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# **Electronic Supplementary Information**

Pt-like catalytic behavior of MoNi decorated CoMoO<sub>3</sub> cuboid arrays for the hydrogen evolution reaction

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# **Experimental Section**

## Materials

Nickel foam (NF) was purchased from Shenzhen Green and Creative Environmental Science and Technology Co. Ltd. KOH, Absolute alcohol and  $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were purchased from Beijing Chemical Corp.  $Co(NO_3)_2\cdot 6H_2O$  was purchased Xilong Scientific Co., Ltd. Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

# Synthesis of MoNi/CoMoO<sub>3</sub>/NF

A piece of Ni foam (2 cm × 4 cm) was cleaned by ultraphonic in HCl solution for 10 min to dissolve the surface oxide layer, and then washed with deionized water several times. Then 40mmol Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 10 mmol (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O were dispersed in 30 mL deionized water and stirred for 30 min. The cleaned Ni foam was submerged into the solution and transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was heated to 150 °C for 6 h in an electric oven, then cooled down to room temperature. The product was washed with water several times, then dried in an oven at 60 °C to obtain NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF precursor (NiMoO<sub>4</sub>, CoMoO<sub>4</sub> and MoO<sub>3</sub> denoted as NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF), the mass loading of NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub> was 50.7 mg cm<sup>-2</sup>. The precursor was then subject to the tube furnace at 500 °C for 2 h in H<sub>2</sub>/Ar (v/v, 5/95) reduction atmosphere to achieve MoNi/CoMoO<sub>3</sub>/NF (mass loading: 40.5 mg cm<sup>-2</sup>). Other samples could be obtained

by adjusted the hydrogen reduction temperature and time.

#### **Materials characterizations**

Powder XRD data were acquired with a RigakuD/MAX 2550 diffractometer with Cu Ka radiation (l=1.5413). SEM measurements were performed with a XL30 ESEM FEG microscope at an accelerating voltage of 20 kV. TEM measurements were made with a Hitachi H-8100 electron microscope (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS measurements were performed with an ESCALABMK II X-ray photoelectron spectrometer by using Mg as the exciting source. The BET surface area was measured on a Quantachrome NOVA 1000 system at liquid N<sub>2</sub> temperature.

#### **Electrochemical measurements**

All electrochemical measurements were performed with a CHI660E electrochemical analyzer (CH Instruments, Inc., Shanghai) at room temperature. MoNi/CoMoO<sub>3</sub>/NF was directly used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and graphite rod as the counter electrode. In this study, E(RHE) E(SCE) + 0.242V + 0.059pH. Pt/C ink was prepared by dispersing 5 mg of Pt/C in 495 µL of ethanol 500µL deionized waterwith and 5 µL of 5 wt % Nafion solution, then the catalyst ink was loaded onto Ni foam surface and air-dried at room temperature (mass loading: 1 mg cm<sup>-2</sup>). The ohmic potential drop losses that arise from the solution resistance have been corrected by *iR* compensation. Tafel plots of the overpotential *vs*. log (j) are recorded with the linear portions at low overpotential

fitted to the Tafel equation ( $\eta = a + b \log j$ , where  $\eta$  is the overpotential, j is the cathodic current density, and b is the Tafel slope). The stability test of the MoNi/CoMoO<sub>3</sub>/NF was also performed using a typical three electrodes system. The capacitances of the double layer (C<sub>dl</sub>) at the solid-liquid interface of materials were measured by CVs collecting between 0.15 V and 0.35 V *vs* RHE in 1.0 M KOH, where the current response should be only due to the charging of the double layer.

## **Calculation Method**

First-principle calculations were performed by the density functional theory (DFT) using the Vienna Ab-initio Simulation Package (VASP) package. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional were used to describe the electronic exchange and correlation effects. Uniform G-centered k-points meshes with a resolution of  $2\pi$ \*0.03 Å<sup>-1</sup> and Methfessel-Paxton electronic smearing were adopted for the integration in the Brillouin zone for geometric optimization. The simulation was run with a cutoff energy of 550 eV throughout the computations. These settings ensure convergence of the total energies to within 1 meV per atom. Structure relaxation proceeded until all forces on atoms were less than 1 meV Å<sup>-1</sup> and the total stress tensor was within 0.01 GPa of the target value.



