Engineering water dissociation sites in MoS₂ nanosheets for accelerated electrocatalytic hydrogen production†

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Earth-abundant MoS₂ is widely reported as a promising HER electrocatalyst in acidic solutions, but it exhibits extremely poor HER activities in alkaline media due to the slow water dissociation process. Here we present a combined theoretical and experimental approach to improve the sluggish HER kinetics of MoS₂ electrocatalysts through engineering the water dissociation sites by doping Ni atoms into MoS₂ nanosheets. The Ni sites thus introduced can effectively reduce the kinetic energy barrier of the initial water-dissociation step and facilitate the desorption of the OH that are formed. As a result, the developed Ni-doped MoS₂ nanosheets (Ni-MoS₂) show an extremely low HER overpotential of ~98 mV at 10 mA cm⁻² in 1 M KOH aqueous solution, which is superior to those (>220 mV at 10 mA cm⁻²) of reported MoS₂ electrocatalysts.

With its high energy density and environmentally friendly advantages, molecular hydrogen has been widely regarded as one of the most promising energy carriers.¹ The scalable and sustainable production of hydrogen fuel through efficient and cost-effective electrocatalytic/photocatalytic/photoelectocatalytic water splitting technologies, e.g., water–alkali and chlor-alkali electrolyzers, is highly promising as a means to meet the future global energy demands.² To this end, active, durable, and earth-abundant electrocatalysts are essential to lower the kinetic overpotentials of the hydrogen evolution reaction (HER) and ultimately accelerate hydrogen production in alkaline solutions.³ Platinum (Pt) has been acknowledged as the most active and stable HER electrocatalyst with a near-zero onset overpotential.⁴ Unfortunately, the large-scale utilization of Pt catalysts in H₂-production electrolyzers is seriously hampered by its scarcity and cost.

In regard to its elemental abundance, high activity, and electrochemical stability, molybdenum disulfide (MoS₂) is a promising catalyst for the electrocatalytic and photocatalytic HER.⁵ Recently, both density functional theory (DFT) calculations and experimental results have demonstrated that the electrocatalytic HER activity of crystalline MoS₂ catalysts originates from the unsaturated Mo–S sites along the edges.⁶ Inspired by this fundamental understanding, extensive efforts have been dedicated to increasing the number of exposed active sites on MoS₂ catalysts by engineering the nanostructures, e.g., double-gyroid mesoporous MoS₂ films,⁷ vertically aligned MoS₂ films,⁸ defect-rich MoS₂ nanosheets,⁹ amorphous MoS₂ films,¹⁰ [Mo₃S₁₃]²⁻ clusters,¹¹ and CoSₓ/MoSₓ hybrids.¹² Unfortunately, although the MoS₂-based electrocatalysts thus developed exhibit enhanced HER activities in acidic solutions, the HER kinetics in alkaline electrolytes still suffer from a high overpotential (>220 mV at a current of 10 mA cm⁻²).¹² The high kinetic energy barrier of

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the initial water dissociation process (the Volmer step) and the strong adsorption of the formed $^\circ$OH on the surfaces of MoS$_2$ are responsible for the sluggish HER kinetics in alkaline solutions.$^{13}$

Herein, we demonstrate a novel strategy to efficiently speed up the sluggish HER kinetics of MoS$_2$ electrocatalysts through doping Ni atoms into crystalline MoS$_2$ nanosheets. The DFT calculations reveal the fact that the kinetic energy barrier of the initial water dissociation step and the adsorption interaction of $^\circ$OH are substantially reduced on Ni-doped MoS$_2$ catalysts (Ni-MoS$_2$). Accordingly, Ni-MoS$_2$ nanosheets with a chemical composition of Ni$_{0.13}$Mo$_{0.87}$S$_2$ were prepared on carbon cloth via a one-pot hydrothermal reaction. The resultant Ni-MoS$_2$ nanosheets exhibit an excellent electrochemical HER activity in 1 M KOH aqueous solution with an extremely low overpotential of ~98 mV at a current density of 10 mA cm$^{-2}$. The achieved overpotential is much lower than those of reported MoS$_2$ electrocatalysts (overpotential is >220 mV at 10 mA cm$^{-2}$ in basic solutions and >110 mV at 10 mA cm$^{-2}$ in acidic solutions).$^{12,14}$

