Electronic Supplementary Material (ESI) for Energy & Environmental Science. This journal is © The Royal Society of Chemistry 2021

Supporting Information for Energy & Environmental Science

Stabilized Hydroxide-Mediated Nickel-Based Electrocatalysts for High-Current-Density Hydrogen Evolution in Alkaline Media

Yuting Luo^{1†}, Zhiyuan Zhang^{1†}, Fengning Yang¹, Jiong Li², Zhibo Liu³, Wencai Ren³, Shuo Zhang^{2*} & Bilu Liu^{1*} **Experimental section.**

1. Synthesis of h-NiMoFe catalysts. We prepared h-NiMoFe catalyst on a Ni foam by a two-step method. First, a piece of Ni foam (purity >99.99%, 20 mm × 30 mm × 1 mm) was cleaned with 1.0 M HCl aqueous solution for 5 min and then flowing ethanol to remove surface oxide layer. Second, amine molybdate ((NH4)6M07O24, 10 mM), nickel nitrate hexahydrate (Ni(NO3)2·6H2O, 40 mM), and iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 5 mM) were added to deionized water (15 mL) and stirred to form a uniform solution. Finally, the aqueous solution contains the Ni, Mo and Fe precursors and the Ni foam were transferred to a Teflon-lined stainless-steel autoclave (50 mL), maintained at 150 °C for 6 h to grow Fe-NiMoO₄ on the Ni foam. The sample was taken out of the autoclave and thoroughly rinsed with ethanol and deionized water, and then dried in vacuum at 60 °C for proper time. Second, the Ni foam with Fe-NiMoO₄ grown on it was put into a 1 in. diameter horizontal quartz tube furnace. The tube flushed with Ar for 30 min to empty air and heated up to 500 °C with a rate of 8 °C min⁻¹. The mixture of Ar (95 standard cubic centimeter per minute (sccm)) and H₂ (5 sccm) was then introduced for 2 h to prepare the h-NiMoFe catalyst. After that, H₂ was turned off and the furnace was cooled to room temperature under Ar (95 sccm). For the NiMo and Ni control samples, their synthesis processes were same to that of h-NiMoFe catalyst, but Fe and/or Mo precursors were not added in solution in the hydrothermal growth step. For the scaling-up synthesis of h-NiMoFe on Ni foam rolls, we prepared it by the same method above. A roll of Ni foam (purity >99.99%, 100 mm \times 1500 mm \times 1 mm) was used as the substrate and Fe-NiMoO4 was grown on it in a Teflon-lined stainless-steel autoclave (900 mL), which was reduced by the same thermal treatment method.

2. Materials characterization. The morphology of the samples was examined by SEM (5 kV, Hitachi

SU8010, Japan). TEM and HRTEM analysis were carried out at an electron acceleration voltage of 300 kV (FEI Titan Cubed Themis G2 300, USA). Raman spectra were collected using 532 nm laser excitation with a beam size of ~1 µm (Horiba LabRAB HR800, Japan). Structural and chemical analyses of the samples were performed by powder XRD (Cu K α radiation, λ =0.15418 nm, Bruker D8 Advance, Germany), high resolution XPS (monochromatic Al Ka X-rays, Thermo Fisher ESCALAB 250Xi, England). The pass energy was 20 eV and energy step size was 0.1 eV. Ni species on the surface of the catalysts were analyzed by high resolution XPS after the samples had been collected and dried inside an Ar-filled glove box. The samples were exposed to air for less than 1 min before the XPS measurements to avoid oxidation in an ambient environment. Each sample for XPS tests after the HER was experienced cyclic voltammetry from 0 to 1000 mA cm⁻² for 100 times. The contact angles of droplets on the sample surfaces were recorded by a contact angle measuring device (MDTC-EQ-M07-01, Japan). The droplet volume (4 µL) was the same in each case and the electrolyte is a 1.0 M KOH solution. The XAS spectra at the Fe, Ni and Mo K-edges were recorded at the BL11B beamline of Shanghai Synchrotron Radiation Facility (SSRF). The beam current of the storage ring was 220 mA in a top-up mode. The incident photons were monochromatized by a Si(111) double-crystal monochromator, with an energy resolution $\Delta E/E \sim 1.4 \times 10^{-4}$. The spot size at the sample was $\sim 200 \,\mu m$ \times 250 µm (H \times V). The XAS spectra of the samples at Fe, Ni, and Mo K-edges were calibrated using the Fe, Ni and Mo reference foils, respectively. Ni and Mo XAS spectra were recorded in the transmission mode, with the ionization chambers filled with N2. The Fe XAS spectra was collected in the fluorescence mode, with a Lytle ionization chamber filled with Ar. For in-situ XAS measurements, the h-NiMoFe catalyst powders were exfoliated from Ni foam supports and then were loaded on carbon papers. In-situ XAFS measurements were performed with the carbon paper as a working electrode

using a homemade in-situ electrochemical cell setup. Graphite rod was used as a counter electrode and a saturated calomel electrode as a reference electrode in 1 M KOH solution. Electrochemical measurements were conducted on CHI 660E electrochemical workstation. XAFS measurement was carried out after the potential was applied for 10 min. All the in-situ XAFS spectra at the Ni and Fe Kedge were collected in fluorescence mode.

