

Original Article

High activity Ni-MoS_{2-x} monolayer nano-sheets fabricated through photo-deposition for highly efficient HER in acid solution

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ABSTRACT

A highly active and stable electro-catalyst for hydrogen evolution was developed by in-situ photo-deposition of Ni metal on MoS₂ nano-sheets with many sulfur vacancies. It was found that Ni metal deposition improved the electrical conductivity of MoS₂ and further enhanced the catalytic activity by synergistic effect with Ni metal with MoS₂ nano-sheets. During photochemical deposition, photo-corrosion moved some sulfur, leading to many sulfur vacancies. Sulfur vacancies further enhance the activity of MoS₂ nano-sheets. Electrochemical experiments demonstrate that the catalyst exhibited excellent hydrogen evolution reaction activity with a large cathode current and a Tafel slope as small as 81 per decade. The high hydrogen evolution activity of Ni-doped MoS₂ was attributed to synergistic electro-catalytic effects between MoS₂ nano-sheets and Ni ions.

1. Introduction

Hydrogen gas has been considered a clean energy source because modern society confronts energy deficits and environmental pollution. Electrochemical-catalytic hydrogen production in an acid solution is one of the most effective and reliable pathways [1-5]. There is no doubt that platinum and its alloys are the most efficient catalysts for hydrogen production. However, the high cost and low reserves have limited their utilization in water electrolysis. Therefore, searching for alternative earth-abundant materials and decreasing the cost of catalysts remain crucial tasks [6-18]. Transition metal disulfides (MS₂) have been considered an up-and-coming alternative to platinum due to their abundance, low cost, and considerable catalytic activity [19-21]. Norskov's group calculated the hydrogen binding energy of MoS₂ and found it was like that of platinum. However, the catalytic activity of 2D MoS₂ was contributed to by its edge sites and sulfur vacancies, leaving many basal plane domains inert for Hydrogen electrochemical revolution (HER) [22]. The HER activity of MoS₂ correlated with the number of catalytically active edge sites and sulfur vacancies that generated new gap states near the Fermi level for hydrogen binding [21,23,24]. As a result, nano-sized MoS₂ is more active than the bulk form due to more exposed sulfur edge sites [25,26]. Based on this understanding, various strategies have been developed to synthesize nano-structured MoS₂ with more defects to improve the HER [6,16,27]. Xie Yi found that the involved oxygen atom can effectively regulate the electronic structure of MoS₂ nano-sheets, enhancing conductivity and HER performance [6]. Zhou Yao *et al.* synthesized Rh_{tin}-MoS_xO_y. Electron-rich tin prefers to stabilize the unstable optical O site in MoS_xO_y, while Rh is a charge regulator, and oxygen in MoS_xO_y provides more activation sites. The triple enhancement effect makes Rh-Sn-MoS_xO_y have high electrochemical activity [28]. Using transition

metal atoms, such as Ni, Co, Fe, Zn, and Mn-doped MoS₂ nano-sheets, could significantly improve the electrochemical activity of MoS [29-34]. Wang *et al.* demonstrated that the exchange current density of MoS₂ can be increased by incorporating transition metal atoms [33]. Activating the MoS₂ basal plane could improve its HER activity compared to growing edge sites. Hong Li *et al.* used Ar plasma to activate the MoS₂ basal plane by increasing sulfur vacancies to increase MoS₂ catalytic activity [23]. By doping with other transition metal sulfides, such as NiS, MnS, ZnS, and CoS, MnS could improve the HER activity of MoS₂ electro-catalysts [35-39].

Herein, we report a novel photochemical strategy to activate MoS₂ monolayer nanosheets' electrocatalytic activity through NiS-incorporated MoS₂ nanosheets and increased sulfur vacancies. Linear sweep voltammetry and Chronoamperometry were used to study the electrochemical activity of MoS₂ nanosheets and Ni-doping MoS_{2-x} nanosheets. Ni displaced some of Mo through photochemical deposition to form the Ni-S band, which had higher electrochemical activity for hydrogen production. Ni dopant and S defects made Ni-doped MoS₂ monolayer nanosheets have higher catalytic activity for HER.

2. Materials and Methods

2.1. Materials

Single MoS₂ nanosheets were purchased from Jiangsu Xianfeng Nanomaterial Technology Co., Ltd. Nickel nitrate and methanol analytical reagents came from Shanghai Aladdin Biochemical Technology Co., Ltd. H₂SO₄ was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. The high-purity water was treated through the Ake water system.

