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One-step liquid phase chemical method to prepare carbon-based amorphous molybdenum sulfides: As the effective hydrogen evolution reaction catalysts



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ABSTRACT

Two different kinds of carbon-based amorphous molybdenum sulfide composite catalysts (activated carbon supported amorphous molybdenum sulfide and acetylene black supported amorphous molybdenum sulfide) had been prepared in a facile and scalable one-step liquid phase chemical method. The morphological and structural information of catalysts was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-Ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and it's electro-catalytic HER activity were evaluated by linear sweep voltammetry(LSV), amperometric i-t technology and AC impedance technology. The as-prepared carbon-based amorphous molybdenum sulfides showed greatly enhanced electro-catalytic activity for HER compared with pure amorphous molybdenum sulfides. Especially, the nano-sized acetylene black supported molybdenum sulfide exhibited excellent electro-catalytic HER performances with a low onset potential of -116 mV versus reverse hydrogen electrode (RHE) and a small Tafel slope of 51 mV per decade.

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1. Introduction

As a renewable and environmentally friendly energy carrier, hydrogen (H₂) had been attracting researchers' eyesight [1]. Currently, the best way to produce hydrogen is electro-catalytic or photo-catalytic "water splitting" [2]. The electro-catalytic "water splitting" reaction consists of two half reactions: the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). And HER (i.e., $2H^+ + 2e^- \rightarrow H_2$) requires a catalyst to decrease the overpotential (η) and consequently increase the efficiency of this significant electrochemical process [3,4]. It is no doubt that the noble metal Platinum and its' composites have the best electrocatalytic HER activity in acid medium [5,6]. However, the high price and scarcity of the natural storage limit it for the practical applications [6,7].

In recent years, Molybdenum sulfides (MoS_x , x = 2, 3) and its' composite materials have been reported to show high eletrocatalytic HER activity and good stability in the acidic medium [2,8-

10]. And it's expected to be able to replace the noble metal in electro-catalytic HER application. It had been proved that the electro-catalytic HER activitiy of Molybdenum sulfides are connected with the amount of the active sulfur edges sites [11,12] (i.e., nano-sized molybdenum sulfides have better electro-catalytic HER activity than micro-sized) and it's conductivity which related to the phase structure [13]. Although, the nano-sized MoS₂ could be obtained from the bulk MoS₂ in many ways, such as liquid exfoliation [14], sonication [12] and mechanical crush [15] and so on, it had been reported by Li et al. [16] that these nanoparticles will aggregate after storage for several days in liquid solution which may reduce the amount of the active S edges, thus leading to an inferior electro-catalytic HER activity. Therefore, there still remains challenge to obtain stable MoS₂ nanosheets or nanospheres from the bulk MoS₂ to meet the practical application.

At the same time, recent work has revealed that the amorphous Molybdenum sulfides(MoS₃) are active catalysts for the HER in acidic medium [10,17–21]. Usually, amorphous molybdenum sulfides (MoS₃) are prepared by wet chemical method through acidification of tetrathiomolybdate or another precursors solutions [19,21,22]. Compared to the hydrothermal synthesis [23–25], solvothermal synthesis [26,27], chemical vapor deposition method [28], chemical method is faster, simpler





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and more scalable. Lots of excellent works which related with amorphous molybdenum sulfides (MoS_3) in solution had been reported by Hu's group [10,18–20] and Jaramillo's group [21]. After centrifugation and drying, these precipitates (MoS_3) will be agglomerated and thus leads to deteriorative electro-catalytic HER activity. Though these agglomerated MoS_3 could be grinded in mortar later; it didn't show favorable activity as the beginning. However, for storage and the practical application, it is optimal to put these amorphous molybdenum sulfides (MoS_3) precipitates into solid powders. Therefore, there need some strategies to prevent the amorphous MoS_3 from agglomerating in order to expose abundant active sites so as to keep the good electrocatalytic HER activity. On the other hand, the electron transport rate of MoS_3 should be considered to promote to get a better electro-catalytic HER activity [19].

