# Supporting Information for

# Atomic origins of nickel doping enhanced electrocatalysis of monolayer MoS<sub>2</sub> for electrochemical hydrogen production

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#### **Experimental Procedures**

Synthesis and characterization of Ni doped MoS<sub>2</sub> (Ni-MoS<sub>2</sub>). The 1.0Ni-MoS<sub>2</sub> catalysts were synthesized by a one-step hydrothermal method. A 20 ml aqueous solution containing 0.5 mmol Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, 0.5 mmol NiSO<sub>4</sub>·6H<sub>2</sub>O and 2.5 mmol L-cysteine was stirred for 0.5 hour, and then transferred into a 25 ml Teflon-line stainless steel autoclave and kept at 200 °C for 24 hours. After rinsing with 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution and deionized water, the precipitates of Ni-MoS<sub>2</sub> were dried in air at 40 °C for 12 h. For comparison, pristine MoS<sub>2</sub> was synthesized through the same process without involving NiSO4·6H2O. The 0.5Ni-MoS<sub>2</sub> and 2.0Ni-MoS<sub>2</sub> samples were synthesized with 0.25 mmol and 1.0 mmol NiSO<sub>4</sub>·6H<sub>2</sub>O, respectively. All the chemicals, Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, NiSO<sub>4</sub>·6H<sub>2</sub>O and L-cysteine were purchased from Aldrich and used as received from commercial suppliers. The microstructures of MoS<sub>2</sub> and Ni-MoS<sub>2</sub> ware characterized by a transmission electron microscope (JEOL ARM 200F) equipped with an aberration corrector for image-forming lens systems. Chemical analyses of the MoS<sub>2</sub> and Ni-MoS<sub>2</sub> were conducted by using X-ray energydispersive spectroscopy and X-ray photoelectron spectroscopy (AXIS ultra DLD, Shimazu). The HAADF-STEM images ware obtained by a transmission electron microscope (JEOL ARM 200F) equipped with a cold emission gun and an aberration corrector for the probe-forming lens system.

Electrochemical measurements. Hydrogen evolution reaction (HER) was tested with cyclic voltammetry (CV) and electrochemical impedance (Iviumstat Technology) in a three-electrode cell with a glassy carbon plate as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode at room temperature. All potentials were referenced to a reversible hydrogen electrode by adding a value of (E (SCE) +  $0.0591PH + E^0$  (SCE)) V. The hydrogen electrode (RHE) scale was calibrated using a pure Pt electrode before each test. For preparing the working electrode, 1 mg of catalyst and 20 µL of Nafion solution (5 wt %, DuPont Corporation) were first dispersed in 500 µL of water-ethanol solution (volume ratio: 3:1). The suspension was then sonicated (bath sonication, 200 W) for 30 min to form a homogeneous ink. Then, 10 µL of the catalyst ink was dripped onto the surface of a glassy carbon electrode (5 mm in diameter). The resulting electrodes were dried at room temperature for 10 h to yield a catalyst loading of approximately 0.77 mg/cm<sup>2</sup>. The CV measurements were taken from -0.50 V to 0 V at a scan rate of 10 mV/s in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. All the electrochemical data in the paper were not iR corrected.

**DFT calculations.** Our calculations were performed using the Vienna ab initio simulation package (VASP) based on the density functional theory  $(DFT)^1$  within the generalized gradient approximations (GGA-PBE)<sup>2</sup>. The projector augmented-wave (PAW)<sup>3</sup> pseudopotential method was used with a cutoff energy of 450 eV. In order to examine the convergence of the results with a supercell size, two supercells with the sizes of  $5 \times 5 \times 1$  and  $6 \times 6 \times 1$  of the MoS<sub>2</sub> primitive cell were used with a separation of 15 Å between two layers. All atomic positions were relaxed using  $6 \times 6 \times 2$  k-point grids, which depend on the size of the supercell. The lattice constant of the MoS<sub>2</sub> monolayer was 3.183 Å. After Ni incorporation, the optimized lattice constant of the

(Mo,Ni)S<sub>2</sub> monolayer was 3.236 Å. The positions of all atoms and lattice parameters were optimized until the residual forces were smaller than 0.01 eV/Å. The total energy in our models was relaxed to be the minimum while a precision of  $10^{-5}$  eV was reached.

