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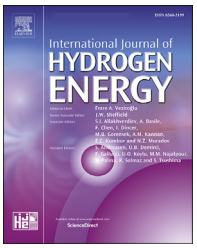

Phosphorus-doped nickel sulfides/nickel foam as electrode materials for electrocatalytic water splitting

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ABSTRACT

Hydrogen production from electrocatalytic water splitting is viewed as one of the most promising methods to generate the clean energy. In this work, we successfully prepared an electrode material by growing phosphorus-doped Ni_3S_2 (PNi_3S_2) on nickel foam substrate (NF) under hydrothermal conditions. The phosphorus-doping has an obvious effect on the morphology of Ni_3S_2 on the surface of the nickel foam, which probably results in more active sites, higher electrical conductivity and faster mass transfer. The resulting electrode material displays excellent electrocatalytic activities and stability towards both OER (oxygen evolution reaction) and HER (hydrogen evolution reaction). A relatively low overpotential of 306 mV is required to reach the current density of 100 mA cm^{-2} for OER and 137 mV at 10 mA cm^{-2} for HER in 1 M KOH solution. When PNi_3S_2/NF was used in an electrolyzer for full water splitting, it can generate a current density of 10 mA cm^{-2} at 1.47 V with excellent stability for more than 20 h.

Introduction

Hydrogen is considered as an alternative energy source due to its high calorific value, zero pollution, high efficiency, renewability, and a substitute for conventional fossil fuels [1,2]. To produce hydrogen through electrochemical water splitting, a low cost and efficient electrocatalyst is indispensable [3,4]. As is known, noble metal-based compounds have the best catalytic activity for OER (oxygen evolution reaction) and HER (hydrogen evolution reaction) [5]. However, these materials are expensive and scarce, which hinders their commercial applications, and most of electrocatalysts reported in the literatures are only active for either OER or HER, but not for the both [6]. Therefore, many efforts have been focused on exploring earth-abundant, relatively cheap, and highly efficient electrocatalysts that can catalyze both OER and HER.

During the past decades, chemists have made a lot of efforts to develop bifunctional electrocatalysts of non-noble transition metal-based materials for water splitting, such as carbides [7], nitrides [8], oxides [9,10], phosphides [11], and sulfides [12,13]. To enhance the electrocatalytic activity, a promising strategy is that the electrocatalyst is loaded or in situ grown on the conductive substrate, such as nickel foam [14], copper foils [15,16], carbon cloth or paper [17], graphene oxide [18], and FTO [19]. However, many substrates are expensive or do not provide sufficient specific surface area. Therefore, it is necessary to develop electrode materials with

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low cost and high specific surface area for successful electrocatalytic applications.

Among various transition metal-based electrocatalysts for water splitting, nickel-containing compounds have shown great activity for both OER and HER [20–22]. Nickel sulfide (Ni_3S_2) has been recognized as a promising water splitting electrocatalyst [23] with excellent activity on various supports [24,25]. Among all the supports, nickel foam (NF) as a cheap commercial material can be used not only as electrode substrate, but also as a nickel source. The high electronic conductivity and high specific surface area made it an excellent electrode material [26]. Wang's group have loaded porous Ni_3S_2 nanorod array on nickel foam, and it can efficiently catalyze the water splitting reaction [23]. Xie and co-workers reported a N-Ni_3S_2/NF material as excellent electrocatalysts for both HER and OER [27]. Recent work in Gao's group stated that a binary metal sulfides on nickel foam substrate (MoS_2-Ni_3S_2/NF) exhibited high stability for water splitting [28]. Although these reported materials have good electrocatalytic activities, their stability still needs to be improved, and also when they are employed as full water splitting electrocatalysts in electrolyzer, the overpotentials are not low enough. Therefore, developing an efficient and stable bifunctional electrocatalyst is critical.

