Supporting information

A Smart Strategy of "Laser-Direct-Writing" to Achieve Scalable Fabrication of Self-Supported $MoNi_4$/Ni Catalysts for Efficient and Durable Hydrogen Evolution Reaction

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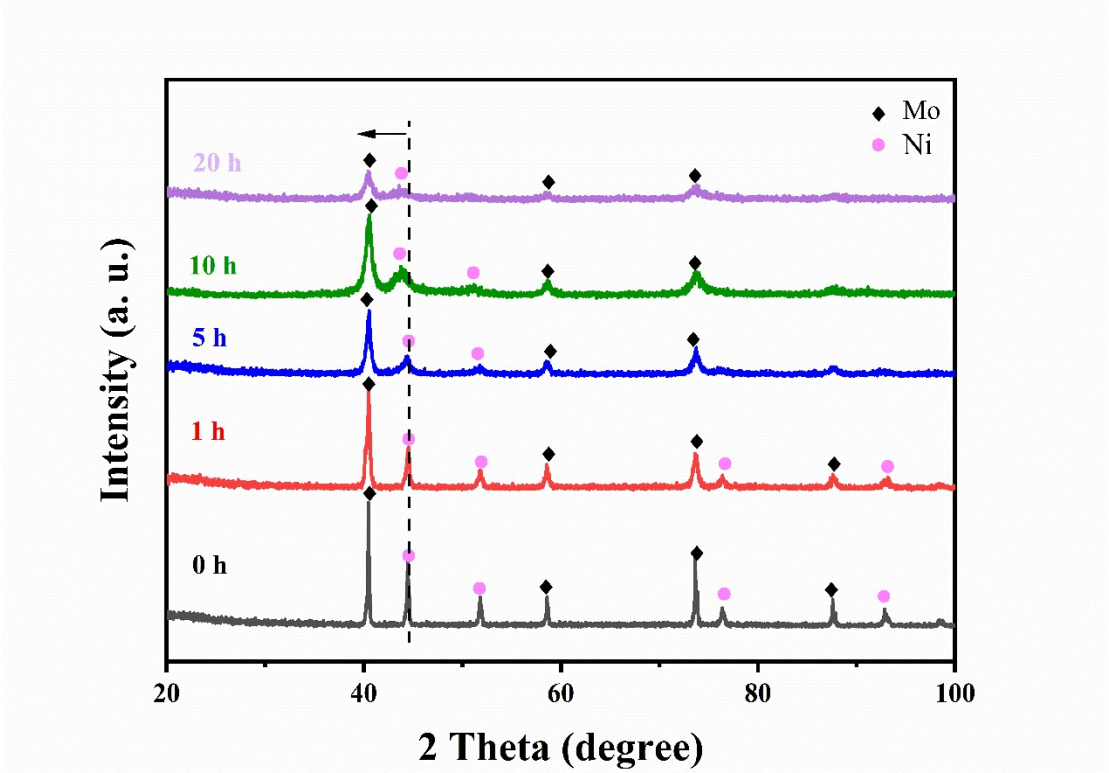

Fig. S1 XRD pattern of the $Ni_{62}Mo_{38}$ powders milled for 0 h, 1 h, 5 h, 10 h, and 20 h.

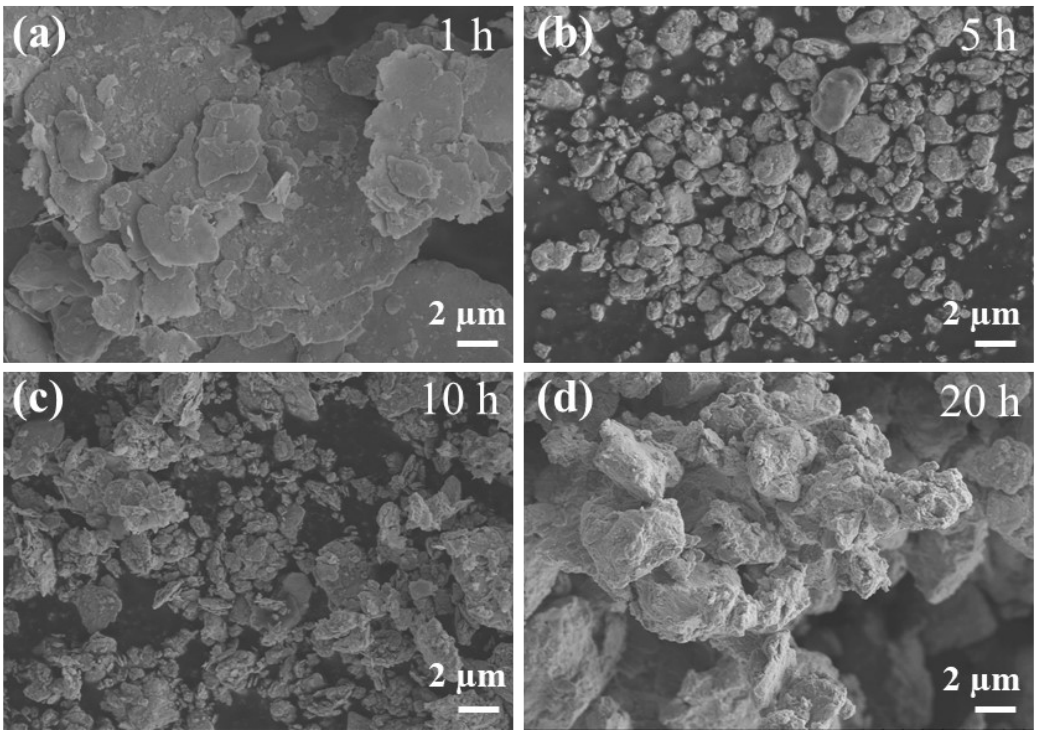

Fig. S2 SEM images of the $Ni_{62}Mo_{38}$ powders milled for (a) 1 h, (b) 5 h, (c) 10 h, and (d) 20 h.