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2.2. Synthesis of catalysts

Typically, 15 mg MoS₂ monolayer nanosheets were dispersed in a 15 mL ethanol solution through ultrasonication. Then, nickel nitrite and 15 mL of pure water were added to the above solution. 0.1 M NaOH and 0.5M H₂SO₄ solution were used to adjust the pH value of the above mixture solution. The MoS₂ nanosheets with different pH values were then illuminated under a 300W Xe light with a 530 nm optical filter for 1 h. The product was washed with a 1:1 ethanol-water solution several times and dried by vacuum cooling drying.

2.3. Preparation of catalyst electrode

Typically, 2 mg of Ni-doping MoS₂ nanosheets catalyst and 30 μL of 0.5% Nafion 717 were dispersed in 1 mL of water by ultrasonication to form a uniform mixture. The catalyst slurry (4 μL) was dropped onto a pure Glass carbon electrode (GCE). Subsequently, a desiccator was used to dry the catalyst-modified GCE at room temperature.

2.4. Electrochemical measurements

Electrochemical measurements were performed through a CHI 660C working station with a standard three-electrode cell. The Ni-MoS₂-modified GCE electrode acted as a working electrode, a Pt electrode as an auxiliary electrode, and a saturated calomel electrode (SCE) as a reference electrode. The electro-catalytic activity of MoS₂ monolayer or Ni doped-MoS₂ was examined through cyclic voltammetry, linear sweep voltammetry, and chrono-amperometry in 0.5M H₂SO₄ solution.

The photochemical deposition experiment was performed in 50 ml reaction tubes with ground glass at room temperature, using a 300W Xe lamp with a 530 nm light filter.

2.5. Characterization

An X-ray diffractometer recorded X-ray diffraction (XRD) patterns. Images were collected using a JEM-2100 transmission electron microscope (TEM). X-ray photoelectron spectroscopy (XPS) was studied to confirm the chemical composition of MoS₂ nanomaterials and nickel-doped MoS₂ nanomaterials. The sample of nickel doping MoS₂ nanosheets (Scanning electron microscope (SEM), XPS, and XRD studied) was prepared with the ratio of MoS₂ to Nickel ions (0.8:1) at a pH value of 2.0.

3. Results and Discussion

3.1 Morphology and structure analysis of MoS₂ and Ni doping MoS₂

The XRD pattern of nickel-doping MoS₂ nanosheets and pure MoS₂ nanosheets were studied to assess their crystal structures. The XRD pattern of MoS₂ nanosheets in Figure 1 revealed the characteristic diffraction of 2H-MoS₂ (JCPDS:73-1508). In contrast, no metallic nickel or nickel oxide diffraction was detected in the sample of nickel-doping MoS₂ nanosheets, confirming the presence of a small amount of nickel

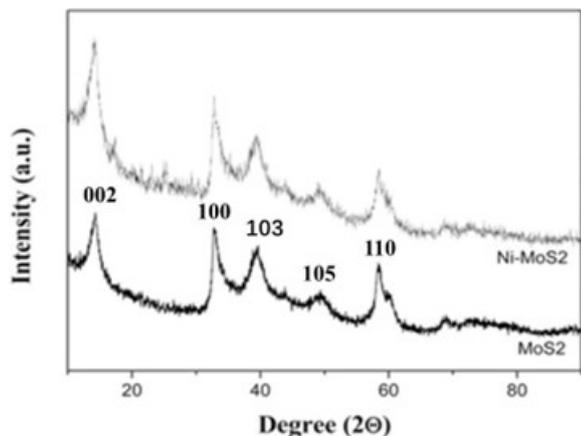


Figure 1. XRD image of MoS₂ nanosheets and Ni doping MoS₂ nanosheets. XRD: X-ray diffraction.

