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Nickel phosphide nanosphere: A high-performance and cost-effective catalyst for hydrogen evolution reaction

Lei Wan ^{a,b,c}, Jinfeng Zhang ^{a,b,c}, Yaqiong Chen ^c, Cheng Zhong ^{a,b},
Wenbin Hu ^{a,b,c}, Yida Deng ^{a,b,*}

^a Key Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education, Tianjin University, Tianjin 300072, PR China

^b Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300072, PR China

^c State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, PR China

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ABSTRACT

Catalyst has been a bottleneck in hydrogen evolution reaction (HER) – a half reaction of water splitting. Hitherto the most efficient HER catalyst in terms of catalytic capacity remains to be those platinum group metals, especially platinum; however, rare metals' exorbitant cost and scarcity inhibit their further application in industry, which therefore call for catalysts prepared from earth-abundant elements. Herein, we introduce nickel phosphide nanospheres (NPNs) bearing excellent HER activity. Prepared via a facile, inexpensive, and eco-friendly preparation procedure, the as-synthesized NPNs have perfect over-potential to reach -100 mA/cm^2 (η_{100}), with η_{100} reaching 251 mV in 0.5 M H_2SO_4 . A series of durability tests, including cyclic voltammetry (CV) and chronoamperometry, also indicate NPNs' favorable stability under both acidic and alkaline conditions. After taking account of a string of factors, including NPNs' mass density, handy preparation process, superior catalytic activity as well as favorable durability, the NPNs bear probable potentiality of taking traditional noble metals' place as the HER catalyst and are worth studying further.

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Introduction

Water-splitting through electrolysis or photoelectrolysis is considered very promising for generating hydrogen under the backdrop of searching for the alternative of fossil fuels [1–5]. Redundant electricity, regardless of their origins, e.g., wind power, solar power, hydroenergy, or traditional fossil fuels,

can be stored as chemical energy and hydrogen counts as a perfect storage form [6]. Noble metal catalysts (often platinum) have so far been the most effective ones to be applied in water splitting [7] and other applications, but their inherent drawbacks (rare and expensive) drive scientists to find a cost-effective and abundant HER catalyst which at the same time is neck-and-neck with noble metals in terms of HER activity [8–11].

* Corresponding author. Key Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education, Tianjin University, Tianjin 300072, PR China. Fax: +86 18622282233.

E-mail address: yida.deng@tju.edu.cn (Y. Deng).

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Micro- and nano-sized nickel phosphides have recently come into researchers' notice, with Ni₂P, Ni₁₂P₅, NiP₂, Ni₅P₄, NiP₂, and so forth being successfully prepared, their HER properties being proved excellent, and their catalytic mechanisms of efficiently activating HER being studied [2,6,12–14]. Their performances in highly acidic environment are also considerably stable. Despite these breakthroughs, the frequently reported methods to prepare Ni–P nanoparticles mostly require high temperature or the involvement of surfactants and organic nickel or phosphorus sources [13,15,16]. The introduction of nanocrystallization of Ni–P alloys and a specific Ni–P phase often requires the abovementioned reaction conditions through a thermal decomposition of organic precursors, hydrothermal, solvothermal or high-temperature solid phase reduction methods [15,17–19], which complicate preparation of Ni–P nanomaterials and hinder Ni–P alloys' further application in large-scale commercial production process. For example, one of the biggest advantage of solvothermal method is a certain Ni–P phase can be easily achieved in a particular reaction condition, but actually, the reported Ni–P phases' HER activities, after taking into consideration of other factors, such as nanoparticles' size and morphology, are not far from one another as expected. Although by far, only Ni₂P and Ni₅P₄'s HER mechanisms have been studied comparatively systematically [2,6,12], other Ni–P phases' HER mechanisms can be analogous to them [13,20]; therefore, a pure Ni–P phase is not necessarily needed to pursue a greater HER property. In some cases, a mixture of different Ni–P may even have better HER catalytic activity [17]. In view of this background, a balance should be struck between Ni–P nanoparticles preparation cost and HER catalytic activity. It has long been proven that Ni has autocatalytic reduction nature, through which Ni–P nanoparticles can be prepared in a comparatively mild condition [21]. And the newly reduced amorphous Ni–P alloys via NaH₂PO₂ as reducing agent are able to transfer to other Ni–P phases through heat treatment procedure. These properties were rarely reported in the preparation of Ni–P nanomaterials that are applied in HER application.

