

Available online at www.sciencedirect.com

ScienceDirect

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

Synthesis of a $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ternary alloy on carbon nanofibers as the high efficient water splitting electrocatalyst

Hui Yang, Ting Zhang, Han Zhu, Ming Zhang, Weiwei Wu, MingLiang Du*

College of Materials and Textiles, Zhejiang Sci-Tech University, Hangzhou, 310018, PR China

ARTICLE INFO

Article history:

Received 19 July 2016

Received in revised form

9 October 2016

Accepted 14 October 2016

Available online 3 November 2016

Keywords:

$\text{MoS}_{2(1-x)}\text{Se}_{2x}$

Ternary alloy

Carbon nanofiber

Hydrogen evolution reaction

Catalyst

ABSTRACT

Binary transition metal dichalcogenides (TMDs) usually exhibit high hydrogen evolution reaction (HER) activities; however, the facile and efficient synthesis of ternary TMDs alloys remains a challenge. In this study, we reported an efficient method of synthesis for a $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ ternary alloy in a CVD system, and carbon nanofibers serve as the substrate. The $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$ hybrids were directly used as hydrogen evolution cathodes and exhibit lower onset potentials and excellent durability, suggesting they have significantly enhanced catalytic activity and could serve as effective and promising catalysts for the HER.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

As a clean and sustainable energy carrier, hydrogen is considered to be a promising and appealing solution to take the place of fossil fuels. Among the hydrogen production methods, the hydrogen evolution reaction (HER) is an efficient electrochemical process to produce hydrogen by water splitting [1,2]. Conventionally, the platinum group metals (e.g., Pt) are demonstrated to be the most effective electrocatalysts for the hydrogen evolution reaction. However, because of the rarity and high cost of the platinum group metals, their extensive application is essentially throttled [2,3]. Extensive investigations about inexpensive alternatives with high electrocatalytic activity have found that layered transition metal

dichalcogenides (TMDs) are especially attractive. Because of the special layered structures, weak van der Waals forces between molecular layers, and strong chemical bonding within the layers, TMDs have demonstrated numerous applications in fields such as water splitting, optoelectronics, and nanoelectronics [4].

Recently, numerous studies have been committed to improve TMDs' electrocatalytic performance [5–9]. As is well known, there are three major approaches to optimize their HER activities: (1) increasing the number of active sites of the catalyst, (2) improving the electrical conductivity of the catalyst, and (3) improving the catalytic effects of the active sites [3]. Cui et al. have fabricated layered MoSe_2 and WSe_2 vertically oriented on curved and rough surfaces that exhibited a significantly enhanced HER activity and an extremely high

* Corresponding author. Fax: +86 571 86843255.

E-mail address: du@zstu.edu.cn (M. Du).

<http://dx.doi.org/10.1016/j.ijhydene.2016.10.075>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

stability because such oriented structures possess maximally exposed active edges [6]. Previously, we reported layered MoSe₂ grown on carbon nanofibers (CNFs), and the obtained nanomaterials exhibited substantially improved catalytic activity because of the large surface area and high conductivity of CNFs.

As is well known, carbonaceous materials, such as graphene, carbon nanotubes and carbon nanofibers, can substantially improve the conductivity of catalysts. Moreover, numerous studies indicate that cation dopants (Ni, Co and etc.) in the layered TMDs could optimize and significantly increase the catalytic activities [10–16]. Considering the similarities in atomic structure and properties of the TMDs' family members (MX₂: M = Mo, W; X = S, Se, Te), it is probable to create a multicomponent alloy system without phase separation by the doping of TMDs with another chalcogen, and the introduction of another chalcogen into TMDs could improve the HER performance [17–20]. Sampath et al. have investigated the introduction of Se substitution into the MoS₂ lattice, and the results suggested that the catalytic activity of sulfoselenides could be optimized by tuning the composition [21]. Bin Xiang et al. have reported one dimensional single-crystal MoS_{2(1-x)}Se_{2x} nanobelts with controllable Se and S content, indicating that the introduction of Se into MoS₂ would change the electronic structures of the MoS_{2(1-x)}Se_{2x} nanobelts and significantly improve the HER electrocatalytic activity [22].

In this study, on the basis of our previous work, we report an efficient method of synthesis for MoS_{2(1-x)}Se_{2x} in a chemical vapor deposition (CVD) system with CNFs serving as substrate. Firstly, electrospinning polyacrylonitrile (PAN) mats were synthesized and then carbonized to CNFs. Subsequently, the rapid sulfurization and selenization of MoO₃ were performed in a CVD system to attain the MoS_{2(1-x)}Se_{2x}/CNFs hybrids. The MoS_{2(1-x)}Se_{2x}/CNFs hybrids were directly employed as the working electrode in a typical three-electrode system and exhibited excellent electrocatalytic activity and stability.

