

Transition-metal Doped Edge Sites in Vertically Aligned MoS₂ Catalysts for Enhanced Hydrogen Evolution

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TABLE OF CONTENTS (TOC)

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ABSTRACT

Highly active and low-cost catalysts for electrochemical reactions such as the hydrogen evolution reaction (HER) are crucial for the development of efficient energy conversion and storage technologies. Theoretical simulations have been instrumental in revealing the correlations between the electronic structure of materials and their catalytic activity, which guide the prediction and development of improved catalysts. However, difficulties in accurately engineering the desired atomic sites lead to challenges in making direct comparisons between experimental and theoretical results. In MoS₂, the Mo-edge has been demonstrated to be active for HER whereas the S-edge is inert. Using a computational descriptor-based approach, we predict that by incorporating transition metal atoms (Fe, Co, Ni, Cu), the S-edge site should also become HER active. Vertically standing, edge-terminated MoS₂ nanofilms provide a well-defined model system for verifying these predictions. The transition metal doped MoS₂ nanofilms show an increase in exchange current densities by at least two-fold, in agreement with the theoretical calculations. This work opens up further opportunities for improving electrochemical catalysts by incorporating promoters into particular atomic sites, and for using well-defined systems in order to understand the origin of the promotion effects.

KEYWORDS

Molybdenum disulfide, chemical vapor deposition, doping, density functional theory

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1. Introduction

As global warming and the need for alternative energy sources becomes a growing concern, hydrogen has gained increased interest as a clean energy carrier.[1, 2] Hydrogen can be sustainably produced via water splitting, which can be driven by either solar energy or electricity.[3-6] The hydrogen evolution reaction (HER) acts as a key step in both photoelectrochemical and electrochemical water splitting, where Pt and other Pt-group metals are recognized as the best catalysts. Due to the high cost of Pt-group metals, efficient and cheap earth-abundant HER catalysts are needed for large scale production. Molybdenum disulfide (MoS_2) has been extensively investigated as an efficient catalyst for hydrodesulfurization for more than ten years,[7, 8] and has recently seen a resurgence in interest as an electrocatalyst due to its high activity in catalyzing HER. In analogy with the active sites in nitrogenase and hydrogenase, the atomic hydrogen adsorption free energy on the Mo-edge sites of MoS_2 was found to be very close to zero,[3] suggesting that MoS_2 can be active for HER if a high number of edge sites are exposed. Theoretical calculations on the edges were confirmed experimentally when it was found that the exchange current density varies linearly with the MoS_2 edge length rather than with the surface area.[4] The high HER activity of molecular electrocatalysts incorporating a MoS_2 edge-site mimic further validated that the edge sites were responsible for HER activity.[9, 10] In order to maximize the exposure of active edge sites and improve the overall activity, significant progress has been made in nanostructuring MoS_2 by creating nanoparticles,[4, 5, 11-14] defective nanosheets,[15] porous films,[16] double-gyroid structures,[17] nanowires,[18] and amorphous films.[19-21] In addition, we have successfully used a rapid sulfurization method to convert Mo or MoO_3 thin films precursors into polycrystalline MoS_2 nanofilms with vertically

aligned molecular layers, maximally exposing the active edge sites to improve HER activity.[14, 22-24]

The overall catalytic activity of the edge-terminated MoS_2 nanofilms can be further improved by activating the S-edge, which is calculated to be inactive for HER.[13, 25] As a hydrodesulfurization catalyst, MoS_2 has been doped with Ni, Co, or other transition metal (TM) ions into the edge sites to modify the activity.[8] The role, effect, location, and coordination of the promoter atoms have also been studied in detail.[8, 26-28] In analogy to hydrodesulfurization, the incorporation of TM atoms into the MoS_2 edge sites could improve the HER catalytic activity. Although some theoretical and experimental studies have demonstrated enhanced HER activities,[13, 29] the effect of doping the S-edges has yet not been explicitly and systematically revealed due to the following reasons: firstly, in the systems studied so far, metal dopants are evenly distributed onto the entire synthesized MoS_2 catalyst, which could also lead to promotion on the terrace sites; secondly, in some cases the morphology or surface area of the catalyst changes after the incorporation of metal atoms, making it difficult to differentiate the promotion effects with doping and the effect of an increased surface area.[13, 29] Our edge-terminated MoS_2 nanofilms thus provides an ideal model system for circumventing the two problems above, since doping can be restricted to the edges and the morphology can be fixed. This enables a systematic investigation of the promotion effects of the metal doped S-edge sites for HER, which could provide meaningful guidance for studying other forms of promoted catalysts.[22]

