Boosting hydrogen evolution on MoS$_2$ via co-confining selenium in surface and cobalt in inner layer

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The lack of highly efficient, inexpensive catalysts severely hinders large-scale application of electrochemical hydrogen evolution reaction (HER) for producing hydrogen. MoS$_2$ as a low-cost candidate suffers from low catalytic performance. Herein, taking advantage of its trilayer structure, we report a MoS$_2$ nanofoam catalyst co-confining selenium in surface and cobalt in inner layer, exhibiting an ultra-high large-current-density HER activity surpassing all previously reported heteroatom-doped MoS$_2$. At a large current density of 1000 mA cm$^{-2}$, a much lower overpotential of 382 mV than that of 671 mV over commercial Pt/C catalyst is achieved and stably maintained for 360 hours without decay. First-principles calculations demonstrate that inner layer-confined cobalt atoms stimulate neighbouring sulfur atoms while surface-confined selenium atoms stabilize the structure, which cooperatively enable the massive generation of both in-plane and edge active sites with optimized hydrogen adsorption activity. This strategy provides a viable route for developing MoS$_2$-based catalysts for industrial HER applications.
The electrochemical splitting of water for producing hydrogen via renewable energy supply is a significant, carbon-neutral technology for clean energy generation\(^1\)-\(^3\). However, the large-scale implementation of the reaction process is severely limited by scarcity of traditional platinum-based catalysts\(^4\),\(^5\). Two-dimensional MoS\(_2\), an earth-abundant material with unique structural and chemical properties, has shown attractive catalytic activity for the reaction and is considered as a potential alternative to the precious platinum-based catalysts in acidic medium\(^6\)-\(^14\). However, only the edge S sites of pure MoS\(_2\) are catalytically active for the HER and the vast amount of S sites in the basal plane are quite inert and not sufficiently utilized\(^15\)-\(^18\). Creating abundant edges is straight-forward but leads to high surface energy and low stability\(^15\),\(^19\),\(^20\). Doping metallic heteroatoms into the MoS\(_2\) lattice, on the one hand can effectively activate the basal plane S atoms and introduce in-plane active sites for the HER\(^19\),\(^21\)-\(^23\), whereas on the other hand it may also unavoidably lead to over-activation of the edges, resulting in overly strong adsorption of hydrogen at the edge sites which is detrimental to the HER activity. Thus, selectively activating the inert basal plane combined with stabilizing the edges without quenching the activity can maximally increase active sites of MoS\(_2\) for the HER, but is highly challenging owing to the difficulty in balancing the activity and stability.

MoS\(_2\) possesses a tri-layer atomic structure, which allows multidimensional manipulation of atomic composition to modulate the catalytic activity. Herein, we report a strategy of co-confining Se in the surface and Co in the inner layer of the MoS\(_2\) lattice, which enables simultaneously activation of the basal plane and stabilization of the edges and optimization of the hydrogen adsorption activity. Combined with a morphology-controlling method of fabricating three-dimensionally nanofoam architecture to promote edge formation, the massive generation of both in-plane and edge active sites are achieved in the synthesized MoS\(_2\) nanofoam with co-confined Co and Se atoms (Co/Se-MoS\(_2\)-NF). Such a catalyst exhibits a high HER activity at large current densities, which, to the best of our knowledge, surpasses those of all previously reported heteroatom-doped MoS\(_2\) catalysts and densities, which, to the best of our knowledge, surpasses those of all previously reported heteroatom-doped MoS\(_2\) catalysts and densities. Raman spectroscopy of a Se-MoS\(_2\)-NF sample displays a new satellite peak at the lower frequency side of the Mo-S vibrational peaks (Supplementary Fig. 3), which can be assigned to the A\(_{1g}\) mode of Mo-Se vibrations and thus indicates that Se atoms are embedded into the MoS\(_2\) lattice replacing the S atoms\(^27\)-\(^30\). In the X-ray absorption near-edge structure (XANES) spectra of Se K-edge, the Se-MoS\(_2\)-NF shows higher absorption edge than that in the MoS\(_2\) (Supplementary Fig. 4), denoting a higher oxidation state of the Se atoms in the Se-MoS\(_2\)-NF. It may be owing to the lower electronegativity of Se atom than that of S atom so that the Se atoms possess less charges in the Se-MoS\(_2\)-NF\(^{31}\)-\(^33\). These results demonstrate that the Se atoms are covalently doped into the MoS\(_2\) lattice rather than forming a new phase of MoSe\(_2\) or being adsorbed on the surface.