Experiments

Synthesis of MoS_{2(1-x)}Se_{2x}/CNFs hybrids

MoS_{2(1-x)}Se_{2x}/CNFs hybrids were synthesized in a quartz tube furnace by the chemical vapor deposition (CVD) method. A ceramic boat with carbon nanofibers was placed in the downstream of the furnace with the temperature at approximately 750 °C. The S powder and Se powder were put into the first and second heating zones, respectively; the boat with the MoO₃ powder was placed between the Se and the CNFs' boat. The loadings of the S powder and Se powder were approximately 0.4 g and 0.2 g. Before the growth, argon gas was flowed through the tube at a flow rate of 70 sccm to remove residual oxygen. Then, we heated the furnace up to 750 °C in an hour and maintained the reaction temperature for an hour. When the temperature of the furnace reached 400 °C, the first heating zone (S powder) was rapidly raised to 150 °C. This was followed by a natural cool-down period during which Ar gas was kept flowing at a rate of 70 sccm to transport sulfur and selenium to the substrate.

Instruments

The sample morphology was observed using a JSM-2100 transmission electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV and a JSM-6700 field-emission scanning electron microscope (JEOL, Japan) at an acceleration voltage of 3 kV. The X-ray photoelectron spectra of the samples were obtained by an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) with an Al (mono) K α source (1486.6 eV). The Al K α source was operated at 15 kV and 10 mA. X-ray diffraction (XRD) patterns were recorded using a Bruker AXS D8 DISCOVER X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of 0.02 2 θ s⁻¹ in a 2 θ range of 10–80°. The Raman spectra of all of the samples were obtained by a Renishaw in Via Raman microscope (LabRAM HR800) using a 532 nm laser excitation source. The excitation light intensity in front of the objective was 10 mW with a spectral collection time of 1 s. The integration time for the measurements was set to 10 s. High-angle annular dark field scanning TEM (HAADF-STEM) images, STEM mapping and line-scan energy dispersive X-ray spectroscopy (EDX) spectra were recorded by a STEM (Tecnai G2 F30S-Twin, Philips-FEI) at an acceleration voltage of 300 kV.

Electrochemical characterization

The electrochemical measurements of all of samples were conducted in a standard three-electrode system in a 0.5 M H₂SO₄ solution (deaerated by Ar for 30 min). The MoS_{2(1-x)}Se_{2x}/CNFs hybrid, platinum mesh electrode and saturated calomel electrode served as the working, counter and reference electrodes, respectively. The HER activity was evaluated by linear sweep voltammetry, which was recorded using a CHI660E workstation (Shanghai Chenhua, Shanghai) at a scan rate of 1 mV/s. The polarization curves were obtained after iR-compensation. In all of the measurements, a Hg/Hg₂Cl₂ electrode was used as the reference, and the potential values were corrected to the reverse hydrogen electrode (RHE).

Results and discussion

In the study, the MoS_{2(1-x)}Se_{2x} alloy nanostructures were synthesized on the CNFs substrate in a home-built quartz tube furnace by the CVD method. The precursors were converted to the vapor phase at a high temperature and transported to the substrate by a carrier gas of argon. In the process, MoS_{2(1-x)}Se_{2x} was obtained by the rapid sulfurization and selenization of MoO₃. Herein, the morphology of the as-grown MoS_{2(1-x)}Se_{2x} nanoflakes is dominated by the hexagonal layer. The SEM images of the low-density MoS_{2(1-x)}Se_{2x}/CNFs (denoted as MoS_{2(1-x)}Se_{2x} (LD)/CNFs) hybrid and the high-density MoS_{2(1-x)}Se_{2x}/CNFs (denoted as MoS_{2(1-x)}Se_{2x} (HD)/CNFs) hybrid are shown in Fig. 1. As illustrated in Fig. 1a and c, the CNFs are a three-dimensional substrate with each fiber approximately 0.2 μm in diameter, and the MoS_{2(1-x)}Se_{2x} nanoflakes were radially grown onto the CNFs. Fig. 1b presents the nanoflakes irregularly stacked together with several layers, and the lengths of the hexagonal nanoflakes are approximately 1 μm . For the MoS_{2(1-x)}Se_{2x} (HD)/CNFs hybrid,

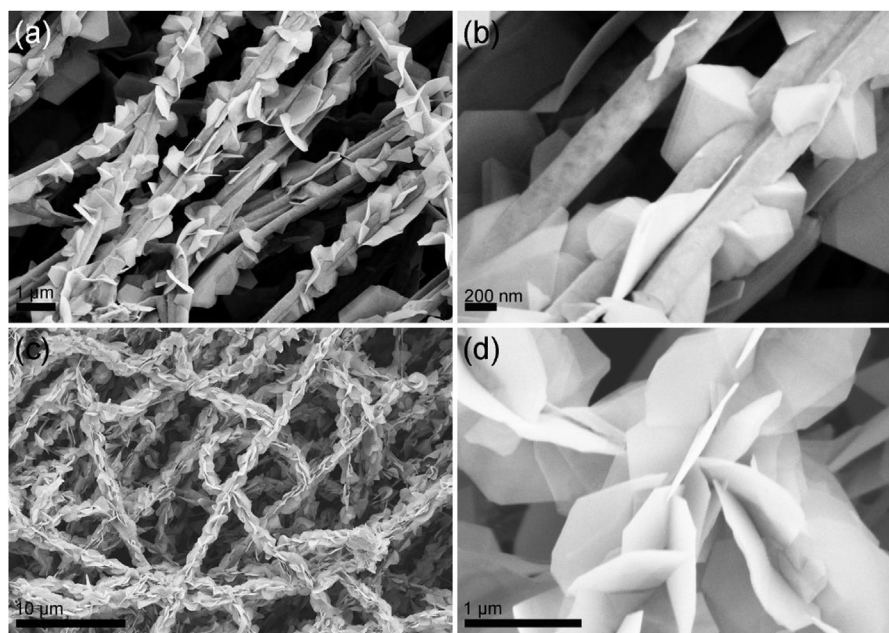


Fig. 1 – FE-SEM images of (a) and (b) the low-density $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$ hybrid, and (c) and (d) the high-density $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$ hybrid.

