Low-cost and highly efficient CoMoS₄/NiMoS₄-based electrocatalysts for hydrogen evolution reactions over a wide pH range

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Abstract

Highly efficient and low-cost electrocatalysts are essential for producing hydrogen through water electrolysis. Here ternary compounds CoMoS₄ and NiMoS₄ were synthesized by a one-step reaction, and further CoMoS₄-H and NiMoS₄-H were obtained by heating the above two samples under Ar atmosphere. The above four materials both show uniformly small irregular nanoparticles. Each element of the four materials exhibits semblable valence without distinct difference of which S was -2, Mo was +6, Ni and Co were +2. We firstly use the above ternary materials as advanced electrocatalysts for HER over a wide pH range, of which CoMoS₄-H displays the best performance with a low onset overpotential at 8 mV in 1.0 M KOH and 83 mV in 0.5 M H₂SO₄. NiMoS₄-H also shows excellent performance with a low onset overpotential at 26 mV in 1.0 M KOH and 160 mV in 0.5 M H₂SO₄. In 1 M phosphate buffer solution, CoMoS₄-H and NiMoS₄-H exhibit onset overpotential at

overpotential of 122 mV and 152 mV, respectively. These results indicate that the combination of earth-abundant sulfur, cobalt (or nickel) and molybdenum elements can provide highly active electrocatalysts for HER over a wide pH range.

Keywords: hydrogen evolution reaction; electrocatalyst; electrocatalytic activity; CoMoS₄; NiMoS₄;

1. Introduction

With the growing of energy demands, the overusing of nonrenewable fossil fuels, and the intensifying of air pollution and global warming, it is an urgent task to explore sustainable and environmentally-friendly energy resources to substitute traditional fossil energy. Among the various energy carriers, hydrogen has attracted extensive attention currently owe to its renewable, clean and high energy density (140 MJ Kg⁻¹) characteristics. Water electrolysis is one of the most promising methods for hydrogen production, which obviously requires effective electrocatalysts for hydrogen evolution reaction (HER) [1–10]. In general, platinum (Pt) and its alloys are currently the most efficient HER catalyst. Nevertheless high cost and low storage of the noble metal limit its wide-scale application [11–14]. In addition, high-performance catalysts in acidic, neutral and alkaline media are required for proton exchange membrane systems, microbial electrolysis cell [15] and alkaline water splitting [16], respectively. For adapting to different systems, HER catalysts need to be applied in different pH. As such, there is highly desirable to develop low-cost and high efficient HER catalysts

operating under acidic, neutral, and basic conditions.

Transition metals and their alloys are economic and abundant on the earth, there have currently been a number of excellent noble-metal-free HER catalysts to compete with Pt [17–19]. Among them, non-noble metal sulfides are a class of promising materials to replace noble metal as the next-generation HER catalysts. As a relative earlier HER catalyst, molybdenum disulfide (MoS_2) has firstly demonstrated to be an highly efficient HER catalyst on the base of experimental and computational studies by Noverskov *et al.* in 2005. From then on, the active catalytic sites of layered MoS_2 crystals were proved to locate at the edges of sulfur, however the basal planes showed catalytically inactive. Therefore HER catalytic performance of MoS_2 was limited by low active sites and poor electron transport [20–22]. To overcome the above weakness, great efforts have been made to develop MoS_2 -based efficient HER catalysts by maximizing the number of active edge sites and enhance conductivity. Zhang *et al.* recently synthesized vertical nanosheets of NiS_2 supported on graphite substrate and used them as HER catalysts in acidic and alkaline solution. The catalyst showed relatively small Tafel slope (40 mV/dec in 0.5 M H_2SO_4 and 80 mV/dec in 1 M NaOH) with low overpotential, which indicated NiS_2 to be one kind of potential HER catalyst over the wide pH range [23]. Even so further investigation is still needed on designing and fabricating NiS_2 -based HER catalysts with excellent property and satisfactory catalytic behavior. Similarly, cobalt sulfides are now emerging as an attractive HER catalysts on account of exceptional activity. Zou *et al.* synthesized carbon-armored Co_9S_8 nanoparticles ($\text{Co}_9\text{S}_8@\text{C}$) that exhibited relatively high activity over a wide pH

range, but Co_9S_8 nanoparticles is unstable in acidic and basic media [24]. More recently, it was found that a second metal to be doped into the metal sulphide-based catalysts could improve HER performance effectively [11,25]. For instance, Fontecave *et al.* used P to modify CoS_2 nanosheet, the doped catalyst showed significantly improved performance [11]. It is due to doping of the other metal into the metal chalcogenides could change the energy and occupation of the anti-bonding defect levels in the band gap, which lead to the changes in the charge states [26]. All of these studies indicated that interaction with metal chalcogenides could effectively improve the HER electrocatalytic activities. Unfortunately, as the HER performance of previously reported non-nobel metal sulphides have yet to achieve perfection, the design and development of highly efficient and low-cost HER electrocatalysts is still an ongoing challenge.

Herein, we have synthesized ternary metal sulphide CoMoS_4 and NiMoS_4 by using Kanatzidis' method [27,28]. $(\text{NH}_4)_2\text{MoS}_4$ has been synthesized first and through a simple one-step reaction CoMoS_4 and NiMoS_4 have been synthesized rapidly. Furthermore $\text{CoMoS}_4\text{-H}$ and $\text{NiMoS}_4\text{-H}$ were obtained by heating the above two samples. For the first time, the above ternary materials were used as HER electrocatalysts in a wide pH range. The composites exhibited an outstanding HER performances with low onset overpotentials and small Tafel slopes in basic solutions, acid solutions, and neutral solutions. Thereinto, $\text{CoMoS}_4\text{-H}$ displayed the best performance with a very low overpotentials of 8 mV in 1.0 M KOH and 83 mV in 0.5 M H_2SO_4 . The synergistic effect between the small amount of amorphous MoS_2 and

CoS₂ may contribute to the high HER activity. In this work, ternary materials CoMoS₄-H and NiMoS₄-H were synthesized by an simplicity and efficient way, the method can be applied to the preparation of similar materials for various applications.