Se-doping combined with fabrication of nanofoam morphology leads to massive generation of edges. High resolution TEM (HRTEM) images show that the Se-MoS\(_2\)-NF possesses abundant edges compared with the MoS\(_2\) nanofoam (MoS\(_2\)-NF) and few-layer MoS\(_2\) (MoS\(_2\)-FL) (Fig. 1c and Supplementary Fig. 5). The clear crystal lattice fringes with an interplanar spacing of 0.66 nm denotes the (002) planes of the 2H phase of MoS\(_2\). X-ray photoelectron spectroscopy (XPS, Fig. 1d) characterizations show that a new doublet peak arises at around 164.9 and 163.7 eV for the Se-MoS\(_2\)-NF and MoS\(_2\)-NF samples, which can be assigned to the bridging disulfide (S\(_2^2\))– ligands at the edges\(^34\)-\(^37\). This confirms that establishing a nanofoam morphology is favorable for the formation of more edges. In addition, the S\(_2^2\)– content of 23% in the Se-MoS\(_2\)-NF sample obtained from the peak area is higher than that of 18% in the MoS\(_2\)-NF, thus implying that Se-doping further promotes the edge formation. This is also reflected by the extended X-ray absorption fine structure (EXAFS) spectroscopy of the Mo K-edge of these samples, which exhibits reduced Mo–Mo coordination of the Se-MoS\(_2\)-NF compared with those of the MoS\(_2\)-NF and MoS\(_2\)-FL (Fig. 1e), thus indicating a decreased lateral sizes and increased exposure of edges in the Se-MoS\(_2\)-NF\(^{21,26,38}\). DFT calculations also show that Se-saturated edge is more stable than S-saturated edge by 0.16 eV per Se replacing a S atom (Fig. 1f). These results demonstrate that Se-doping can promote the formation of abundant edges via stabilizing the edges. The Se-dopants were directly observed in the atomic-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of the Se-MoS\(_2\)-NF, showing the homogeneous dispersion of the Se atoms in the basal plane and at the edge of the Se-MoS\(_2\)-NF (Fig. 1g). The magnified image in Fig. 1h clearly illustrates that the S atoms are substituted by the Se atoms in accordance with the simulated image of the atomic model.

**Results**

**Se-doping promotes edge formation.** The terminating atoms of the MoS\(_2\) edges determine the stability and reactivity of the edges. Selenium being in the same group with S was introduced into MoS\(_2\) to modify the edge properties. A series of Se-doped MoS\(_2\) nanofoam (Se-MoS\(_2\)-NF) with different Se content were synthesized via a one-pot solvothermal method by using (NH\(_4\))\(_6\)MoO\(_4\)\(_2\)\(_4\)H\(_2\)O, CS\(_3\), and Se powder as precursors. Monodispersed SiO\(_2\) nanospheres were used as templates to fabricate a foam-like morphology. As shown in scanning electron microscopy (SEM) (Fig. 1a) and transmission electron microscopy (TEM) (Supplementary Fig. 1) images, the Se-MoS\(_2\)-NF possesses a nanofoam morphology with abundant spherical cavities (average pore size ~100 nm), which will favor the mass transportation of reactants to access more active sites of the catalysts\(^15\),\(^19\),\(^21\),\(^26\).

Comprehensive spectroscopic characterizations of the Se-MoS\(_2\)-NF samples were performed to investigate the geometric distribution and electronic states of the Se atoms. Energy-dispersive X-ray (EDX) analysis shows that the Mo, S, and Se elements are homogeneously distributed in the nanofoam framework (Fig. 1b). X-ray diffraction (XRD) analysis show no obvious difference in the crystallographic structure and lattice parameters of the Se-MoS\(_2\)-NF compared with those of the pure MoS\(_2\)-NF, which excludes the formation of new crystal phases after the Se doping (Supplementary Fig. 2 and Table 1). Raman spectroscopy of a Se-MoS\(_2\)-NF sample displays a new satellite peak at the lower frequency side of the Mo-S vibrational peaks (Supplementary Fig. 3), which can be assigned to the A\(_{1g}\) mode of Mo-Se vibrations and thus indicates that Se atoms are embedded into the MoS\(_2\) lattice replacing the S atoms\(^27\)-\(^30\). In the X-ray absorption near-edge structure (XANES) spectra of Se K-edge, the Se-MoS\(_2\)-NF shows higher absorption edge than that in the MoS\(_2\) (Supplementary Fig. 4), denoting a higher oxidation state of the Se atoms in the Se-MoS\(_2\)-NF. It may be owing to the lower electronegativity of Se atom than that of S atom so that the Se atoms possess less charges in the Se-MoS\(_2\)-NF\(^{31}\)-\(^33\). These results demonstrate that the Se atoms are covalently doped into the MoS\(_2\) lattice rather than forming a new phase of MoSe\(_2\) or being adsorbed on the surface.

**HER performance of the Se-MoS\(_2\)-NF.** The Se-MoS\(_2\)-NF samples present obviously enhanced HER activity compared with those of bulk MoS\(_2\), MoS\(_2\)-FL, and MoS\(_2\)-NF (Fig. 2a). The sample with Se doping content of 9.1% (Se(9.1)-MoS\(_2\)-NF)
exhibits the highest HER activity with overpotentials of 132, 187, and 224 mV at current densities of 10, 50, and 100 mA cm$^{-2}$, respectively (Fig. 2b). The decrease in activity as the Se doping content exceeds 9.1% may be resulted from the significantly weakened adsorption of H* at the over-doped Mo-edge Se sites with much positive adsorption free energies (Supplementary Fig. 6). The slopes of linear part of the Tafel plots were used to investigate the HER mechanism over these catalysts. The introduction of Se atoms leads to slight decrease in the Tafel slope of MoS$_2$ ranging from 75 to 80 mV dec$^{-1}$, which indicates a Volmer–Heyrovsky mechanism (Supplementary Fig. 7). From the electrochemical impedance spectroscopy (EIS) of the electrode kinetics, the Nyquist plots (Supplementary Fig. 8 and Table 2) reveal a remarkable decrease in the charge-transfer resistance ($R_{ct}$) from 44.1 $\Omega$ of the MoS$_2$-NF to 11.6 $\Omega$ of the Se(9.1)-MoS$_2$-NF, demonstrating the prominently improved interfacial electron-transfer kinetics over the Se(9.1)-MoS$_2$-NF. Durability tests show that the HER performance of the Se(9.1)-MoS$_2$-NF is well maintained for over 30 h at a current density of 10 mA cm$^{-2}$, whereas those of the MoS$_2$-NF and Pt/C (40 wt.%) drop rapidly (Supplementary Fig. 9). These results demonstrate the positive effect of Se doping in enhancing both the HER activity and stability of the MoS$_2$.

