

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ijhydene](http://www.elsevier.com/locate/ijhydene)

# Efficient and durable electrochemical hydrogen evolution using cocoon-like MoS<sub>2</sub> with preferentially exposed edges

Wei Li, Xiaoguang Wang, Dehua Xiong, Lifeng Liu\*

International Iberian Nanotechnology Laboratory (INL), Av. Mestre José Veiga, 4715-330, Braga, Portugal

## ARTICLE INFO

### Article history:

Received 25 January 2016

Received in revised form

30 March 2016

Accepted 31 March 2016

Available online 23 April 2016

### Keywords:

Molybdenum sulfide

Hydrogen evolution reaction

Electrocatalysis

Earth-abundant catalyst

## ABSTRACT

High-density cocoon-like molybdenum sulfide (MoS<sub>2</sub>) nanostructures have been fabricated by thermal oxidation of a metallic Mo foil, followed by a simple sulfurization process under hydrothermal conditions. The MoS<sub>2</sub> layer thickness is determined by that of the pre-formed oxide layer on Mo foils which can be readily tuned by thermal oxidation duration. The morphology and microstructure of the as-fabricated MoS<sub>2</sub> nano-cocoons are investigated in detail by SEM, XRD, Raman spectroscopy, and TEM. The results show that the cocoons consist of many vertically aligned ultrathin MoS<sub>2</sub> nanosheets with preferentially exposed edges, and that the MoS<sub>2</sub> layer is intimately bonded to the underneath Mo substrate for samples having a small layer thickness. Electrochemical tests demonstrate that all MoS<sub>2</sub>-Mo cathodes exhibit high electrocatalytic activities, small Tafel slopes and good long-term stability for the hydrogen evolution reaction (HER). The outstanding HER performance can be attributed to the existence of abundant electrocatalytically active edge sites and structural defects, and to the intimate electrical contact between MoS<sub>2</sub> and metallic Mo and the bind-free nature of the electrode, which facilitate electron transfer. Given the high electrocatalytic performance and the easy fabrication procedure, Mo supported cocoon-like MoS<sub>2</sub> holds substantial promise to substitute platinum for use to catalyze HER in water electrolyzers.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Electrochemical water splitting has long been known to be a clean and sustainable way to produce hydrogen (H<sub>2</sub>) fuel, a promising carbon-neutral energy carrier that has been proposed to be a primary renewable source for both stationary and transportation applications in the future [1]. H<sub>2</sub> produced by water electrolysis usually has high purity [2], and therefore

can be directly fed to H<sub>2</sub>-O<sub>2</sub> proton-exchange membrane fuel cells (PEMFCs) without the risk of poisoning the platinum (Pt) anode catalysts. Water electrolyzers together with PEMFCs have been suggested to be the major components of a decentralized grid in the future energy infrastructure [3]. However, the global H<sub>2</sub> production is only ca. 4% from water electrolysis at the moment [4], primarily because the electrolyzed H<sub>2</sub> is currently not economically competitive and viable compared to that produced by steam reforming of natural gas.

\* Corresponding author. Fax: +351 253140119.

E-mail address: [lifeng.liu@inl.int](mailto:lifeng.liu@inl.int) (L. Liu).<http://dx.doi.org/10.1016/j.ijhydene.2016.03.209>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

At present, Pt is the most efficient and commonly used electrocatalyst to catalyze the hydrogen evolution reaction (HER) in electrolyzers. But Pt is expensive and has limited availability in the earth's crust, and practically cannot be employed on a large scale that is commensurate with global demand. Therefore, many research efforts have recently been devoted to the search for non-precious, earth-abundant catalysts as alternatives to Pt, such as transition metal sulfides [5–9], phosphides [10–15], carbides [16–18], borides [18], and nitrides [19].

Molybdenum sulfide ( $\text{MoS}_2$ ), among many earth-abundant HER catalysts reported to date, has attracted considerable research interest because of its high activity and excellent long-term stability. According to density functional theory (DFT) calculations, the free energy of atomic hydrogen adsorption on  $\text{MoS}_2$ , a primary descriptor of the HER activity, is only ca. 0.1 eV [5], and therefore  $\text{MoS}_2$  should be able to accomplish HER with a small overpotential. This has been experimentally demonstrated in many works published in recent years [20–25]. It is now clear that the edges of  $\text{MoS}_2$  are electrocatalytically active sites for the HER [5,6]. However, due to the crystal habit, crystalline  $\text{MoS}_2$  prefers to form a layered structure with its basal planes exposed to electrolyte, which is not favorable to catalyze the HER. For this reason, a lot of efforts have been made to engineer the microstructure of  $\text{MoS}_2$  to make more catalytically active edge sites exposed. For example, Kibsgaard et al. synthesized three-dimensional mesoporous  $\text{MoS}_2$  network structure with double gyroid morphology where the active edge sites are preferentially exposed [20]. Hu et al. has developed amorphous  $\text{MoS}_x$  catalysts by electrochemical deposition which contain more coordinatively unsaturated sites contributing to the proton reduction [7]. Recently, vertically aligned layers of  $\text{MoS}_2$  were also reported, in which the density of active edge sites could be exposed to a great extent [21].