3. Electrochemical measurements. The h-NiMoFe catalyst loading was measured to be about 0.5 mg cm⁻². A standard three-electrode electrolyzer with KOH (1.0 M) was used in all tests, with a saturated calomel electrode (SCE) (or a Hg/HgO electrode) and a graphite rod as the reference and counter electrodes, respectively. For the standard electrochemical tests, a H-cell with a membrane separating the catholyte and anolyte is used (see Fig. S17 for details). The scan rate was 0.5 mV s^{-1} for linear sweep voltammetry tests and 50 mV s⁻¹ for long-term cyclic voltammetry tests. The steady-state polarization curves were obtained using chronoamperometry (CA) method by increasing overpotential at a step of 10 mV. Before each test, electrolyte was bubbled with Ar for 15 min to remove dissolved oxygen in the solution. Then, catholyte and anolyte were pre-saturated by H₂ and O₂ respectively, at 1 atm, before collecting electrochemical data. For fair comparisons, a 90% iR correction was taken and the distance between reference electrode and working electrode was fixed by H-cell. Electrochemical active surface areas (ECSA) were obtained by measuring electrochemical double layer capacitance (Cdl) of catalysts. Faradaic efficiencies were defined as the ratio of H₂ amount collected in experiment to the amount in theory, where H₂ was collected by water drainage method (see Fig. S21 for details). Stability tests were performed by chronoamperometry measurements method. The Pt sample used for comparison was prepared by depositing commercial Pt/C catalysts on Ni foam. Specifically, 20 wt%

Pt/C (10 mg), Nafion solution (5%, 0.2 mL), and isopropanol (0.5 mL) were mixed into a uniform ink, which was then casted onto Ni foam with a controlled loading of 2 mg cm⁻².

4. DFT modelling calculations. All the calculations were carried out using the Vienna Ab-initio Simulation Package (VASP).^{1, 2} The exchange-correlation potential was described by the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) exchange model.³ The electronic wave functions were expanded using a plane-wave basis set with an energy cutoff of 400 eV. The structures were relaxed until the forces are smaller than 0.02 eV Å⁻¹ and the energy difference is less than 10^{-5} eV. The p (3×3)-Pt (111), p (2×2)-Ni4Mo (002), and p (2×2)-Ni4Mo with Fe(OH)4Ni4 motif on its surface were used to model the Pt, NiMo, and h-NiMoFe catalysts. Four layers of Pt (111) and Ni4Mo (002) were used and the top two layers were relaxed during the structural optimization, and other layers were fixed to their bulk structures. A vacuum layer of 15 Å was used to avoid interactions between periodic images. The Brillouin zone was sampled in a Monkhorst–Pack $3\times3\times1$ k-points mesh. The Gibbs reaction free energies of adsorption of species X (ΔG_X) were calculated following previous method⁴:

$$\Delta G_{\rm X} = \Delta E_{\rm X} + \Delta E_{\rm ZPE} - T \Delta S_{\rm X} \tag{3}$$

where ΔE_X is the adsorption energy of X obtained from DFT calculations, ΔE_{ZPE} is the difference in the zero point energy between the adsorbed X and the gas phase, and S_X is the entropy at 298.15 K. The nudged elastic band (NEB) method was used to obtain the transition states of the H₂O dissociation reactions.

5. Calculation of specific activity and TOF. The specific activity of catalysts was normalized by their electrochemical surface area (ECSA). To get ECSA of each sample, their capacitances were got firstly

by sweeping the potential at different scan rates (see Fig. S12 for details). Then, ECSA were calculated from the following formula.⁵

$$A_{ECSA} = \frac{C_{dl}}{C_s}$$

Where C_{dl} is electrochemical double-layer capacitance and C_s is the specific capacitance of materials. The specific capacitance of platinum and h-NiMoFe were assumed as 62 µF cm⁻² and 40 µF cm⁻², respectively.^{6, 7} Thus, the A_{ECSA} of h-NiMoFe and Pt foil were calculated as ~100 cm² and ~8.9 cm². The specific activity was then obtained. The TOF was calculated from the following formula.^{7, 8}

$$TOF = \frac{number of total H2 turnovers per geometric area}{number of active sites per geometric area}$$

