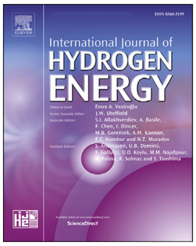
Available online at www.sciencedirect.com

ScienceDirect

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



Efficient hydrogen evolution catalyzed by amorphous molybdenum sulfide/N-doped active carbon hybrid on carbon fiber paper

Lun Yang [a,*], Xinyue Xiao [a], Zhan Yang [a], Yu Cai [a], Bo Xie [a], Nian Zhao [a], Xiang Li [a], Yu Wang [a], Meifeng Liu [a], Xiuzhang Wang [a], Guohong Wang [a], Zhixing Gan [b], Ming Meng [c], Wenyuan Yang [d], Jun Zhang [e], Jun-Ming Liu [a,f]

[a] Institute for Advanced Materials, Hubei Key Laboratory of Pollutant Analysis & Reuse Technology, Hubei Normal University, Huangshi 435002, China
[b] Key Laboratory of Optoelectronic Technology of Jiangsu Province, School of Physics and Technology, Nanjing Normal University, Nanjing 210023, China
[c] School of Physics and Telecommunication Engineering, Zhoukou Normal University, Zhoukou 466001, China
[d] Yunnan Jingxi New Material Technology Co., Ltd, Qujing 655000, China
[e] Faculty of Mathematics and Physics, Huaiyin Institute of Technology, Huaian 223003, China
[f] National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history:
Received 27 April 2018
Received in revised form
2 June 2018
Accepted 8 June 2018
Available online xxx

Keywords:
Amorphous
Molybdenum sulfide
Active carbon
Hydrogen evolution

ABSTRACT

Among numerous noble-metal-free electrocatalysts, molybdenum sulfides are recognized as promising candidates for hydrogen evolution reaction (HER). Owing to abundant under-coordinated sulfur atoms serving as catalytically active centers, intensive spectra studies have revealed that the HER property of amorphous molybdenum sulfide (a-MoS_x) is superior to crystal molybdenum sulfide (c-MoS_2). In this work, nitrogen-doped active carbon (NAC) is obtained through plasma treatment and amorphous MoS_x/NAC hybrid catalyst films are electrodeposited on carbon fiber papers (CFP) which are employed as porous three-dimensional electrodes with low resistivity. The incorporation of NAC increases the electrochemically active surface area, enhances the electron transport, and facilitates the reaction kinetics. Moreover, the functionality durability benefits from synergistic effect between a-MoS_x and NAC. Thus, the obtained hybrid catalyst delivers the excellent HER activity, requiring only 203 mV overpotential to achieve a geometrical current density of 100 mA cm^{-2} with a Tafel slope of ~43.9 mV per decade.

Introduction

Hydrogen has been recognized as an attractive energy source to achieve a low-carbon economy [1–3]. Once powered by electricity from solar and/or wind energy, hydrogen could be produced by water splitting, which requires efficient, low-cost, and stable HER catalysts [4–6]. Despite noble metal Pt has been identified as a benchmark catalyst for HER, its practical application is limited by the scarcity [7,8]. Recently,

---

* Corresponding author.
E-mail address: yanglun@hbnu.edu.cn (L. Yang).

https://doi.org/10.1016/j.ijhydene.2018.06.061

Please cite this article in press as: Yang L, et al., Efficient hydrogen evolution catalyzed by amorphous molybdenum sulfide/N-doped active carbon hybrid on carbon fiber paper, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.06.061

plenty of materials free of noble metals including transition metal sulfides, phosphides, borides, carbides, nitrides, and metal-free electrocatalysts such as FeS_2 [9], $NiSe_2$ [10,11], CoP [12], CoB [13], Mo_2C [14], WN [15], and (N,P)-codoped carbon networks [16] have been reported as potential HER catalysts. These materials deliver rather high HER efficiency and are composed only of earth-abundant elements [17–19].

Especially, molybdenum sulfide stands out due to its facile synthesis approaches, extraordinary catalytic activity, and good electrochemical robustness [20,21]. It has been clarified that edge sites instead of the inert (0 0 0 1) basal planes are catalytically active [7,22]. Considering that both Mo sites and S sites on edges are chemically under-coordinated, the coordination environment and surface electronic states of molybdenum sulfide determine the Gibbs free energy for adsorbed atomic hydrogen (ΔG_H) [23]. This free energy ΔG_H is the crucial parameter for hydrogen generation and its optimum value should be zero, which means that the hydrogen binding should be neither too strong nor too weak [7,24].

