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Construct hierarchical electrode with $Ni_xCo_{3-x}S_4$ nanosheet coated on $NiCo_2O_4$ nanowire arrays grown on carbon fiber paper for high-performance asymmetric supercapacitors

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HIGHLIGHTS

- Hierarchical $NixCo_{3-x}S_4$@$NiCo_2O_4$/CFP pseudo-capacitive based electrode was designed.
- High discharge gravimetric capacitance of 1501 Fg^{-1} was achieved.
- Ni_2CoS_4@$NiCo_2O_4$/CFP//carbon xerogel device delivers a energy density of 32.2 $Whkg^{-1}$.
- The device shows an excellent cycling ability (87.6% retention after 10,000 cycles).

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ABSTRACT

In order to boost the energy density of supercapacitors, the strategy of using advanced pseudo-capacitive electrode and asymmetric device architecture is feasible and effective. Herein, we report a significant advance in the design and synthesis of a new hierarchically nanostructures with a series of controllable Ni/Co molar ratios of $Ni_xCo_{3-x}S_4$ (i.e., $NiCo_2S_4$ and Ni_2CoS_4) nanosheets coatings have in situ grown on $NiCo_2O_4$ nanowires arrays on a flexible carbon fiber paper (CFP). Remarkably, the hybrid Ni_2CoS_4@$NiCo_2O_4$ composite electrode delivers the highest discharge gravimetric capacitance of 1501 F g^{-1}, and areal capacitance of 1.86 F cm^{-2} at 1 mA cm^{-2}. Furthermore, coupled with nitrogen-doped carbon xerogels anode, we have fabricated a 1.6 V asymmetric supercapacitor (Ni_2CoS_4@$NiCo_2O_4$//nitrogen-doped carbon xerogels), such device delivers a maximum energy and power densities of 32.2 Wh kg^{-1} and 2.5 kW kg^{-1} in 1.0 M KOH electrolyte, respectively, and an excellent cycling stability (~87.6% retention after 10,000 cycles).

1. Introduction

The tremendous demand for energy storage devices with high energy density and power density, long lifespan, and short charging time characteristic is urgently needed to meet the rapid development of electric vehicles (EVs) or hybrid electric vehicles (HEVs), portable electronic products and large-scale grid energy storage in our daily life [1–3]. Supercapacitors are emerging as attractive energy storage devices due to their high power density, excellent cyclability (over 500,000 cycles) and fast charge time (few minutes) [4,5]. However, supercapacitors suffer from their lower energy density (<5Wh kg^{-1}) as compared to rechargeable lithium ion batteries (120–200 Wh kg^{-1}) [4]. According to the energy density calculation formula ($E = 0.5CV^2$, where C is specific capacitance and V is working voltage) [3], one way to increase the energy density of supercapacitors is to use pseudo-capacitive materials, such as transition metal oxides (MnO_2, NiO, Co_3O_4, V_2O_5, etc.), hydroxides ($Ni(OH)_2$) and conductive polymers [6–14], where reversible Faradaic redox reactions occured at the electrode surface enable charge storage, thus offering much higher specific capacitance compared with electrical double-layer capacitors (EDLCs), whereas its charge storage only rely on electrostatic accumulating in the electric double-layer near interfaces of the electrode/electrolyte.

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However, most of pseudocapacitive materials show either low electronic conductivity or poor electrochemical stability, which limited electrode to support ultra-fast electron transport toward high rate charge-discharge capability. To solve this problem, numerous efforts have been focused on developing three-dimensional (3D) additive/binder-free electrode architectures to avoid the "dead surface" effect existed in traditional slurry derived film electrode and allow for more efficient ion and electron transport, those include 3D conducting carbonaceous network nanostructures (for example, graphene, carbon nanotubes and carbon nanofibers) as backbone to scaffold the pseudo-capacitive electrode materials [15–18,43,44], "core-shell" coaxial nanostructure arrays [12,13,19], meso-porous/macro-porous architecture foams [6,20], free-standing papers/cloths/textiles or sponges [21–24], and so forth. Despite that great progresses have been achieved on the aspect of the rate capability and cycling stability of those electrodes, there is still a big challenge in further improving the capacitance.

