



Pt nanoparticles/MoS₂ nanosheets/carbon fibers as efficient catalyst for the hydrogen evolution reaction



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ABSTRACT

Advanced materials for electrocatalytic water splitting are central to renewable energy research. In this study, we describe a two-step reaction for preparing hydrogen evolution reaction (HER) electrodes composed of Pt nanoparticles and MoS₂ nanosheets grown on carbon fibers. The morphology and the structures are characterized by a variety of techniques including SEM, TEM, XRD and XPS. Detailed electrochemical characterizations demonstrate that the Pt nanoparticles/MoS₂ nanosheets/carbon fibers electrode (2.03 w% Pt) exhibited an excellent catalytic activity for HER in an acidic electrolyte with an overpotential of -5 mV (vs. HER). And the corresponding Tafel slope is estimated to be 53.6 mV/dec. Stability tests through long-term potential cycles and extended electrolysis confirm the exceptional durability of the catalyst.

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1. Introduction

Hydrogen has been deemed to be a promising alternative and renewable energy source that may take the place of fossil fuels in future. Toward this end, one effective approach of hydrogen production is the environmentally friendly electrochemical water-splitting [1–4]. In these studies, advanced catalysts for the hydrogen evolution reaction (HER) are generally needed to reduce the overpotential and increase the catalytic current density. To date, the most effective electrocatalysts for HER are based on Pt-group metals, which are capable of catalyzing HER at a significant rate with almost no overpotential [5–7]. However, their scarcity and high costs of Pt-group metals have hindered their wide applications. Recently, inorganic catalysts, such as MoS₂, WS₂ and CoSe₂, have drawn great attention due to their low costs, high chemical stability, and excellent catalytic properties in HER [8–14]. However, the catalytic activity of the above reported catalysts can't be compared with that of Pt-based electrocatalysts. It remains a great challenge to minimize the use of platinum to obtain the same high active HER catalysts [5,15,16].

In additions, using MoS₂ and related metal sulfides as water-splitting electrocatalysts has been intensified, and extensive research efforts have been devoted toward the enhancement of the material catalytic properties by loading catalysts on all kinds of conductive substrates (e.g., graphene-protected 3D Ni foams, graphene nanosheets, and fiber paper) [17–20]. For instance, MoS₂ nanoparticles have been grown on reduced graphene oxide nanosheets via a facile solvothermal procedure and the resulting composites exhibited excellent HER activity with a small overpotential of 100 mV, large cathodic currents, and a Tafel slope as small as 41 mV/dec [18]. Desheng Kong et al. [19] reported a two-step reaction for preparing three-dimensional electrodes composed of CoSe₂ nanoparticles grown on carbon fiber paper. The electrode exhibits excellent catalytic activity for a hydrogen evolution reaction in an acidic electrolyte (100 mA/cm² at an overpotential of ~ 180 mV).

In our previous reports, we have found that the carbon fibers have high electrochemical active area, which can be used as supercapacitor electrode materials [21]. Therefore, in this report, we used the carbon fibers as HER electrode materials, and MoS₂ nanosheets were grown on the surface of carbon fibers. Using MoS₂ nanosheets as substrate can reduce the loading of Pt, and obtain the higher catalytic activity [15]. Pt nanoparticles/MoS₂ nanosheets/carbon fibers were synthesized by hydrothermal reaction,

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followed by electro-deposition process, which possessed the efficient HER activity.

2. Experimental

2.1. Materials

All reagents were of analytical grade and used without further purification. Sulfuric acid (H_2SO_4), nitric acid (HNO_3), sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$), thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, TAA), and chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were obtained from Sinopharm Chemical Reagents Beijing Co., and Carbon fibers and carbon paper were obtained from Fiber Glast Development Corporation in the USA.

