# Transition-metal Doped Edge Sites in Vertically Aligned MoS<sub>2</sub> Catalysts for Enhanced Hydrogen Evolution

Haotian Wang<sup>1</sup>§, Charlie Tsai<sup>2,3</sup>§, Desheng Kong<sup>4</sup>, Karen Chan<sup>2,3</sup>, Frank Abild-Pedersen<sup>3</sup>, Jens K. Nørskov<sup>2,3</sup>(⊠), and Yi Cui<sup>4,5</sup>(⊠)

*Nano Res.*, Just Accepted Manuscript • DOI: 10.1007/s12274-014-0677-7 http://www.thenanoresearch.com on December 8 2014

© Tsinghua University Press 2014

# Just Accepted

This is a "Just Accepted" manuscript, which has been examined by the peer-review process and has been accepted for publication. A "Just Accepted" manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides "Just Accepted" as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these "Just Accepted" manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.



#### TABLE OF CONTENTS (TOC)

Transition-metal Doped Edge Sites in Vertically	
Aligned MoS <sub>2</sub> Catalysts for Enhanced Hydrogen	
Evolution	Insert your TOC graphics here.
Haotian Wang <sup>1§</sup> , Charlie Tsai <sup>2,3§</sup> , Desheng Kong <sup>4</sup> , Karen Chan <sup>2,3</sup> , Frank Abild-Pedersen <sup>3</sup> , Jens K. Nørskov <sup>2,3*</sup> , and Yi Cui <sup>4,5*</sup>	
<sup>1</sup> Department of Applied Physics, Stanford University,	
Stanford, CA 93205, USA	
<sup>2</sup> Department of Chemical Engineering, Stanford	
University, Stanford, CA 94305, USA	
<sup>3</sup> SUNCAT Center for Interface Science and Catalysis,	
SLAC National Accelerator Laboratory, 2575 Sand Hill	1–2-sentence summary of the paper. The font is Times New Roman
Road, Menlo Park, CA 94025, USA	9
<sup>4</sup> Department of Materials Science and Engineering,	
Stanford University, Stanford, CA 94305, USA	
<sup>5</sup> Stanford Institute for Materials and Energy Sciences,	
SLAC National Accelerator Laboratory, 2575 Sand Hill	
Road, Menlo Park, CA 94025, USA	
§ These authors contributed equally to this work.	

# **Transition-metal Doped Edge Sites in Vertically Aligned MoS<sub>2</sub> Catalysts for Enhanced Hydrogen Evolution**

Haotian Wang<sup>1</sup>, Charlie Tsai<sup>2,3</sup>, Desheng Kong<sup>4</sup>, Karen Chan<sup>2,3</sup>, Frank Abild-Pedersen<sup>3</sup>, Jens K. Nørskov<sup>2,3</sup>( $\boxtimes$ ), and Yi Cui<sup>4,5</sup>( $\boxtimes$ )

<sup>1</sup> Department of Applied Physics, Stanford University, Stanford, CA 93205, USA

<sup>2</sup> Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA

<sup>3</sup> SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA

<sup>4</sup> Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA

<sup>5</sup> Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA

§ These authors contributed equally to this work.

Received: day month year / Revised: day month year / Accepted: day month year (automatically inserted by the publisher) © Tsinghua University Press and Springer-Verlag Berlin Heidelberg 2011

### 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 MoS<sub>2</sub>, 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 MoS<sub>2</sub> nanofilms provide a well-defined model system for verifying these predictions. The transition metal doped MoS<sub>2</sub> 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

Address correspondence to J. K. Nørskov, norskov@stanford.edu; Yi Cui, yicui@stanford.edu