In this work, we demonstrate a novel strategy using commercial and cheap carbon resources (activated carbon and acetylene black), which can effectively prevent the agglomeration during the formation process of amorphous MoS₃ in liquid, to prepare the carbon-based amorphous molybdenum sulfides catalysts. To the best of our knowledge, it is the first time for the carbon-based amorphous molybdenum sulfides composite catalysts to be prepared into solid powder directly by one-step liquid phase chemical method and the as-prepared catalysts show highly performances for the electro-catalytic HER. And the influence of the composition of materials (including different carbon resources and different atom ratios of molybdenum to carbon within the same carbon resource), the dispersing agents, the concentration of bulk electrolytes and the loading amount of catalyst on the HER activity of catalysts has been systematically investigated.

2. Experimental

2.1. Apparatus and reagents

Scanning electron microscopy (SEM) images were taken on S-4800 field-emission scanning electron microscope (Hitachi, Japan). Powder X-ray diffraction (XRD) data were recorded with a Japan Rigaku D/Max-Ra using Cu K α radiation (λ = 0.15406 nm) at 40 kV and 200 mA. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo ESCALAB 250Xi spectrometer equipped with an Al anode (Al K α = 1486.6 eV) and the energy valued were calibrated by using the C1s level of 284.8 eV.

All the electrochemical tests were carried out in a threeelectrode cell with the volume of 5 mL. Saturated calomel electrode (SCE) was used as the reference electrode, Pt wire electrode as the counter electrode and the glassy carbon electrode (GCE, diameter: 3 mm) as the working electrode. Linear sweep voltammetry (LSV) with a scan rate of 5 mV/s (or 10 mV/s) was conducted in 0.5 M H₂SO₄ or 1 M H₂SO₄. AC impedance measurements were carried out in the same configuration at overpotential (η) was 145 mV from 10⁵ to 0.02 Hz with an AC voltage was 5 mV. Amperometric i-t technology was conducted 4000s at the constant potential: -245 mV (versus RHE) in different electrolytes. In order to compare the electrochemical surface area, electrochemical capacitance of pure MoS3 (loading amount: 0.283 mg cm⁻²) and MoS3/AB with different loading amount including 0.142, 0.283, 0.425 and 0.566 $\mathrm{mg}\,\mathrm{cm}^{-2}$, was obtained by cyclic voltammetry at different scan rates in H₂SO₄. The scan rates are 5, 10, 25, 50, 100, 200, and 300 mV s^{-1} . The electrochemical capacitance is the slop of current density against scan rate line. The Tafel plots of catalysts were obtained from the corresponding polarization curves which were recorded by linear sweep voltammetry (LSV) at 5 mV/s in in 1 or 0.5 M H₂SO₄. The loading amount for pure MoS_3 and MoS_3/AC was 0.283 $mg\,cm^{-2}$ and that for MoS3/AC was 0.425 mg cm $^{-2}$ in 1 M $\rm H_2SO_4$ and 0.566 mg cm $^{-2}$ in 0.5 M H₂SO4. The electrode potentials were recorded (after several polarizations) versus SCE reference, which was calibrated with respect to RHE. Before all the electrochemical measurements, the electrolyte solution was degassed by bubbling N_2 for 30 min at least. All the electrochemical measurements were taken on CHI660C electrochemical workstation (Chenhua Instruments, Shanghai, China).

Granular activated carbon, acetylene black powder, sodium sulfide nonahydrate (Na₂S·9H₂O, \geq 98.0%), sodium molybdate dehydrate (Na₂MoO₄·2H₂O, \geq 99.0%), concentrated hydrochloric acid (HCl, \geq 36%) and other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. All the solutions were prepared with Milli-Q purified water (Millipore, >18.2 M\Omega cm).

2.2. Synthesis of amorphous MoS₃

Amorphous MoS_3 has been prepared according to the procedures reported by Jaramillo's group [21] and Hu's group [19]. Typically, 0.01 mol Na_2MoO_4 ·2H₂O and 0.04 mol Na_2S ·9H₂O were added into 50 mL H₂O and stirred for 0.5 h, and then kept under stir during the slow addition of 9 mL concentrated HCl within 50 mL H₂O. Next, the solution has been heated at 140 °C for 20 minutes in oil bath and then cooled to room temperature. After removing the supernatant, the sediment was cleaned by 600 mL H₂O. In the end, the amorphous MoS₃ was collected after vacuum suction filtration and vacuum drying (5 h at 60 °C).