2.2. Preparation of MoS_2 nanosheets/carbon fibers (MoS_2/CFs)

5 cm of carbon fibers were immersed into a mixture of concentrated H_2SO_4 (30 mL) and HNO_3 (10 mL), which was sonicated for 2 h to remove organic matter. The carbon fibers were then removed from the solution and washed with a copious amount of water, and dried in an electrical oven at 60°C for 6 h. Typically, 30 mg sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) and 60 mg thioacetamide ($\text{C}_2\text{H}_5\text{NS}$) were dissolved in 20 mL deionized water to form a transparent solution. Then carbon fibers were added into the above solution, then was transferred to a Teflon-lined stainless steel autoclave and then heated in an electric oven at 200°C for 24 h. MoS_2/CFs was harvested after washing by water and dried at 50°C for 12 h. In order to study the effect of carbon fibers on HER performance, the MoS_2/CPs (MoS_2 nanosheets/carbon papers) was synthesized by the same process using carbon papers instead of carbon fibers.

2.3. Preparation of Pt nanoparticles/ MoS_2 nanosheets/carbon fibers ($\text{Pt}/\text{MoS}_2/\text{CFs}$)

Pt nanoparticles were loaded on MoS_2/CFs by electro-deposition. A saturated calomel electrode (Hg/HgCl_2 in saturated KCl) and a platinum wire were used as the reference and counter electrode, respectively. MoS_2/CFs was used as working electrodes and 0.5 M H_2SO_4 aqueous solution used as electrolyte. Before the electro-deposition, 0.04 mL of chloroplatinic acid aqueous solution (1 mg/mL) was added into H_2SO_4 electrolyte as platinum source. The process was carried out via cyclic voltammetry with voltage range from 0 to -0.6V (vs. SCE) at a sweep speed of 100 mV/s. Pt/CFs was prepared as the same process using carbon fibers instead of MoS_2/CFs .

2.4. Characterizations

Field-emission scanning electron microscopic (FESEM, Model JSM-7600F) measurements were employed to characterize the morphologies of the obtained samples. Transmission electron microscopic (TEM) measurements were carried out with a JOEL JEM 2100 F microscope. Powder X-ray diffraction (XRD) patterns of the samples were recorded with a Bruke D8 Advance powder X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 0.15406\text{ nm}$) radiation. X-ray photoelectron spectroscopic (XPS) measurements were performed using an ESCALAB 250. TGA analysis was taken on a TGA/DSC 1 analyzer (METTLER TOLEDO) from 30 to 800°C under air with a heating rate of $10^\circ\text{C}/\text{min}$.

2.5. Electrochemistry

Electrochemical measurements were performed with an electrochemical workstation (Solartron Analytical 1287+1260)

in a 0.5 M H_2SO_4 aqueous solution. A saturated calomel electrode (Hg/HgCl_2 in saturated KCl) and a platinum wire were used as the reference and the counter electrode, respectively. The MoS_2/CFs and $\text{Pt}/\text{MoS}_2/\text{CFs}$ were used as the working electrodes, respectively. The current densities were evaluated in terms of the mass of MoS_2 and Pt/MoS_2 . The polarization curves were obtained by sweeping the potential from 0 to -0.8V (vs. SCE) at a potential sweep rate of 5 mV/s. The accelerated stability tests were performed in 0.5 M H_2SO_4 at room temperature by potential cycling between +0.1 and -0.5V (vs. SCE) at a sweep rate of 100 mV/s for a given number of cycles. Current-time responses were monitored by chronoamperometric measurements for up to 10 h. Hydrogen production was carried out at -0.5V (vs. SCE) and the hydrogen gas production rate was quantified by gas chromatographic measurements (GC-2060F, Lu Nan Analytical Instruments, LTD, China).

3. Results and discussion

Fig. 1 shows the SEM and HRTEM images of the synthesized MoS_2/CFs and $\text{Pt}/\text{MoS}_2/\text{CFs}$. The carbon fibers with the diameters of 7–10 μm possess smooth surface (Fig. S1). The thin MoS_2 nanosheets as shell are uniformly coated on the carbon fibers (Fig. 1a and b). Under the high magnification, the MoS_2 nanosheets are interconnected with each other, forming the 3D nanosheets networks (Fig. 1c) with high contact area with electrolyte, which enable the fast HER reactions. However, the MoS_2 can't be detected by XRD due to low loading (Fig. S2). The diffraction peak at 25.9° in the XRD pattern of MoS_2/CFs and $\text{Pt}/\text{MoS}_2/\text{CFs}$ corresponds to the diffraction of graphite (002) of CFs [22,23].

