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A novel three-dimensional hierarchical $NiCo_2O_4/Ni_2P$ electrode for high energy asymmetric supercapacitor

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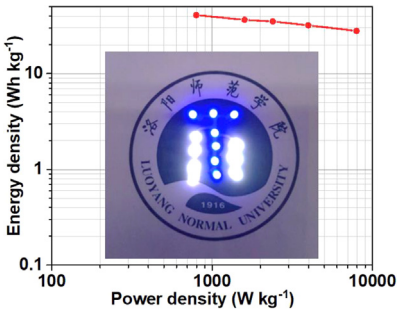
HIGHLIGHTS

- Hierarchical $NiCo_2O_4/Ni_2P$ electrodes on nickel foam are rationally constructed.
- This unique structure provides more electroactive sites for Faradaic reaction.
- The $NiCo_2O_4/Ni_2P$-30 electrode exhibits a high specific capacity of 2900 F g^{-1}.
- The assembled asymmetric supercapacitor can easily power 14 LEDs.

GRAPHICAL ABSTRACT

Three-dimensional hierarchical $NiCo_2O_4/Ni_2P$ electrodes have been successfully synthesized for advanced asymmetric supercapacitors.



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ABSTRACT

Herein, a novel three-dimensional hierarchical $NiCo_2O_4/Ni_2P$ structure is successfully fabricated through a facile hydrothermal and subsequent electrodeposition process. One-dimensional Ni_2P nanoneedles decorate on two-dimensional $NiCo_2O_4$ nanosheets can effectively enhance the electrical conductivity and surface area of $NiCo_2O_4$ to promote fast Faradaic reaction. The optimized $NiCo_2O_4/Ni_2P$-30 electrode exhibits a high specific capacity of 2900 F g^{-1} at 0.008 A cm^{-2}. Moreover, an asymmetric supercapacitor (ASC) is fabricated by using the $NiCo_2O_4/Ni_2P$-30 as positive electrode and activated carbon as the negative electrode, the device achieves an excellent electrochemical property with the energy density of 40.7 W h kg^{-1} at 800 W kg^{-1}. Besides, the as-assembled device also exhibits an excellent cycling performance of ~92.0% of initial capacitance after 5000 cycles indicating its outstanding conductivity and structural stability. All of the results demonstrate that the hierarchical $NiCo_2O_4/ Ni_2P$ composites are electrodes in energy storage application.

1. Introduction

With increasing demand of hybrid electric vehicles and portable electronic devices, supercapacitors are of great interest due to their ultrahigh power density, near-infinite long cycling life and fast recharge capability [1,2]. However, the relatively low energy density restricts its extensive practical applications for next generation supercapacitors. Based on the equation of energy density (E), $E = 0.5C\Delta V^2$, seeking for

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appropriate electrode materials and maximizing the specific capacitance (C) is an effective method to improve the energy density of supercapacitors [3,4]. According to the storage mechanism, pseudocapacitor electrode always exhibit more superior capability than that of double layer capacitor [5,6]. Transition metal oxides are considered to be one of the most potential pseudocapacitor electrode materials due to their various oxidation states for the redox reaction process that enable a high theoretical capacity [7–9]. Among which, $NiCo_2O_4$ with high theoretical specific capacitance, high availability and low toxicity has received tremendous interest recently. More importantly, it is reported that $NiCo_2O_4$ nanosheets possesses large surface area can be served as a backbone to form 3D hierarchical hybrid nanostructures with other highly active electrode materials [10–14]. However, the semiconducting nature of $NiCo_2O_4$ determines there is no obvious superiority when compared with conductors, which limiting the enhancement of rate capacity and cycling stability [15,16].

Combination of other materials with good electrical conductivity and high capacity into $NiCo_2O_4$ is conductive to defects introduction and charge transfer, which is a potential route to solve above problem. Conducting polymers, metal sulfides and metal phosphide had been integrated with $NiCo_2O_4$ to generate the synergistic effect of all individual components [17–20]. Among which, nickel phosphide is an ideal novel electrode material not only possesses high capacity, but also provides high electrical conductivity due to the existence of covalent bonds and metal bonds. Several nickel phosphide-based electrode materials such as Ni_2P, Ni_7P_3, Au/$Ni_{12}P_5$, Ni_2P/Ni and Ni_2P@CoAl-LDH had been reported as high performance supercapacitor electrodes [21–24]. Liu et al. reported a hybrid supercapacitor electrode consisting of honeycomb-like biphasic Ni_5P_4–Ni_2P (Ni_xP_y) nanosheets. Benefiting from the synergistic effect of the multicomponent systems and unique structure, the synthesized Ni_xP_y delivers an ultrahigh specific capacity (1272 C g^{-1} at 2 A g^{-1}) as well as good cycling stability (90.9% capacity retention after 5000 cycles). In addition, an asymmetric capacitor employing Ni_xP_y as the positive electrode and activated carbon as the negative electrode, displayed a significantly high energy density of 67.2 W h kg^{-1} at 0.75 kW kg^{-1} [21]. Besides, amorphous Ni_2P nanoparticles reported by Wang et al., when served as pseudocapacitive materials, which exhibit a large specific capacitance of 1597 F g^{-1} at a current density of 0.5 A g^{-1} and good cycling stability of 71.4% after 1000 cycles [25]. To further improve the performance of Ni_2P, An et al. fabricated Ni_2P/reduced graphene oxide composites via a low-temperature solid state reaction method, The as-prepared electrode demonstrates interesting supercapacitive properties of 2266 F g^{-1} and superior cycling stability [26].

