INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–8

Available online at www.sciencedirect.com

ScienceDirect

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

Carbon-coated molybdenum carbide nanosheets derived from molybdenum disulfide for hydrogen evolution reaction

Yunjie Huang[*], *Chenshuai Wang, Huaibing Song, Yaqi Bao, Xiaoqing Lei*

Faculty of Materials Science and Chemistry, China University of Geosciences (Wuhan), Wuhan, Hubei, 430074, PR China

ARTICLE INFO

Article history:
Received 14 January 2018
Received in revised form
8 February 2018
Accepted 19 March 2018
Available online xxx

Keywords:
Hydrogen evolution reaction
Molybdenum carbide
Nanosheet
Molybdenum disulfide

ABSTRACT

The design and synthesis of efficient non-noble metal catalyst is important for the practical application of hydrogen evolution reaction (HER) from water electrolysis. In this study, molybdenum carbides were prepared by a novel synthetic method, which involved the first exfoliation of 2D MoS_2 based on the principle of cold expansion of water below 4 °C and then carburization of exfoliated MoS_2. In this method, MoS_2 played roles of morphology template and molybdenum source simultaneously. Carbon-coated molybdenum carbide nanosheets were obtained and confirmed by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy. The stripping degree of MoS_2 was found to have an important influence on physical properties and catalytic performance of molybdenum carbides. Interestingly, Mo_2C nanosheets encapsulated in carbon nanotubes were observed when the MoS_2 with a high peeling degree was used in the preparation. It showed high activity and good durability towards HER in acid solution.

Introduction

Hydrogen energy is one of the most promising alternative energy for fossil energy due to its high energy density, cleanness and renewability. However, the current industrial production of hydrogen depends mainly on steam reforming from fossil hydrocarbons, which is contradictory to the renewability of hydrogen energy [1]. Hydrogen evolution reaction (HER) from water electrolysis provides a favorable approach for hydrogen production, especially when it is driven by the surplus electrical energy of renewable sources [2–5]. For HER, an electrocatalyst is generally needed to decrease overpotential and then energy consumption. It is encouraging that the element Pt has been found to show a high activity even at nearly zero overpotential. However, the scarcity and high price of Pt restricts its global-scale application [6–9]. Therefore, much attention has been paid to exploit non-noble HER catalyst such as transition metal carbides [7,10–15], nitrides [16–19], phosphides [20–26] and sulfides [27–34]. Among them, molybdenum carbide exhibits great application potential because of its platinum-like electronic properties [10,35]. Most research involved in molybdenum carbide is about the crystal structure, morphology, support and electron modification. For example, Huang et al. reported a high-utilization Mo_2C catalyst for HER, in which 3 nm Mo_2C nanoparticles were well dispersed on hierarchical carbon microflowers [36]. Shi et al. demonstrated in both theoretically

* *Corresponding author.*
E-mail address: yjhuang@cug.edu.cn (Y. Huang).

https://doi.org/10.1016/j.ijhydene.2018.03.233

and experimentally that phosphorus doping into Mo_2C was an effective way to modify the electronic configuration of Mo_2C and then benefit the catalytic activity towards HER [37]. Fe was incorporated into the lattice of Mo_2C, which causes a broader valence band and then result in the enhancement of catalytic activity for the HER [38]. MoC–Mo_2C heteronanowires composed of well-defined nanoparticles were prepared by a controlled carbonization method with aniline as template. The optimized electron density in the surface of MoC–Mo_2C composite was thought to contribute its high activity towards HER [39]. Another recent research focus is carbon-coated molybdenum carbides, which have been confirmed to show both high activity and good durability toward HER [10,40–42]. The carbon layer in the surface of molybdenum carbide could efficiently prevent the corrosion of molybdenum carbide in the electrolyte medium while electron penetration from the encapsulated molybdenum carbide was thought to benefit the HER. As summarized from these literature, it was the rational preparation approach that decided the catalyst formation and catalytic performance towards HER.

In this study, 2D MoS_2 was applied as both morphology template and Mo source for the preparation of molybdenum carbide. In order to study the effect of exfoliation degree of MoS_2 on the formation of molybdenum carbide, a simple freezing/unfreezing exfoliation method based on cold expansion principle of water below 4 °C was also developed. This simple preparation method was found to bring out carbon-coated molybdenum carbide nanosheets. Interestingly, molybdenum carbide nanosheets encapsulated in carbon nanotubes (CNTs) were formed when well-defined exfoliated MoS_2 was used in the preparation. It was very active and stable towards HER under acid condition.

