Applied Surface Science 439 (2018) 343–349

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Improving the catalytic activity of amorphous molybdenum sulfide for hydrogen evolution reaction using polydihydroxyphenylalanine modified MWCNTs

Maoguo Li *, Muping Yu, Xiang Li

Anhui Key Laboratory of Chemo-Biosensing, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, PR China

ARTICLE INFO

Article history:
Received 12 October 2017
Revised 3 January 2018
Accepted 7 January 2018
Available online 9 January 2018

Keywords:
Hydrogen evolution reaction
Amorphous MoS_x
PDOPA
MWCNTs

ABSTRACT

Molybdenum sulfides are promising electrocatalysts for hydrogen evolution reaction (HER) in acid medium due to their unique properties. In order to improve their HER activity, different strategies have been developed. In this study, amorphous molybdenum sulfide was prepared by a simple wet chemical method and its HER activity was further improved by using polydihydroxyphenylalanine (PDOPA) modified MWCNTs as supports. It was found that the PDOPA can effectively improve the hydrophilic properties of multiwalled carbon nanotubes (MWCNTs) and amorphous MoS_x can uniformly grow on the surface of PDOPA@MWCNTs. Compared with MoS_x and MoS_x/MWCNTs, MoS_x/PDOPA@MWCNTs show obviously enhanced HER activities due to the superior electrical conductivity and more exposed active sites. In addition, the effect of the ratio of MoS_x and PDOPA@MWCNTs and the loading amount of catalysts on the electrodes are also investigated in detail. At the optimum conditions, MoS_x/PDOPA@MWCNTs display an overpotential of 198 mV at 10 mA/cm^2, a Tafel slope of 53 mV/dec and a good long-term stability in 0.5 M H_2SO_4, which make them promising candidates for HER application.

1. Introduction

Water splitting is an attracting strategy to produce clean and highly efficient hydrogen energy due to its environmentally friendly process and utilization of renewable and intermittent sources such as solar energy [1,2]. However, the sluggish kinetics of hydrogen evolution reaction (HER) on the cathode hamper the development of this technique. To overcome this bottleneck, effective, stable and low-cost HER electrocatalysts are desperately required. Despite the excellent HER catalytic activity, Pt-based material are not ideal catalysts because of their low abundance and high cost.

Recently, molybdenum sulfide materials have been intensively investigated as HER electrocatalysts due to their catalytic activity, high stability in acid medium and low cost [3–7]. Nevertheless, the HER catalytic activity of molybdenum sulfide is much poorer than that of Pt-based catalysts and unable to meet the requirement of practical application. Many efforts have been dedicated to improving the catalytic activity of molybdenum sulfide. Considering that the catalytic active site of such materials is the sulfur atoms on the edges [8], the first strategy is to prepare ultrathin [9,10] or amorphous molybdenum sulfide [11–15] to expose more active sites. Secondly, molybdenum sulfide can be integrated with electrically conductive support to avoid their agglomeration and accelerate the electron transport [16–19]. In addition, doping molybdenum sulfide with transition elements such as Fe and Co has proved to be an effective method to improve the catalytic activity [20,21].

Combining the above two strategies, amorphous molybdenum sulfide supported on (multiwalled carbon nanotubes) MWCNTs was designed as the HER electrocatalysts in this study. Amorphous molybdenum sulfide generally exists in the form of $Mo^{IV}S_2^{2-}S^{2-}$ [22]. Compared with crystalline MoS_2, amorphous molybdenum sulfide not only can provide more active sites and faster diffusion of electrolyte but also can be prepared by a facile and scalable wet chemical method. However, the aggregation of pure amorphous molybdenum sulfide limits its catalytic activity. Thus, MWCNTs with large surface area and high electrical conductivity is chosen as the support of amorphous molybdenum sulfide.

It is well known that the surface properties of supports can greatly affect the dispersity of catalysts, the interaction between catalysts and support, and further the catalytic activity [23]. To improve the catalytic activity of the composites, hydrophilic groups are often introduced on the surface of CNTs by refluxing

---

* Corresponding author.
E-mail address: limaoguo@mail.ahnu.edu.cn (M. Li).

https://doi.org/10.1016/j.apsusc.2018.01.063
0169-4332/

them in concentrated nitric acid for a long time [24] or doping heteroatoms under high temperature [25].

In contrast, polydopamine (PDA) provides a facile route to modify diverse substrates by the self-polymerization of dopamine under mild conditions [26–28]. They can bring abundant hydrophilic groups such as hydroxyl (—OH) and amino (—NH_2) on the surface of the substrates without impairing the properties of the substrates.

3,4-L-Dihydroxyphenylalanine (DOPA) is a compound with a similar structure to dopamine, which contains amino acid and catechol groups. It has been reported that DOPA can be self-polymerized under the similar conditions to DA [29]. The structures of DOPA and the corresponding polymer are shown in Fig. 1. The polymer of DOPA (PDOPA) has been used as surface modification materials for water purification membranes to improve the hydrophilic and fouling resistance properties [30,31]. However, up to now, the PDOPA has rarely been used to modify substrates such as CNTs or other carbon materials, although it has more functional groups (e.g. —COOH) than PDA.

In this research, PDOPA is used to functionalize CNTs by the oxidative polymerization of DOPA in alkaline medium for the first time. The CNTs modified by PDOPA (PDOPA@MWCNTs) were then used as the support to grow amorphous MoS_x in situ. The synthesized MoS_x/PDOPA@MWCNTs shows enhanced HER catalytic activity in comparison with MoS_x/MWCNTs. Thus, PDOPA is expected to be applied to functionalize other carbon-based material as a new modification material and to find applications in wide fields.