2.3. Synthesis of micro-sized amorphous activated carbon supported amorphous MoS₃

Since the commercial amorphous carbon is nubby, it isn't suitable for direct application. Thus, the activated carbon has been crushed for 30 min in a mortar for further use. Amorphous activated carbon supported amorphous MoS_3 (denoted as MoS_3 /AC), including MoS_3 /AC (1:2), MoS_3 /AC (1:4), MoS_3 /AC (1:10), MoS_3 /AC (1:20), and MoS_3 /AC (1:20), which were obtained with different atom ratios of Mo to C (1:2, 1:4, 1:10, 1:20, 1:30) and were prepared by the same strategy.

For example, in a typical process, for preparation of MoS_3/AC (1:2), 0.01 mol $Na_2MoO_4 \cdot 2H_2O$ and 0.04 mol $Na_2S \cdot 9H_2O$ were added into 250 mL beaker which contained 50 mL H_2O and the mixture has been stirred for 0.5 h. In a second beaker, 0.02 mol activated carbon with 41 mL H_2O and 9 mL concentrated HCl has been sonicated for 20 minutes. During sonicating, the solution of the first beaker was transferred into the second beaker. The sediment was cleaned by 600 mL H_2O after removing the supernatant. At last, the product was harvested after vacuum suction filtration and vacuum drying (5 h at 60 °C).

To keep the amount of the activated carbon immobile, the other catalysts can be prepared by adding of the corresponding mole of Na_2MoO_4 ·2H₂O and Na_2S ·9H₂O. In order to keep sulfur sources enough, the mole ratio of Na_2S ·9H₂O to Na_2MoO_4 ·2H₂O has been set as 4:1 during the preparation of all catalysts.

2.4. Synthesis of nano-sized acetylene black supported amorphous MoS_3

In a typical process, 0.025 g acetylene black (0.002 mol) and 5 mL concentrated HCl were added into 250 mL beaker which contained 50 mL H₂O and sonicated for 20 minutes. In the second beaker, 0.0478 g Na₂MoO₄·2H₂O (0.0002), 0.2184 g Na₂S·9H₂O (0.0008) and 50 mL H₂O were added and stirred for 0.5 h. Then the solution of the second beaker was transferred into the first beaker during the process of sonicating. 600 ml H₂O was used to clean the sediment after removing the supernatant.



Scheme 1. Prepare of MoS₃ in solution with and without carbon resources.

Finally, the acetylene black supported amorphous MoS_3 (denote as MoS_3/AB) powders was collected after vacuum suction filtration and vacuum drying (5 h at 60 °C).

2.5. Preparation of modified electrodes

Three kinds of ultrasonic dispersing agents (i.e., H_2O , Ethanol aqueous solution with the volume fraction 45% of ethanol (45% EtOH), N, N-dimethylformamide (DMF)) were chosen to disperse the different amount of MoS₃/AC and MoS₃. For MoS₃/AB catalyst only 45% EtOH solution was chosen as ultrasonic dispersing agent. The concentration of catalysts in different dispersing agent was 4 mg/mL. For MoS3/AC, different amount of catalysts including 0.113, 0.226, 0.283, 0.396 mg/cm² were loaded on the electrodes. For MoS₃/AB, different amount of

catalysts including 0.283, 0.142, 0.425, and 0.566 mg/cm² were loaded on the electrodes. For comparison, 0.283 mg/cm² MoS3 were loaded on the electrodes. After modified with each of catalysts, 2.0 μ L 0.5% Nafion solution was added onto GCE for fixing.

3. Results and discussion

3.1. Characterization

The MoS₃, MoS₃/AC, and MoS₃/AB were synthesized by a simple wet chemical method. When the solution contained another phase carbon resource, amorphous MoS_3 will deposit on it preferentially and thus can effectively prevent the agglomeration of amorphous MoS_3 , and thereby the substantial catalytic sites can be exposed (Scheme 1).

