Amorphous nickel/cobalt tungsten sulfide electrocatalysts for high-efficiency hydrogen evolution reaction

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The hydrogen evolution reaction (HER), an appealing solution for future energy supply, requires efficient and inexpensive electrocatalysts with abundant active surface sites. Although crystalline MoS$_2$ and WS$_2$ are promising candidates, their activity is dominated by edge sites. Amorphous tungsten sulfide prepared so far lacks the required active sites and its application has thus been hampered. In this work, nickel and cobalt incorporated amorphous tungsten sulfide synthesized by a thermolytic process is demonstrated to enhance the HER efficiency dramatically. The amorphous nickel tungsten sulfide (amorphous NiWS) annealed at 210°C delivers the best HER performance in this system boasting a Tafel slope of 55 mV per decade and current density of 8.6 mA cm$^{-2}$ at 250 mV overpotential in a sustained test for 24 h. The introduction of Ni or Co into the catalyst and subsequent thermal treatment alters the porous structure and chemical bonding states thereby increasing the density of active sites on the surface.

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1. Introduction

Hydrogen produced by electrolysis or solar-driven water splitting offers an environmentally acceptable and technologically promising approach to fulfill future energy demand [1–3]. Platinum group metals are the most electroactive catalysts but their rareness limits the applicability. Recently, transition-metal dichalcogenides MX$_2$ (M = Mo, W; X = S, Se) have drawn much attention as efficient and low-cost catalysts [4–8]. MX$_2$ is a bio-inspired catalyst [9] and has been used in the hydrotreating (HDT) process [10]. Containing Fe, Ni, Mo, S in the active sites, hydrogenases and nitrogenases exhibit excellent HER activity [11]. Many HDT catalysts such as molybdenum carbide [12,13], molybdenum nitride [13], tungsten carbide [14], tungsten carbonitride [15], and nickel phosphide [16] are good HER candidates [10]. These electrocatalysts also have potentials as photocatalysis and photoelectrocatalysis [17–21]. 2H-MX$_2$ is a general phase and the edge sites in lieu of the inert (0 0 0 1) basal planes have been identified experimentally and theoretically to be catalytically active. This indicates the importance of uncoordinated centers [9,22].

In order to achieve better performance, much effort has recently been made to produce various MX$_2$-based catalysts by taking advantage of the edge sites on nanosheets [23,24], double-gyroid networks [25], and molecular mimicking systems [26]. Particularly, crystalline WS$_2$ nanoribbons [27], WS$_2$ nanosheets produced by ball-milling method [28], and WS$_2$ nanoflakes prepared by sonochemistry [29] or solution-phase method [30] expose dense edge sites. It has been shown that the WS$_2$/Au hybrid [31] and WS$_2$/graphene hybrid produced by hydrothermal reaction [32] or electrodeposition [33] can facilitate charge transport. WS$_2$ nanosheets prepared by lithium intercalation [34] or microwave-assisted reaction [35] display impressing HER efficiency due to the existence of strained metallic 1T-WS$_2$. Crystalline catalyst is usually more stable and it is relatively easy to elucidate the catalytic mechanism compared to that of amorphous materials [8,22]. However, amorphous materials have a high concentration of unsaturated sites and can yield high activity with the proper structure [36,37]. Recently, amorphous molybdenum sulfide (MoS$_x$) has been shown to be an effective HER catalyst by electro-deposition [38], ...
Considering the nickel center in hydrogenase [11] and extensive use of Ni and Co as promotional elements for 2H-MS2 (M = Mo, W) in hydrodesulfurization (HDS) [5,10,46,47], we fabricate amorphous nickel and cobalt tungsten sulfides by a simple thermolysis process at low temperature in this work and the amorphous structure is demonstrated to be highly active for HER. The Ni2+ or Co2+ cations can interact with tetrathiomolybdate or tetrathioltungstate anions (MS2−) to form complexes like [M′(MS4)n− or M′MS4 (M′ = Ni, Co; M = Mo, W; n = 2, 3) which exhibit strong M′ → MS4 electron delocalization [48–52]. Hence, Ni/Co incorporation and thermal treatment can be implemented together to optimize the amorphous structure. Our results reveal that although the undoped catalyst shows slow HER kinetics, the modified catalyst film with a porous morphology and larger density of active surface sites exhibits enhanced catalytic activity. By adopting the optimal synthesis conditions, the HER performance is comparable to that of crystalline WS2 and metal pyrite families [53].

2. Experimental

2.1. Materials

Unless otherwise stated, the reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification.

2.2. Electrode pretreatment

The fluorine-doped tin oxide electrode (FTO-coated glass, Nippon Sheet Glass, 14 Ω/sq) was cleaned in a bath containing isopropanol and then thoroughly rinsed with acetone, deionized water, and ethanol prior to use. The glassy carbon (GC, Tianjin Aida-hengsheng Technology Co., 2 cm × 1 cm) substrate was polished with 1.0 μm alpha alumina and 0.05 μm gamma alumina powders (CH Instrument) suspended in de-ionized water on a Microcloth polishing pad (CH Instruments). The GC electrode was treated in an ultrasonic bath of deionized water and ethanol for 15 min.

2.3. Sample preparation

The catalyst films were synthesized by thermolysis in a CVD furnace under nitrogen atmosphere at different temperatures. In a typical procedure to prepare the amorphous nickel tungsten sulfide, 0.345 mmol (120.0 mg) of ammonium tetrathiotungstate (NH4)2WS4, 0.115 mmol (27.3 mg) nickel(II) chloride hexahydrate (NiCl2·6H2O) were dissolved in 3 mL of water to form a dark red solution, followed by ultrasonic treatment for several minutes. 600 μL of the stock solution was dropped onto a 10 mm × 20 mm FTO sample, desiccated, and kept in a vacuum dryer at room temperature immediately. Afterwards, the FTO substrate was put in a quartz tube, heated to 210 °C in 20 min, and kept at this temperature for 30 min in a nitrogen atmosphere at a flow rate of 100 standard-state cubic centimeter per minute (scm). Finally, the FTO substrate was coated in a bath containing isopropanol and then thoroughly rinsed with acetone, deionized water, and ethanol prior to use. The glassy carbon (GC, Tianjin Aida-hengsheng Technology Co., 2 cm × 1 cm) substrate was polished with 1.0 μm alpha alumina and 0.05 μm gamma alumina powders (CH Instrument) suspended in de-ionized water on a Microcloth polishing pad (CH Instruments). The GC electrode was treated in an ultrasonic bath of deionized water and ethanol for 15 min.