The loading of MoS_2 is measured by thermogravimetric analysis (Fig. S3), which is about 6.7 wt%. After loading of Pt nanoparticles on MoS_2/CFs , the morphology is not changed due to low content and small size of Pt (Fig. 1d). The existence of Pt on the MoS_2/CFs is further confirmed by HRTEM image (Fig. 1f) and XPS results (Fig. 2). From the HRTEM images in Fig. 1e, the lattice fringes of MoS_2 nanosheets can be clearly observed. The fringes with a lattice spacing of 0.6 nm correspond to the (002) plane of MoS_2 with the layered structures. The (111) plane of Pt with a lattice spacing of 0.265 nm is also observed in Fig. 1f, which implies that Pt nanoparticles are successfully load on MoS_2/CFs .

X-ray photoelectron spectroscopic (XPS) measurements were then carried out to further investigate the chemical composition and valence states of different samples. From the survey spectra in panel (a) of Fig. 2, the elements of Mo, C, O and S can be clearly identified for MoS_2/CFs . Except for the above elements, the Pt element was also observed in $\text{Pt}/\text{MoS}_2/\text{CFs}$. Fig. 2b and c depict the high-resolution scans of the Mo3d, S2p and S2s electrons, with the characteristic peaks for Mo^{4+} at 232.8 eV and 230 eV, 235.8 eV for Mo^{6+} and those for S^{2-} at 163.8 eV and 227.8 eV, signifying the formation of MoS_2 on the surface of carbon fibers. The Pt peaks at 72.7 eV and 76.1 eV were only observed in survey spectrum for $\text{Pt}/\text{MoS}_2/\text{CFs}$. Furthermore, based on the peak areas of the C1s and Pt4f electrons, the loading of Pt was estimated to be $\sim 2.03\text{ wt}\%$. However, after loading Pt nanoparticles on MoS_2 nanosheets, the characteristic peak of S2p shift from 163.8 eV to 163.5 eV, which possibly due to the bonding effect between Pt and S. As we known, the catalytic sites of MoS_2 originated from the exposure of Mo atoms [24]. The changed electronic state density of S can affect catalytic activity of the exposed Mo, which is one possible reason of the enhanced HER catalytic activity for $\text{Pt}/\text{MoS}_2/\text{CFs}$.

MoS_2/CFs , Pt/CFs and $\text{Pt}/\text{MoS}_2/\text{CFs}$ are used directly as HER electrodes without binder and conducting additive because of their good conductivity and excellent mechanical strength. Linear sweeps of the different electrodes normalized by weight of MoS_2 and Pt into current density are shown in Fig. 3a. As can be seen, the cathodic current density of $\text{Pt}/\text{MoS}_2/\text{CFs}$ (90.6 A/g) at