The kinetic energy barriers of the prior water dissociation step ($\Delta G(H_2O)$, Volmer step), the Gibbs free energy of adsorbed $^\circ$OH ($\Delta G(OH)$), and the concomitant combination of H* intermediates into molecular hydrogen ($\Delta G(H)$, Tafel step) were firstly investigated using the DFT calculations according to the as-built catalyst models including MoS$_2$, Ni-MoS$_2$, Co-doped MoS$_2$ (Co-MoS$_2$), and Fe-doped MoS$_2$ (Fe-MoS$_2$) (Fig. S1, ESI†). As shown in Fig. 1 and Table S1 (ESI†), MoS$_2$ exhibits a very high $\Delta G(H_2O)$ up to 1.17 eV and an extremely low $\Delta G(OH)$ (~5.24 eV). Substituting a Mo atom with a metal (Ni, Co, or Fe) atom along the edge of MoS$_2$ dramatically decreases the $\Delta G(H_2O)$ value in the order of: Ni-MoS$_2$ ($\Delta G(H_2O)$ = 0.66 eV) < Co-MoS$_2$ ($\Delta G(H_2O)$ = 0.76 eV) < Fe-MoS$_2$ ($\Delta G(H_2O)$ = 0.96 eV). In contrast to MoS$_2$, the $\Delta G(OH)$ value is reduced to $^-3.46$ eV for Ni-MoS$_2$, $^-3.46$ eV for Co-MoS$_2$, and $^-3.36$ eV for Fe-MoS$_2$. These greatly reduced $\Delta G(H_2O)$ and $\Delta G(OH)$ values on Ni-MoS$_2$ suggest that the kinetics of the initial water dissociation step and the concomitant desorption of the formed $^\circ$OH can be effectively promoted after the doping of a Ni atom into the edge of MoS$_2$. In addition, the $\Delta G(H)$ is $^-0.06$ eV for Ni-MoS$_2$, $^0.13$ eV for Co-MoS$_2$, and $^-0.10$ eV for Fe-MoS$_2$, which are much lower than 0.60 eV for MoS$_2$. The negative value of $\Delta G(H)$ for Ni-MoS$_2$ catalysts shows that the subsequent Tafel step towards molecular hydrogen can spontaneously occur in thermodynamics.

Encouraged by these DFT results, we prepared metal-doped MoS$_2$ nanosheets (M-MoS$_2$), where the metal (Ni, Co, or Fe) atoms are homogeneously doped into the crystalline MoS$_2$ nanosheets, as schematically illustrated in Fig. S2 (ESI†). Specifically, the Ni-MoS$_2$ nanosheets were constructed on carbon cloth (1 x 3 cm$^2$) through a one-pot hydrothermal reaction at 200 °C for 24 h, involving NiSO$_4$·6H$_2$O, Na$_2$MoO$_4$·2H$_2$O, and l-cysteine in 15 mL deionized water. The molar content (x, expressed in Ni$_{1-x}$Mo$_x$S$_2$) of Ni in the as-obtained Ni-MoS$_2$ nanosheets could be tuned from 6.2% to 19.1% by adjusting the dosage of NiSO$_4$·6H$_2$O. The loading weight of Ni-MoS$_2$ nanosheets on the carbon cloth was approximately 0.89 mg cm$^{-2}$. Under the same hydrothermal conditions, Co-MoS$_2$ (Co$_{0.03}$Mo$_{0.97}$S$_2$) and Fe-MoS$_2$ (Fe$_{0.12}$Mo$_{0.88}$S$_2$) nanosheets on carbon cloth were also prepared utilizing CoSO$_4$·7H$_2$O and FeSO$_4$·7H$_2$O as Co and Fe sources, respectively. For comparison, pristine MoS$_2$ nanosheets were synthesized through the same process without involving NiSO$_4$·6H$_2$O.

The crystalline structure of the M-MoS$_2$ nanosheets was first confirmed by X-ray diffraction (XRD) measurements. As shown in Fig. S3 (ESI†), the Ni-MoS$_2$ nanosheets show the diffraction peaks at diffraction angles similar to semiconducting MoS$_2$.$^{15}$ To probe the morphologies of the as-obtained Ni-MoS$_2$, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) were employed. Fig. 2a and Fig. S4 (ESI†) reveal numerous sheet-like nanostructures, which are vertically aligned and inter-connected on the carbon cloth. The thickness and length of the Ni-MoS$_2$ nanosheets are approximately 5–10 nm and 40–100 nm, respectively. Elemental mappings of
field-emission SEM (FE-SEM) reveal the homogenous distributions of Ni, Mo, and S elements over the Ni-MoS2 nanosheets (Fig. S3a–e, ESI†). The corresponding energy dispersive X-ray spectroscopy (EDS) analysis further suggests a chemical elemental composition of Ni0.13Mo0.87S2 (Fig. S5f, ESI†). Fig. 2b and c show the HRTEM images of the Ni-MoS2 nanosheets. Lattice fringes with lattice distances of 0.75 and 0.28 nm correspond to the (002) edge and (100) plane facets of the Ni-MoS2 nanosheets, respectively.16 Scanning TEM (STEM)-EDS characterization was utilized to analyze the elemental distributions in the Ni-MoS2 nanosheets (Fig. 2d). Apparently, the Ni atoms are homogeneously distributed in the Ni-MoS2 nanosheets. Similarly, the morphologies and chemical compositions of the as-prepared MoS2, Co-MoS2, and Fe-MoS2 nanosheets were also investigated by SEM, XRD and EDS analyses (Fig. S6–S8, ESI†).