2. Experimental

2.1. Reagents

$Na_2MoO_4 \cdot 2H_2O$, $Na_2S \cdot 9H_2O$, were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. The MWCNTs, multiwalled carbon nanotubes (diameter 20–40 nm, length 5–15 μm) were purchased from Tokyo Chemical Industry CO., Ltd. (Japan) and used as received. 3,4-Dihydroxy-L-phenylalanine (DOPA) was obtained from Sangon Biotech Co., Ltd (Shanghai). Deionized H_2O (Millipore, Resistivity ≥18. 2 MΩ·cm at 25 °C) was used throughout.

2.2. Synthesis of electrocatalysts

2.2.1. The modification of MWCNTs with PDOPA

20 mg multi-wall carbon nanotubes (MWCNTs) and 40 mg 3,4-dihydroxy-L-phenylalanine (DOPA) were sonicated for 30 min in 40 mL H_2O, and then tris-(hydroxylmethyl) aminomethane was added to adjust pH to 8.5 [29]. After vigorous stirring for 6 h, cleaning with water and vacuum filtration, the PDOPA functionalized MWCNTs (PDOPA@MWCNTs) were obtained.

2.2.2. Synthesis of MoS_x/PDOPA@MWCNTs

As-prepared PDOPA@MWCNTs and 50 mL H_2O were sonicated for 5 min to form a uniform suspension and then 0.4 mmol $Na_2MoO_4 \cdot 2H_2O$ and 1.6 mmol $Na_2S \cdot 9H_2O$ were mixed with the suspension. Next, 4 mL 3 M HCl was added drop by drop into the mixture. After vigorously stirring for 0.5 h and boiling for 0.5 h to ensure complete reaction, the product was filtrated off, washed with water and dried in air. For control experiments, PDOPA@MWCNTs was replaced by original MWCNTs and the procedures were carried out in the same manner as aforementioned.

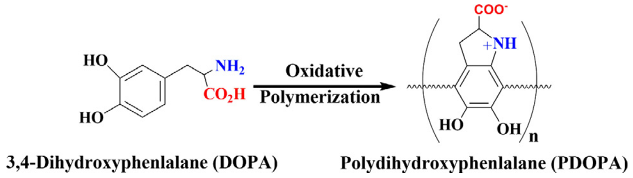

Fig. 1. The structure of DOPA and PDOPA.

To optimize the ratio of MoS_x/PDOPA@MWCNTs, the amount of $Na_2MoO_4 \cdot 2H_2O$ varied from 0.1, 0.4 to 0.8 mmol, but the mole ratio of $Na_2MoO_4 \cdot 2H_2O/Na_2S \cdot 9H_2O$ was set to be 1:4.

2.3. Structural characterizations

Transmission electron microscopy (TEM) and high resolution TEM (HR-TEM) images were carried out on a Tecnai G2F20 microscope operating at 200 kV. Scanning electron microscopy (SEM) images were performed on S-4800 field-emission scanning electron microscope (Hitachi, Japan). Powder X-ray diffraction (XRD) data were recorded with a D8 Advance using Cu Kα radiation (λ = 0.15406 nm) at 40 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo ESCALAB 250Xi spectrometer equipped with an Al anode (Al Kα = 1486.6 e V) and the energy valued were calibrated by using the C1s level of 284.8 eV.

2.4. Electrochemical characterizations

To evaluate the electrochemical HER activity of catalyst, 4 mg of catalyst was sonicated for 30 min in 1 mL 45 v% ethanol aqueous solution to form a homogeneous ink. Drop-coating technique was used to prepare catalyst modified glassy carbon electrode (diame ter = 3 mm). Then, 5 μL 0.5 wt% Nafion solution was added onto glassy carbon electrode (GCE) for fixing. The catalyst modified GCE was used as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and a glassy carbon rod as the counter electrode. Electrical impedance spectroscopy (EIS) was recorded under the following conditions: Potential −0.4 V (*vs.* SCE), AC voltage amplitude 5 mV, frequency ranges $1 \times 10^5 \sim 0.01$ Hz. Linear sweep voltammetry with a scan rate of 5 mV/s was tested in 0.5 M H_2SO_4 electrolytes. Amperometric i-t technology was conducted 4000 s at the constant potential: −0.5 V (*vs.* SCE) in different electrolytes to examine its electrocatalytic stability. In order to compare the results with the literature, all the potentials reported here were converted from *vs.* SCE to *vs.* RHE according to the equation: $E\ (\mathrm{RHE}) = E\ (\mathrm{SCE}) + 0.2415 + 0.059\ pH$ and the current density was normalized to the geometrical area of the GCE. Before all electrochemical measurements, the electrolyte solution was degassed by bubbling N_2 for 30 min at least. All electrochemical measurements were taken on CHI660E.

3. Results and discussion

3.1. Characterization of prepared HER electrocatalysts

MoS_x/PDOPA@MWCNTs were prepared by directly growing MoS_x on the PDOPA modified MWCNTs via a simple wet chemical method. It was expected that the functionalization of MWCNTs with PDOPA could improve the dispersity of MoS_x on MWCNTs and enhance the interaction between them due to its functional groups such as —NH_2, —COOH, and —OH.

First of all, the PDOPA@MWCNTs was successfully prepared, which can be confirmed by the different morphology and wettability between original MWCNTs and PDOPA@MWCNTs. Fig. 2a and b shows the SEM images of original MWCNTs and PDOPA@MWCNTs. The original MWCNTs display morphology of gathered bundles, while the PDOPA@MWCNTs disperse uniformly with much less aggregation. In the case of the wettability, as can be seen in the