In this article we use a computational descriptor-based approach to predict the trends in HER activity of MoS_2 structures doped with several TM dopants (Co, Fe, Ni, Cu). We confirm experimentally that by incorporating these dopants into the edge sites of the vertically aligned MoS_2 nanofilms that the catalytic activity in HER can be significantly improved. Benefiting from the precise edge-terminated MoS_2 structures, the promotion effects of the metal dopants in the S-edge can be quantitatively determined. We are then able to make a quantitative

comparison between the experimental and theoretical results, finding agreement in the activity trends.

2. Theoretical Calculations

The hydrogen adsorption free energy, ΔG_{H} , was previously found to be an accurate descriptor for HER activity,^[30] with the optimal HER catalyst having a thermo-neutral ΔG_{H} . Herein, we used density functional theory (DFT) to calculate the ΔG_{H} on the S-edges of Co-, Fe-, Ni-, and Cu-doped MoS₂ to elucidate the trends in predicted activity for these structures. In order to accurately determine the ΔG_{H} at the doped edges, it is crucial to model the correct concentration of dopant metals, sulfur atoms, and hydrogen atoms, as variations in any of these could significantly alter the predicted ΔG_{H} . Experimental work by Kibsgaard *et al.*[31] on MoS₂ nanoclusters showed that dopant substitution at the S-edge was 100%, with negligible doping of the Mo-edges in most cases. Theoretical work[32] has further shown that the preferential doping of the S-edge is a general phenomena arising from the relative stabilities of the Mo-edge and the S-edge, where the Mo-edge is generally more stable. Schweiger *et al.*[32] showed that Co could only dope the S-edge, whereas Ni could dope both edges, in agreement with previous experimental work [26]. Following the methodology outlined in ref. [32], we confirmed that only Ni can dope the Mo-edge whereas the others cannot. Since previous theoretical calculations and our own predictions on the isolated edge sites confirmed what was found experimentally[31], we will first assume that what is observed on the MoS₂ nanoclusters is a good approximation of the relative stabilities of the edge sites. To a first approximation, all S-edges should be doped whereas Ni should only dope the Mo-edge. We will seek to validate these assumptions with the experimental results. We have assumed 100% substitution at the edges. If there was partial substitution, the effect should be intermediate

between the pristine case, and the doped cases. Either way, the S-edge should be improved and the Mo-edge should be worsened.

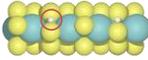
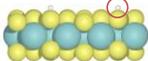
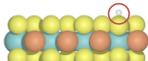
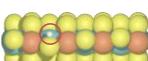
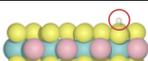
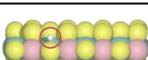
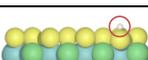
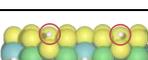
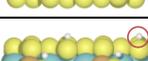
The relevant equilibrium edge configuration of sulfur and hydrogen for each structure was determined in the same way as in ref. [33], which is a more thorough treatment of the competing reaction pathways during HER than was previously considered.[3, 13] It involves calculating a large range of structures with various S and H coverages and comparing their surface energies. We show the relevant edge structures and their respective differential hydrogen adsorption free energies in Table 1. The hydrogen atoms bound at the most thermoneutral ΔG_{H} are circled in red, whereas the other hydrogen atoms are bound too strongly and can be considered poisoned at the edge.

The doped S-edges all have a smaller coverage of sulfur compared to the pristine MoS₂ S-edge, indicating that the direct effect of dopant substitution is to modify how strongly the edge sulfur is bound. In the case of the Cu-doped S-edge, even the sulfur atoms at the terrace adjacent to the edge are able to bind hydrogen.