2. Experiment

2.1. Materials

Ammonium sulfide ((NH₄)₂S), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) were purchased from Aladdin Ltd. (Shanghai, China). 5 wt% Nafion Solutions were purchased from Sigma-Aldrich and commercial Pt/C were purchased from HeSeng Ltd. (Shanghai, China). All chemicals were used without further purification.

2.2. Synthetic procedures

2.2.1. Synthesis of (NH₄)₂MoS₄

To prepare (NH₄)₂MoS₄, 15.0 g (NH₄)₆Mo₇O₂₄·4H₂O was dissolved in 10 mL ammonia with stirring for approximately 10 min until solid matter was homogeneously dissolved. Then 120.0 g 20% (NH₄)₂S was added to the above solution at room temperature ($n_S=0.357$ mol, $n_{Mo}=0.085$ mol, $n_{S/Mo} = 4.2$). The system was heated at 60 °C for 2 hours. After that, the obtained red-brown solution was transferred into ice-bath, the solution cooled down and crystallized out (NH₄)₂MoS₄ crystals. Finally, the crystals were collected by Buchner funnel and washed ten times with cold water.

2.2.2. Synthesis of CoMoS₄, NiMoS₄, CoMoS₄-H and NiMoS₄-H

CoMoS₄ and NiMoS₄ were synthesized by Kanatzidis' method. Firstly, 10.0 g (NH₄)₂MoS₄ were dispersed in 20 mL water to form homogenous solution. Then 10.9 g Co(NO₃)₂·6H₂O, 10.9 g Ni(NO₃)₂·6H₂O was added to (NH₄)₂MoS₄ aqueous solution ($n_{\text{Mo/Co}} = 1$, $n_{\text{Mo/Ni}} = 1$), respectively. The black deposits produced in the system were collected by centrifuging at 2000 rpm for 5 min, washed with distilled water and absolute ethanol several times, finally vacuum drying at room temperature. CoMoS₄ and NiMoS₄ were placed in tubular furnace and heated under Ar atmosphere at 450 °C for 2 h with a heating rate of 5 °C/min. The resultant were denoted as CoMoS₄-H and NiMoS₄-H, respectively.

2.3. Characterizations

The X-ray diffraction (XRD) measurements were carried out on a Miniflex600 diffractometer at 40 kV and 40 mA for Cu K α ($\lambda = 0.15406$ nm). The samples were scanned in steps of 5° in the range of 5–85° with a counter time of 60 s per step. Scanning electron microscopy (SEM) was obtained on a Hitachi S-4800 instrument operating at 5 kV. X-ray photoelectron spectrometer (XPS) was measured on an ESCALAB 250 by using Mg K α radiation exciting source. To ensure the data of samples aligned and avoid differential charging effects convoluting the data, all binding energies were referenced to the C1s peak at 285.0 eV. Raman spectra were recorded with a BAC151A Video Microscope Raman Sampling System spectrometer.

2.4. Electrochemical measurements

HER catalytic performance measurements were conducted in a standard three-electrode system by using a CHI 660E electrochemistry workstation. A glass

carbon electrode (GCE, 3 mm in diameter) contained catalyst powders was served as working electrode (WE), an Ag/AgCl with saturated KCl solution and a Pt disk worked as the reference electrode (RE) and the counter electrode (CE), respectively. Linear sweep voltammograms (LSVs) were conducted to examine catalytic activity. For HER tested in alkaline solution, LSVs were obtained with a scan rate of 5 mV s^{-1} in the range from -1.8 to -0.8 V vs. Ag/AgCl in 1 M KOH electrolyte. 0.5 M H_2SO_4 and 1 M phosphate buffer solution were respectively used as acid electrolyte and neutral electrolyte, the corresponding LSVs were collected by sweeping from -1 V to 0 V and from -1.5 V to -0.5 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) measurements were performed in the same configuration at $\eta = 0.24 \text{ mV}$ within the frequency range of 100 kHz to 100 mHz. In this work, all the potentials were referenced to the reversible hydrogen electrode (RHE). The potentials were converted as follows, in 1 M KOH, $E(\text{RHE}) = E(\text{Ag/AgCl}) + 1.059 \text{ V}$, in 0.5 M H_2SO_4 , $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.232 \text{ V}$, in 1 M phosphate buffered saline (PBS), $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.646 \text{ V}$.

The detailed method to prepare working electrodes coated catalysts could be obtained as follows. 2 mg catalysts and 40 μL 5 wt% Nafion solution were dispersed with the mixed solution of 365 μL distilled water and 95 μL absolute ethanol, then the mixture was ultrasonicated for 30 min to form a homogeneous ink solution. And further 5 μL dispersion was dropped onto a glassy carbon electrode, which giving a catalyst loading of 0.262 mg/cm^2 . Finally, the as-prepared working electrodes were dried at room temperature.