Recently, binary transition metal oxides (for example, $NiCo_2O_4$) and sulfides (such as $NiCo_2S_4$ and Ni_2CoS_4) nanostructures have been investigated as a new type electrode material due to their capability of providing multiple Faradaic redox reactions for pseudo-capacitor with excellent performance [25–30]. Particularly, binary nickel cobalt sulfides electrode exhibited an electric conductivity of ~100 times higher than that of $NiCo_2O_4$ [31,32], although $NiCo_2O_4$ is higher than the corresponding single component oxides (either nickel oxides or cobalt oxides) by over 2 orders of magnitude in electric conductivity [33]. Furthermore, with both cobalt and nickel ions, binary nickel cobalt sulfides can offer much richer Faradaic redox reactions than corresponding single component sulphides. Taking all these considerations into account, high electric conductivity of binary nickel cobalt sulfides nanostructures can be considered as a good functionalized material for constructing hybrid electrodes for pseudo-capacitors. Herein, we report a significant advance in the design and synthesis of a new hierarchically hybrid nanostructures for pseudo-capacitors. A series of controllable Ni/Co molar ratios of binary nickel cobalt sulfides (typically expressed as $Ni_xCo_{3-x}S_4$, i.e., $NiCo_2S_4$ and Ni_2CoS_4) nanosheets coatings were in situ grown $NiCo_2O_4$ nanowires arrays on a flexible CFP. Such a hierarchical electrode design has following characteristics: (1) Firstly, one-dimensional (1D) structure of $NiCo_2O_4$ nanowire uniformly grown on CFP was acted as backbone to support and provide reliable electrical connection to the binary nickel cobalt sulfides nanosheet coatings with large surface areas accessible to electrolyte, enabling fast ionic diffusion and electronic conduction through the electrode; (2)In addition, the nanosheet morphology of binary nickel cobalt sulfides coatings posses richer Faradaic redox reaction due to its larger interlayer space and higher electronic conductivity; (3) Finally, the synergistic effect of this hierarchical nanostructure will contribute to improve the specific capacity, rate capability and cycle-life of these pseudo-capacitive materials. As a result, the hybrid Ni_2CoS_4@$NiCo_2O_4$/CFP electrode delivers the highest discharge gravimetric capacitance of 1501 F g^{-1}, and areal capacitance of 1.86 F cm^{-2} at 1 mA cm^{-2}. In addition, when coupled with nitrogen-doped carbon xerogels anode, we have fabricated a 1.6 V asymmetric supercapacitor, such device delivers a maximum energy and power densities of 32.2 Wh kg^{-1} and 2.5 kW kg^{-1} in 1.0 M KOH electrolyte, and an excellent cycling stability (~87.6% retention after 10,000 cycles).

2. Experimental section

2.1. Preparation of $Ni_xCo_{3-x}S_4$ nanosheets coatings on $NiCo_2O_4$ nanowires arrays on the CFP

Firstly, $NiCo_2O_4$ nanowires arrays were prepared by a facile hydrothermal synthesis method. In a typical procedure, the solution containing 30 mM $Co(NO_3)_2$, 15 mM $Ni(NO_3)_2$ and 50 mM urea was transferred into a 30 mL Teflon-lined stainless steel autoclave. One piece of carbon fiber paper (1.5 × 3 cm^2) vertically inserted into the holder and followed by heating the solution to 120 °C in an electric oven, then kept at this temperature for 16 h. The as synthesized electrode was washed in the DI water and rinsed with ethanol for several times, dried at 70 °C for 12 h under the vacuum environment, and annealed at 350 °C in air for 2 h to get the $NiCo_2O_4$/CFP electrode. Then, the growth of $Ni_xCo_{3-x}S_4$ nanosheets coatings on this $NiCo_2O_4$/CFP electrode was carried out through a simple electrochemically co-deposition method with some modifies [30]. The electrodeposition solution contains 5 mM $CoCl_2 \cdot 6H_2O$ with different concentrations of $NiCl_2 \cdot 6H_2O$ (2.5 mM for $NiCo_2S_4$ preparation and 7.5 mM for Ni_2CoS_4 preparation) and 0.75 M thiourea. The electrochemical deposition process was carried out in a three-electrode cell using $NiCo_2O_4$/CFP electrode as the working electrode, Pt as counter electrode, and Ag/AgCl as reference electrode by cyclic voltammetry method at a scan rate of 5 mVs^{-1} for 15 cycles within a voltage range between 0.2 V and −1.2 V. This prepared $Ni_xCo_{3-x}S_4$@$NiCo_2O_4$/CFP electrode was washed by DI water and ethanol for several times and then vacuum drying at 70 °C for 12 h.

2.2. Characterization

The morphology and microstructure of the samples were systematically investigated by scanning electron microscopy (SEM, Hitachi S-5200), transmission electron microscopy (TEM, JEOL 2010), high resolution transmission electron microscopy (HRTEM, Field Emission JEOL 2100), X-ray photoelectric spectroscopy (XPS, ESCALAB 250XI, Al Kα, 150) and X-ray diffraction (XRD, Rigaku D/Max Ultima II Powder X-ray diffractometer equipped with Cu kα radiation (λ = 0.15406 nm)) measurements.

2.3. Electrochemical measurements

The effective area of all the samples above immersed inside the electrolyte is controlled at around 1.5 × 3 cm^2. The electrochemical performance tests were carried out at room temperature in both three-electrode (half-cell) and two-electrode (full-cell) configurations. In the typical three-electrode measurements, the electrochemical tests were conducted with a CHI 660E electrochemical workstation (Chenhua, Shanghai) in an aqueous 1.0 M KOH electrolyte where nickel-cobalt sulfide coated on $NiCo_2O_4$ nanowires arrays grown on CFP serves as the working electrode, platinum foil as the counter electrode and a standard calomel electrode (SCE) as the reference electrode. In the full-cell measurement, an asymmetric supercapacitor with nickel-cobalt sulfide coated on $NiCo_2O_4$ nanowires arrays grown on CFP acting as positive electrode and a nitrogen-doped carbon xerogels film as negative electrode was assembled in the pouch cells. A 1 M KOH solution was used as electrolyte for all electrochemical measurements. The electrochemical performance was tested in the above mentioned electrochemical workstation by the techniques of cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy (EIS). The gravimetric and area specific capacitance values were calculated from the galvanostatic charge-discharge curves according to the following equations (1)–(4):

half-cell:

$$C_s = \frac{I}{\frac{\Delta V}{\Delta t} m} \quad (1)$$