X-ray photoelectron spectroscopy (XPS) was applied to probe the composition and valence state of the Ni-MoS2 nanosheets. The survey spectrum demonstrates a chemical composition of Ni0.12Mo0.88S2, which is consistent with inductively coupled plasma mass spectrometry (ICP-MS) analysis (Ni0.13Mo0.87S2) (Fig. S9–S11, ESI†). The peaks of Ni 2p3/2 and Ni 2p1/2 were observed at 857.9 eV and 876.0 eV, respectively (Fig. 2c). The binding energies of Mo 3d5/2 and Mo 3d3/2 in the Ni-MoS2 nanosheets shifted to 228.8 and 232.1 eV, respectively (Fig. 2f), in contrast to those (Mo 3d5/2 at 228.5 and Mo 3d3/2 at 231.8 eV) in the pristine MoS2 nanosheets. Likewise, the S 2p3/2 and S 2p1/2 signals in the Ni-MoS2 also have a shift of ~0.3 eV, relative to those in the MoS2 nanosheets (Fig. 2g and Fig. S9, ESI†). Raman spectroscopy was further used to survey the Ni-MoS2 nanosheets. The characteristic Raman bands of the A1g and E2g modes of Ni-MoS2 shifted to 406 and 376 cm−1, relative to the MoS2 nanosheets (A1g at 412 cm−1; E2g at 388 cm−1) (Fig. S12, ESI†). These XPS and Raman results highlight the strong influence of Ni atom doping on the electronic structure of MoS2.

To evaluate the electrocatalytic HER activities of the catalysts, a three-electrode configuration in Ar-saturated 1 M KOH aqueous solution was applied using a Hg/HgO electrode and a graphite rod as the reference and counter electrodes, respectively (Fig. S13, ESI†). All potentials are referenced to the reversible hydrogen electrode (RHE) and the ohmic potential drop caused by the solution resistance has been deducted unless noted (Fig. S13, ESI†). As shown in Fig. 3a, although MoS2 can act as a HER catalyst, the hydrogen evolution reaction occurred at an overpotential of ~197 mV and the cathodic current density reached 10 mA cm−2 at a high overpotential of ~308 mV. Noticeably, the doping of Ni, Co, or Fe atoms into MoS2 nanosheets leads to profound enhancements of the HER activities. Specifically, Co-MoS2 and Fe-MoS2 catalysts show overpotentials of only 203 and 163 mV at a current density of 10 mA cm−2, respectively. Remarkably, the onset overpotential of Ni-MoS2 catalysts was as low as 45 mA and a current density of 10 mA cm−2 was delivered at an extremely low overpotential of ~98 mA cm−2. It is much lower than those of the as-prepared MoS2 catalysts (~308 mA at 10 mA cm−2) and the reported MoS2-based catalysts (regardless of whether in basic and acidic solutions) including amorphous MoS2 film (~500 mA at 4 mA cm−2)10 MoS2 nanoparticles grown on graphene (~155 mA at 10 mA cm−2),17 defect-rich MoS2 nanosheets (~190 mA at 10 mA cm−2),18 double-gyroid mesoporous MoS2 films (~235 mA at 10 mA cm−2),19 Li-MoS2 films (~168 mA at 10 mA cm−2),18 and CoS/CoS2 hybrids (~220 mA at 5 mA cm−2)20 (Table S2, ESI†). Moreover, the HER overpotential achieved by the Ni-MoS2 catalysts is comparable to those of highly active NiO/Ni heterostructures (~80 mA at 10 mA cm−2),19 CoP nanowires on carbon cloth (~209 mA at 10 mA cm−2),40 porous MoC nanooctahedra (~151 mA at 10 mA cm−2),41 cobalt-sulfide films (~180 mA at 10 mA cm−2),22 and CoO/Co/N-doped carbon hybrids (~232 mA at 10 mA cm−2)23 (Table S3, ESI†).

Fig. 3b displays Tafel plots of the corresponding polarization curves, which provide further insights into the HER reaction pathways on the surfaces of the catalysts. The Tafel slope of the MoS2 catalysts is as high as 201 mV per decade. However, the Tafel slope of the Ni-MoS2 catalysts is significantly decreased to 60 mV per decade. Compared with the MoS2 catalysts, the greatly decreased Tafel slope highlights that the kinetics of the water dissociation step is effectively facilitated on the Ni-MoS2 catalysts. On the basis of the Tafel analysis, the exchange current density of the Ni-MoS2 catalysts was estimated to be ~0.98 mA cm−2 (Fig. S15, ESI†). Meanwhile, the turnover frequency (TOF) of the Ni-MoS2 catalysts was up to 0.32 s−1 at an overpotential of 150 mV (Fig. S16, ESI†). In addition, the electrochemical impedance spectroscopy (EIS) analyses also confirmed a faster HER kinetic process on the Ni-MoS2 catalysts than on the MoS2 catalysts (Fig. S17, ESI†).

