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Hierarchical MoS_2 nanoflowers on carbon cloth as an efficient cathode electrode for hydrogen evolution under all pH values

*Baodong Mao [a], Bo Wang [a], Furong Yu [a], Kewei Zhang [a], Zhengyuan Zhang [a], Jinhui Hao [a], Junbo Zhong [b], Yanhong Liu [a,**], Weidong Shi [a,*]*

[a] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, PR China
[b] Key Laboratory of Green Catalysis of Higher Education Institutes of Sichuan, College of Chemistry and Environmental Engineering, Sichuan University of Science and Engineering, Zigong, 643000, PR China

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ABSTRACT

In this paper, a facile hydrothermal synthetic strategy was developed for MoS_2 nanoflowers with enlarged interlayer spacing on the carbon cloth (CC) as a high efficiency cathode electrode for hydrogen evolution reaction (HER) under wide pH condition. It was observed that the loading amount of MoS_2 has a major impact on the HER performance, where the optimized MoS_2/CC exhibited a low onset potential of 94 mV and a small Tafel slope of 50 mV dec^{-1} in strong acid solution (pH = 0). The improved HER performance can be contributed to the enlarged interlayer spacing, abundant defects and more exposed active sites in the small size MoS_2 nanosheets as revealed by XRD and HRTEM. Meanwhile, it also exhibited relatively good performance for HER under basic and neutral conditions with the overpotentials of 188 (pH = 14) and 230 (pH = 7) mV to achieve current density of 10 mA cm^{-2} and the Tafel slopes of 52 and 84 mV dec^{-1}, respectively.

Introduction

With the global energy and environmental crisis intensified, hydrogen generation through electro-hydrolysis will be an effective way to replace traditional fossil fuels to cope with the growing energy crisis and environmental pollution [1,2]. However, it requires highly efficient electrocatalysts for hydrogen evolution reaction (HER) to provide high current with low potential [3,4]. Pt group metals have been well known as the most popular electrocatalytic materials. Nevertheless, the high cost and rare reserves of Pt group materials limit their application [5,6]. Moreover, the electrochemical water splitting system requires the capability of working under different conditions, such as in strong acid (in proton exchange membrane (PEM) technology) [7], neutral solution (in microbial electrolysis cell) [8], or strong basic solution (in industrial alkaline electrolysis) [9]. It is also worth mentioning that Pt catalysts are not ideal for HER in neutral and alkaline solutions. As such, developing efficient electrocatalysts from

* Corresponding author.
** Corresponding author.
E-mail addresses: liuyh@ujs.edu.cn (Y. Liu), swd1978@ujs.edu.cn (W. Shi).
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earth-abundant inexpensive materials for HER in broad pH solution have attracted great interest [10]. Recently, two-dimensional (2D) layered transitional-metal dichalcogenides, such as MoS_2 [11], WS_2 [12], $MoSe_2$ [13] and WSe_2 [12], exhibited unique advantages as electrocatalysts for HER.

Among these materials, MoS_2 has drawn great attention as an active HER catalyst in acid solution. MoS_2 possesses the structure of 2D layers similar to that of graphene, with stacked S-Mo-S layers through weak van der Waals interactions [14]. Both theoretical and experimental researches have demonstrated that MoS_2 has the catalytic active edge sites for HER [15,16]. The active edge sites will increase significantly when the size of MoS_2 is reduced to the nanoscale, resulting in an increase of HER performance, such as, ultrathin defective MoS_2 nanosheets [17], nanostructured hollow spheres [18], nanoflowers [19], MoS_2 nanodots [20], and edge-exposed porous films [21]. Moreover, researchers recently have found that enlarged interlayer spacing of MoS_2 can increase the HER performance of these MoS_2-based electrocatalysts [22–24]. Lan et al. synthesized an ultrathin MoS_2/N-RGO nanocomposite with enlarged interlayer spacing for enhanced HER in acid by a simple hydrothermal method [23]. Xue et al. reported P-doped MoS_2 nanosheets with increased active sites and enlarged interlayer spacing for improved HER [24]. Additionally, the exceedingly low conductivity of MoS_2 itself significantly limit the overall HER rate. Furthermore, prior to electrochemical tests, such catalysts were required to effectively regulate on glassy carbon electrode with polymer binders, which might increase the series resistance, hide catalytic active site and affect diffusion to reduced electrocatalytic activity [25,26]. Therefore, combining with conductive substrates to form a three-dimensional catalyst has attracted considerable interest for the development of efficient electrocatalysts with increased surface area and charge transportation. However, these electrocatalysts were mainly studied in acid solution for HER, while only very few literature aimed in neutral and alkaline conditions due to the insufficient H^+ to react on the electrode surface [27]. The relatively low catalytic activity may be attributed to the fact that it quires to break the H-O-H bond that is more difficult than the reduction of H_3O^+ [28]. Liu et al. prepared MoS_2 on the carbon cloth (CC) with low catalytic activity in neutral electrolyte due to the low H^+ concentrations and poor conductivity [29]. Similarly, MoS_2 nanosheets array supported on CC shows low HER performance in alkali. However, as far as we know, no research work has been contributed to the structure manipulation of MoS_2-based HER catalysts under a wide pH range, which is necessary to study.

