into the mixture of ethanol and deionized water (10/10 mL) under stirring to obtain a clear solution. Then the solution and the clean Ni foam were transferred into a Teflon-lined autoclave and maintained at 100 °C for 8 h. After cooling, the coated Ni foam was picked out, washed with deionized water and dried at 60 °C to obtain $NiCoO_2$ precursor/Ni foam. The $NiCoO_2$ precursor/Ni foam was annealed at 300 °C for 3 h in N_2 atmosphere to achieve $NiCoO_2$/Ni foam.

2.3. Preparation of rGO

The graphite was oxidized into graphene oxide (GO) by a modified Hummer' method [23]. Then GO was reduced into rGO by hydrazine hydrate at 90 °C.

2.4. Characterization

The scanning electron microscopy (SEM) measurement of $NiCoO_2$/Ni foam and rGO was performed using S4800 microscope (Hitachi Limited, Japan). Transmission electron microscopy (TEM) images of $NiCoO_2$ and rGO were got using Philips Tecnai G2F20 microscopy (Netherlands). The X-ray diffraction (XRD) patterns of $NiCoO_2$/Ni foam and rGO were measured with the given step (4° min^{-1}) using a D8 FOCUS diffractometer with Cu Ka radiation as reference target. The X-ray photoelectron spectrum (XPS) measurement of $NiCoO_2$ was conducted using a PHI1600 ESCA System spectrometer (PERKIN ELMER, USA) with Al Kα radiation.

2.5. Electrochemical measurement

The $NiCoO_2$/Ni foam (1 × 1 cm^2) was directly used as the working electrode. The rGO, carbon black and polytetrafluoroethylene with a mass ratio of 75:15:10 were mixed and coated on Ni foam (1 × 1 cm^2) and then used as a working electrode. The large-area Pt mesh and HgO/Hg were assigned as counter and reference electrode, respectively. The performance tests of $NiCoO_2$/Ni foam and rGO single electrodes were conducted in a three-electrode system in 1 M KOH electrolyte.

The hybrid supercapacitor was assembled with $NiCoO_2$/Ni foam (1 × 1 cm^2) and rGO as positive and negative electrodes, cellulose membrane as separator, KOH (1 M) as electrolyte. Before assembling the device, the two electrodes and separator were immersed into 1 M KOH for 2 h. The performances of this $NiCoO_2$/Ni foam//rGO hybrid supercapacitor was studied using a two-electrode system.

The testing technologies contain cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) cycles and electrochemical impedance spectroscopy (EIS). In the EIS measurements, the frequency range is from 10 mHz to 100 kHz with the applied potential amplitude (5 mV). The specific capacitances of the single electrode based on the mass of active materials (*Cm*, F/g), hybrid supercapacitor device based on the total mass of active materials (C_M, F/g) and hybrid supercapacitor device based on the total mass of the device (*Cd*, F/g) were determined according to Eqns. (1)–(3) respectively. The energy density (*E*, Wh/kg) and power density (*P*, W/kg) based on the total mass of active materials for the hybrid supercapacitor were calculated using the following Eqns. (4) and (5). The energy density (*Ed*, Wh/kg) and power density (*Pd*, W/kg) based on the total mass of the device for the hybrid supercapacitor were also determined using Eqns. (6) and (7).

$$Cm = \frac{i \times \Delta t}{\Delta v \times m} \quad (1)$$

$$C_M = \frac{i \times \Delta t}{\Delta V \times M} \quad (2)$$

$$Cd = \frac{i \times \Delta t}{\Delta V \times Md} \quad (3)$$

$$E = \frac{1000}{2 \times 3600} C_M (\Delta V)^2 \quad (4)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (5)$$