3. Results and discussion

3.1. Catalyst structure and composition

To investigate the structural morphologies of the as-prepared samples, scanning electron microscopy (SEM) were conducted for CoMoS₄, NiMoS₄, CoMoS₄-H and NiMoS₄-H. As shown in Fig. 1, the images of all samples didn't show a clear crystal lattice except for uniformly small irregular nanoparticles relatively.

The X-ray diffraction (XRD) patterns were recorded for CoMoS₄, NiMoS₄, CoMoS₄-H, and NiMoS₄-H. As shown in Fig. 2, both XRD patterns of NiMoS₄ and CoMoS₄ showed predominant broad features which indicated the materials were amorphous. A similar result has been reported in relevant literature [28]. After CoMoS₄ and NiMoS₄ underwent a heating process, the intensities of these broad peaks were gradually reduced and sharp peaks gradually appeared. Apparently the characteristic peak at $2\theta = 14.05$ was the (0 0 2) basal planes of crystalline MoS₂, which indicated that MoS₂ with a rather smaller size of (0 0 2) phase was generated and that the Ni or Co promoter interaction with the (0 0 2) phase of MoS₂ [29–32]. Other several MoS₂ diffraction peaks of CoMoS₄-H and NiMoS₄-H could be found at $2\theta = 32.65$ and 58.83 that assigned to MoS₂(1 0 1) and (1 1 3), respectively (JCPDS: 65-3656, hexagonal). For CoMoS₄-H, other diffractograms showed strong similarity to CoS₂ (JCPDS: 41-1471). Several well-defined peaks appeared at 30.15 , 36.93 , 38.81 , 46.57 , 55.03 , corresponding to CoS₂ (2 0 0) (2 1 0) (2 1 1) (2 2 0) (3 1 1). These results suggested the formation of ternary Co–Mo–S material that to be called CoMoS₄-H here. Similarly, the XRD pattern of NiMoS₄-H exhibited an excellent

assignment with the prominent peaks of the standard diagram (JCPDS: 73-0574). The distinct five peaks could be found around 2θ values at 30.09, 33.29, 38.85, 45.91 and 53.39, and the diffractograms corresponded to cubic pyrite phase from the (2 0 0), (2 1 0), (2 1 1), (2 2 0) and (3 1 1) of NiS_2 , respectively. These results suggested the formation of ternary Ni–Mo–S phases that to be called $\text{NiMoS}_4\text{-H}$ here. The diffractograms of prepared $(\text{NH}_4)_2\text{MoS}_4$ showed strong similarity to standard pattern of $(\text{NH}_4)_2\text{MoS}_4$ (JCPDS: 48-1662), which indicated that $(\text{NH}_4)_2\text{MoS}_4$ was successfully synthesized.

Raman spectroscopy was conducted to check out electronic properties of the as-prepared CoMoS_4 , NiMoS_4 , $\text{CoMoS}_4\text{-H}$ and $\text{NiMoS}_4\text{-H}$. Raman spectroscopy confirmed the few-layer structure of MoS_2 in the hybrids as shown in Fig. 3. Herein, due to the two peaks of CoS_2 were coincide with MoS_2 , the peak position changed a little compared with the literature. The appearance of two characteristic peaks at 397 cm^{-1} and 411 cm^{-1} shifted blue compared with pure MoS_2 and CoS_2 . The hexagonal MoS_2 showed two characteristic peaks at 381 cm^{-1} and 404 cm^{-1} corresponded to the E_{2g}^1 (the in-plane vibration of the S atoms) and A_{1g} (the out-of-plane vibration of the S atoms) vibrational modes of MoS_2 , respectively [33]. CoS_2 showed two obvious peak at about 389 cm^{-1} and 412 cm^{-1} assigned to A_g and F_g [34]. All Raman conclusion were reasonable and agreed with those of XRD.

To obtain the chemical state and composition of both samples, X-ray photoelectron spectroscopy (XPS) analysis was performed. Fig. 4 showed the Ni 2p, Co 2p, S 2p and Mo 3d XPS spectra of CoMoS_4 , NiMoS_4 , $\text{CoMoS}_4\text{-H}$ and $\text{NiMoS}_4\text{-H}$. Fig. 4a and

4b showed that the S 2p peak were splitted into three peaks. The two sharp peaks with binding energy values (B.E.) at 162.2 eV and 163.4 eV for CoMoS₄-H, 161.5 eV and 162.8 eV for NiMoS₄-H actually corresponded to the spectra of S 2p_{3/2} and S 2p_{1/2}, which were agreed with the sulfur element in the sulfides. The peaks at 167.3 and 168.8 eV for CoMoS₄-H and NiMoS₄-H respectively were attributed to presence of SO₃²⁻ in the materials, which might account for the samples were oxidation partially during the pyrolyze processes [35–38]. For CoMoS₄ and NiMoS₄, S 2p spectra showed similar peaks to CoMoS₄-H and NiMoS₄-H.

