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Broader context

Outstanding hydrogen evolution reaction catalyzed by porous nickel diselenide electrocatalysts†

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To relieve our strong reliance on fossil fuels and to reduce greenhouse effects, there is an ever-growing interest in using electrocatalytic water splitting to produce green, renewable, and environment-benign hydrogen fuel *via* the hydrogen evolution reaction. For commercially feasible water electrolysis, it is imperative to develop electrocatalysts that perform as efficiently as Pt but using only earth-abundant commercial materials. However, the highest performance current catalysts consist of nanostructures made by using complex methods. Here we report a porous nickel diselenide (NiSe₂) catalyst that is superior for water electrolysis, exhibiting much better catalytic performance than most first-row transition metal dichalcogenide-based catalysts, well-studied MoS₂, and WS₂-based catalysts. Indeed NiSe₂ performance, we use first-principles calculations to identify the active sites. This work demonstrates the commercial possibility of hydrogen production *via* water electrolysis using porous bulk NiSe₂ catalysts.

Hydrogen is a clean, environmentally benign and renewable energy carrier. The hydrogen evolution reaction is a simple and cost-effective route to produce hydrogen from water splitting, which requires cheap, earth-abundant, and efficient catalysts instead of precious Pt catalysts. Although tremendous effort has been dedicated to fabricating robust catalysts from earth-abundant materials, it remains a great challenge to make an efficient catalyst directly from commercial materials without involving complex synthetic methods. Here we demonstrate that commercially available nickel (Ni) foam, which is very cheap, highly conductive and has rich macroporosity, can be effectively utilized as the starting materials to fabricate robust porous NiSe₂ electrocatalysts with tunable surface porosities by simple acetic acid treatment and thermal selenization in an Ar atmosphere. Remarkably, this NiSe₂ catalyst exhibits outstanding catalytic activity that is better than many other robust catalysts consisting of nanostructures and approaches the benchmark Pt catalysts. First-principles calculations further shed light on the origin of the active sites. This indicates that NiSe₂ holds the potential to replace Pt in possible industrial applications of electrocatalytic water splitting.

Concerns about the continued significant deterioration of the Earth's ecological environment make it imperative to explore alternative energy resources to reduce the consumption of fossil fuels. Since water is an abundant and renewable resource on earth, the best solution is to use hydrogen (H₂) produced from water splitting as a green and renewable energy carrier to reduce our reliance on limited natural energy resources.¹

Electrochemical water splitting *via* the hydrogen evolution reaction (HER) is a straightforward and clean route to produce H_2 with high efficiency on a large scale. However, this route is still not widely deployed primarily due to the high production costs of the electrocatalysts, compared to Pt.^{2,3} Thus the search for efficient and durable electrocatalysts from earth-abundant and cost-effective elements to replace the scarce and precious Pt-group metals is a central research topic for energy.⁴

Currently, a number of earth-abundant compounds are found to be competitive alternatives,^{4–7} including layered transition metal dichalcogenides (edge-active MoS_2 , WS_2 ; surface-active NbS_2 and TaS_2 , *etc.*), first-row transition metal dichalcogenides (CoS_2 , $CoSe_2$, *etc.*), transition metal carbides (WC, Mo_2C), transition metal phosphides (Ni_2P , CoP), and so on. Although great progress has been made on these catalysts, the majority of the

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Paper

catalysts are in the form of nanostructures including nanoparticles, nanosheets, and nanoribbons,5,6,8-11 which involve complex preparation methods and require expensive conductive polymers for electrode fabrication, making scale-up quite challenging. Due to the high surface area and good conductivity (carbon cloth, carbon fiber paper, carbon nanotube arrays), the most practical fabrication is nothing more than using hydrothermal or solvothermal methods to grow nanostructured catalysts anchored on self-standing conductive carbon supports.^{8,9,12-14} However, this is still too complicated to be applied for industrial applications. Rather than carbon supports, commercial nickel (Ni) foam is an attractive starting material because of its low price, high conductivity, rich macroporosity, and structural integrity.¹⁵⁻¹⁸ Thus, it is highly desirable to find a novel strategy to prepare exceptional catalysts using only commercial materials like Ni foam without involving complicated procedures.17,18

