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Full Length Article

One-step integration of the C/$NiCo_2O_4$ mesoporous nanoneedle arrays on Ni foam for high-performance hybrid supercapacitors

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ABSTRACT

In this work, the uniform C/$NiCo_2O_4$ mesoporous nanoneedle arrays grown on Ni foam (NF) as a composite electrode are synthesized by a facile one-step hydrothermal and annealing processes. Due to the introduction of the carbon originating from glucose in hydrothermal process, the electrochemical performances of the hybrid electrode are effectively improved compared to the $NiCo_2O_4$. The unique structure is beneficial for facilitating ion transport between electron and electrolyte and accelerating the redox reaction, which makes the composite deliver prominent electrochemical properties, including a high areal capacitance (4.974 F/cm^2 at 2 mA/cm^2), remarkable rate capability and cycling stability. In addition, the C/$NiCo_2O_4$ electrode has a bright prospect for high performance supercapacitor applications because of excellent electrochemical performances and an easy synthetic method.

1. Introduction

With the development of social economic, the demand for high-efficiency, eco-friendly energy storage devices gradually increases for solving energy depletion and environmental pollution [1–5]. Supercapacitors (SCs) have been widely investigated as electrical energy storage devices because of high power density, fast charge/discharge rate and long cycle life [6–8]. The electrochemical performances of supercapacitors are depended on electrode materials, mainly including carbon-based materials [9–11], transition metal oxides/hydroxides [12–16] and conducting polymers [17,18]. Besides, the suitable base also plays a vital role. Such as Ni foam, as a result of high porosity, large ratio surface area and unique three-dimensional network structure, has been widely used in storage devices [19,20].

The electrode materials based on carbon that have aroused attention for supercapacitors owing to high power capability, long cycle stability and high safety. A variety of carbon materials such as reduced graphene oxide (RGO) [21,22], carbon nanotubes (CNTs) [23], carbon nanofibers (CNFs) [24], carbide-derived carbons (ACs) [25,26], hollow carbon nanospheres (HCNs) [27], nitrogen-doped mesoporous hollow carbon spheres (NHCS) [28], 3D graphene foams (GFs) [29] had been reported on previous literatures.

Beyond that, the transition metal oxides have caused great concerns due to different electrochemical valence states that offer richer redox reactions. At present, $NiCo_2O_4$ as a ternary oxide compared with the binary nickel or cobalt oxides, has more advantages, such as better electrical conductivity and higher theoretical specific capacitance [30–32]. However, the $NiCo_2O_4$ supercapacitor electrode material encounters several major problems such as low practical capacitance, inferior rate performance, and poor cycling stability [33]. Recently, many researches have devoted to solve these problems. He et al. had prepared $NiCo_2O_4$ hollow microspheres with tunable numbers and thickness of shell by hard templates method, which exhibits remarkable rate capability [34]. Through a controlled hydrolysis process and followed by a thermal annealing treatment, Hao et al. have prepared hierarchically yolk-shelled $NiCo_2O_4$ spheres, which showed a capacitance up to 835.7 F/g at 0.5 A/g and excellent cycling stability of 93% retention after 10,000 cycles [35]. The $NiCo_2O_4$/NF presented a specific capacitance of 835 F/g at 2 A/g [36]. The PPy-$NiCo_2O_4$@CPF electrode displayed the specific capacitance of 910 F/g at a current density of 1 A/g and cyclic stability was 88% after 10,000 cycles [37]. Zhang et al. have prepared the unique heterostructured rGO/$NiCo_2O_4$, which delivers high area capacitance (up to 4.37 F cm^{-2} at the current density of 2 mA cm^{-2}) and outstanding cycling stability with capacitance retention of 90% after 2000 charge–discharge cycles [38]. The hybrid Ni_2CoS_4@$NiCo_2O_4$ composite electrode shows a high areal capacitance of 1.86 F cm^{-2} at 1 mA cm^{-2} [39].

In this work, the C/$NiCo_2O_4$ mesoporous nanoneedle arrays fabricated on NF as a composite electrode were synthesized by one-step hydrothermal and annealing processes. The facile synthetic method directly aligned on NF and the mesoporous structure of the nanoneedle arrays offer superior electron transport between the electrolyte and

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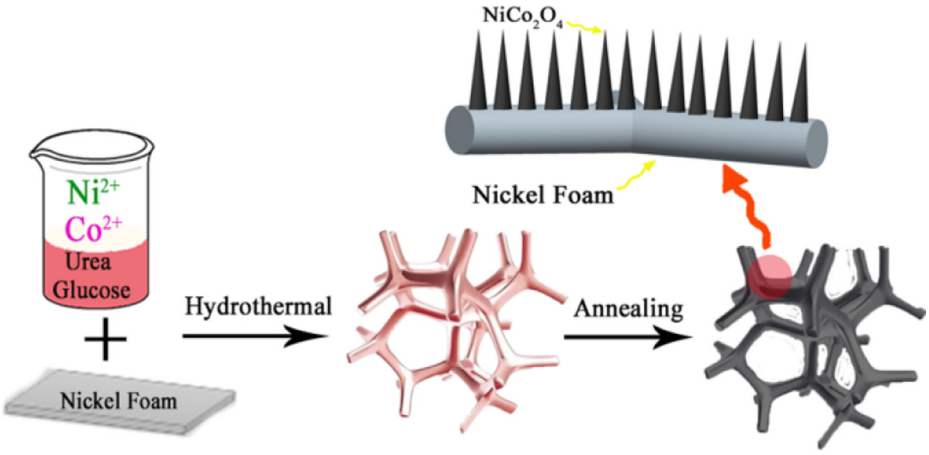

Scheme 1. Schematic illustration of the fabrication of the C/$NiCo_2O_4$ composite on NF.

electrode material. Besides, the composite combining conductive carbon material and transition metal oxide has some synergistic effects, including excellent cycling stability of carbon material, the larger areal capacitance of transition metal oxide [40].