Varied strategies have been proposed to modulate the coordination states including exposing edges [25], generating sulfur vacancies [7,26], Ni/Co doping [27,28], or designing stepped surface structures [23]. Thus, the quantity of active sites on molybdenum sulfide is largely increased, the per-site catalytic activity is significantly promoted, and finally the HER performance is remarkably enhanced [27,29]. The electronic structure could be optimized and the reaction barrier could be further lowered by forming $W_xMo_{1-x}S_2$ alloys [30] or electron doping of 1T-MoS_2 (trigonal symmetry) [31]. Besides, increased carrier concertation and electron injection result in the adjustment of Fermi level and activation of basal planes for 2H–MoS_2 (hexagonal symmetry) through reducing the contact resistance [32], field effect [4], or proton intercalation [33].

Compared with *c*-MoS_2, amorphous molybdenum sulfide possesses vast coordinately unsaturated sulfur centers [34,35], which are catalytically active for HER [36]. Despite the controversy about which is more active between terminal S_2^{2-} ligands and bridging S_2^{2-} ligands [37,38], *a*-MoS_x provides more degrees of freedom to tune its local stoichiometry and electronic structure [36,39]. Even without purposely structural design, *a*-MoS_x fabricated by electrodeposition, wet-chemical synthesis, or thermolysis exhibits impressive HER activity, making it even a better choice for hydrogen generation [39–41]. However, as a consequence of amorphous atomic structure, *a*-MoS_x still suffers from small specific surface area, large electronic resistance, and unsatisfactory durability till now [20].

To overcome those drawbacks, one sees that the charge transport could be improved by using conductive substrates such as graphene [42], carbon nanotube [43,44], and polypyrrole [45]. Interactions between substrate and catalyst are usually not strong enough to robustly anchor disulfide ligands and efficiently modify the coordination environment, which are crucial to HER kinetics [32,38].

Here, we prepare an amorphous MoS_x/NAC hybrid catalyst on CFP through a two-step fabrication process, *i.e.* a plasma treatment followed by electrodeposition. Nitrogen doping is an efficient method to ameliorate conductivity and surface energy of carbon materials, leading to a more reasonable affinity for substrate to anchor catalyst [44,46]. In our approach, nitrogen is introduced to active carbon through plasma treatment. Utilization of appropriate hierarchical structure and application of porous electrode have been proved to maximize the electrochemically active surface area sufficiently, which is the most direct way to increase the quantities of active sites [43]. The rational design of MoS_x/NAC hybrid films benefits from porous structure and good electroconductivity of NAC and CFP. In addition, the electron-rich nitrogen doping brings in a synergistic effect between *a*-MoS_x and NAC, increasing and stabilizing the active S_2^{2-} content. Therefore, the obtained *a*-MoS_x/NAC/CFP catalyst boosts hydrogen evolution reaction efficiently with a small Tafel slope of ~43.9 mV per decade.

Experimental section

Sample preparation

Nitrogen-doped active carbon (NAC) particles are synthesized by plasma treatment. For this sequence, an alumina boat loaded with active carbon (50 mg, YP-50F, Kuraray Chemical Co., Ltd.) is inserted into a vacuum tube furnace (BTF-1200C-II-AS-PECVD, Anhui BEQ Equipment Technology Co., Ltd.). The sample is then treated by nitrogen plasma at 200 °C for 120 min utilizing an inductively coupled radio frequency power source (13.56 MHz) operated at 100 W. The pressure is kept around 1×10^{-2} mBar with a nitrogen flow rate of 3 standard-state cubic centimeter per minute (sccm). Ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$, 99.95%, J&K Scientific Ltd) is dissolved in high-purity de-ionized water (18.2 $M\Omega\ cm^{-1}$) with a concentration of 10 mmol L^{-1}. Then, different amount of NAC is added. The mixture solution is intensively stirred and let stand for about 6 h. After that, the catalyst film on the carbon fiber paper (CFP, HCP030 N, Shanghai Hesen Electric Co., Ltd.) is produced by an electrochemical method. A potentiostatic electrodeposition is performed in the mixture solution at +0.40 V vs. Ag/AgCl for 20 min. For simplification, the samples are designated as MoS_x/NAC–xx, where xx labels the content of NAC in mixture solution in unit of mg per 10 mL. Besides, the amorphous molybdenum sulfide (MoS_x) films on CFP are prepared too, for reference and comparison in the similar way expect that no NAC was added.

Characterization

The as-prepared samples are characterized in microstructure by field-emission scanning electron microscopy (FE-SEM, FEI SIRION 200), X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB250Xi), and X-ray powder diffraction (XRD, Bruker D8 advanced). Here, the nitrogen adsorption and desorption isotherms are obtained at 77 K on an adsorption analyzer (Micromeritics Instrument Co. ASAP2020). The specific surface area is derived from nitrogen adsorption according to the Brunauer-Emmett-Teller (BET) method.

Electrochemical measurements

The electrochemical measurements are performed on a three-electrode system using a CHI 660E workstation (CH Instrument)

Please cite this article in press as: Yang L, et al., Efficient hydrogen evolution catalyzed by amorphous molybdenum sulfide/N-doped active carbon hybrid on carbon fiber paper, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.06.061