## **Supplementary Materials**

## Self-templated construction of 1D NiMo nanowires via a Li electrochemical tuning method for hydrogen evolution reaction

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**Fig. S1** (a) Cyclic voltammogram of the NiMoO<sub>4</sub>/Ni foam electrode for the initial cycle at a scan rate of 0.1 mV s<sup>-1</sup> in the potential window of 0.01-3.0 V; (b) discharge curve of the NiMoO<sub>4</sub>/Ni foam electrode.

As shown in Fig. S1a, in the cathodic sweep, there are three reduction peaks at 1.68 V, 1.33 V, and 0.62 V, which can be assigned to Li insertion into the lattice of NiMoO<sub>4</sub> crystal structure, the formation of metallic Ni and Mo nanoparticles, and the generation of a solid-electrolyte interphase (SEI) layer, respectively. In the anodic sweep, another three peaks are observed, which can be attributed to the oxidation of metallic Ni and Mo to NiO and MoO<sub>3</sub>, respectively. Fig. S1b displays the discharge curve of the NiMoO<sub>4</sub>/Ni foam electrode at the current density of 0.1 mA cm<sup>-2</sup>, in which the plateaus coincide well with the reduction peaks in Fig. S1a.



Fig. S2 Digital images of Ni foam, NiMoO<sub>4</sub>/Ni foam, and NiMo/Ni foam.



Fig. S3 XRD pattern of C-NiMo supported on the commercial carbon cloth (CC).



Fig. S4 Low-magnification FESEM images of Ni foam (a), NiMoO<sub>4</sub>/Ni foam (b), and NiMo/Ni foam (c).



Fig. S5 Diameter distribution histograms for NiMoO<sub>4</sub> (a) and NiMo (b).

100 nanorods and nanowires in Fig. 1c and 1d were randomly selected and manually measured to obtain the diameter distribution histograms.



Fig. S6 (a, b) FESEM images of C-NiMo/Ni foam.



Fig. S7 High resolution of Li 1s spectrum of NiMo without Ar ion etching treatment.



**Fig. S8** Line-scanning profile of high magnification TEM image of NiMoO<sub>4</sub>, indicating a lattice fringe spacing of 0.202 nm.



Fig. S9 XRD patterns of NiMoO<sub>4</sub> and NiMo supported on the commercial carbon cloth (CC).

The broad two peaks at 24.6° and 43.2° (marked with diamonds) were attributed to the (002) and (100) planes of graphitic carbon, respectively.



Fig. S10 XPS survey spectrum of NiMo/Ni foam without Ar ion etching treatment.



**Fig. S11** LSV curves of NiMo samples prepared under different discharge current densities (a) and cutoff potentials (b).

Catalyst	Loading (mg cm <sup>-2</sup> )	Tafel slope (mV dec⁻¹)	η (mV) at j=10 mA cm <sup>-2</sup>	Electrolyte	Reference
NiMo/Ni foam	0.88	37.2	73	1 M KOH	This work
MoNi microspheres	N/A	36.6	72	1 M KOH	1
Mo <sub>0.6</sub> Ni <sub>0.4</sub>	0.05	72	65	1 M KOH	2
Holey graphene covered NiMo	25.5	37	22	$0.5 \text{ M H}_2\text{SO}_4$	3
NiMo-EDA	0.37	89	72	1 M KOH	4
Ni–Mo/Cu Nanowire	2.17	107	115	1 M KOH	5
Ni-Mo alloy nanosheet	0.8	45	35	1 M KOH	6
MoNi₄/MoO₂@Ni foam	~43.4	30	~15	1 M KOH	7
NC/NiMo/NiMoO <sub>x</sub> / Ni faom	~20	46	29	1 M KOH	8
Ni–Mo microspheres/Cu	4.2	49	47	1 M KOH	9
MoNi <sub>4</sub> /MoO <sub>3-x</sub>	8.7	36	17	1 M KOH	10
NiMo nanowires/Ni foam	0.41	86	30	1 M KOH	11
NiMo hollow nanorods	0.68	76	92	1 M KOH	12
Ni-Mo nanopowder	1	N/A	89	1 M NaOH	13
Ni₄Mo nanoclusters	1.2	78	76	1 M KOH	14
MoNi <sub>4</sub> /Ni foam	1.09	36	~28	1 M KOH	15
NiMo/NiMoO <sub>4</sub> /NC	~0.8	98.9	80	0.5 M H <sub>2</sub> SO <sub>4</sub>	16
NiMo-Mo <sub>2</sub> C/C	0.75	73	<sup>a</sup> η <sub>1</sub> =70	0.5 M H <sub>2</sub> SO <sub>4</sub>	17

**Table S1.** Comparison of HER activity for various NiMo HER electrocatalysts.

<sup>a</sup> Overpotential at 1 mA cm<sup>-2</sup>

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Fig. S12 Nyquist plots of Ni foam, NiMoO4/Ni foam, and NiMo/Ni foam.



**Fig. S13** (a) CV curves for Ni foam and NiMo/Ni foam in 0.5 M PBS (pH=7) at a scan rate of 50 mV s<sup>-1</sup>; (b) comparison of the TOFs of Ni foam and NiMo/Ni foam.



**Fig. S14** CV curves of NiMo/Ni foam (a) and C-NiMo/Ni foam (c) at different scan rates; double-layer charging currents of NiMo/Ni foam (b) and C-NiMo/Ni foam (d) at 0.275 V (vs. RHE) with respect to the potential scan rate.



Fig. S15 (a, b) FESEM images of NiMo/Ni foam after a long-term HER stability test.