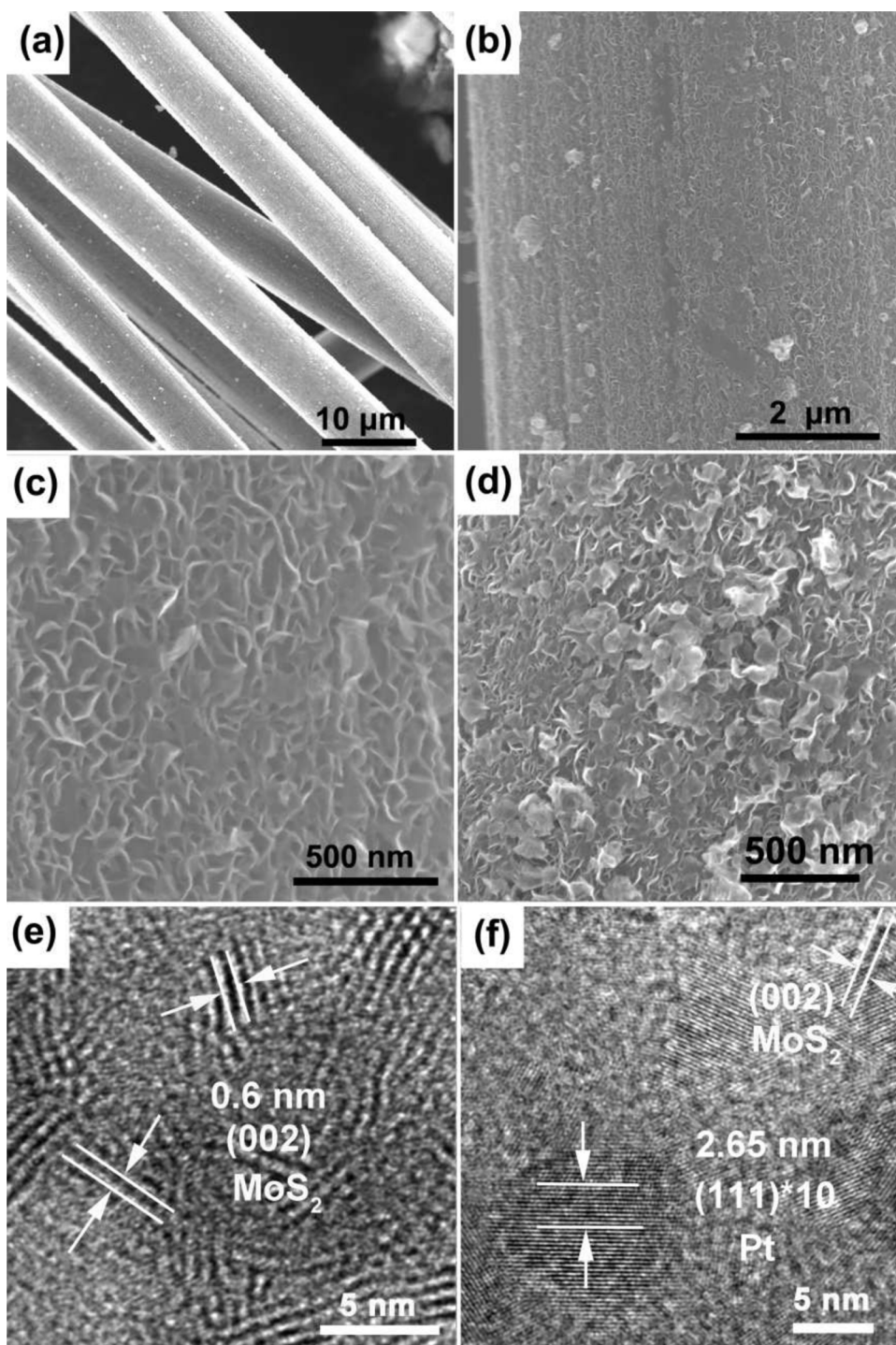
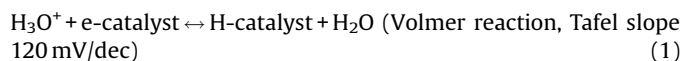


Fig. 1. SEM images of (a–c) MoS₂/CFs and (d) Pt/MoS₂/CFs, HRTEM images of (e) MoS₂ and (f) Pt from Pt/MoS₂/CFs.

−0.2 V is also much higher than those of MoS₂/CFs (10.5 A/g) and Pt/CFs (39.7 A/g). The cyclic voltammetry curves of MoS₂/CFs before and after adding the H₂PtCl₆ aqueous solution were shown in Fig. S4. The current densities of MoS₂/CFs, Pt/CFs and Pt/MoS₂/CFs were also normalized by electrochemical area, which were shown in Fig. S5. So, the enhanced HER activity of Pt/MoS₂/CFs is due to not only high electrochemical area but also the synergistic effect between MoS₂ nanosheets and Pt nanoparticles. The above HER current densities of Pt/MoS₂/CFs (−90.3 A/g) and MoS₂/CFs (−10.5 A/g) are also much better or similar with the reported results, such as MoS₂/graphene/Ni

foam (~5 A/g) [17], MoS₂/graphene hierarchical framework (~9 A/g) [25] and Li-MoS₂/carbon fiber paper (~52 A/g) [20] (Table S1).