In the present work, we report the direct growth of 3D hierarchical MoS_2 nanoflower arrays on CC towards efficient HER over a wide pH range. With phosphomolybdic acid as the Mo source, MoS_2 nanoflowers with small lateral size and enlarged interlayer spacing were obtained. As a result, an excellent HER performance of the MoS_2/CC was achieved over a wide pH range with small overpotentials of 160, 230 and 188 mV at a current density of 10 mA cm^{-2} and small Tafel slopes of 50, 84 and 52 mV dec^{-1} in pH = 0, 7 and 14, respectively. The improved HER performance may be ascribed to the cooperative effect of the massive exposed active edge sites from the more defect structure and small lateral size, enlarged interlayer spacing, and the inherent electrical conductivity of CC. This work suggests the great potential of rational nanostructure design of MoS_2 for the development of efficient HER cathode under all pH values.

Experimental section

Reagents and materials

All chemicals are analytically pure and used without further purification. Carbon cloth (CC) was bought from Hesenbio Ltd. (Shanghai, China). Phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot xH_2O$) was purchased from Sinopharm Chemical Reagent Co. Ltd. Thiourea (CN_2H_4S, $\geq$99.0%) was purchased from Shanghailingfeng Chemical Reagent Co. Ltd. Nafion solution (5%) and graphite rod (99.9995%) were purchased from Sigma-Aldrich. Absolute ethanol and sulphuric acid (H_2SO_4, 95.0–98.0%) were purchased from Beijing Chemical Co. (China). Potassium hydroxide (KOH), sodium dihydrogen phosphate (NaH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4) were purchased from Aladdin Reagent. The water used in the experiments was ultra-pure water.

Preparation of MoS_2/CC

Firstly, CC was sonicated with acetone, ethanol and deionized water several times to clean the CC surface before use. In brief, 2 mL of 0.014 mM PMo_{12} solution was added to deionized water (25 mL) by stirring to form a homogeneous solution. Then, 2 mL of 0.67 mM thiourea solution was added into the above solution (Mo:S molar ratio = 1:4). The solution and CC (1×2 cm^2) were transferred into a 50 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 24 h, which was then cooled down to room temperature naturally. The final product (denoted as MoS_2/CC-1) was washed with deionized water and absolute ethanol, and dried in a vacuum oven at 60 °C overnight. Similarly, the synthesis step of MoS_2/CC-x (x = 2, 3, 4) nanocomposites was the same with the above method except for the different amounts of MoS_2. MoS_2/CC-2, MoS_2/CC-3, MoS_2/CC-4 samples were prepared using 4, 6, 8 mL of 0.014 mM PMo_{12} and 0.67 mM thiourea as the precursors at 180 °C for 24 h, respectively.

Characterizations

Crystal structure of the samples were studied by X-ray diffraction (XRD) using Cu-Kα radiation source (λ = 1.54056 Å) under 40 kV and 40 mA ranging from 5° to 75° at a scanning rate of 7.0° min^{-1} (Bruker AXS, Germany). Raman spectra were recorded with an America ThermoFisher (DXR) Laser Raman Spectrometer with a 532 nm laser. The morphology of the samples was observed using a field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan). Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and scanning transmission electron microscopy (STEM) were also used to explore the structure of the samples with a Tecnai G2 F30 S-Twin (FEI) electron microscope with an accelerating voltage of 200 kV.

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