The adsorption energy is estimated as  $\Delta E_{H} = E_{Mo(Ni)S2+nH} - E_{Mo(Ni)S2+(n-1)H} - E_{H2}/2$ , where  $E_{Mo(Ni)S2+nH}$  is the total energy of the Mo(Ni)S<sub>2</sub> system with n hydrogen atoms adsorbed on the surface,  $E_{Mo(Ni)S2+(n-1)H}$  is the total energy for (n-1) hydrogen atoms adsorbed on the surface and the  $E_{H2}$  is the energy for a hydrogen molecule in the gas phase. The Gibbs free energy for hydrogen adsorption is calculated by including this correction:  $G_{H} = \Delta E_{H} + \Delta E_{ZPE} - T\Delta S_{H}$ . Here the  $\Delta E_{ZPE}$  is the difference in zero point energy between the adsorbed hydrogen and hydrogen in the gas phase and  $\Delta S_{H}$  is the entropy between the adsorbed state and the gas phase.

$MoS_2: G_H = \Delta E_H + 0.235 \text{ eV}$	$Ni_{0.04}Mo_{0.96}S_2$ : $G_H = \Delta E_H + 0.374 eV$
$Ni_{0.06}Mo_{0.94}S_2$ : $G_H = \Delta E_H + 0.369 \text{ eV}$	$Ni_{0.12}Mo_{0.88}S_2$ : $G_H = \Delta E_H + 0.274 \text{ eV}$
$Ni_{0.16}Mo_{0.84}S_2$ : $G_H = \Delta E_H + 0.272 \text{ eV}$	$Ni_{0.19}Mo_{0.81}S_2$ : $G_H = \Delta E_H + 0.256 \text{ eV}$

#### **Results and Discussion**

1. The HER performance of pristine MoS<sub>2</sub> and 1.0Ni-MoS<sub>2</sub> in KOH



Figure S1. HER measurements of pristine  $MoS_2$  and  $1.0Ni-MoS_2$  in 1 M KOH. (a) Polarization curves; and (b) corresponding Tafel plots.

2. The layer numbers and interlayer spacings in the pristine MoS<sub>2</sub> and 1.0Ni-MoS<sub>2</sub>.



Figure S2. TEM characterization of pristine  $MoS_2$  and  $1.0Ni-MoS_2$ . (a) Low magnification TEM image of pristine  $MoS_2$ ; (b) Enlarged TEM image showing the layer numbers and interlayer distance of pristine  $MoS_2$ ; (c) Low magnification TEM image of  $1.0Ni-MoS_2$ ; (d) Enlarged TEM image showing the layer numbers and interlayer distance of  $1.0Ni-MoS_2$ . The blue numbers in (b) and (d) represent the layer numbers and the red lines as used as the marks for measuring the interlayer distance. The scale bar in (a) and (c) is 200 nm and in (b) and (d) is 1 nm, respectively.

3. XRD patterns of the pristine MoS<sub>2</sub>, 0.5Ni-MoS<sub>2</sub>, 1.0Ni-MoS<sub>2</sub>, and 2.0Ni-MoS<sub>2</sub>.

As shown in Figure S3, the peaks representing (002) plane of  $MoS_2$  in Ni-MoS<sub>2</sub> have a significant shift compared with standard and pristine  $MoS_2$ , indicating a distance expansion of the interlayer space. Besides, in the XRD pattern of the 2.0Ni-MoS<sub>2</sub>, extra peaks emerged, revealing the formation of NiS in the highly Ni doped sample.



**Figure S3.** XRD patterns of the pristine  $MoS_2$ , 0.5Ni- $MoS_2$ , 1.0Ni- $MoS_2$ , and 2.0Ni- $MoS_2$ . The standard pattern of  $MoS_2$  and NiS are shown as reference.

#### 4. TEM characterization of 0.5Ni-MoS<sub>2</sub>

As shown in Figure S1a and b, 0.5Ni-MoS<sub>2</sub> has a similar morphology with 1.0Ni-MoS<sub>2</sub>, with the layer number of 1-7 and the interlayer distance is ~ 0.86 nm, larger than that of pure MoS<sub>2</sub> but smaller than that of 1.0Ni-MoS<sub>2</sub>. The STEM-EDS mappings in Figure S2d–g show that Mo, S and Ni elements are homogeneously dispersed over the 0.5Ni-MoS<sub>2</sub> nanosheets. The quantitative EDS analysis suggests the chemical composition is Ni<sub>0.04</sub>Mo<sub>0.96</sub>S<sub>2</sub>. Particulaly, Figure S2c shows the atomic HAADF-STEM image of 0.5Ni-MoS<sub>2</sub>, and the Ni atom found here doesn't have a significant offset distance, while in 1.0Ni-MoS<sub>2</sub> the average offset distance is ~ 0.05 nm.