2.4. Characterization

The samples were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S4800), high-resolution transmission electron microscopy (HR-TEM, JEOL-2100), X-ray powder diffraction (XRD, Philips, Xpert), and X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbe). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a STA-449C (Netzsch Instruments) thermomicrobalance under nitrogen. The nitrogen adsorption and desorption isotherms were acquired at 77 K on a TriStar 3000 (Micromeritics Instrument Co.) adsorption analyzer and the specific surface areas were determined from nitrogen adsorption according to the Brunauer–Emmett–Teller (BET) method.

2.5. Electrochemical measurements

The electrochemical measurements were carried out using a three-electrode system on the CHI 660D workstation (CH Instrument) at ambient temperature in a 0.5 M H2SO4 solution. The catalyst films deposited on FTO-coated glass were used as the working electrode, whereas the Ag/AgCl (in 3.5 M KCl solution) electrode and platinum mesh served as the reference and counter electrodes, respectively. All of the potentials reported were calibrated to the reversible hydrogen electrode (RHE) using the following equation: \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{V} \times \text{pH} + 0.205 \text{V} \). Polarization curves and Tafel analysis acquired from the catalyst films in 0.5 M H2SO4 at a scanning rate of 2 mV s−1. Electrochemical impedance spectroscopy (EIS) measurements were performed using the same configuration at −0.10 V vs. RHE from 105 to 0.1 Hz with an AC voltage of 5 mV. The impedance experiments were conducted to determine the series resistance and subsequent correct the Tafel analysis for iR losses. In the galvanostatic polarization experiment, the headspace of the cathodic compartment was purged with high purity nitrogen for 2 h with vigorous stirring before the measurement. The evolved hydrogen was quantified by a GC-8A (Shimadzu Co., Ar carrier gas) gas chromatograph.
are homogeneously distributed (Fig. S5). The amorphous nature is further confirmed by the broad XRD peaks (Fig. S6) [55]. When the annealing temperature reaches 400 °C, the morphology of catalysts changes slightly. Both samples show polycrystalline 2H-WS2 XRD patterns. No crystalline nickel sulfide side-phase like Ni3S2 is observed from nickel tungsten sulfide, indicating that the catalyst processed at 400 °C is a single NiWS phase, corroborated by TEM and SAED (Figs. S2g–l, S4g–l and S6).

To investigate the electrocatalytic activity of the samples, linear sweep voltammetry is performed in 0.5 M H2SO4 at 2 mV s⁻¹. Fig. 2a shows the polarization curves of the a-WS2, prepared at 210 °C with different Ni concentrations. The HER efficiency reaches a maximum when the Ni to W ratio is 1:3. The non-baseline current cannot be observed from the a-WS2 before a 300 mV overpotential, but the optimal NiWS structure with optimal loading shows an onset potential of ~100 mV and a current density of 14.1 mA cm⁻² at −0.30 V vs. RHE (Fig. S7). Fig. 2b illustrates the influence of the annealing temperature on the HER performance of NiWS (Ni:W = 1:3). According to the above analysis, NiWS is amorphous at below 300 °C and polycrystalline over 350 °C. The HER activity shows an ‘N’ shape relationship with annealing temperature. The amorphous NiWS (a-NiWS) processed at 210 °C exhibits the highest activity and a minimal efficiency is observed at 240 °C. In contrast, poor HER efficiency is observed from the undoped catalysts produced in the same temperature range, as shown in Fig. S8. This unusual temperature dependence of the HER activity observed from NiWS is quite different from that of MoS2 nanosheets [56] and amorphous MoSx [40].

After replacing Ni²⁺ with Co²⁺, the catalyst film again unambiguously shows enhanced activity at an onset potential of ~120 mV (Fig. S9). Consistent with the best amorphous NiWS structure, the Co to W ratio is 1:3 and the catalyst is treated at 210 °C. To achieve a current density of 10 mA cm⁻², overpotentials of 604, 330, and 265 mV are required for the amorphous WS2, CoWS, and NiWS films, respectively. A drastic decrease of 339 mV is observed from NiWS compared to a-WS2. Herein, the effect of Ni is much more pronounced than previously reported Ni-promoted MoS2 microspheres [57], Co-doped 2H-MoS2 [5], and Fe/Co/Ni-promoted amorphous MoS2 [49]. This activity enhancement is further confirmed by using nickel(II) acetate and cobalt(II) acetate as the Ni²⁺ and Co²⁺ sources (Fig. S10). After correcting for the ohmic potential drop (IR) loss, rather small overpotentials of 189 and 250 mV are needed to deliver a current density of 10 mA cm⁻² for the Ni and Co doped catalysts, respectively (Figs. S9 and S11).

With regard to the amorphous NiWS annealed below 180 °C and CoWS annealed at 210 °C, a reduction peak emerges prior to hydrogen evolution in the first polarization scan and disappears from the second scan (Fig. S12). The reduction peak of NiWS becomes smaller as the annealing temperature increases from 160 to 180 °C and completely vanishes from the film annealed at 210 °C. The reduction process is also observed from electro-polymerized amorphous MoSx [38] and crystalline Cu2MoS4 [53]. In the XPS spectra
Overpotential (V)

WS as cobalt and nickel incorporated catalyst films, respectively. The

After iR correction, the linear segments are fitted to the Tafel
different temperature. Curves of 160 and 180
of a Pt foil is shown for comparison. (b) Nickel tungsten sulfide films annealed at

Fig. 2. Polarization curves acquired from the catalyst films on FTO in 0.5 M H2 SO4
160 and 180 °C are from the second polarization
in 0.5 M H2 SO4 to obtain the exchange current den-

The Tafel plots in Fig. 3a provide insights into the mechanism

Fig. 3. (a) Tafel plots of unpromoted, nickel and cobalt promoted amorphous tung-
sto S2− is observed from the first polarization scan acquired from the NiWS annealed at 180 °C and CoWS at 210 °C. This also reflects the reduction process [38].

