Efficient hydrogen evolution by ternary molybdenum sulfoselenide particles on self-standing porous nickel diselenide foam

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With the massive consumption of fossil fuels and its detrimental impact on the environment, methods of generating clean power are urgent. Hydrogen is an ideal carrier for renewable energy; however, hydrogen generation is inefficient because of the lack of robust catalysts that are substantially cheaper than platinum. Therefore, robust and durable earth-abundant and cost-effective catalysts are desirable for hydrogen generation from water splitting via hydrogen evolution reaction. Here we report an active and durable earth-abundant transition metal dichalcogenide-based hybrid catalyst that exhibits high hydrogen evolution activity approaching the state-of-the-art platinum catalysts, and superior to those of most transition metal dichalcogenides (molybdenum sulfide, cobalt diselenide and so on). Our material is fabricated by growing ternary molybdenum sulfoselenide particles on self-standing porous nickel diselenide foam. This advance provides a different pathway to design cheap, efficient and sizable hydrogen-evolving electrode by simultaneously tuning the number of catalytic edge sites, porosity, heteroatom doping and electrical conductivity.
The large consumption of fossil fuels and its impact on the environment make it urgent to develop environmentally friendly and renewable energy sources. Hydrogen (H₂) is an attractive and promising energy carrier because of its high energy density and no pollution gas emission. One direct and effective route to generate H₂ is based on electrocatalytic hydrogen evolution reaction (HER) from water splitting, in which an efficient catalyst is required to ensure the energy efficiency. Platinum (Pt)-based noble metals are by far the most active catalysts; however, they are not suitable for large-scale applications because of the high cost and scarcity of Pt on earth. Thus, we aim to identify alternative electrocatalysts based on earth-abundant and cost-effective elements. Until now, various classes of earth-abundant transition metal compounds are confirmed to be promising candidates, such as metal sulfides, selenides, phosphides, carbides and the composites. However, far most of the catalysts exhibit inferior efficiency to Pt, while many involve complicated preparation methods and multiple steps that increase costs. Great progress has been obtained for HER on layered transition metal dichalcogenides (LTMDs) such as molybdenum disulfide (MoS₂) either in the form of crystalline or amorphous states, and even in molecular mimics. However, it remains a challenge to get catalytic performance comparable to that of Pt, which is probably due to the low density and reactivity of active sites, poor electrical transport and inefficient electrical contact to the catalyst.

On the basis of the above results, fabricating MoS₂ or its derivatives into hybrids or composites might be an interesting strategy to promote the catalytic performance. Currently, carbon-based materials are generally used as the catalyst support because of their high surface area and good conductivity. However, complex catalyst synthesis procedures are typically required. As an alternative, arranging the catalysts into double-gyroid structures with numerous nanopores might lead to improved HER activity because of preferential exposure of catalytic active edges rather than the inactive basal planes. This approach reminds us of the necessity to make three-dimensional (3D) catalysts with high surface area loaded on porous supports, fast proton transfer and greater contact areas with reactants during the catalytic process. Meanwhile, the bottleneck of the double-gyroid structures is the intrinsically poor conductivity of the catalysts. Thus, even though MoS₂ is established as an effective HER catalyst since 2005, it is still difficult to obtain satisfactory catalysts in low costs on par with the current Pt catalysts. In the light of these challenges, we conclude that the best strategy is to improve the dispersion and electrical conductivity of these catalysts on the supports and to expose a large number of active edge sites. Furthermore, we propose using 3D catalysts with high surface area loaded on porous supports, which are the promising candidates.

In this work, we propose a strategy of growing ternary molybdenum sulfoselenide MoS₂(1−x)Se₂x particles with vertically aligned layers on a 3D porous HER-active conductive nickel diselenide (NiSe₂) scaffold, which takes advantage of the merits of highly conductive support, double-gyroid structures (3D, porous and lots of exposed edge sites) and synergistic effects between two different catalysts. Indeed, we measure excellent HER performance for this hybrid catalyst that is superior to most reported transition metal dichalcogenides (MoS₂, cobalt diselenide CoSe₂ and so on).

