Full Length Article

A novel composite of network-like tungsten phosphide nanostructures grown on carbon fibers with enhanced electrocatalytic hydrogen evolution efficiency

Keke Xu[a,b], Xiuli Fu[a,*], Hong Li[a,b], Zhijian Peng[b,*]

[a] State Key Laboratory of Information Photonics and Optical Communications, and School of Science, Beijing University of Posts and Telecommunications, Beijing 100876, PR China
[b] School of Science, China University of Geosciences, Beijing 100083, PR China

ARTICLE INFO

ABSTRACT

Enhancing the electrocatalytic activity of transition metal phosphides (TMPs) for hydrogen evolution has become an attractive way for noble-metal-free electrocatalysts. In this work, a novel composite of network-like tungsten phosphide nanostructures on carbon fibers (CFs@WP) was prepared by a two-step high-temperature calcination strategy. Owing to the high electrochemical active surface area originating from the WP nanostructures of network-like morphology and the enhanced conductivity caused by the introduction of carbon fibers, the obtained CFs@WP composite, as an integrated hydrogen evolution cathode, exhibits much higher electrocatalytic activity for hydrogen evolution than pure WP nano-/micro-particles after toasting their corresponding suspension onto bare CFs. This catalyst could, in 0.5 mol·L^{-1} H$_2$SO$_4$, deliver a current density of 10 and 100 mA·cm^{-2} respectively at the over-potential of merely 137 mV and 215 mV, and present a small Tafel slope of 69 mV·dec^{-1} as well as excellent stability at various current densities, although it may exhibit relatively inferior catalytic activity in hydrogen evolution in neutral and alkaline conditions. The present strategy may also offer a straight-forward model to enhance the hydrogen evolution activity of other TMPs catalysts.

1. Introduction

Electrochemical water splitting for hydrogen evolution represents a promising approach to produce clean and high-purity hydrogen fuel, which has been proposed as a "core clean energy technology" and would be essential for the future energy infrastructure based on hydrogen economy [1]. Today, some catalysts based on noble metals, such as platinum (Pt), ruthenium (Ru) and palladium (Pd) materials, exhibit great electrocatalytic activity, which can accomplish the hydrogen evolution reaction (HER) at a low over-potential and with a small Tafel slope especially under acidic conditions [2]. However, the high cost and limited supply from the nature sources hinder their large-scale employment. Therefore, it is of critical importance to search for efficient, inexpensive, and durable electrocatalysts to replace the noble metal catalysts for expediting the HER.

However, only till recent years, the scientists have understood that hydrogen evolution proceeds via a similar pathway with hydrogenation (hydrotreating process) such as hydrodesulfurization and hydrodenitrogenation, during which the reversible adsorption/desorption of hydrogen over the catalysts are the critical step for achieving fast

kinetics [3]. This correlation establishes a new avenue to find noble-metal-free catalysts for HER. For instance, transition metal phosphides (TMPs) like Ni$_2$P [4], previously employed as the catalyst for hydrodesulfurization and hydrodenitrogenation, could currently also be used as the active catalyst for HER. Because the elements in TMPs are earth-abundant and TMPs have desirable catalytic performance, after the discovery of Ni$_2$P catalyst for HER, various TMPs such as NiP$_2$ [5], Cu$_3$P [6], MoP [7], CoP [8], Co$_2$P [9] and FeP [10] have been reported as efficient and inexpensive electrocatalysts for HER.