Properties of Co/Se-codoped MoS$_2$. Substituting the Mo with Co atoms can effectively activate the adjacent S atoms and improve markedly the HER performance over the MoS$_2$ basal plane. To combine the activating effect of Co-doping with the effect of Se-doping in enriching the edges and boosting the HER activity, we designed a series of Co/Se-codoped MoS$_2$ nanofoam (Co/Se-MoS$_2$-NF) to study the synergistic interplay between the dual-elements codoping.

The TEM (Supplementary Fig. 10) and SEM (Supplementary Fig. 11) images show that the Co/Se-MoS$_2$-NF possesses a similar morphology with that of the Se-MoS$_2$-NF, containing assemble of small-sized MoS$_2$ nano-flakes with abundant edges as presented in the HRTEM images (Supplementary Fig. 12). No nanoparticles or large clusters were observed in the TEM and HRTEM images of the Co/Se-MoS$_2$-NF. The HAADF-STEM and corresponding EDX mappings (Fig. 3a) demonstrate the well-dispersion of Co atoms (Supplementary Fig. 9). These results demonstrate the positive effect of Se doping in enhancing both the HER activity and stability of the MoS$_2$.
and Se atoms in the structure. This is also confirmed by the XRD analysis showing no other diffraction peaks of Co- or Se-related crystal phases until the Co-doping content reaches 12.2% or more (Supplementary Fig. 13). In addition, the Co K-edge EXAFS characterizations indicate that the Co atoms in the Co/Se-MoS2-NF are mainly coordinated by S atoms and the Co–S bond in Co/Se-MoS2-NF is shorter compared with that of the standard CoS sample (Fig. 3g). A Co–Se bond (2.54 Å) is notably longer than a Co–S bond (2.41 Å) according to our DFT calculations but is not observed, which indicates that CoSe phase should not be formed. Besides, the Co valence state in the Co/Se-MoS2-NF is totally different from those of the Co foil, Co3O4, and CoS standard samples and falls in between those of the CoS and CoO4 standard samples (Fig. 3g and Supplementary Fig. 14). Combined with the EXAFS results, it demonstrates that the Co atoms are covalently confined into the MoS2 lattice rather than being adsorbed on the surface or forming non-MoS2 hetero-phases such as CoS, CoSe, and CoO4. Atomic-resolution HAADF-STEM imaging of a monolayer Co/Se-MoS2-NF shows the embedding of Co atoms with a lower contrast at the Mo site and Se atoms being obviously brighter at the S site (Fig. 3b), as confirmed by simulated HAADF-STEM image in Fig. 3c. The Co atom is further identified by using atomic-resolution electron energy loss spectroscopy (EELS), which shows the feature peaks of L2 and L3 edges of the Co atom at the site A with lower contrast (Fig. 3c). Distribution of Co and Se atoms being adjacent or separated to each other were observed in the HAADF-STEM image according to the contrast analysis (Fig. 3d), and were confirmed by the simulated HAADF-STEM images and the line intensity profiles (Fig. 3e, f).

Compared with pure Se-doping which can reduce the Mo–Mo coordination and increase the edge formation, Co/Se-codoping can further decrease both the Mo–Mo and Mo–S coordination as shown in the Mo K-edge EXAFS spectra (Figs. 1e, 3h). This is also reflected by the increasing peaks of bridging disulfide S22− in the S 2p XPS spectra of the Co/Se-MoS2-NF compared with those of Se-MoS2-NF and MoS2-NF (Supplementary Fig. 15), thus demonstrating the effect of the Co/Se-codoping in further promoting the formation of edges. Co/Se-codoping also leads to significant changes to the electronic structures of the S atoms. A notably negative shift in S 2p binding energies of the XPS was observed after the Co/Se coding (Supplementary Fig. 16). In addition, the S L-edge XANES characterization shows that the intensity of the white line grows obviously higher after the Co/Se codoping compared with that of single-element Co- or Se-doped MoS2 with similar morphology (Fig. 3i). Co and Se atoms possess lower electronegativities than those of Mo and S atoms, so that the S atoms adjacent to the Co and Se dopants are more enriched with electrons, which synergistically modifies the electronic structures and hence the reactivity of S atoms39,40.

**HER performance of the Co/Se-MoS2-NF.** Considering the optimum Se-doping content of 9.1% in the Se-MoS2-NF offering the lowest overpotential, we adopted the same weight ratio of precursors for the Se and MoS2 and prepared a series of Co/Se-MoS2-NF samples with varied Co content from 4.0% to 14.6% to investigate the synergistic effect of Co/Se-codoping in tuning the HER activity. The onset overpotential of Co(4.0)/Se-MoS2-NF is significantly decreased compared with those of Se(9.1)-MoS2-NF and MoS2-NF (Fig. 4a). As the content of Co increases, the Co(10.4)/Se-MoS2-NF sample presents the lowest overpotentials of 104, 157, and 188 mV under the current densities of 10, 50, and 100 mA cm−2, respectively, which is superior to those of doped MoSe2 and MoS2 catalysts (Supplementary Fig. 17 and Table 3). Then the activity decreases as the Co content further grows to 12.2% or larger, which may be due to the formation of other crystal phases at high Co content21. The Co(10.4)/Se-MoS2-NF sample also presents a much lower Tafel slope of 67 mV dec−1 than those of 77 mV dec−1 for the Co(10.4)-MoS2-NF, 75 mV dec−1 for the Se(9.1)-MoS2-NF and 83 mV dec−1 for the undoped MoS2-NF, respectively (Fig. 4b). This clearly demonstrates the superior HER kinetics over the Co/Se-codoped MoS2 via the Volmer–Heyrovsky mechanism, which differs from that over the Pt/C (40 wt.%) electrocatalyst via the Volmer–Tafel mechanism with a Tafel slope of 29 mV dec−141,42.