## 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 earthabundant HER catalysts are needed for large scale production. Molybdenum disulfide (MoS<sub>2</sub>) 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<sub>2</sub> was found to be very close to zero,[3] suggesting that MoS<sub>2</sub> 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<sub>2</sub> edge length rather than with the surface area.[4] The high HER activity of molecular electrocatalysts incorporating a MoS<sub>2</sub> 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, made significant progress has been in nanostructuring MoS<sub>2</sub> 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 MoO3 thin films precursors into polycrystalline MoS<sub>2</sub> 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<sub>2</sub> nanofilms can be further improved by activating the S-edge, which is calculated to be inactive for HER.[13, 25] As a hydrodesulfurization catalyst, MoS2 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 MoS2 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 studies so far, metal dopants are evenly distributed onto the entire synthesized MoS<sub>2</sub> 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<sub>2</sub> 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,  $\Delta G_{H}$ , was previously found to be an accurate descriptor for HER activity,[30] with the optimal HER catalyst having a thermo-neutral  $\Delta G_{\rm H}$ . Herein, we used density functional theory (DFT) to calculate the  $\Delta G_{\rm H}$  on the Sedges of Co-, Fe-, Ni-, and Cu-doped MoS2 to elucidate the trends in predicted activity for these structures. In order to accurately determine the  $\Delta G_{\rm H}$ 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  $\Delta G_{\rm H}$ . 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 doped 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  $\Delta G_{\rm H}$  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 MoS<sub>2</sub> 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  $|\Delta G_H|$  that are closer to thermo-neutral than the pristine MoS<sub>2</sub> S-edge, indicating improved activity at the S-edge. In the cases of MoS<sub>2</sub> 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  $\Delta G_{\rm H}$  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 MoS<sub>2</sub>, 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  $MoS_2$  and doped  $MoS_2$  catalysts. The adsorbed hydrogen atoms that is the most thermo-neutral is circled in red. For the S-edge of Ni-doped  $MoS_2$ , 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 <sub>2</sub> catalyst	Edge	Structure	$\theta_{\rm H}({\rm ML})$	Active Sites	$\Delta G_{\rm H}({ m eV})$	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 MoS<sub>2</sub> nanofilm structures,[22] the layers stack with alternating Moand 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  $\Delta G_{\rm H}$  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  $\Delta G_{\rm H}$  values suggest that when compared to pristine MoS<sub>2</sub>, Fe-doped MoS<sub>2</sub> and Co-doped MoS<sub>2</sub> should have higher activity per active site, while Cu-doped MoS<sub>2</sub> should have similar activity per active site.

For the Ni-doped S-edge, two H atoms have very similar  $\Delta G_{H}$ , 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

MoS<sup>2</sup> 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 though 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 MoS<sup>2</sup> nanofilms were synthesized by chemical vapor deposition of rapid sulfurization method.[22] The schematic of the top-view of the layer vertically aligned MoS<sub>2</sub> 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 layervertically-aligned  $MoS_2$ nanofilm (Supporting Information). Since the diffusion of the TM atoms into the MoS<sub>2</sub> 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 MoS<sub>2</sub>. (B) Schematic of the top view of the edge-terminated surface of MoS<sub>2</sub>. (C) Schematic of the chemical vapor deposition synthesis of TM doped MoS<sub>2</sub> 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 MoS<sub>2</sub> matrix. The color gradient represents the gradually reduced concentration of the TM atoms.

#### 3.2. Characterizations

Characterizations were performed on the Co-doped MoS<sub>2</sub> as an example to understand the differences in material properties between the pristine and the TMdoped MoS<sub>2</sub> (characterizations of other TM-doped MoS<sub>2</sub> are also included in the Supporting Information). Transmission electron microscopy (TEM) images in Figure 2 show the texture of the MoS<sub>2</sub> nanofilms before and after Co doping. Figure 2A shows the pristine MoS<sub>2</sub> 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  $MoS_2$  nanofilm. The grains are around 10 nm with random orientations within the plane. (B) TEM image of the Co-doped  $MoS_2$  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 MoS<sub>2</sub> 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 MoS<sub>2</sub> 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 MoS<sub>2</sub> 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<sub>5/3</sub> and Mo 3d<sub>3/2</sub> in the pristine MoS<sub>2</sub> 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<sub>3/2</sub> binding energy of 161.8 eV confirms the -2 oxidation state for the sulfur.[17, 34, 35] Since the XPS spectra of MoS<sub>2</sub> and Co-doped MoS<sub>2</sub> 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 MoS<sub>2</sub> nanofilm. The weak signal implies the small amount of Co atoms in the MoS<sub>2</sub> 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 MoS<sub>2</sub> layers. (C) Mo 3d regions of the pristine and Co-doped MoS<sub>2</sub> nanofilms. (D) S 2p regions of the pristine and Co-doped MoS<sub>2</sub> nanofilms.