All doped S-edges have values of $|\Delta G_{\text{H}}|$ that are closer to thermo-neutral than the pristine MoS₂ S-edge, indicating improved activity at the S-edge. In the cases of MoS₂ doped with Fe and Co, there is even improvement over the pristine Mo-edge by at least 0.02 eV. Doping with Co, Fe, Ni, and Cu therefore increases the S-edge activity to make it comparable to or better than the pristine Mo-edge.

The steady-state structures for the doped Mo-edges consist of the bare edge with no terminating sulfur atoms, unlike the pristine Mo-edge, which has S-monomers. The ΔG_{H} of the doped Mo-edges are all further uphill from thermo-neutral than the pristine Mo-edge, which indicates that the Mo-edges should be deactivated when doped. The exception is the Ni-doped MoS₂, where the doped Mo-edge could still be considered active, though less so than the pristine Mo-edge.

Table 1. Relevant edge structures, hydrogen adsorption free energies, and hydrogen coverages for pristine MoS₂ and doped MoS₂ catalysts. The adsorbed hydrogen atoms that is the most thermo-neutral is circled in red. For the S-edge of Ni-doped MoS₂, the final two adsorbed hydrogen atoms have very similar adsorption free energies, which suggests that they are relatively unaffected by each other’s presence and could simultaneously evolve hydrogen.

MoS ₂ catalyst	Edge	Structure	θ_H (ML)	Active Sites	ΔG_H (eV)	Doped
Pristine	Mo-edge		0.50	1	0.06	–
	S-edge		1.00	0	–0.45	–
Fe-doped	Mo-edge		0.25	0	0.48	No
	S-edge		0.25	1	0.04	Yes
Co-doped	Mo-edge		0.25	0	0.30	No
	S-edge		0.25	1	0.01	Yes
Ni-doped	Mo-edge		0.25	1	0.15	Yes
	S-edge		0.75 1.00	2	–0.18 –0.15	Yes
Cu-doped	Mo-edge		0.25	0	0.47	No
	S-edge		1.00	1	0.05	Yes

In our vertically standing MoS₂ nanofilm structures,[22] the layers stack with alternating Mo- and S-edges exposed on the surface. However, since only the Mo-edge shows significant HER activity, and both Mo- and S-edges are exposed on the surface, only every other edge on the surface can be considered very active. Furthermore, at the equilibrium coverage, only one in four sites on the Mo-edge is catalytically active.

For Fe, Co, and Cu, where the Mo-edge is expected to be unaffected by doping, the results from the ΔG_H indicate that HER should be activated on the S-edge,

making it comparable to the Mo-edge and thereby increasing the active sites by at least two-fold. The theoretical ΔG_H values suggest that when compared to pristine MoS₂, Fe-doped MoS₂ and Co-doped MoS₂ should have higher activity per active site, while Cu-doped MoS₂ should have similar activity per active site.

For the Ni-doped S-edge, two H atoms have very similar ΔG_H , which suggests that the adsorption of hydrogen on one site is not affected by adsorption on the other; we thus count two active sites on the S-edge. The S-edge should also be activated, but the activity

of the Mo-edge could be reduced if it was doped. We should thus expect the active sites to triple, but the activity per active site to decrease.

In the cases of Fe, Co, and Cu, the total activity should not change significantly if both Mo-edge and S-edge are doped, since the activation of one edge would be offset by the deactivation of the other.

3. Experimental

3.1. Synthesis

MoS₂ is a hexagonal layered structure as shown in Figure 1A. Mo and S atoms are covalently bonded to form single layers, which stack together along the z direction through weak van der Waals interactions. The strong anisotropy induces large surface energy of the edge sites, which makes it difficult in the previous synthesis methods to maximally expose the edge sites.[22] In our previous work, edge-terminated MoS₂ nanofilms were synthesized by chemical vapor