The traditional and effective way to boost catalytic performance is increasing the effective surface areas of the catalyst through fabricating nanostructures (nanowire or nanosheet arrays),19-21 introducing porous structures14,18,22,23 or utilizing conductive carbon supports.^{8,12,13,24,25} Even though these three routes can result in robust and stable catalysts for the HER, such material synthesis still involves complicated recipes. Therefore, to boost the hydrogen economy to reduce the use of fossil fuels in the near future, we consider that it is urgent to develop a simple route for large scale HER. Following this line of thought, we have devoted our efforts to developing a simple and novel strategy to fabricate robust catalysts from commercially available Ni foam by surface engineering, leading to large scale and low-cost preparation of robust HER catalysts. Indeed, we demonstrate that surface engineering using a mild acetic acid is a simple but very effective means to achieve outstanding NiSe₂ electrocatalysts, leading to hydrogen evolution with a Faradaic yield of nearly 100%. This catalytic performance is better than most robust catalysts composed of nanostructures, and is very close to the state-of-the-art Pt catalysts with almost the same Faradaic efficiency. This indicates that NiSe₂ has the potential to replace Pt in commercial applications.

The pyrite-type transition metal dichalcogenides $(MX_2,$ where M = Fe, Co, or Ni and X = S or Se), which are abundant minerals in the Earth's crust, have proved to be promising lowcost materials with high catalytic activities.^{13,26-28} However, almost all reported catalysts failed to catalyze hydrogen evolution with the activity comparable to Pt in acidic media. It is worth mentioning that the bulk crystals for these materials are good conductors but show poor catalytic performance, whereas their nanostructures exhibit better activity but lower conductivity.29 We believe that high surface area and good conductivity must be combined to obtain outstanding catalytic performance for this kind of catalyst, and we demonstrate a simple two-step process for achieving this from commercial Ni foams (Fig. 1a): immersing the Ni foam in HAc solution and drying, followed by gas-phase selenization in an Ar atmosphere (Fig. 1b-e). Notably, this facile design endows the NiSe₂ foam with four characteristics: high porosity, good conductivity, sharp surface features with many active sites, and rigid support provided by a bulk NiSe₂ foam

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Fig. 1 Synthesis and microscopic characterization of the as-prepared NiSe₂ samples from commercial Ni foam. (a) A typical SEM image of the commercial Ni foam. The inset shows the Ni grains and grain boundaries. (b and c) Typical SEM images showing the surface roughness of the as-prepared NiSe₂ foam from HAc-treated commercial Ni foam (H-NiSe₂). (d and e) Typical SEM images showing the surface roughness of the as-synthesized NiSe₂ foam from HAc and PVP co-treated commercial Ni foam (HP-NiSe₂). (f) High-resolution TEM image. (g) The bright field TEM image and the corresponding elemental mapping showing the uniform distribution of Ni and Se. (a, b and d) Scale bar: 200 μ m. (c, e and g) Scale bar: 1 μ m. (f) Scale bar: 1 nm.

without the presence of contact resistance between the catalyst and its support since they are the same materials, which are the key factors contributing to the excellent catalytic performance.

In particular, we find that the utilization of polyvinylpyrrolidone (PVP) and HAc plays a significant role in enhancing the surface roughness of the NiSe₂ catalysts. Obviously, among these three kinds of samples, the NiSe2 made from HAc and PVP co-treated Ni foam (HP-NiSe2, Fig. 1d and e) exhibits the roughest surface, the one from the HAc-treated Ni foam (H-NiSe₂, Fig. 1b and c) is the second roughest, and the as-prepared one from the original Ni foam without other treatment (A-NiSe₂, Fig. S1, ESI⁺) is the least rough. This means that the effective electrochemical surface area of the NiSe₂ catalysts can be effectively tuned by the HAc treatment.²² To gain further insight into the crystal structure of the as-prepared NiSe₂ foam, we performed detailed transmission electron microscopy (TEM) characterization to gain elemental composition and distribution information. It is apparent from the highresolution TEM image (HRTEM, Fig. 1f) that there are two lattice fringes with inter-plane spacings of 0.24 nm and 0.30 nm, corresponding to the (211) and (200) planes of pyrite NiSe₂, respectively.¹² We find that Ni and Se are the only two elements with an atomic ratio of 1:2.04 (Fig. S2, ESI⁺) and that they are distributed uniformly (Fig. 1g). These results confirm the successful conversion of commercial Ni foam to a three-dimensional porous NiSe₂ foam with engineered surface roughness.

