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Sputtering nickel-molybdenum nanorods as an excellent hydrogen evolution reaction catalyst

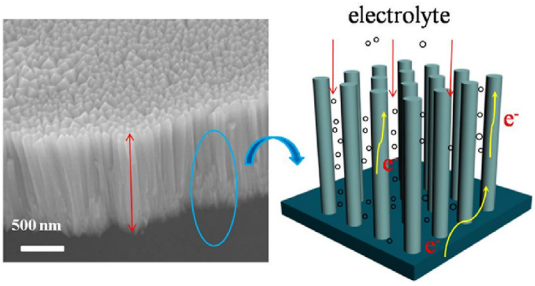
Li Zhang, Kun Xiong, Yao Nie, Xiaoxue Wang, Jianhua Liao, Zidong Wei*

Chongqing Key Laboratory of Chemical Process for Clean Energy and Resource Utilization, School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

HIGHLIGHTS

- Ni–Mo alloy nanorods have been constructed on Ni foam by sputtering method.
- The electrode has a large surface area and small charge transfer resistance.
- The synergistic interaction between Ni and Mo enhances the intrinsic activity.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a novel fabrication of nickel-molybdenum alloy nanorods catalyst for hydrogen evolution reaction (HER), which is prepared by co-deposition of pure nickel and molybdenum in a multisource sputtering system on the surface of Ni foam substrate. The Ni–Mo alloy film exhibits favorable vertical nanorods structure and presents the most efficient activity for HER compared to the film only including one metal element. The remarkably enhanced catalytic activity is attributed to its ordered array geometry as well as the synergistic interaction between Ni and Mo. Meanwhile, the open space within nanorod arrays facilitates the electrolyte penetration and diffusion of ionic species, allowing high utilization efficiency of active species as well as rapidly release of evolved hydrogen gas from the electrode surface.

1. Introduction

Hydrogen seems to be the most likely fuel of the future, concerning about the issues of sustainability, environmental emissions and energy security [1,2]. A clean and renewable method of hydrogen production is electrolysis of water using renewable energies, in particular solar energy [2,3]. Pt-group metals are the best catalysts for hydrogen production, unfortunately, the scarcity and the prohibitive cost of platinum catalysts make them impractical for global-scale application. There is a strong demand for developing cheap and abundant materials to reduce the cost of hydrogen production technologies [4–8].

Ni–Mo alloy is one of the best binary metal alloys among all of non-precious metals for hydrogen production as it is in the form of nanoparticles or planar porous morphology [9–13]. However, to the best of our knowledge, Ni–Mo alloy nanostructured arrays for hydrogen evolution reaction (HER) are seldom reported in the literatures yet. Compared with the common nanoparticles or planar

* Corresponding author.
E-mail address: zdwei@cqu.edu.cn (Z. Wei).

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porous electrodes, the well-aligned nanorod arrays with catalytically active components directly grown on the metallic substrate can provide a larger surface area of active materials. The open space within nanorod arrays facilitates the electrolyte penetration and diffusion of ionic species, allowing high utilization efficiency of active species as well as the in-time leaving of as-formed H_2 bubbles [8,14–16]. Conveyance of the H_2 bubbles away from the electrode surface maintains the integrity of the solid–liquid interface necessary for HER electrocatalysis and keeps the real contact area of electrolyte and electrode almost constant [17]. Accordingly, designing nanostructured arrays of Ni–Mo alloy catalyst well grown onto Ni foam is highly desirable for the HER.

It is well known that magnetron sputtering is a controllable and versatile physical technique to prepare nanostructured films, of which the preparation condition and the chemical composition could be precisely controlled [18,19]. Therefore, in this work, we describe a magnetron sputtering method for synthesizing vertical Ni–Mo alloy nanorods on the surface of Ni foam as a binder-free integrated catalyst for the HER. The as-obtained Ni–Mo electrocatalyst presents excellent catalytic activity for the HER in the light of inosculating the merits of large active surface area provided by its unique nanorods structure, and high intrinsic activity benefited from the synergistic effect between Ni and Mo. This nanoscaled design of electrode architecture provides a valuable strategy for catalyst development and should be applicable for other gas evolution catalytic materials.

2. Experimental section

2.1. Fabrication of Ni–Mo alloy nanorods on a Ni foam substrate

The Ni foam was immersed in a 3.0 mol L^{-1} HCl solution for 15 min to get rid of the surface oxide layer and cleaned with acetone and ethanol in an ultrasonic bath for 15 min. Subsequently, it was washed with deionized water and then dried in a dry oven at 60 °C.

