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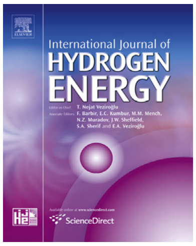

Hydrogen evolution reaction performance of the molybdenum disulfide/nickel–phosphorus composites in alkaline solution

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ABSTRACT

The low phosphorus (LP), medium phosphorus (MP), and high phosphorus (HP) three nickel–phosphorus (Ni–P) powders were employed as supports of molybdenum disulfide (MoS_2) to fabricate MoS_2/Ni–P composites (MoS_2/Ni–LP, MoS_2/Ni–MP, and MoS_2/Ni–HP) via a hydrothermal technique. Crystal structures, morphologies, components and hydrogen evolution reaction (HER) performances of them were characterized and evaluated. During the incorporation between MoS_2 and Ni–P, the crystallization of Ni–P powders and the presence of metastable nickel phosphides can be validated; also, the 2H-MoS_2 tends to transfer to the phase of 1T-MoS_2. Compared with MoS_2 and Ni–P samples, MoS_2/Ni–P composites show a higher HER property. Prominent HER behaviors of the composites can be due to the presence of monolayer 1T-MoS_2 on the surface, the excellent conductivity of Ni–P powder at the bottom, as well as the coexistence of nickel phosphides. Among the three composites, MoS_2/Ni–MP exhibits the remarkably electrocatalytic activity.

Introduction

The clean and efficient energy carrier of hydrogen derived from the electrocatalytic hydrogen evolution reaction (HER), has been intensively explored to alleviate the severe energy shortage and environmental deterioration caused by the excessive consumption of coal and petroleum fuels [1]. It is well known that platinum (Pt) and Pt-based electrocatalysts are competent for the HER applications, whereas high costs and scarcities of these metals hinder their widespread commercializations [2–4]. Thus, the ongoing exploitation of cost-effective and earth-abundant substitutes employed for HER to replace the Pt-based metals has attracted enormous attention. Various non-noble materials including nickel-based alloys [5–9], Fe-based alloys [10–12], Co-based alloys [13,14], transition/alkaline earth metal oxide [15], metal sulfides [16–19], metal carbides/carbon materials [20–24], nitrides [25,26] as well as phosphides [27–29] have been tested for catalyzing the electrochemical HER.

Among various candidates, molybdenum disulfide (MoS_2) in the form of crystalline [30,31] and amorphous states [32,33] has received tremendous attention due to its abundance and high activity. However, HER performance of MoS_2 has been limited because of the insufficient active edge sites and the

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poor electrical transport. To unravel the conundrum of the inferior HER performance of MoS_2, three main issues have been proposed [34–37]: (1) the increase in the electrocatalytic activity of active sites, (2) the improvement in the electrical contact to the active sites, and (3) the enhancement in the number of active sites of this catalyst. Thus, a great deal of efforts have been made for modifying the surface structures of MoS_2-based materials, aiming at enhancing the HER properties of these materials. Among the reported efforts, the phase transformation from 2H-MoS_2 to the metallic 1T-MoS_2 [38,39], gentle oxidation [40,41], functional structural design [42,43], and stabilizing the edge layers with organic molecules [39] have been extensively attempted. Up to now, many reports have focused on the reduction in the stacked layers of the as-prepared MoS_2 to increase the number of edge sites for enhancing the electrocatalytic performance of this catalyst. Unquestionably, the presence of abundant active sites will be valuable for the increase in HER performance. But, a high stacked height along the (002) basal plane of MoS_2 is required to gain a maximum value of edge/basal ratio, which is crucial for the enhancement in HER property.

It should be pointed out that the drawbacks of poor bulk conduction and anisotropic electrical transport of MoS_2 restrict its overall HER efficiency. For this nano-structured material, the poor conductivity within the interparticle and interdomain can reduce the total HER activity. The improvement in the electrical contact between the active sites deserves to be considered to increase the intrinsic activity. Some promoters such as gold [44], core–shell MoO_3 [45], macroporous and mesoporous carbon materials [36,46–48], graphene [37,49], and graphene oxide [42,50] have been employed as electrical conduction supports to improve the electrical contact between the active sites of this catalyst. Compared with the above-mentioned supports, the electroless nickel–phosphorus (Ni–P) coating or powder exhibits the advantages of facile fabrication, anticorrosion, excellent wear resistance, prominently electrical conductivity, and the promisingly electrocatalytic activity of HERs [51–55]; thus, this material may be competent for the candidate employed as a support to enhance the HER performance of MoS_2. However, to the best of our knowledge, the electroless Ni–P coating or powder applied as the supporting substrate to enhance the HER property of MoS_2 has not yet been reported. We are sure that this work will offer a significant guidance for the exploitation of HER catalysts.

