

# Ni<sub>x</sub>S<sub>y</sub>-MoS<sub>2</sub> hybrid microspheres: One-pot hydrothermal synthesis and their application as a novel hydrogen evolution reaction electrocatalyst with enhanced activity



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## ARTICLE INFO

### Article history:

Received 31 March 2014

Received in revised form 5 June 2014

Accepted 5 June 2014

Available online 12 June 2014

### Keywords:

Nickel sulfide

Molybdenum sulfide

Hybrid microspheres

One-pot hydrothermal synthesis

Electrocatalyst

Hydrogen evolution reaction

## ABSTRACT

The present work reports on the preparation of Ni<sub>x</sub>S<sub>y</sub>-MoS<sub>2</sub> hybrid microspheres (NMSHMs) via one-pot hydrothermal treatment of aqueous solutions of Na<sub>2</sub>MoO<sub>4</sub>•2H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O and H<sub>2</sub>NCSNH<sub>2</sub>. As an electrocatalyst toward hydrogen evolution reaction, the NMSHMs exhibit superior activity over MoS<sub>2</sub>, Ni<sub>x</sub>S<sub>y</sub> and the physical mixture of MoS<sub>2</sub> and Ni<sub>x</sub>S<sub>y</sub> in acidic solutions. Such NMSHMs catalyst also shows good durability.

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## 1. Introduction

Direct electrochemical splitting of water is an attractive method to generate the renewable energy carrier hydrogen, and hydrogen evolution reaction (HER) is one key step in this process [1–5]. Usually, an efficient electrocatalyst is required to accelerate the HER rate due to the multi-electronic nature of reduction of protons to form dihydrogen (2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>2</sub>) [6]. Although Pt is the most efficient HER catalyst, it suffers from low abundance and high cost [7]. Therefore, development of low-cost Pt-free alternatives is highly desirable.

MoS<sub>2</sub>, a kind of two-dimensional (2D) layered metal chalcogenide material, is considered as one promising non-precious-metal alternative to Pt with high HER activity [8,9]. Recently, much effort has been made to prepare MoS<sub>2</sub> nanostructures with more exposed sulfur edges, leading to promoted HER activity [10–14]. Introducing promoters such as Co or Ni to MoS<sub>2</sub> also enhance greatly its HER activity [15,16]. It is reported that nickel sulfides exhibit good HER activity with low Tafel slopes in acidic

electrolyte [17]. It is thus expected that integrating nickel sulfides and MoS<sub>2</sub> could lead to a HER catalyst with greatly enhanced activity. Herein, we report on the preparation of Ni<sub>x</sub>S<sub>y</sub>-MoS<sub>2</sub> hybrid microspheres (NMSHMs) via one-pot hydrothermal process using Na<sub>2</sub>MoO<sub>4</sub>•2H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O and H<sub>2</sub>NCSNH<sub>2</sub> as precursors. As a HER electrocatalyst, such NMSHMs were found to exhibit superior activity over MoS<sub>2</sub>, Ni<sub>x</sub>S<sub>y</sub> and the physical mixture of MoS<sub>2</sub> and Ni<sub>x</sub>S<sub>y</sub> (mNM) with good durability.

