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One-step synthesis of self-supported Ni_xP nanowires/Ni hybrid foam as battery-like electrode for high-performance supercapacitors

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HIGHLIGHTS

- Ni_xP nanowires/Ni hybrid foam is obtained by a facile and large-scale method.
- Supercapacitor performance for Ni_xP nanowires/Ni hybrid foam is investigated.
- Ultrahigh rate performance is observed for Ni_xP nanowires/Ni hybrid foam.
- Ni_xP nanowires/Ni hybrid foam shows long-term cycling stability.

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ABSTRACT

The search of low-cost, earth-abundant and high electro-capacitive electrode materials is significant for the practical application of supercapacitors. Here we introduce a simple and cost-effective strategy for one-step synthesis of self-supported Ni_xP nanowires/Ni hybrid foam electrodes from commercially available Ni foams via low-temperature thermal phosphorization. This electrode exhibits superior electrochemical capacitive performance featured by an ultrahigh-rate performance (0.36 C cm^{-2} at 100 mA cm^{-2}) and long cycling stability (a stable capacitance of 0.74 C cm^{-2} at 20 mA cm^{-2} for 5000 cycles), which benefits from the good electrical conductivity of Ni_xP nanowires active materials on Ni foam and one-dimensional structure for Ni_xP. This work demonstrates a facile and effective avenue to prepare a cheap and efficient super-capacitive electrode for the practical application of supercapacitors.

1. Introduction

Supercapacitors have attracted great interest in recent years for high-power electric vehicles due to their high power density with good cycling performance [1]. The properties of supercapacitors largely depend on electrode materials. Many researchers work hard to develop new types of electrode materials and electrochemical energy storage systems which can balance the relationship between the optimal electrochemical performance and cost [2–4]. In particular, nickel phosphides (Ni_2P, $Ni_{12}P_5$ et al.), which possess much higher intrinsic conductivity than nickel oxides and have abundant natural resources, are promising pseudo-capacitor materials [5]. The first paper on the supercapacitor materials for Ni_2P was reported by An and coworkers [6]. They used Ni_2S/graphene oxide as the precursor to prepare Ni_2P/reduced graphene oxide (Ni_2P/rGO) composites by 500 °C solid state reaction method. The as-prepared composite electrodes exhibited a high specific capacitance of 2266 F g^{-1} at 5 mA cm^{-2} and superior cycling performance. Tu's group [7] developed the electro-less nickel plating process based on Ni_2P particle to obtain Ni-coated Ni_2P (Ni_2P/Ni) composites. The as-obtained composite electrodes delivered high specific capacitances of 581 F g^{-1} at 1 A g^{-1} and 464 F g^{-1} at 40 A g^{-1}, respectively. Wang and coworkers [8] prepared amorphous Ni-P (Ni and Ni_3P phase) by a facile solvothermal method. The amorphous Ni-P material exhibited larger specific capacitance and better cycling stability than the crystalline Ni-P material. In order to further enhance the electrochemical capacitive performance of nickel phosphides, metal doped (NiCoP sample) [9] and material coating [10–12] were also reported using complex methods. However, it is still a challenge to prepare nickel phosphides using a simple, large scale and low-cost synthetic method for practical application of supercapacitors. Recently, Ni foam has been extensively used as a conductive substrate to prepare the

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binder-free supercapacitor electrode [13–15]. Herein, inspired by Xiao's work [16], they developed a facile method for nickel phosphide nanowire array/Ni foam electrode by direct phosphorization treatment of commercial Ni foam. The as-prepared samples exhibit outstanding overall water splitting catalytic performance. Therefore, we modify this method to prepare self-supported Ni_xP nanowires/Ni hybrid foam, which can be directly as a supercapacitor electrode without adding additional conductive agents and binders. The as-prepared Ni_xP nanowires/Ni hybrid foam displays a high specific capacitance of 0.36 C cm^{-2} even at a high current density 100 mA cm^{-2}, enhanced rate and excellent cycling stability, which can make it for the practical application of supercapacitors.

2. Experimental section

2.1. Self-supported Ni_xP nanowires/Ni hybrid foam

The Ni foam (1 cm*4 cm) was pretreated with 6 M hydrochloric acid in an ultrasonic bath for 30 min to remove the nickel oxide layer. After acid treated, the Ni foam was cleaned with de-ionized water and ethanol for several times. NaH_2PO_2 was used as the P source, which was placed under foam nickel in one porcelain boat. The mole ration of P:Ni was control to be 5:1. The porcelain boat was placed at the center of the alumina tube furnace. Before heating, the high-pure N_2 gas was introduced into the tube furnace for 1 h to exclude the air. Then the tube furnace was heated to 300 °C at a rate of 1 °C min^{-1} and kept at this temperature for 2 h in a static N_2 atmosphere. After this, the as-obtained sample was washed with de-ionized water by ultrasonic treatment for three times and dried at 60 °C for 12 h in a vacuum oven. The loading mass of active materials is about 1 mg cm^{-2}.

