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Phase and composition controllable synthesis of nickel phosphide-based nanoparticles via a low-temperature process for efficient electrocatalytic hydrogen evolution

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ABSTRACT

Nickel phosphide has been shown to be active toward hydrogen evolution reaction (HER). In this paper, we demonstrate the phase and composition controllable synthesis of nickel phosphide-based nanoparticles (Ni–P-based NPs) via a low-temperature phosphidation reaction (250 °C) using NaH₂PO₂ as the phosphorus source and the as-prepared Ni(OH)₂ precursor as the nickel source. Interestingly, by changing the NaOH concentration and nickel source used to fabricate Ni(OH)₂ precursors, we could adjust the phases and compositions of as-synthesized Ni–P-based nanocatalysts from Ni₅P₄, Ni₂P to Ni₁₂P₅. The different steric hindrance and the electrostatic repulsion of synthesized β-Ni(OH)₂ precursors result in the formation of three Ni–P phases with various Ni:P ratios. Electrochemical characterizations reveal that the Ni–P-based NPs with P-rich phase (Ni₅P₄+Ni₂P) exhibit remarkable electrocatalytic HER property, with low overpotential (η) of 111 mV to reach a current density of 10 mA cm⁻² in a 0.5 M H₂SO₄ media, which is superior than those of pure Ni₂P (η = 118 mV) and the Ni-rich Ni–P-based counterpart (Ni₁₂P₅+Ni₂P) (η = 131 mV). This is attributed to the stronger ensemble effect of P and more active sites provided by P-rich Ni–P-based NPs. Our results demonstrate that by tailoring the surface properties of Ni(OH)₂ precursors, the phases and compositions of Ni–P-based nanoparticles could be easily tuned, which provides a simple, economic, and green strategy to optimize the HER performance of transition metal phosphide-based electrocatalysts.

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1. Introduction

Being faced with the over-consumption of energy and the environment crisis, scientists have been searching renewable and environmentally friendly alternative energy sources. As an ideal energy carrier candidate to substitute traditional fossil fuels, hydrogen has the highest gravimetric energy density and zero carbon emission [1]. Free hydrogen does not exist in nature freely. Comparing to the dominant and conventional productive process to pass steam through hydrocarbons to produce H₂ and CO₂ in industry, electrocatalytic splitting of water holds tremendous promise as an efficient and clean approach to produce hydrogen [2]. Exploiting efficient catalysts for proton reduction is the prime challenge to

produce hydrogen via hydrogen evolution reaction (HER). Platinum group metals are recognized as the most active HER catalysts, therefore, they generate large cathodic current densities at very low overpotentials [3]. However, their feasible large-scale application is restricted by the high cost and scarcity of these materials. Thus, it is an urgent affair to design and develop alternative electrocatalysts with high activity and long-term stability based on earth-abundant elements [4].

During the past few years, transition-metal compounds, including transition metal sulfides, selenides, borides, carbides, nitrides have been exploited [5–11]. Moreover, transition metal phosphides (TMPs) have emerged as a new class of low-cost and earth-abundant catalysts and their electrocatalytic properties towards HER have been evaluated, such as Ni–P [12–14], Co–P [15–17], Fe–P [18], Cu–P [1] and Mo–P [19]. These catalysts display considerable HER activities in acidic environment, in which proton exchange membrane-based electrolysis is viable and operational [20,21].

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Among them, nickel phosphides have attracted extensive research interest for HER electrocatalysis during the last decades, since they share a similar mechanism to the hydrogenases in nature [22–25]. For example, Laursen et al. reported the nanocrystalline Ni_5P_4 as a HER electrocatalyst with exceptional efficiency in both acidic and alkaline media [26]. Popczun et al. developed the nanostructured Ni_2P with exposed (001) facets, which could be used as highly efficient catalyst for HER to replace noble metals [22]. However, conventional phosphide catalysts were generally synthesized via relatively complex and laborious steps, comprising several heating procedures and subsequent phosphidation treatments above 500 °C [20,27,28]. Another representative class of alternative synthetic route to produce Ni–P catalysts was based on the wet-chemical solution strategy, which was considerably controllable and reacted under a relative low temperature (300–400 °C) [29–31]. However, these methods typically involve the utilization of organophosphorus, organometallic precursors and organic solvents, which are poisonous and environmentally contaminative, preventing the large-scale practical production of the nickel phosphide-based materials. Moreover, the nickel phosphides are featured with various crystallographic structures including Ni_3P , Ni_2P , Ni_5P_2 , Ni_{12}P_5 , and Ni_5P_4 , which brings a great challenge to the phase-controlled synthesis and clarification of the relationship between the phases and the catalytic properties of Ni–P series. In conclusion, controllable fabrication of Ni–P nanocatalysts with different phases and compositions through a facile, mild, and environmentally friendly technology remains a big challenge up to now.

Herein, a facile, two-step, and organic solvent-free strategy has been proposed to synthesize Ni–P-based nanocatalysts with controllable phases and compositions under mild conditions. With the first step to hydrothermally synthesize $\text{Ni}(\text{OH})_2$ nanostructures, the $\text{Ni}(\text{OH})_2$ precursors were chemically converted into Ni–P-based nanoparticles via a low-temperature phosphidation reaction (250 °C) using the NaH_2PO_2 as the phosphorus species during the second step. Interestingly, the phases and compositions of Ni–P-based NPs can be simply tailored by adjusting the anions of nickel source and the NaOH molarity used to prepare $\text{Ni}(\text{OH})_2$. Followed electrochemical tests reveal that the Ni–P-based nanoparticles with P-rich phase ($\text{Ni}_5\text{P}_4+\text{Ni}_2\text{P}$) display superior electrocatalytic HER performance than those of Ni_2P and the Ni-rich benchmark ($\text{Ni}_{12}\text{P}_5+\text{Ni}_2\text{P}$), which was attributed to the stronger ensemble effect of P and more active sites in P-rich Ni–P-based NPs.