Binary Ni–Mo alloy nanorods were prepared by co-deposition of pure nickel (99.9%) and pure molybdenum (99.9%) in a multi-source sputtering system. The vacuum chamber was pumped to a residual pressure lower than 1×10^{-3} Pa before sputtering. High purity argon at 40 sccm was served as a working gas and the sputtering pressure was kept at 4.0 Pa throughout the deposition process. Cathode powers for nickel and molybdenum were kept at 80 W and 180 W, respectively. A pre-sputtering process (5 min) was conducted to clean the target surface and remove any possible contamination. The substrate holder was rotated at 9.5 rpm in order to ensure the lateral compositional homogeneity of the alloys. After sputtering for 1 h, the Ni–Mo nanorods were successfully grown on a Ni foam substrate or on a Si sheet substrate in order to eliminate the influence of Ni substrate for the sake of XRD analysis. For the purposes of comparison, single element Ni or Mo was also synthesized on Ni foam as described above without using Mo or Ni target.

2.2. Characterization techniques

The surface morphology and the microstructure of the samples were analyzed by field-emission scanning electron microscopy (FE-SEM, JSM-7800, Japan) and X-ray diffraction (XRD-6000, Shimadzu), respectively. An electron microscope with EDX (FEI, model Quanta 200) was used to observe the composition of the catalysts. Electrochemical measurements (CHI 660D electrochemical workstation) were conducted in a three-electrode configuration at 25 °C using a 6.0 mol L^{-1} NaOH as electrolyte. A Pt foil in parallel orientation to the working electrode was used as the counter electrode and Hg/HgO (1 M KOH) as the reference electrode, the area of the working electrode is 1 cm^2. All potentials mentioned in this work were converted to the values with reference to a reversible hydrogen electrode (RHE). Double layer capacitance of the electrodes was obtained by cyclic voltammetry experiments in the potential range of 0.1–0.2 V vs. RHE at scan rate from 5 to 200 mV s^{-1}. The mean current obtained from the average of the absolute values in the cathodic and anodic wave at 0.15 V vs. RHE was plot against the scan rate. The EIS measurements were conducted at different over-potentials in the frequency range of 10 kHz to 0.01 Hz, and with the perturbation amplitude of 5 mV. Experimental EIS data were analyzed and fitted with the software EIS Spectrum Analyzer.

3. Results and discussion

The structural characterization of the catalysts synthesized by sputtering was given by X-ray diffraction (XRD). As seen from the XRD patterns in Fig. 1, there is no significant diffraction peak of Ni or Mo for the Ni–Mo film, compared to that of the films consisting of only one metal element, indicating that the synthesized Ni–Mo alloy has an amorphous or microcrystalline structure. As is well known [12,20], the surface of amorphous alloy is beneficial for the electrochemical desorption of H_{ads} because of the short-range order of the amorphous structure. What's more, the amorphous alloy existing in a meta-stable state with high free energy on the surface is more active and favorable for the mechanical strength and corrosion resistance.

Scanning electron microcopy (SEM) was employed to study the microstructure of the sputter-deposited catalyst. As Fig. 2 (a) shown, the pre-treatment Ni foam holds a wrinkle-like structure, thus, offering a large surface area for the growth of nanostructured active materials. The surface of as-deposited Ni–Mo alloy film is composed of highly uniform nanoparticles, with a diameter of about 50 nm, as clearly demonstrated in Fig. 2 (b). More importantly, the cross-sectional SEM image of Ni–Mo alloy from Fig. 3 clearly reveals the morphology of vertically aligned nanorods, of which the length is about 1 μm. EDS and the corresponding elemental mapping of Ni and Mo for Ni–Mo alloy nanorods in Fig. 2(c–e) display that the two elements are homogeneously

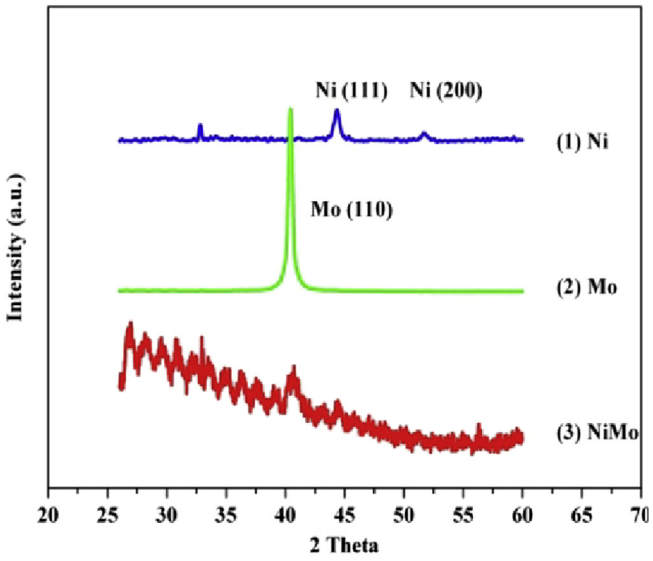

Fig. 1. XRD patterns of (1) Ni/Si, (2) Mo/Si, and (3) Ni–Mo/Si catalysts synthesized by sputtering.