From Fig. 4d and 4c, the Mo 3d spectra of all samples have four peaks, and one of those at 226.2eV could be attributed to S 2s. The other two strong and sharp peaks were observed, with binding energy values of 230.3 eV and 232.5 eV for CoMoS₄, 229.5 eV and 232.7 eV for NiMoS₄, 229.5 eV and 232.5 eV for CoMoS₄-H while 232.3 eV and 233.4 eV for NiMoS₄-H, which corresponded to Mo 3d_{5/2} and Mo 3d_{3/2}. It confirmed that molybdenum existed its VI oxidation state, which in accordance with that in the (NH₄)₂[Mo^{VI}S₄] precursor [27]. However, the peak at about 236 eV could be identified as Mo⁶⁺ for MoO₃ or MoS₃ which was consistent with the result of S 2p spectra [38]. The Ni 2p spectra of NiMoS₄-H were shown in Fig. 4f, two groups of peaks that generated from the spin–orbit interaction were shown in the spectrum. The group in lower B.E. at about 858.6 eV and in higher B.E. at about 876.5 eV could be attributed to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively. This illustrated that Ni was in its II oxidation state in the all samples. As shown in Fig. 4e, the Co 2p_{3/2} region showed one main peak at 781.6 eV and one satellite peak at 785.5 eV for CoMoS₄, 781.7 eV and

785.9 eV for CoMoS₄-H. The Co 2p_{1/2} region also exhibited a main peak at 797.8 eV and one satellite peak at 802.2 eV for CoMoS₄, similarly 797.9 eV and 802.5 eV for CoMoS₄-H. The intense satellite peaks in Co 2p spectra at about 786.0 eV and 802.5 eV have been ascribed to shake up excitation of the high-spin Co²⁺ ions in the samples [39]. Furthermore, the Co 2p_{3/2} B.E. at about 781.6 eV was a little higher than 778.5 eV of Co₉S₈ energy, the value was close to that of the Co–Mo–S phase reported by Okamoto [40] and Alstrup *et al.*[41], which indicated that Co²⁺ ions were bonded to MoS₄²⁻ and then the CoMoS₄ phase was generated. Similarly, Ni 2p_{3/2} with B.E. values of 858.6 eV could be ascribed to Ni (II) species that were bonded to MoS₄²⁻, leading to the production of NiMoS₄ phase. As a result, the state of each element has not changed after the samples were calcined.

3.2. Electrocatalytic activity and stability toward HER

The electrocatalytic activity of samples toward HER were tested in solutions with various pH. In alkaline solution, electrochemical analysis was conducted in 1 M KOH (aq) electrolyte. Additionally, commercial Pt/C (20 wt% Pt on Vulcan carbon black) was tested under same condition for comparison.

Fig. 5a showed the corresponding polarization curves in 1 M KOH. All of the as-prepared CoMoS₄, NiMoS₄, CoMoS₄-H and NiMoS₄-H showed excellent HER activity in alkaline solutions, which reflected by extremely low onset overpotential (the overpotential required to reach a current density of 1 mA cm⁻²) and high current density at low overpotential. The commercial Pt/C catalyst as comparison exhibited high HER catalytic performance reflected by a onset overpotential nearly zero. It is

noteworthy that the CoMoS₄-H material gave a very small onset overpotential of 8 mV, which got close to that of commercial Pt/C. NiMoS₄-H also showed a small onset overpotential at 26 mV. Besides, CoMoS₄ and NiMoS₄ exhibited the low onset potential of 66 mV and 74 mV respectively. All of the above samples could be comparable to that of other earth-abundant HER electrocatalysts smoothly [2–8], [42–48]. In addition, it need 78 mV for CoMoS₄-H to reach the current density of 10 mA cm⁻² (an important factor in water electrolysis), lower than CoMoS₄ (about 153 mV). NiMoS₄-H need 152 mV to reach the current density of 10 mA cm⁻², lower than NiMoS₄ (about 191 mV). It suggested the heated samples showed higher current density at low overpotentials than the primary samples.

The Tafel slope was an inherent property of the catalyst, which was determined by the rate-limiting step of the HER and calculated from the linear portion of the Tafel plots by fitting the experimental data to the Tafel equation ($\eta = b \log(j) + a$, j is the current density and b is the Tafel slope). With applied overpotential increasing, a smaller Tafel slope will lead to a faster increase of the current. As shown in Fig. 5b, in 1 M KOH, commercial Pt/C catalyst exhibited the Tafel slope of 28.1 mV/dec, which agreed well with the reported values [4]. CoMoS₄-H and NiMoS₄-H gave a small Tafel slope of 89 mV/dec and 94.4 mV/dec respectively. Although showed lower onset potential than the heated samples, CoMoS₄ had a lower Tafel slope of 77.6 mV/dec. NiMoS₄ was calculated to a little higher Tafel slope of 145.4 mV/dec.

Additionally, EIS was performed in potentiostatic mode at $\eta = 0.24$ V with the frequencies ranging from 100 kHz to 100 mHz. The charge transfer resistances (R_{ct})

for the different samples were put down to the semicircle recorded at the same overpotential. As shown in Fig. 5c, there was one semicircle observed in Nyquist plots of each sample, which indicated that the equivalent circuit for the electrocatalysis was characterized by one time constant. Therefore it was believed that there were only one charge transfer resistor and one double layer capacitor existed in the equivalent circuit. CoMoS₄-H exhibited lower R_{ct} (~72 Ω) than CoMoS₄ (~100 Ω). Similarly, NiMoS₄-H showed lower R_{ct} (~85 Ω) than NiMoS₄ (~105 Ω). The lower R_{ct} of CoMoS₄-H and NiMoS₄-H might be attributed to the interaction between MoS₂ and Co or Ni component that promote the HER activity, which indicated that CoMoS₄-H and NiMoS₄-H have higher conductivity, of which effectively reduce the resistance of CoMoS₄ and NiMoS₄.