the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ nanoflakes grew vertically on the CNFs (as shown in Fig. 1c), and the surface of CNFs is uniformly covered with nanoflakes. In Fig. 1d, the lengths of the hexagonal nanoflakes are also approximately $1\ \mu\text{m}$. Moreover, we can observe that the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ nanoflakes were a hexagonal layer in structure, not a pure hexagon, but a structure more like a triangle that intercepted at the three corners. Such edge-terminated nanoflakes were expected to be highly efficient HER catalysts because they expose the edge sites maximally [5].

Fig. 2a presents the obtained $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ (LD) nanoflakes wrapping the surface of the CNFs, and herein, the nanoflakes

are of irregular shapes. Moreover, we can observe the thickness of each nanoflake is several nanometers. The inset of Fig. 2a presents a high-resolution transmission electron microscope (HRTEM) image of a typical nanoflake, indicating the high-quality crystallinity with the lattice fringes of $0.25\ \text{nm}$, which is in good agreement with (102) lattice planes. The HRTEM image of a typical nanoflake is shown in Fig. 2b and demonstrates that the nanoflake is not a pure hexagon but a structure more like a triangle with three corners intercepted, in good agreement with the SEM results. As presented in the inset of Fig. 2b, the selected area electron diffraction (SAED) pattern shows six-fold symmetry diffraction spots, further

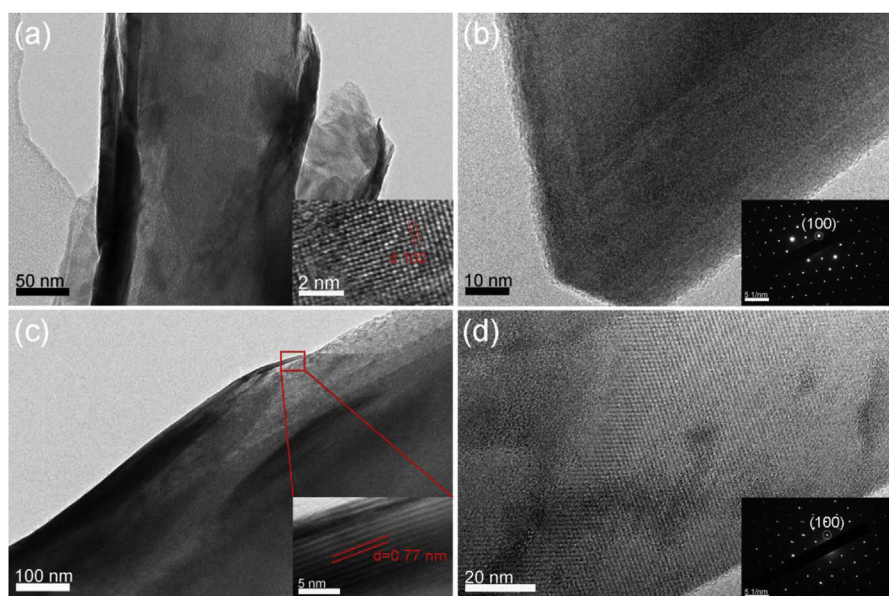


Fig. 2 – TEM images of (a) the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ (LD)/CNFs hybrid and (b) an HRTEM image of a typical $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ nanoflake; (c) the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ (HD)/CNFs hybrid and (d) an HRTEM image of a typical $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ nanoflake.

confirming the single-crystalline nature of the nanoflakes. In Fig. 2c, the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ (HD) nanoflakes stuck to the surface of the CNFs. In the inset, the corresponding selected area image is shown, revealing that the nanoflake consists of many layers, and the space between the layers is approximately 0.77 nm. As shown in Fig. 2d and the inset, we can observe a fringe in the nanoflake, and the SAED pattern shows six-fold symmetry diffraction spots, also confirming the single-crystalline nature of the nanoflakes. To unambiguously determine the distribution of elements, we employed elemental mapping by scanning transmission electron microscopy (STEM), and the high-resolution EDS elemental mapping images are shown in Fig. 3a and b. This confirms the homogeneous distribution of Mo, S and Se elements across the substrate, and a high spatial correlation is presented over the entire area mapped, demonstrating the single-phase construction of S and Se without the phase separation of MoS_2 and MoSe_2 .

