INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–12

Available online at www.sciencedirect.com

ScienceDirect

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

Facile synthesis of MoS_2/N-doped macro-mesoporous carbon hybrid as efficient electrocatalyst for hydrogen evolution reaction

Xiaoling Chen [a], Kangning Zhang [a], Zhenzhen An [a], Lina Wang [a], Yan Wang [a], Sen Sun [a], Tong Guo [a], Dongxia Zhang [a], Zhonghua Xue [b], Xibin Zhou [a,*], Xiaoquan Lu [b,**]

[a] Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, College of Geography and Environment Science, Northwest Normal University, Lanzhou 730070, China
[b] College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China

ARTICLE INFO

Article history:
Received 25 November 2017
Received in revised form
21 February 2018
Accepted 26 February 2018
Available online xxx

Keywords:
Molybdenum disulfide
N-doped macro-mesoporous carbon
Solvothermal method
Hydrogen evolution reaction

ABSTRACT

A novel three-dimensional (3D) hybrid consisting of molybdenum disulfide nanosheets (MoS_2) uniformly bound at N-doped macro-mesoporous carbon (N-MMC) surface was fabricated by the solvothermal method. The resulting MoS_2/N-MMC hybrid possesses few-layer MoS_2 nanosheets structure with abundant edges of MoS_2 exposed as active sites for hydrogen evolution reaction (HER), in sharp contrast to large aggregated MoS_2 nanoflowers without N-MMC. The high electric conductivity of N-MMC and an abundance of exposed edges on the MoS_2 nanosheets make the hybrid excellent electrocatalytic performance with a low onset potential of 98 mV, a small Tafel slope of 52 mV/decade, and a current density of 10 mA cm^{-2} at the overpotential of 150 mV. Moreover, the MoS_2/N-MMC hybrid exhibits outstanding electrochemical stability and structural integrity owing to the strong bonding between MoS_2 nanosheets and N-MMC.

Introduction

Nowadays, the rapid consumption of fossil fuels has brought about a sequence of serious environmental issues and energy crisis. Thus, developing green, economical, and renewable energy is a solution with great promise to solve this problem [1–4]. Hydrogen energy has been considered as a promising alternative energy source to substitute for traditional sources in the future, and drawn extensive attention because of the fact that it is an environmentally friendly [5]. Hydrogen can be sustainably produced by electrochemical of water splitting, the essential step in water electrolysis is the hydrogen evolution reaction (HER, $2H^+ + 2e^- \rightarrow H_2$) [6–8]. In general, Pt-group metals, such as Pt and Pd, are considered as the most efficient electrochemical catalysts for HER due to the exceptionally low overpotential [9]. However, large scale applications of noble metals have been further confined due to their expensive cost and low abundance [10]. Thus, it is desirable to develop inexpensive and earth-abundant catalysts with non-platinum rare metals for efficient hydrogen evolution,

* Corresponding author.
** Corresponding author.
E-mail addresses: zhouxb@nwnu.edu.cn (X. Zhou), Luxq@nwnu.edu.cn (X. Lu).
https://doi.org/10.1016/j.ijhydene.2018.02.163
0360-3199/

preferably based upon economic, non-poisonous and stable materials.

In recent years, many effective noble-metal-free electrocatalysts for HER including transitional metal sulfides [11–13], selenides [14], phosphides [15–17], nitrides [18,19], and carbides [20–22] have been explored. Among them, molybdenum disulfide (MoS_2) is proved to be a promising candidate in HER [23–26]. Both computational and experimental results verify that the HER catalytic activity derives from the sulfur edges of MoS_2 plates [27]. However, dispersed MoS_2 nanostructures easily aggregate and stack by reason of their high surface energy and interlayer van der Waals interaction, which limits the number of exposed active sites [28]. In addition, as a typical semiconductor material, the extremely low electrical conductivity of MoS_2 nanostructure, especially along the adjacent interlayers, hampers the electron transfer for highly efficient HER [29]. Taking these factors into account, the researchers mainly focus on following key strategies: (1) increasing the exposed active sites of sulfur edges, and preventing MoS_2 from agglomerating, and (2) further improving closely electronic contact between catalysts and electrode to accelerate H^+ adsorption and conversion into H_2 [30]. Thus developing MoS_2-based catalysts with layers on highly conductive substrate have been put forward as a promising solution, due to the fact that good conductivity of the substrates can lower the resistance of the catalysts. Carbon materials are ideal substrates for loading MoS_2 to enhance their electrocatalytic performance due to the remarkable conductivity and stability, including graphene [31], graphene oxide (GO) [32,33], graphene aerogels [34], graphene quantum dots [35], carbon cloth [36], carbon nanotubes (CNTs) [37], CNTs aerogel [38] and amorphous carbon [39].