Fig. S1 XRD pattern of the NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub> precursor.



Fig. S2 The a)TEM image and b) corresponding EDX spectrum of the MoNi nanoparticles which obtained from the area marked with red rectangle.

\*\*\*Peak Fitting Results\*\*\*

Integrated	
Intensity	Uncertainty
891.434	300.598
571.634	302.157
606.657	219.009
676.818	231.868
	Integrated Intensity 891.434 571.634 606.657 676.818

Input FWHM = 134 eV @ 5.9 keV Measured FWHM = 137.154 eV @ 5.9 keV Calibration: 10.0044 eV/ch, -11.8651 eV at channel 0 Accelerating voltage: 187 kV Alpha tilt: 15 degrees

\*\*\*Quantification Results\*\*\*

Correction method: None

Element	Weight	% Atomic %	Uncert. %	Detector Correction	k-Factor
Ni(K)	33.61	45.28	1.01	0.99	1.521
Mo(K)	66.39	54.72	2.15	0.99	4.417



Fig. S3 a) Nitrogen adsorption-desorption isotherm of MoNi/CoMoO<sub>3</sub>/NF and b) the corresponding pore size distributions.



Fig. S4 a) Nitrogen adsorption-desorption isotherm of NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF and b) the corresponding pore size distribution.



Fig. S5 SEM image of MoNi/CoMoO<sub>3</sub>. It can be seen clearly that lots of pores are

distributed on the CoMoO<sub>3</sub> cuboid.



Fig. S6 XRD patterns of the electrocatalysts when  $NiMoO_4$ -MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF was calcined for different temperature in H<sub>2</sub>/Ar atmosphere.



Fig. S7 SEM images of the electrocatalysts when NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF cuboids are calcined for different temperature in H<sub>2</sub>/Ar atmosphere: a-b) 400 °C; c-d) 500 °C; e-f) 600 °C.



Fig. S8 XRD patterns of the MoNi/CoMoO<sub>3</sub> when NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF was calcined for different lengths of time at 500 °C in  $H_2$ /Ar atmosphere.



Fig. S9 SEM images of the MoNi/CoMoO<sub>3</sub>/NF cuboids when NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF cuboids are calcined for different time at 500 °C in a  $H_2$ /Ar atmosphere: a-b) 1 h; c-d) 2 h; e-f) 3 h.



Fig. S10 STEM image of a MoNi/CoMoO<sub>3</sub> cuboid.



Fig. S11 The XPS spectra of MoNi/CoMoO<sub>3</sub> (black) and NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub> (blue) in O 1s.



Fig. S12 LSV curves of the products when NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF cuboids are calcined for 400, 500 and 600 °C in  $H_2$ /Ar atmosphere.



Fig. S13 LSV curves of the products when NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF cuboids are calcined for 1, 2 and 3 h at 500 °C in a  $H_2$ /Ar atmosphere.



Fig. S14 The exchange current densities of the catalysts.



Fig. S15 CV curves for MoNi/CoMoO<sub>3</sub>/NF recorded between -0.2 V and 0.6 V vs. RHE in 1.0 M PBS (pH=7) at a scan rate of 50 mV s<sup>-1</sup>.

Since the difficulty in attributing the observed peaks to a given redox couple, the number of active sites should be proportional to the integrated charge over the CV curve. Assuming a one-electron process for both reduction and oxidation, the upper limit of active sites (n) for MoNi/CoMoO<sub>3</sub>/NF could be calculated according to the follow equation:

## N=Q/2F

where F and Q are the Faraday constant and the whole charge of CV curve, respectively.



Fig. S16 The calculated TOF of MoNi/CoMoO<sub>3</sub>/NF.

Assuming that all of active sites were entirely accessible to the electrolyte, the TOF values were calculated and plotted against the potential. The following formula was used to calculate TOF:

where *F* and *n* are the Faraday constant and the number of active sites, respectively; *I* is the current density of LSV curve.



Fig. S17 a-b) SEM images of MoNi/CoMoO<sub>3</sub>/NF after long-time stability test.



Fig. S18 XRD patterns of MoNi/CoMoO<sub>3</sub> before and after long-term stability tests.