In this article, we report a simple and convenient method for the fabrication of Mo foil supported cocoon-like  $\text{MoS}_2$  nanostructures having a high density of exposed edge sites and structural defects (hereafter denoted as  $\text{MoS}_2$ -Mo foils). The  $\text{MoS}_2$ -Mo foils were obtained by thermal oxidation of metallic Mo substrates, followed by a sulfurization treatment using thiourea under hydrothermal conditions. By changing the thermal oxidation durations, we obtained  $\text{MoS}_2$ -Mo foils with different thicknesses of  $\text{MoS}_2$  catalyst layers, and thoroughly characterized these samples using scanning electron microscopy, X-ray diffractometry, Raman spectroscopy, and transmission electron microscopy. Furthermore, we used these  $\text{MoS}_2$ -Mo foils as binder-free cathodes, and investigated their catalytic performance towards the HER in acidic solution. In the end, we have discussed why the unique electrode structure of  $\text{MoS}_2$ -Mo foils renders high HER performance.

## Experimental

### Thermal oxidation of Mo foils

$\text{MoO}_3$ -Mo foils with tunable thicknesses of  $\text{MoO}_3$  layers were obtained by thermal oxidation of metallic Mo foils for varying durations. Prior to thermal oxidation, the Mo foil ( $4 \times 1 \text{ cm}^2$ ,

0.05 mm thick, 99.95%, Alfa Aesar) was cleaned by ultrasonication in 6 M HCl for 10 min, washed successively in water and acetone, and finally dried at 60 °C for 1 h under vacuum. Subsequently, the Mo foil was put into a muffle furnace that was pre-heated to 500 °C, and kept at that temperature in static air for different periods of time (i.e., 0.5 h, 1 h, 2 h, 3 h or 6 h) to obtain a  $\text{MoO}_3$  layer with different thicknesses. Finally, the foil was quickly taken out from the muffle furnace for quenching. The oxidized Mo foils are denoted as  $\text{MoO}_3$ -Mo-T, where T represents the oxidation time.

### Fabrication of $\text{MoS}_2$ -Mo foils

Following thermal oxidation, the obtained  $\text{MoO}_3$ -Mo foil was further subjected to a hydrothermal sulfurization treatment using thiourea (99.0%, Sigma-Aldrich) as the source of sulfur. Specifically, 0.5 g thiourea was dissolved in 30 mL de-ionized (DI) water under vigorous magnetic stirring for 30 min to form a homogenous solution. Subsequently, the solution was transferred to a Teflon-lined stainless steel autoclave reactor (Parr Instrument Company) with an inner volume of 45 mL. The  $\text{MoO}_3$ -Mo foils were then placed in the Teflon liner against the inner wall. The autoclave reactor was sealed, heated to 180 °C, maintained at that temperature for 18 h, and in the end cooled down to room temperature naturally. After the sulfurization, the foil was washed in sequence with DI water, ethanol and acetone, and dried at 40 °C under vacuum. The sulfurized foils are denoted as  $\text{MoS}_2$ -Mo-T, where T again stands for the oxidation duration of the Mo foil.

### Materials characterization

Scanning electron microscopy (SEM) examination was performed on a FEI Quanta 650 FEG microscope equipped with INCA 350 spectrometer (Oxford Instruments) for energy dispersive X-ray spectroscopy (EDX). Powder X-ray diffraction (XRD) experiments were conducted on a X'Pert PRO diffractometer (PANalytical) set at 45 kV and 40 mA, using Cu  $K\alpha$  radiation ( $\lambda = 1.541874 \text{ \AA}$ ) and a PIXcel detector. Data were collected with the Bragg-Brentano configuration in the  $2\theta$  range of 10–90° at a scan speed of  $0.01^\circ \text{ s}^{-1}$ . Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected-area electron diffraction (SAED) and EDX mapping studies were carried out on a probe-corrected transmission electron microscope operating at 200 kV (FEI Titan ChemiSTEM 80-200). Raman spectra were collected using the WITec Alpha 300R confocal Raman system with a laser excitation wavelength of 532 nm.

### Electrochemical measurements

All electrochemical measurements were performed on a Biologic VMP-3 potentiostat/galvanostat at room temperature (ca. 25 °C) in a typical three-electrode configuration. The HER performance was evaluated in 0.5 M  $\text{H}_2\text{SO}_4$  (pH = 0.40) solution using the as-fabricated  $\text{MoS}_2$ -Mo foil as the working electrode, a gold foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference. In our experiments, a Au foil (0.1 mm, 99.99%, Sigma-Aldrich), instead of Pt, was utilized as the counter electrode because Au is catalytically inactive for

Download English Version:

<https://daneshyari.com/en/article/7710439>

Download Persian Version:

<https://daneshyari.com/article/7710439>

[Daneshyari.com](https://daneshyari.com)