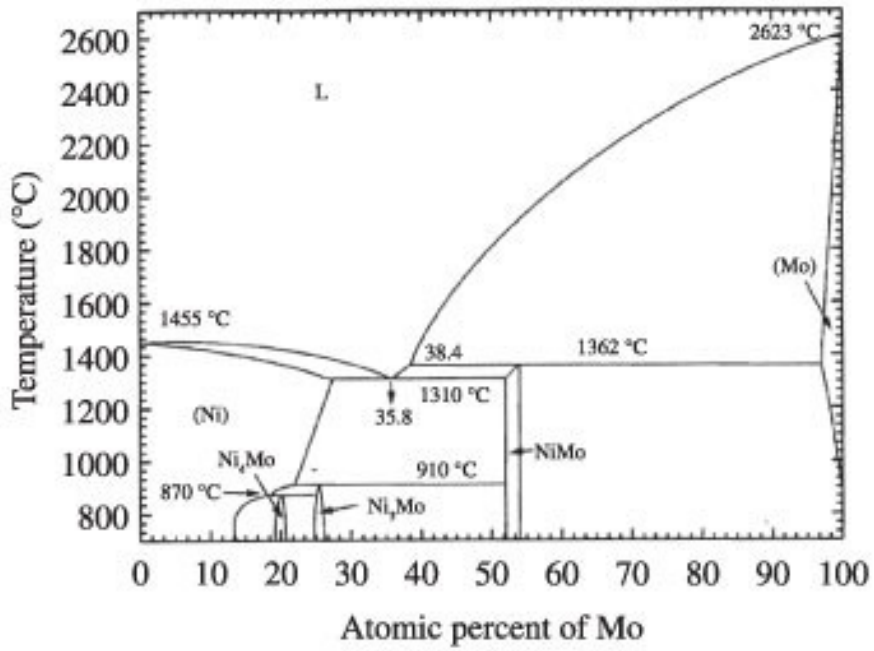

Fig. S3 Phase diagram for high temperature for Ni-Mo system.[1]

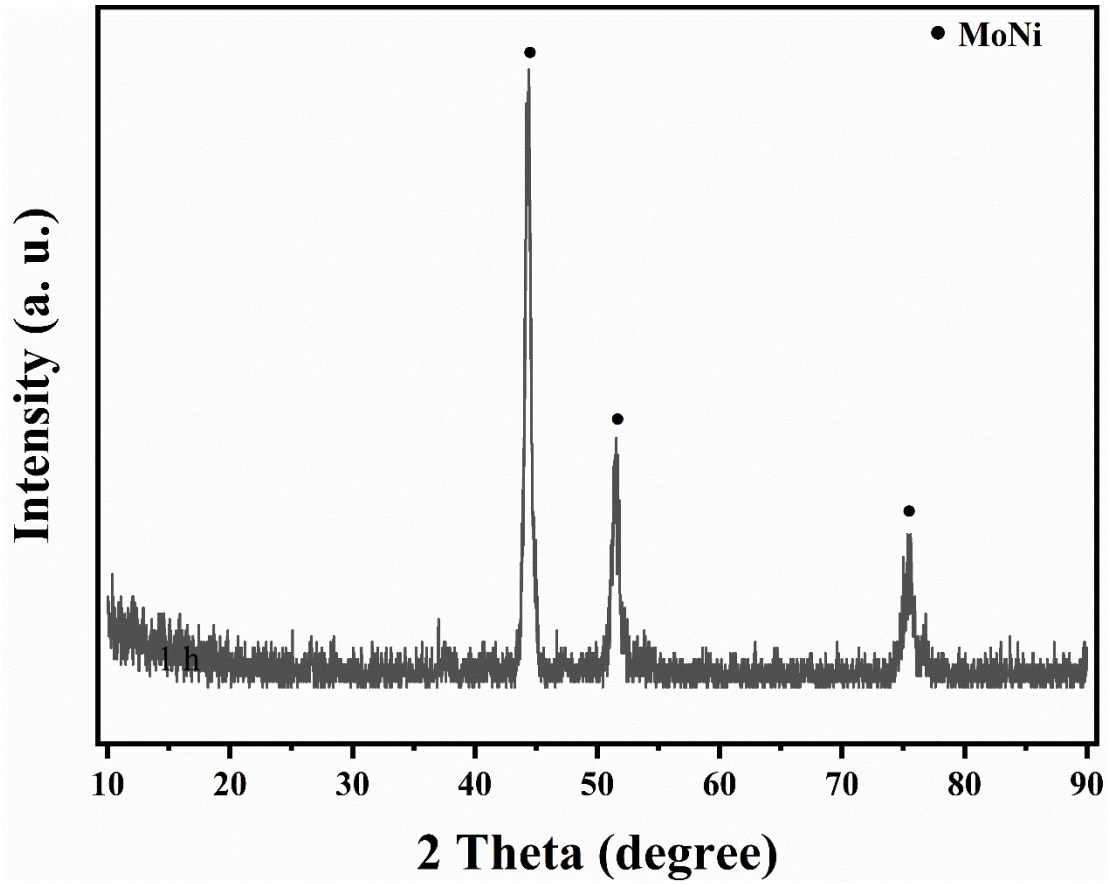

Fig. S4 XRD patterns of $Ni_{80}Mo_{20}$ powders after laser treatment.