The EIS measurements at a constant potential of 150 mV vs. reversible hydrogen electrode (RHE) indicate that the Co(10.4)/Se-MoS2-NF possesses the lowest Rct value comparing with all other samples (Fig. 4c and Supplementary Table 2). The Tafel slope derived from the EIS reflects purely the charge-transfer kinetics of the catalytic process and is different from that derived from the linear sweep voltammetry (LSV) curves, where the difference stems from the electronic resistances of the catalysts43,44. The much similar values of the EIS and LSV Tafel slopes for the Co(10.4)/Se-MoS2-NF sample indicates an improved conductivity of the catalyst (Supplementary Fig. 18). The double-layer capacitance (Cdl) extracted from the cyclic
voltammetry (CV) measurements was used to estimate the electrochemically active surface areas. The Co(10.4)/Se-MoS2-NF shows a higher $C_{dl}$ of 45.7 mF cm$^{-2}$ compared with those of 26.3 mF cm$^{-2}$ for the Co(10.4)-MoS2-NF, 30.7 mF cm$^{-2}$ for the Se(9.1)-MoS2-NF, and 15.8 mF cm$^{-2}$ for the MoS2-NF, respectively (Supplementary Figs. 19 and 20). This demonstrates that the Co(10.4)/Se-MoS2-NF possesses a higher catalytically active surface area and exposes more active sites.

More interestingly, the Co(10.4)/Se-MoS2-NF exhibits both superior HER activities and stability at practically high current densities. At 208 mA cm$^{-2}$, the overpotential becomes lower than that of the 40 wt.% Pt/C catalyst (Fig. 4d and Supplementary Fig. 21). At a higher large current density of 1000 mA cm$^{-2}$, the overpotential is only 382 mV and significantly lower than that of 671 mV over the Pt/C catalyst. The faradic efficiency for H2 production in a wide range of working potential is well maintained at ~100%, which indicates that there is almost no other reduction product (Supplementary Fig. 22). To the best of our knowledge, such HER activity of the catalyst also surpasses those of all previously reported heteroatom-doped MoS2 catalysts (Supplementary Table 3). More importantly, the activity can be well maintained for more than 360 h without decay at the large current density of 1000 mA cm$^{-2}$, while the activity of Pt/C catalyst will drop quickly within 50 h at the same test condition (Fig. 4e). The XRD (Supplementary Fig. 23) and SEM image (Supplementary Fig. 24) of the Co(10.4)/Se-MoS2-NF show no

**Fig. 3 Structural and electronic properties of the Co/Se-doped MoS2 nanofoam (Co/Se-MoS2-NF).** a HAADF-STEM image and corresponding EDX mappings of the Co/Se-MoS2-NF. b Atomic-resolution HAADF-STEM image of the Co/Se-MoS2-NF. c Enlarged and simulated images of the white dashed line region in b and the EELS spectra obtained at the site A and B via line scan. d Low pass filtered large area atomic-resolution HAADF-STEM image of the Co/Se-MoS2-NF. e Enlarged and simulated images of the white dashed line in d. f The measured intensity profile along three lines labeled in e. g Co K-edge $k^3$-weighted EXAFS spectra of Co/Se-MoS2-NF sample in comparison with CoS, Co3O4, and Co foil, respectively. Mo K-edge $k^3$-weighted EXAFS spectra (h) and S L-edge total electron yield X-ray absorption spectra (i) of Co/Se-MoS2-NF sample compared with Co-MoS2-NF, Se-MoS2-NF, and MoS2-NF. The Co/Se-MoS2-NF sample with 10.4% Co-doping content in atomic percentage was employed in these series of characterizations.

voltammetry (CV) measurements was used to estimate the electrochemically active surface areas. The Co(10.4)/Se-MoS2-NF shows a higher $C_{dl}$ of 45.7 mF cm$^{-2}$ compared with those of 26.3 mF cm$^{-2}$ for the Co(10.4)-MoS2-NF, 30.7 mF cm$^{-2}$ for the Se(9.1)-MoS2-NF, and 15.8 mF cm$^{-2}$ for the MoS2-NF, respectively (Supplementary Figs. 19 and 20). This demonstrates that the Co(10.4)/Se-MoS2-NF possesses a higher catalytically active surface area and exposes more active sites.

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change in the crystallographic and morphology structure after the 360 h of durability test. The inductively coupled plasma optical emission spectrometry (ICP-OES) measurement shows that the content of Pt in the sample after the durability test is below the detection limit, thus indicating that Pt is not likely deposited on the Co(10.4)/Se-MoS2-NF sample. These results demonstrate that the dual-element Co/Se-codoping can synergistically enhance both the HER activity and stability of MoS2, even under industrial-level large current densities.