The aim of this study is to reveal the effect of Ni–P addition with different phosphorus content on the structure and HER activity of the fabricated MoS_2/Ni–P composite. Three Ni–P powders, i.e. low phosphorus- (Ni–LP), medium phosphorus- (Ni–MP), and high phosphorus-type Ni–P (Ni–HP) were employed as the supports for the fabrications of MoS_2/Ni–P composites via a hydrothermal synthesis process. Crystal structures, morphologies, components, and porosities of the three MoS_2/Ni–P composites (MoS_2/Ni–LP, MoS_2/Ni–MP, and MoS_2/Ni–HP) were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), Raman spectroscopy, energy dispersive X-ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), and the nitrogen gas adsorption/desorption test. The electrocatalytic performances in HER of these composites were evaluated by techniques of linear sweep voltammetry (LSV), Tafel polarization, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS).

Material and methods

Material

Analytical grade reagents of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 99 wt%), thiourea ($CH_4N_2S$, 99 wt%), nickel sulfate hexahydrate ($NiSO_4\cdot 6H_2O$), citric acid monohydrate ($C_6H_8O_7\cdot H_2O$), sodium hypophosphite monohydrate ($NaH_2PO_2\cdot H_2O$), succinic acid ($C_4H_6O_4$), ammonium hydrogen fluoride (NH_4HF), sodium acetate trihydrate ($NaAc\cdot 3H_2O$), ammonia solution (25 wt%), sodium hydroxide (NaOH), hydrochloric acid (36.5 wt%), and sulfuric acid (H_2SO_4, 98 wt%) were purchased from Jingchun Scientific Co. Ltd. (Shanghai, China). The 5 wt% of Nafion solution was provided by Alfa Aesar Chemicals Co. Ltd. (Shanghai, China). The above mentioned reagents were used as received and without further purification.

Synthesis of Ni–P powders

A kind of stainless steel slice was employed as the substrate for the fabrication of three nickel–phosphorous (Ni–P) powders (Ni–LP, Ni–MP, and Ni–HP). The chemical composition in weight content (wt%) of this slice was as follows: 0.08% for carbon, 0.03% for sulfur, 0.045% for phosphorous, 1.0% for silicon, 2.0% for manganese, 8.0% for nickel, 18.0% for chromium, and 70.845% for iron. First of all, the stainless steel slices with a dimension of 5 cm × 5 cm × 0.5 cm were polished mechanically to mirror finish and cleaned with absolute ethanol and distilled water successively. Then, they were immersed into 3 mol/L of HCl solution at room temperature for 3 min, followed by cleaned with distilled water and placed into the electroless plating bath for the preparation of Ni–P coatings.

The compositions of the electroless Ni–P bath were described as follows: 30 g/L of $NiSO_4\cdot 6H_2O$, 20 g/L of $C_6H_8O_7\cdot H_2O$, 15 g/L of NaAc, 5 g/L of $C_4H_6O_4$, 5 g/L of NH_4HF, and 7.5 g/L of $NaH_2PO_2\cdot H_2O$ for Ni–LP coating (15 g/L for Ni–MP coating, and 30 g/L for Ni–HP coating). The pH value of this bath was adjusted to 4.6 by adding ammonia solution. The temperature of this solution during the electroless plating process was kept at 85 ± 2 °C; the plating time was controlled for 1 h. After the plating, the stainless steel slices loading Ni–P coatings removed from the bath were cleaned using deionized water adequately. Then, the deposited Ni–P coatings were scraped away from the substrate and milled in the agate-vibrating mill with the agate balls for 3 h. The size of the obtained Ni–P powders ranged from 1.5 to 15 μm. The determined weight content of phosphorus element for the three powders was that: 3.2 wt% of P for Ni–LP, 7.9 wt% of P for Ni–MP, and 11.1 wt% of P for Ni–HP.

Synthesis of the MoS_2/Ni–P composites

The preparation processes of the three MoS_2/Ni–P composites (denoted as MoS_2/Ni–LP, MoS_2/Ni–MP, and MoS_2/Ni–HP) were

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