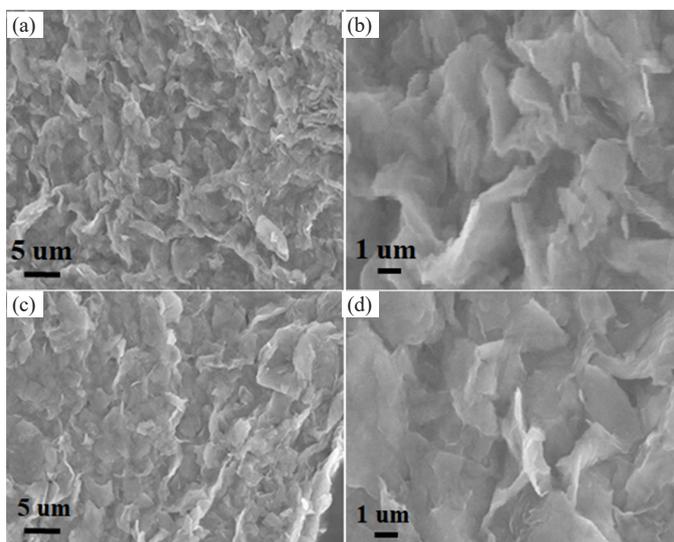


Figure 2. (a) SEM image of MoS₂ nanosheets and (b) enlarged image of MoS₂ nanosheets, (c) SEM image of Ni doping MoS₂ nanosheets and (d) enlarged image of Ni doping MoS₂ nanosheets. SEM: Scanning electron microscope.

in the nickel-doping MoS₂ nanosheets. SEM and TEM characterized the MoS₂ nano-sheet and Ni metal-doped MoS₂ nano-sheet morphology. It can be seen in the SEM image in Figure 2 that there is no significant difference between the pure MoS₂ nano-sheets and Ni-doped MoS₂ nano-sheets. The MoS₂ nano-sheet was larger than 1 μm in both pure MoS₂ nanosheets and nickel-doping MoS₂ nanosheets.

The MoS₂ nanosheets in Figure 3(a) present a folded nano-sheet-like structure, and the morphology of NiS-doped MoS₂ in Figure 3(b) also presents folded nanosheets with some small particles attached to the surface, which may be attributed to NiS produced by the photo-deposition process. High resolution transmission electron microscope (HRTEM) of the MoS₂ nanosheets in Figure 3(c) presents a clear and coherent lattice structure. Many tiny particles are scattered on the

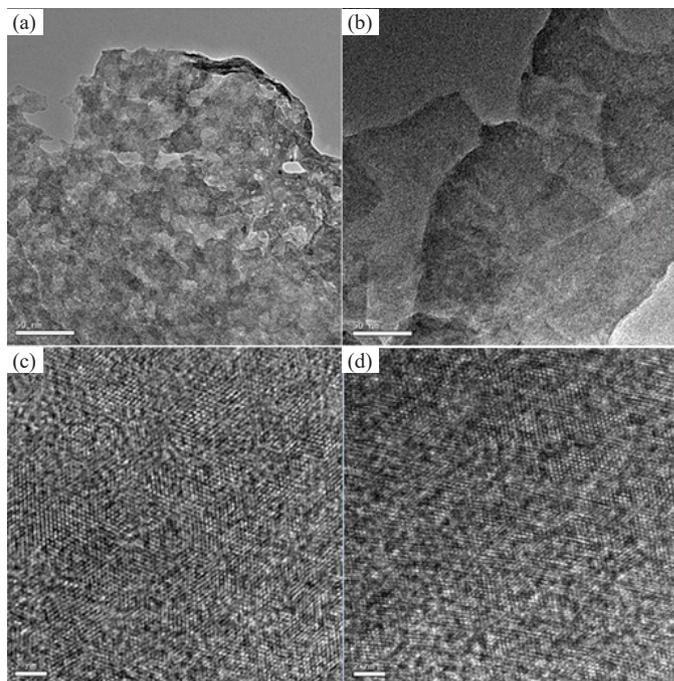


Figure 3. The MoS₂ nanosheets in (a) present a folded nano-sheet-like structure, and the morphology of NiS-doped MoS₂. (b) Presents folded nanosheets with some small particles attached to the surface, which may be attributed to NiS produced by the photo-deposition process. (c-d) HRTEM of the MoS₂ nanosheets (c) presents a clear and coherent lattice structure, (d) with a lattice structure different from the lattice structure of MoS₂, which are NiS particles formed during the photochemical deposition process. HRTEM: High resolution transmission electron microscope.