The Tafel plots in Fig. 3a provide insights into the mechanism [10]. After iR correction, the linear segments are fitted to the Tafel equation ($\eta = a + b \log |j|$) to obtain the exchange current density ($j_0$) and Tafel slope ($b$) [59]. Exchange current densities of 0.86, 3.2, and 3.5 μA cm$^{-2}$ are obtained from the undoped as well as cobalt and nickel incorporated catalyst films, respectively. The WS$_x$ exhibits a large Tafel slope of 129 mV per decade, indicating that the discharge process is slow and rate-determining (see Tafel analysis in Supporting Information) [12]. A Tafel slope of 55 mV per decade observed from the amorphous NiWS film reveals the Volmer–Heyrovsky mechanism and the rate limiting step is the electrochemical desorption reaction [13]. Hence, it is likely that Ni reduces the free energy barrier in the discharge reaction to at least that of the following desorption reaction resulting in the obvious decrease in the Tafel slope [6]. Besides, a more complex HER mechanism is suggested for amorphous CoWS with a higher Tafel slope of 74 mV per decade. This Tafel slope cannot be simply ascribed to a purely activation controlled dynamic process [58]. The Ni/Co doped catalysts with enhanced HER kinetics have enormous potential in water-splitting devices [60].

Galvanostatic polarization is performed to determine the sta-

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bility of the amorphous NiWS (Fig. 3b) [61]. An overpotential of

An overpotential of 188 mV is required to reach a current density of 4 mA cm$^{-2}$ with slight degradation during the 5 h span. The amount of evolved hydrogen determined by gas chromatography demonstrates unity Faradaic efficiency. The durability is further confirmed by constant-

gas chromatography (red square dots) as a function of time. (For interpretation of

tion in Supporting Information) [16]. The calculated TOFs of the

In catalysis, the turnover frequency (TOF) of each active site is commonly employed to evaluate the intrinsic activity [11]. Assuming that all the surface sites are catalytically active, we can estimate the TOF values (see Figs. S16 and S17 and TOF calcula-

although the amorphous NiWS is comparable to other non-

Although the amorphous NiWS is comparable to other non-

precious HER catalysts, its electrocatalytic property is still inferior to that of Pt. Pt(1 1 1) exhibits a Tafel slope of 29 mV dec$^{-1}$, exchange current density of 450 μA cm$^{-2}$, and TOF of 0.9 s$^{-1}$ [22]. The performance gap is probably due to the intrinsically low
electric conductivity of the amorphous films and poor synergistic effects between the catalyst and substrate \[64\]. This is similar to the case of amorphous molybdenum sulfide. The activity of the MoS\(_2\)/NCNT (N-doped carbon nanotube) hybrid is superior to that of the electro-deposited MoS\(_2\) film \[38,64\], but surprisingly, the MoS\(_2\)/PPy (polypyrrole) copolymer displays even much higher efficiency comparable to that of commercial Pt/C catalysts \[62\]. Hence, more work is needed to elucidate the HER mechanism and improve the activity \[65\]. In addition, we have evaluated the performance of the catalyst films on the GC electrode (Fig. S18). Remarkable increase in the exchange current density is observed as demonstrated by values of 17.4 and 13.4 \(\text{mAcm}^{-2}\) observed from the amorphous NiWS and CoWS, respectively. Here, we would like to mention that better performance can be expected by coupling with conductive electrode like graphene \[59\].

To obtain more knowledge about the chemical nature of the catalysts, XPS is performed to determine the atomic composition and bonding states. As shown in Fig. 4, the Ni 2p spectrum of the NiWS film annealed at 210 °C shows two peaks corresponding to the Ni 2p\(_{1/2}\) and 2p\(_{3/2}\) \(\text{NiW}\) (see the XPS results of amorphous CoWS in Supporting Information, Figs. S20 and S21) \[66\]. The Ni 2p\(_{3/2}\) peak at 853.54 eV is attributed to the Ni 2p in NiWS phase as it differs from the typical Ni 2p\(_{3/2}\) signal from Ni\(_3\)S\(_2\) at 853.0 eV \[51,66\]. The W 4f spectra are fitted to several doublets including W\(_{6+}\) 4f\(_{7/2}\)-7/2, W\(_{5+}\) 4f\(_{7/2}\)-7/2, and W\(_{4+}\) 4f\(_{5/2}\)-7/2 \[44\]. Signals of W\(_{4+}\) and W\(_{5+}\) species are commonly observed from amorphous WS\(_2\) and its derivatives \[67\], but the ratios of the contents are smaller in amorphous NiWS than crystalline WS\(_2\). The W\(_{6+}\) peaks representing oxidation of W are more obvious in NiWS, as the precursor becomes more unstable after WS\(_2\)-bonding interacts with Ni\(_2\) \[48,67\]. In the S 2p spectrum, the peaks at 162.47–162.75 and 161.37–161.65 eV correspond to the S 2p\(_{1/2}\) and 2p\(_{3/2}\) of S\(^{2-}\) ligand \[38\]. Previous studies have revealed that the S\(^{2-}\)-ligand may play an important role in the HER activity of amorphous MoS\(_2\) \[40,62\]. In NiWS, the intensity of the S 2p\(_{1/2}\) and 2p\(_{3/2}\) peaks at 164.05–164.20 and 162.95–163.10 eV, which indicate the presence of bridging S\(^{2-}\)- and/or apical S\(^{2-}\) \[62\], is larger than that in WS\(_2\). By integrating the XPS data, the amorphous NiWS structure is derived to be Ni\(_{0.36}\)WS\(_{2.78}\).