Understanding the synergistic effect of Co/Se-codoping. DFT calculations were performed to study the synergistic effect of dual-element Co/Se-codoping in improving the HER performance of MoS2 (Fig. 5). Co-doping significantly enhances the adsorption of hydrogen on the basal plane S site with adsorption free energy of $H^*$ ($\Delta G_{H^*}$) decreasing from 2.01 to $-0.32$ eV (Fig. 5a). However, it also inevitably strengthens the adsorption of hydrogen on the Mo-edge S site with $\Delta G_{H^*}$ of $-0.47$ eV, which leads to over-binding of $H^*$ and is unfavorable for the HER at the Co-doped Mo-edge sites. Introducing Se into the Co-doped MoS2 compensates the over-strong adsorption of $H^*$ on both the Co-doped in-plane and edge sites and thereby moderately weakens their adsorption activity for $H^*$. At the Co/Se-codoped in-plane, Mo-edge, and S-edge sites, the $\Delta G_{H^*}$ are increased to $-0.21$, $-0.14$, and $0.10$ eV, respectively, from those of $-0.32$, $-0.46$, and $-0.10$ eV at the corresponding Co-doped sites (Fig. 5a, b). This indicates an improved HER activity at the Co/Se-codoped in-plane...
and Mo-edge sites with reduced overpotentials. In comparison, pure Se-doping only notably weakens the H\(^*\) adsorption at the Mo-edge but still lead to a good HER activity at the Mo-edge and S-edge sites with \(\Delta G_{H^*}\) of 0.08 eV and \(-0.10\) eV, respectively (Fig. 5a). Thus, the Co/Se-codoping brings a compromise between the enhancement effect of Co-doping and weakening effect of Se-doping on the hydrogen adsorption at the codoped sites, leading to more favorable hydrogen adsorption activities for the HER. In addition, Se-doping also prominently stabilizes the Co-doped basal plane and edges by forming Co–Se bonds (Fig. 5c, d), where the formation energies of Co/Se-codoped basal plane, Mo-edge, and S-edge can be reduced by 0.21, 0.12, and 0.07 eV per Co–Se bond formed, respectively, compared with those with Co and Se separated from each other. These results demonstrate a synergy between the activating effect of inner-layer Co-doping and the stabilizing effect of surface Se-doping in the Co/Se-codoped MoS\(_2\), which significantly improves the HER performance by simultaneously enriching active sites and optimizing their hydrogen adsorption activities.

**Discussion**

In summary, via co-confining Se in the surface and Co in the inner layer of the MoS\(_2\) combined with fabricating a nanofoam architecture, we achieve both ultrahigh activity and stability for the acidic HER. The activating effect of the inner-layer Co-doping combined with the stabilizing effect of the surface Se-doping enables the formation of abundant active sites in both the basal plane and the edges with optimized hydrogen adsorption activity at the codoped sites. The Co-Se-MoS\(_2\)-NF presents the highest HER activity among the previously reported heteroatom-doped MoS\(_2\) catalysts under industrial-level large current densities. At a high current density of 1000 mA cm\(^{-2}\), the Co-Se-MoS\(_2\)-NF exhibits a much lower overpotential of 382 mV than that of 671 mV over the 40 wt.% Pt/C catalyst, and the high activity can be maintained with long-term stability of more than 360 h without decay. Such a strategy of engineering the HER activity of MoS\(_2\) via co-confining multielements offers a promising and feasible route of developing high-performance and low-cost MoS\(_2\) catalysts for large-scale production of clean energy hydrogen.

**Methods**

**Synthesis of SiO\(_2\) template.** The uniform SiO\(_2\) nanosphere template was prepared by adding 9.6 g tetraethyl orthosilicate into 200 mL of ethanol solution under stirring for 10 min, followed by adding 8 mL of deionized water and 8 mL of ammonia. Then, the mixture was continuously stirred under room temperature until all the solvent was evaporated and was dried at 60 °C to obtain SiO\(_2\) template.
Synthesis of Se-doped MoS2 nanofoam (Se-MoS2-NF). The Se-MoS2-NF was synthesized through a one-pot chemical synthesis method. First, 0.4 g (NH4)6Mo7O24·4H2O, specified amount of selenium powder and 1.6 g MoS2 nanosheet powder were dispersed in 25 mL deionized water, followed by continuously stirring under room temperature until all the solvent was evaporated. Then, the gained solid was dried under 80 °C for 12 h. After that, the gained powder and 10 mL CS2 were both transferred into 40 mL stainless steel autoclave in a three-electrode electrochemical cell equipped with a gas flow controlling system. For the preparation of the working electrode, 4 mg catalyst and 2 mg carbon black (Vulcan XC-72) were suspended in 25 mL Nafion solution (5 wt.%, Du Pont) to form a homogeneous ink assisted by ultrasonication. Then, the ink was dropped on CFPs (1 cm × 1 cm) and dried under room temperature. For the characterization of HER polarization curves, an Ag/AgCl (saturated KCl-filled) electrode and graphite rod were used as reference and counter electrode, respectively. For the characterization of chronopotentiometric test, Pt mesh was used as the counter electrode owing to the instability of graphite rod under large current densities. In order to avoid effectively the possible Pt contamination during measurements, cathode and anode compartments were separated with Nafion 117 membrane in H-type electrochemical cell. To weaken the influence of reactant concentration for catalyst activity, the electrolyte was replaced every 72 h.