Fig. S19 The XPS spectra of MoNi/CoMoO<sub>3</sub> in a) Ni 2p, b) Co 2p, c) Mo 3d and d) O 1s after long-term stability test.



Fig. S20 CVs for a) MoNi/CoMoO<sub>3</sub>/NF, b) NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF and c) NF.



Fig. S21 SEM images MoNi/CoMoO<sub>3</sub>/NF after thermal oxidation.

The MoNi/CoMoO<sub>3</sub>/NF is exposed to air and oxidized at 300 °C for 2 h.



Fig. S22 XRD pattern of MoNi/CoMoO<sub>3</sub>/NF after thermal oxidation.



Fig. S23 XPS spectra of MoNi/CoMoO<sub>3</sub> (black) and the product of MoNi/CoMoO<sub>3</sub> after thermal oxidation (blue). High-resolution XPS signals in a) Ni 2p, b) Co 2p, c) Mo 3d and d) O 1s.



Fig. S24 LSV curves of MoNi/CoMoO<sub>3</sub>/NF for HER before and after thermal

oxidation.



Fig. S25 XRD patterns of the NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF precursor (red) and the product of NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF calcined for 2 h at 500 °C in Ar atmosphere (black).



Fig. S26 SEM images of the product when  $NiMoO_4$ -MoO<sub>3</sub>-CoMoO<sub>4</sub>/NF was calcined for 2 h at 500 °C in Ar atmosphere.



Fig. S27 XPS spectra of MoNi/CoMoO<sub>3</sub> (black) and the product of NiMoO<sub>4</sub>-MoO<sub>3</sub>-CoMoO<sub>4</sub> after annealed in Ar atmosphere (blue). High-resolution XPS signals in a) Ni 2p, b) Co 2p, c) Mo 3d and d) O 1s.



Fig. S28 LSV curves of MoNi/CoMoO<sub>3</sub>/NF (black) and sample calcined for 2 h at 500  $^{\circ}$ C in an Ar atmosphere (red).

Name	Peak	FWHM	Area (P)	Atomic %	Q
	(BE)	(eV)	CPS.eV		
Ni 2p	855.52	1.83	3367.9	2.64	1
Co 2p	780.66	2.88	7824.33	6.96	1
Mo 3d	230.2	1.68	6636.65	9.15	1
O 1s	530.6	2	24108.6	81.25	1

 $\label{eq:table_state} Table \ S1 \ The \ surface \ compositions \ of \ MoNi/CoMoO_3.$ 

Electrocatalysts	Electrolyte	Overpotential (mV)	Tafel solp	TOF	Ref.
		at 10 mA/cm <sup>2</sup>	(mV dec <sup>-1</sup> )	(S <sup>-1</sup> )	
MoNi/CoMoO <sub>3</sub> /NF	1 M KOH	18	35	0.56	This work
				(100 mV)	
CoMoP@C	1 М КОН	81	55.5	N/A	Energy Environ. Sci. 2017, 10, 788
NiCo <sub>2</sub> P <sub>x</sub>	1 M KOH	58	34.3	0.056	<i>Adv. Mater.</i> <b>2017</b> , <i>29</i> , 1605502
				(100 mV)	
Ni–MoO <sub>2</sub> -450	1 M KOH	40	30	N/A	J. Mater. Chem. A
NWs/CC					<b>2017</b> , <i>5</i> , 24453–24461
NC/NiMo/NiMoO <sub>x</sub>	1 M KOH	29	46	N/A	Small
					<b>2017</b> , <i>13</i> , 1702018
Zn-doped MoS <sub>2</sub>	0.5 M	Onset Potential	51	~6	J. Am. Chem. Soc.
	$H_2SO_4$	(130 mV)		(200 mV)	<b>2017</b> , <i>139</i> , 15479
Ni <sub>3</sub> S <sub>2</sub> @NPC	1 M KOH	60.8	67.5	N/A	Nano Energy <b>2017</b> , 36, 85
Zn <sub>0.3</sub> Co <sub>2.7</sub> S <sub>4</sub> polyhedra	1 M KOH	100	48	N/A	J. Am. Chem. Soc.
					<b>2016</b> , <i>138</i> , 1359-1365
Ni-Mo nanopowders	1 M KOH	90	N/A	N/A	ACS Catal.
					<b>2013</b> , <i>3</i> , 166-169.
Co/Co <sub>3</sub> O <sub>4</sub>	1 М КОН	90	44	N/A	Nano Lett.