To investigate the electrochemical performance of samples in acid and neutral solution, electrochemical analysis was conducted in 0.5 M H₂SO₄ solution and 1 M phosphate buffer solution, respectively. Similarly, commercial Pt/C was also tested under same condition for comparison. The polarization curves of samples in acid were displayed in Fig. 6a. It was worth noticing that CoMoS₄-H and NiMoS₄-H exhibited low onset overpotentials of about 83 mV and 160 mV respectively. CoMoS₄ and NiMoS₄ exhibited relatively high onset potential of 221 mV and 254 mV respectively. Moreover, the overpotentials of CoMoS₄-H, NiMoS₄-H, CoMoS₄ and NiMoS₄ required to approach current densities at 10 mA cm⁻² were 170 mV, 254 mV, 515 mV and 536 mV, respectively. Accordingly, CoMoS₄-H gives a small Tafel slope of 79.9 mV/dec as shown in Fig. 6b. The Tafel slope of NiMoS₄-H was calculated to be 93.9

mV/dec. It was an undeniable fact that CoMoS₄ and NiMoS₄ showed low catalytic activity by giving Tafel slope of 308.6 and 232.7 mV/dec. It could get conclusion that CoMoS₄-H and NiMoS₄-H exhibit relatively high HER electrocatalytic activity in acid environment.

Under neutral media, electrocatalytic reactions are generally conducted more moderately and most catalysts are stable against oxidation and corrosion [49]. We additionally investigated catalytic activity in neutral media after investigating the catalytic performance in acidic and alkaline media, although HER showed slow kinetics inherently under neutral condition. Reasonably, electrocatalytic activity of all samples at pH = 7 were relatively lower than the ones in acid and alkaline solutions. Specifically, while CoMoS₄-H gave onset overpotentials of 8 mV and 83 mV at pH = 14 and pH = 0, respectively, it exhibited the same current density at a much higher overpotential of 122 mV in neutral media. NiMoS₄-H, CoMoS₄ and NiMoS₄ showed 162 mV, 152 mV and 218 mV, respectively. Nevertheless, the performance of the above samples were not inferior to other earth-abundant HER electrocatalysts under the same condition. Co₉S₈@C and were reported to give an onset overpotentials of 150 mV [24]. Additionally, Mo₂C [50] and MoB [50] were recently shown to need 200 and 250 mV to approach 1 mA/cm⁻², which is larger than the value of CoMoS₄-H NiMoS₄-H CoMoS₄ ,and NiMoS₄. Undeniable, the overpotentials required to approach current densities at 10 mA cm⁻² of the above samples were between 500 mV and 600 mV, which were highly than non-noble HER catalysts reported for neutral media [49]. For example, MoS₂ NAs/Ti showed a small overpotential of 200 mV at

the current density of 10 mA cm^{-2} [51]. Bulk MoB need 225 mV to approach the same current density [50]. As shown in Fig. 6d, the Tafel slope of CoMoS₄-H, NiMoS₄-H, CoMoS₄, and NiMoS₄ was calculated to be 253.7, 307.5, 370.0 and 314.2 mV/dec, respectively.

Due to the high HER catalytic activity of CoMoS₄-H, NiMoS₄-H, CoMoS₄ and NiMoS₄ under all pH conditions observed by experiment, it is necessary to explore the reaction mechanism for HER. Generally speaking, for a wide variety of catalysts ΔG_H is supposed to a suitable indicator of HER activity. The higher ΔG_H value will lead to weak bonding force between the protons on the surface of catalyst, which cause the slow HER kinetics. Conversely, the lower ΔG_H value will contribute to relatively higher surface coverage of H_{ads} and accelerate the reaction rate [2,52,53]. Density functional theory (DFT) calculations from previous research indicated that unsaturated sulfur atoms of MoS₂ edge sites can reduce ΔG_H as low as 0, which was greatly beneficial to improve electrocatalytic activity of HER. This theory was experimentally verified by Jaramillo *et al.* [54]. Additionally, first-row transition metal ions such as Ni and Co can make a faster proton adsorption rate by coupling with the edges of sulfur, which can lower the ΔG_H from 0.18 to 0.10 eV and promote the HER activity of MoS₂ effectively [52,55,56]. For CoMoS₄-H and NiMoS₄-H catalyst, a few MoS₂ appeared through heating CoMoS₄ and NiMoS₄, the interaction between MoS₂ and Co or Ni component might promote the HER activity.

4. Conclusion

In conclusion, effective and robust hydrogen evolution catalysts were synthesized

by marrying inexpensive transition metal chalcogenides. All the materials were inexpensive and earth abundant. The synthetic method was simple and efficient. Thereinto, the new CoMoS₄-H and NiMoS₄-H electrocatalysts exhibited excellent HER catalytic properties in a wide pH electrolyte. In alkaline solution (pH = 14), CoMoS₄-H exhibited a low onset potential of 8 mV and a small Tafel slope of 89 mV/dec, indicating that the performance of non-noble metal catalyst could be close to Pt/C catalyst. NiMoS₄-H also showed a excellent onset overpotential at 26 mV. And CoMoS₄ and NiMoS₄ exhibited the small onset potential of 66 mV and 74 mV respectively. All of the prepared samples could compete with that of other reported non-nobel HER electrocatalysts in alkaline environment. In 0.5 M H₂SO₄ solution (pH = 0), CoMoS₄-H exhibited a low onset potential of 64 mV and a small Tafel slope of 94.4 mV/dec. In 1 M phosphate buffer (pH = 7), CoMoS₄-H exhibited onset potential of 122 mV. The better catalyst CoMoS₄-H and NiMoS₄-H activity might be benefit from the small amount of amorphous MoS₂ around the CoS₂ or NiS₂, which bring in more active edge sites. The low-cost and highly efficient CoMoS₄ and NiMoS₄ electrocatalysts are promising materials for HER.

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References

- [1] X. Zou, Y. Zhang, Noble metal-free hydrogen evolution catalysts for water splitting, Chem. Soc. Rev. 44 (2015) 5148–5180.