deposition of rapid sulfurization method.[22] The schematic of the top-view of the layer vertically aligned MoS₂ nanofilms is illustrated in Figure 1B. Since the two-dimensional surface is totally covered by the edge sites, it is straightforward to modify the edge by doping transition metal atoms and examine the changes of the HER activities, with minimized effects from the terrace sites. Figure 1C illustrates the material synthesis process. Specifically, 5 Å of TM was deposited onto the 16 nm Mo on glassy carbon, followed by the rapid sulfurization process in the quartz tube (see Methods). The Mo film was successfully converted into a 54 nm thick layer-vertically-aligned MoS₂ nanofilm (Supporting Information). Since the diffusion of the TM atoms into the MoS₂ matrix is limited by the short time of the rapid synthesis, it is expected that the surface edge sites are rich of the TM atoms. Away from the surface edge sites the concentration of the TM atoms will decrease dramatically as illustrated in Figure 1D.

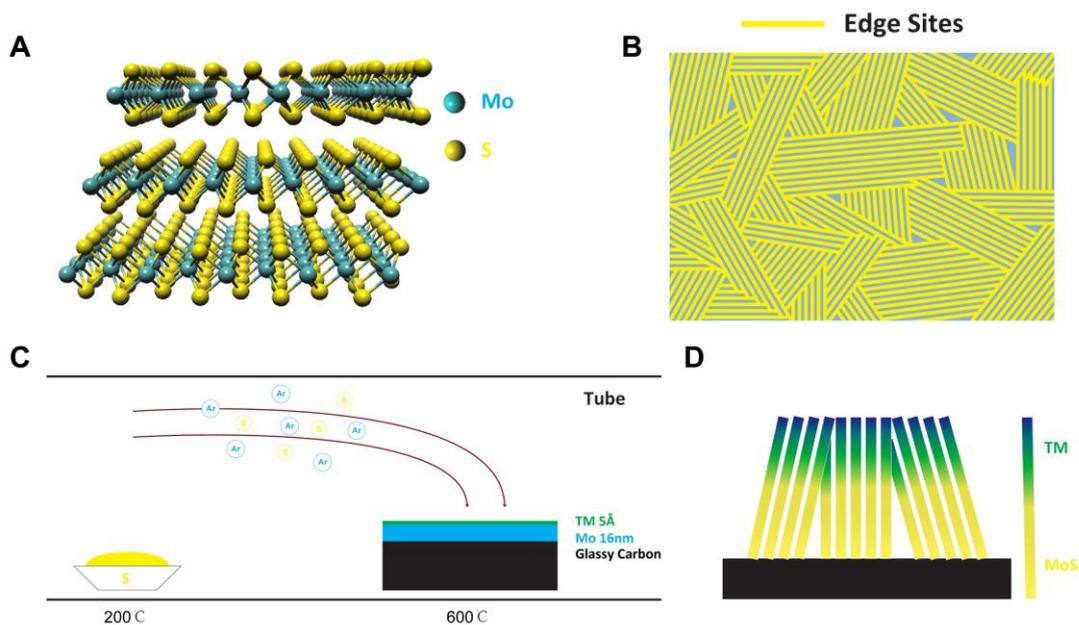


Figure 1. Schematics of material structure and synthesis. (A) Layered crystal structure of MoS₂. (B) Schematic of the top view of the edge-terminated surface of MoS₂. (C) Schematic of the chemical vapor deposition synthesis of TM doped MoS₂ nanofilm. Only 5 Å of TM was deposited onto the 16 nm Mo thin film on glassy carbon substrate. (D) Schematic of the concentration profile of the TM atoms in the MoS₂ matrix. The color gradient represents the gradually reduced concentration of the TM atoms.

3.2. Characterizations

Characterizations were performed on the Co-doped MoS₂ as an example to understand the differences in material properties between the pristine and the TM-doped MoS₂ (characterizations of other TM-doped MoS₂ are also included in the Supporting Information). Transmission electron microscopy (TEM) images in Figure 2 show the texture of the MoS₂ nanofilms before and after Co doping. Figure 2A shows the pristine MoS₂ nanofilm with densely packed, stripe-like grains. Each grain consists of vertically aligned molecular layers, which terminate the surface of the nanofilm with the edge sites. There are hardly any changes of the nanofilm morphology after the edge sites were modified by Co atoms as illustrated in Figure 2B. No particles or clusters are observed rules out the possibility of the formation of cobalt sulfide compounds on the surface, which reveals that the Co atoms are uniformly distributed on the surface edge sites.