Herein, we prepared an electrode material by growing phosphorus-doped Ni_3S_2 (PNi_3S_2) on nickel foam substrate through a hydrothermal method. This materials displayed superior electrocatalytic activity for HER, OER, and overall water splitting in alkaline condition. This is because that the phosphorus doping modified the nanostructure of Ni_3S_2, which probably further results in higher specific surface and more exposed catalytic active centers. Furthermore, PNi_3S_2/NF was used as both cathode and anode electrodes in an alkaline electrolyzer for overall water splitting, and this electrolyzer generates a current density of 10 mA cm^{-2} at a quite low cell voltage of 1.47 V with excellent stability for more than 20 h, demonstrating that PNi_3S_2/NF is a bifunctional electrocatalyst with high-efficiency for water splitting.

Experimental

Materials

All the chemicals including nickel foam (thickness: 1.6 mm, surface density: 350 g/m^2), thioacetamide (TAA), sodium hypophosphite (NaH_2PO_2), hydrochloric acid, potassium hydroxide (KOH) and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai China), and all the chemicals were used as purchased without further purification.

Synthesis of PNi_3S_2/NF

In a typical experiment, commercial nickel foam (NF, 1 cm × 1 cm) was pretreated based on published procedures [29]. Afterward, the NF was immersed in a Teflon-lined stainless steel autoclave with TAA (160 mg) and deionized water (10 mL) in it, and heated at 180 °C for 6 h. Then, the NF, NaH_2PO_2 (15.5 mg, 0.146 mmol) and deionized water (10 mL) were placed in a Teflon-lined stainless autoclave at 150 °C for 6 h. Then the samples were rinsed with deionized water and dried in a vacuum oven at 60 °C for 6 h. After that, PNi_3S_2/NF material was prepared. For comparison, Ni_3S_2/NF was prepared in the same procedure as the above described except that sodium hypophosphite was not added [22].

Characterization

A field emission scanning electron microscope (FESEM, S-4800) with an accelerating voltage of 5 kV was used to observe the morphology of the catalysts and the phase composition of the samples was determined by EDX. High resolution transmission electron microscopy (HRTEM, JEM-2100) was applied to obtain more detailed information of morphologies. X-ray photoelectron spectroscopy (XPS, Escalab 250) measurements were carried out on catalysts to investigate the compositions and valance states of the elements on the surface. X-ray powder diffraction (XRD, D/max-2550VB+/PC) patterns of the samples were recorded with Cu-Kα radiation (λ = 0.15418 nm). Elemental analysis for N element was performed by Elmentar, Vario EL III instrument. Inductive Coupled Plasma Emission Spectrometer (ICP, Leeman Prodigy) was employed to measure the amount of P and S elements in the electrode materials. N_2 adsorption/desorption isotherms were recorded at −196 °C by TriStar II 3020 adsorption analyzer. The Brunauer Emmett Teller (BET) surface area was calculated from adsorption data.

Electrochemical measurements

The OER and HER electrochemical activities were tested in 1 M aqueous KOH solution by setting up a standard three-electrode system on an electrochemical workstation (CHI 760D, CH Instruments, Inc., Shanghai, China), and the overall water splitting was studied by applying a two-electrode system. The OER and HER electrochemical activities were measured against a platinum wire as counter electrode, and a silver chloride electrode (Ag/AgCl) with saturated potassium chloride as the reference electrodes (CH Instruments, Inc., Shanghai, China). PNi_3S_2/NF was directly used as a working electrode. Linear sweep voltammetry (LSV) for OER and HER were conducted with a scan rate of 10 mV s^{-1} in aqueous electrolyte. The stability of the PNi_3S_2/NF electrode was studied with the given operating conditions when the current density is 100 mA cm^{-2} for OER and 50 mA cm^{-2} for HER. The electrochemical impedance spectra (EIS) of the electrodes were obtained from AC impedance spectroscopy under the conditions that the amplitude is 5 mV and the frequency is ranging from 10 mHz to 100 kHz. All potential of vs. Ag/AgCl conversion to vs. RHE were calibrated by the Nernst equation, and the detailed calculation was described in the supplementary data.

Results and discussion

Material characterization

The powder XRD patterns of as-synthesized PNi_3S_2/NF is shown in Fig. 1. All the diffraction peaks can be well indexed to

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