To further probe the chemical composition of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ /CNFs hybrids, XPS characterizations were conducted. Fig. 4a–d presents the survey, and Mo 3d, S 2p, and Se 3d high-resolution spectra of the as-grown hybrid. As shown in Fig. 4a, the result indicates that a composition of C, Mo, S, and Se exists in the hybrid, in good accordance with the mapping result. The intensity of the C 1s is the strongest among all of peaks, revealing that the carbonaceous material is dominant in the hybrid, and it could improve the conductivity of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ semiconductor. In Fig. 4b, the two clear peaks located at 232.5 eV and 229.4 eV are the characteristic Mo 3d_{3/2} and Mo 3d_{5/2} peaks, respectively, and are consistent with values from MoS_2 and MoSe_2 systems [23–25]. The Mo 3d_{5/2} peak located at 229.4 eV is the characteristic peak of the Mo +4 oxidation state in the hexagonal 2H phase [2,26]. The peaks for S 2p between 158 eV and 170 eV can be deconvoluted into four peaks (Fig. 4c). The S 2p_{1/2} and 2p_{3/2} peaks emerge with binding energies of 163.7 eV and 162.4 eV, respectively [21,22,25]. They are in agreement with the binding energies of the corresponding peaks in MoS_2 , demonstrating the existence of Mo–S bonding instead of elemental S [27,28]. Whereas the other two obvious peaks located at approximately 167.0 eV and 161.2 eV are assigned to Se 3p_{1/2} and 3p_{3/2}, respectively [3,25,29]. The peaks at approximately

55.7 eV and 54.9 eV are attributed to Se 3d_{3/2} and 3d_{5/2}, respectively, as shown in Fig. 4d.

XRD and Raman spectroscopy were utilized to investigate the nanostructure information of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ /CNFs hybrid. The diffraction peaks of the samples in the XRD pattern reveal the good purity of the products, as shown in Fig. 5a. The good crystallinity of the samples is likely advantageous for the catalytic activity and stability [20]. The broad diffraction peak at a 2θ value of 23.3° is attributed to the diffraction plane of (002) for graphitic carbon. The characteristic diffraction peaks in the case of MoSe_2 /CNFs located at 2θ value of 13.60°, 31.71°, 37.35°, and 57.09° correspond to the (002), (100), (103), and (110) diffraction planes, respectively. Moreover, the characteristic diffraction peaks of the $\text{MoS}_{0.44}\text{Se}_{1.56}$ /CNFs slightly shift to higher angles, and such a slight displacement is expected as S has a smaller ionic radius than Se [3,30,31], which indicates that the mixing of Se and S is on the atomic scale.

Raman spectroscopy was used to characterize the composition-dependent vibration modes of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ /CNFs hybrid, as presented in Fig. 5b. As is well known, two kinds of characteristic Raman vibrational modes can be gained in 2D metal dichalcogenides: the in-plane vibrational mode (E mode) and the out-plane vibrational mode (A mode). In the case of the ternary alloy $\text{MoS}_{2(1-x)}\text{Se}_{2x}$, the vibrational modes can be classified into two sets of composition-dependent modes: Mo–Se-related modes at low frequency (200–300 cm⁻¹) and Mo–S-related modes at high frequency (350–410 cm⁻¹) [2]. For the low frequency modes of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ /CNFs hybrid, two identifiable peaks can be found at approximately 233.54 cm⁻¹ and 248.90 cm⁻¹, corresponding to the MoSe_2 -like A_{1g} and E_{2g}, respectively. The intensities of the MoS_2 -like vibration modes are less than those of MoSe_2 , and the peaks located at approximately 380.88 cm⁻¹ and 441.23 cm⁻¹ can be assigned to the MoS_2 -like E_{2g} and A_{1g}, respectively. Moreover, for the high frequency modes of the hybrid, two sharp peaks at 1334.29 cm⁻¹ and 1584.78 cm⁻¹ can be ascribed to the D and G bands of the carbon nanofibers substrate.

Based on the above discussion, the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ nanoflakes with a hexagonal morphology were successfully prepared on the surface of the CNFs. The characterizations reveal

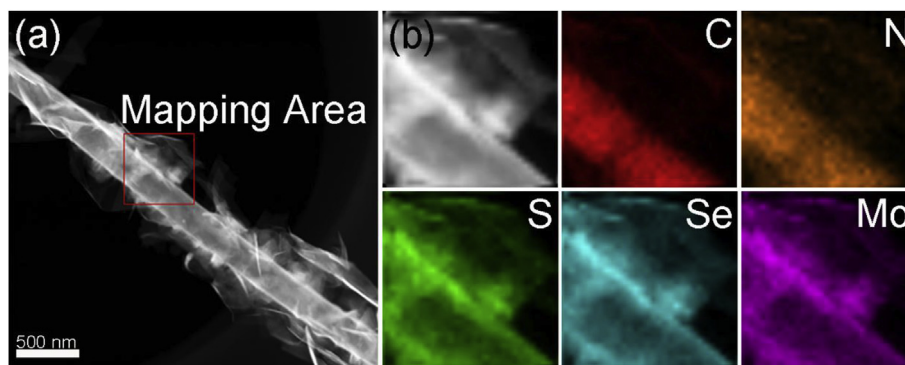


Fig. 3 – (a) HAADF STEM image of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ /CNFs hybrids, and (b) the corresponding elemental distribution obtained from the mapping area in (a).

