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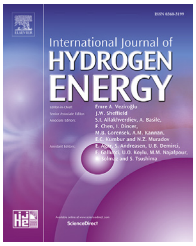

Self-supported Ni_3S_2@MoS_2 core/shell nanorod arrays via decoration with CoS as a highly active and efficient electrocatalyst for hydrogen evolution and oxygen evolution reactions

Wenqing Lu, Ye Song, Meiling Dou, Jing Ji, Feng Wang***

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing, 100029, China

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ABSTRACT

A hierarchically porous MoS_2 on Ni_3S_2 nanorod array on Ni foam (MoS_2/Ni_3S_2/NF) was firstly fabricated through a simple microwave-assisted hydrothermal method, and then followed by electrochemical deposition approach in which MoS_2/Ni_3S_2/Ni foam is decorated with CoS (CoS–MoS_2/Ni_3S_2/NF). In contrast to conventional hydrothermal approach, microwave irradiation accelerates the synthesis of MoS_2/Ni_3S_2/Ni foam from time of >20 h –2 h. The characterization of CoS–MoS_2/Ni_3S_2/NF by scanning electron microscope (SEM) and high resolution transmission electron microscope (HRTEM) indicate that a whole scale of 1D the Ni_3S_2 nanorods were hierarchically integrated with MoS_2 and CoS nanosheets. The as-synthesized CoS–MoS_2/Ni_3S_2/NF hybrid not only endows the ease transport of electrons along Ni_3S_2 nanorods to Ni foam, but also accommodates maximal exposure of active edge sites to the reactants through hierarchically porous CoS doped MoS_2 nanosheets, accomplishing the promoted kinetics and activity for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). By electrochemical measurements such as linear sweep voltammetry (LSV) and electrochemical impedance spectroscope (EIS), we find that the CoS–MoS_2/Ni_3S_2/NF hybrid shows markedly enhanced electrochemical performance for both HER and OER. Specifically, the optimal CoS–MoS_2/Ni_3S_2/NF–8C possesses the low overpotentials (η_{10}) of 85 and 225 mV at current density ($|j|$) of 10 mA cm^{-2} in 1.0 M KOH and the small 62.3 and 46.1 mV dec^{-1} Tafel slope for HER and OER, respectively, outperforming those of most of the current noble metal-free electrocatalysts. These results highlight the fact that CoS–MoS_2/Ni_3S_2/NF is a high-performance, noble-metal-free electro-catalyst, and provide a potential avenue toward achieving an enhanced electrocatalytic activity towards both in HER and OER. Yet the duration of the as prepared catalyst in OER still need to be improved.

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* *Corresponding author.*
** *Corresponding author.*
E-mail addresses: jijing@mail.buct.edu.cn (J. Ji), wangf@mail.buct.edu.cn (F. Wang).

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Introduction

Water splitting by electrocatalysis is one of the promising and appealing approach to produce H_2 and O_2 [1–4]. Efficient cathode and anode catalysts for hydrogen evolution reaction (HER) and oxygen revolution reaction (OER), respectively, are crucial for water splitting. The well known for HER and OER are Pt, RuO_2 and IrO_2 [5–9]. However, the application of these noble-metal-based catalysts is limited by their high cost and scarcity. Transition metal sulfides are the attractive catalysts in many applications because of their unique properties [10,11]. Among the transition metal sulfides, single crystalline Ni_3S_2 is a good metallic conductor with a room temperature resistivity of about 1.8×10^{-5} Ω cm. The Ni_3S_2 with low resistivity allows ease in transportation for ions and electrons [12], and has been proven to be an effective catalyst for OER [13–15] due to its rich and unusual valence states of Ni (Ni^0, $Ni^+$and Ni^{2+}) in the Ni_3S_2 electrode which allows water adsorbing favorably on their surfaces, similarly for the disproportionation and comproportionation of Mn^{3+} in MnO_2 OER catalysts reported [16]. More importantly, Ni_3S_2 has been also verified to exhibit electrocatalytic activity for HER [17,18]. Although the catalytic activity and stability for HER are still far from satisfactory, Ni_3S_2, supported on Ni substrate possesses proper energy for reversible binding of the hydrogen at adsorption site of the catalyst [19], and exhibits the potential for HER electrocatalyst [20]. Different from Ni-based alloy materials, which is only used in HER [21–25], Ni_3S_2 is stable in both acidic and alkaline environments [26,27]. Therefore, Ni_3S_2 is expected to be active for both HER and OER [28–30].