2.2. Material characterization

The structures of as-prepared samples were carried out on Bruker D8 Advanced X-ray diffractometer (XRD) with a Cu Ka radiation. Scanning electron microscope (SEM) with energy dispersive X-ray (EDX) of as-prepared samples was determined on Hitachi S3400N.

2.3. Electrochemical measurements

A three-electrode system, (a Pt plate as the counter electrode, Hg/HgO electrode as a reference and as-prepared Ni_xP nanowires/Ni hybrid foam as a working electrode), was used to perform supercapacitive measurements in 2M KOH electrolyte. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) were carried on CHI 660E electrochemical workstation.

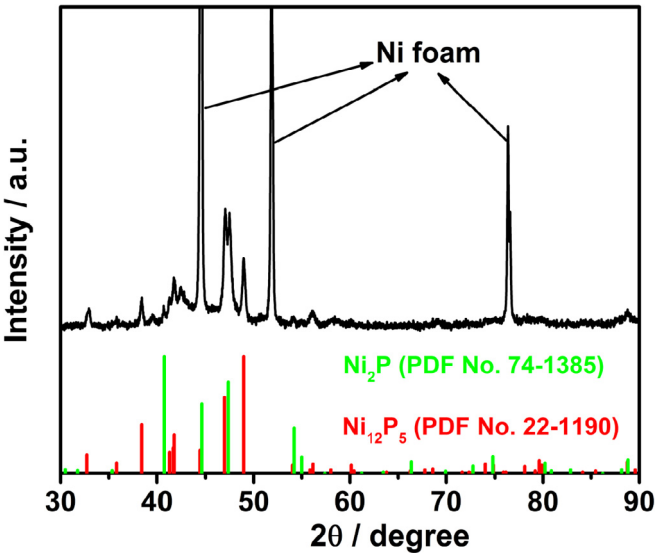


Fig. 1. XRD pattern of as-prepared Ni_xP nanowires/Ni hybrid foam.

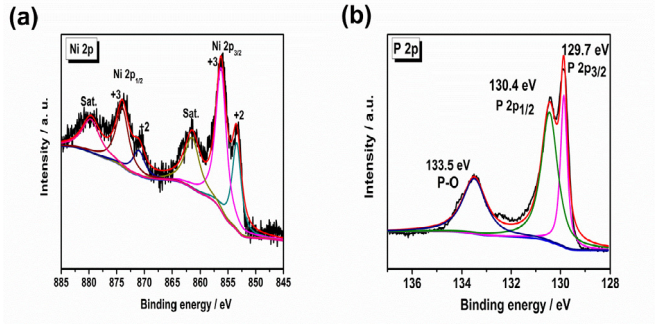
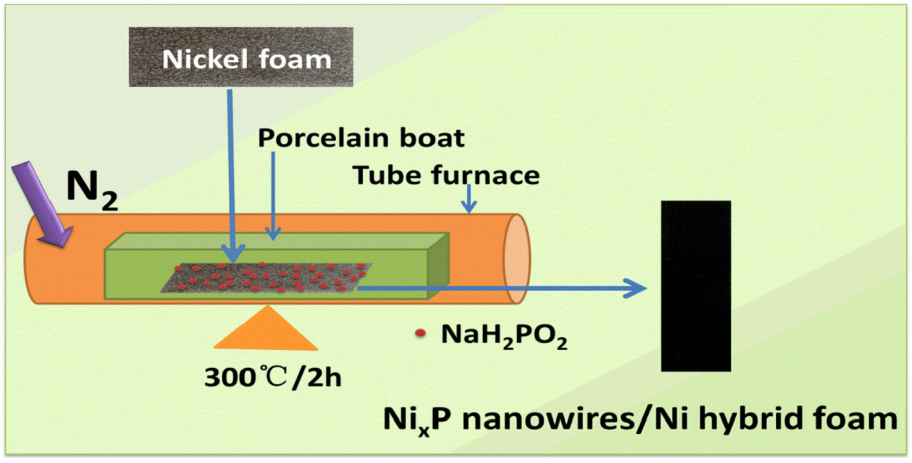


Fig. 2. XPS spectra of Ni_xP nanowires/Ni hybrid foam in the (a) Ni 2p and (b) P 2p regions.



Scheme 1. Diagrammatic sketch of the formation process for self-supported NixP nanowires/Ni hybrid foam.