In particular, amorphous tungsten phosphide (WP) nanoparticles have been developed by Schaak's group as an efficient HER catalyst operating in acidic solution [11]. They reported that in 0.50 mol·L^{-1} H$_2$SO$_4$ (aq) the as-prepared electrode for HER could produce a current density of 10 and 20 mA·cm^{-2} at an over-potential of only 120 and 140 mV, respectively. However, a substrate like Ti foam was required to support the amorphous WP nanoparticles (forming a WP/Ti composite) to complete the electrochemical process; and the introduction of non-conductive polymers to protect the Ti foam makes the electrochemical process much complicated and unstable. Later, Sun et al. [12] successfully prepared a composite of tungsten phosphide nanorod arrays

---

* Corresponding authors.
  E-mail addresses: xiulifu@bupt.edu.cn (X. Fu), pengzhijian@cugb.edu.cn (Z. Peng).

on carbon cloth, which exhibited high HER activity with an over-potential of 130 and 230 mV to afford a current density of 10 and 100 mA·cm^{-2}, respectively. But in their work, the applied WO$_3$ precursor was prepared by hydrothermal process, which may cause many defects and relatively low crystallinity for the composite compared with those prepared by high temperature calcination. However, to the best of our knowledge, as a hot topic in this filed, although several literatures have been reported on tungsten phosphides as HER catalysts [11–18], there are rare publications on network-like nanostructured tungsten phosphides [17,18], which have relatively large specific area and thus more active sites for hydrogen evolution.

On the other hand, prior to electrochemical tests, most of the reported HER catalysts are required to be effectively immobilized on current collectors by using a polymer binder like Nafion or PTFE as the film-forming agent. The polymer binder will generally increase the electrical resistance of the composite catalysts [19], block the active sites and inhibit the diffusion of H$^+$, leading to a reduced effective catalytic activity [20]. However, it is known that, if the electrocatalysts can be grown directly on three-dimensional (3D) structures to form 3D self-supported electrodes, polymer binders could be free of use to avoid the above disadvantages [16,21]; and 3D self-supported electrodes possess robust skeleton and large surface area, thus effectively increasing the contact area between the catalyst and electrolyte, compared with the traditional electrodes coated on 2D substrates by spin-coating, dip-coating, or sputtering. Therefore, 3D electrodes can always exhibit much better performance than the planar ones [21,22]. In addition, it was reported that the direct growth of metal salt (the precursor of phosphide) could be realized via electrodeposition, hydrothermal synthesis and high-temperature calcination [23–26]. And compared with electrodeposition or hydrothermal synthesis, the direct growth of the precursor of phosphides on current collectors by high-temperature calcination and its post-phosphorization allows for a better mechanical adhesion of the catalyst to the substrate [27]. And also, the high-temperature calcination could avoid low purity of products because of the by-products of electrodeposition or hydrothermal synthesis, and low crystallinity due to their low formation temperature by hydrothermal synthesis [28].

Therefore, in this paper, a novel composite of network-like tungsten phosphide nanostructures on carbon fibers (CFs@WP) was prepared by a two-step high-temperature calcination strategy. During the preparation, a composite of network-like WSe$_2$ nanostructures on carbon fibers (CFs@WSe$_2$) was first synthesized in a tube furnace by the selenylation of WO$_3$ powder on preoxidized polyacrylonitrile (PAN) fibers; and then, the phosphorization was carried out to chemically convert the CFs@WSe$_2$ into CFs@WP. The obtained CFs@WP composite, which can directly be used as an integrated hydrogen evolution cathode, exhibits much better electrocatalytic activity for HER than pure WP nano-/micro-particles (NMPs) after toasting their corresponding suspension onto bare CFs (NMPs/CFs) in acidic media. Furthermore, the as-prepared CFs@WP composite needs an over-potential of 137 and 215 mV to afford a current density of 10 and 100 mA·cm^{-2}, respectively. The present strategy may also offer a straight-forward model to enhance the HER activity of other TMPs composite catalysts by simultaneously constructing TMPs network-like nanostructures and introducing high conductive, cost-effective carbon substrate via high-temperature calcination to enhance the adhesion between the catalyst and substrate.

2. Experimental section

2.1. Samples preparation

Chemicals and materials. All the applied chemicals were of analytical grade and used as received without further purification. Among them, selenium powder, tungsten trioxide and sulphuric acid were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Red P and 10 wt% Pt/C were bought from Aladdin Industrial Corporation,

China.