Moreover, the linear portion of the Tafel plots (Fig. 3b) is fit to the Tafel equation ($\eta = b \log j + a$, where j is the current density and b the Tafel slope). Note that for hydrogen evolution in acid on metal electrode surfaces, the mechanism typically involves three major reactions [12,18,26],



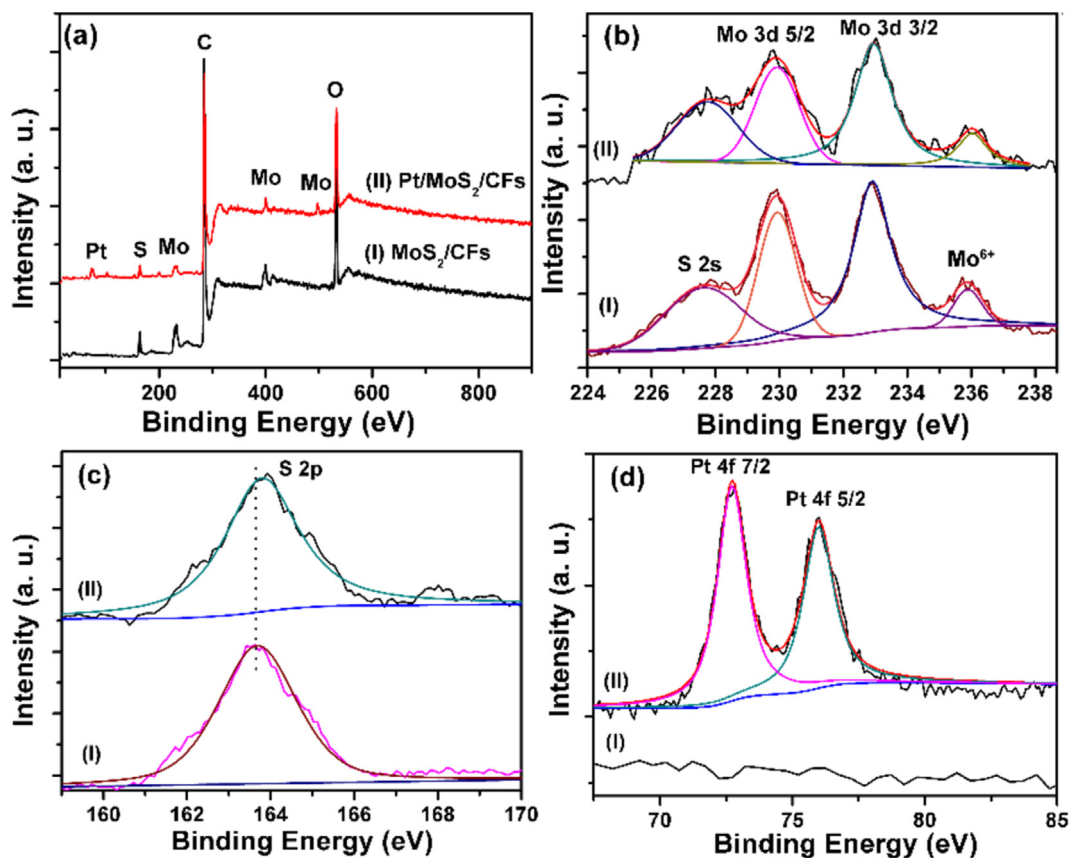


Fig. 2. XPS survey spectra (a) and high-resolution scans for the (b) Mo, (c) S and (d) Pt of (I) MoS₂/CFs and (II) Pt/MoS₂/CFs.