Without adding solid phase carbon resource, amorphous MoS₃ agglomerated seriously after centrifugation and drying, and it wasn't suitable for electro-catalytic HER (Fig. S1a in the Supporting Information). The addition of carbon resources can effectively prevent amorphous MoS₃ from agglomerating so as to expose the larger surface area. To confirm it, the morphologies of MoS₃/AC have been characterized. Fig. 1a shows the SEM image of MoS₃ deposited on the surface of activated carbon. The other MoS₃/AC samples with different ratio of MoS₃ and activated carbon were also characterized by SEM. As can be seen from Fig. S2, all the MoS₃ in the composites grew on the surfaces of activated carbon. In contrast, the nano-sized acetylene black was mixed with the amorphous MoS₃ and the size of the MoS₃/AB kept on nano-sized (Fig. S3). Since the SEM images of MoS₃/AB is difficult to demonstrate that the acetylene black was mixed with the MoS₃, the TEM image and corresponding elemental mapping images of the MoS₃/AB are given in Fig. 1(b-f). According to the elemental



Fig. 1. (a) SEM image of MoS₃/AC (1:20) (the AC marked by white arrow and the MoS₃ marked by the black arrow), (b) TEM image of MoS₃/AB (1:10), and (c) the corresponding elemental mapping images of MoS₃/AB. The elemental mapping images of the MoS₃/AB (d) S, (e) C, (f) Mo atoms.

mapping images, we can conclude that the carbon sources were really mixed with the MoS_3 . The above results indicate that the added carbon resources can effectively absorb the forming MoS_3 precipitates and thus to prevent the MoS_3 from agglomerating. It should be noted that not all carbons are covered by MoS_3 (Fig. 1c) because the addition of acetylene black is more abundant than source of molybdenum and sulfurs, in accordance with the previously reported amorphous MoS_3 [21,22].

To further verify the as-prepared carbon-based composites, X-ray diffraction (XRD) analysis was first performed. As shown in Fig. S4, besides a hump between $30-50^{\circ}$, there is a weak and broad peak appearing at about 15° for pure MoS₃, which corresponds to the (002) diffraction peak of MoS₂ indicating the existence of MoS₂ clusters among amorphous products [29]. In fact, many so-called MoS₃ synthesized by a wet chemical method displayed a very similar XRD pattern to ours [29,30,22]. However, the XRD plot of

the amorphous MoS_3 synthesized by Jaramillo's group showed no peaks except a hump between 20 to 40° [21]. The difference in XRD patterns may be related to the difference in starting material. Compared with pure MoS3, there are two extra peaks appearing at 25 and 45° for MoS_3/AB , which are in accordance with the (002) and (101) diffraction peaks of graphitic carbon [31]. In comparison, the XRD pattern of MoS_3/AC is almost the same to that of pure MoS_3 , which reveals the amorphous structure of AC. The results of XRD also indicate that MoS_3/AB may possess higher conductivity than MoS_3/AC due to the graphitic structure of AB. Obviously, the XRD results exhibit the poor crystalline of MoS_3 , but they can't verify the chemical composition of MoS_3 .

XPS is a powerful technique to carry out the research on amorphous MoS_3 materials. The XPS survey spectra of MoS_3 , $MoS_3/$ AB, MoS_3/AC (1:10) are shown in Fig. 2 and Fig. S5. It has been reported that the binding energy of Mo $3d^{5/2}$ and Mo $3d^{3/2}$ of pure



Fig. 2. XPS spectra of (a) MoS₃. Left: Mo 3*d* and S 2*s* region; right: S 2*p* region; binding energies (eV): doublet I $2p_{3/2}$, 162.0; $2p_{1/2}$, 163.0; doublet II $2p_{3/2}$, 163.5; $2p_{1/2}$, 164.5. (b) MoS₃/AB. Left: Mo 3*d* and S 2*s* region; right: S 2*p* region; binding energies (eV): doublet I $2p_{3/2}$, 162.2; $2p_{1/2}$, 163.3; doublet II $2p_{3/2}$, 163.7; $2p_{1/2}$, 164.8. (c) MoS₃/AC (1:10) composites. Left: Mo 3*d* and S 2*s* region; right: S 2*p* region; binding energies (eV): doublet I $2p_{3/2}$, 162.0; $2p_{1/2}$, 163.1; doublet II $2p_{3/2}$, 163.8; $2p_{1/2}$, 164.9.



Fig. 3. (a) The influences from the different ultrasonic time (at 10 mV/s) and (b) dispersing agents on the HER activity of MoS₃/AC (1:10) (at 5 mV/s). (c) The influences from the same dispersing agents on the HER activity of MoS₃/AC (1:20) (at 5 mV/s).