And the total number of H turnovers can be calculated from the current density as follows:

No. of
$$H_2 = \left(j\frac{mA}{cm^2}\right) \left(\frac{1\ Cs^{-1}}{1000\ mA}\right) \left(\frac{1\ mol\ e^-}{96485.3\ C}\right) \left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right) \left(\frac{6.022 \times 10^{23}H_2\ mol\ ecues}{1\ mol\ H_2}\right)$$

= $3.12 \times 10^{15} \frac{H_2/s}{cm^2}\ per\ \frac{mA}{cm^2}$

To estimate the number of active sites, we counted all the metal atoms (Ni, Fe, and Mo) in h-NiMoFe,

because the exact hydrogen binding site and the exact cell parameters of h-NiMoFe is not known.



| Element | Line | Intensity (c/s) | Atomic content (at%) | Weight content (wt%) |
|---------|------|-----------------|----------------------|----------------------|
| Fe | Ka | 20.68 | 5.47 | 4.26 |
| Ni | Ka | 138.35 | 59.31 | 48.58 |
| Mo | La | 256.25 | 35.22 | 47.16 |



of h-NiMoFe catalysts. The results show that the amount of Fe element is about 5 at%.



Figure S2. XRD pattern of h-NiMoFe. (a) XRD pattern and the (b) enlarged view of the h-NiMoFe. The results show that the catalyst is mainly composed of Ni₄Mo and MoO₂ compounds.



Figure S3. Raman pattern of h-NiMoFe. The result shows the Mo-O bending and stretching peaks,⁹,

¹⁰ confirming the existence of molybdenum oxides in h-NiMoFe.



Figure S4. Fourier transformed EXAFS of h-NiMoFe catalyst and controls at Fe K-edge. These results confirm that iron is in oxidation state in h-NiMoFe and is possibly in form of mononuclear FeO_x cluster that lacks long-range crystal structure.



Figure S5. X-ray absorption spectroscopies. (a) X-ray absorption and (b) Fourier transformed EXAFS of h-NiMoFe catalyst and controls at Mo *K*-edge, showing Mo is in both oxidized state and metallic state.



Figure S6. Fitting result of the FT-EXAFS of h-NiMoFe catalyst and controls at Ni K-edges. These

results confirm that nickel is mainly in metallic state in h-NiMoFe.



Figure S7. XPS patterns of h-NiMoFe and the control samples. (a) Ni 2p, (b) Mo 3d, and (c) Fe 2p XPS spectrum. These results confirm the presentence of Mo/Fe in h-NiMoFe modulates the local electronic structures of the Ni sites.



Figure S8. XPS Ni 3s patterns of h-NiMoFe and the control samples. These results show that the

surface Ni species are different due to the presentence of Mo/Fe in h-NiMoFe.



Figure S9. XPS Ni 3s patterns of h-NiMoFe and the control samples before and after HER cycles.

(a) Ni, (b) NiMo, and (c) h-NiMoFe samples. These results show that the changes of surface Ni species are different before and after HER cycles of of 100 times from 0 to 1000 mA cm⁻².



Figure S10. HER performance of h-NiMoFe and the controls. (a) Polarization curves and (b) the corresponding overpotentials at 50 mA cm⁻² of the catalysts. These results show that h-NiMoFe shows better performance than the controls.



Figure S11. CV curves at different scan rates and the calculated C_{dl} of (a) Ni, (b) NiMo, and (c) h-NiMoFe catalysts, and (d) their corresponding the double layer capacitance (C_{dl}). These results indicate that the C_{dl} as well as the electrochemical surface areas of the three samples are close to each other.



Figure S12. In-situ X-ray absorption spectroscopies of Ni K-edge in h-NiMoFe. (a) X-ray absorption and (b) Fourier transformed EXAFS of h-NiMoFe catalyst and controls at Ni K-edge. The results show that Ni in h-NiMoFe keeps metallic state under HER condition, indicating that Ni₄Mo nanoparticle bulks keep alloys even though their surfaces are decorated by hydroxides groups.



Figure S13. In-situ X-ray absorption spectroscopies of Fe K-edge in h-NiMoFe. (a) X-ray absorption and (b) Fourier transformed EXAFS of h-NiMoFe catalyst and controls at Fe K-edge. The results show that a new catalyst species containing Fe-O(H)-Ni motif forms under HER condition.



Figure S14. Fitting result of the FT-EXAFS of h-NiMoFe catalyst and controls at Fe K-edge.

These results confirm that iron changes under HER condition.



Figure S15. Relaxed configurations for calculating adsorption energies of dissociated H₂O. The

top and side views of the corresponding optimized structures, where orange, green, purple, grey, red,

and white spheres represent Mo, Ni, Fe, Pt, O, and H atoms, respectively.