- [2] M.R. Gao, J.X. Liang, Y.R. Zheng, Y.F. Xu, J. Jiang, Q. Gao, J. Li, S.H. Yu, An efficient molybdenum disulfide/cobalt diselenide hybrid catalyst for electrochemical hydrogen generation, *Nat. Commun.* 6 (2015) 5982–5988.
- [3] M. Gong, W. Zhou, M.-C. Tsai, J. Zhou, M. Guan, M.-C. Lin, B. Zhang, Y. Hu, D.Y. Wang, J. Yang, S.J. Pennycook, B.J. Hwang, H. Dai, Nanoscale nickel oxide/nickel heterostructures for active hydrogen evolution electrocatalysis, *Nat. Commun.* 5 (2014) 4695.
- [4] M.S. Faber, R. Dziedzic, M.A. Lukowski, N.S. Kaiser, Q. Ding, S. Jin, High-performance electrocatalysis using metallic cobalt pyrite (CoS(2)) micro- and nanostructures, *J. Am. Chem. Soc.* 136 (2014) 10053–10061.
- [5] J. Guo, F. Li, Y. Sun, X. Zhang, L. Tang, Oxygen-incorporated MoS₂ ultrathin nanosheets grown on graphene for efficient electrochemical hydrogen evolution, *J. Power Sources* 291 (2015) 195–200.
- [6] Y. Zheng, Y. Jiao, Y. Zhu, L.H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec, S.Z. Qiao, Hydrogen evolution by a metal-free electrocatalyst, *Nat. Commun.* 5 (2014) 4783.
- [7] C. Ouyang, X. Wang, S. Wang, Phosphorus-doped CoS₂ nanosheet arrays as ultra-efficient electrocatalysts for the hydrogen evolution reaction, *Chem. Commun.* 51 (2015) 14160–14163.
- [8] X. Yan, L. Tian, M. He, X. Chen, Three-dimensional crystalline/amorphous Co/Co₃O₄ core/shell nanosheets as efficient electrocatalysts for the hydrogen evolution reaction, *Nano Lett.* 15 (2015) 6015–6021.

- [9] Q. Lu, G.S. Hutchings, W. Yu, Y. Zhou, R.V. Forest, R. Tao, J. Rosen, B.T. Yonemoto, Z. Cao, H. Zheng, J.Q. Xiao, F. Jiao, J.G. Chen, Highly porous non-precious bimetallic electrocatalysts for efficient hydrogen evolution, *Nat. Commun.* 6 (2015) 6567.
- [10] M.R. Tarasevich, O.V. Korchagin, Electrocatalysis and pH (a review), *Russ. J. Electrochem.* 49 (2013) 600–618.
- [11] A.L. Goff, V. Artero, B. Jusselme, P.D. Tran, N. Guillet, R. Métayé, A. Fihri, S. Palacin, M. Fontecave, From hydrogenases to noble metal-free catalytic nanomaterials for H₂ production and uptake, *Science* 326 (2009) 1384–1387.
- [12] R.B. Gordon, M. Bertram, T.E. Graedel, Metal stocks and sustainability, *Sci. USA* 103 (2006) 1209–1214.
- [13] G.M. Walter, E.L. Warren, J.R. McKone, S.W. Boettche, Q. Mi, E.A. Santori, N. S. Lewis, Solar water splitting cells, *Chem. Rev.* 110 (2010) 6446–6473.
- [14] A. Standing, S. Assali, L. Gao, M.A. Verheijen, D. van Dam, Y. Cui, P.H.L. Notten, J.E.M. Haverkort, E.P.A.M. Bakkers, Efficient water reduction with gallium phosphide nanowires, *Nat. Commun.* 6 (2015) 8824.
- [15] A. Kundu, J.N. Sahu, G. Redzwan, M.A. Hashim, An overview of cathode material and catalysts suitable for generating hydrogen in microbial electrolysis cell, *Int. J. Hydrogen Energy* 38 (2013) 1745–1757.
- [16] R.L. LeRoy, Industrial water electrolysis present and future, *Int. J. Hydrogen Energy* 8 (1983) 401–478.

- [17] Y.G. Li, H.L. Wang, L.M. Xie, Y.Y. Liang, G.S. Hong, H.J. Dai, MoS₂ nanoparticles grown on graphene: An advanced catalyst for the hydrogen evolution reaction, *J. Am. Chem. Soc.* 133 (2011) 7296–7299.
- [18] J. Tian, Q. Liu, A. M. Asiri, X. Sun, Self-supported nanoporous cobalt phosphide nanowire arrays: An efficient 3D hydrogen-evolving cathode over the wide range of pH 0–14, *J. Am. Chem. Soc.* 136 (2014) 7587–7590.
- [19] L. Tao, X. Duan, C. Wang, X. Duan, S. Wang, Plasma-engineered MoS₂ thin-film as an efficient electrocatalyst for hydrogen evolution reaction, *Chem. Commun.* 51 (2015) 7470–7473.
- [20] B. Hinnemann, P.G. Moses, J.k. Noverkov, Biornimetic hydrogen evolution: MoS₂ nanoparticles as catalyst for hydrogen evolution, *J. Am. Chem. Soc.* 127 (2005) 5308–5309.
- [21] Jaramillo T. F., Jørgensen K. P., Bonde J., Nielsen, J. H.;Horch, S., Chorkendorff, I., Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts, *Science* 317 (2007) 100–102.
- [22] A. Sobczynski, Molybdenum disulfide as a hydrogen evolution catalyst for water photodecomposition on semiconductors, *J. Catal.* 131 (1991) 156–166.
- [23] X.L. Wu, B. Y, Z.J. Li, Synthesis of supported vertical NiS₂ nanosheets for hydrogen evolution reaction in acidic and alkaline solution, *RSC Adv.* 5 (2015) 32976–32982.
- [24] L.L. Feng, G.D. Li, Y. Liu, Y. Wu, H. Chen, Y. Wang, Y.C. Zou, D. Wang, X. Zou,

Carbon-armored Co_9S_8 nanoparticles as all-pH efficient and durable H_2 -evolving electrocatalysts, *ACS Appl. Mater. Interfaces* 7 (2015) 980–988.