With regard to the amorphous NiWS after the HER studies, the W\(_{6+}\) signal increases slightly, while the S\(^{2-}\)-content decreases slightly (Figs. S22 and S23). We have also acquired XPS spectra from the NiWS annealed at 180 and 240 °C (Figs. S24–S26). Notable difference is from the W 4f and S 2p regions compared to the NiWS annealed at 210 °C, especially the signal of S\(^{2-}\) decreases with increasing annealing temperature. For the NiWS annealed at 400 °C, the Ni 2p spectrum is similar to that from the NiWS annealed at 210 °C. However, in the W 4f and S 2p regions, both the undoped and nickel incorporated catalysts show similar features as 2H-WS\(_2\) (Figs. S28 and S29) \[27,52\]. XPS indicates that the proper Ni:W:S ratio and concomitant binding structures formed at 210 °C are responsible for the excellent catalytic activity.

Fig. 4. XPS spectra obtained from amorphous nickel tungsten sulfide (NiWS) and amorphous tungsten sulfide (WS): (a) Ni 2p, (b) W 4f, and (c) S 2p. The black circle line represents the experimental data and the cyan line is the fitted curve (Fig. S19).
have oxidation state IV or V and the W$_2$ dimer is bridged to S$_2$\(^{-2}\). Hence, Ni/Co introduction and heating treatment are utilized together to optimize the amorphous structure in an attempt to enhance the HER activity and as a result, the chemical structure is altered significantly as disclosed by the XPS spectra.

To further elucidate the effects of Ni or Co incorporation, the electrochemically active surface area ($S_{\text{echem}}$) is assessed by capacitance measurements (Fig. 5) because $S_{\text{echem}}$ is assumed to be linearly proportional to the double layer capacitance ($C_d$)\(^{-1}\). The relative value ($S_{\text{chem}}^*$) of $S_{\text{echem}}$ can be obtained by normalizing of $C_d$ and the relative geometric surface area ($S_{\text{geom}}^*$) is derived from the BET data (Figs. S29–S32). It is generally supposed that $S_{\text{chem}}$ is directly proportional to the amount of active sites in HER\(^{-1}\). After doping, $S_{\text{chem}}^*$ becomes larger compared to the relatively small increase in $S_{\text{geom}}$ (Table 1). In addition, for amorphous NiWS, the values of $S_{\text{chem}}^*$ at 180 and 240 °C are smaller than that at 210 °C, but still much larger than those of a-W$_x$S. The relative surface density of the active sites ($\sigma_{\text{eff}}$) can be determined by dividing $S_{\text{chem}}^*$. Compared to WS$_x$, the $\sigma_{\text{eff}}$ values of amorphous NiWS and CoWS are 263 and 124 times larger, respectively, indicating pronounced increase in the active site density due to incorporation of Ni or Co.

In contrast to the Co/Ni-S centers in the crystalline CoWS and NiWS,\(^{-43}\) it is more likely that the enhanced activity arises from the structure of Ni–W–S or Co–W–S, as the performance of the catalysts is not directly related to the Ni/Co concentration\(^{-49}\). Dopant atoms and thermal treatment greatly alter the electronic structure, especially the coordination states, and so $\Delta G_H$ can be tuned\(^{-5}\). Under optimal conditions, the average $\Delta G_H$ is expected to be largely reduced and inert surface sites are galore activated based on the previously theoretical analyses\(^{-5,49}\). Therefore, the active site density is increased, especially in amorphous NiWS annealed at 210 °C. The discharge reaction barrier is reduced by reformative bonding of the intermediates and closer proximity among active sites\(^{-70}\). Consequently, the electrochemical desorption reaction becomes more rate determining and the HER dynamics is accelerated\(^{-6,70}\). Hence, the intrinsic activity in amorphous NiWS and CoWS is significantly improved and comparable to that of other MX$_2$-based catalysts (Table S1).

### 4. Conclusion

In conclusion, amorphous nickel/cobalt tungsten sulfide is synthesized by a thermolysis and the catalysts, especially amorphous NiWS, deliver outstanding catalytic performance. Hence, utilization of tungsten sulfide derived materials in HER catalysis is no longer limited to the crystalline 2H or 1T phase. Ni/Co incorporation and thermal treatment alter the morphology and chemical structure of the amorphous WS$_x$ and produce numerous surface sites. By adopting the optimal conditions, the density of active surface sites is significantly increased and the HER kinetics is largely promoted compared to WS$_x$. The results clearly indicate that amorphous NiWS and CoWS catalysts have immense potentials in water splitting devices.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apsusc.2015.03.018.

### References


### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>$b$ (mV dec$^{-1}$)</th>
<th>$j_0$ ($\mu$A cm$^{-1}$)</th>
<th>$S_{\text{chem}}^*$</th>
<th>$S_{\text{geom}}^*$</th>
<th>$\sigma_{\text{eff}}$</th>
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<tr>
<td>WS$_x$</td>
<td>129</td>
<td>0.86</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<tr>
<td>CoWS</td>
<td>74</td>
<td>3.2</td>
<td>1.89</td>
<td>234</td>
<td>124</td>
</tr>
<tr>
<td>NiWS</td>
<td>55</td>
<td>3.5</td>
<td>1.30</td>
<td>342</td>
<td>263</td>
</tr>
</tbody>
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Supporting Information

Amorphous nickel/cobalt tungsten sulfide electrocatalysts for high-efficiency hydrogen evolution reaction

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13. Tafel analysis and HER mechanism.


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16. References.
Fig. S1. TG/DSC curves of three precursors. Thermal decomposition is performed at a heating rate of 10 °C min⁻¹ in nitrogen.