Results
Preparation of 3D porous hybrid electrocatalyst. To the best of our knowledge, the majority of HER catalysts reported thus far are based on nanostructures (nanoparticles, nanosheets and so on); thus, binder polymers (for example, nafion solution) are necessary to fasten the catalysts on the conducting substrates such as glassy carbon electrodes, which somewhat increases the cost. This problem can be avoided by growing the active catalysts directly on self-standing conducting skeletons as the current collectors. The key challenge is to find a suitable 3D supports with high surface area, high porosity and good conductivity. Graphene or carbon nanotube is not feasible because of their high costs. Instead, nickel (Ni) foam is suitable because of its low price, commercial availability and 3D skeleton structure. We find that numerous additional pores are generated in the NiSe₂ foil, which provides preferential sites for growing LTMD catalysts with high-density active edges. Thus, we propose using 3D porous NiSe₂ foam as a conductive skeleton to load ternary MoS₂(1−x)Se₂x catalysts.

Structural characterizations of the electrocatalyst. The chemical composition of the as-grown particles was examined using high-resolution transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and energy-dispersive X-ray spectroscopy. TEM images (Fig. 2a,b and Supplementary Fig. 2) clearly resolve a large amount of vertically aligned MoS₂(1−x)Se₂x layers, suggesting that many active edge sites are exposed at the surface of MoS₂(1−x)Se₂x particles. It is reasonable since the porous structure of NiSe₂ foam with high surface area is favourable for the growth of layered materials with vertically aligned layers. Meanwhile, XPS spectra in the hybrid reveal the presence of Ni, Mo, S and Se elements (Fig. 2c–e). However, since the Se in NiSe₂ foam has a similar state to that in the molybdenum compound, we put a precursor-decorated Si substrate underlying the NiSe₂ foam during the second selenization. It is clear that the (NH₄)₂MoS₄ precursor has been converted to a distinctive ternary alloy phase at 500°C from the prominent Mo, S and Se signals in the XPS spectra (Fig. 2c–e). Especially in the Raman spectra (Fig. 2f), in comparison with pure MoS₂ that exhibits two prominent peaks at 380 cm⁻¹ (E₁g) and 406 cm⁻¹ (A₁g), there is another obvious peak located at 264 cm⁻¹ for the samples with a ternary phase, which can be ascribed to the A₁g mode of the Mo–Se bond. Compared with the Raman mode of the bulk MoS₂ crystals (~242 cm⁻¹), the blueshifts of this peak to 264 cm⁻¹ suggest a ternary MoS₂(1−x)Se₂x compound rather than a mixture of two solid phases. This Raman feature is also observed from the ternary phase grown on porous NiSe₂ foam, which is consistent with previously reported results on ternary MoS₂(1−x)Se₂x single crystals. By comparing the relative peak intensity between 264 and 380 cm⁻¹, we estimate that the atomic ratio between S and Se is ~1, which is further supported by the energy-dispersive X-ray spectroscopy analysis (Supplementary Fig. 3).

Hydrogen evolution catalysis. Considering the metallic and porous feature in the NiSe₂ foam, and the good dispersion and preferential orientation of ternary MoS₂(1−x)Se₂x.
particles, it is expected that this 3D architecture should have outstanding HER activity, such as low overpotentials, low Tafel slopes and large exchange current densities. To evaluate the catalytic performance of these ternary MoS$_2$-$x$Se$_2x$ particles on 3D porous NiSe$_2$ foam, we performed detailed electrocatalytic measurements via a standard three-electrode set-up in a 0.5 M H$_2$SO$_4$ electrolyte de-aerated with high-purity N$_2$. The loading of MoS$_2$-$x$Se$_2x$ catalysts is ~4.5 mg cm$^{-2}$. Figure 3a shows that the self-standing porous hybrid catalyst can afford a geometric current density of $-10$ mA cm$^{-2}$ at a very low overpotential of $-69$ mV for the ternary MoS$_2$-$x$Se$_2x$/NiSe$_2$ hybrid electrode (Supplementary Table 1). In contrast, for binary MoS$_2$ on NiSe$_2$ foam and pure NiSe$_2$ foam, overpotentials of $-118$ and $-153$ mV are needed to achieve $-10$ mA cm$^{-2}$, respectively. The catalytic overpotential ($-69$ mV) of the MoS$_2$-$x$Se$_2x$/NiSe$_2$ hybrid is also much lower than those of the best catalysts thus far based on LTMDs MoS$_2$ ($-110$ mV)\textsuperscript{18}, WS$_2$ ($-142$ mV)\textsuperscript{15} and WS$_2$-$x$Se$_2x$ ($-170$ mV)\textsuperscript{30}, and first-row transition metal dichalcogenides CoSe$_2$ ($-139$ mV)\textsuperscript{24}, NiSe$_2$ ($-136$ mV)\textsuperscript{26} and CoS$_2$ ($-142$ mV)\textsuperscript{31}, suggesting that our ternary MoS$_2$-$x$Se$_2x$ particles/NiSe$_2$ foam hybrid is an outstanding HER catalyst. Meanwhile, a Tafel slope, which is an inherent property of the catalyst, can be obtained by extracting the slopes from the linear regions in Tafel plots (Fig. 3b). We find that the ternary electrode possesses a smaller Tafel slope of $42.1$ mV per decade than that of binary MoS$_2$ on NiSe$_2$ foam ($58.5$ mV per decade) and pure NiSe$_2$ foam ($46.4$ mV per decade). In addition, our hybrid catalyst leads to a Tafel slope much lower than many previously reported cheap and efficient HER catalysts in the same electrolyte (Supplementary Table 2). More interestingly, based on the intercept of the linear region of the Tafel plots, the exchange current densities ($j_{th,geo}$) at the thermodynamic redox potential ($\eta = 0$) can be calculated to be $299.4 \mu$A cm$^{-2}$ for the ternary-phase hybrid catalysts. This exchange current density is one to two orders of magnitude larger than those of well-known LTMDs MoS$_2$ and WS$_2$, or first-row transition metal dichalcogenides CoSe$_2$ and CoS$_2$ catalysts (Supplementary Table 2). Thus, considering the small overpotential ($-69$ mV to reach $10$ mA cm$^{-2}$), low Tafel slope ($42.1$ mV per decade) and large exchange current density ($299.4 \mu$A cm$^{-2}$), it is worth pointing out that the catalytic performance of our as-prepared catalyst is superior to most of the MoS$_2$-based catalysts.