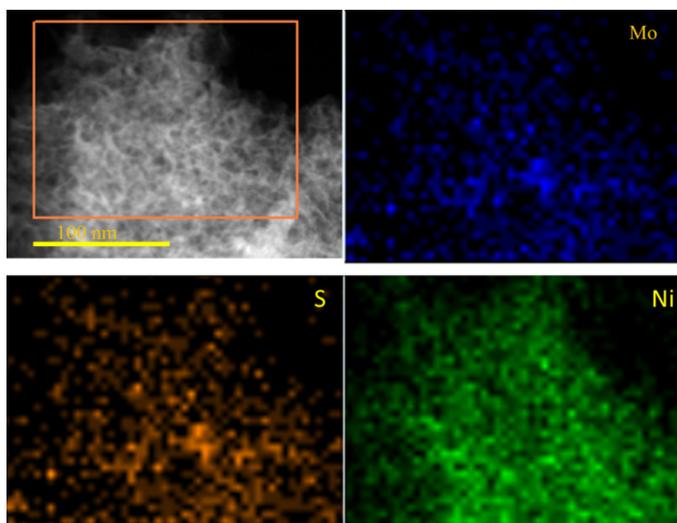


Figure 4. EDX mapping of elements in Ni-doping MoS_{2x} nano-sheets.

surface of MoS_2 nanosheets in Figure 3(d) with a lattice structure different from the lattice structure of MoS_2 , which are NiS particles formed during the photochemical deposition process. This phenomenon, which showed that Ni-doped MoS_2 nano-sheets had little difference from pure MoS_2 nano-sheets, could contribute to that small amount of Ni doping in the Ni- MoS_2 . The SEM and XRD images had the same phenomena as the TEM images, further confirming the small amount of nickel in Ni- MoS_2 nano-sheets.

To further study that Ni had inserted into MoS_2 nano-sheets, the EDX mapping method was used to study the Ni further doping MoS_2 monolayer nano-sheets fabrication. EDX mapping in Figure 4 showed the homogenous distribution of Mo, S, and Ni elements, further confirming that the Ni doping MoS_2 nano-sheet was successfully fabricated using photo-chemical deposition. The EDX and EDX mapping in Figure 4 confirmed that nickel had successfully inserted into MoS_2 nano-sheets.

The Mo, Ni, and S chemical states in the Ni-doped single nanosheets are analyzed using the X-ray photoelectron spectroscopy technique (XPS). The 232.2 and 229 eV peaks belong to Mo 3d 3/2 and 3d 1/2 binding energies (Figure 5a), respectively, which were constant with the structure of MoS_2 nanosheets. The peak (223) belongs to MoO_3 , and the binding energy located at 232 belongs to molybdic acid, formed by MoS_2 oxidized by photochemical corrosion. There are also

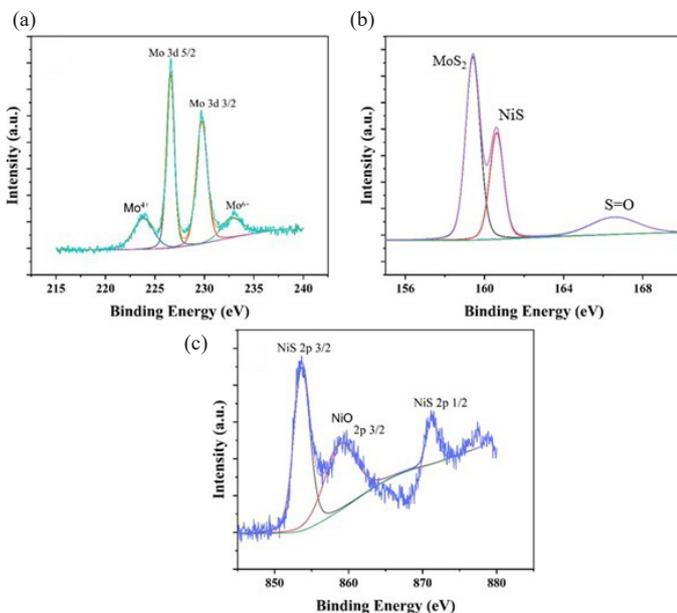


Figure 5. XPS image of (a) Mo 3d, (b) S 1s, and (c) Ni 2p in Ni doping MoS_2 nanosheet. XPS: X-ray photoelectron spectroscopy.

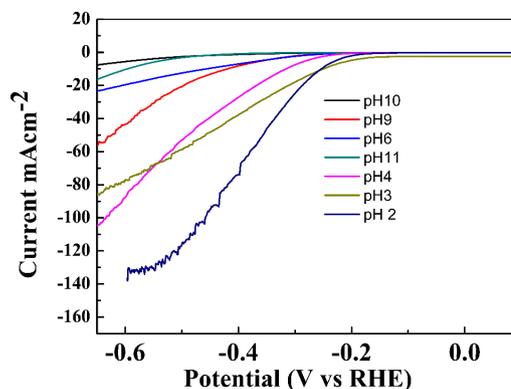


Figure 6. Linear sweep scan image of Ni- MoS_2 in 0.5M H_2SO_4 at a scan rate of 20 mV/s (fabricated in different pH values).