[25] M. Daniel, V. Heron, R. Lorenzo, F. Stéphane, X. Hu, Fe, Co, and Ni ions promote the catalytic activity of amorphous molybdenum sulfide films for hydrogen evolution, *Chem. Sci.* 3 (2012) 2515–2525.

[26] J. Deng, H. Li, J. Xiao, Y. Tu, D. Deng, H. Yang, H. Tian, J. Li, P. Ren, X. Bao, Triggering the electrocatalytic hydrogen evolution activity of the inert two-dimensional MoS_2 surface via single-atom metal doping. *Energy Environ. Sci.* 8 (2015) 1594–1601.

[27] X. Zheng, J. Guo, Y. Shi, F. Xiong, W.H. Zhang, T. Ma, C. Li, Low-cost and high-performance CoMoS_4 and NiMoS_4 counter electrodes for dye-sensitized solar cells, *Chem. Commun.* 49 (2013) 9645–9647.

[28] K. Polychronopoulou, C.D. Malliakas, J.Q. He, M.G. Kanatzidis, Selective surfaces: Quaternary $\text{Co}(\text{Ni})\text{MoS}$ -based chalcogels with divalent (Pb^{2+} , Cd^{2+} , Pd^{2+}) and trivalent (Cr^{3+} , Bi^{3+}) metals for gas separation, *Chem. Mater.* 24 (2012) 3380–3392.

[29] P. Żabiński, K. Mech, R. Kowalik, Co-Mo and Co-Mo-C Alloys Deposited in a magnetic field of high intensity and their electrocatalytic properties, *Arch. Metall. Mater.* 57 (2012) 127–133.

[30] B. Yoosuk, J.H. Kim, C. Song, C. Ngamcharussrivichai, P. Prasassarakich, Highly active MoS_2 , CoMoS_2 and NiMoS_2 unsupported catalysts prepared by hydrothermal synthesis for hydrodesulfurization of 4,6-dimethyldibenzothiophene,

Catal. Today 130 (2008) 14–23.

[31] B. Yoosuk, D. Tumnantong, P. Prasassarakich, Amorphous unsupported Ni-Mo sulfide prepared by one step hydrothermal method for phenol hydrodeoxygenation, Fuel 91 (2012) 246–252.

[32] W. Wang, L. Li, K. Wu, K. Zhang, J. Jie, Y. Yang, Preparation of Ni-Mo-S catalysts by hydrothermal method and their hydrodeoxygenation properties, Appl. Catal. A 495 (2015) 8–16.

[33] R.D. Nikam, A.Y. Lu, P.A. Sonawane, U.R. Kumar, K. Yadav, L.J. Li, Y.T. Chen, Three-dimensional heterostructures of MoS₂ nanosheets on conducting MoO₂ as an efficient electrocatalyst to enhance hydrogen evolution reaction, ACS Appl. Mater. Interfaces 7 (2015) 23328–23335.

[34] E. Anastassakis and C. Perry, Light scattering and ir measurements in XS₂ pyrite-type compounds, J. Chem. Phys. 64 (1976) 3604–3609.

[35] T.W. Lin, C.J. Liu, J.Y. Lin, Facile synthesis of MoS₃/carbon nanotube nanocomposite with high catalytic activity toward hydrogen evolution reaction, Appl. Catal. B: Environ. 75 (2013) 134–135.

[36] X.L. Zheng, J.B. Xu, K.Y. Yan, H. Wang, Z.L. Wang, S.H. Yang, Space-confined growth of MoS₂ nanosheets within graphite: The layered hybrid of MoS₂ and graphene as an active catalyst for hydrogen evolution reaction, Chem. Mater. 26 (2014) 2344–2353.

[37] A.J. Smith, Y.H. Chang, K. Raidongia, T.Y. Chen, L.J. Li, J.X. Huang, Molybdenum sulfide supported on crumpled graphene balls for electrocatalytic

hydrogen production, *Adv. Energy Mater.* 4 (2014) 1400398–1400404.

[38] X. Dai, Z. Li, K. Du, H. Sun, Y. Yang, X. Zhang, X. Ma, J. Wang, Facile synthesis of in-situ nitrogenated graphene decorated by few-layer MoS₂ for hydrogen evolution reaction, *Electrochim. Acta* 171 (2015) 72–80.

[39] Matthew S. Faber, Rafal Dziedzic, Mark A. Lukowski. High-performance electrocatalysis using metallic cobalt pyrite (CoS₂) micro- and nanostructures. *J. Am. Chem. Soc.* 136 (2014) 10053–10061.

[40] Y. Okamoto, K. Ochiai, M. Kawano, K. Kobayashi and T. Kubota, Effects of support on the activity of Co-Mo sulfide model catalysts, *Appl. Catal. A* 226 (2002) 115–127.

