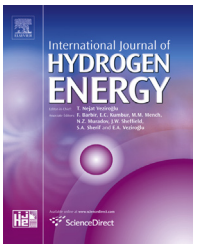
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–13

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Two-dimensional molybdenum disulfide and tungsten disulfide interleaved nanowalls constructed on silk cocoon-derived N-doped carbon fibers for hydrogen evolution reaction

QingFa Wang [a,**], RuoPing Yanzhang [a], XiaoNa Ren [a], Han Zhu [b,*], Ming Zhang [b], MingLiang Du [b]

[a] Key Laboratory for Green Chemical Technology of the Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, 92 Weijin Road, Tianjin, 300072, PR China

[b] Department of Materials Engineering, College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou, 310018, PR China

ARTICLE INFO

Article history:
Received 14 June 2016
Received in revised form
23 July 2016
Accepted 28 July 2016
Available online xxx

Keywords:
Silk derived N-doped carbon
Molybdenum sulfides
Tungsten disulfide
Hydrogen evolution reaction
Electrocatalysts

ABSTRACT

Finding cost-effective, active and durable catalyst materials for energy applications, such as electrocatalytic hydrogen production, is an intriguing challenge. Here, a facile and effective approach to the design and construction of two-dimensional MoS_2 and WS_2 interleaved nanowalls with maximum exposures of active edges on silk-derived N-doped carbon fibers (SNCF) was demonstrated. The morphological evolutions of the MoS_2 and WS_2 nanocrystals on the SNCF from crescent-like nanosheets to an interleaved nanowall network can be obtained by adjusting the concentrations of the Mo and W precursors. These robust MoS_2/SNCF and WS_2/SNCF electrocatalysts exhibit prominent hydrogen evolution reaction (HER) activities with onset potentials of −40 and −96 mV and Tafel slopes of 60 and 66 mV dec^{-1}, respectively. The overpotentials (η) at $j = -10$ mA cm^{-2} for MoS_2/SNCF and WS_2/SNCF are −102 and −157 mV, respectively. In addition, MoS_2/SNCF and WS_2/SNCF are both able to sustain continuous HER operation for 10 h under working conditions with only a slight degradation in current densities, implying excellent durability and a prospect for practical applications.

Introduction

Hydrogen is a clean and sustainable energy carrier that provides an environmentally friendly alternative energy source to meet future global energy demands [1]. The production of hydrogen by electrocatalytic or solar-driven water splitting requires highly efficient and robust catalyst materials [1,2]. The platinum group is at present the most active catalysts for the hydrogen evolution reaction (HER). Unfortunately, the high cost and low elemental abundance of the platinum group metals limit their application in large-scale hydrogen

* *Corresponding author*. Fax: +86 571 86843255.
** *Corresponding author*. Fax: +86 22 27892340.
E-mail addresses: qfwang@tju.edu.cn (Q. Wang), zhuhanfj@zstu.edu.cn (H. Zhu).

http://dx.doi.org/10.1016/j.ijhydene.2016.07.257
0360-3199/

production [3,4]. Motivated by this challenge, the search for cost-effective, Earth-abundant materials with both high HER activity at low overpotentials and excellent stability has recently attracted significant research interest and has become an important pursuit toward enabling a hydrogen economy [5,6].

Various classes of Earth-abundant transition metal compounds, such as MoS_2 [7], WS_2 [8], CoS_2 [1], $CoSe_2$ [9], and MoP [10] have been recently identified as promising HER electrocatalysts. Two-dimensional MoS_2 or WS_2 have been considered as the most promising catalysts because their hydrogen binding energies are comparable to that of the Pt-group metals, as determined by density functional theory calculations [7,8]. From both theoretical calculations and experimental studies, it is known that the HER active sites arise from the edges rather than the basal plane of an MoS_2 sheet [7,8]. Therefore, to realize the ideal catalytic activity of MoS_2, we should find an effective approach to design and construct novel structures of MoS_2 with exposed active edges. In addition, the poor conductivity of semiconducting MoS_2 limits the electron transfer and the electrocatalytic efficiency for the HER.