**Figure S4.** TEM characterization of 0.5Ni-MoS<sub>2</sub>. (a) Low magnification TEM image; (b) high reselusion TEM image; (c) HAADF-STEM image; (d), (e) (f) and (g) STEM-EDS mappings of Mo, S, Ni and mix, respectively. The scale bar in (a), (b) and (c) is 50 nm, 5 nm and 0.5 nm, and in (d) - (g) is 50 nm, respectively.

## 5. TEM characterization of 2.0Ni-MoS<sub>2</sub>

Figure S2a shows the morphology of 2.0Ni-MoS<sub>2</sub>. Selected aera electron diffraction (SAED) (Figure S2b) reveals the formation of NiS with a hexagonal structure. Figure S2c shows the HAADF-STEM image of the NiS phase. Many brighter atoms are embedded in the NiS lattices, suggesting the NiS phase contains Mo.



**Figure S5.** TEM characterization of 2.0Ni-MoS<sub>2</sub>. (a) Low magnification TEM image; (b) SAED; (c) HAADF-STEM image; (d), (e) (f) and (g) STEM-EDS mappings of Mo, S, Ni and mix, respectively. The scale bar in (a) and (c) is 500 nm and 2 nm, and in (d) - (g) is 200 nm respectively.



6. XPS characterization of pristine  $MoS_2$  and  $Ni-MoS_2$ 

**Figure S6.** XPS spectra of (a) pristine  $MoS_2$ , (b) 0.5Ni-MoS<sub>2</sub>, (c) 1.0Ni-MoS<sub>2</sub> and (d) 2.0Ni-MoS<sub>2</sub>, respectively.

7. Atomic models and corresponding simulated STEM images of monolayer and bilayer  $MoS_2$ 

Figure S4 shows the projective atomic models and corresponding simulated STEM images of monolayer and bilayer  $MoS_2$  from top view. The difference of the two samples can be easily distinguished from the HAADF-STEM images as shown in (e) and (f).<sup>4</sup> Therefore, the deconvoluted HAADF-STEM image of Ni-MoS<sub>2</sub> showing in Figure 3a can be confirmed from the monolayer structure.



Monolayer 1H MoS<sub>2</sub>

**Bilayer 2H MoS<sub>2</sub>** 

**Figure S7.** Projected structure models of (a) monolayer 1H  $MoS_2$  and (b) bilayer 2H  $MoS_2$  from side view; projected structure models of (c) monolayer 1H  $MoS_2$  and (d) bilayer 2H  $MoS_2$  from top view, i.e. [001] direction. Corresponding stimulated HAADF-STEM images of (e) monolayer 1H  $MoS_2$  and (f) bilayer 2H  $MoS_2$  from top view.

8. Comparison between original and deconvoluted STEM images of 1.0Ni-MoS<sub>2</sub> We used ultra thin carbon TEM grid with 300 mesh to hold our samples when observing under TEM and STEM. The 3nm amorphous carbon film, unfortunately, still affected the contrast of monolayer MoS<sub>2</sub>, as shown in figure S5a. To eliminate the substrate influence, we used a deconvolution method to filter the image with *HREM DeConvHAADF* software,<sup>5</sup> and the result is shown in Figure 3a and S5b. Figure S5c shows the difference of the intensity between the original and deconvoluted images.



**Figure S8.** (a) Original atomic HAADF-STEM image of 1.0Ni-MoS<sub>2</sub>; (b) corresponding deconvoluted HAADF-STEM image of 1.0Ni-MoS<sub>2</sub> with red false colour; (c) the intensity line profiles in image (a) along the red rectangle and image (b) along the green dashed rectangle. The scale bar in (a) and (b) is 0.5 nm.

9. The chemical bonding structures of Mo-S in  $2H-MoS_2$  and Ni-S bond in NiS.



Figure S9. (a) The trigonal prism coordination for the Mo atom in  $2H-MoS_2$  and (b) the octahedral coordination for the Ni atom in NiS.



10. DFT-optimized structure models of  $Ni-MoS_2$  with different Ni contents

Figure S10. DFT-optimized structure models of (a)  $Ni_{0.04}Mo_{0.96}S_2$ , (b)  $Ni_{0.08}Mo_{0.92}S_2$ , (c)  $Ni_{0.12}Mo_{0.88}S_2$  and (d)  $Ni_{0.16}Mo_{0.84}S_2$ , respectively.