MoS₂ is 228.5 and 231.8 eV [32], and that of pure MoS₃ is 230.8 and 233.8 eV, respectively [21]. The binding energy of Mo 3d of our three catalysts all falls in between that of pure MoS₂ and pure MoS₃, indicating the coexistence of MoS₂ and MoS₃ in our products. The S2p spectra of these catalysts are almost the same and they consist of two doublets with S $2p^{3/2}$ energies, implying the presence of both S^{2–} and S₂^{2–} [19]. Additionally, the chemical composition of these catalysts was evaluated by both XPS and EDX. According to XPS tests, the atom ratios of S/Mo for MoS3, MoS3/AC

(1:10) and MoS3/AB are 4.60, 4.45 and 5.89. The high values may be due to the adsorption of element S on the surface of the catalysts. The EDX results (Fig. S6) show that the atom ratios of S/Mo for MoS₃, MoS₃/AC (1:10) and MoS₃/AB are 3.12, 2.44 and 2.97, which agrees well with the coexistence of MoS₂ and MoS₃.

To sum up, amorphous MOS_3 is present in all the catalysts we studied. In spite of the existence of some MOS_2 cluster impurities, it is acceptable to denote our catalysts as amorphous MOS_3 , MOS_3/AC and MOS_3/AB .

3.2. The HER activity of MoS₃/AC

Firstly, the effect from the ultrasonic time and the solvents used for dispersing the catalysts on the HER activity was investigated. As shown in Fig. 3a, the catalytic activity of MoS₃/AC (1:10) in 1 M H₂SO₄ increased the ultrasonic time and did not increase after 2 h. According to the previous reports [33,34], the HER activity of catalysts is also significantly be dependent on the dispersing agents due to the dispersing ability of different dispersing agents. The results showed that the dispersing ability to MoS₂ is DMF > 45% EtOH > H₂O. In this present work, the HER activity of MoS₃/AC (1:10) and MoS₃/AC (1:20) is both related to the dispersing agents. As shown in Fig. 3b and c, the dispersing ability of MoS₂.

Then, the effect from the composition and the loading amounts of MoS_3/AC on the HER activity was examined. To verify the influence from the composition of MoS_3/AC , the polarization curves of catalysts with different atom ratios of Mo to C were recorded in Fig. 4a. From the polarization curves, it can be found the HER activity remained invariable with the increasing content of activated carbon when the atom ratio of Mo:C reached 1:10.

The relationship between the HER activity and the loading amount of MoS_3/AC was further investigated and the data is shown in Fig. 4b. Obviously, with the loading amount increasing from 0.113 to 0.283 mg cm⁻², the HER performance increases obviously. However, the thick layer of MoS_3/AC can hinder the charge transport between the catalyst and electrolyte (Fig. S7), leading to the decrease of HER activity. Thus, the high loading amount of MoS_3/AC with 0.396 mg cm⁻² exhibits slightly lower activity than that of with 0.283 mg cm⁻². After the catalytic sites being saturated, some inner catalytic sites will be buried with further increasing of the loading amount of catalyst.

For understanding whether the loss of the HER activity was caused by the catalyst's expansion during the formation of hydrogen, the *i*-*t* curve and the stability of MoS_3/AC had been



Fig. 4. (a) The polarization curves of different composition of catalysts with the loading amount of 0.283 mg/cm² in 1 M H₂SO₄ at 5 mV/s (b) The polarization curves of different loading amounts of MoS₃/AC (1:20) at 5 mV/s.



Fig. 5. (a) The current density versus time on $MoS_3/AC(1:20)$ modified electrode at the constant potential of -245 mV in $1 \text{ M } H_2SO_4$ at 5 mV/s. (b) The polarization curves of $MoS_3/AC(1:20)$ before and after a 4000 s constant voltage test, and dried naturally after a 4000 s test in $1 \text{ M } H_2SO_4$ at 5 mV/s.

investigated. As shown in Fig. 5a, a slight and acceptable loss was found like Jaramillo's work [21]. At the same time, the GC electrode modified with MoS_3/AC (1:20) which had used to perform the *i*-*t* test, was taken out from the electrolyte and the HER activity was tested again after being dried naturally. As shown in Fig. 5b, the HER activity of those electrodes was found to be of good recovery. The above results indicate that the slight loss of the HER activity was not caused by the inherent catalytic performance of catalyst [21] when take into account some catalyst leaking from the GC electrode surface.