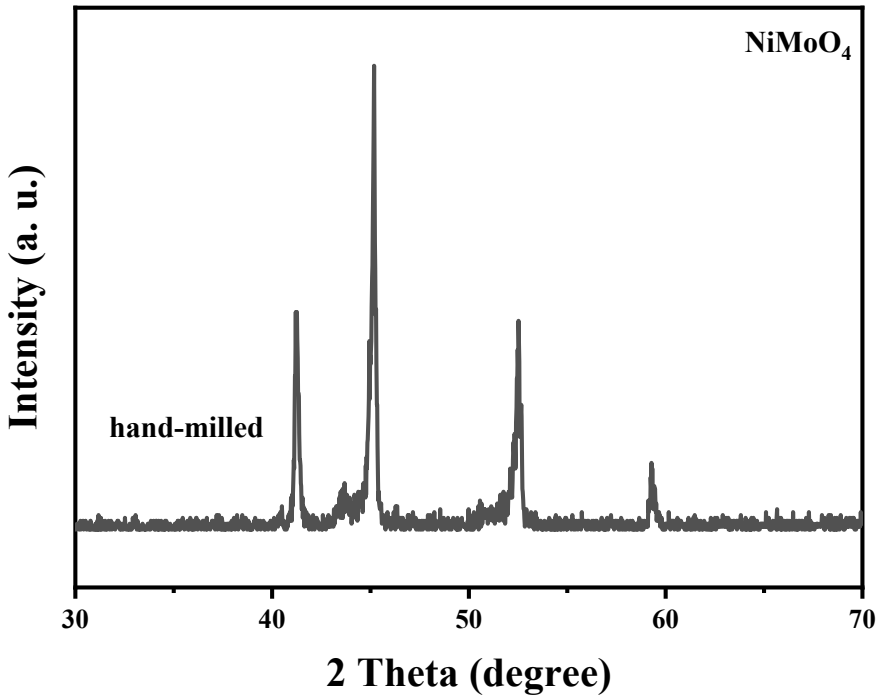

Fig. S5 XRD patterns of physically mixing Ni and Mo powders without ball milling after laser treatment.

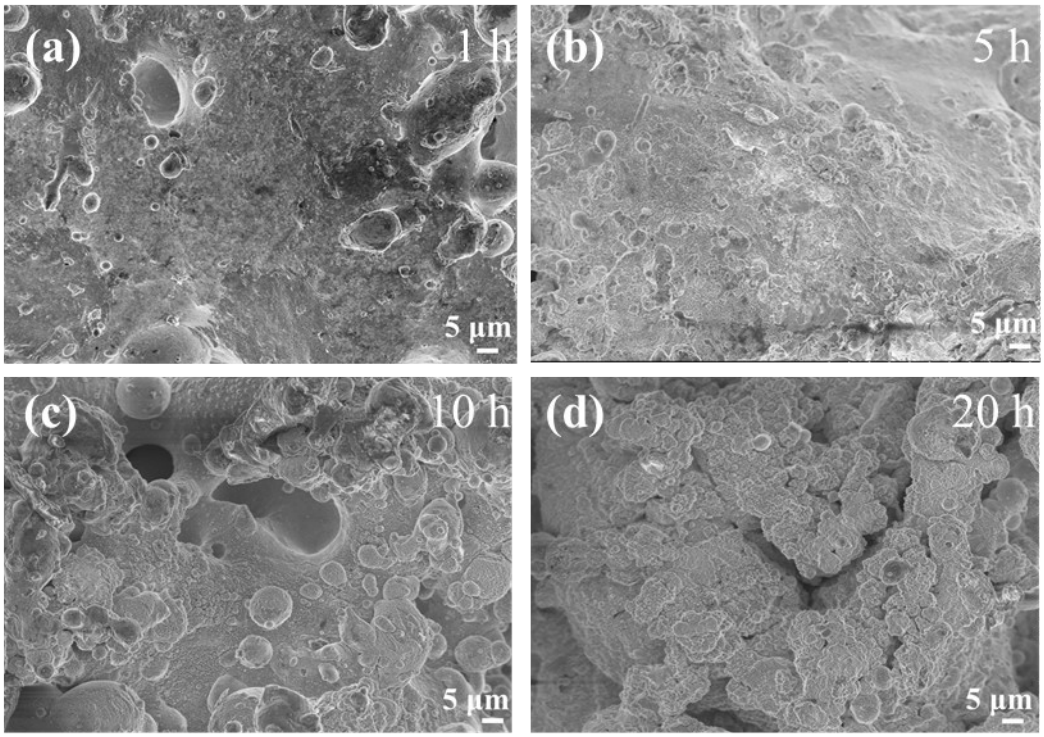

Fig. S6 Low magnification SEM images of the Ni and Mo powders with the milled time of (a) 1 h, (b) 5 h, (c) 10 h, and (d) 20 h after laser treatment.