Raman spectroscopy is employed to test both the composition and orientation of the as-grown pristine and Co-doped MoS<sub>2</sub> nanofilms on glassy carbon. Pristine MoS<sub>2</sub> in Figure 4A has three distinct vibration modes located at 287, 381, and 409 cm<sup>-1</sup>, corresponding to the E1g, E2g1, and A1g first-order phonon modes of  $MoS_2$  at the  $\Gamma$  point of the Brillouin zone respectively (Figure 4B).[17, 22, 36-40]. The relative integrated intensity ratio of the E2g1 to A1g peaks in Figure 4A provides rich texture information about the thin films. The vibration direction of A1g mode is c-axis, which is preferentially excited for the edge-terminated structure and results in a small E2g1 to A<sub>1g</sub> peak ratio of ~ 30 %.[22] E<sub>2g</sub><sup>1</sup> 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 MoS<sup>2</sup> spectrum has almost the same features with the pristine one, suggesting that the MoS<sup>2</sup> 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 MoS<sup>2</sup> surface edge sites.



**Figure 4.** Raman spectra of the as-synthesized materials. (A) The Raman spectra of the pristine MoS<sub>2</sub>, Co-doped MoS<sub>2</sub>, and mechanically exfoliated MoS<sub>2</sub>. 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 MoS<sub>2</sub> layers.

#### 4. Results and Discussion

Electrochemical characterizations were performed on the Fe, Co, Ni, Cu-doped MoS<sub>2</sub> 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 MoS<sub>2</sub> reaches - 0.6 mA/cm<sup>2</sup> 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/cm<sup>2</sup> 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 MoS<sub>2</sub>. 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 MoS<sub>2</sub> and TM-doped MoS<sub>2</sub> 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 MoS<sub>2</sub> nanofilms. (B) Tafel plots of the as-synthesized catalysts corresponding to those in (A).

Since the synthesized vertical MoS<sub>2</sub> layers stack with alternatingly 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 Moedge 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 MoS<sub>2</sub> samples (Table 2). For Cu-doped MoS<sub>2</sub>, 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 MoS<sub>2</sub> 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 MoS<sub>2</sub> and Cu-doped MoS<sub>2</sub> are similar, whereas the Fe-doped MoS<sub>2</sub> and Codoped MoS<sub>2</sub> have much higher values, an the Nidoped MoS<sub>2</sub> has a much lower value. This confirms the theoretical trends in  $\Delta G_H$  where the order of activity should be Fe-doped MoS<sub>2</sub>, Co-doped MoS<sub>2</sub> > pristine MoS<sub>2</sub>, Cu-doped MoS<sub>2</sub> > Ni-doped MoS<sub>2</sub> based on how thermo-neutral the values of  $|\Delta G_{\rm H}|$  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 jo(p	$i_{0}(\mathbf{u} \wedge l_{0}m^{2})$	$\eta$ (mV/decade)	Normalized	TOF (a-1)
	<i>J</i> <sub>0</sub> (μΑ/cm <sup>-</sup> )		Per-active Site $j_0$ ( $\mu$ A/cm <sup>2</sup> )	101 (8)
Pristine MoS <sub>2</sub> *	2.20	118	25.9	0.054
Fe-doped MoS <sub>2</sub>	6.34	117	37.4	0.078
Co-doped MoS <sub>2</sub>	5.65	110	33.3	0.069
Ni-doped MoS <sub>2</sub>	5.50	117	21.6	0.045
Cu-doped MoS <sub>2</sub>	4.90	109	28.8	0.060

#### 5. Conclusions

In summary DFT calculations were performed to predict the effect of doping vertically aligned MoS<sub>2</sub> 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.

#### Acknowledgements

H.W., D.K. and Y.C. acknowledge support by the Department of Energy, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, under contract DE-AC02-76-SFO0515. C.T., K.C., F.A-P., and J.K.N. acknowledge support from the Center on Nanostructuring for Efficient Energy Conversion (CNEEC) at Stanford University, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Basic Energy Sciences under award number DE-SC0001060. F.A.-P. and J.K.N. acknowledge financial support from the U.S. Department of Energy, Office of Basic Energy Sciences to the SUNCAT Center for Interface Science and Catalysis. C.T. acknowledges financial support from the NSF GRFP Grant DGE-114747.