**Table S2** Comparison of HER performances for MoNi/CoMoO<sub>3</sub>/NF with otherselected electrocatalysts.

					2015, <b>15</b> , 6015–6021
MoS <sub>2</sub> /Ni <sub>3</sub> S <sub>2</sub>	1 M KOH	110	83	N/A	Angew. Chem. Int. Ed.
					<b>2016</b> , <i>55</i> , 6702–6707.
Co <sub>9</sub> S <sub>8</sub> –Ni <sub>x</sub> S <sub>y</sub> /NiF	1 M KOH	163	88	N/A	J. Mater. Chem. A <b>2016</b> , 4, 9744
Fe <sub>0.54</sub> Co <sub>0.46</sub> S <sub>0.92</sub> /CN Ts/CC	1 М КОН	70	55	N/A	ACS Energy Lett.
					<b>2017</b> , <i>2</i> , 2778–2785
TiO <sub>2</sub> NDs/Co	1 M KOH	108	62	~28	Angew. Chem. Int. Ed.
NSNTs-CFs				(100 mV)	<b>2017</b> , <i>56</i> , 2960 –2964
NiCo <sub>2</sub> O <sub>4</sub> hollow	1 M KOH	110	49.7	N/A	Angew. Chem. Int. Ed.
microcuboids					<b>2016</b> , <i>55</i> , 6290 –6294
CP/CTs/Co-S	1 M KOH	190	131	0.12	ACS Nano
				(250 mV)	<b>2016</b> , <i>10</i> , 2342–2348
Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub> /NFs	1 M KOH	190	110	N/A	Adv. Mater.
					<b>2015</b> , <i>27</i> , 4752–4759
N-Ni <sub>3</sub> S <sub>2</sub> /NF	1 M KOH	110	N/A	N/A	Adv. Mater.
					<b>2017</b> , <i>29</i> , 701584
NiFe/NiCo <sub>2</sub> O <sub>4</sub> /NF	1 M KOH	105	88	N/A	Adv. Funct. Mater.
					<b>2016</b> , <i>26</i> , 3515–3523
Ni/Mo <sub>2</sub> C-PC	1 М КОН	179	101	N/A	Chem. Sci.
					2017, 8, 968–973
NiMo <sub>3</sub> S <sub>4</sub>	0.1 M KOH	257	98	N/A	Angew. Chem. Int. Ed.
					<b>2016</b> , <i>55</i> , 15240

Ni-C-N	1 М КОН	30.8	40	8.52	J. Am. Chem. Soc.
				(200 mV)	<b>2016</b> , <i>138</i> , 14546
Mo <sub>2</sub> C nanotubes	0.1 M KOH	112	55	N/A	Angew. Chem. Int. Ed.
					<b>2015</b> , <i>54</i> , 15395
N,P-doped Mo2C@carbon	1 М КОН	50	71	3.71× 10 <sup>-3</sup> (10 mV)	ACS Nano
nanospheres					<b>2016</b> , <i>10</i> , 8545
Mo <sub>2</sub> C/carbon/graph ene	0.5 M	34	34	N/A	Nat. Commun.
	$H_2SO_4$				<b>2016</b> , <i>7</i> , 11204-11211
Mo <sub>x</sub> C/Ni@N- doped carbon	1 M KOH	126	N/A	N/A	J. Am. Chem. Soc.
					2015, 137, 15753
Pt <sub>3</sub> Ni <sub>2</sub> NWs-S/C	1 M KOH	70 (7.2 mA cm <sup>-2</sup> )	N/A	N/A	Nat. Commun.
					<b>2017</b> , <i>8</i> , 14580
Pt <sub>3</sub> Ni <sub>3</sub> nanowires	1 M KOH	50	N/A	N/A	Angew. Chem.
					<b>2016</b> , <i>128</i> , 13051
Pt anowires/single layer Ni(OH) <sub>2</sub>	1 M KOH	98 (5 mA cm <sup>-2</sup> )	N/A	N/A	Nat. Commun.
nanosheets					<b>2015</b> , <i>6</i> , 6430-6437