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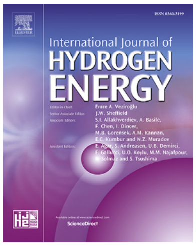

Preparation of mesoporous Ni_2P nanobelts with high performance for electrocatalytic hydrogen evolution and supercapacitor

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ABSTRACT

The development of bifunctional electrochemically-active materials for both hydrogen evolution reaction (HER) and supercapacitors enables the possibility to integrate energy storage and production into one single system. Here, we report a novel bifunctional mesoporous Ni_2P nanobelt-like architecture prepared via the hydrothermal synthesis of $Ni(SO_4)_{0.3}(OH)_{1.4}$ nanobelt precursor and subsequent low temperature phosphorization process under Ar atmosphere. Composed of numerous cross-linked Ni_2P nanoparticles, the as-obtained Ni_2P nanobelts exhibit a two dimensional leaf-like morphology, allowing remarkable enhancement of mesoporosity as well as active surface area. The HER electrocatalytic test in acid medium show a current density of 16 mA cm^{-2} at an overpotential of 187 mV, Tafel slope of 62 mV dec^{-1} and long-term durability. Investigation of this Ni_2P nanobelts as supercapacitor materials in 2M KOH electrolyte display a high specific capacity ranging from 1074 F g^{-1} at 0.625 A g^{-1} to 554 F g^{-1} at 25 A g^{-1}, and notable cycling life with 86.7% retention after 3000 cycles at 10 A g^{-1}. With the simplicity of the synthetic routine and the outstanding performance as both HER catalysts and supercapacitors, the Ni_2P nanobelts provide promising potential for energy devices.

Introduction

Transition metal phosphides (TMPs) have been attracting wide attention in the energy applications (electrocatalysis [1], photocatalysis [2], battery [3] and supercapacitor [4]) due to their low cost and high active properties [5–7]. Recently, Ni_2P nanomaterials were shown to be electrochemically active for hydrogen evolution reaction (HER) due to synergistic effects between exposed proton-acceptor and hydride-acceptor centers on the surface of Ni_2P [8,9]. At the same time, Ni_2P nanomaterials are also effective for energy storage in supercapacitors due to superior electrical conductivity and much higher pseudocapacitance. Therefore, Ni_2P nanomaterials hold significant potential applications for electrocatalytic hydrogen evolution as well as supercapacitor.

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The pioneering work on Ni_2P materials as a HER catalyst was reported in 2013 by Popczun and coworkers [9]. They investigated a solution-phase reaction to synthesis Ni_2P nanoparticle with impressive HER activity due to a high accessible surface area and a high density of exposed (001) facets. Nevertheless, this reaction is highly corrosive and flammable. Hu and Feng [10] reported a simple and scalable solid-state reaction by heating NaH_2PO_2 and $NiCl_2 \cdot 6H_2O$ at 250 °C. The obtained Ni_2P nanoparticles exhibited a high catalytic activity and improved stability for HER in both acidic and basic solutions. Moreover, Ni_2P and Ni_2P-based materials with unique morphologies (peapod-like [11], nanorod-like [12]), Ni_2P nanoparticle supported on a Ti plate [13], Ni_2P nanorods [14] and urchin-like [15]/Ni electrode, Ni_2P-graphene@Nickel foam [16] et al.) were reported to be effective catalysts for HER. Also a novel Ni_2P/rGO composite [17] with Ni_2P nanoparticles grown on reduced graphene oxide (rGO) prepared by a low-temperature solid state reaction method has revealed a high specific capacitance of 2266 F g^{-1} at 5 mA cm^{-2}. Tu' group [18] reported an electroless plating process to obtain Ni_2P nanoparticles coated self-made Ni substrate. The materials deliver specific capacitance can reach 1115 F g^{-1} at 2 A g^{-1}. Very recently, Zhang and coworkers [19] reported a facile hydrothermal-phosphorization method for fabrication of conductive porous Ni_2P nanowall arrays on nickel foam. Coupled with activated carbon (AC) anode, the integrated Ni_2P nanowall arrays cathode exhibits notable energy storage performance with high capacity (125 mAh g^{-1}), desirable high-rate ability and long-term cycling stability (99% retention after 6000 cycles at 1 A g^{-1}). Therefore, it can be concluded that Ni_2P materials can be used as high performance electrocatalytic hydrogen evolution catalysts and supercapacitors. However, uniform two dimensional nanobelt-like Ni_2P mesoporous structure with enlarged active surface area, which affects its supercapacitive and electrocatalytic performance, is rarely reported.