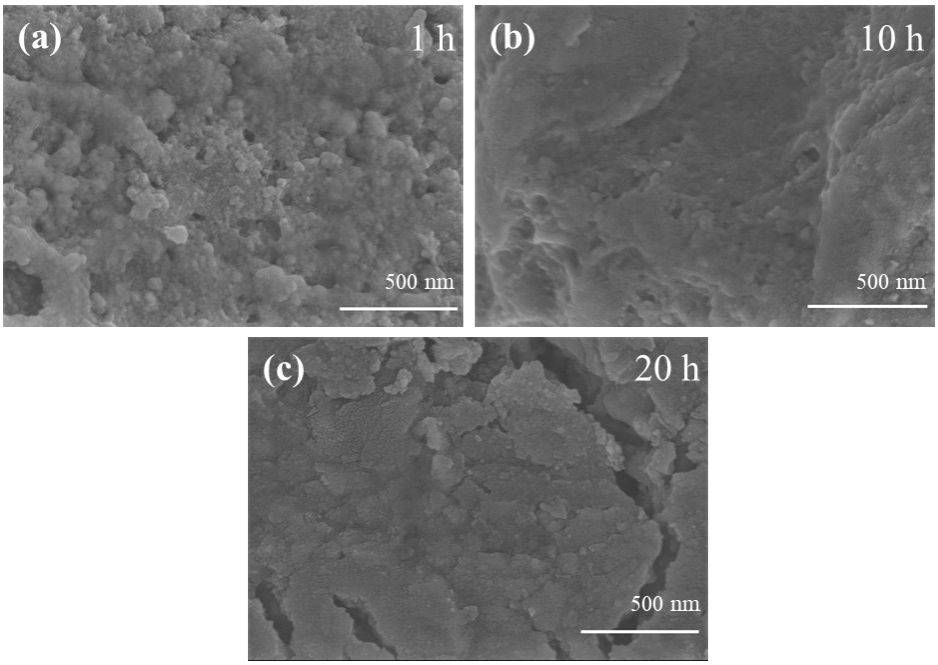

Fig. S7 High magnification SEM images of the Ni and Mo powders with the milled time of (a) 1 h, (b) 10 h, and (c) 20 h after laser treatment.

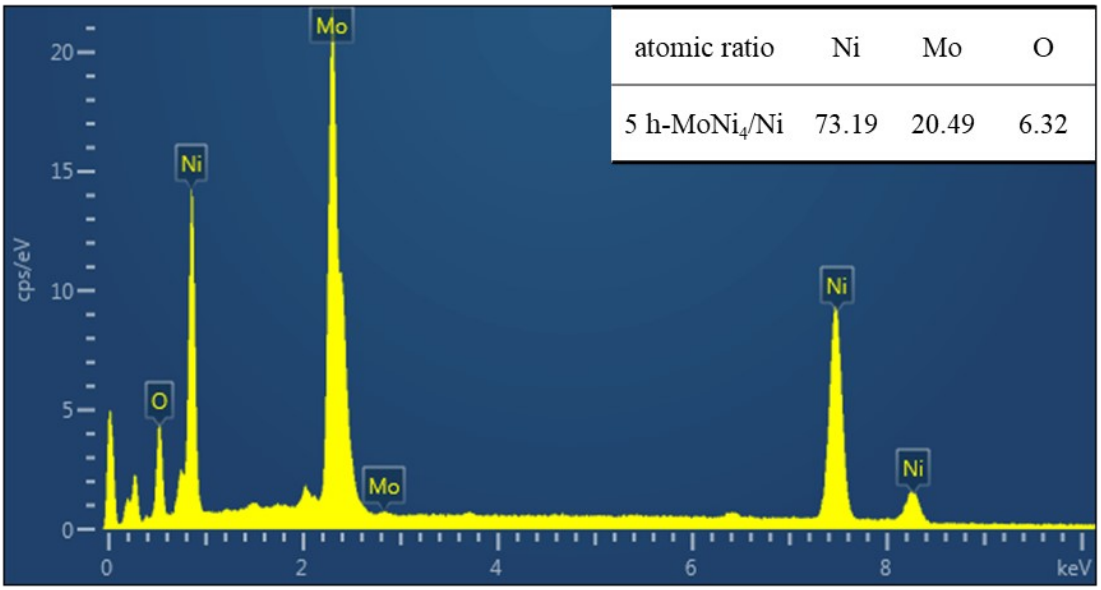

Fig. S8 EDS spectra of the 5 h-$MoNi_4$/Ni sample.