11. Band structures of pristine MoS<sub>2</sub> and Ni-MoS<sub>2</sub>

Figure S11. Band structures of (a) pristine  $MoS_2$ , (b)  $Ni_{0.04}Mo_{0.96}S_2$ , (c)  $Ni_{0.08}Mo_{0.92}S_2$ , (d)  $Ni_{0.12}Mo_{0.88}S_2$  (e)  $Ni_{0.16}Mo_{0.84}S_2$ , and (f)  $Ni_{0.19}Mo_{0.81}S_2$ , respectively.



12. The total density of states (TDOS) and projected density of states (PDOS) of pristine  $MoS_2$  and  $Ni-MoS_2$ 

Figure S12. The TDOS and PDOS on (a) pristine  $MoS_2$  (b)  $Ni_{0.04}Mo_{0.96}S_2$ , (c)  $Ni_{0.08}Mo_{0.92}S_2$ , (d)  $Ni_{0.12}Mo_{0.88}S_2$  (e)  $Ni_{0.16}Mo_{0.84}S_2$ , and (f)  $Ni_{0.19}Mo_{0.81}S_2$ , respectively.



13. Charge distributions in Ni-MoS<sub>2</sub> with different Ni contents

**Figure S13.** Partial charge density of of (a)  $Ni_{0.04}Mo_{0.96}S_2$ , (b)  $Ni_{0.08}Mo_{0.92}S_2$ , (c)  $Ni_{0.12}Mo_{0.88}S_2$  and (d)  $Ni_{0.16}Mo_{0.84}S_2$ , respectively. Yellow and blue isosurfaces represent positive and negative charges, respectively.

**Table S1.** Table Caption Calculated adsorption energy  $[\Delta E_H (H^*)]$  and Gibbs free energy  $[G_H (H^*)]$ .

Catalysts	Adsorption energy $\Delta E_{H}$ (eV)	Gibbs free energy G <sub>H</sub> (eV)	
$MoS_2$	-0.952	-0.717	
Ni <sub>0.04</sub> Mo <sub>0.96</sub> S <sub>2</sub>	-0.610	-0.236	
$Ni_{0.06}Mo_{0.94}S_2$	-0.591	-0.222	
Ni <sub>0.12</sub> Mo <sub>0.88</sub> S <sub>2</sub>	-0.463	-0.189	

$Ni_{0.16}Mo_{0.84}S_2$	-0.445	-0.173
Ni <sub>0.19</sub> Mo <sub>0.81</sub> S <sub>2</sub>	-0.391	-0.135

**Table S2.** The HER activities of the as-prepared Ni-MoS<sub>2</sub> and the reported  $MoS_2$ -based non-noble metal catalysts.

Catalyst	Electrolyte	Overpotential (mV) at 10 mA/cm <sup>2</sup>	Tafel slope (mV/decade)	References (Year)
1.0Ni-MoS <sub>2</sub>	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	173	69	This work
1.0Ni-MoS <sub>2</sub>	1.0 m KOH	124	64	This work
Ni-Co-MoS <sub>2</sub> nanobox	0.5 M H <sub>2</sub> SO <sub>4</sub>	155	51	6 (2016)
Cu–MoS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	211	86	7 (2017)
Co-MoS <sub>2</sub> mesoporous foam	$0.5 \text{ M} \text{ H}_2 \text{SO}_4$	156	74	<sup>8</sup> (2017)
Ni-MoS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	300 (11 mA/cm2)	89	9 (2017)
Ni-MoS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	~170	/	<sup>10</sup> (2016)
Ni-MoS <sub>2</sub>	1.0 m KOH	98	60	<sup>10</sup> (2016)
Amorphous Co/Ni with 1T-MoS <sub>2</sub>	1.0 m KOH	70	38.1	11 (2017)
Co-MoS <sub>2</sub> /BCCF-21	1.0 m KOH	48	52	12 (2018)
Strained MoS <sub>2</sub> with S vacancies	0.3 M H <sub>2</sub> SO <sub>4</sub>	170	60	<sup>13</sup> (2016)
1T-MoS <sub>2</sub>	$0.5 \text{ M H}_2 \text{SO}_4$	175	41	<sup>14</sup> (2016)
Amorphous MoS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	143	39.5	15 (2016)
highly porous MoS <sub>2</sub> nanostructures	0.5 M H <sub>2</sub> SO <sub>4</sub>	130	69	16 (2017)

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