**Electronic Supplementary Material**: Supplementary material (details of the experiments and calculation details) is available in the online version of this article at <u>http://dx.doi.org/10.1007/s12274-\*\*\*\_\*\*\*\_\*</u>.

#### References

- Dresselhaus, M. S.; Thomas, I. L. Alternative energy technologies. *Nature* 2001, 414, 332-337.
- [2] Lewis, N. S.; Nocera, D. G. Powering the planet: Chemical challenges in solar energy utilization. *Proceedings of the National Academy* of Sciences 2006, 103, 15729-15735.
- [3] Hinnemann, B.;Moses, P. G.;Bonde, J. L.;Jørgensen, K. P.;Nielsen, J. H.;Horch, S.;Chorkendorff, I.; Nørskov, J. K. Biomimetic Hydrogen Evolution: MoS<sub>2</sub> Nanoparticles as Catalyst for Hydrogen Evolution. *J. Am. Chem. Soc.* 2005, *127*, 5308-5309.
- [4] Jaramillo, T. F.;Jorgensen, K. P.;Bonde, J.;Nielsen, J. H.;Horch, S.; Chorkendorff, I. Identification of Active Edge Sites for Electrochemical H2 Evolution from MoS2 Nanocatalysts. *Science* 2007, 317, 100-102.
- [5] Li, Y.;Wang, H.;Xie, L.;Liang, Y.;Hong, G.; Dai,
  H. MoS2 Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction. *Journal of the American Chemical Society* 2011, 133, 7296-7299.
- [6] Zong, X.;Yan, H.;Wu, G.;Ma, G.;Wen, F.;Wang,
  L.; Li, C. Enhancement of Photocatalytic H2 Evolution on CdS by Loading MoS2 as Cocatalyst under Visible Light Irradiation. *Journal of the American Chemical Society* 2008, 130, 7176-7177.
- [7] Prins, R.;De Beer, V. H. J.; Somorjai, G. A. Structure and Function of the Catalyst and the Promoter in Co-Mo Hydrodesulfurization Catalysts. *Catalysis Reviews* 1989, *31*, 1-41.
- [8] Coulier, L.;de Beer, V. H. J.;van Veen, J. A. R.; Niemantsverdriet, J. W. On the formation of cobalt-molybdenum sulfides in silicasupported hydrotreating model catalysts. *Topics in Catalysis* 2000, 13, 99-108.
- [9] Jaramillo, T. F.;Bonde, J.;Zhang, J.;Ooi, B. L.;Andersson, K.;Ulstrup, J.; Chorkendorff, I.
   Hydrogen Evolution on Supported

Incomplete Cubane-type [Mo3S4]4+ Electrocatalysts. *The Journal of Physical Chemistry C* 2008, 112, 17492-17498.

- Karunadasa, H. I.;Montalvo, E.;Sun, Y.;Majda,
   M.;Long, J. R.; Chang, C. J. A Molecular MoS2
   Edge Site Mimic for Catalytic Hydrogen
   Generation. *Science* 2012, 335, 698-702.
- [11] Vrubel, H.;Merki, D.; Hu, X. Hydrogen evolution catalyzed by MoS3 and MoS2 particles. *Energy & Environmental Science* 2012, 5, 6136-6144.
- [12] Laursen, A. B.;Kegnaes, S.;Dahl, S.; Chorkendorff, I. Molybdenum sulfidesefficient and viable materials for electro - and photoelectrocatalytic hydrogen evolution. *Energy & Environmental Science* 2012, 5, 5577-5591.
- Bonde, J.;Moses, P. G.;Jaramillo, T. F.;Nørskov,
   J. K.; Chorkendorff, I. Hydrogen evolution on nano-particulate transition metal sulfides.
   *Faraday Discuss.* 2008, 140, 219.
- [14] Wang, H.;Lu, Z.;Kong, D.;Sun, J.;Hymel, T. M.; Cui, Y. Electrochemical Tuning of MoS2 Nanoparticles on Three-Dimensional Substrate for Efficient Hydrogen Evolution. ACS Nano 2014, 8, 4940-4947.
- [15] Xie, J.;Zhang, H.;Li, S.;Wang, R.;Sun, X.;Zhou, M.;Zhou, J.;Lou, X. W.; Xie, Y. Defect-Rich MoS2 Ultrathin Nanosheets with Additional Active Edge Sites for Enhanced Electrocatalytic Hydrogen Evolution. Advanced Materials 2013, 25, 5807-5813.
- [16] Lu, Z.;Zhang, H.;Zhu, W.;Yu, X.;Kuang, Y.;Chang, Z.;Lei, X.; Sun, X. In situ fabrication of porous MoS2 thin-films as highperformance catalysts for electrochemical hydrogen evolution. *Chemical Communications* 2013, 49, 7516-7518.
- [17] Kibsgaard, J.;Chen, Z.;Reinecke, B. N.;Jaramillo, T. F. Engineering the surface