Herein, we present a facile and efficient method to prepare three-dimensional (3D) hierarchical $NiCo_2O_4$/Ni_2P onto nickel foam through a mild hydrothermal synthesis and an electrodeposition technique for the first time. In the unique hybrid nanostructures, One-dimensional Ni_2P nanoneedles decorated on two-dimensional $NiCo_2O_4$ nanosheets could evidently increase the active surface area and provide effective exposure of active sites for Faradaic redox reaction, which is beneficial for ion diffusion and promoting electrolyte accessibility. When assembled a $NiCo_2O_4$/Ni_2P//activated carbon asymmetric supercapacitor, the device can reach a maximum energy density of 40.7 W h kg^{-1} and the corresponding power density of 800 W kg^{-1}, as well as a good long-term cycling stability of 92.0% capacity retention after 5000 cycles.

2. Experimental

2.1. Synthesis of Ni foam supported $NiCo_2O_4$ nanosheets

Prior to the synthesis, a piece of Ni foam (1 × 2 cm^2) was washed ultrasonically with 3 M HCl, deionized water and ethanol in sequence. Next, a certain amount of $Ni(NO_3)_2{\cdot}6H_2O$ (0.96 mmol), $Co(NO_3)_2{\cdot}6H_2O$ (1.92 mmol), NH_4F (1.6 mmol) and urea (4.8 mmol) were dissolved in 20 mL deionized water. After stirring for 30 min and forming a pink solution, a piece of treated Ni foam was added into above pink solution. Then, an autoclave contained above mixture was maintained at 110 °C for 4 h in an oven. Finally, the $NiCo_2O_4$ nanosheets coated on Ni foam substrate were obtained and washed with deionized water and absolute ethanol before drying under vacuum at 60 °C. The final products were further treated by calcining at 320 °C in static air for 2 h [18].

2.2. Synthesis of the hierarchical $NiCo_2O_4$/Ni_2P core-shell composites

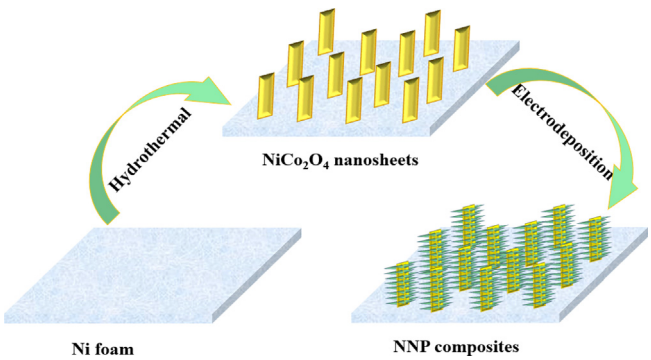
CHI 760E electrochemical workstation (CH Instruments Inc, China) was used to carry out the electrochemical measurements. Hierarchical $NiCo_2O_4$/Ni_2P core-shell nanosheets arrays were synthesized by electrodepositing Ni_2P nanoneedles on the surface of $NiCo_2O_4$ nanosheets in a standard three electrode configuration. A Pt foil and silver/silver chloride (Ag/AgCl) electrode were used as the counter electrode and reference electrode, respectively. The $NiCo_2O_4$/ Ni foam electrode immersed in 100 mL electrolyte containing of 0.7 mmol $NaH_2PO_2{\cdot}H_2O$, 0.2 mmol $C_6H_5Na_3O_7{\cdot}2H_2O$ and 1.75 mmol $NiSO_4{\cdot}6H_2O$. The cyclic voltammetry (CV) deposition process was conducted in the potential range from −1 to 0 V with a sweep rate of 20 mV s^{-1} for different cycles. Then, the obtained $NiCo_2O_4$/Ni_2P electrode was washed with deionized water and absolute ethanol before drying at 60 °C. The obtained composite electrode materials with different scanning cycles (15, 20, 25, 30 and 35 cycles) were named as NNP-15, NNP-20, NNP-25, NNP-30 and NNP-35, respectively (Scheme 1).

2.3. Materials characterization

The crystallographic phases of as-prepared products were determined by an X-ray diffraction (XRD D/MAX-2500) diffractometer equipped with Cu-Kα radiation source. The morphology and microstructure of as-fabricated products were investigated by using a field emission scanning electron microscope (FESEM, Hitachi Japan S-4800) and a transmission electron microscope (TEM, Tecnai FEI, G2F20 S-Twin) with an accelerating voltage of 200 kV. Further evidence for the composition of the product was recorded from X-ray photoelectron spectroscopy (XPS using an ESCALAB_250Xi) with 150 W Al Kα X-ray sources.

2.4. Electrochemical performance measurements

All of the electrochemical performance was measured in 3 M KOH aqueous solution. During the three-electrode system, Ni foam supported NNP, a platinum plate and a saturated calomel electrode were served as the working electrode, counter electrode and reference electrode, respectively. Cyclic voltammetry (CV) and constant-current galvanostatic (GV) charge-discharge curves were recorded to evaluate the electrochemical behaviors. Electrochemical impedance spectroscopy (EIS) was



Scheme 1. Schematic fabrication process of $NiCo_2O_4$/Ni_2P core–shell nanoarrays on Ni foam.