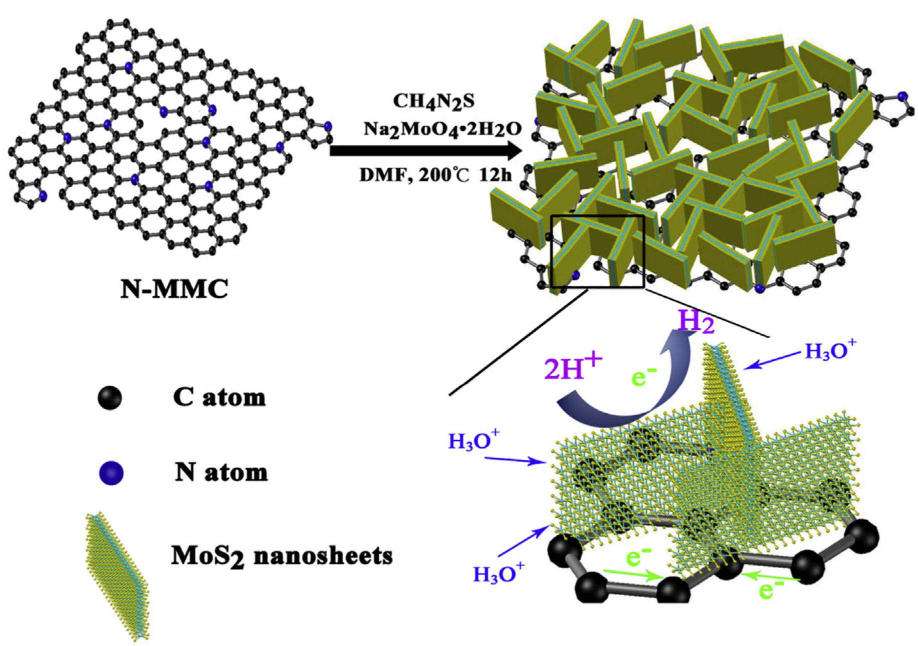
Hierarchical macro-mesoporous carbons (MMC) with mesopores located at the walls of the macropores have been drawn extensively interests due to large surface area, tunable pore structure, uniform and adjustable pore size, chemically inert nature, mechanical stability, good conductivity, and efficient mass transfer through macropores [40]. These outstanding features make them ideal candidates in the applications of electrochemical energy storage and conversion [41]. Later on, some researches indicate that the incorporation of heteroatoms, such as B, N and O, into the carbon lattice can significantly enhance the mechanical, semiconducting, field-emission, and electrical properties of carbon materials [42]. Particularly, N doping can enhance the surface polarity, electric conductivity, and electron-donor tendency of the porous carbons [43]. By far, N-MMC has been successfully used in many fields including ORR [44], gas adsorption [45], biosensing research [46], supercapacitors [47], and so on.

Based on above viewpoints, we describe the preparation of 3D hierarchical frameworks by the self-assembly of MoS_2 nanosheets on N-MMC via a simple one-step hydrothermal process. In this process, N-MMC acting as the 3D conductive substrate not only provides matrix for the nucleation and subsequent growth of MoS_2, but also improves the conductivity of the MoS_2/N-MMC, thus facilitating electron transfer during the HER electrocatalytic process. The fabrication procedure of MoS_2/N-MMC hybrid electrocatalyst is shown in Scheme 1.

Experimental

Materials

All chemicals were reagent grade and used as received without further purification in this work. Thiourea (CH_4N_2S, 99%), sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$, 99%) were purchased from Aladdin, N,N-dimethylformamide (DMF, ≥99.5%), and anhydrous ethanol were obtained from Tianjin Chemical Reagent plant, hydrazine hydrate was purchased



Scheme 1 – Schematic diagram of the fabrication procedure of MoS_2/N-MMC hybrid.

Please cite this article in press as: Chen X, et al., Facile synthesis of MoS2/N-doped macro-mesoporous carbon hybrid as efficient electrocatalyst for hydrogen evolution reaction, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.02.163