Experimental section

Reagents

Commercial MoS_2, Nafion® (5 wt%), gas (CH_4 and H_2, 99.999%) and ethanol (99.7%) were purchased from Alfa Aesar, Sigma-Aldrich, Guangzhou Yuejia Gas and Sinopharm Chemical Reagent Co., Ltd, respectively. Pt/C (20 wt%) was from Johnson Matthey Company.

Exfoliation of MoS_2

The cold expansion principle of water at temperature of below 4 °C was applied for the exfoliation of layered 2D MoS_2. The exfoliation procedure was shown in Fig. 1. Firstly, 10 g of commercial MoS_2 (C–MoS_2) was added into 900 mL of deionized water. It was stirred for 48 h at room temperature and then transferred into a refrigerator which was set at −20 °C. After 24 h, it was taken out from the refrigerator and kept at room temperature until the ice thawed totally. This freezing/unfreezing process was repeated for 8 times. Next, the obtained black suspension was centrifuged at 3000 rpm for 10 min. The MoS_2 in the supernatant was collected by filtrating and drying treatment and referred to U–MoS_2 while the downside MoS_2 precipitation after drying was referred to D–MoS_2.

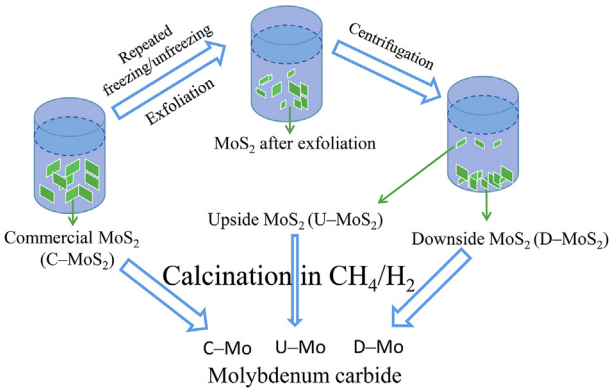

Fig. 1 – The schematic preparation process of molybdenum carbides.

Preparation of molybdenum carbide

As shown in Fig. 1, the molybdenum carbide was prepared by calcinating MoS_2 under CH_4/H_2 atmosphere. The carbonization temperature, carbonization time, heating-up rate, flow rate of H_2 and CH_4 was set as 1000 °C, 2 h, 8 °C min^{-1}, 80 mL min^{-1} and 20 mL min^{-1} in sequence. Three kinds of molybdenum carbide were prepared by using C–MoS_2, D–MoS_2 and U–MoS_2 as precursor and denoted as C–Mo, D–Mo and U–Mo, respectively.

Physical characterization

X-ray diffraction (XRD) patterns were obtained on a D8-Focus X-ray diffractometer equipped with a Cu K_α radiation source ($\lambda = 0.154$ nm). X-ray photoelectron spectroscopy (XPS) measurement was carried out using a Kratos XSAM-800 spectrometer with an Mg Kα radiator. The electron beam was corrected by C1s and the correction value was 284.6 eV. Raman spectra were processed on RM-1000 Raman spectrometer with a laser wavelength of 532 nm. Transmission electron microscopy (TEM) investigations were performed on a Philips TECNAI G2 microscope with an acceleration voltage of 200 kV.

Electrochemical measurements

The electro-catalytic performance of the prepared carbon molybdenum towards HER was tested by using a Gamry potentiostat/galvanostat instrument (Interface 1000, USA).

Before measurements, the practical potential of saturated calomel electrode (SCE) which was used as reference electrode in the following tests was calibrated and converted to reversible hydrogen electrode (RHE). The traditional three-electrode system with Pt working, Pt counter and SCE reference electrode was used for the calibration [43]. First, 0.5 M H_2SO_4 electrolyte were purged with H_2 for 30 min. A linear scanning voltammetry (LSV) with a scan rate of 0.1 mV S^{-1} was then run from −0.21 V to −0.30 V. The potential at the current of zero is considered as the thermodynamic potential (vs. SCE) and was found to be −0.268 V in this study.

Please cite this article in press as: Huang Y, et al., Carbon-coated molybdenum carbide nanosheets derived from molybdenum disulfide for hydrogen evolution reaction, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.03.233