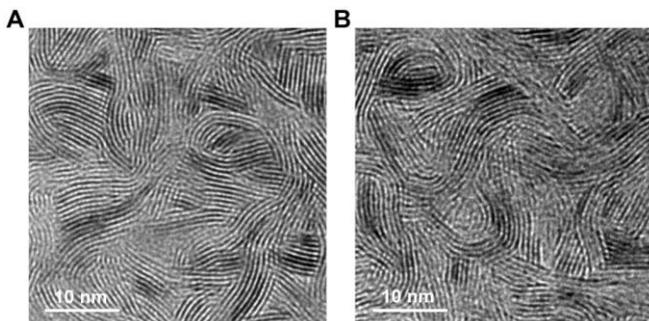


Figure 2. TEM images of the as-synthesized materials. (A) TEM image of the pristine MoS₂ nanofilm. The grains are around 10 nm with random orientations within the plane. (B) TEM image of the Co-doped MoS₂ nanofilm. The morphology is not changed compared with the pristine one in (A).

The X-ray photoelectron spectroscopy (XPS) Co 2p region at 778.8 eV shown in Figure 3A suggests the presence of Co on the surface of the MoS₂ nanofilm.[8,

27] In addition, the diffusion of Co atoms along the vertical direction must be considered. During the sulfurization reaction, Co atoms mix with Mo atoms on the surface and diffuse into the growing MoS₂ slabs. As illustrated by the schematic in Figure 1D, it is expected that the concentration of the dopants is decreasing along the vertical direction due to the limited time for the uniform distribution of the metal atoms though the whole MoS₂ matrix. This is confirmed by the XPS atomic ratio measurement of Co to Mo as shown in Figure 3B. The Co/Mo ratio on the surface of Co-doped MoS₂ is 0.29, which is much larger than the average ratio calculated by the deposition thickness. The ratio decays dramatically to 0.19 at a depth of 5.2 nm after the Ar plasma sputtering (see Methods). The Co concentration continuously decreases to 0.062 and 0.036 at depths of 31 and 57 nm respectively. From the Co concentration profile along the vertical direction of MoS₂ film we can conclude that the Co atoms in MoS₂ vertical layers are concentrated on the surface, in which case the small amounts of Co atoms can be fully used for the promotion effects in HER. Mo 3d and S 2p regions of the pristine and Co-doped MoS₂ are presented in Figures 3C and 3D. The binding energies of Mo 3d_{5/3} and Mo 3d_{3/2} in the pristine MoS₂ are located at 228.9 and 232.1 eV respectively, indicating the + 4 oxidation state of Mo.[34, 35] The corresponding S 2p doublets with an S 2p_{3/2} binding energy of 161.8 eV confirms the -2 oxidation state for the sulfur.[17, 34, 35] Since the XPS spectra of MoS₂ and Co-doped MoS₂ in Figures 3C and 3D have almost the same peak shapes and positions, it is concluded that the chemical states of Mo and S are not affected by the incorporation of Co atoms.