Aside from a stringent requirement for high HER activity, stability is another important criterion in evaluating the performance of an electrocatalyst. In our experiment, a long-term cyclic voltammetry (CV) test between $-0.20$ and $0.07$ V versus RHE shows no significant degradation of cathodic current densities for the hybrid catalyst after 1,000 cycles (Fig. 3c). Particularly, the cathodic current density for the hybrid catalyst remains stable and exhibits no obvious degradation for electrolysis at a given potential ($-69$ or $-121$ mV) for over a long period ($> 16$ h; Fig. 3d), suggesting the potential use of this catalyst over a long time in an electrochemical process. Even after long-term stability and cyclability tests, the catalytic performance of this hybrid catalyst still shows no degradation compared with...
spectra measured on different samples.

In different samples, such as binary MoS2 particles on Si, MoS2(110) surfaces of NiSe2. Molybdenum dichalcogenide with Se:S ratios of 0:1, 1:1, 1:0 are modelled, and, in the 1:1 case, the S and Se alternate above and below the plane to avoid strain. As shown in Fig. 4a, $\Delta G_{\text{H}}^\circ$ is 8.4 kcal mol$^{-1}$ for hydrogen adsorbed on

its initial state (Fig. 3c). In addition, the Faradaic efficiency for hydrogen evolution of this hybrid catalyst was evaluated (Supplementary Note 4). The efficiency is determined to be nearly 100% during 60 min of electrolysis (Supplementary Fig. 4).

To elucidate the origin of the differences in the overall catalytic performance among different catalysts, a simple CV method$^{15,20,24}$ was utilized to measure the corresponding electrochemical double-layer capacitances ($C_{\text{dl}}$) for evaluation of the electrochemically effective surface areas (Supplementary Fig. 5). Taking consideration of the direct proportion between the effective surface area and double-layer capacitance, we need to compare the capacitance values $C_{\text{dl}}$. By plotting the positive and negative current density differences ($\Delta j = j_a - j_c$) at a given potential (0.15 V versus RHE) against the CV scan rates, we can directly get the $C_{\text{dl}}$, which is equal to half the value of the linear slopes of the fitted lines in the plots. As shown in Fig. 3e, the MoS2(1−x)Se2x/NiSe2 hybrid electrode exhibits a $C_{\text{dl}}$ value of 319.15 mF cm$^{-2}$, which is one order of magnitude larger than that of pure MoS2/NiSe2 (30.88 mF cm$^{-2}$), and ~43 times larger than that of pure NiSe2 foam (7.48 mF cm$^{-2}$), demonstrating the proliferation of active sites in the porous hybrid catalyst, which accordingly results in the improved catalytic performance. From these capacitance values, we can roughly calculate the electrochemically effective surface area, and thus the turnover frequency per site (0.030 s$^{-1}$ at 100 mV and 0.219 s$^{-1}$ at 150 mV, see Supplementary Table 3) by using a similar calculation method developed by Jaramillo et al.$^{32}$ (Supplementary Note 5). The turnover frequency values are larger to that of transition metal phosphide-based electrocatalysts (Supplementary Table 3). On the other hand, electrochemical impedance spectroscopy was carried out to examine the electrode kinetics under the catalytic HER-operating conditions (Fig. 3f).