It is generally understood that thermal decomposition of \((NH_4)_2WS_4\) takes place by the following reactions:\(^1\)

\[
(NH_4)_2WS_4 \rightarrow WS_3 + H_2S + 2NH_3
\]

\[
WS_3 \rightarrow WS_2 + S
\]

Amorphous tungsten trisulfide is produced in an inert ambient at a temperature between 170 and 310 °C and the materials are stable between 310 and 350 °C. The amorphous WS\(_3\) begins to decompose into crystalline 2H-WS\(_2\) and S above 350 °C.\(^1,2\) It is noted that decomposition of NiCl\(_2\)/(NH\(_4\))\(_2\)WS\(_4\) occurs at a temperature as low as 110 °C and the amorphous phase begins to crystallize at 320 °C.\(^2\)
Fig. S2. FE-TEM images of the catalyst films prepared by thermolysis on FTO. (a, b, c) Tungsten sulfide film annealed at 210 °C. (d, e, f) Cobalt tungsten sulfide film annealed at 210 °C. (g, h, i) Tungsten sulfide film annealed at 400 °C. (j, k, l) Nickel tungsten sulfide film annealed at 400 °C.
**Fig. S3.** (a, b) Cross-sectional FE-SEM images of the amorphous nickel tungsten sulfide film deposited on FTO electrode. The average film thickness is 18 μm (varying from 15 to 20 μm).
**Fig. S4.** Low magnification TEM images, high-resolution TEM images, and SAED patterns of nanoparticles deposited from the diluted catalyst suspension. (a, b, c) Tungsten sulfide annealed at 210 °C. (d, e, f) Cobalt tungsten sulfide annealed at 210 °C. (g, h, i) Tungsten sulfide annealed at 400 °C. (j, k, l) Nickel tungsten sulfide annealed at 400 °C. HR-TEM images (b, e) and SAED patterns (c, f) revealing the amorphous structure of tungsten sulfide and cobalt tungsten sulfide annealed at 210 °C. Typical polycrystalline structures revealed by the HR-TEM images (h, k) and SAED patterns acquired from the tungsten sulfide and nickel tungsten sulfide annealed at 400 °C. No crystalline nickel sulfide side-phase like Ni$_3$S$_2$ is observed from nickel tungsten sulfide annealed at 400 °C from Fig. S4k, l, indicating that the catalyst is a single NiWS phase.
Fig. S5. Ni, W, and S elemental mapping images of three films deposited from the diluted catalyst suspension utilizing TEM: (a) NiWS film annealed at 180 °C (scale bar = 500 nm), (b) NiWS film annealed at 400 °C (scale bar = 500 nm), (c) CoWS annealed at 210 °C (scale bar = 250 nm). The elemental mapping images indicate that Ni/Co, W, and S in the catalysts are homogeneously distributed.
**Fig. S6.** XRD patterns acquired from the unpromoted, nickel and cobalt promoted tungsten sulfide films (WS, NiWS, CoWS) processed at 210 and 400 °C on FTO-coated glass. (*) represents the peaks from (NH₄)₂WS₄ which appear at 2θ of about 17° and 23° corresponding to the [(120), (111)] and [(100), (101)] reflections (JCPDS card No. 48-1663). (●) indicates the peaks from 2H-WS₂. The broad diffuse features at 2θ ca. 14° and 33° stem from the (002) and [(100), (101)] reflections of 2H-WS₂ (JCPDS card No. 08-0237), respectively. Nickel/Cobalt clusters or phase segregation of the NiWS into Ni₃S₂ and WS₂ is not observed as a result of the relatively small Ni or Co concentration and low processing temperature.¹"
Fig. S7. Polarization curves of amorphous nickel tungsten sulfide films annealed at 210 °C for different precursor mass loadings in 0.5 M H₂SO₄ at a scanning rate of 2 mV s⁻¹.
**Fig. S8.** Polarization curves of the unpromoted tungsten sulfide on FTO electrode for different annealing temperature. The potential scanning rate is 2 mV s\(^{-1}\). The inset shows the corresponding current density at –0.65 V vs. RHE as a function of heating temperature, indicating poor catalytic activity of the unpromoted tungsten sulfide annealed below 400 °C. The error bars are presented according to several measurements on multiple samples.
Fig. S9. Polarization curves of unpromoted, nickel and cobalt promoted amorphous tungsten sulfide films (WS, NiWS, and CoWS) on FTO electrode in 0.5 M H₂SO₄ at 2 mV s⁻¹ with and without correction for iR losses (Fig. S11). The curve of the CoWS film is from the second polarization scan which shows a reduction process in the first scan. The curve of the Pt foil is shown for comparison.
**Fig. S10.** Polarization curves of the catalyst films produced from different precursors. They are put together to estimate the effects of hydrogen and chloride ions. The curve acquired from pure FTO electrode is shown for comparison. Compared to previous results, similar catalytic activity is observed with nickel(II) acetate (Ni(Ac)\(_2\)) as the Ni\(^{2+}\) source, cobalt(II) acetate (Co(Ac)\(_2\)) as the Co\(^{2+}\) source, and HCl added to (NH\(_4\))\(_2\)WS\(_4\) as the precursor of the unpromoted tungsten sulfide. The results indicate that hydrogen ions do not make a big difference and the activity does not depend on the original Ni\(^{2+}\) or Co\(^{2+}\) counter ions.
Fig. S11. Nyquist plots of the amorphous tungsten sulfide (WS), amorphous nickel tungsten sulfide (NiWS), and amorphous cobalt tungsten sulfide (CoWS) films on the FTO electrode at −0.10 V vs. RHE in 0.5 M H₂SO₄. All of the series resistances are in the range of 6-10 Ω cm² and the average values are 7.7 Ω cm² for WS, 7.9 Ω cm² for amorphous NiWS, and 8.0 Ω cm² for amorphous CoWS. The series resistance mainly comes from the catalyst film, FTO substrate, and electrolyte.
Fig. S12. First (dark line) and second (red dashed line) polarization curves of the freshly prepared catalyst films on FTO electrode in 0.5 M H₂SO₄ solution at a scanning rate of 2 mV s⁻¹. Nickel tungsten sulfide film annealed at 160 °C (a), 180 °C (b), 210 °C (c), and cobalt tungsten sulfide film annealed at 210 °C (d). The polarization curves in (a), (b) and (d) suggest a reduction process prior to hydrogen evolution as indicated in Fig. S12. This reduction peak is probably related to the interaction between Ni²⁺/Co²⁺ and WS₄²⁻ as a result of incomplete thermolysis (Fig. S6).⁴⁻⁵
**Fig. S13.** S 2p XPS spectra of the Ni and Co tungsten sulfide films before (a, c, e) and after (b, d, f) the first polarization experiment. Nickel tungsten sulfide is annealed at 180 °C (a, b) and 210 °C (c, d). Cobalt tungsten sulfide is annealed at 210 °C (e, f). The S 2p data are extracted from Fig. 5 in the manuscript and Figs. S19-S24 in Supporting Information. Similar reduction peak is also observed from amorphous molybdenum sulfide by electro-deposition\textsuperscript{S6} or acidification.\textsuperscript{S7} After the polarization testing, the S 2p spectrum of the NiWS annealed at 210 °C changes slightly. For the NiWS
annealed at 180 °C and CoWS annealed at 210 °C, the $S_2^{2-}$ features become weak, but do not disappear, indicating the reduction of portion $S_2^{2-}$ to $S^{2-}$.