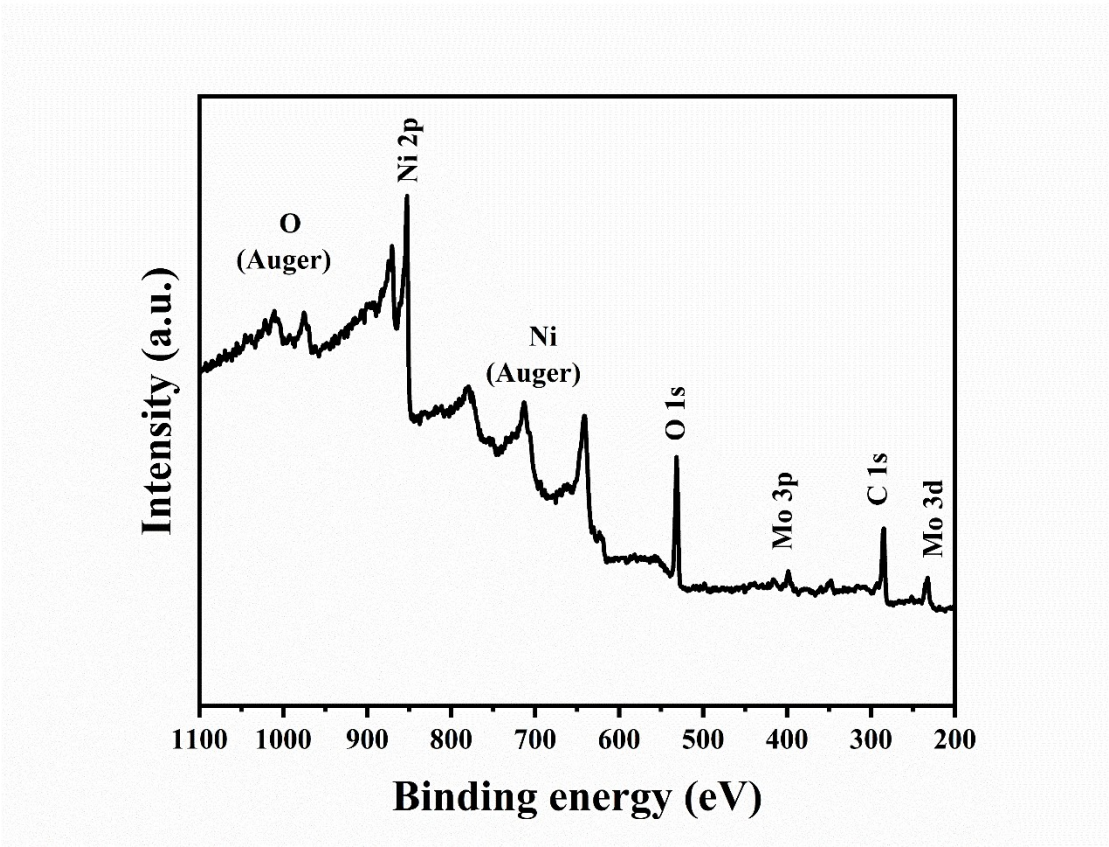

Fig. S9 XPS survey spectrum of the 5 h-$MoNi_4$/Ni sample.

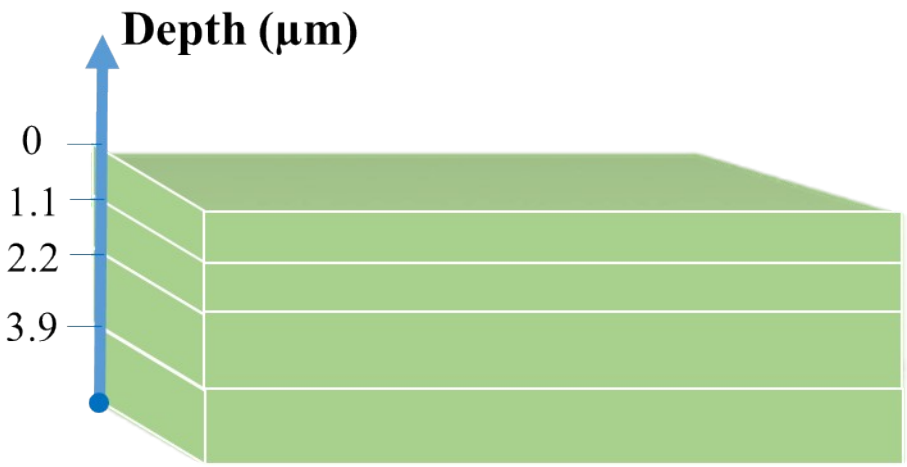

Fig. S10 XPS with Ar^{+} etching to observe the as-prepared 5 h-$MoNi_4$/Ni operation in KOH solution at different depths.

$h = St$ (Etching layer depth)

$S = (I.Y.M)/(100\rho)[nm/sec]$ (Etching rate)

$I = 15.56\ [\mu A.mm^{-2}]$ (Ionic current density)

$Y = 6.61$ (Sputtering output)

$M = 330.72$ (Atomic mass)

$\rho = 9.17\ [g.cm^{-3}]$ (Material density)

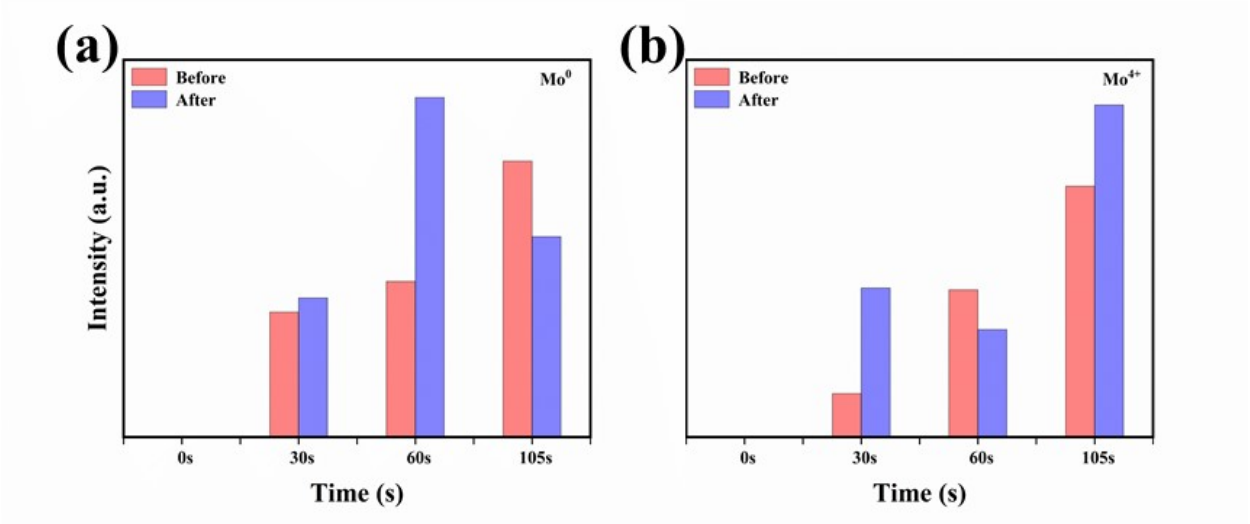

Fig. S11 Histogram of the mass percentages of Mo^{0+} and Mo^{4+} species before and after 1 h operation: a) Mo^{0+} species, b) Mo^{4+} species.