3.3. The HER activity of MoS₃/AB

In this work, the HER activity of MoS₃/AB was also investigated in detail. For comparison with the previous reports, the HER performance of MoS₃/AB has been studied in two kinds of electrolytes (i.e., 1 M H₂SO₄ and 0.5 M H₂SO₄). For MoS₃/AB, the 30 min of ultrasonic time is enough to disperse the catalysts in 45% ethanol-water solution owing to the nano-sized acetylene black as support materials. The electrochemical measurements (Fig. 6a and b) indicated that in 1 M H₂SO₄ and 0.5 M H₂SO₄ solution, the optimal loading amounts of MoS₃/AB are 0.425 mg cm⁻² and 0.566 mg cm⁻², respectively. This may be due to the more bubbles generated in the higher concentration of H₂SO₄.

The electrochemical surface area (ECSA) is an important metric to evaluate the performance of catalyst [35,36]. Therefore, the determination of ECSA enables independent estimation of the current density of electrochemically active sites and provides useful insights for future improvements to catalyst design. As



Fig. 6. (a) Polarization curves of MoS₃/AB tested in 0.5 M H₂SO₄ at 5 mV s⁻¹. (B) Polarization curves of MoS₃/AB tested in 1 M H₂SO₄ at 5 mV s⁻¹. (c) The capacitive current ($|\Delta J| = |J_{anode} - J_{cathode}|$) measured at 0.255 V vs. RHE was plotted as a function of scan rate for the catalysts: (1) pure MoS₃ with the loading amount of 0.283 mg cm⁻², and (2–5) MoS₃/AB modified GC electrodes with different loading amounts in 1 M H₂SO₄. The loading amount is (2) 0.142 mg cm⁻², (3) 0.283 mg cm⁻², (4) 0.425 mg cm⁻² and (5) 0.566 mg cm⁻², respectively.

ladie I		
The slope of linear	regression equation of each catalyst.	

Catalyst	MoS ₃	MoS ₃ / AB	MoS ₃ / AB	MoS ₃ / AB	MoS ₃ /AB
Loading amount (mg cm ⁻²)	0.283	0.142	0.283	0.425	0.566
Slope	0.00013	0.0076	0.012	0.017	0.018



Fig. 7. The polarization curves of pure MoS₃, MoS₃/AC and MoS₃/AB with the loading amount of 0.283, 0.283, and 0.425 mg cm⁻², respectively.



Fig. 8. Tafel plots of MoS_3, MoS_3/AC and MoS_3/AB obtained from the polarization curves recorded in 0.5 M $\rm H_2SO_4.$

shown in Fig. S8, the double-layer capacitance of various samples was determined by the cyclic voltammetry (CV), which is considered to be linearly proportional to the effective surface. For the capacitance measurements, a potential range of 0.155–0.355 V vs. RHE was selected, because no obvious electrochemical features corresponding to faradic current were detected in this region. The results were summarized in Fig. 6c. The slope of linear regression equation can reflect the relative size of the ECSAs of the electrodes in a certain extent. And the slope of linear regression

equation of each catalyst was listed in Table 1. The slope of GC electrode modified with MoS_3/AB (0.283 mg cm⁻²) is about 92 times that of MoS_3 (0.283 mg cm⁻²), which can explain the higher HER activity of MoS3/AB. Moreover, notably, the ECSA of the modified electrode increased with the increase of the loading amount of catalyst. However, once loading amount of MoS_3/AB exceeded 0.425 mg cm⁻², the ECSA will reach the saturation value.

3.4. Comparison

In this work, three kinds of catalysts, MoS₃, MoS₃/AC and MoS₃/ AB, were synthesized. To intuitively display the HER activity, the comparisons with themselves and previously reported catalysts were performed. Fig. 7 shows the polarization curves of the asprepared catalysts in the optimal conditions. Obviously, the MoS₃/ AB has the highest HER activity regarded as both catalytic current and onset potential.