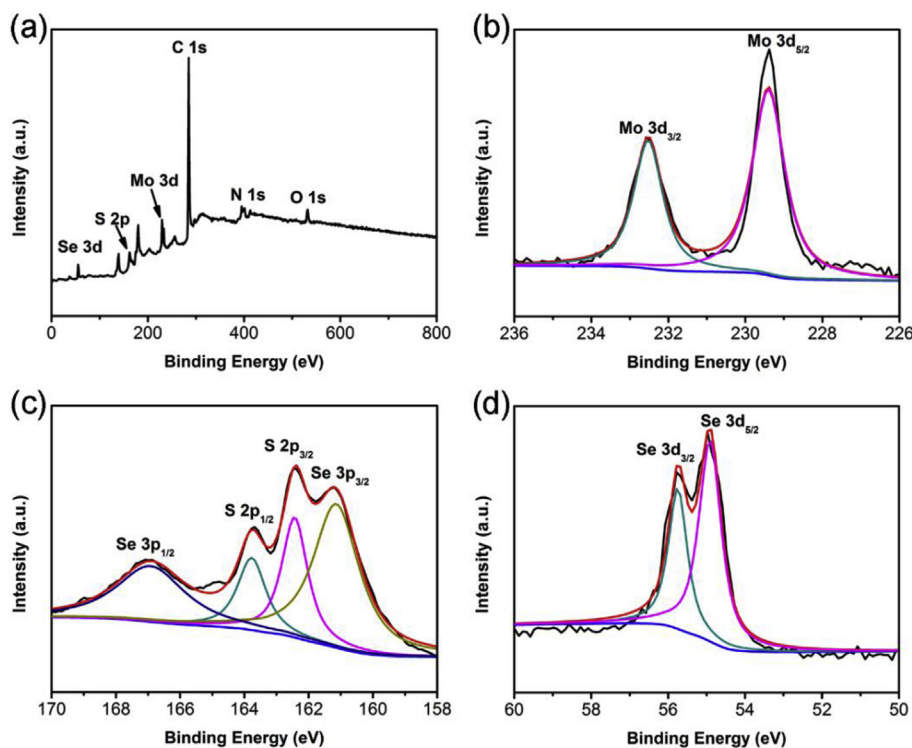


Fig. 4 – XPS spectra of (a) the survey, (b) Mo 3d, (c) S 2p, and (d) Se 3d of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$ hybrid.

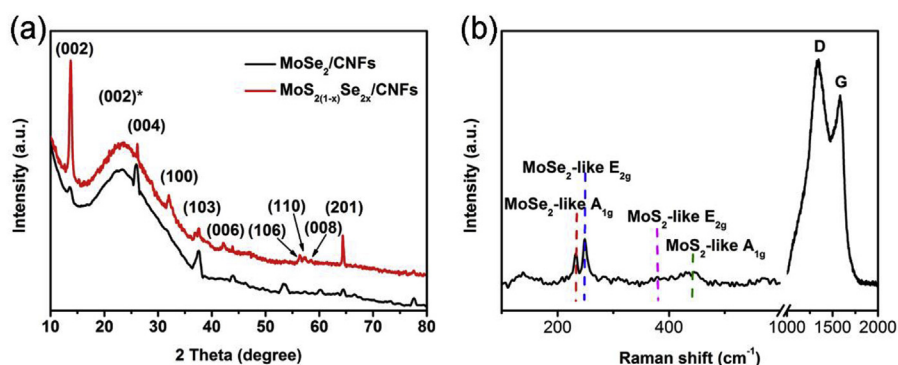


Fig. 5 – (a) XRD patterns of the $\text{MoSe}_2/\text{CNFs}$ hybrid (black) and the $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$ hybrid (red); (b) the Raman spectrum of $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$ hybrid. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the good crystallinity of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ nanoflakes and their maximally exposed edge sites, which are critical for HER catalysts. A typical three-electrode system and 0.5 M H_2SO_4 (aq) was utilized to evaluate the HER activity. The hybrid was directly assembled as the working electrode. The platinum mesh electrode and the saturated calomel electrode were used as the counter electrode and the reference electrode, respectively. The polarization curves reveal that the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ (HD)/CNFs hybrid exhibited the smallest onset potential of approximately 54 mV vs. RHE, as shown in Fig. 6a. Significantly, in the case of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ (LD)/CNFs hybrid, the onset potential is substantially higher than that of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ (HD)/CNFs hybrid (approximately 104 mV vs. RHE). Moreover, the onset potential of the $\text{MoSe}_2/\text{CNFs}$ hybrid is approximately 137 mV vs. RHE. And the MoS_2/CNFs hybrid

exhibits higher onset potential of 167 mV vs. RHE. Interestingly, the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ (HD)/CNFs hybrid demonstrated the best activity for the HER with an overpotential of 150 mV (vs. RHE) at a current density of 10 mA/cm² and the $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ (LD)/CNFs hybrid possesses a higher overpotential of 272 mV (vs. RHE), which is less than that of the $\text{MoSe}_2/\text{CNFs}$ hybrid (approximately 345 mV vs. RHE) and the MoS_2/CNFs hybrid (approximately 281 mV vs. RHE).