According to the Nyquist plots and data fitting to a simplified Randles circuit, our results clearly reveal that the charge-transfer resistance ($R_{\text{ct}}$) for the MoS2(1−x)Se2x/NiSe2 hybrid is much smaller than that for pure MoS2/NiSe2 ($R_{\text{ct}}$~ 8 Q) or for porous NiSe2 foam alone ($R_{\text{ct}}$~ 22 Q). In addition, all the catalysts have very small series resistances ($R_s$~ 0.6 – 1.2 Q), suggesting high-quality electrical integration of the catalyst with the electrode.

Quantum mechanics calculations. To understand the improvement on the catalytic hydrogen evolution of the MoS2(1−x)Se2x/NiSe2 hybrid catalyst, quantum mechanics calculations at the density functional theory (DFT) level (PBE-D3 flavor, see Supplementary Note 6) were performed to calculate the binding free energies of hydrogen on the Mo atom.$^{11,23}$ Although it was originally suggested that the edge S atom is the catalytic atom in hydrogen evolution on MoS2 (ref. 11), we find that H$_2$ formation going through the Mo atom via the Heyrovsky reaction$^{33}$ has a lower barrier than the Heyrovsky and Volmer$^{34}$ reaction on the S atom. Therefore, we use a lower hydrogen-binding energy on the Mo atom as the indicator of a lower barrier in the Heyrovsky step. Since there are various exposed facets in our as-prepared NiSe2 foam (Supplementary Fig. 1), we modelled the reaction on the simple low-index (100), (110) and (111) surfaces of NiSe2. Molybdenum dichalcogenide with Se:S ratios of 0:1, 1:1, 1:0 are modelled, and, in the 1:1 case, the S and Se alternate above and below the plane to avoid strain. As shown in Fig. 4a, $\Delta G_{\text{H}}^\circ$ is 8.4 kcal mol$^{-1}$ for hydrogen adsorbed on...
Figure 3 | Electrocatalytic performance of different catalysts. (a) The polarization curves recorded on MoS$_2$(1-x)Se$_2$/NiSe$_2$ foam hybrid, MoS$_2$/NiSe$_2$ foam hybrid and pure NiSe$_2$ foam electrodes compared with a Pt wire. (b) Tafel plots recorded on the catalysts in a. (c) Polarization curves showing negligible current density loss of ternary MoS$_2$(1-x)Se$_2$/NiSe$_2$ hybrid electrodes initially, after 1,000 CV cycles and after the stability test. (d) Time dependence of current densities $-10$ and $-140$ mA cm$^{-2}$ recorded on the MoS$_2$(1-x)Se$_2$/NiSe$_2$ hybrid electrode under given potentials of $-69$ and $-121$ mV, respectively. (e) Plot showing the extraction of the $C_{dl}$ from different electrodes. (f) Electrochemical impedance spectroscopy (EIS) Nyquist plots of different electrocatalysts. The data were fit to the simplified Randles equivalent circuit shown in the inset. The loading of MoS$_2$(1-x)Se$_2$/NiSe$_2$ catalyst is 4.5 mg cm$^{-2}$.

MoS$_2$(1-x)Se$_2$/NiSe$_2$ which is more reactive than MoS$_2$/MoS$_2$ with a $\Delta G^{*}$ of 10.6 kcal mol$^{-1}$, agreeing with the reported experimental results (Supplementary Figs 6 and 7)\textsuperscript{35,36}.

