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Highly active and inexpensive iron phosphide nanorods electrocatalyst towards hydrogen evolution reaction

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ABSTRACT

Herein for the first time we report a novel approach to prepare well-controlled iron phosphide nanorods (FeP NRs) via low-temperature phosphidation of Fe salt with a porous anodic aluminum oxide (AAO) template. The as prepared FeP NRs exhibit high catalytic activity toward hydrogen evolution reaction (HER) in acidic solutions, showing an onset potential of ~45 mV, a Tafel slope of 55 mV/dec and nearly 100% Faradaic yield (FY) with good stability. Additionally, the catalyst can deliver current density of 2 and 10 mA/cm² for HER with low overpotentials of 67 and 120 mV, respectively. Up to date the FeP NRs should be the inexpensive electrocatalyst while offering high activity toward HER, thus holding a great promise for practical applications for water electrolysis in large scale production.

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Introduction

Hydrogen is an abundant, renewable and clean energy source and has been considered as a promising replacement for today's fossil fuels [1]. Electrocatalysis of water splitting is a simple way to produce hydrogen with high purity at the most economical price [2]. In order to improve the reaction rate and lower the overpotential for reduction of energy consumption, an efficient HER electrocatalyst is urgently demanded. It is known that Pt-based noble metals are the best HER catalysts, but their wide use is greatly limited by terrestrial scarcity and

high cost [3]. The highly acidic conditions in proton exchange membrane technology require compatible HER catalyst [4]. Therefore, it is highly desired to develop noble-metal-free and acid-stable HER catalysts [5]. Intensive effort has been paid to develop efficient transition metal compounds based HER catalysts [6], among which molybdenum-based compounds such as sulfides, selenides, carbides, borides and nitrides have achieved success [7–11].

Transition metal phosphides (TMPs) are an important class of compounds with good electrical conductivity [12] and have been widely studied as catalysts for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) as well as anode materials

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for Li-ion batteries [13]. Recently, TMPs based materials including Ni₂P nanoparticles [14,15], FeP nanosheets [16], FeP nanorod arrays [17], CoP hollow nanoparticles [18], CoP nanotube [19], self-supported CoP/CC [20], CoP nanocrystals decorated carbon nanotubes [21] and 3D interconnected network of CoP nanowires [22] have been developed as efficient HER catalysts in acidic solutions. Iron is the most inexpensive and one of the most abundant transition metals, thus FeP could be an excellent one over other TMPs-based HER catalysts toward large-scale applications.

Herein, we develop a hard template strategy for well-controlled FeP NRs fabrication involving low-temperature phosphidation of Fe salt with the help of a porous anodic aluminum oxide (AAO) template, subsequently the template was removed by HF solution. In acidic electrolyte, the FeP NRs exhibit superior HER catalytic activity over previously reported FeP nanosheets [16], with a low onset potential of ~45 mV, a Tafel slope of 55 mV/dec, nearly 100% Faradaic yield and good stability.

Experimental

Materials

Al foil (0.3 mm, 99.99%) was purchased from Alfa Aesar. NaH₂PO₂ was purchased from Aladdin Ltd. (Shanghai, China). Nafion (5 wt%) was bought from Sigma–Aldrich. Other chemicals used were bought from Beijing Chemical Corporation. All the reagents were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of FeP NRs and bulk FeP

Porous AAO films were prepared according to previously reported method [23]. As-synthesized AAO films (1 g) were soaked in 3 M ferrous chloride ethanol solution for 0.5 h, followed by drying in a vacuum oven at 80 °C. In order to fill the holes of the AAO template with ferrous chloride completely, the soaking process was assisted with sonication. The as-treated films and NaH₂PO₂ were put in a porcelain boat at two separate positions with NaH₂PO₂ at the upstream side of the furnace, followed by heating to 350 °C for 2 h in a static Ar atmosphere. Then the films were collected after cooling down to ambient temperature under Ar atmosphere. Finally the FeP NRs were obtained by etching AAO template with 5% HF solution. The bulk FeP was prepared by direct phosphidation of ferrous chloride powder without using the template but with the same experimental conditions as the templating approach.

Characterizations

The powder XRD data were acquired with a RigakuD/MAX 2550 diffractometer under Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS measurements were performed on an

ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements

All electrochemical measurements were performed at room temperature with a CHI660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A typical three-electrode setup with glassy carbon electrode (GCE, $\Phi = 4 \text{ mm}$), graphite rod and saturated calomel electrode (SCE) as working, counter and reference electrode, respectively was used. Catalyst ink was prepared by dispersing 5 mg catalyst into 1 mL ethanol containing 20 μL 5 wt% Nafion followed by sonication for 30 min. Then 5 μL of the catalyst ink was coated on the GCE with a loading of 0.2 mg/cm². 0.5 M H₂SO₄ solution was used as electrolyte. Polarization curves were collected at a sweep rate of 2 mV/s. All potentials in this report are versus the reversible hydrogen electrode (RHE). In 0.5 M H₂SO₄, $E \text{ (RHE)} = E \text{ (SCE)} + 0.281 \text{ V}$ [24].

Results and discussion

The X-ray diffraction (XRD) patterns (Fig. S1) of FeP NRs and bulk FeP indicate that both samples have same characteristic diffraction peaks of FeP (JCPDS No. 78-1443), which is well consistent with the reported work [25,26]. Confirming the FeP material was successfully synthesized by a simple phosphidation reaction. The scanning electron microscopy (SEM) image of FeP NRs (Fig. 1a) indicates the formation of a large amount of one-dimensional (1D) nanostructures about 100 nm in diameter. Transmission electron microscopy (TEM) observation (Fig. 1b) further confirms the formation of nanorod structure. The high-resolution TEM (HRTEM) image taken from a nanorod (Fig. 1c) reveals clear lattice fringes with an interplane distance of 0.242 nm corresponding to (111) plane of FeP [26]. The corresponding selected area electron diffraction (SAED) pattern (Fig. 1d) shows several bright rings made up of discrete spots with d values of 0.273, 0.242, 0.193, 0.188, 0.164 and 0.155 nm, which can be indexed to the (011), (111), (202) (211), (212) and (020) planes of FeP [27], respectively. The scanning TEM (STEM) and corresponding EDX elemental mapping images (Fig. 1e) demonstrate that both P and Fe elements are uniformly distributed throughout the nanorod. All these results strongly confirm the successful synthesis of FeP NRs. However, without using AAO template a preparation with the same procedure only produced bulk irregular structures with bigger diameters (Fig. S2).

The HER activity of FeP NRs was studied in 0.5 M H₂SO₄ solution. For comparison, bare GCE, bulk FeP and commercially available Pt/C (20 wt%) with same loading were also examined. Owing to as-measured reaction currents cannot directly reflect the intrinsic catalytic behavior of catalysts for the effect of ohmic drop, an iR correction was applied to all initial data for further analysis. The polarization curves of FeP NRs, bulk FeP, bare GCE and Pt/C in Fig. 2a show that the bare GCE has poor electrocatalytic activity toward HER while Pt/C exhibits excellent catalytic activity with a near zero onset potential. Bulk FeP is an active material toward HER, which needs overpotentials of 172 and 285 mV to drive current

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