structure of MoS2 to preferentially expose active edge sites for electrocatalysis. *Nat Mater* **2012**, *11*, 963-969.

- [18] Chen, Z.;Cummins, D.;Reinecke, B. N.;Clark, E.;Sunkara, M. K.; Jaramillo, T. F. Core-shell MoO3-MoS2 Nanowires for Hydrogen Evolution: A Functional Design for Electrocatalytic Materials. *Nano Letters* 2011, 11, 4168-4175.
- [19] Merki, D.;Fierro, S.;Vrubel, H.; Hu, X. Amorphous molybdenum sulfide films as catalysts for electrochemical hydrogen production in water. *Chemical Science* 2011, 2, 1262-1267.
- Benck, J. D.;Chen, Z.;Kuritzky, L. Y.;Forman, A.
   J.; Jaramillo, T. F. Amorphous Molybdenum Sulfide Catalysts for Electrochemical Hydrogen Production: Insights into the Origin of their Catalytic Activity. ACS Catalysis 2012, 2, 1916-1923.
- [21] Merki, D.;Vrubel, H.;Rovelli, L.;Fierro, S.; Hu, X. Fe, Co, and Ni ions promote the catalytic activity of amorphous molybdenum sulfide films for hydrogen evolution. *Chemical Science*, 3, 2515-2525.
- [22] Kong, D.;Wang, H.;Cha, J. J.;Pasta, M.;Koski, K. J.;Yao, J.; Cui, Y. Synthesis of MoS2 and MoSe2 Films with Vertically Aligned Layers. *Nano Letters* 2013, 13, 1341-1347.
- [23] Wang, H.;Lu, Z.;Xu, S.;Kong, D.;Cha, J. J.;Zheng, G.;Hsu, P.-C.;Yan, K.;Bradshaw, D.;Prinz, F. B.; Cui, Y. Electrochemical tuning of vertically aligned MoS2 nanofilms and its application in improving hydrogen evolution reaction. *Proceedings of the National Academy of Sciences* 2013, 110, 19701-19706.
- [24] Wang, H.;Kong, D.;Johanes, P.;Cha, J. J.;Zheng,
   G.;Yan, K.;Liu, N.; Cui, Y. MoSe2 and WSe2
   Nanofilms with Vertically Aligned Molecular
   Layers on Curved and Rough Surfaces. *Nano Letters* 2013, 13, 3426-3433.
- [25] Tsai, C.;Abild-Pedersen, F.; Nørskov, J. K.

Tuning the MoS2 Edge-Site Activity for Hydrogen Evolution via Support Interactions. *Nano Letters* **2014**, *14*, 1381-1387.