three pairs of characteristic peaks belonging to S elements. The 159.4, 160.6, and 166.6 eV peaks in Figure 5(b) contributed to MoS_2 , NiS, and S partly oxidizing, respectively. The electronic valence state of nickel in the above materials was also studied by XPS spectroscopy, with the peak located at 857.8, 871.2 eV in Figure 5(c) contributing to Ni 2p 2/3 and 2p 1/2. Meanwhile, the peak located at 859.1 belongs to nickel oxide. The XPS image research confirms that the Ni-doped MoS_2 nanosheets contain Ni, Mo, and S elements. Nickel exists in the form of nickel sulfide in nickel-doped molybdenum disulfide materials. Like molybdenum disulfide, NiS has good electro-catalytic activity for hydrogen production. The synergistic effect of NiS and MoS_2 gives Ni- MoS_2 higher electrocatalytic activity for hydrogen production.

3.2 Electrochemical performance

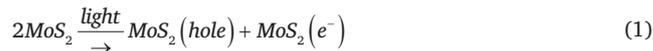
3.2.1 pH value affects the catalyst activity

MoS_2 monolayer nanosheets have been widely studied in the electrocatalytic hydrogen reaction. Still, due to their activity, they only originated from edge sites and sulfur vacancies, leaving a tremendous amount of in-plane domains inert. To enhance the catalytic activity of MoS_2 nanosheets, the photochemical method was used to fabricate Ni metal-doped MoS_2 nanosheets. Furthermore, some sulfur atoms were moved by the photochemical corrosion reaction during the photochemical reaction. Subsequently, Ni-doped MoS_2 with many sulfur vacancies has super catalytic activity in hydrogen production.

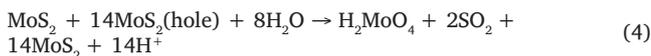
The pH value of the synthesis environment has dramatically affected the activity of the catalyst. It can be seen in Figure 6 that the pH value has significantly impacted the electro-catalytic activity of Ni- MoS_2 . When the pH value decreased from 11 to 2, the electro-catalytic activity of Ni- MoS_2 increased with the pH value decreased. When the pH value was 2, the electrochemical activity got the highest value. pH value has dramatically impacted the activity of Ni-doped MoS_2 nano-sheets for Ni metal deposition, which has been significantly affected by the pH value for hydrogen ions participating in Ni-doped MoS_2 nano-sheet fabrication.

3.2.2 The possible mechanism of Ni- MoS_2 fabrication by photochemical deposition

Ni ions were unstable in the alkaline solution, almost wholly changing into $\text{Ni}(\text{OH})_2$. Under the photochemical system, there is a reversible process of Ni ions and $\text{Ni}(\text{OH})_2$. The Ni ions were reduced to Ni metal on the surface of the MoS_2 nano-sheet by following the chemical Eqs. (1) to (3):



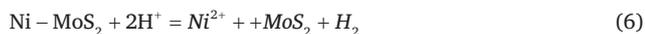
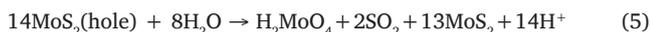
At the same time, some of part of MoS_2 nano-sheets were decomposed by the following photochemical reaction (Eq. 4):



Some molybdenum ions in the solution had reacted with oxygen to form molybdenum oxide, and other molybdenum ions dissolved in the solution as molybdic acid.

In the basement of the photochemical reaction, Ni metal was reduced by electrons, which were produced by light illumination on MoS_2 nano-sheets to make holes and electrons. The holes were depleted by hole receptor ethanol. The Ni metal kept being deposited until the Ni ions were transferred to NiS and NiO or the light was suddenly shut down.

Under weak acid solution, Ni- MoS_{2-x} was formed through chemical Eqs. (1)-(3). However, under an acid environmental system, the corrosion of MoS_2 would become serious for hydrogen ions to take part in the corrosion process, as shown in the following Eqs. (5)-(7). The nickel metal cluster or nickel oxide particles were unstable and could be dissolved in a robust acid solution. With strong photo-corrosion, many molybdenum or Sulphur lose and leave many active sites; the Ni ions could be coordinated with S and form a Ni-S bond. So, nickel ions were inserted into the structure of MoS_2 and displaced some of the Mo element. The XRD image (Figure 1) of Ni- MoS_2 nano-sheets and MoS_2 nano-sheets had no difference, which confirmed that nickel doping was not only mixed with nickel metal or nickel oxide.