The Tafel slope is another critical factor for the HER, and an inherent property of the rate-determining step in the HER. The slopes were obtained by the fitting of the linear regions, according to the Tafel equation: $\eta = b \log j + a$, where η is the overpotential, b is the Tafel slope, and j is the current density. As shown in Fig. 6b, the $\text{MoSe}_2/\text{CNFs}$ hybrid exhibits the largest Tafel slope (166 mV/dec), and the value for the

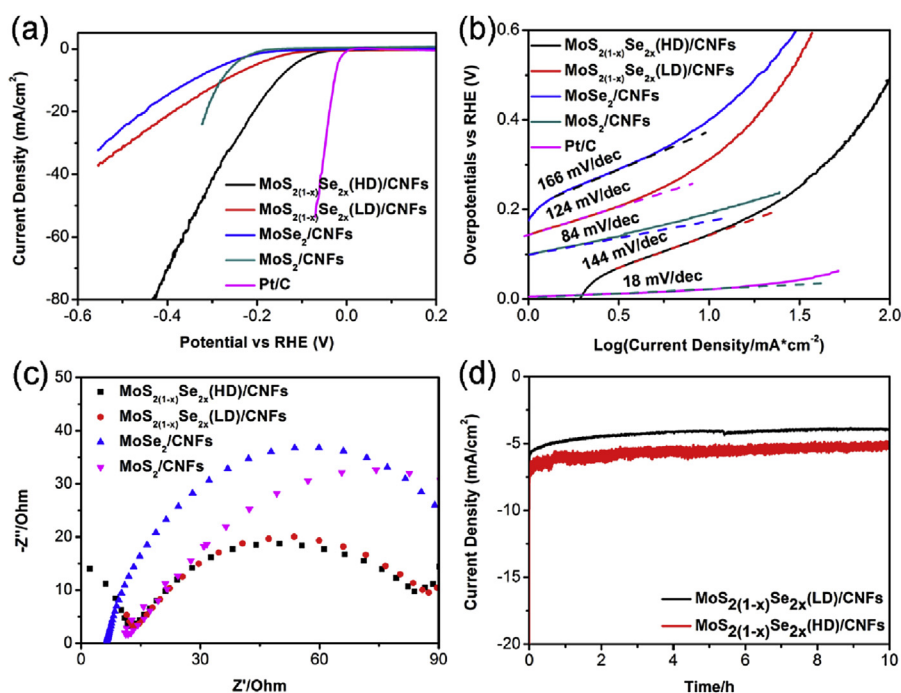


Fig. 6 – (a) Polarization curves obtained for $\text{MoSe}_2/\text{CNFs}$, MoS_2/CNFs , $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{LD})/\text{CNFs}$, $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{HD})/\text{CNFs}$, and Pt/C as indicated, (b) the corresponding Tafel plots and (c) the electrochemical impedance spectra of $\text{MoSe}_2/\text{CNFs}$, MoS_2/CNFs , $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{LD})/\text{CNFs}$ and $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{HD})/\text{CNFs}$, and (d) the time dependence of the current density under a static overpotential of -0.5 V .

$\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{HD})/\text{CNFs}$ hybrid is 144 mV/dec , which suggests it follows the Volmer-Heyrovsky or the Volmer-Tafel process with the Volmer reaction as the rate-determining step. Strangely, an abnormal phenomenon occurred with the $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{LD})/\text{CNFs}$ hybrid yielding a value of the Tafel slope as 124 mV/dec , which is substantially less than that of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{HD})/\text{CNFs}$ hybrid. Generally, a smaller Tafel slope means an improvement in the HER rate at a moderate increase of overpotential [3,22,32,33]. Besides the HER catalysis active sites, the enhanced charge transfer kinetics also contribute to the improved HER efficiency of a catalysts [3]. We evaluated the AC impedance at an overpotential of -300 mV (as shown in Fig. 6c). The ternary alloy hybrid exhibits a smaller charge transfer impedance at range of $70\text{--}80\text{ Ohm}$ than that of the $\text{MoSe}_2/\text{CNFs}$ hybrid ($\sim 120\text{ Ohm}$) and MoS_2/CNFs hybrid ($\sim 150\text{ Ohm}$), suggesting faster HER kinetics with $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$.

The durability of the catalysts is another important property for the HER. The time dependence of the current density was investigated at an overpotential of -0.5 V for $36,000\text{ s}$. As shown in Fig. 6d, the current density of the ternary alloy hybrid remained stable for 10 h , and only a slight decrease was observed, indicating the excellent electrocatalytic durability of the $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$ hybrids.

In the present investigations, we investigated and determined the elements by XPS characterizations. We calculated the ratio of Se/S by the formula: $\text{Se}/\text{S} = (I_{\text{Se}} \cdot F_{\text{S}}) / (I_{\text{S}} \cdot F_{\text{Se}})$, where I_{Se} and I_{S} are the areas under the peaks of Se $3p_{3/2}$ and S $2p_{3/2}$, respectively; F_{Se} and F_{S} represent the relative symmetric factors (R.S.F) for Se $3p_{3/2}$ (0.4453) and S $2p_{3/2}$ (0.8493) respectively

[21,22]. In the case of $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{HD})/\text{CNFs}$ and $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{LD})/\text{CNFs}$, the x is determined as 0.78 and 0.64 , respectively.