X-ray powder diffraction (XRD), Raman spectroscopy, and X-ray photoelectron microscopy (XPS) were employed to further determine the phase, purity, and elemental composition of the final products (Fig. 2). As expected, the typical XRD spectra (Fig. 2a) show that all the as-prepared porous materials are composed of pyrite NiSe₂ with the peaks in a one-to-one correspondence with the standard XRD pattern (ICSD no. 40330), confirming the observations by TEM (Fig. 1f, g and Fig. S2, ESI[†]). It is worth noting that nearly no XRD peaks are observed corresponding to metallic Ni, suggesting the very high purity of the as-grown samples and nearly complete conversion of the Ni foam to porous NiSe₂ foam. On the other hand, four Raman peaks are clearly detected with frequencies located at around 152.7 cm⁻¹, 171.5 cm⁻¹, 217.2 cm⁻¹, and 243.3 cm⁻¹, corresponding to the T_g , E_g , A_g , and T_g modes of NiSe₂, respectively. These observations are in good agreement with the literature results on pyrite $NiSe_2$.^{16,26,30} As shown in Fig. 2c and d, XPS data show clearly the main signals of Ni and Se elements, carbon contamination, and adsorbed oxygen (Fig. S3, ESI[†]). Deconvoluting the Se peak, we find four peaks with the binding energies Se $3d^{5/2}$ at 54.3 eV and Se $3d^{3/2}$ at 55.1 eV originating from a pyrite NiSe₂ compound,^{13,16,27} and two other peaks with binding energies Se $3d^{5/2}$ at 55.6 eV and Se $3d^{3/2}$ at 56.4 eV that correspond to residual Se species. This suggests that a very small amount of residual Se is observed on the surface. Thus, despite the differences in the three preparation methods, XPS, XRD, and Raman characterization indicate that all the final products are pyrite NiSe₂ foams.

Surface pre-treatment of the Ni foam can change the surface roughness of the as-grown NiSe₂ foams, endowing them with some unique attributes toward hydrogen evolution: high porosity to ensure fast exchange of the protons,^{18,31} high-density sharp features to expose many active catalytic sites,^{8,22} the absence of



Fig. 2 Characterization of the as-prepared NiSe₂ foams by XRD, Raman, and XPS. (a) Typical XRD patterns of different porous NiSe₂ foams compared to the standard index cards Ni and NiSe₂. (b) Raman spectra of different porous NiSe₂ foams. (c and d) XPS analysis of the Ni 2p and Se 3d spectra of different NiSe₂ foams. It is noted that a small amount of elemental Se is deposited on the samples.

contact resistance between the NiSe₂ catalyst and its support, and good conductivity to facilitate electron transfer between the catalyst and electrode, all of which should play positive roles in the enhancement of catalytic properties. To verify this point, the HER performance (Fig. 3) for different NiSe₂ catalysts were tested via a three-electrode electrochemical configuration in an N₂-saturated 0.5 M H₂SO₄ electrolyte (Fig. S4, ESI⁺).^{16,18} Since the NiSe₂ foam is self-supported, there is no necessity to use polymers for electrode fabrication, and the catalyst can be directly connected to the working electrode for electrochemical tests. All the potentials shown here were referenced to the reversible hydrogen electrode (RHE). Fig. 3a shows the polarization curves recorded on different as-grown NiSe₂ foams in comparison to a Pt wire. Obviously, the H-NiSe₂ and HP-NiSe₂ catalysts exhibit an enormous increase in the cathodic current density (Table S1, ESI[†]) compared to the A-NiSe₂ foam. A normal criterion is to compare the overpotential vs. RHE at a geometric current density of 10 mA cm⁻². The A-NiSe₂ foam requires a large overpotential of -153 mV vs. RHE to yield such a current density of 10 mA cm⁻². In contrast, this overpotential is greatly reduced to -107 mV vs. RHE for H-NiSe₂ catalysts and to -57 mV vs. RHE for HP-NiSe₂ catalysts, which is lower than those for first-row transition metal dichalcogenides CoSe2



Fig. 3 The electrocatalytic performance of different NiSe₂ catalysts toward hydrogen evolution. (a) The polarization curves of the as-prepared NiSe₂ catalysts from original (A-NiSe₂), HAc-treated (H-NiSe₂), HAc and PVP-treated Ni foams (HP-NiSe₂) in comparison with a Pt wire. (b) Relevant Tafel plots of different catalysts. (c) Hydrogen amount from theoretical calculations (solid) and experimental tests (sphere) *versus* time for the NiSe₂ catalyst at -20 mA for 60 min. (d) The extracted double-layer capacitances (C_{dl}) of different NiSe₂ electrodes using a cyclic voltammetry method. (e) EIS Nyquist plots recorded on different NiSe₂ electrodes with the potential set at -0.14 V *vs.* RHE. (f) Stability tests of H-NiSe₂ and HP-NiSe₂ catalysts.