[41] J. Ladrière, S. Göbölös , F. Delannay, B. Delmon, Mössbauer emission spectroscopy of an unsupported cobalt-molybdenum hydrodesulfurization catalyst, *J. Radioanal. Nucl. Chem.* 109 (1987) 213–222.

[42] J. Kibsgaard, T.F. Jaramillo, F. Besenbacher, Building an appropriate active-site motif into a hydrogen-evolution catalyst with thiomolybdate [Mo₃S₁₃]²⁻ clusters, *Nat. Chem.* 6 (2014) 248–253.

[43] E. J. Popczun, J.R. McKone, C.G. Read, A.J. Biacchi, A.M. Wiltrout, N.S. Lewis, R.E. Schaak, Nanostructured nickel phosphide as an electrocatalyst for the hydrogen evolution reaction, *J. Am. Chem. Soc.* 135 (2013) 9267–9270. [44] E. J. Popczun, C.G. Read, C.W. Roske, N.S. Lewis, R.E. Schaak, Highly active electrocatalysis of the hydrogen evolution reaction by cobalt phosphide nanoparticles, *Angew. Chem. Int. Ed.* 53 (2014) 5427–5430.

- [45] Y. Sun, C. Liu, D.C. Grauer, J. Yano, J.R. Long, P. Yang, C.J. Chang, Electrodeposited cobalt-sulfide catalyst for electrochemical and photoelectrochemical hydrogen generation from water, *J. Am. Chem. Soc.* 135 (2013) 17699–17702.
- [47] J.D. Benck, Z.B. Chen, L.Y. Kuritzky, A.J. Forman, T.F. Jaramillo, Amorphous molybdenum sulfide catalysts for electrochemical hydrogen production: insights into the origin of their catalytic activity, *ACS Catal.* 2 (2012) 1916–1923.
- [48] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D.C.B. Alves, T. Fujita, M. Chen, T. Asefa, V.B. Shenoy, G. Eda, M. Chhowalla, Enhanced catalytic activity in strained chemically exfoliated WS₂ for hydrogen evolution, *Nat. Mater.* 12 (2013) 850–855.
- [49] X. Zou, X. Huang, A. Goswami, R. Silva, B.R. Sathe, E. Mikmekova, T. Asefa, Cobalt-embedded nitrogen-rich carbon nanotubes efficiently catalyze hydrogen evolution reaction at all pH values, *Angew. Chem. Int. Ed. Engl.* 53 (2014) 4372–4376.
- [50] H. Vrubel, X. Hu, Molybdenum boride and carbide catalyze hydrogen evolution in both acidic and basic solutions, *Angew. Chem. Int. Ed.* 51 (2012) 12875–12878.
- [51] J. Shi, J. Hu, Molybdenum sulfide nanosheet arrays supported on Ti plate: an efficient hydrogen-evolving cathode over the whole pH range, *Electrochim. Acta* 168 (2015) 256–260.
- [52] Parsons, R. The rate of electrolytic hydrogen evolution and the heat of adsorption of hydrogen. *Trans. Faraday Soc.* 54 (1958) 1053–1063.
- [53] J.K. Nørskov, T. Bligaard, A. Logadottir, J.R. Kitchin, J.G. Chen, S. Pandelov, U. Stimming, Trends in the exchange current for hydrogen evolution, *J. Electrochem.*

Soc. 152 (2005) J23–J26.

[54] H.I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J.R. Long, C.J. Chang, A molecular MoS(2) edge site mimic for catalytic hydrogen generation, *Science* 335 (2012) 698–702.

[55] J. Bonde, P.G. Moses, T.F. Jaramillo, J.K. Nørskov, I. Chorkendorff, Hydrogen evolution on nano-particulate transition metal sulfides, *Faraday Discuss.* 140 (2008) 219–231.

[56] D. Merki, X.L. Hu, Recent developments of molybdenum and tungsten sulfides as hydrogen evolution catalysts, *Energy Environ. Sci.* 4 (2011) 3878–3888.

Figures Captions

Fig. 1. SEM images of (a)(b) CoMoS₄, (c)(d) NiMoS₄, (e)(f) CoMoS₄-H and (g)(h) NiMoS₄-H.

Fig. 2. XRD patterns of CoMoS₄, NiMoS₄, CoMoS₄-H, NiMoS₄-H and (NH₄)₂MoS₄.

Fig. 3. Raman spectra of CoMoS₄, NiMoS₄, CoMoS₄-H and NiMoS₄-H.

Fig. 4. High resolution X-ray photoelectron spectroscopy (XPS) of the S 2p region of CoMoS₄, CoMoS₄-H (a) and NiMoS₄, NiMoS₄-H (b); Mo 3d region of CoMoS₄, CoMoS₄-H (c) and NiMoS₄, NiMoS₄-H (d); Co 2p region of CoMoS₄, CoMoS₄-H (e), Ni 2p region of NiMoS₄, NiMoS₄-H (f).

Fig. 5. The HER activity of CoMoS₄, NiMoS₄, CoMoS₄-H and NiMoS₄-H in 1 M KOH. (a) I–V polarization curve. (b) The Tafel plot derived from I–V polarization curve. (c) The Nyquist plots.

Fig. 6 The HER activity of CoMoS₄, NiMoS₄, CoMoS₄-H and NiMoS₄-H in 0.5 M H₂SO₄. (a) I–V polarization curve. (b) The Tafel plot derived from I–V polarization curve. The HER activity of CoMoS₄, NiMoS₄, CoMoS₄-H and NiMoS₄-H in 1 M phosphate buffer solution. (c) I–V polarization curve. (d) The Tafel plot derived from I–V polarization curve.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6