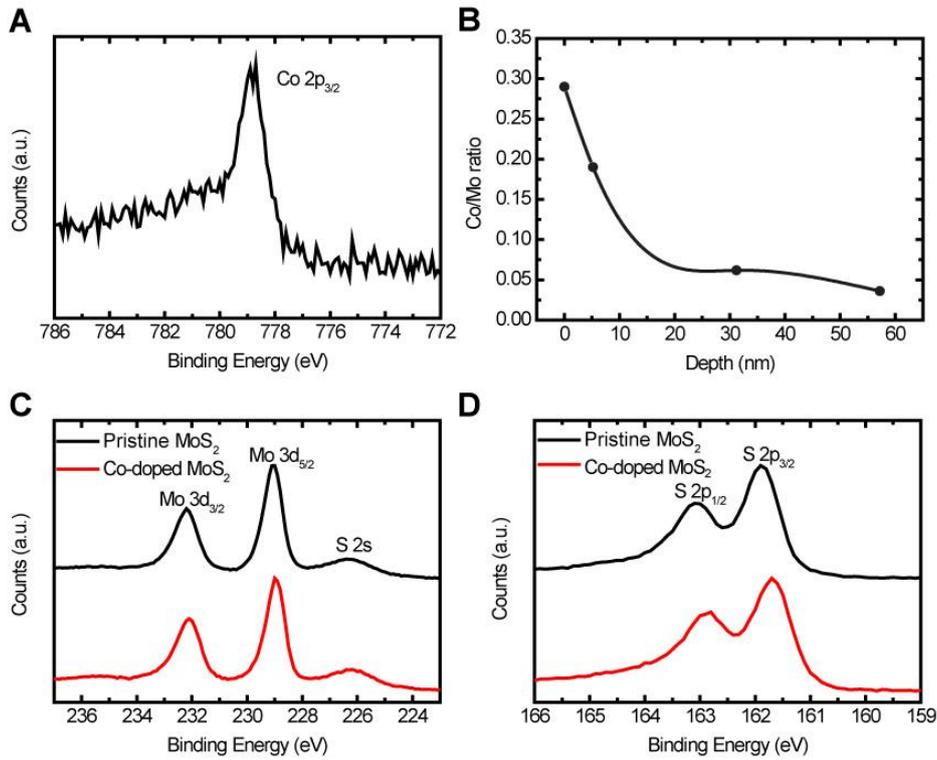


Figure 3. XPS of the as-synthesized materials. (A) Co 2p region of the Co-doped MoS₂ nanofilm. The weak signal implies the small amount of Co atoms in the MoS₂ matrix. (B) The atomic ratio of Co to Mo as a function of the film depth. The diffusion length is around 10 nm along the MoS₂ layers. (C) Mo 3d regions of the pristine and Co-doped MoS₂ nanofilms. (D) S 2p regions of the pristine and Co-doped MoS₂ nanofilms.

Raman spectroscopy is employed to test both the composition and orientation of the as-grown pristine and Co-doped MoS₂ nanofilms on glassy carbon. Pristine MoS₂ in Figure 4A has three distinct vibration modes located at 287, 381, and 409 cm⁻¹, corresponding to the E_{1g}, E_{2g}¹, and A_{1g} first-order phonon modes of MoS₂ at the Γ point of the Brillouin zone respectively (Figure 4B).[17, 22, 36-40]. The relative integrated intensity ratio of the E_{2g}¹ to A_{1g} peaks in Figure 4A provides rich texture information about the thin films. The vibration direction of A_{1g} mode is c-axis, which is preferentially excited for the edge-terminated structure and results in a small E_{2g}¹ to A_{1g} peak ratio of ~ 30 %.[22] E_{2g}¹ mode vibration direction is within basal plane and preferentially excited for the terrace-terminated film obtained by mechanical exfoliation, with the integrated intensity of E_{2g}¹ mode close to that of A_{1g} shown in Figure

4A.[22, 37] The Co-doped MoS₂ spectrum has almost the same features with the pristine one, suggesting that the MoS₂ layer-vertically-aligned structure is not affected. By integrating all of the characterization results together we conclude that the Co atoms make a uniform doping in the MoS₂ surface edge sites.