2H-catalyst \leftrightarrow H₂-catalyst (Tafel reaction, Tafel slope 30 mV/dec) (2)

H₃O⁺ + e-catalyst + H-catalyst \leftrightarrow H₂-catalyst + catalyst + H₂O (Heyrovsky reaction, Tafel slope 40 mV/dec) (3)

where e-catalyst denotes metal-bound electrons, and H-catalyst and H₂-catalyst represent a hydrogen atom and a hydrogen molecule adsorbed on to a surface metal atom, respectively. The Tafel slopes are estimated to be 88.7 mV/dec for MoS₂/CFs, 97.8 mV/dec for Pt/CFs and 53.6 mV/dec for Pt/MoS₂/CFs, which suggests that the rate-determining step of HER is most likely the Volmer reaction, a discharge step that converts protons into adsorbed hydrogen atoms on the catalyst surface. Electrochemical impedance spectroscopy (EIS) is a useful technique to characterize interface reactions and electrode kinetics in HER. Fig. 3c showed the representative Nyquist plots of the EIS response of the Pt/MoS₂/CFs at various potentials. The fast electron transfer between the catalytic edge sites of MoS₂ and CFs is one of the key factors contributing to the superior HER kinetics. In the high frequencies zone, the Pt/MoS₂/CFs electrode exhibits one capacitive semicircle, indicating that the corresponding equivalent circuit (inset of Fig. 3c) for the HER was characterized by one time constant and the reaction was kinetically controlled. The resistance (R_s) of solution and the electrochemical workstation is overpotential independent \sim 3.2 Ω . The charge transfer resistance R_{ct} is related to the electrocatalysis kinetics and a lower value corresponds to a faster reaction rate [10]. In this system, the values of R_{ct} is very small, which decreases significantly with increasing potentials, from 15.5 Ω at 50 mV to only 4.2 Ω at 150 mV. The value of R_{ct} for Pt/MoS₂/CFs is much less than the reported result for MoS₂ nanoparticles on mesoporous graphene foams (\approx 33 Ω at 150 mV

[8], which implies the fast charge transfer characteristics of carbon fibers. In addition, the EIS of Pt/MoS₂/CFs, Pt/CFs, MoS₂/CFs and CFs are involved in Fig. S6. The R_s values of the Pt/MoS₂/CFs, Pt/CFs, MoS₂/CFs and CFs have no significant differences, which are about 3 Ω due to good conductivity of carbon fibers. While, their R_{ct} values are significantly different due to the various overpotentials, which are 8.5, 10.8, 240.8 and 320 Ω for Pt/MoS₂/CFs, Pt/CFs, MoS₂/CFs and CFs, respectively.

In addition to the good catalytic activity, the Pt/MoS₂/CFs electrodes also perform good stability for HER in acidic environment. Fig. 3d shows that even after 2000 potential cycles, the *j*-V curve of the Pt/MoS₂/CFs electrode is almost the same as the initial one. This suggests strong bonding interactions between the MoS₂ nanosheets and the carbon fibers, which enables fast electron transfer and collection. To further investigate the stability of the MoS₂/CFs and Pt/MoS₂/CFs in HER, the cathodic currents at the applied potential of -0.236 V were acquired for up to 10 h, as presented in Fig. 3e. It can be seen that the MoS₂/CFs and Pt/MoS₂/CFs electrodes exhibited the large HER current of -30.1 A/g and -62.8 A/g, respectively; and the currents remain almost unchanged even for over 10 h of continuous operation, suggesting excellent durability of the MoS₂/CFs and Pt/MoS₂/CFs electrodes for HER. A lot of bubbles are also observed on the surface of the Pt/MoS₂/CFs electrode (Fig. S7). It is worth noting that the bubbles are easy to escape from the electrodes due to the cambered surface of carbon fibers (The corresponding video is shown in Fig. S8), which is the superiority of CFs as HER electrode. The result is also verified by the current-time response of MoS₂/CFs and Pt/MoS₂/CFs electrodes, which possess no obvious fluctuations of cathodic currents during the hydrogen production process. The gas is confirmed to be hydrogen by gas chromatography, and the amounts of hydrogen produced at MoS₂/CFs and Pt/MoS₂/CFs