During the photochemical deposition, some Ni-S or MoS_2 decomposed to ions and then combined with oxygen to form NiO, MoO_2 , and molybdic acid. The Ni-S, NiO, MoO_2 , and molybdic acid could enhance MoS_2 's electrochemical activity. Compared to the high amount of NiS, NiO, MoO_2 , and molybdic acid are lesser. A small amount of transition metal, transition sulfide, or transition oxide doping in MoS_2 could enhance the electrocatalytic activity of MoS_2 [37,38,40-43]. The existence of NiS, NiO, MnO_2 , and molybdic acid in Ni doping MoS_2 nanosheets gives the Ni doping MoS_2 nanosheets a higher electrocatalytic activity than pure MoS_2 nanosheets. The hydrogen ions taking part in photochemical corrosion and Ni- MoS_2 dissolution made a significant amount of MoS_2 decomposed, which led to the lower yield of Ni- MoS_{2-x} .

3.2.3 Electrochemical hydrogen evolution research

Electrochemical hydrogen evolution reactions were studied with different amounts of Ni to Ni- MoS_{2-x} and pure MoS_2 nano-sheets in 0.5M H_2SO_4 solution. Linear sweep voltammetry studies at a scan rate of 20 mv/s exhibit the current density as a function of applied potential. Figure 7 shows that pure MoS_2 exhibited great over-potential value and low current density, contributing to low edge concentration and poor

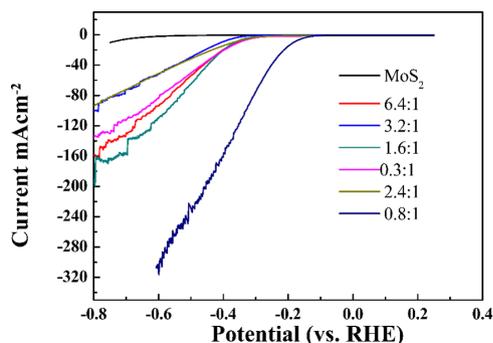


Figure 7. LSV image of Ni- MoS_{2-x} in 0.5M H_2SO_4 solution fabricated with different ratios of Ni ions compared with MoS_2 at a scan rate of 20 mv/s.

conductivity. In comparison, all the Ni metal doping MoS_{2-x} nano-sheets possessed much lower onset over-potentials than the pure MoS_2 nano-sheets. When the Ni to Mo molar rate was 3.2, the current was 80 mA cm^{-2} , eight times larger than a pure MoS_2 nano-sheet. Under optimized synthesis conditions, the amount of Ni affected the electrochemical activity of the catalyst's HER. When the molar rate of Ni ions to MoS_2 was 0.80, the current of Nickel - MoS_{2-x} was 320 mA cm^{-2} , almost 32 times bigger than pure MoS_2 . Under optimized conditions, the over-potential of Ni- MoS_2 was smaller than 100 mV. This phenomenon was relevant to the complication of photochemical deposition. The photochemical deposition is always accompanied by photo-corrosion. Photo-corrosion would lead to S and Mo loss, which would result in more sulfur vacancies and further enhance the MoS_2 catalyst's activity. The higher electrochemical activity of Ni-doping MoS_{2-x} could be attributed to the following reasons: photo-deposition corrosion left many S vacancies and defects, which enhanced HER activity. Ni doping further increased the HER activity of MoS_2 . In all, Ni doping and photo-deposition method in acid circumstances made NiS- MoS_{2-x} have higher HER activity. The existence of NiO, MoO_2 , and molybdic acid on MoS_2 further enhances the electrochemical activity for hydrogen production. The anisotropic factor of 2D nanomaterials towards their catalytic performance is demonstrated in the active edges.

