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Ultra-long life nickel nanowires@nickel-cobalt hydroxide nanoarrays composite pseudocapacitive electrode: Construction and activation mechanism

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ABSTRACT

A three dimensional hierarchical composite electrode composed of nickel nanowires@nickel-cobalt double hydroxide aligned on nickel foam is successfully fabricated by an in-situ growth route. In this composite electrode, the nickel nanowires are used as core materials to support high-pseudocapacitance nickel-cobalt double hydroxide and construct the typical Ni nanowires core@Ni-Co double hydroxide shell hierarchical structure on Ni foam. Compared with Ni-Co double hydroxide/Ni foam electrode (without nickel nanowires), the electrochemical performance of the obtained composite electrode is apparently improved, which shows a high areal specific capacitance (2.25 F cm^{-2} at 5 mA cm^{-2}), excellent rate capability (1.65 F cm^{-2} at 100 mA cm^{-2}) and superior cycle stability (151.2% retained in the 20000th cycle). And the activation mechanism of ultra-long cycle life of the obtained composite electrode is studied in this work, which indicates that the transforms of surface atoms on Ni nanowires into high-pseudocapacitance $Ni(OH)_2$ and NiOOH during cycles make major contributions for the performance improvement.

1. Introduction

The growing demand of energy has deeply promoted the research on electrode materials with high performance for energy storage and conversion devices [1–3]. Supercapacitors, considered as one of the most promising candidates for the next generation of energy storage and conversion devices, have drawn a lot of attention for their high power density, short charge/discharge time and long cycling lifetime among various power source devices [4–7]. Metals double hydroxides (M-DH), as the typical pseudocapacitive active materials for supercapacitors, attract the extensive attention owing to their high redox activity, low cost and environmentally friendly nature [8]. Such as NiAl-DH, CoAl-DH, NiMn-DH and NiCo-DH etc [9–19]. Among these metals double hydroxides, NiCo-DH is one of the most studied positive electrode materials due to its relatively high redox activity and highly reversible charge/discharge abilities [20]. For example, the Ni-Co binary hydroxides nanorods exhibit 1030 F g^{-1} at 3 A g^{-1} [21]. Layered Co–Ni hydroxide hierarchical structure is up to 1965.6 F g^{-1} at 5 A g^{-1} [22]. A mesoporous Co_xNi_{1-x} layered double hydroxide shows a specific capacitance of 1809 F g^{-1} at 1 A g^{-1} and remains at about 90.2% of the initial value after 1000 cycles at 10 A g^{-1} [23]. However, the unsatisfactory cycling stability has been difficult to achieve due to poor intrinsic conductivity and aggregation of active species during in the process of making electrodes. More troublesome, the electrochemical mechanism of cycling stability decline is very poorly explained only in a few references.

An efficient method to solve the unsatisfactory cycling stability and break through charge storage capability is to grow active materials on current collectors with special structure, such as, carbon fiber, graphene, carbon nanotubes (CNTs) and Ni Foam [24–27]. Beyond that, forming a typical core-shell nanostructure in which structural features of each component are thoroughly present to

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guarantee sufficient exposure of active sites, fast ion/electron transport to realize the full potential of the composite materials. Based on these advantages, the electrode with well-organized nanoarrays grown directly on a collector tends to show a high electrochemical performance. For instance, the Co_xNi_{1-x} LDHs deposited onto stainless steel electrode has a specific capacitance of 2104 F g^{-1} [28]. The Ni-Co hydroxide film on Ni foam displays a significantly enhanced specific capacitance of 2682 F g^{-1} at 3 A g^{-1} [22]. Thus it can be seen that these electrode designs are particularly significant for the performance improvement of electrode materials.

In this work, we fabricated a novel 3D nickel nanowires@nickel-cobalt double hydroxide core-shell structure aligned on nickel foam (NiNW@NiCo-DH/NF) electrode by a facile hydrothermal method. The nickel nanowires are used as core materials to support high-pseudocapacitance NiCo-DH, and the integrated NiNW/NF composite substrate are worked as an excellent binder-free current collector. It is worth mentioning that both of the growth of NiNW on NF and NiCo-DH on NiNW is by an in-situ growth route, leading to the robust interfacial adhesion between NiCo-DH nanoarrays, NiNW backbone and NF substrate. Benefited from the design of 3D hierarchical nanostructure and highly active NiNW, the NiNW@NiCo-DH/NF electrode exhibits ultra-long cycle stability in addition to excellent charge storage capability.

2. Experiment section

2.1. Materials

Ni foam (110 PPI; 1.7 mm thick) was soaked in diluted hydrochloric acid solution (0.35 M) for 15 min under ultrasonic condition. Then, the resulting foam was washed several times with deionized water and dried at 60 °C under vacuum for further use. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification.