Materials characterization. TEM, HAADF-STEM, HRTEM, and EDX mappings measurements were carried out on the Phillips Analytical FEI Tecnai20 electron microscope. Atomic-resolution HAADF-STEM images and EELS mapping were performed on a schematic aberration-corrected Nion Σ-HERMES100. The experiments were conducted at 60 kV accelerating voltage to reduce radiation damage and also with relatively low electron dose. EELS spectra processing was performed using the open-source software HYPERSPY (former EELSLAB) to remove X-ray strikes45. Atomic-resolution HAADF-STEM image simulation was performed in the QSTEM software. XRD patterns were recorded on Rigaku Ultima IV diffractometer. Cu Ka radiation (λ = 0.15406 nm) at 40 kV and 30 mA was used as the X-ray source. XPS measurements were carried out on a Thermo ESCALAB 250Xi spectroscope using Al Kα x-rays as the excitation source. Raman measurements were performed on a home-built Invia confocal Raman microscope (Renishaw, UK) with Leica DM2500 microscopes, which was operated with a 633 nm excitation laser at a power of 26.7 μW. XANES and EXAFS measurements were carried out on the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) recorded in a transmission mode. The 5 l-edge XANES spectra were collected with a synchrotron electron yield mode at the beamline BL10 in Hefei National Synchrotron Radiation Laboratory (NSRL). ICP-OES test was conducted on Shimadzu ICP-S800.

Electrochemical measurements. Electrochemical measurements were performed in a three-electrode electrochemical cell equipped with a gas flow controlling system on electrochemical workstations (CHI 760E and CHI 680 C). We employed which was operated with a 633 nm excitation laser at a power of 26.7 μW to obtain the CV curve for H2 evolution. The long-term stability tests were performed by using a three-electrode H-type electrochemical cell with a gas flow controlling system. For the preparation of the working electrode, 4 mg catalyst and 2 mg carbon black (Vulcan XC-72) were suspended in 0.5 mL ethanol with 25 μL Nafion solution (5 wt.%, Du Pont) to form a homogeneous ink assisted by ultrasonication. Then, the ink was dropped on CFPs (1 cm × 1 cm) and dried under room temperature. For the characterization of HER polarization curves, an Ag/AgCl (saturated KCl-filled) electrode and graphite rod were used as reference and counter electrode, respectively. For the characterization of chronopotentiometric test, Pt mesh was used as the counter electrode owing to the instability of graphite rod under large current densities. In order to effectively the possible Pt contamination during measurements, cathode and anode compartments were separated with Nafion 117 membrane in H-type electrochemical cell. To weaken the influence of reactant concentration for catalyst activity, the electrolyte was replaced every 72 h.

All potentials were 85% iR corrected and referenced to the RHE by the equation E(RHE) = E(Ag/AgCl, saturated KCl-filled)−IR + 0.2427. The R for iR correction was determined by impedance measurements.

Calculation of the faradic efficiency. The controlled potential electrolysis was carried out to determine the faradic efficiency of H2 using a three-electrode H-type electrochemical cell. During the controlled potential electrolysis, the electrolyte in both anodic and cathodic compartments were stirred slightly to enhance the diffusion of reactant. Quantification of the H2 were performed using the gas chromatograph (Shimadzu GC 2014) with a thermal conductivity detector. The faradic efficiency of H2 are calculated from GC chromatogram peak areas at a given potential as follow:

\[ i_{\text{th}} = i_{\text{vis}} \times \frac{2F \rho}{RT} \]

\[ FE_{\text{H2}} = \frac{i_{\text{th}}}{i_{\text{vis}}} \times 100\% \]

where \( i_{\text{vis}} \) is partial current density for H2, \( i_{\text{th}} \) is total current density, \( F \) is Faraday's constant, \( V \) is gas volume flow rate, and \( T = 298.15 \) K.

DFT calculations. DFT calculations were performed using the Vienna Ab-initio Simulation Package. The projector augmented-wave pseudopotential method with Perdew–Burke–Ernzerhof exchange-correlation functional and a plane-wave cutoff energy of 400 eV was adopted. The standard version of PAW pseudopotentials without using semi-core states were used for all elements. Van der Waals correction was calculated using the Zero-damping DFT-D3 method of Grimme. A tri-layer model of MoS2 was built in a 6 × 6 supercell to simulate the in-plane doping of Co and Se. A nanoribbon model of MoS2 with six repeated sections was used as the counter electrode owing to the instability of graphite rod under large current densities. In structural optimizations, the forces between atoms were converged below 0.02 eV/Å. Dipole correction was applied to correct the interactions between the slabs or nanoribbons.

The free energy of (H1+v+e−) was calculated as that of % H2. The free energy of gas molecules was calculated as \( E_{\text{total}} + ZPE + \sum_{i} E_{\text{ vib}} \), where \( E_{\text{total}} \) is DFT calculated total energy, ZPE is the zero-point energy, \( T \) is temperature, \( \sum_{i} E_{\text{ vib}} \) is the integrated heat capacity from 0 K to \( T \) and \( S \) is the entropy. For the ZPE

\[ F_{\text{E}} = \frac{i_{\text{th}}}{i_{\text{vis}}} \times 100\% \]

where \( i_{\text{vis}} \) is partial current density for H2, \( i_{\text{th}} \) is total current density, \( F \) is Faraday's constant, \( V \) is gas volume flow rate, and \( T = 298.15 \) K.

The free energy of adsorbed species were calculated as \( E_{\text{total}} + ZPE + \sum_{i} E_{\text{ vib}} \), where \( \sum_{i} E_{\text{ vib}} \) is the integrated heat capacity from 0 K to \( T \) and \( S \) is the entropy. The electrons from adsorbed atoms were converged below 0.02 eV/Å. Dipole correction was applied to correct the interactions between the slabs or nanoribbons.