(-139 mV vs. RHE),¹³ NiSe₂ (-117 mV vs. RHE),²⁷ and FeS₂ (-104 mV vs. RHE),²⁹ non-pyrite metal phosphides CoP $(-75 \text{ mV } \nu s. \text{ RHE})^{20}$ and Mo-W-P $(-100 \text{ mV } \nu s. \text{ RHE})$,¹⁴ wellstudied layered transition metal dichalcogenides like MoS₂/CNT $(-110 \text{ mV } \nu s. \text{ RHE})$,¹² MoS_{2(1-x)}Se_{2x}/NiSe₂ (-69 mV $\nu s. \text{ RHE})$,¹⁸ WS₂ (-142 mV vs. RHE),¹⁰ and WS_{2(1-x)}Se_{2x}/NiSe₂ (-88 mV vs. RHE),³¹ and transition metal oxides such as $WO_{2.9}$ (-70 mV vs. RHE),³² and MoO₂ (-64 mV vs. RHE).³³ These results are still inferior to a few reported electrocatalysts (Table S2, ESI[†]). Meanwhile, the superior catalytic performance of the H-NiSe₂ and HP-NiSe₂ catalysts is evidenced in the Tafel slopes typically utilized to evaluate HER electrocatalytic activity (Fig. 3b). Notably, the H-NiSe₂ (42.6 mV dec⁻¹) and HP-NiSe₂ (43.0 mV dec⁻¹) catalysts possess much lower Tafel slopes than A-NiSe₂ (46.0 mV dec⁻¹), which is desirable for practical applications since it ensures a dramatic increase in the HER rate with increased potential. In addition, the Faradaic efficiency, which is defined as the ratio between the experimental and theoretical (based on 100% yield) H₂ production, is found experimentally to be nearly 100% (Fig. 3c). This is comparable to that of noble Pt catalysts (10 mA cm⁻² at 32 mV vs. RHE) for hydrogen evolution in acid, indicating that NiSe₂ is a promising nonnoble and cost-effective electrocatalyst with excellent catalytic HER performance.

The exchange current density (j_0) at the thermodynamic redox potential ($\eta = 0$), which is another important metric to show the inherent activity, can be derived using the extrapolation method on the basis of the Tafel equation (Table S1, ESI⁺). It is interesting to note that the HP-NiSe₂ electrode has the highest j_0 (612 µA cm⁻²), which is around 9.5 times larger than that of H-NiSe₂ (64.6 μ A cm⁻²) and 71 times that of A-NiSe₂ (8.6 μ A cm⁻²). This value is also in the same order as reported for competitive catalysts consisting of low-cost and earth-abundant non-noble metal compounds (Table S2, ESI⁺), indicating the excellent catalytic activity of the HP-NiSe₂ catalysts. All these properties demonstrate that high porosity or surface roughness plays a dominant role in the improved catalytic performance of the HP-NiSe₂ catalysts, which can be further supported by measuring the electrochemically effective surface areas using a simple cyclic voltammetry (CV) method (Fig. 3d and Fig. S5, ESI†).8,16,18,31 The double-layer capacitance C_{dl} is half the value of the linear slope that describes the relationship between the current difference and scan rate. Supposing that the active surface area is proportional to the capacitance, a larger C_{dl} represents a higher surface area of the investigated catalyst. Thus, HP-NiSe2 has the highest surface area in our case, and the enhancement of the catalytic performance is mainly attributed to the increased active surface area from the engineered surface morphologies.

Good electrical conductivity is another important contributor to the outstanding catalytic activity of the H-NiSe₂ and HP-NiSe₂ catalysts, which is well manifested in their low Tafel slopes. This is in contrast to previous investigations on first-row transition metal dichalcogenides^{26,29,34} like FeS₂ and CoS₂ where poor conductivity in the nanostructures is a major obstacle to improving the catalytic activity. To clarify this point, we utilized electrochemical impedance spectroscopy (EIS) to reveal the electrode kinetics at the electrode/electrolyte interface of the electrocatalysts (Fig. 3e). The Nyquist plots for all the NiSe₂ electrodes can be well fitted with a simplified Randles model, from which we can gain the relevant series resistances (R_s) and charge-transfer resistances (R_{ct}). It is clearly revealed that the series resistances are in the range of 0.5–0.8 Ω , while all R_{ct} are very small, confirming that good conductivity is beneficial for the efficient charge transfer, which agrees well with the low Tafel slopes in Fig. 3b. This is reasonable since the as-prepared NiSe₂ foam is a bulk material, which is confirmed to show a metal-like electrical conductivity (Fig. S6, ESI†). Furthermore, these two catalysts H-NiSe₂ and HP-NiSe₂ show nearly negligible degradation in the current densities after 1000 cycles (Fig. 3f), corroborating their electrochemical stability in acid.