2.2. Preparation of integrated Ni nanowires grown on Ni foam composite substrate

The integrated NiNW/NF composite substrate was synthesized by a simple water bath method. First, a prepared solution of $NiCl_2$ aqueous solution (0.05 M) was mixed with triton X-100 aqueous solution (0.05 M) according to the scale of one to one under continues stirring conditions. After 30 min, the resulting light blue solution (200 mL) was transferred to a 250 mL beaker. Then, a piece of treated Ni foam, used as the substrate for the growth of Ni nanowires, was upright in the middle of the 250 mL beaker and treated by ultrasonication for a few minutes. After that, the beaker containing the mixed solution was transferred to the water bath pot and heated up to 70 °C. Next the mixed solution of 15 mL $N_2H_4 \cdot H_2O$ (85%) with 0.75 mL NaOH solution (1 M) was added. After 1.5 h, the Ni foam coated with a layer of black and fluffy NiNW was obtained leaving aside the clear solution. The product (NiNW/NF) was washed with deionized water and ethanol for several times and treated by ultrasonication to remove unstable Ni nanowires attached on the surface. Finally, the NiNW/NF was dried at 60 °C under vacuum for further use. If no NF was used in the synthetic procedure of NiNW/NF, then the NiNW would be obtained.

2.3. Synthesis of 3D Ni nanowire@NiCo-DH/Ni foam

For the synthesis of 3D core-shell structured NiNW@NiCo-DH/NF, the as-prepared NiNW/NF composite substrate was placed vertically in the middle of 100 mL Teflon lining. After that, the well-prepared mixed solution of 0.75 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 1.5 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 4.5 mmol hexamethylenetetramine (HMT) in the 60 mL deionized water was added, followed by ultrasonication for 15 min. Then, the Teflon lined autoclave was sealed and heated at 120 °C for 8 h. After being cooled to ambient temperature, the product (NiNW@NiCo-DH/NF) was collected, followed by ultrasonication with deionized water and ethanol. In the end, the NiNW@NiCo-DH/NF was vacuum dried for 12 h to prepare for the next step. For the sake of comparison, NiCo-DH/NF was synthesized with a similar process to that of NiNW@NiCo-DH/NF except NF which was directly used as substrate instead of NiNW/NF. If no substrate was used, then the pure NiCo-DH power would be obtained.

2.4. Materials characterization

X-ray diffraction (XRD) patterns were performed by Bruker D8 Advance diffractometer with Cu Kα radiation at 40 KV, 40 mA. The morphology and size of the samples were investigated by scanning electron microscope (SEM, JEOL JSM-7100F). Fourier transform infrared (FT-IR) spectra was recorded on a Nicolet Nexus 470 spectrometer with KBr pellets. X-ray photoelectron spectroscopy (XPS) measurements were characterized using Thermo Fisher Scientific Escalab 250Xi spectrometer with Al Kα radiation.

2.5. Electrochemical measurements

Electrochemical measurements were performed in a three-electrode system using a CHI 760D electrochemical workstation. The 6 M KOH, platinum foil and Hg/HgO electrode were used as the electrolyte, counter and reference electrodes, respectively. The as-obtained samples were pressed into thin flake and directly used as working electrode without further processing, the mass loading value of NiNW@NiCo-DH/NF is about 1.1–1.2 mg cm^{-2}. The electrochemical properties of the as-prepared electrodes were evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) technique.

3. Results and discussion

The general fabrication processes of 3D NiNW@NiCo-DH/NF are illustrated in Fig. 1. First, the NiNW/NF was obtained with the assistance of hydrazine hydrate as a reducing agent in alkaline conditions and nickel ions as the metal ion sources. Then, the NiCo-DH nanoarrays grown on the nickel nanowires by a simple hydrothermal method. In this reaction, HMT solution produces OH^- ions by the heat, which reacted with Ni^{2+} and Co^{2+} to form nickel and cobalt hydroxide monomers on the surface of nickel nanowires, and then nickel and cobalt hydroxide monomers were converted to NiCo-DH by olation reactions and crystallization. For the next step, the as-obtained sample was directly used as working electrode. In present study, nickel nanowires worked as core materials to support high-pseudocapacitance NiCo-DH and formed the well-defined NiCo-DH shell/NiNW core hierarchical structure on nickel foam. The growth of NiNW on NF is an in-situ self-assembly process, which enables the robust interfacial adhesion between NiNW and NF substrate. Combined with the advantages of large specific surface area, high intrinsic conductivity and robust interfacial adhesion, the integrated NiNW/NF composite substrate can work as an excellent binder-free current collector and serve as a good template to synthesize 3D hierarchical core-shell structured NiNW@NiCo-DH/NF electrode for the applications of supercapacitors.

The morphologies of Nickel nanowires and NiNW@NiCo-DH/NF are shown in Fig. 2 by SEM. The low-magnification image of NiNW (Fig. 2a and b) shows an all direction extending network structure