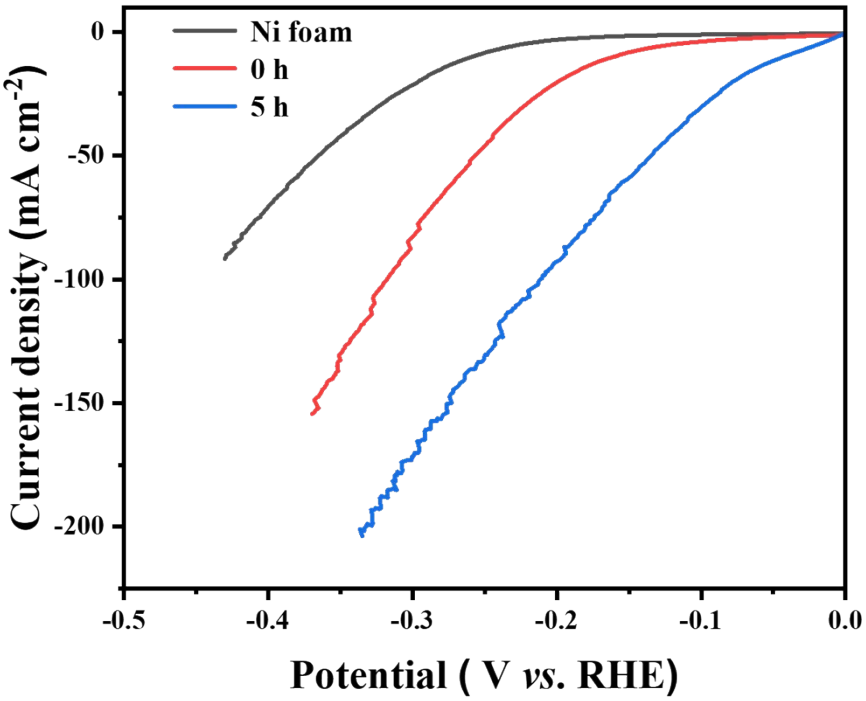

Fig. S12 LSV curves for Ni foam, the 0 h-$NiMoO_4$/Ni sample, and the 5 h-$MoNi_4$/Ni sample.

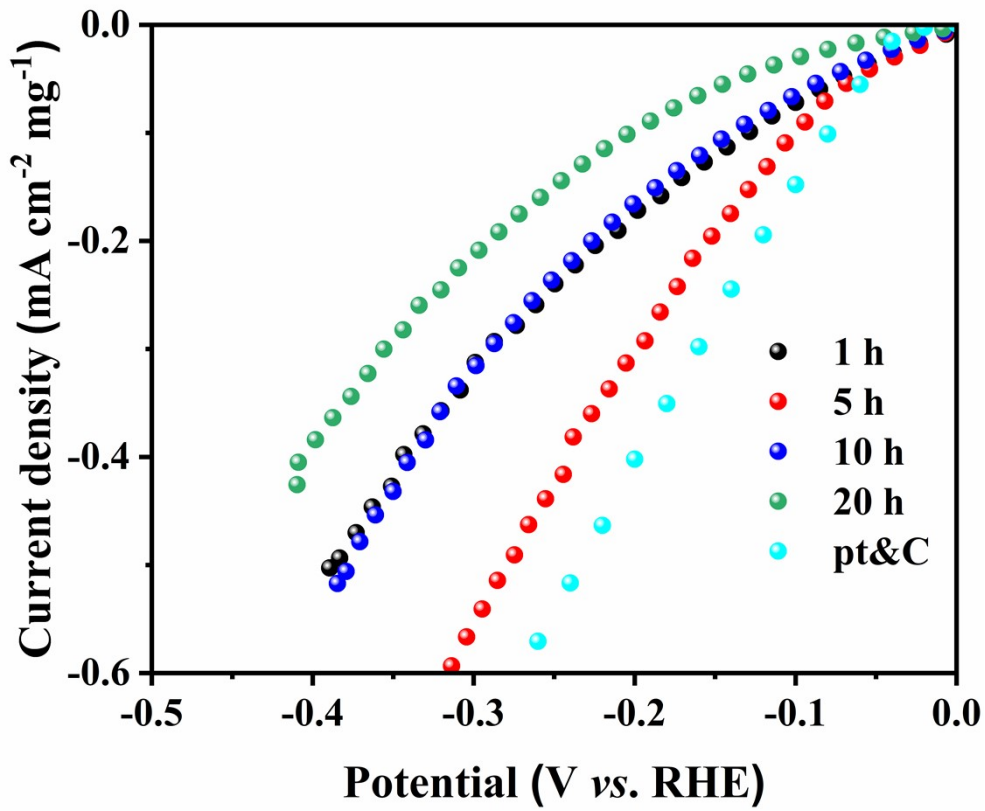

Fig. S13 LSV curves for normalizing the mass of samples.