In earlier theoretical calculations, the results revealed that the ΔG_{H} of hydrogen adsorption for Mo–S edges is 80 meV and that of Mo–Se edges is -140 meV [22,34,35]. It reaches the thermoneutral with the free energy of adsorbed atomic hydrogen to $\Delta G_{\text{H}} \approx 0$. With the introduction of Se into MoS_2 lattice, the oxidation state of Mo would be changed. The increasing of Se content, the energy barrier in the chemical reaction would decrease, resulting lower hydrogen adsorption energy and higher HER performance [22]. As a consequence, the $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{HD})/\text{CNFs}$ and $\text{MoS}_{2(1-x)}\text{Se}_{2x}(\text{LD})/\text{CNFs}$ catalysts exhibit much higher electrochemical activity compared with $\text{MoSe}_2/\text{CNFs}$ and MoS_2/CNFs .

Conclusions

In summary, the hexagonal layered $\text{MoS}_{2(1-x)}\text{Se}_{2x}$ nanoflakes were successfully grown onto carbon nanofibers by the CVD method. The ternary alloy nanoflakes with an abundance of exposed active edge sites were uniformly stacked on the surface of the CNFs. The as-prepared $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$ hybrids were directly used as hydrogen evolution cathodes, and all of the samples exhibited a lower onset potential, a higher current density, and excellent durability, suggesting $\text{MoS}_{2(1-x)}\text{Se}_{2x}/\text{CNFs}$ hybrid has significantly enhanced catalytic activity and could serve as an effective and promising catalyst for the HER.

Acknowledgments

This study was supported by the National Natural Science Foundation of China (NSFC) (Grant number. 51373154, 51573166), the Program for Innovative Research Team of Zhejiang Sci-Tech University and the 521 Talent Project of Zhejiang Sci-Tech University.