**Fig. S14.** (a) Long-term electrochemical stability test showing the variation of the current density measured from the amorphous nickel tungsten sulfide film on the FTO electrode at −0.25 V vs. RHE in 0.5 M H$_2$SO$_4$ with time. The current density is around 8.6 mA cm$^{-2}$ and is sustained for 24 h, revealing the excellent catalytic activity and robustness of the materials. (b) Electrochemical activities of the freshly prepared amorphous nickel tungsten sulfide film (black line) on the FTO electrode in 0.5 M H$_2$SO$_4$ and the same catalyst left in air for a month (red dashed line).
**Fig. S15.** (a, b) FE-SEM images of the amorphous nickel tungsten sulfide film after conducting the electrochemical stability test for 24 h.
Fig. S16. Nitrogen adsorption-desorption isotherms of the amorphous tungsten sulfide (WS), amorphous nickel tungsten sulfide (NiWS), and amorphous cobalt tungsten sulfide (CoWS). The Brunauer-Emmett-Teller (BET) model is adopted to assess the surface area. The BET surface areas of the amorphous WS, NiWS, and CoWS are 6.31, 6.79, and 9.78 m² g⁻¹, respectively.
Fig. S17. Calculated lower limit turnover frequency versus overpotential of the amorphous nickel tungsten sulfide (NiWS, red line) and amorphous cobalt tungsten sulfide (CoWS, green line). The obtained results are based on data of the linear polarization curves from the catalyst films on FTO electrodes. The onset potential of amorphous WSₙ is ~300 mV according to previous experimental results.
**Fig. S18.** HER activities of amorphous WS$_x$, CoWS, and NiWS films on GC electrodes. (a) Polarization curves of the catalyst films in 0.5 M H$_2$SO$_4$ at a scanning rate of 2 mV s$^{-1}$. The curve from CoWS in (a) is the second polarization scan. It also exhibits a reduction process in the first scan, as shown in (b). The HER performance of amorphous nickel tungsten sulfide on glassy carbon is quite impressive, as overpotentials of 260, 349, 658 mV are required to achieve a current density of 40 mA cm$^{-2}$ for the amorphous WS$_x$, CoWS, and NiWS films, respectively. (c) Corresponding Tafel plots of the catalyst films after correction for iR losses. (d) Nyquist plots of the catalyst films at $-0.10$ V vs. RHE. Based on the Tafel plots in (c), the Tafel slopes and exchange current densities are obtained to be 142 mV dec$^{-1}$ and 3.6 $\mu$A cm$^{-2}$ for amorphous WS$_x$, 74 mV dec$^{-1}$ and 13.4 $\mu$A cm$^{-2}$ for amorphous CoWS, 56 mV dec$^{-1}$ and 17.4 $\mu$A cm$^{-2}$ for amorphous NiWS.
Fig. S19. (a) XPS survey spectrum of amorphous nickel tungsten sulfide (NiWS) annealed at 210 °C. The ratio of Ni: W: S is 0.36:1:2.78. (b) XPS survey spectrum of the amorphous tungsten sulfide (WS) annealed at 210 °C. The S to W ratio is 2.62:1.
Fig. S20. XPS spectra of the amorphous cobalt tungsten sulfide (CoWS) annealed at 210 °C: (a) XPS survey spectrum, (b) Co 2p region, (c) W 4f region, and (d) S 2p region. The Co:W:S ratio is 0.36:1:2.86. In the Co 2p spectrum in (b), the two peaks correspond to Co 2p$_{1/2}$ and 2p$_{3/2}$ binding energies. Similar to the NiWS annealed at 210 °C, the bonding states of the amorphous CoWS are quite different from those of WS$_x$ in the W 4f and S 2p regions. The present W$^{6+}$ and S$^{2-}$ features are more obvious than those of WS$_x$. Moreover, the relative intensity ratio of S$^2$ to S$^{2-}$ is even larger than that from the NiWS annealed at 210 °C.
Fig. S21. XPS spectra of the amorphous cobalt tungsten sulfide (CoWS) annealed at 210 °C after the first polarization experiment: (a) XPS survey spectrum, (b) Co 2p region, (c) W 4f region, and (d) S 2p region. After testing, the Co 2p and W 4f spectra display relatively small changes. However, the S^{2-} signal increases and S_{2^{2-}} signal decreases obviously. The S 2p XPS spectra indicate that portion S_{2^{2-}} is reduced to S^{2-} after the voltammetry measurement, comporting with the reduction peak in the polarization curve in Fig. S11(d).
Fig. S22. XPS spectra of the amorphous nickel tungsten sulfide (NiWS) annealed at 210 °C after the first polarization experiment: (a) XPS survey spectrum, (b) Ni 2p region, (c) W 4f region, and (d) S 2p region. In contrast to the XPS spectra of the amorphous NiWS annealed at 180 °C and CoWS at 210 °C, the XPS spectra in the Ni 2p, W 4f, and S 2p regions of the amorphous NiWS annealed at 210 °C present little changes after the polarization scan. This result reveals the stability of the Ni-promoted catalyst annealed at 210 °C. This is in accordance with the linear sweep voltammetry shown in Fig. S11(c).
Fig. S23. XPS spectra of the amorphous nickel tungsten sulfide (NiWS) annealed at 210 °C after conducting the electrocatalytic reaction for 3 h: (a) XPS survey spectrum, (b) Ni 2p region, (c) W 4f region, and (d) S 2p region. After the HER test, the peak positions of Ni 2p1/2 and 2p3/2 in (b) alter a little. The W⁶⁺ signal in the W 4f region and S²⁻ signal in S 2p region slightly increases and decreases, respectively. In addition, the W⁵⁺/W⁴⁺ ratio becomes larger after the HER testing.
