Defect-rich MoS$_2$ nanowall catalyst for efficient hydrogen evolution reaction

Junfeng Xie$^{1,2}$ ($^{\star}$), Haichao Qu$^1$, Jianping Xin$^1$, Xinxia Zhang$^1$, Guanwei Cui$^1$, Xiaodong Zhang$^2$, Jian Bao$^2$, Bo Tang$^1$, and Yi Xie$^2$ ($^{\star}$)

$^1$ College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Institute of Molecular and Nano Science, Shandong Normal University, Jinan 250014, China

$^2$ Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

Received: 20 November 2016
Revised: 10 December 2016
Accepted: 15 December 2016

© Tsinghua University Press and Springer-Verlag Berlin Heidelberg 2017

KEYWORDS
molybdenum disulfide (MoS$_2$), nanowall, water splitting, electrocatalysis, hydrogen evolution reaction

ABSTRACT
Designing efficient electrocatalysts for the hydrogen evolution reaction (HER) has attracted substantial attention owing to the urgent demand for clean energy to face the energy crisis and subsequent environmental issues in the near future. Among the large variety of HER catalysts, molybdenum disulfide (MoS$_2$) has been regarded as the most famous catalyst owing to its abundance, low price, high efficiency, and definite catalytic mechanism. In this study, defect-engineered MoS$_2$ nanowall (NW) catalysts with controllable thickness were fabricated and exhibited a significantly enhanced HER performance. Benefiting from the highly exposed active edge sites and the rough surface accompanied by the robust NW structure, the defect-rich MoS$_2$ NW catalyst with an optimized thickness showed an ultralow onset overpotential of 85 mV, a high current density of 310.6 mA·cm$^{-2}$ at $\eta = 300$ mV, and a low potential of 95 mV to drive a 10 mA·cm$^{-2}$ cathodic current. Additionally, excellent electrochemical stability was realized, making this freestanding NW catalyst a promising candidate for practical water splitting and hydrogen production.

1 Introduction

Designing efficient and robust electrocatalysts for the hydrogen evolution reaction (HER) has become increasingly important owing to the urgent requirement of high-energetic and environmentally benign energy carriers to solve the energy crisis and relevant pollution concerns [1–4]. Among the large variety of the as-explored HER electrocatalysts, molybdenum disulfide (MoS$_2$) has been considered as one of the classical candidates to replace state-of-the-art noble metal catalysts owing to its low price, abundance, high
efficiency, and definite catalytic mechanism [5–16]. Theoretical and experimental evidence indicates that the HER active sites in MoS2-based catalysts are located at the edges where abundant unsaturated sulfur atoms exist, while the thermodynamically favorable basal planes are catalytically inert, which significantly impedes the further optimization of MoS2-based catalysts towards an enhanced HER performance [5, 6].

In the past few years, many approaches have been developed that focus on the enrichment of active sites for earth-abundant-metal HER catalysts, including defect engineering [11, 12, 17–19], preferential exposure of active facets [7–9, 20–22], amorphization [23–25], and scaling catalysts to the nanoscale [26–29]. Among various morphological configurations, the nanowall (NW) structure comprising vertically aligned ultrathin nanosheets (NSs) may be a beneficial model for improving the HER performance of MoS2-based HER catalysts owing to its highly exposed edges, vertical channels for ion penetration, and intimate attachment between the active NW and the arbitrary substrate [30, 31]. For example, Cui et al. proposed that the sulfurization of a Mo thin film can lead to the generation of a vertically aligned MoS2 film with an enhanced HER performance, but the stringent experimental conditions may hinder practical applications [8–10]. Recently, our group explored the hydrothermal synthesis of defect-rich (DR) MoS2 NSs with additional active edge sites, but the poor charge transport between individual NSs unfortunately hampered the optimization of the HER activity [11].

In this study, using highly conductive indium tin oxide (ITO) glass as the substrate, a mild hydrothermal reaction was conducted, yielding the in situ growth of DR-MoS2 NW catalysts with tunable thickness. Detailed characterizations revealed that the DR-MoS2 NW catalyst had a porous surface with a high roughness, which is considered to be beneficial for HER owing to its superaerophobic feature and highly exposed edge sites [20]. Furthermore, the DR nature of the NS building blocks can provide additional active edge sites, which synergistically guarantees the high catalytic activity for the HER. Additionally, in sharp contrast to layer-by-layer (LbL) thin-film catalysts assembled from freestanding NSs, the intimate connection between the NW structure and the ITO substrate can result in an improved electrochemical stability during continuous HER operation. Owing to these benefits, the DR-MoS2 NW catalyst has great potential for replacing noble metal-based HER catalysts in practical water electrolysis.

2 Experimental

2.1 Fabrication of DR-MoS2 NW catalyst

In a typical procedure, (NH4)6Mo7O24·4H2O and thiourea were dissolved in 35 mL of distilled water under vigorous stirring in a Mo:S ratio of 1:5 to form a homogeneous solution. The concentration of (NH4)6Mo7O24·4H2O was selected in the range of 1/56 to 1/7 mmol, which corresponds to an $n_{Mo}$ range of 0.125–2 mmol. After 30 min of stirring, the solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave, and a piece of ITO-coated glass with 1.5 cm × 5 cm in size was completely cleaned by acetone, dried, and placed inside the autoclave with the conductive surface obliquely facing the bottom of the autoclave. The autoclave was maintained at 220 °C for 10 h. Then, the reaction system was cooled to room temperature. The as-obtained MoS2 NW electrode was rinsed with distilled water and ethanol at least three times and then dried naturally at room temperature. The thickness of the DR MoS2 NW electrodes was readily controlled by modifying the concentration of the precursors. For the synthesis of DR-MoS2 NW–200, 1/14 mmol of (NH4)6Mo7O24·4H2O was added, whereas for the synthesis of NW catalysts with thicknesses of 50, 100, and 300 nm, the amount of (NH4)6Mo7O24·4H2O was modified to 1/56, 1/28, and 1/7 mmol, respectively. The Mo:S ratio of the precursors was maintained at 1:5 for all the NW catalysts to ensure the formation of rich defects.

2.2 Fabrication of DR and defect-free (DF) MoS2 NSs

The DR-MoS2 NSs were prepared according to a previous study [11]. In a typical procedure, 1 mmol of (NH4)6Mo7O24·4H2O and 30 mmol of thiourea were dissolved in 40 mL of deionized water under vigorous stirring to form a transparent solution. Then, the solution was transferred into a 50 mL Teflon-lined