Accordingly, here, we reported the hydrothermal-phosphorization method for construction of highly mesoporous Ni_2P nanobelts. When tested our Ni_2P nanobelts as an HER catalyst in acid media, which showed Tafel slope of 62 mV dec^{-1} and good durability. We also tested as the electrode for supercapacitors, the Ni_2P nanobelt electrodes exhibit impressive performance with a high specific capacity ranging from 1074 F g^{-1} at 0.625 A g^{-1} to 554 F g^{-1} at 25 A g^{-1}, and remarkable cycling life with 86.7% retention after 3000 cycles at 10 A g^{-1}. These results have demonstrated promising application of mesoporous Ni_2P nanobelts in the development of high performance HER catalysts and supercapacitors.

Experimental section

Preparation of $Ni(SO_4)_{0.3}(OH)_{1.4}$ nanobelts and Ni_2P nanobelts

In a typical synthesis, 2 mmol $Ni(SO_4)_2 \cdot 7H_2O$ and 0.1 g urea were dissolved in the mixed solution (57.5 ml of de-ionized water and 2.5 ml of glycerol) under stirring at ambient temperature. Then the suspension was transferred into a 100 ml Teflon-lined autoclave, followed by maintaining at 200 °C for 6 h in an electric oven. After that, the as-prepared green Ni-precursor product ($Ni(SO_4)_{0.3}(OH)_{1.4}$ nanobelt) was collected by centrifugation and washed with deionized water and ethanol for at least 3 times, and then dried at 70 °C overnight. To obtain Ni_2P, the prepared Ni-precursor product was put at one porcelain boat, and then NaH_2PO_2 as P source was put at the other porcelain boat in the upstream side of the furnace. Subsequently, the two porcelain boats were calcined at 300 °C for 2 h with a heating speed of 1 °C min^{-1} under the Ar atmosphere.

Characterization

The X-ray diffraction (XRD) data of the as-prepared samples were obtained on Bruker D8 Advanced X-ray diffractometer. X-ray photoelectron spectroscopy (XPS) was conducted on ESCALAB 250 instrument. N_2 adsorption and desorption isotherm was obtained using Quantachrome AutoSorb6 ISA. Scanning electron microscope (SEM) with energy dispersive X-ray (EDX) was performed on Hitachi S3400N. High resolution transmission electron microscopy (HRTEM) was carried out on a JEM-2100.

Electrochemical measurements

For HER measurement, Catalyst ink was obtained by dispersing 5.0 mg of as-prepared Ni_2P nanobelt sample into 0.9 mL of ethanol containing 0.1 mL Nafion solution (5 wt%) and sonication for 1 h. Then 10 μL of the obtained catalyst ink was added on a glassy carbon electrode (GCE, 5 mm in diameter). All the electrochemical measurement was carried out on CHI 660E using a standard three-electrode system with a Pt plate as the counter electrode and saturated calomel electrode as a reference. The electrolyte is 0.5 M H_2SO_4 solution. Linear sweep voltammetry (LSV) was measured with a scan rate of 2 mV s^{-1}. All the potentials reported here are calibrated to the reversible hydrogen electrode (RHE).

For supercapacitive measurement, the working electrode was prepared according our previous report [20]. The mass of the active materials is tested as 5–6 mg for each electrode. Cyclic voltammogram (CV) and galvanostatic charge-discharge (GCD) were conducted on CHI 660E using a typical three-electrode system with a Pt plate as the counter electrode and Hg/HgO electrode as a reference. The electrolyte is 2 M KOH solution.

Results and discussion

Structural and morphology characterization

The synthesizing process of the Ni_2P nanobelts, as illustrated in Fig. 1, involves two steps: firstly, the green Ni-precursor is prepared by the hydrothermal method; secondly, the Ni_2P nanobelts are obtained by low temperature phosphorization of the precursor. It is obvious that the color of Ni-precursor is changed from green into black after phosphorization. Moreover, during the phosphidation process, the mesoporous structure is formed due to the dehydration and gas release, which could be the key factor for high surface area, uniform

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