Fig. S24. XPS spectra of the amorphous nickel tungsten sulfide (NiWS) annealed at 180 °C: (a) XPS survey spectrum, (b) Ni 2p region, (c) W 4f region, and (d) S 2p region. As shown in (b), the two peaks correspond to the Ni 2p\textsubscript{1/2} and 2p\textsubscript{3/2} binding energies and their positions are close to those of the NiWS annealed at 210 °C. However, the W 4f spectra are different in the two samples. The W\textsuperscript{5+} and W\textsuperscript{6+} signals are more obvious and the W\textsuperscript{4+} signal is relatively small in the NiWS annealed at 180 °C. In the S 2p region, the S\textsubscript{2}\textsuperscript{2-} peaks are stronger than that in the NiWS annealed at 210 °C but they decrease after the polarization scan, as shown in Fig. S24.
**Fig. S25.** XPS spectra of the amorphous nickel tungsten sulfide (NiWS) annealed at 180 °C after the first polarization experiment: (a) XPS survey spectrum, (b) Ni 2p region, (c) W 4f region, and (d) S 2p region. After the polarization scan, relatively small changes are observed in the Ni 2p and W 4f spectra. However, the S$_{2}^{2-}$ and S$_{2}^{-}$ signals decreases and increases, respectively. This indicates the reduction of portion S$_{2}^{2-}$ to S$^{2-}$. The relative intensity of the S$_{2}^{2-}$ peak after the test is even lower than that in the amorphous NiWS annealed at 210 °C.
**Fig. S26.** XPS spectra of the amorphous nickel tungsten sulfide (NiWS) annealed at 240 °C: (a) XPS survey spectrum, (b) Ni 2p region, (c) W 4f region, and (d) S 2p region. The two peaks in the Ni 2p spectrum which correspond to the Ni 2p$_{1/2}$ and 2p$_{3/2}$ binding energies indicate the incorporation of Ni element. Compared to the amorphous NiWS annealed at 210 °C, the peak intensity ratios of W$^{5+}$/W$^{4+}$ in the W 4f region and S$_2^{2-}$/S$^2^{-}$ in the S 2p region decrease. The W$^{6+}$ peaks in the W 4f spectrum are still more apparent than those from the unpromoted catalyst.
Fig. S27. XPS spectra of the nickel tungsten sulfide (NiWS) annealed at 400 °C: (a) XPS survey spectrum, (b) Ni 2p region, (c) W 4f region, and (d) S 2p region. In the Ni 2p region, the two peaks correspond to the Ni 2p$^{3/2}$ and 2p$^{1/2}$ binding energies. The peak position of Ni 2p$^{3/2}$ is a little larger than that from the NiWS annealed at 210 °C. But in the W 4f and S 2p regions, the W$^{5+}$ and S$^{2-}$ signals vanish and the W$^{4+}$ and S$^{2-}$ peaks become the main features of the spectra. Besides, the W$^{6+}$ peaks representing oxidation of W still exist. The XPS data coincide with the previous TGA, XRD, TEM, and SAED results.
**Fig. S28.** XPS spectra of the unpromoted tungsten sulfide (WS) annealed at 400 °C: (a) XPS survey spectrum, (b) W 4f region, and (c) S 2p region. Similar to the case from the NiWS annealed at 400 °C, the W^{5+} and S^{2−} signals disappear and the W^{4+} and S^{2−} signals become the main features of the W 4f and S 2p spectra for the unpromoted tungsten sulfide annealed at 400 °C. In addition, the W^{6+} peaks are smaller compared to those in the promoted catalyst. This is similar to the case from the NiWS annealed at 210 °C. The XPS results further confirm that the tungsten sulfide annealed at 400 °C is a crystalline 2H-WS₂.
Fig. S29. (a) Cyclic voltammograms of the amorphous cobalt tungsten sulfide (CoWS) film annealed at 210 °C on FTO electrode acquired at different scanning rates (10-100 mV s⁻¹) in 0.5 M H₂SO₄. (b) Corresponding scanning rate dependence of the current density at 0.20 V vs. RHE. The calculated double layer capacitance of amorphous CoWS is 4460 μF cm⁻².
**Fig. S30.** (a) Cyclic voltammograms of the amorphous tungsten sulfide film annealed at 210 °C obtained at different scanning rates (10-100 mV s⁻¹). (b) Corresponding scanning rate dependence of the current density at 0.20 V vs. RHE. The calculated capacitance of amorphous WSₓ is 19 μF cm⁻². By normalizing the capacitance to the value of WSₓ, the relative geometric surface areas (Sₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑ) are 1, 234, and 342 for amorphous WSₓ, CoWS, and NiWS, respectively.
Fig. S31. (a) Cyclic voltammograms of the amorphous NiWS annealed at 180 °C obtained at different scanning rates (10-100 mV s⁻¹). (b) Corresponding scanning rate dependence of the current density at 0.20 V vs. RHE. \( C_{dl} \) of the amorphous NiWS annealed at 180 °C is 4715 μF cm⁻² and \( S_{echem} \) is 248. These values are in accord with the previous HER performance, indicating that the activity of the amorphous NiWS annealed at 180 °C is inferior to the amorphous NiWS annealed at 210 °C, but it is still much better than that of the amorphous WSₓ annealed at 210 °C.
Fig. S32. (a) Cyclic voltammograms of the amorphous NiWS annealed at 240 °C obtained at different scanning rates (10-100 mV s\(^{-1}\)). (b) Corresponding scanning rate dependence of the current density at 0.20 V vs. RHE. \(C_{dl}\) of the amorphous NiWS annealed at 240 °C is 4220 μF cm\(^{-2}\) and \(S_{echem}^*\) is 222. Similar to the case in the NiWS annealed at 180 °C, these values are smaller than those from the NiWS annealed at 210 °C, but they are still much larger than those from the amorphous WS\(_x\). This is in line with the previous HER activity.
Tafel analysis and HER mechanism