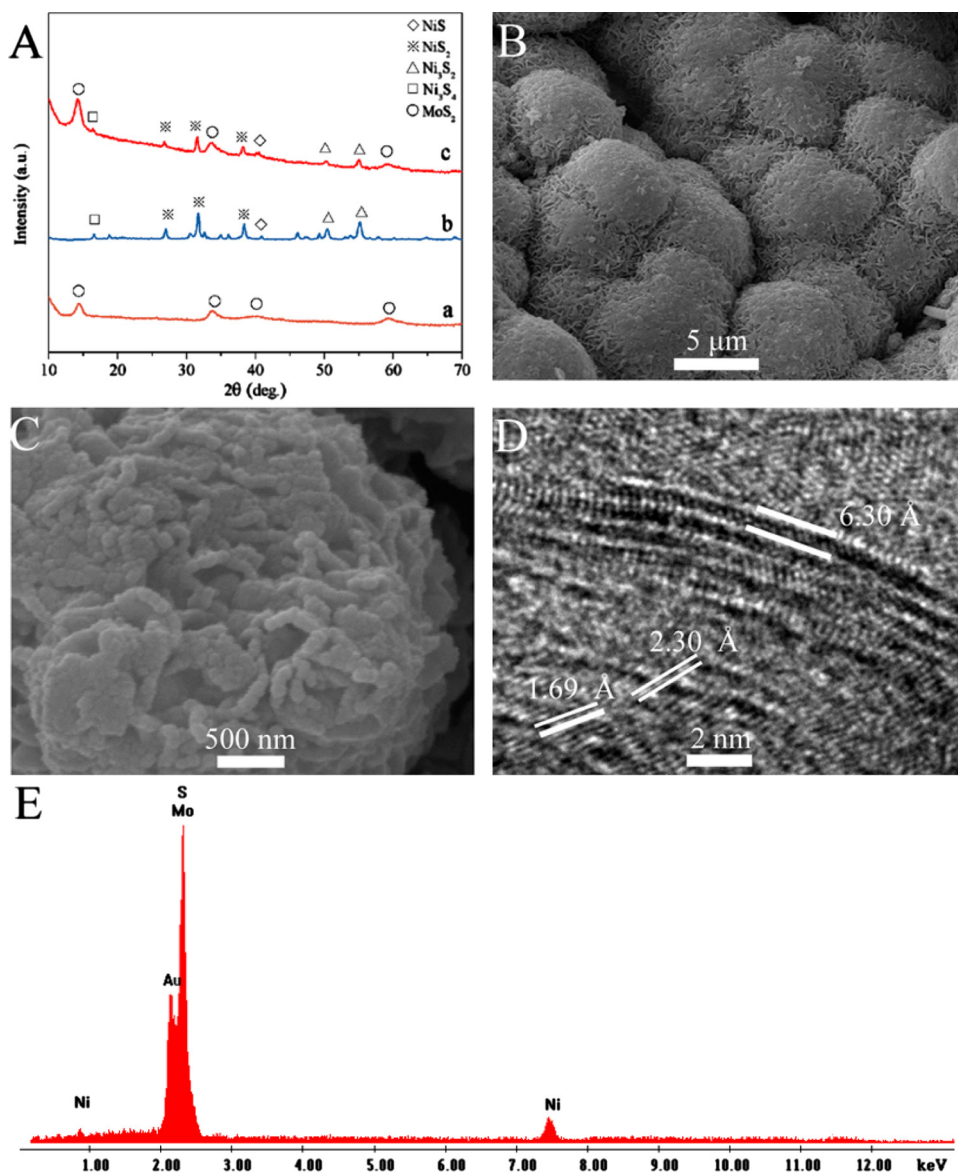
## 2. Experimental

### 2.1. Synthesis of NMSHMs, MoS<sub>2</sub> and Ni<sub>x</sub>S<sub>y</sub>

The NMSHMs were prepared as follows. In a typical synthesis, 0.872 g Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, 1.452 g Na<sub>2</sub>MoO<sub>4</sub>•2H<sub>2</sub>O and 1.035 g H<sub>2</sub>NCSNH<sub>2</sub> (mole ratio of Ni/Mo: 1:2) were dissolved in 35 mL deionized water. The mixture was ultrasounded for 30 mins and then transferred to a 50 mL autoclave for hydrothermal reaction at 200 °C for 24 h. After cooled to room temperature naturally, the products were collected by filtration, washed with distilled water and ethanol several times to remove the residue of reactants, and finally dried in vacuum at 80 °C. MoS<sub>2</sub> and Ni<sub>x</sub>S<sub>y</sub> were prepared

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**Fig. 1.** (A) XRD patterns of (a) MoS<sub>2</sub>, (b) Ni<sub>3</sub>S<sub>2</sub> and (c) NMSHMs. (B) Low and (C) high-magnification SEM images, (D) HRTEM image and (E) EDS of NMSHMs.

by the same procedure without the presence of Ni and Mo salt, respectively.

## 2.2. Characterizations

Scanning electron microscope (SEM) measurements were made on a XL30 ESEM FEG microscope. Transmission electron microscopy (TEM) measurements were made on a Hitachi H-8100 electron microscope (Hitachi, Tokyo, Japan). Powder X-ray diffraction (XRD) data were recorded on a RigakuD/MAX 2550 diffractometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The Brunauer-Emmett-Teller (BET) surface area was measured on a Quantachrome NOVA 1000 system at liquid N<sub>2</sub> temperature.

## 2.3. Electrochemical Measurements

Electrochemical measurements were performed with a CHI614D electrochemical analyzer (CH Instruments, Inc.,

Shanghai) with the use of a glassy carbon electrode (GCE, geometric area = 0.07 cm<sup>2</sup>) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire as the counter electrode. To prepare the working electrode, 5 mg of the catalyst and 10 μL of 5 wt% Nafion solution were dispersed in 1 mL of water/ethanol (49:50 v/v) mixed solvent, followed by ultrasonication for 30 min. Then 5 μL of the ink thus prepared was dropped onto the GCE surface. Linear sweep voltammetry (LSV) was performed in 0.5 M H<sub>2</sub>SO<sub>4</sub> with a scan rate of 2 mV s<sup>-1</sup>. Durability in 0.5 M H<sub>2</sub>SO<sub>4</sub> was tested by cyclic voltammetry (CV) with a scan rate of 100 mV s<sup>-1</sup> for 3000 cycles.

All voltages reported in our work were corrected for the ohmic resistance. The ohmic resistance used for iR-correction was obtained from electrochemical impedance spectroscopy (EIS) measurements. Catalysts-modified GCE were examined in the frequency range of 100 to 0.01 Hz at open circuit potential in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

In all measurements, SCE was used as the reference, but all potentials reported in our work are vs. the reversible hydrogen

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