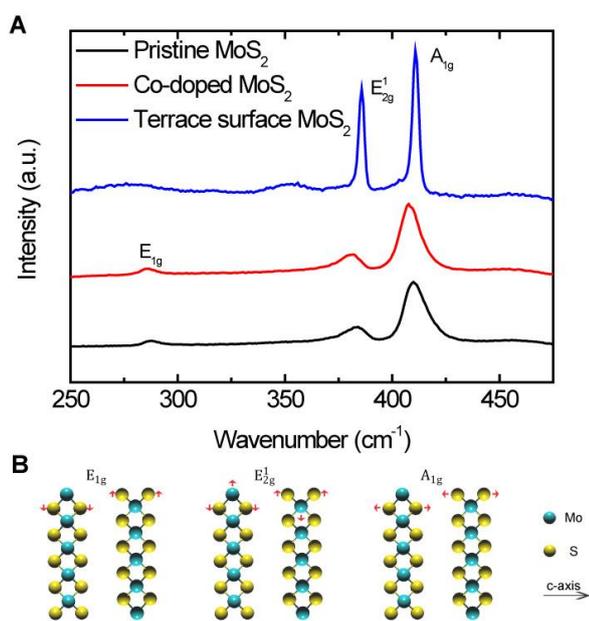


Figure 4. Raman spectra of the as-synthesized materials. (A) The Raman spectra of the pristine MoS₂, Co-doped MoS₂, and mechanically exfoliated MoS₂. The relative integrated intensity ratio of the E_{2g}¹ to A_{1g} peaks suggests the layer orientation on the substrate. (B) Schematic of different vibration modes of the MoS₂ layers.

4. Results and Discussion

Electrochemical characterizations were performed on the Fe, Co, Ni, Cu-doped MoS₂ samples as well as the pristine one by a standard three-electrode electrochemical cell (see Methods). The impedance test of the samples were performed at -0.1 V vs reversible hydrogen electrode (RHE) in Figure S1, which indicates that those films have similar

resistances. Polarization curves shown in Figure 5A were obtained after iR-correction at a scan rate of 2 mV/s. Pristine MoS₂ reaches -0.6 mA/cm² at 300 mV overpotential, which is largely improved after the transition metal atoms incorporated into the edge sites. The roughness of the thin film does not change much after the TM incorporation, with only ~3% increase in the surface area as measured by atomic force microscopy. Fe, Co, Ni, and Cu-doped MoS₂ nanofilms achieve -2.3, -3.5, -2.4, and -2.6 mA/cm² at 300 mV respectively, around 4 times of the pristine one. Figure 5B presents the Tafel plots corresponding to the polarization plots. Analyzing the Tafel slopes and exchange current densities can offer rich information about the density and activity of the active sites.[4] The Tafel slope of pristine MoS₂ results in 118 mV/decade, indicating that the rate-limiting step of HER is the discharge step with a very small surface coverage of adsorbed hydrogen.[22, 24] The doping process does not affect the Tafel slopes by much, resulting in a range of 117 to 103 Tafel slopes of those TM-doped MoS₂. The unaffected Tafel slopes suggest that the rate-limiting step is not changed after the doping process, and thus the comparison of the exchange current densities as well as the turnover frequency (TOF) per active site is meaningful. The exchange current densities of the pristine MoS₂ and TM-doped MoS₂ obtained by averaging three identical samples of each material are summarized in Table 2.

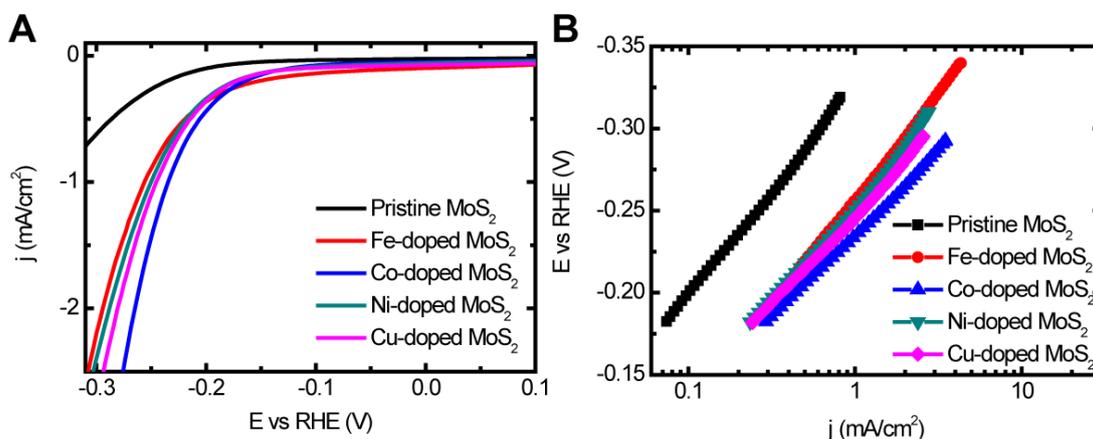


Figure 5. Electrochemical characterizations of the as-synthesized materials. (A) Polarization curves of the pristine and TM-doped MoS₂ nanofilms. (B) Tafel plots of the as-synthesized catalysts corresponding to those in (A).