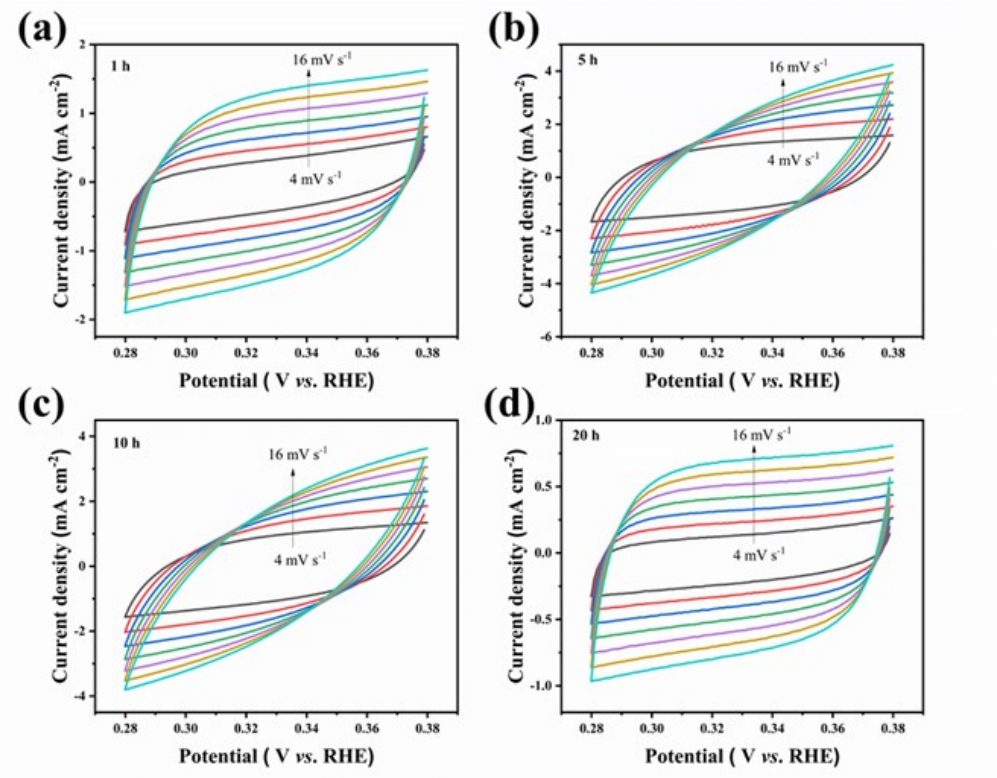

Fig. S14 (a, b, c, d) CV curves of the Ni and Mo powders with the milled time of (a) 1 h, (b) 5 h, (c) 10 h, and (d) 20 h after laser treatment.

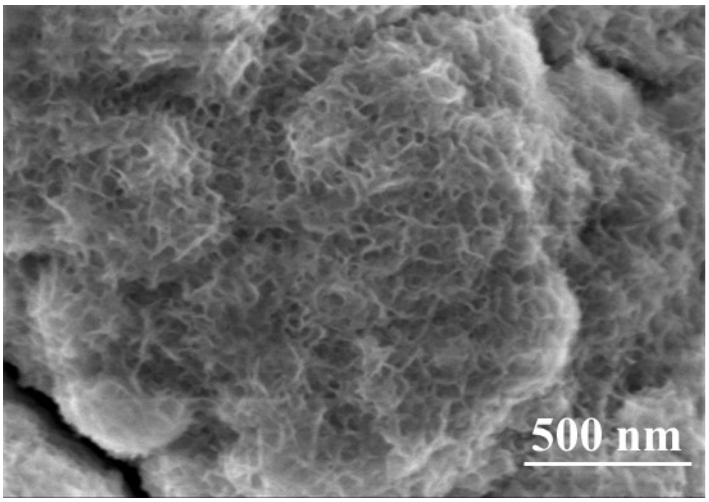

Fig. S15 SEM image of the 5 h-$MoNi_4$/Ni sample after the stability test of 100 h.

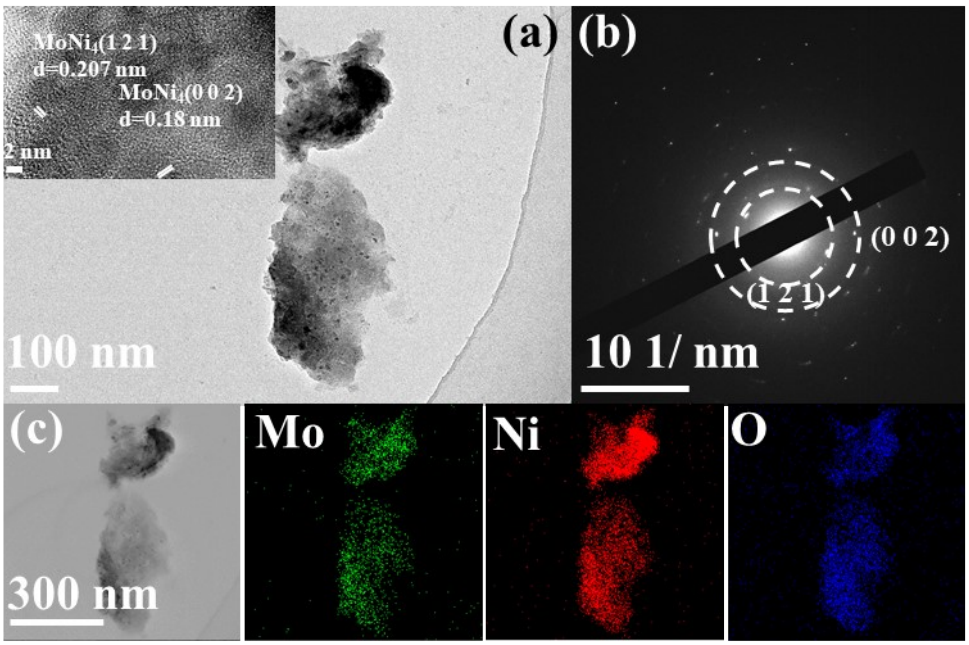

Fig. S16 Structure characterizations of the 5 h-$MoNi_4$/Ni sample after the stability test of 100 h a) TEM image, b) SAED pattern, c) elemental mapping images.