The free energy of (H1+v+e−) was calculated as that of % H2. The free energy of gas molecules was calculated as \( E_{\text{total}} + ZPE + \sum_{i} E_{\text{ vib}} \), where \( E_{\text{total}} \) is DFT calculated total energy, ZPE is the zero-point energy, \( T \) is temperature, \( \sum_{i} E_{\text{ vib}} \) is the integrated heat capacity from 0 K to \( T \) and \( S \) is the entropy. For the ZPE

\[ \mu(H) = 1/2G(H_2) \]

\[ \mu(S) = (G(HS) - G(H)) \]

\[ \mu(Mo) = G(MoS2) - 2\mu(S) \]

\[ \mu(Se) = 1/2(G(MoS2) - 2\mu(Mo)) \]

\[ \mu(Co) = 1/2(G(Co) - \mu(\text{bulk})) \]

\[ i_{\text{vis}} = i_{\text{th}} \times \frac{2F \rho}{RT} \]

\[ FE_{\text{H2}} = \frac{i_{\text{th}}}{i_{\text{vis}}} \times 100\% \]

The supercell of hcp Co bulk contains two Co atoms.
Then the formation energy ($E_{\text{form}}$) of a structure $\text{Mo}_x\text{Co}_y\text{S}_z\text{Se}_w$ is given by:

$$E_{\text{form}} = E_{\text{total}}(\text{Mo}_x\text{Co}_y\text{S}_z\text{Se}_w) - xy(Mo) - yz(\text{Co}) - zw(S) - mw(Se).$$ (8)

The relative formation energy of a Co-doped, Se-doped, or Co/Se-codoped MoS$_2$ edge is calculated by using its formation energy minus that of the corresponding undoped pure MoS$_2$ edge. This is to decouple the doping effect on the formation energy from the that of creating undoped pure MoS$_2$ edges.

Data availability

The data that support the findings of this study are available from the corresponding authors on request.