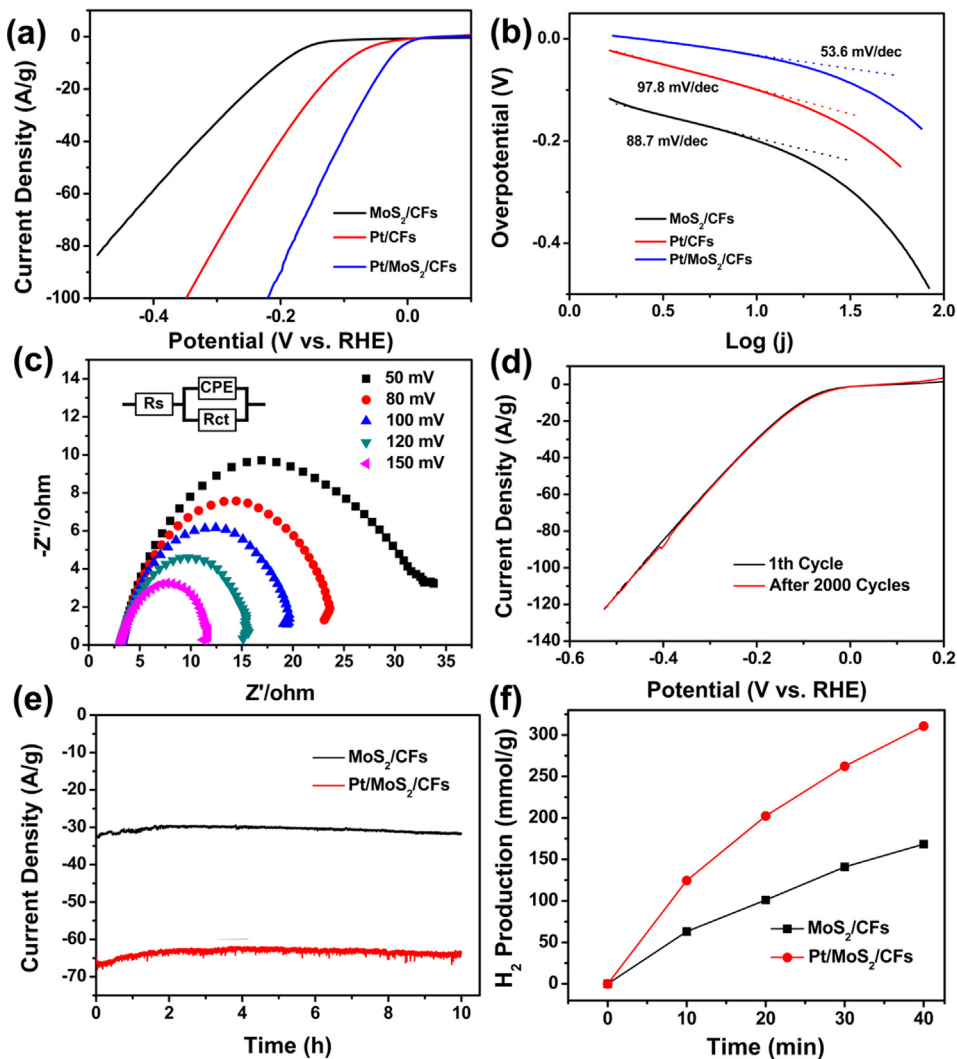


Fig. 3. (a) Polarization curves of MoS₂/CFs, Pt/CFs, and Pt/MoS₂/CFs; (b) Tafel plot for Fig. 3a; (c) Electrochemical impedance spectra of Pt/MoS₂/CFs electrodes at various HER overpotentials in 0.5 M H₂SO₄; (d) HER polarization curves for Pt/MoS₂/CFs electrode before and after 2000 cycles in the stability test; (e) Current-time responses of the MoS₂/CFs and Pt/MoS₂/CFs at the applied potential of -0.236 V (vs. RHE); (f) Production of hydrogen gas normalized by the weight of MoS₂ nanosheets and Pt/MoS₂ nanosheets at different reaction time.

electrodes are shown in Fig. 3f. Linear regressions of the experimental data yield the corresponding hydrogen production rates, which are 281.7 mmol/g h and 524.5 mmol/g h for MoS₂/CFs and Pt/MoS₂/CFs, respectively.