The HER activity of a site is reflected by the free energy of H adsorption, ΔG_{H^*} (ESI[†]). A site with ΔG_{H^*} closer to zero usually has a higher catalytic activity.³⁵ Our NiSe₂ catalysts have a pyrite structure as confirmed by the XRD patterns. The most commonly found surface of pyrite is the stoichiometric (001), which has been shown to have the lowest surface energy.³⁶ Therefore, we consider (001) here as a representative example. This surface has Ni atoms in a square lattice with Se dimers in the centers of the squares (Fig. 4a and b). We find that H prefers to be adsorbed at the top of a Ni site rather than to the Se site; however, its ΔG_{H^*} is rather high (>0.6 eV); therefore, the pristine surface is not active for HER. The ΔG_{H^*} becomes lower for some of the surface defect sites; for example, at the vacancies (e.g., Ni vacancy, Se monomer vacancy, and Se dimer vacancy), ΔG_{H^*} is further reduced to below 0.5 eV, but it is still significantly higher than 0.3 eV. Our calculations also show that the Ni atom adsorbed on the surface is not active ($\Delta G_{H^*} \sim 0.7 \text{ eV}$). Interestingly, with a Se monomer or dimer adsorbed on the surface, we find that $|\Delta G_{H^*}|$ is greatly reduced to ~0.1 eV close to that of the best HER catalyst Pt.35 Indeed, for our as-prepared NiSe₂ samples, a small fraction of elemental Se is detected on the surface from the XPS peak deconvolution of Se spectra and EDX analysis (atomic ratio Se/Ni = 2.04), suggesting that a Se rich condition might increase the catalytic sites of pyrite NiSe₂ for HER. This is consistent with the findings in the literature reports.^{27,37,38} Moreover, our calculations show that the binding energies of Se monomers and dimers to the NiSe2 surface are 2.49 eV and 0.75 eV, respectively, and the etching of these adsorbates into H₂Se is endothermic by 0.45 and 0.99 eV, suggesting that the Se monomers and dimers are stable on the surface.

Considering the nearly bulk state and metallic feature of the NiSe₂ foam, the superior performance we find for HP-NiSe₂ and H-NiSe₂ can probably be attributed to the enhanced surface roughness (or active surface area) resulting from the porous structures. That is, the superior catalytic activity of a bulk HP-NiSe₂ catalyst is a direct outcome of the following factors: (1) high electrochemically active surface area resulting from three-dimensional porous structures of the NiSe₂ foam, which ensures the catalyst has a greater contact area with reactants and sufficient transport of reactants and products; (2) good electrical conductivity from the bulk NiSe₂ crystal and the lack of contact resistance between the catalyst and the support



Reaction coordinate

Fig. 4 Identification of active sites for HER by DFT calculations. (a and b) Atomic structures of the active sites with H adsorption. For clarity, only the top stoichiometric layer of the (001) surface is shown. The bottom panel shows the side view. Grey: Ni; green: Se; white: H. (c) Calculated free energies of H adsorption on different sites, perfect: ideal surface; V-Ni: Ni vacancy; V-Se: Se monomer vacancy; V-2Se: Se dimer vacancy; ad-Ni: Ni atom adsorbed on the surface; ad-Se: Se monomer adsorbed on the surface.

facilitating the charge transfer from the electrode to the catalyst surface; (3) very low Gibbs free energy of H adsorption on a Se-adsorbed $NiSe_2$ catalyst toward hydrogen evolution, ensuring fast proton/electron adsorption and hydrogen release from the catalyst surface. Thus, on the basis of surface engineering, we can endow the as-prepared electrocatalysts with high surface area, good electrical conductivity, and considerable active sites.

Conclusions

In conclusion, we found a novel robust and stable porous $NiSe_2$ electrocatalyst for hydrogen evolution from the commercial Ni foam by simple acid treatment and direct selenization. Our experimental data confirm that surface engineering is a versatile route to construct porous $NiSe_2$ catalysts with outstanding catalytic activity better than most of the reported results on well-studied WS₂ and MoS₂ catalysts and first-row transition metal pyrites (CoSe₂, CoS₂, *etc.*), and nearly as good as the noble Pt catalysts. The fabrication procedure used here can be possibly scaled-up with low cost with potential use toward water electrolysis commercially.

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