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References

1. Dresselhaus, M. S. & Thomas, I. L. Alternative energy technologies. *Nature* **414**, 332–337 (2001).
2. Turner, J. A. Sustainable hydrogen production. *Science* **305**, 972 (2004).
3. Stamenkovic, V. R., Strmcnik, D., Lopes, P. P. & Markovic, N. M. Energy and fuels from electrochemical interfaces. *Nat. Mater.* **16**, 57–69 (2017).
4. Zou, X. & Zhang, Y. Noble metal-free hydrogen evolution catalysts for water splitting. *Chem. Soc. Rev.* **45**, 5148–5180 (2015).
5. Chen, Z. et al. A review on non-precious metal electrocatalysts for PEM fuel cells. *Energy Environ. Sci.* **4**, 3167–3192 (2011).
6. Norskov, J. K. & Christensen, C. H. Toward efficient hydrogen production at surfaces. *Science* **312**, 1322 (2006).
7. Hinnemann, B. et al. Biomimetic hydrogen evolution: MoS$_2$ nanoparticles as catalyst for hydrogen evolution. *J. Am. Chem. Soc.* **127**, 5308–5309 (2005).
8. Jaramillo, T. F. et al. Identification of active edge sites for electrochemical H$_2$ evolution from MoS$_2$ nanocatalysts. *Science* **317**, 100 (2007).
9. Deng, J. et al. Highly active and durable non-precious-metal catalysts encapsulated in carbon nanotubes for hydrogen evolution reaction. *Energy Environ. Sci.* **7**, 1919–1923 (2014).
10. Deng, J. et al. Triggering the electrocatalytic hydrogen evolution activity of the inert two-dimensional MoS$_2$ surface via single-atom metal doping. *Energy Environ. Sci.* **8**, 1594–1601 (2015).
11. Mao, J., Wang, Y., Zheng, Z. & Deng, D. The rise of two-dimensional MoS$_2$ for catalysis. *Front. Phys.* **13**, 138118 (2018).
12. Wang, Y. et al. Catalysis with two-dimensional materials and their heterostructures. *Nat. Nanotechnol.* **11**, 218–230 (2016).
13. Xiao, J., Wang, Y., Zhang, W. & Lan, Q. The two-dimensional transition metal dichalcogenides for electrochemical water splitting. *Adv. Mater.* **25**, 3575–3609 (2013).
14. Deng, D. et al. Catalysis with two-dimensional materials and their heterostructures. *Nat. Nanotechnol.* **11**, 218–230 (2016).
15. Mao, J., Wang, Y., Zheng, Z. & Deng, D. The rise of two-dimensional MoS$_2$ for catalysis. *Front. Phys.* **13**, 138118 (2018).
16. Wang, Y. et al. Catalysis with two-dimensional materials confining single atoms: concept, design, and applications. *Chem. Rev.* **119**, 1806–1854 (2019).
17. Qi, K. et al. Single-atom cobalt array bound to distorted 1T MoS$_2$ with ensemble effect for hydrogen evolution catalysis. *Nat. Commun.* **10**, 5231 (2019).
18. Kibsgaard, J., Chen, Z., Reinecke, B. N. & Jaramillo, T. F. Engineering the surface structure of MoS$_2$ to preferentially expose active edge sites for electrocatalysis. *Nat. Mater.* **11**, 963–969 (2012).
19. Xie, J. et al. Defect-rich MoS$_2$ ultrathin nanosheets with additional active edge sites for enhanced electrocatalytic hydrogen evolution. *Adv. Mater.* **25**, 5807–5813 (2013).
20. Deng, J. et al. High-performance hydrogen evolution electrocatalysis by layer-controlled MoS$_2$ nanosheets. *Rsc. Adv.* **4**, 34733–34738 (2014).
21. Li, H. et al. Activating and optimizing MoS$_2$ basal planes for hydrogen evolution through the formation of strained sulphur vacancies. *Nat. Mater.* **15**, 364–364 (2016).
22. Albu-Yaron, A. et al. MoS$_2$ hybrid nanomaterials: from octahedral to quasi-spherical shells within Individual nanoparticles. *Angew. Chem. Int. Ed.* **50**, 1810–1814 (2011).
23. Shi, Y. et al. Three-dimensional architectures constructed from transition-metaldichalcogenide nanomaterials for electrochemical energy storage and conversion. *Angew. Chem. Int. Ed.* **56**, 626–648 (2017).
24. Deng, J. et al. Multiscale structural and electronic control of molybdenum disulhide foam for highly efficient hydrogen production. *Nat. Commun.* **8**, 14430 (2017).
25. Wu, W. et al. Activation of MoS$_2$ basal planes for hydrogen evolution by Zinc. *Angew. Chem. Int. Ed.* **58**, 2029–2033 (2019).
26. Meng, X. et al. Three-dimensionally hierarchical MoS$_2$/graphene architecture for high-performance hydrogen evolution reaction. *Nano Energy* **61**, 611–616 (2019).
27. Li, H. et al. Growth of alloy Mo$_2$Se$_2$(1–x) nanosheets with fully tunable chemical compositions and optical properties. *J. Am. Chem. Soc.* **136**, 3756–3759 (2014).
28. Mann, J. et al. 2-dimensional transition metal dichalcogenides with tunable direct band gaps: MoS$_2$–Mo$_2$Se$_2$ monolayers. *Adv. Mater.* **26**, 1399–1404 (2014).
29. Zhang, X. et al. Phonon and raman scattering of two-dimensional transition metal dichalcogenides from monolayer, multilayer to bulk material. *Chem. Rev.* **144**, 2775–2785 (2015).
30. Konkena, B. et al. MoS$_2$Se$_2$nanoheterostructures as efficient and stable electrocatalysts for the hydrogen evolution reaction. *Nano Energy* **29**, 46–53 (2016).
31. Alfred, A. L. Electronegativity values from thermochemical data. *J. Inorg. Nucl. Chem.* **47**, 215–221 (1961).
32. Li, K. & Xue, E. Determination of electronegativity values of elements in different valence states. *J. Phys. Chem. A* **110**, 11332–11337 (2006).
33. Diener, A., Neumann, T., Kramar, U. & Schütt, C. Structure of selenium incorporated in pyrite and mackinawite as determined by XAFS analyses. *J. Contam. Hydrokol.* **133**, 30–39 (2012).
34. Wang, Y. et al. Structural and electronic properties of MoS$_2$ nanosheets. *Adv. Mater.* **22**, 123–128 (1995).
35. Albu-Yaron, A. et al. MoS$_2$ hybrid nanostructures: from octahedral to quasi-two-dimensional. *Adv. Mater.* **28**, 3649–3653 (2016).
36. Liu, T. H. M. et al. Transition metal atom doping of the basal plane of MoS$_2$ monolayer nanosheets for electrochemical hydrogen evolution. *Chem. Sci.* **9**, 4769–4776 (2018).
37. Wang, Y. et al. Catalysis with two-dimensional materials and their heterostructures. *Nat. Nanotechnol.* **11**, 218–230 (2016).
38. Deng, J. et al. Multiscale structural and electronic control of molybdenum disulhide foam for highly efficient hydrogen production. *Nat. Commun.* **8**, 14430 (2017).
39. Shi, Y. et al. Energy level engineering of MoS$_2$ by transition-metal doping for accelerating hydrogen evolution reaction. *J. Am. Chem. Soc.* **139**, 15479–15485 (2017).
40. Xiong, Q. et al. Cobalt covalent doping in MoS$_2$ to induce bifunctionality of overall water splitting. *Adv. Mater.* **30**, 1801450 (2018).
41. Deng, J. et al. Transition metal atom doping of the basal plane of MoS$_2$ monolayer nanosheets for electrochemical hydrogen evolution. *Chem. Sci.* **9**, 4769–4776 (2018).
54. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
55. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
56. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104 (2010).
57. Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **32**, 1456–1465 (2011).
58. Lauritsen, J. V. et al. Atomic-scale insight into structure and morphology changes of MoS2 nanoclusters in hydrotreating catalysts. *J. Catal.* **221**, 510–522 (2004).
59. Raybaud, P. et al. Ab initio study of the H2-H2S/MoS2 gas-solid interface: the nature of the catalytically active sites. *J. Catal.* **189**, 129–146 (2000).
60. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**, 5188–5192 (1976).

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**Author contributions**

D.D. conceived the project and designed the experiments. Z.Z performed the materials synthesis, materials characterization, and electrochemical measurements. L.Y. conducted the DFT calculations. M.G., X.C., W.Z., and C.M. performed the atomic-resolution HAADF-STEM measurements. L.W. and J.Z. assisted with the S L-edge XANES measurements. X.M., J.H., Y.T., and J.M. assisted with partial materials characterization. S.W. conducted the Raman measurements. Z.T. gave the valuable discussions and suggestions. Z.Z., L.Y., and D.D. co-wrote the paper.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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