- [26] Lauritsen, J. V.;Kibsgaard, J.;Olesen, G. H.;Moses, P. G.;Hinnemann, B.;Helveg, S.;Nørskov, J. K.;Clausen, B. S.;Topsøe, H.; Lægsgaard, E. Location and coordination of promoter atoms in Co-and Ni-promoted MoS2-based hydrotreating catalysts. *J. Catal.* 2007, 249, 220-233.
- [27] Bouwens, S. M. A. M.;Vanzon, F. B. M.;Vandijk, M. P.;Vanderkraan, A. M.;Debeer, V. H. J.;Vanveen, J. A. R.; Koningsberger, D. C. On the Structural Differences Between Alumina-Supported Comos Type I and Alumina-, Silica-, and Carbon-Supported Comos Type II Phases Studied by XAFS, MES, and XPS. *Journal of Catalysis* 1994, 146, 375-393.
- [28] Byskov, L. S.;Nørskov, J. K.;Clausen, B. S.; Topsøe, H. DFT Calculations of Unpromoted and Promoted MoS2-Based Hydrodesulfurization Catalysts. J. Catal. 1999, 187, 109-122.
- [29] Merki, D.;Vrubel, H.;Rovelli, L.;Fierro, S.; Hu, X. Fe, Co, and Ni ions promote the catalytic activity of amorphous molybdenum sulfide films for hydrogen evolution. *Chemical Science* 2012, *3*, 2515-2525.
- [30] Nørskov, J. K.;Bligaard, T.;Logadóttir, Á.;Kitchin, J. R.;Chen, J. G.;Pandelov, S.; Stimming, U. Trends in the Exchange Current for Hydrogen Evolution. In *J. Electrochem. Soc.*, 2005; pp J23-J26.
- [31] Kibsgaard, K. J.;Tuxen, A.;Knudsen, G.;Brorson, M.;Topsøe, H.;Lægsgaard, Besenbacher, E.;Lauritsen, J. V.; F. atomic-scale Comparative analysis of promotional effects by late 3d-transition metals in MoS<sub>2</sub> hydrotreating catalysts. J. Catal. 2010, 272, 195-203.
- [32] Hannes Schweiger, P. R., Hervé Toulhoat Promoter Sensitive Shapes of Co(Ni)MoS

Nanocatalysts in Sulfo-Reductive Conditions. *Journal of Catalysis* **2002**, *212*, 33-38.

- [33] Tsai, C.;Chan, K.;Abild-Pedersen, F.; Norskov,
   J. K. Active edge sites in MoSe2 and WSe2 catalysts for the hydrogen evolution reaction:
   a density functional study. *Physical Chemistry Chemical Physics* 2014, 16, 13156-13164.
- [34] Patterson, T. A.;Carver, J. C.;Leyden, D. E.; Hercules, D. M. A surface study of cobaltmolybdena-alumina catalysts using x-ray photoelectron spectroscopy. *The Journal of Physical Chemistry* **1976**, *80*, 1700-1708.
- [35] Muijsers, J. C.;Weber, T.;Vanhardeveld, R. M.;Zandbergen, H. W.; Niemantsverdriet, J. W. Sulfidation Study of Molybdenum Oxide Using MoO3/SiO2/Si(100) Model Catalysts and Mo-IV3-Sulfur Cluster Compounds. *Journal of Catalysis* 1995, 157, 698-705.
- [36] Stacy, A. M.; Hodul, D. T. Raman spectra of IVB and VIB transition metal disulfides using laser energies near the absorption edges.

Journal of Physics and Chemistry of Solids **1985**, 46, 405-409.

- [37] Wieting, T. J.; Verble, J. L. Infrared and Raman Studies of Long-Wavelength Optical Phonons in Hexagonal MoS\_{2}. *Physical Review B* 1971, 3, 4286-4292.
- [38] Castellanos-Gomez, A.;van der Zant, H. J.; Steele, G. Folded MoS2 layers with reduced interlayer coupling. *Nano Res.* **2014**, *7*, 1-7.
- [39] Zhou, H.;Yu, F.;Liu, Y.;Zou, X.;Cong, C.;Qiu, C.;Yu, T.;Yan, Z.;Shen, X.;Sun, L.;Yakobson, B.; Tour, J. Thickness-dependent patterning of MoS2 sheets with well-oriented triangular pits by heating in air. *Nano Res.* 2013, *6*, 703-711.
- [40] Huang, Y.;Wu, J.;Xu, X.;Ho, Y.;Ni, G.;Zou, Q.;Koon, G.;Zhao, W.;Castro Neto, A. H.;Eda, G.;Shen, C.; Özyilmaz, B. An innovative way of etching MoS2: Characterization and mechanistic investigation. *Nano Res.* 2013, 6, 200-207.