Graphene like MoS_2 is composed of three atom layers of S–Mo–S stacked together through Vander Waals interactions, and considered as a potential of substitute for replacing Pt-based HER electrocatalysts. The electrocatalytic activity for HER derives of its close hydrogen binding energy to Pt-group metals [31] and abundant unsaturated S at edges of MoS_2 [32–37]. The layered structure confines thickness on the atomic scale, and enables the maximal exposure of abundant active sites [35,37–39] and large specific surface to the reactant, rendering it enhanced electrocatalytic activity for HER [40].

Furthermore, binary TMD composites have been verified to exhibit better electrocatalytic activities than the related unary counterparts. The coordination of two or more TMD species would offer more active sites due to defects derived of doping, which are beneficial to electrocatalytic applications [41]. Besides, differential combination and tunable proportion of TMD species offer great opportunities to tune the physical/chemical properties.

From the view point of electrocatalytic kinetics, vertically aligned 2D nanostructures on the conductive substrate is an ideal morphology for enhancing the electrocatalytic activity due to their abundant active sites, large specific surface and easy electron transportation. Much enthusiasm has been focused on the well-defined morphologies and tunable functions thereof [42]. To increase the utilization efficiency of the electrocatalyst and promote the electron transportation, 1D nanoarray structures, such as various nanowire arrays [43] and nanosheets arrays [44,45], which are directly grown on conductive substrate, are also preferred to form an integrated electrode. Recent related investigations have indicated that electrochemical activity of Ni_3S_2 for HER can be improved by combining Ni_3S_2 with other TMDs [46]. Specifically, the as prepared nanostructures are characterized by the combination of highly porous hierarchical MoS_2 nanosheets with 1D Ni_3S_2 nanoarrays. Wherein, the highly conductive 1D Ni_3S_2 nanorods is prepared by the direct hydrothermal growth of Ni_3S_2 nanorods on Ni foam, and hierarchically structured MoS_2 nanosheets can be formed simultaneously when the molybdates is present [47]. However, such catalysts are commonly fabricated through a hydrothermal method, which usually take more time (more than 20 h) for the formation of the as designed structure. Up till now, there still lack simple and high efficiency approaches to prepared the as designed metal sulfide arrays. Therefore, it is highly desirable to develop a simple and time saving method to fabricate metal sulfide arrays with well-defined morphologies and thereof tunable functions with high HER and OER activity.

In this work, a hierarchically porous MoS_2 on Ni_3S_2 nanorod arrays on Ni foam (MoS_2/Ni_3S_2/Ni foam) was firstly fabricated through a simple microwave-assisted hydrothermal method, and then followed by electrochemical deposition approach in which MoS_2/Ni_3S_2/Ni foam is decorated with CoS nanosheets. In contrast to conventional hydrothermal approach, microwave irradiation accelerates the synthesis of MoS_2/Ni_3S_2/Ni foam from time of >20 h–2 h owing to the special heating via dipolar polarization and ionic conduction [48]. In this strategy, the direct growth of MoS_2/Ni_3S_2 nanorods on Ni foam, which is binder free, provides a strong combination with substrate, leading to enhanced electron transport and stability over the long-term operation. In this well-defined heterostructure, Ni_3S_2 nanorod endows the ease transport of electrons along Ni_3S_2 nanorods to Ni foam, and highly porous MoS_2 nanosheets doped by CoS accommodates maximal exposure of active edge sites to the reactants. As expected, the optimal CoS–MoS_2/Ni_3S_2/NF–8C exhibits superior electrocatalytic activity toward both HER and OER. The low overpotentials (η_{10}) of 85 and 225 mV at current density (|j|) of 10 mA cm^{-2} in 1.0 M KOH for HER and OER, respectively outperform those of most of the current noble metal-free electrocatalysts. Considering the outstanding HER and OER performance, CoS–MoS_2/Ni_3S_2/NF–8C is a compatibly integrating HER and OER activity material.

Experimental section

Materials

Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) was obtained from Sigma-Aldrich. Hexaammonium heptamolybdate tetrahydrate, cobalt(II) chloride hexahydrate, L-Cysteine and hydrochloric acid was purchased from Sinopharm Chemical Reagent Co., Ltd. Potassium hydroxide and thiourea was obtained from aladdin. Ni foam (100*25 cm^2) was purchased from Changsha force yuan new material Co., Ltd. Deionized water (Resistivity > 18.4MΩ/cm) was produced using a pure water system (TTL-6B). All chemical reagents were used without further purification.