The polarization curves were also measured in 0.5M H_2SO_4 electrolyte with a scan rate of 20 mv/s, as shown in Figure 8(a). To evaluate the electrochemical activity of Ni- MoS_2 , the HER activity of the commercial Pt/C acted as a reference for assessing Ni- MoS_2 performance. Undoubtedly, the Pt/C electro-catalyst exhibits the best electrochemical activity for HER with nearly zero over-potential. The electrochemical activity of H- MoS_2 was poor, with the highest over-potential. The electrochemical activity of Pt- MoS_2 is better than that of MoS_2 nano-sheets, and its over-potential is lower than that of pure MoS_2 , which means that noble Pt has excellent catalytic activity. Tafel slope is often utilized to evaluate the catalyst's performance, and the smaller Tafel slope means a faster increase in the HER rate with a decrease in over-potentials. The results of the Tafel slope of MoS_2 nano-sheets in Figure 8(b) is 294 mV Dec^{-1} , which matches several earlier reports for MoS_2 nano-sheet catalysts. The Tafel slope of Ni doping MoS_{2-x} is 81 mV decade^{-1} , which is almost as good as Pt/C. To reach the current density of 10 mA cm^{-2} , the reference point, the over-potential of -300mv, is required for the pure MoS_2 . Compared with pure MoS_2 , the over-potential is only -200mv for the Ni-doped MoS_{2-x} monolayer nano-sheets.

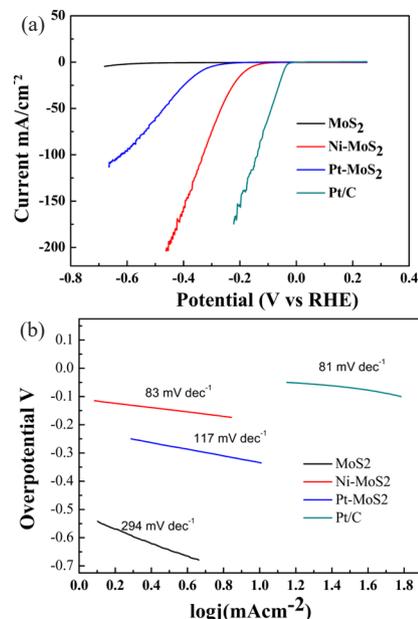


Figure 8. (a) Polarization curves of different electrodes at a scan rate of 20 mv/s. (b) Tafel plots of different materials modified electrodes.

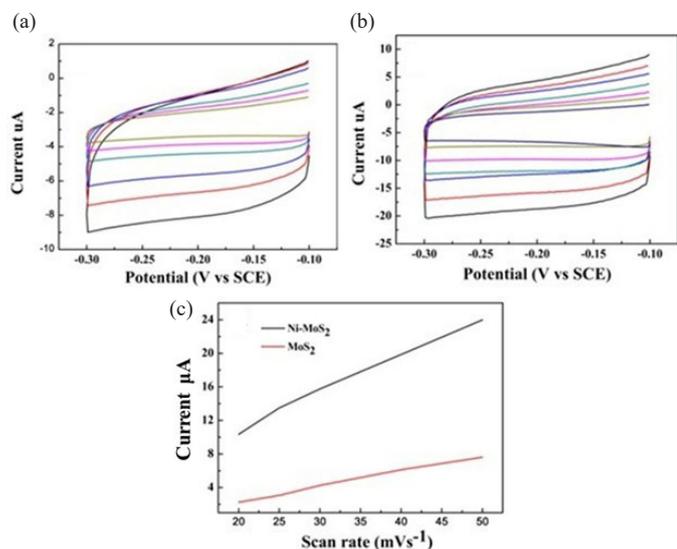


Figure 9. (a) Cyclic voltammograms of MoS₂ nanosheets modified GCE in 0.5M H₂SO₄ at different scan rates. (b) Cyclic voltammograms of Ni-MoS₂ modified GCE in 0.5M H₂SO₄ at different scan rates. (c) Capacitive currents over nickel doping MoS₂ nanosheets and pure MoS₂ nanosheets vs scan rate. GCE: Glass carbon electrode.

To initiate HER in the acid electrolyte, three principal steps would involve H⁺ to H₂, which contain the Volmer equation, Herrovsky equation, and Tafel reaction equation. The Ni-MoS₂ nano-sheets exhibit a Tafel slope of 83 mv/dec, which is lower than pure MoS₂ (294 mv/dec) and Pt-MoS₂ (197 mv/dec) nano-sheets. The Ni-MoS₂ is almost as super as Pt/C (81 mv/dec), which gives them great potential in electrochemical hydrogen production. The Tafel plot of Ni-MoS₂ nano-sheets is shallow, meaning that the electrochemical reaction on the surface of Ni-MoS₂ proceeds through the Volmer-Herrvosky mechanism step.