In this paper, we therefore introduce a facile preparation process of NPNs and report their HER properties. Inspired by the tradition chemical nickel-plating process and nickel's autocatalytic reduction property, the nano-sized nickel phosphide was prepared through a facile, surfactant-free and mild autocatalytic reduction reaction [22]. The as-synthesized NPNs' catalytic properties after different heat treatment processes were studied. As-prepared amorphous nickel phosphide nanoparticles were heat treated under 350 °C by different durations. These nanoparticles, being sphere-like, have shown distinguished HER property in their amorphous state and furthermore, after the annealing processes, HER properties of these nanoparticles, mainly comprised by a combination of Ni₃P and Ni₅P₂, were enhanced substantially. All of the samples show outstanding catalytic properties in both H₂SO₄ and NaOH in which they also have considerable stability. The minimum over-potential required for –100 mA/cm² on the cathode is 251 mV in H₂SO₄ and is achieved in the 8-h heat-treated sample. The promoted performance is attributable to superior dispersity, nanostructure bearing more active sites, increased crystallinity and nickel

phosphide's nature. After comparing HER properties of HPNs before and after heat treatment procedure, the crystallized phases of Ni_xP_y should be considered better than amorphous one in terms of HER activity. The comparatively low-cost raw materials of the NPNs, produced from earth-abundant elements, if studied searchingly, may pave the way for their future application.

Experimental

Materials

Nickel sulfate (NiSO₄), sodium hydroxide (NaOH), sodium hypophosphite (NaH₂PO₂), palladium chloride (PdCl₂), acetic acid (CH₃COOH), all in analytical pure and without purification, were purchased from National Chemical Reagent Ltd., Shanghai, China. A Millipore water system was applied to prepare deionized water throughout experiment procedure.

Preparation and annealing processes of NPNs

The first step is to prepare α-Ni(OH)₂ nanowire precursor through a hydrothermal synthesis method [23]. The key point of forming wire-like morphology is to mix twofold excess NiSO₄ into NaOH and heat-treat them under 120 °C for 24 h. Drawing on these as-synthesized α-Ni(OH)₂ precursors, and capitalizing on NaH₂PO₂ as reducing reagent, CH₃COOH as pH regulator, and PdCl₂ as nucleate agent, the NPNs were prepared through an auto-catalytic reduction [22]. Adequately rapid reaction rate, comparatively high reaction temperature (90 °C) as well as the addition of PdCl₂ prior to NaH₂PO₂ [24] would ensure solid and spherical morphology, rather than some novel morphologies like hollow spheres, nanotubes or yolk-in-shell nanospheres. The as-prepared NPNs was annealed under 350 °C and amid 5% H₂/Ar in different time periods, 0 h (non-heat treated), 4 h, and 8 h, respectively.

Characterization

A Pyris 1 TGA Thermo Gravimetric, working from room temperature (300 K) to 550 °C, was applied to get differential scanning calorimetry and thermogravimetric analysis (DSC/TGA) plots. X-ray diffraction (XRD) patterns of NPNs annealed through different time periods were obtained via a D/max-III A X-ray diffractometer, with 40 kV as the accelerating voltage and Cu-Kα (λ = 1.540 56 Å) as the radiation source. NPNs' morphology was observed by a JEM-2100F transmission electron microscope (TEM) whose samples were prepared by depositing ultra-dilute NPNs (mixed with ethanol) onto carbon copper grids. NPNs' molar ratio of Ni to P (n(Ni):n(P)) was determined through a Thermo's iCAP6300 inductively coupled plasma optical emission spectrometer (ICP).

Working electrodes and electrochemical measurements

NPNs of different annealing times and Pt/C (purchased from Hispec 3000, 20 wt. %), diluted by ethanol, served as electrode materials that were uniformly dropped on L-shaped glass carbon electrodes (GCE, 5 mm as diameter). Then the working

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