In an acidic medium, hydrogen evolution is considered to involve the following three elementary reactions:\(^{S8}\)

\[
\text{H}_3\text{O}^+ + e^- + \text{cat} \rightleftharpoons \text{H-cat} + \text{H}_2\text{O}, \text{discharge step (Volmer reaction)} \tag{1}
\]

\[
\text{H-cat} + \text{H-cat} \rightleftharpoons \text{H}_2 + 2\text{cat}, \text{recombination step (Tafel reaction)} \tag{2}
\]

\[
\text{H}_3\text{O}^+ + e^- + \text{H-cat} \rightleftharpoons \text{H}_2 + \text{cat} + \text{H}_2\text{O}, \text{desorption step (Heyrovsky reaction)} \tag{3}
\]

The Tafel slope is an intrinsic property of electrocatalysts and determined by the rate-limiting step of HER. In the Volmer-Tafel mechanism, if a fast discharge reaction is followed by a rate-determining recombination reaction, a Tafel slope of 29 mV dec\(^{-1}\) should be observed, as is well known for Pt(111). In the Volmer-Heyrovsky mechanism, if the discharge reaction is fast and the electrochemical desorption reaction is slow, the Tafel slope should be 38 mV dec\(^{-1}\). In both mechanisms, a rate-determining discharge reaction results in a theoretical Tafel slope of 116 mV dec\(^{-1}\).

The Tafel slope depends on many factors such as the reaction pathway and adsorption conditions in a complex way and the influencing factors in Tafel analysis are not completely clear with respect to MX\(_2\)-based catalysts.\(^{S8}\) More work is needed to elucidate the HER mechanism clearly.
Calculation of the lower limit for turnover frequency (TOF).

The method used to determine the lower limit of the TOF values shown below is similar to that described in Refs. S9 and S10. The relative roughness factor is obtained from the BET and XPS measurements\textsuperscript{S9} and the hypothetical geometry of the 2H-WS\textsubscript{2} surface is adopted to calculate the surface site density\textsuperscript{S10} in order to derive the lower limit of the TOF values at the specified current density.

In the typical procedure, the initial loading of (NH\textsubscript{4})\textsubscript{2}WS\textsubscript{4} is 6 mg cm\textsuperscript{-2} for unpromoted and promoted catalyst films. The elemental composition is calculated from XPS spectra and considering the fixed W content, the final loading values are 4.18 mg cm\textsuperscript{-2} for WS\textsubscript{x}, 5.07 mg cm\textsuperscript{-2} for amorphous NiWS, and 5.11 mg cm\textsuperscript{-2} for amorphous CoWS. The relative roughness factor (RF\textsubscript{BET}) is defined as the quotient of the actual surface area of the catalyst films divided by the FTO substrate area. Utilizing the BET data, the RF\textsubscript{BET} values are 264.3 for WS\textsubscript{x}, 344.3 for amorphous NiWS, and 499.5 for amorphous CoWS. By normalization of these values, the relative geometric surface areas (S\textsuperscript{geom}) are obtained to be 1, 1.30, and 1.89 for amorphous WS\textsubscript{x}, NiWS and CoWS, respectively.

To estimate the upper limit for the surface density of active sites, it is assumed that all the surface sites are catalytically active. The quantity of surface sites is calculated based on the geometry of 2H-WS\textsubscript{2}.\textsuperscript{S10} As an approximation, it is postulated that the average area of surface sites has the same value as the WS\textsubscript{2} unit in the 2H-WS\textsubscript{2} basal planes.\textsuperscript{S10} The calculated surface area of a WS\textsubscript{2} unit is 0.26 nm\textsuperscript{2}, according to the hexagonal arrangement of sulfur atoms and S-S bond length of 0.318 nm on the 2H-WS\textsubscript{2} surface.\textsuperscript{S11}

The lower limit TOF per site at a given current density of j mA cm\textsuperscript{-2} is calculated as follows:
\[
\text{TOF} = j \text{mA cm}^{-2} \times 1 \text{cm}^2 \times \frac{1}{1.602 \times 10^{-19} \text{C}} \times \frac{1}{2} \times \frac{1}{\text{RF}_{\text{BET}} \times 1 \text{cm}^2 / 0.26 \text{nm}^2}
\]

\[
= 8.2 \times \frac{j}{\text{RF}_{\text{BET}}} \text{ s}^{-1}
\]

Using this formula, the TOF values of hydrogen molecules evolved per second are calculated to be 0.34 and 0.12 s\(^{-1}\) at 300 mV overpotential for the amorphous NiWS and CoWS films on FTO electrodes, respectively.
Table S1. Comparison of various MX$_2$-based HER catalysts in acid media.

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<th>Catalyst</th>
<th>$b$ (mV dec$^{-1}$)</th>
<th>$j_0$ (μA cm$^{-2}$)</th>
<th>$\eta$ (mV) at 10 mA cm$^{-2}$</th>
<th>Ref</th>
</tr>
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(*) Calculated or read based on their data.
References