2. Experimental section

2.1. Pretreatment of NF

A piece of NF (3.5 cm × 1 cm) was processed under ultrasonication for 20 min in acetone, distilled water and ethanol sequentially. NF substrate treated was dried at 60 °C all night in a vacuum drying oven [41].

2.2. One-step hydrothermal synthesis of the C/$NiCo_2O_4$ nanoneedle arrays on NF

Here, 0.0216 g (0.12 mmol) of glucose monohydrate ($C_6H_{12}O_6{\cdot}H_2O$), 0.2908 g (1mmol) of nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), 0.5821 g (2mmol) of cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and 0.6006 g (10 mmol) of urea (H_2NCONH_2) were dissolved in 35 mL of distilled water, leading to a homogeneous mixture solution under stirring for 30 min constantly. A piece of treated NF and the above solution were transferred together into 50 mL Teflon-linked stainless autoclave, maintained at 180 °C for 4.5 h. The NF depositing with the pink substance was washed with distilled water and alcohol after the autoclave was cooled. Finally, the sample was dried at 60 °C all night. The sample with the pink precursor was annealed at 350 °C for 5 h to transform into the C/$NiCo_2O_4$ under N_2 atmosphere. For comparison, pure $NiCo_2O_4$ was synthesized in the absence of glucose but with the other experimental parameters constant.

2.3. Structural characterization

SEM images were investigated with JEOLJSM-7800F field-emission scanning electron microscope to obtain the morphologies of the samples. The morphologies were further observed by Transmission electron microscope (TEM; Zeiss LIBRA 200 FEG TEM) and high resolution TEM (HRTEM, 200 kV). The X-ray diffraction (XRD) information was collected to characterize the phase of the sample on a PANalytical Empyrean Diffractometer, operated from the 2θ = 5–90° with Cu (Ka) radiation. The chemical states were characterized by using X-ray photoelectron spectroscopy (XPS, VG Escalab 250 spectrometer). Micromeritics ASAP 2020 Surface Area and Porosity Analyzer using Nitrogen adsorption at 77 K was used to investigate the surface area and pore structure of the samples.

2.4. Electrochemical measurements

Three-electrode system was made up for the electrochemical measurements of the as-prepared electrodes in 3 mol/L KOH, operated with an electrochemical workstation (CHI760E, Shanghai Chenhua, China). A platinum sheet (1 cm × 1 cm) and Hg/HgO electrode were used as the counter and reference electrodes. And the C/$NiCo_2O_4$ grown on NF (1 cm × 1 cm) was used as a work electrode. cyclic voltammetry (CV) tests, galvanostatic charge − discharge (GCD) tests and electrochemical impedance spectroscopy (EIS) tests were recorded sequentially from 0 to 0.7 V at various scan rates, 2–10 mA/cm^2 and 100 kHz to 0.01 Hz.

3. Results and discussion

3.1. Material characterizations

The one-step fabrication procedure of the C/$NiCo_2O_4$ grown on NF is illustrated in Schematic 1. Firstly, the pink precursor of the C/$NiCo_2O_4$ grown on NF was synthesized by one-step hydrothermal. Then, the black C/$NiCo_2O_4$ nanoneedle arrays were achieved through the annealing process.

Typically, to analyze the morphologies of the prepared samples, the scanning emission microscopy (SEM) was performed. Fig. 1a and b show the low magnification images of the $NiCo_2O_4$ and the C/$NiCo_2O_4$, respectively. It can be seen from the pictures that the $NiCo_2O_4$ and the C/$NiCo_2O_4$ have been loaded on NF, and outside NF both are spinous microspheres agglomerating together. Seen from Fig. 1c and d, the morphology of the samples on NF consists of the nanoneedle arrays, and a few were reunited as like-spinous microspheres. It is worth noting that the nanoneedle arrays of the C/$NiCo_2O_4$ are more homogeneous and uniform than the $NiCo_2O_4$. Fig. 1e and f, the nanoneedle arrays of the C/$NiCo_2O_4$ are smaller in diameter than the $NiCo_2O_4$ on NF with the addition of glucose in hydrothermal process. To sum up, the composite of the C/$NiCo_2O_4$ was fabricated on Ni foam in the form of the smaller and homogeneous nanoneedle arrays, which could shorten ion diffusion distance to promote the ion exchange between solution and material. So, the presence of carbon may be able to optimize the morphology and improve electrochemical performances of composite. As shown in Fig. 1(g–j), the elemental mappings of the composites were obtained to clarify the composition and distribution of elements. It is obvious that Ni, Co, O and C are distributed uniformly in composites.

The X-ray diffraction (XRD) patterns of the C/$NiCo_2O_4$ and the $NiCo_2O_4$ were shown in Fig. 2a to analyze the crystal structure of the samples. There are no appreciable distinctions in the diffraction peaks of the C/$NiCo_2O_4$ and the $NiCo_2O_4$ at 2θ = 18.9°, 31.3°, 36.8°, 44.5°, 59.1° and 65.1°, corresponding to planes of (1 1 1), (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) crystal planes of cubic spinel $NiCo_2O_4$ phase