The Tafel slope is a virtual parameter to evaluate the electrocatalyst and determined by the rate-limiting step of the HER. As shown in Fig. 8, the Tafel slopes of MoS₃/AB (0.425 mg cm⁻²) and MoS₃/AB (0566 mg cm⁻²) MoS3/AB are 51 and 50 mV/dec, smaller than that of MoS₃/AC (0.283 mg cm⁻²) and pure MoS₃ (0.283 mg cm⁻²). The reason can be attributed to the good dispersity of MoS₃ among AB and the high conductivity of AC with graphitic structure which has been verified by XRD. In addition, the higher conductivity and electron transfer rate of MoS₃/AB compared with pure MoS₃ and MoS₃/AC are proved by the Fe(CN)₆^{3-/4-} probe, as shown in Fig. S9.

Further, the exchange current densities (J_0) of the catalysts were calculated by applying extrapolation methods (Fig. S10). The HER performances of the catalysts prepared in this work are listed in Table S1. The results show that the exchange current density of MoS₃/AC is larger than that of MoS₃/AB, indicating the lower activation energy of HER with MoS₃/AC as catalysts. It can be concluded that although MoS₃/AC have a more effective catalytic sites due to their high dispersing ability, the poor conductivity may hinder the electron and proton transfer and lead to higher overpotential and lower current density. The Tafel slope of 51 or 50 mV/decade for MoS₃/AB means that the HER mechanism is a rapid discharge reaction followed by either a rate-limiting Heyrovsky reaction or Tafel reaction [24], since the two possible mechanisms cannot be distinguished from the Tafel analysis alone [11].

The electrochemical parameters of catalysts for the HER based on carbon materials reported in recent years were also compared in Table 2. An advanced catalyst for the HER should reduce the overpotential and increase the current density at the same time [37]. The low onset potential and the large current density suggest that the as-prepared MoS_3/AB is a good candidate for the HER applications.

It should be pointed out that according to the previous report, Pt particles might be deposited onto the modified electrodes during

Table 2

Comparison of the electrochemical performances of the different catalysts for the HER.

Catalyst	Onset potential (mV)	Tafel slope ($mV/decade$)	$I_1 ({\rm mA cm^{-2}})$	l_0 (µA cm ⁻²)	Electrolyte	Ref.
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MoS ₃ /AB	-116	50	-25	6.31	$I M H_2 SO_4$	this work
Fe-MoS ₃ ^a	-140	39	-24.9	0.2	1 M H ₂ SO ₄	[18]
MoS ₃ /MWCNT ^b	-140	42	-4.8	0.126	1 M H ₂ SO ₄	[19]
MoS ₃ -CV ^c	-120	40	-14	0.13	1 M H ₂ SO ₄	[20]
MoS ₃ ^d	-150	60	-10	-	0.5 M H ₂ SO ₄	[21]

Note: J_0 is exchange current density calculated using the geometric area of GC electrode; J_1 is current densities calculated at the overpotential of 200 mV (vs. RHE). ^a Fe-MoS₃ films-modified GC electrode prepared by CV in aqueous solutions containing of FeCl₂ and (NH₄)₂[MoS₄].

^b MoS₃-modified GCE blended with multi-walled carbon nanotubes.

^c MoS₃ films-modified GCE prepared by electrodepositing method from (NH₄)₂[MoS₄] solution.

 $^{\rm d}\,$ Amorphous ${\rm MoS}_3$ synthesized by wet chemical method.

polarization scans when the Pt wire or plate was used as the counter electrode and there is a slight possibility that the activity of the modified electrodes is due to Pt contamination [38]. To rule out this possibility, the polarization scans were carried out using a glassy carbon rod counter electrode. The MoS₃/AB-modified electrode shows the same activity, as shown in Fig. S11. Thus, the catalytic activity is due to MoS₃-based catalysts, not Pt contamination, in agreement with the Hu's work [19].

4. Conclusions

Two kinds of carbon-based MoS₃ powders, MoS₃/AC and MoS₃/ AB have been successfully synthesized via a facile, versatile and scalable wet chemically heterogeneous precipitation method. The addition of carbon resources can effectively prevent amorphous MoS₃ to agglomerate during the drying process. Thus, the catalysts can expose substantial catalytic sites. The HER activity of catalysts was enhanced greatly due to the good electrical conductivity of carbon resources. The proposed method makes possible the simple and scale preparation of carbon-based MoS₃ catalysts. Though the catalytic performance of the as-prepared catalysts in this work should be further improved, the proposed strategy may inspire the researchers for preparing other catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2017. 03.193.

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