Carbon materials, such as graphene [11], carbon nanotubes [12], porous carbon [13] and carbon nanofibers [14], have been widely used to improve the electrochemical performance of catalysts. Recently, our group has reported that carbon materials not only serve as substrates but can also confine the growth of MoS_2 or WS_2, leading to novel nanostructures of two-dimensional transition metal sulfides with abundant active sites and high electrocatalytic activity toward the HER [15–17]. Carbon materials derived from natural resources and their conversion into functional building units are highly desirable [18,19]. Silk fiber is a filamentous natural protein fiber made of repeated amino acid patterns [20]. Researches on silk fibers are generally focused on its applications in the biomedical and clinical fields because of its excellent biocompatibility and biodegradability [21–23]. Moreover, silk fibers have a wealth of polypeptides and a high content of C, N, and O elements [21–25], which might provide a great opportunity for conversion into naturally derived heteroatom-doped carbon catalysts.

Herein, we utilized the chemical composition and fibrous structure of silk fibers to produce N-doped carbon fibers through simple pyrolysis. The resulting silk-derived N-doped carbon fibers (SNCF) serve as an effective substrate for the design and construction of MoS_2 and WS_2 nanowalls with exposed active-edges. The morphological evolution of MoS_2 and WS_2 nanocrystals on the SNCF from crescent-like nanosheets to an interleaved nanowall network can be obtained by adjusting the concentrations of the Mo and W precursors. The HER performances of various catalysts were measured to confirm the realization of the active-edge control, and a comprehensive investigation of the growth mechanisms was provided. The present investigation aimed to determine whether nanowalls with vertically aligned and densely packed MoS_2 and WS_2 nanosheets on SNCF possess the most exposed active edges and obtained outstanding HER performance. The robust MoS_2/SNCF and WS_2/SNCF electrocatalysts exhibit preeminent HER activity with onset potentials of −40 and −96 mV and Tafel slopes of 60 and 66 mV dec^{-1}, respectively. The overpotentials (η) at $j = -10$ mA cm^{-2} (mV) for MoS_2/SNCF and WS_2/SNCF are −102 and −157 mV, respectively. In addition, MoS_2/SNCF and WS_2/SNCF are both able to sustain continuous HER operation for 10 h under working conditions with only a slight degradation in the current density. The results reveal a stability under HER conditions and a strong coupling of the MoS_2 and WS_2 nanowalls to the SNCF, implying excellent durability and a prospect for practical applications.

Experiment section

Materials

Silk cocoons were prepared by feeding the Bombyx mori in our lab. Pt/C (20 wt %) and the Nafion solution (5 wt %) were purchased from Sigma–Aldrich. $(NH_4)_2MoS_4$, $(NH_4)_2WS_4$ and dimethyl formamide (DMF, 95%) were obtained commercially from Shanghai Civi Chemical Technology Co., Ltd. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of the silk-derived carbon fibers (SNCF)

Natural silk cocoons were prepared by feeding the *Bombyx mori* in our lab. In brief, the obtained silk cocoons were treated with distilled water in an ultrasonic bath for 2 h to remove adsorbed impurities. Then, the silk cocoons were dried at 50 °C for 12 h. The cleaned silk cocoons were placed into a chemical vapor deposition (CVD) furnace and carbonized at 900 °C at a heating rate of 4 °C/min for 3 h in an Ar/NH_3 atmosphere. The obtained silk-derived N-doped carbon fibers were treated with 1 M HNO_3 three times, washed with deionized water and dried at 60 °C for 24 h in a vacuum oven.

Preparation of the two-dimensional MoS_2 and WS_2 nanowall network on silk-derived carbon fibers

The as-prepared silk-derived carbon fibers served as the substrate for the growth of the two-dimensional MoS_2 and WS_2 nanosheets. Briefly, 110 mg of $(NH_4)_2MoS_4$ was dissolved in 50 mL of a DMF solution containing 330 mg of the as-prepared silk-derived N-doped carbon fibers. The mixture was stirred at room temperature for 2 h, transferred to a 50 mL Teflon-lined autoclave and kept in an oven at 200 °C for 12 h. Finally, the product was centrifuged, washed with distilled water, and then centrifuged repeatedly to remove the DMF. Pure MoS_2 nanoflowers were prepared using the same procedure in the absence of the SNCF. The preparation of WS_2 nanowalls were using the same procedure.

Fabrication of the catalyst-modified glassy carbon electrode (GCE)

To prepare the working electrode, 3 mg of the catalyst and 25 μL of the 5 wt % Nafion solution were dispersed in 1 mL of an isopropanol/water (3:1, v/v) mixed solvent, followed by ultrasonication for at least 30 min. Then, 5 μL of the mixture

Please cite this article in press as: Wang Q, et al., Two-dimensional molybdenum disulfide and tungsten disulfide interleaved nanowalls constructed on silk cocoon-derived N-doped carbon fibers for hydrogen evolution reaction, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.07.257