Electrocatalytic stability is another important criterion for the HER catalysts. For the Ni-MoS2 catalysts, after 2000 cyclic voltammetry (CV) cycles in 1 M KOH aqueous solution, the overpotential required for a current density of 10 mA cm−2 increased by only 5 mA (Fig. 3c). A long-term HER process was
performed at a current density of 10 mA cm\(^{-2}\) (Video S1, ESI\(^\dagger\)).

Fig. 3d manifests that the Ni-MoS\(_2\) catalysts retained a steady HER activity and no noticeable increase in potential was observed for hydrogen production over a period of 100 h. After the above HER durability assessment, the structural information of the Ni-MoS\(_2\) catalysts was scrutinized using SEM. The morphology of the Ni-MoS\(_2\) catalysts showed no structural variations, suggesting their superior structural stability during the HER process (Fig. S18, ESI\(^\dagger\)). The electrochemical stability of the Ni-MoS\(_2\) catalysts was further confirmed by element mapping, EDX, and XPS analysis (Fig. S19 and S20, ESI\(^\dagger\)).

To clarify the influence of the active surface area on the electrocatalytic HER activity, the active surface areas of the as-synthesized catalysts were analyzed through their electrochemical double layer capacitances \(C_p\).\(^2,4\) For comparison, the \(C_p\) of the MoS\(_2\) catalysts was approximately 0.54 F. However, the Ni-MoS\(_2\), Co-MoS\(_2\), and Fe-MoS\(_2\) catalysts showed low \(C_p\) values of \(~0.35\ F, 0.32\ F,\) and \(0.27\ F\), respectively (Fig. 4a and Fig. S21, ESI\(^\dagger\)). These results demonstrate that the excellent HER activity of the Ni-MoS\(_2\) catalysts originates from the improved HER kinetics, rather than the active surface area. As illustrated in the reported volcano plots, under acidic conditions, the HER kinetics of a catalyst is strongly correlated with its hydrogen adsorption ability.\(^5,25\) To further understand the roles of hydrogen adsorption and water dissociation in electrocatalytic HER kinetics of the Ni-MoS\(_2\) catalysts, the electrochemical HER activities of the catalysts were tested under acidic conditions. As shown in Fig. 4b and c, in comparison with the MoS\(_2\) catalysts, the HER overpotential of the Ni-MoS\(_2\) catalysts at 10 mA cm\(^{-2}\) was decreased by only 43 mV in 0.5 M H\(_2\)SO\(_4\) aqueous solution, which was far less than 209 mV in 1 M KOH aqueous solution. These studies clearly manifest that the greatly enhanced HER activity of the Ni-MoS\(_2\) catalysts in 1 M KOH aqueous solution is mainly attributed to the initially accelerated water dissociation, rather than the hydrogen adsorption properties.

We also investigated a series of Ni-MoS\(_2\) catalysts with different molar contents of Ni \([\text{Ni-MoS}_2-x; x \text{ is expressed in Ni}_x\text{Mo}_{10-x}\text{S}_8] \) in 1 M KOH aqueous solution (Fig. S22, ESI\(^\dagger\)). As shown in Fig. S23 (ESI\(^\dagger\)), the HER polarization curves of the Ni-MoS\(_2\) catalysts dramatically shifted towards lower overpotentials along with the increased Ni content. When the molar content of Ni was \(~13.3\%\), the Ni-MoS\(_2\) catalysts exhibited the lowest HER overpotential \([\sim 98\ mV \text{ at } 10\ mA\ cm^{-2}]\). The overpotential increased if the molar content of Ni was more than 13.3% and even the overpotential of the NiS\(_2\) catalysts at 10 mA cm\(^{-2}\) was approximately 201 mV.

In summary, we have demonstrated a novel strategy to greatly accelerate the sluggish HER kinetics of MoS\(_2\) electrocatalysts through engineering the water dissociation sites in alkaline environments. The combined DFT and experimental results show that the doping of Ni atoms into crystalline MoS\(_2\) nanosheets can efficiently lower the kinetic energy barrier of the initial water dissociation step and facilitate the desorption of the formed \(\text{OH}\) from the surface of the Ni-MoS\(_2\) catalysts. Therefore, this work opens up a favorable direction for exploring efficient and robust water-splitting catalysts, which have promising applications in alkali electrolyzers and solar-driven photocatalytic/photoelectrocatalytic devices.

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**Notes and references**