In contrast, once the MoS$_2$/MoS$_2$ and MoS$_2$(1-x)Se$_2$/MoS$_2$(1-x)Se$_2$ hybrid structures of HER-active NiSe$_2$ foam: first, similar to MoS$_2$, the catalytic property of MoS$_2$(1-x)Se$_2$/NiSe$_2$ hybrid catalyst is greatly related to the number of exposed edge sites\textsuperscript{1,13,17}. Indeed, in our experiments, because of the porous structure and curved surface of as-grown NiSe$_2$ foam, ternary MoS$_2$(1-x)Se$_2$ layers tend to exhibit vertical orientation on the NiSe$_2$ surface as demonstrated using high-resolution TEM, indicating that abundant active edge sites
are exposed in these MoS$_2$–x$\rightarrow$Se$_2$x particles. Second, the electrical conductivity of MoS$_2$(1–x)S$_2$/NiSe$_2$ catalysts is another crucial factor to the electrocatalytic activity since the intrinsic conductivity is extremely low between two adjacent van der Waals bonded S–Mo–S layers. In our case, the MoS$_2$(1–x)Se$_2$x layers are vertically oriented, which enhance the electron transfer from the electrode to the MoS$_2$(1–x)Se$_2$x layers. Furthermore, the underlying NiSe$_2$ foam is metallic and is composed of lots of 3D porous structures that ensure rapid electron transport from the less-conducting MoS$_2$(1–x)Se$_2$x to the electrodes, and easy diffusion of the electrolyte into the active sites. Finally, the Gibbs free energy for hydrogen adsorption on MoS$_2$(1–x)Se$_2$x edges plays significant roles in this HER process, which is much lower compared with MoS$_2$, leading to higher coverage of hydrogen adsorption at the active sites. Thus, by using this strategy, we can simultaneously engineer the catalysts with high surface area, 3D porous structures, good electrical conductivity and a large number of exposed active edge sites.

In summary, we propose and validate a simple and efficient strategy to synthesize a robust and stable self-standing hydrogen-evolving catalyst by simply growing ternary MoS$_2$(1–x)Se$_2$x particles on 3D porous and metallic NiSe$_2$ foam. According to our experimental results and quantum mechanics DFT calculation, these MoS$_2$(1–x)Se$_2$x/NiSe$_2$ hybrid catalysts exhibit an outstanding catalytic performance superior to that of the widely reported LTMD catalysts (especially MoS$_2$, WS$_2$ and so on) and first-row transition metal pyrites (Co$_2$Se$_2$, Co$_2$S and so on). Our catalysts are very effective in catalysing hydrogen production by integrating metal dichalcogenides and pyrites into 3D hybrid architectures that possess high surface area, porous structures, good electrical conductivity and abundant active edge sites, making it promising to realize large-scale water splitting.

Methods

**Material synthesis.** 3D porous NiSe$_2$ foam was directly synthesized by thermal selenization of commercial Ni foam in a tube furnace. Then, the as-prepared NiSe$_2$ foam was immersed in (NH$_4$)$_2$MoS$_4$ solution in dimethylformamide (DMF) solvent (5 wt% (NH$_4$)$_2$MoS$_4$ in DMF) and dried on the hot plate, followed by thermolysis or second selenization at 500 °C in the tube furnace. The details are shown in the Supplementary Information.

**Electrochemical measurements.** The electrochemical measurements were conducted in a three-electrode setup with an electrochemical station (Gamry, Reference 600). The polarization curves were collected by linear sweep voltammetry with a scan rate of 0.5 mV s$^{-1}$ in 82 ml of 0.5 M H$_2$SO$_4$, so as to suppress the capacitive current due to the high surface area and high porosity of the porous samples. A saturated calomel electrode was used as the reference electrode, a Pt wire (CH Instruments Inc.) as the counter electrode and as-prepared hybrid catalysts as the self-supported working electrodes. During the electrochemical measurements, high-purity N$_2$ gas was continually bubbled throughout the whole electrochemical measurement. Potentials versus RHE can be calculated by comparing with saturated calomel electrode by adding a value of 0.263 V after calibration. The electrochemical stability of the catalyst was evaluated by continuously cycling the catalyst for 1,000 times at a scan rate of 50 mV s$^{-1}$. Chronoamperometry was performed under a given potential for the MoS$_2$(1–x)Se$_2$x/NiSe$_2$ hybrid electrode. The electrochemical impedance spectroscopy test was carried out in the same device configuration at a potential of –0.15 V versus RHE with the frequency ranging from 10 mHz to 1 MHz with a 10 mV AC dither. All the potentials used here were referred to RHE.

**Data availability.** The data that support the findings of this study are available from the corresponding author upon request.

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Author contributions
Z.R. guided the project and discussed the experimental results. H.Z. conceived, designed and performed the experiments (SEM, Raman, XPS and HER tests) and analysed the data. F.Y. conducted catalyst synthesis by CVD method and helped to collect the HER data. Y.H., R.J.N. and W.A.G. carried out the first-principles calculations. J.S. performed TEM characterizations. R.H. carried out XRD characterization. S.C. contributed to the result discussion, device design and measurements. Z.Z. and J.B. measured the Faradaic efficiency. H.Z., S.C. and Z.R. wrote the paper. All the authors discussed the results and revised the paper.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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