In order to highlight the advantages of carbon fibers as HER electrodes, we compare the HER performance of MoS₂/CFs and MoS₂/CPs. As shown in Fig. 4a, the current density of MoS₂/CFs (-1.6 A/g) is much better than that of MoS₂/CPs (-0.28 A/g) with same total mass of MoS₂/carbon at the potential of -0.3 V vs RHE. The effective surface areas play very important role in the overall HER performance. To estimate the effective surface areas, we employ the CV method to measure the electrochemical double-layer capacitances (Fig. 4b and c). The potential range where no faradic current is selected for the MoS₂/CFs and MoS₂/CPs. The halves of the positive and negative current density differences at the center of the scanning potential ranges are plotted versus the voltage scan rates in Fig. 4d, in which the slopes are the electrochemical double-layer capacitances. The electrochemical effective surface area of MoS₂/CFs is 250.2 mF/g, which is about 2 times more than that of MoS₂/CPs (85.9 mF/g). The value of electrochemical surface area for MoS₂/CFs is similar with or much higher than many reported results, such as CoSe₂ nanoparticle/

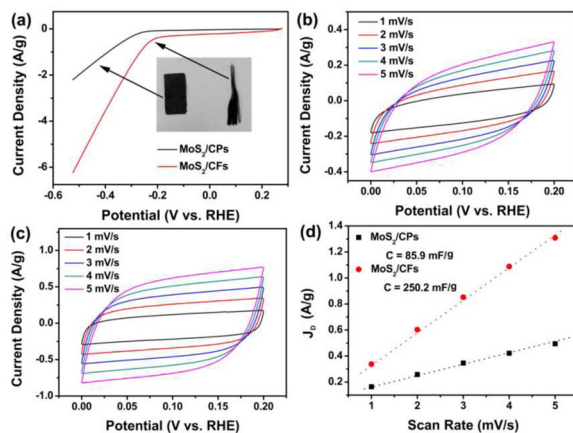


Fig. 4. (a) Polarization curves at a scan rate of 5 mV/s (the current density was calculated by total mass of MoS₂/CFs and MoS₂/CPs, respectively), (b, c) electrochemical cyclic voltammogram of MoS₂/CFs and MoS₂/CPs with same MoS₂ loading at different potential scanning rates. The scan rates are 1, 2, 3, 4 and 5 mV/s. The selected potential range where no faradic current was observed is 0 to 0.2 V vs RHE. (d) Linear fitting of the capacitive currents of the catalysts vs scan rates.

carbon fiber paper electrode (14.1 mF/cm²) [19], Li-MoS₂ (345 mF) [20] and 1T-WS₂ nanosheets (48 mF/cm²) [27]. The high HER activity as well as good stability of the Pt/MoS₂/CFs can be attributed to the following aspects: (I) the good conductivity of the carbon fibers allows for effective charge collection-transfer, which is confirmed by electrochemical impedance results (Fig. 3c); (II) the high electrochemical effective surface area of MoS₂/CFs (250.2 mF/g) is obtained; (III) the MoS₂ nanosheets with large surface area are vertically grown on surface of the carbon fibers, which possesses permeable channels for ion absorption and transport; and (IV) the synergetic effect between MoS₂ nanosheets and Pt nanoparticles also play the important role in the enhancement of HER activity, which is confirmed XPS results (Fig. 2) and other reports [15].

4. Conclusions

Pt nanoparticles/MoS₂ nanosheets/carbon fibers are synthesized by hydrothermal reaction, followed by electro-deposition process. The obtained Pt/MoS₂/CFs exhibits apparent and stable HER electrocatalytic activity with an overpotential of -5 mV, a Tafel slope of 53.6 mV/dec, and almost no change of the cathodic currents in HER for up to 10 h of continuous operation. Thus, the fast electron transfer between the catalytic edge sites of MoS₂ and carbon fibers, and high electrochemical effective surface area of the electrode substrate are the key factors contributing to the superior HER kinetics. This study highlights the significance of carbon fibers as support for the growth of MoS₂ nanosheets in the enhancement of the HER electrocatalytic activity.

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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.2015.03.067>.

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