Since the synthesized vertical MoS₂ layers stack with alternately exposed Mo-edges and S-edges, only every other layer in the pristine MoS₂ catalysts should be active for HER. According to the predictions from DFT, the S-edges should become similarly active or more active than the pristine Mo-edge once they are doped with TM atoms. Accordingly, the experimental total exchange current density has been at least doubled in the Fe-, Co-, and Cu-doped MoS₂ samples (Table 2). For Cu-doped MoS₂, where the S-edge binds hydrogen with the same strength as the pristine Mo-edge, we see that the exchange current density is almost exactly doubled, indicating a doubling of active sites with the same intrinsic activity. This also confirms our assumption that the Mo-edge should not be affected by doping in these cases. The Mo-edge becomes deactivated if there is significant doping, which would not lead to the doubling of exchange current density. The Ni-doped MoS₂ shows a total exchange current density that is slightly less than tripled, which also confirms our

theoretical calculations, which indicated that active sites should be tripled, but the per-site activity should be worse.

In order to compare the intrinsic activity of the catalysts with the theoretical trends, the experimental exchange current densities were normalized to the theoretical active site density, estimated from the number of active sites in each type of edge, the experimental lattice constant, and the experimental van der Waals interlayer distance (details in the supporting information). The numbers of active sites on the S-edges are shown in Table 1. The normalized exchange current densities and turnover frequencies (Table 2) show that the pristine MoS₂ and Cu-doped MoS₂ are similar, whereas the Fe-doped MoS₂ and Co-doped MoS₂ have much higher values, and the Ni-doped MoS₂ has a much lower value. This confirms the theoretical trends in ΔG_{H} where the order of activity should be Fe-doped MoS₂, Co-doped MoS₂ > pristine MoS₂, Cu-doped MoS₂ > Ni-doped MoS₂ based on how thermo-neutral the values of $|\Delta G_{\text{H}}|$ are.

Table 2. Exchange current densities and turnover frequencies for each catalyst normalized to the active site density. The exchange current densities are obtained by averaging three identical samples. The Tafel slopes are obtained from Figure 5B. The exchange current densities are normalized to the same number of active sites for Pt(111) in order to compare the intrinsic rates to the transition metals, as was done in [4].

Materials	$j_0(\mu\text{A}/\text{cm}^2)$	η (mV/decade)	Normalized Per-active Site j_0 ($\mu\text{A}/\text{cm}^2$)	TOF (s^{-1})
Pristine MoS ₂ *	2.20	118	25.9	0.054
Fe-doped MoS ₂	6.34	117	37.4	0.078
Co-doped MoS ₂	5.65	110	33.3	0.069
Ni-doped MoS ₂	5.50	117	21.6	0.045
Cu-doped MoS ₂	4.90	109	28.8	0.060

5. Conclusions

In summary DFT calculations were performed to predict the effect of doping vertically aligned MoS₂ layers with TM atoms. The S-edges, which constitute approximately half of the exposed catalyst surface, are predicted to become similarly active to the pristine Mo-edge upon TM doping. The experimentally determined total exchange current densities confirm that the activity is approximately doubled, and the normalized exchange current densities confirm the predicted trends in activity amongst the doped catalysts. Our study shows how the activity of a cheap, earth-abundant catalyst can be further improved by incorporating TM atoms. Furthermore, the vertically aligned MoS₂ catalysts provide a well-defined system for verifying the predicted effect of doping with TM atoms, which is to modify the activity of the S-edge. The success of the computational descriptor-based analysis in predicting the effect of TM doping and in describing the trends in HER activity suggests that a large scale screening of MoS₂ doped with various transition metal dopants could be performed to discover new MoS₂-based catalysts in the future.

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