2. Experimental

2.1. Materials

Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Sulfuric acid (H_2SO_4 , 95%–98%) purchased from Tianjin Yuanli Chemical Co., Ltd. Nafion perfluorinated resin solution (5 wt% in a mixture of lower aliphatic alcohols and water, contains 45% water) was obtained from Sigma Aldrich Co., Ltd. Commercial Pt/C (20 wt%) catalyst was purchased from Shanghai Hesen Electric Co., Ltd. All chemicals were used as received without further purification and all solutions in our work were prepared using Millipore-MiliQ water (resistivity: $\rho \geq 18 \text{ M}\Omega \text{ cm}^{-1}$).

2.2. Synthesis of the Ni_2P , $\text{Ni}_5\text{P}_4+\text{Ni}_2\text{P}$ and $\text{Ni}_{12}\text{P}_5+\text{Ni}_2\text{P}$ nanoparticles

According to our previous report [32], the nickel hydroxide precursor was synthesized by hydrothermally reacting fresh

precipitated sodium hydroxide with nickel chloride. In a typical synthesis, 15 mL of 2 M NaOH solution was slowly added into 15 mL $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ aqueous solution (2 M) (noting that a viridescence precipitation formed immediately upon mixing). The mixture was kept stirring for 10 min so as to form a uniform suspension, which was subsequently transferred into a Teflon-lined stainless steel autoclave (50 mL in volume), sealed, and maintained at 120 °C for 24 h. After that, the autoclave was naturally cooled down to room temperature and the light green precipitate was thoroughly washed with deionized water for six times. Finally, the sample was mixed with NaH_2PO_2 aqueous (4 M, 40 ml) and the mixture was dried by lyophilization overnight.

Ni_2P nanoparticles were prepared by a low-temperature phosphidation process between $\text{Ni}(\text{OH})_2$ precursors and NaH_2PO_2 at 250 °C under the protection of static Ar atmosphere. The system was raised to 250 °C at a heating rate of 5 °C min^{-1} and maintained for 60 min. After naturally cooling, the products were washed with water and ethanol to remove the unreacted salts and dried at 60 °C overnight in air. $\text{Ni}_5\text{P}_4+\text{Ni}_2\text{P}$ nanoparticles were synthesized by the same process except using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in place of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ while $\text{Ni}_{12}\text{P}_5+\text{Ni}_2\text{P}$ nanoparticles were synthesized using $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 4.8 M NaOH in preparing the $\text{Ni}(\text{OH})_2$ precursors.

2.3. Materials characterization

The powder X-ray diffraction (XRD) was performed on Bruker/D8 Advance X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418$) as irradiation source. The samples were scanned from 10° to 80° at a scanning rate of 6° min^{-1} . The morphologies and micro/nanostructures of samples were characterized using scanning electron microscopy (SEM, Hitachi, S-4800, 5 kV) and transmission electron microscopy (TEM, JEOL JEM-2100 F, 200 kV) equipped with energy dispersive spectrometer (EDS). TEM samples were prepared by dispersing various Ni–P NPs in ethanol and depositing the dispersion liquids onto carbon-coated copper grids. The surface chemical valence states of the catalysts were analyzed by using a Kratos AXIS Ultra X-ray photoelectron spectroscope with an incident radiation of Monochromatic Al KR X-rays at 150 W.

2.4. Electrochemical measurements

The HER performances of the Ni–P-based catalysts were evaluated on the electrochemical workstation (PARSTAT 4000) in a typical three-electrode testing system. The catalysts deposited on glassy carbon electrode were served as the working electrode, a platinum foil and Ag/AgCl with saturated KCl were used as the counter and reference electrode, respectively. For preparing the working electrode, 5 mg Ni–P-based nanoparticles or commercial Pt/C catalyst (20 wt%) were dispersed in ethanol (1 ml) by at least 30 min ultrasonication, and a homogeneous ink would be formed. The glassy carbon electrode (GCE) was polished with 300 and 50 nm alumina slurries for several minutes, then 20 μL of catalyst ink were drop-coated onto the glass carbon electrode (GCE, 5 mm in diameter) with the mass loading of about 0.5 mg cm^{-2} 10 μL Nafion solution (0.2 wt%) were loaded onto GCE. The tested electrolyte was oxygen-free 0.5 M H_2SO_4 solution, which was achieved by bubbling N_2 for 20 min before the experiments. Catalytic activity of HER was analyzed by methods of multi-cyclic voltammetry (CV), linear sweep voltammetry (LSV) and potentiostatic electrolysis. Before collecting the electrochemical data, several CV cycles were scanned to activate the catalyst samples until the system was stabilized. The LSVs were collected at a scan rate of 5 mV s^{-1} . The electrochemical impedance spectroscopy (EIS) measurements were carried out at -0.149 V vs. RHE from 100 kHz to 100 mHz at an amplitude of 5 mV. All the polarization

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