The electrochemical capacitance surface area measurements were also researched to study the electrochemical active area of MoS₂ and Ni-MoS₂ nano-sheets. The electrochemical double layer charge of MoS₂ and Ni single atom doped MoS₂ were measured. As shown in Figure 9(a) and 9(b), the capacitive current of Ni-doped MoS₂ nano-sheets is more significant than that of pure MoS₂ nano-sheets at the scan rate of 40mv/s. Fig exhibits that the calculated capacitive current of Ni-MoS₂ is more significant than pure MoS₂. Figure 9(c) displays the measured capacitive currents plotted as a function of scan rate, and it also reveals that Ni-doped MoS₂ shows a larger double-layer capacitance than pure MoS₂ nano-sheets, which further confirmed that Ni-doping MoS₂ nano-sheets had high catalytic activity than pure MoS₂ nano-sheets.

Stability is another essential criterion used to evaluate the catalyst's HER activity. Continuous HER at a given over-potential was conducted to explore the durability of the Ni-doped MoS₂ nano-sheets in a 0.5M H₂SO₄ environment. As shown in Figure 10(a), the stability of the cathodic current of Ni-MoS₂ is higher than 10 mAcm⁻², which is five times higher than pure MoS₂. The 2H-MoS₂ can act as HER catalyst,

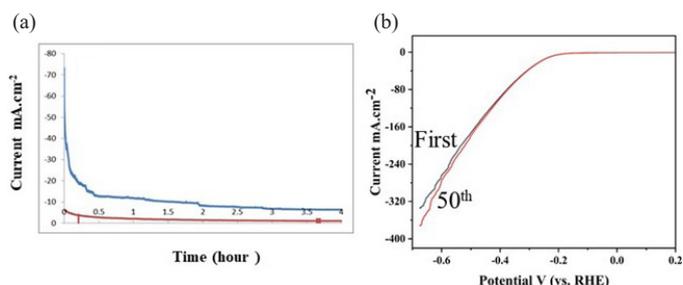


Figure 10. (a) Stability test at the fixed potential of -1.0 vs. SCE in 0.5M H₂SO₄ solution (blue line: Ni-MoS₂ nano-sheets, red line: pure MoS₂ nano-sheets). (b) Stability of nickel doping MoS₂ nanosheets modified electrode by LSV methods. SCE: Saturated calomel electrode.

and the hydrogen evolution reaction occurred at a higher over-potential than Ni-doped MoS₂ nano-sheets. The doping of Ni into MoS₂ nano-sheets leads to profound enhancements of HER activities. The recycle stability test was also studied through the LSV method in 0.5 M H₂SO₄ solution at a scan rate of 20 mV/s on the nickel doping MoS₂ nanosheet-modified electrode. As shown in Figure 10(b), there is no significant difference between the first scan of LSV of nickel doping MoS₂ nanosheets and the 50th cycle, which further confirms that nickel doping MoS₂ has stable catalytic activity for hydrogen production in acid solution.

4. Conclusions

We fabricated Ni doping MoS_{2-x} nano-sheets using the photochemical method. The electrochemical activity of Ni-MoS_{2-x} was greatly influenced by pH value. The Ni-doped MoS₂ nano-sheets were fabricated using two different photochemical deposition mechanisms: acid and alkaline. The Ni-doped monolayer MoS₂ fabricated in an acid solution with a pH value of 2 had the highest electrochemical activity. The Ni-doped monolayers fabricated in an acid solution were compared in terms of MoS₂ corrosion and Ni deposition, leading to more S defects. Ni was inserted into the structure of MoS₂ to displace some Mo elements. Ni displacement, S defects, NiO, MnO₂, and molybdic acid in MoS₂ made Ni-MoS_{2-x} have the highest activity for hydrogen production in acid solution. This is a new method to fabricate high electro-catalytic nanomaterials with great potential in the hydrogen production industry.

CRedit authorship contribution statement

Yonging Du: Experimental program design, nanomaterial synthesis, electrochemical testing, and manuscript writing; **Xuanye Du:** electrochemical test of MoS₂ nanosheets and NiS-doping MoS₂ nanosheets; **Yunming Du:** stability test of NiS doping MoS_{2-x} and the Figures plotted; **Xiaolong Li:** XRD and XPS test and related data process; **Yuhao Li:** nanomaterials synthesis; **Xuezhao Shi:** English polishing for the manuscript; **Zhixiang Zheng:** Funding supporting.

Declaration of competing interest

The authors declare no competing interest.

Declaration of Generative AI and AI-assisted technologies in the writing process

The authors confirm that there was no use of artificial intelligence (AI)-assisted technology for assisting in the writing or editing of the manuscript and no images were manipulated using AI.

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