Fabrication of CFs@WSe$_2$. The CFs@WSe$_2$ composite was fabricated by a modified method as previously reported [28]. In a typical process, a bunch of PAN fibers (100 mg) was first rinsed in turn with de-ionized water and ethanol, and then dried under N$_2$ flow at room temperature. Afterwards, the PAN fibers were soaked in a WO$_3$ suspension (2 g of WO$_3$ powder dispersed in 5 ml of ethanol) for 1 min, and then laid on a quartz plate for drying. After drying, the sample was moved into a double-temperature-zone vacuum tube furnace, settling at the heating center, while an alumina ceramic boat loaded with about 2 g of Se powder was located at 40 cm away from the sample in the upstream zone of the carrier gas. Before heating, the furnace was evacuated and flushed with argon gas (Ar, 99.99%) for several times. For the heating, the furnace was first heated up to 400 °C in 20 min and maintained at 400 °C for 10 min, then to 700 °C in 40 min and held at 700 °C for 60 min, and finally to 1075 °C in 40 min and soaked at 1075 °C for 60 min. After heating, the furnace was naturally cooled down to room temperature. During the experiment, the Ar flow (200 sccm) was maintained throughout the whole process. The resultant dark-blue fiber-like products (denoted as CFs@WSe$_2$ in this work) were then collected for the following experiment.

Fabrication of CFs@WP. The as-obtained CFs@WSe$_2$ precursor was first loaded into an alumina ceramic boat. Afterwards, the ceramic boat was located at the center of a microwave vacuum tube furnace, while a ceramic boat loaded with 1 g of red P was placed at 8 cm away from the CFs@WSe$_2$ in the upstream of the carrier gas. The furnace was then purged with argon gas (Ar, 99.99%) for several times, and heated up to the optimized 1000 °C at a ramping rate of 40 °C·min^{-1}, soaking at this temperature for 1 h. Finally, the furnace was naturally cooled down to room temperature. Throughout the whole heating process, an Ar gas flow (140 sccm) was maintained. Finally, a bunch of dark-grey fiber-like products (denoted as CFs@WP composite) was collected.

Fabrication of WP NMPs and CFs. For comparison, pure WP NMPs were synthesized through the same route for the synthesis of CFs@WP without using PAN fibers. Bare CFs were prepared by pyrolyzing PAN fibers alone under the same conditions for the preparation of CFs@WSe$_2$.

2.2. Materials characterization

The phase composition of the samples was identified by X-ray powder diffraction (GI-XRD, D/max-RB, Japan; Cu Kα radiation, λ = 1.5418 Å) in a 2θ range of 10–90° under a continuous scanning mode with a scanning rate of 6°/min at an incidence angle of 1° of the X-ray. The morphology and microstructure of the samples were examined by field emission scanning electron microscopy (SEM, S4800, Japan), transmission electron microscopy (TEM, Tecnai G2 F20 U-TWIN, America) and high resolution TEM (HRTEM). The composition of the samples was measured by the energy dispersive X-ray (EDX) spectroscopes attached to the SEM and TEM, respectively. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB MKII, Thermo VG Scientific Ltd., America) was employed to investigate the chemical state of the elements, in which the results were calibrated by the binding energy of C 1s line (284.8 eV).

2.3. Electrochemical measurements

Working electrodes preparation. The obtained CFs@WP composite was first cut into short-cuttings in a length of 2 cm, which were then horizontally connected by conducting adhesive tape on a copper foil in a width of 1 cm. The finally obtained electrode would contain the CFs@WP composite in a mass density of 4 mg·cm^{-2}. During electrochemical measurement, the immersed part of the electrode in the electrolyte was in a geometry of 1 × 1 cm^2. Besides, the electrode of bare CFs was also fabricated by this method.

To prepare the electrode of WP NMPs, a suspension with a