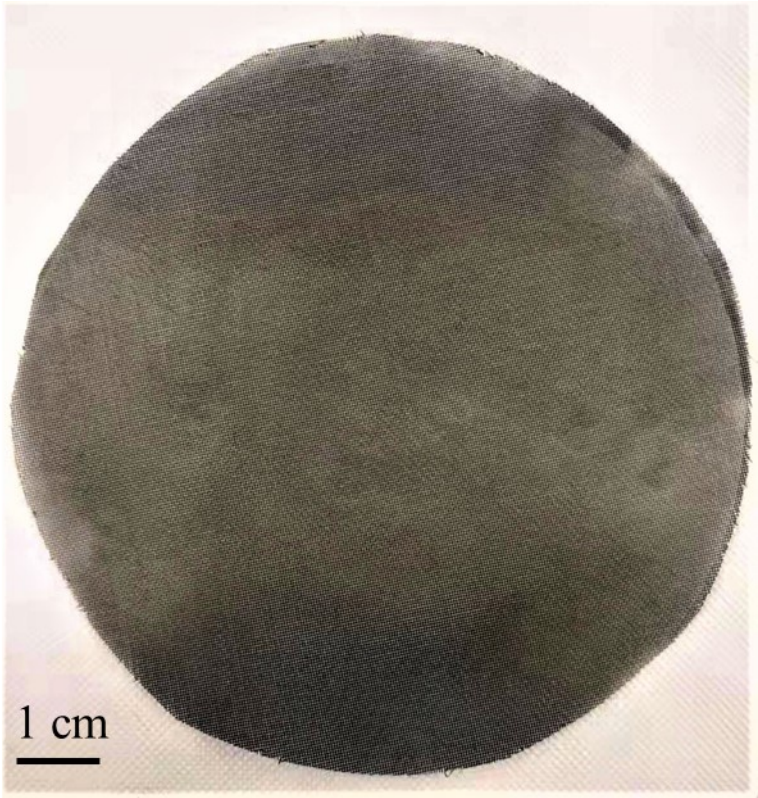

Fig. S17 The $MoNi_4$ catalyst with an area of 100 cm^2 (10 cm in width and 10 cm in length) on a nickel mesh substrate.

Table S1. The ICP-OES results of 5 h-$MoNi_4$.

Solution label	Mo	Ni
Blank	0.00 (ppm)	0.00 (ppm)
Standard sample 1	3.00 (ppm)	3.00 (ppm)
Standard sample 2	6.00 (ppm)	6.00 (ppm)
Standard sample 3	9.00 (ppm)	9.00 (ppm)
5 h-$MoNi_4$	155864.71 o (ppm)	376546.63 o (ppm)

Table S2. The mass of Nickel foam before and after laser treatment.

Time (h)	The mass of nickel foam (mg)	Mass after laser treatment (mg)	Net mass (mg)
1	38.1	336.3	298.2
5	37.8	343.7	305.9
10	37.0	349.3	312.3
20	38.0	337.5	299.5

Table S3. A comparison of the prices of catalysts in this work compared to commercial electrocatalysts for HER.

Catalysts	**Materials**	**Price (US$)**	**Price per 1 m^2 catalyst (US$)**
$MoNi_4$/Ni (This work)	Mo powders	56.7 kg^{-1}	43.1
$MoNi_4$/Ni (This work)	Ni powders	59.9 kg-1	45.5
Supports (This work)	Ni foam	30 m^{-2}	30
Pt/C	20 wt.% Pt/C powder	206 g^{-1}	4120 (2 mg cm^{-2}, w/o support)

Table S4. Electrochemical data obtained via equivalent circuit fitting of the EIS curves.

Time (h)	R_s (Ω cm^{-2})	CPE_1-T (Ω^{-1} S^n)	CPE_1-P (Ω^{-1} S^n)	R_1 (Ω cm^{-2})	CPE_2-T (Ω^{-1} S^n)	CPE_2-P (Ω^{-1} S^n)	R_{ct} (Ω cm^{-2})
1	1.759	0.010616	0.68712	1.421	0.11543	0.76646	1.883
5	1.675	0.062402	0.49935	0.54077	0.20093	0.76832	1.455
10	1.661	0.018695	0.62577	1.263	0.07652	0.74176	2.242
20	1.836	0.011324	0.65146	1.326	0.055482	0.72654	5.444

Table S5. HER activities of our results and some reported Ni-Mo catalysts in alkaline solution.

Catalyst	Electrolyte	ŋ (mV)	J (mA cm^2)	Durable time (h)	Preparation time (h)	Reference
$MoNi_4$/Ni	**1 M KOH**	**43**	**10**	**100**	**0.004**	**This work**
$MoNi_4$-$NiMoO_4$/NF	1 M KOH	55	10	50	34	2
CoP_3/$NiMoO_4$–NF	1 M KOH	92	10	12	8	3
MoP NTs/Mo	1 M KOH	269	10	2	3	4
$MoNi_4$/MoOx@NF	1 M KOH	160	200	16	14	5
Al-$NiMoO_4$ -rods	1 M KOH	131	10	30	14	6
Ni_3S_2/MoS_2	1 M KOH	89	10	50	11	7
NiMo/$NiMoO_4$@NC/NF	1 M KOH	80	10	24	63	8
NiMo/Ni	1 M KOH	73	10	20	6	9

Supplementary References

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