REFERENCES

- Morales-Guio CG, Stern LA, Hu X. Nanostructured hydrotreating catalysts for electrochemical hydrogen evolution. *Chem Soc Rev* 2014;43:6555–69.
- Gong Q, Cheng L, Liu C, Zhang M, Feng Q, Ye H, et al. Ultrathin $\text{MoS}_2(1-x)\text{Se}_{2x}$ alloy nanoflakes for electrocatalytic hydrogen evolution reaction. *ACS Catal* 2015;5:2213–9.
- Xu C, Peng S, Tan C, Ang H, Tan H, Zhang H, et al. Ultrathin S-doped MoSe_2 nanosheets for efficient hydrogen evolution. *J Mater Chem A* 2014;2:5597–601.
- Feng Q, Mao N, Wu J, Xu H, Wang C, Zhang J, et al. Growth of $\text{MoS}_2(1-x)\text{Se}_{2x}$ ($x = 0.41-1.00$) monolayer alloys with controlled morphology by physical vapor deposition. *ACS Nano* 2015;9:7450–5.
- Kong D, Wang H, Cha J, Pasta M, Koski K, Yao J, et al. Synthesis of MoS_2 and MoSe_2 films with vertically aligned layers. *Nano Lett* 2013;13:1341–7.
- Wang H, Kong D, Johannes P, Cha J, Zheng G, Yan K, et al. MoSe_2 and WSe_2 nanofilms with vertically aligned molecular layers on curved and rough surfaces. *Nano Lett* 2013;13:3426–33.
- Wu Z, Fang B, Wang Z, Wang C, Liu Z, Liu F, et al. MoS_2 nanosheets: a designed structure with high active site density for the hydrogen evolution reaction. *ACS Catal* 2013;3:2101–7.
- Kim J, Byun S, Smith A, Yu J, Huang J. Enhanced electrocatalytic properties of transition-metal dichalcogenides sheets by spontaneous gold nanoparticle decoration. *J Phys Chem Lett* 2013;4:1227–32.
- Chhowalla M, Shin H, Eda G, Li L, Loh K, Zhang H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat Chem* 2013;5:263–75.
- Merki D, Vrubel H, Rovelli L, Fierro S, Hu X. Fe, Co, and Ni ions promote the catalytic activity of amorphous molybdenum sulfide films for hydrogen evolution. *Chem Sci* 2012;3:2515–25.
- Lv X, She G, Zhou S, Li Y. Highly efficient electrocatalytic hydrogen production by nickel promoted molybdenum sulfide microspheres catalysts. *RSC Adv* 2013;3:21231–6.
- Li J, Tang W, Yang H, Dong Z, Huang J, Li S, et al. Enhanced electrocatalytic activity of $\text{Ni}_{1-x}\text{Fe}_x$ alloy supported on polyethyleneimine functionalized MoS_2 nanosheets for hydrazine oxidation. *RSC Adv* 2014;4:1988–95.
- Zhou T, Yin H, Liu Y, Chai Y, Zhang J, Liu C. Synthesis, characterization and HDS activity of carbon-containing Ni–Mo sulfide nano-spheres. *Catal Lett* 2010;134:343–50.
- Alvarez L, Berhaut G, Alonso-Nunez G. Unsupported NiMo sulfide catalysts obtained from nickel/ammonium and nickel/tetraalkylammonium thiomolybdates: synthesis and application in the hydrodesulfurization of dibenzothiophene. *Catal Lett* 2008;125:35–45.
- Liu B, Chai Y, Liu Y, Wang Y, Liu Y, Liu C. A simple method for preparation of presulfidized eggshell $\text{CoMoS}/\gamma\text{-Al}_2\text{O}_3$ catalysts for hydrodesulfurization of dibenzothiophene. *Fuel* 2012;95:457–63.
- Okamoto Y, Hioka K, Arakawa K, Fujikawa T, Ebihara T, Kubota T. Effect of sulfidation atmosphere on the hydrodesulfurization activity of SiO_2 -supported Co–Mo sulfide catalysts: local structure and intrinsic activity of the active sites. *J Catal* 2009;268:49–59.
- Li H, Duan X, Wu X, Zhuang X, Zhou H, Zhang Q, et al. Growth of alloy $\text{MoS}_2x\text{Se}_{2(1-x)}$ nanosheets with fully tunable chemical compositions and optical properties. *J Am Chem Soc* 2014;136:3756–9.
- Tongay S, Narang D, Kang J, Fan W, Ko C, Luce A, et al. Two-dimensional semiconductor alloys: monolayer $\text{Mo}_{1-x}\text{W}_x\text{Se}_2$. *Appl Phys Lett* 2014;104:012101.
- Zhang W, Li X, Jiang T, Song J, Lin Y, Zhu L, et al. CVD synthesis of $\text{Mo}_{(1-x)}\text{W}_x\text{S}_2$ and $\text{MoS}_2(1-x)\text{Se}_{2x}$ alloy monolayers aimed at tuning the bandgap of molybdenum disulfide. *Nanoscale* 2015;7:13554–60.
- Zou M, Chen J, Xiao L, Zhu H, Yang T, Zhang M, et al. WSe_2 and $\text{W}(\text{Se}_x\text{S}_{1-x})_2$ nanoflakes grown on carbon nanofibers for the electrocatalytic hydrogen evolution reaction. *J Mater Chem A* 2015;3:18090–7.
- Kiran V, Mukherjee D, Jenjeti R, Sampath S. Active guests in the $\text{MoS}_2/\text{MoSe}_2$ host lattice: efficient hydrogen evolution using few-layer alloys of $\text{MoS}_2(1-x)\text{Se}_{2x}$. *Nanoscale* 2014;6:12856–63.
- Lei Yang, Wang W, Fu Q, Zhang J, Xiang. $\text{MoS}_2(1-x)\text{Se}_{2x}$ nanobelts for enhanced hydrogen evolution. *Electrochimica Acta* 2015;185:236–41.
- Bougouma M, Batan A, Guel B, Segato T, Legma J, Reniers F, et al. Growth and characterization of large, high quality MoSe_2 single crystals. *J Cryst Growth* 2013;363:122–7.
- Abdallah W, Nelson A. Characterization of MoSe_2 (0001) and ion-sputtered MoSe_2 by XPS. *J Mater Sci* 2005;40:2679–81.
- Gong Y, Liu Z, Lupini A, Shi G, Lin J, Najmaei S, et al. Band gap engineering and layer-by-layer mapping of selenium-doped molybdenum disulfide. *Nano Lett* 2014;14:442–9.
- Kibsgaard J, Chen Z, Reinecke B, Jaramillo T. Engineering the surface structure of MoS_2 to preferentially expose active edge sites for electrocatalysis. *Nat Mater* 2012;11:963–9.
- Benoist L, Gonbeau D, Pfister-Guillouzo G, Schmidt E, Meunier G, Lévassieur A. XPS analysis of lithium intercalation in thin films of molybdenum oxysulphides. *Surf Interface Anal* 1994;22:206–10.
- Wang H, Skeldon P, Thompson G. XPS studies of MoS_2 formed in associated with anodizing process. *Surf Coat Technol* 1997;91:200–7.
- Ueno T. Chemical shifts of photoelectron and Auger lines in Ag- or Cu-doped amorphous GeSe_2 and As_2Se_3 . *Jpn J Appl Phys* 1983;22:1469.
- Yang C, Qin M, Wang Y, Wan D, Huang F, Lin J. Observation of an intermediate band in Sn-doped chalcopyrites with wide-spectrum solar response. *Sci Rep* 2013;3:1286.
- Wang G, Yang M, Li Z, Lin K, Jin Q, Xing C, et al. Synthesis and characterization of Zn-doped MgAl-layered double hydroxide nanoparticles as PVC heat stabilizer. *J Nanopart Res* 2013;15:1–8.
- Li Y, Wang H, Xie L, Liang Y, Hong G, Dai H. MoS_2 nanoparticles grown on graphene: an advanced catalyst for the hydrogen evolution reaction. *J Am Chem Soc* 2011;133:7296–9.
- Xie J, Zhang H, Li S, Wang R, Sun X, Zhou M, et al. Defect-rich MoS_2 ultrathin nanosheets with additional active edge sites for enhanced electrocatalytic hydrogen evolution. *Adv Mater* 2013;25:5807–13.
- Hinnemann B, Moses P, Bonde J, Jørgensen K, Nielsen J, Horch S, et al. Biomimetic hydrogen evolution: MoS_2 nanoparticles as catalyst for hydrogen evolution. *J Am Chem Soc* 2005;127:5308–9.
- Jaramillo T, Jørgensen K, Bonde J, Nielsen J, Horch S, Chorkendorff I. Identification of active edge sites for electrochemical H_2 evolution from MoS_2 nanocatalysts. *Science* 2007;317:100–2.