Figure S16. Standard electrochemical tests. (a) Schematic and (b) photo showing an electrochemical configuration and corresponding conditions used for standard electrochemical tests. First, the anolyte and catholyte is separated by a membrane in a H-cell. Second, the Hg|HgO|OH⁻ reference electrode (RE) connected to a Luggin capillary was used and the distance between head of Luggin capillary and working electrode was fixed and optimized in the cell. Third, anolyte and catholyte were pre-saturated by O₂ or H₂ respectively under 1 atm pressure. (c) Calibration of the Hg|HgO|OH⁻ reference electrode in high-purity hydrogen saturated 1 M KOH electrolyte with a Pt wire as working electrode. (d) The comparison between steady-state method and linear sweep voltammetry method. The results show that the capacitance current can be avoid using a slow voltage scan rate (0.5 mV s⁻¹).



Figure S17. Comparison between h-NiMoFe, Pt, and freshly flame-annealed Pt foil. (a) Specific activity normalized by the electrochemical surface area (ECSA), and (b) Turnover frequency (TOF) of h-NiMoFe, Pt, and fleshly flame-annealed Pt foil. The results show that the h-NiMoFe has a high intrinsic activity for alkaline HER, which is comparable to Pt catalysts.



Figure S18. EIS curves of h-NiMoFe and the controls in 1.0 M KOH. These results show that the

h-NiMoFe has the lowest charge transfer resistance among the samples.



Figure S19. Uniformity of the h-NiMoFe catalyst. (**a**) Photo and (**b**) corresponding SEM images of the catalysts. (**c**) XRD spectrum. (**d**) EDS spectrum and corresponding elemental contents of catalyst. These results show that morphology, structure, and elemental contents of scaling-up sample are similar to those of small sample.



Figure S20. Faradaic efficiency (FE) test. (a) Schematic showing setup for measuring FE of catalyst for a long operation time in a sealed H-cell. H₂ is collected by water drainage method, and the water is saturated by H₂ before collecting. (b) Volumes of hydrogen and FE. HER is operated at 150 mA cm⁻² for continuous 40 hours, and the H₂ volumes is recorded for 1 hour (volumes of H₂ are read every 20 mins for three times in each rounds of recording) every 10 hours.



Figure S21. (a-d) HRTEM images of h-NiMoFe after HER in 1.0 M KOH. These results show that

the h-NiMoFe catalyst maintain its structure well after HER.



Figure S22. Selective selected area electron diffraction (SEAD) patterns of h-NiMoFe after HER

in 1.0 M KOH. These results show that the h-NiMoFe catalyst maintain its crystalline structure well after HER.



Figure S23. XPS spectra of h-NiMoFe before and after HER. (**a**) Ni 2p, (**b**) Mo 3d, and (**c**) Fe 2p XPS spectra.

| Samula | Atomic | No. of atoms | Interatomic | ΔE_0 | Debye-Waller factor | R |
|----------|---------|--------------|--------------|--------------|---------------------------------|--------|
| Sample | scatter | (CN) | distance (Å) | (eV) | $(10^{-3} \times \text{\AA}^2)$ | factor |
| Ni foil | Ni-Ni | 12.00 | 2.48±0.003 | 5.34 | 6.2±0.3 | 0.001 |
| NiMo | Ni-Ni | 6.3±0.7 | 2.51±0.03 | 6.02 | 6.8 ± 0.8 | |
| | Ni-Mo | 2.7±0.3 | 2.53±0.03 | 6.02 | 16.7±3.7 | 0.003 |
| | Ni-Ni | 1.8±0.2 | 2.55±0.03 | 6.02 | 16.7±3.7 | |
| h-NiMoFe | Ni-Ni | 4.83±2.46 | 2.57±0.05 | 7.43 | 8.8±4.3870 | |
| | Ni-Mo | 2.07±1.05 | 2.58±0.06 | -10.60 | -2.45±3.0 | 0.0002 |
| | Ni-Ni | 2.07±1.05 | 2.61±0.06 | 7.43 | -2.45±3.0 | |

Table S1. Structural parameters of h-NiMoFe and reference samples that are extracted from the Ni *K*-edge EXAFS fitting (S_0^2 =0.77).

Note: The background subtraction, merging, normalization, and fitting of the XAS data were performed by Demeter software package.¹¹ The k³-weighted EXAFS of Ni *K*-edge was Fourier transformed to real (R) space using a hanning window (dk = 1.0 Å^{-1}) in k-space between 2.858 and 11.693 Å⁻¹. The amplitude-reduction factor S₀² was determined by fitting the experimental data of Ni foil. The R-ranges for the fitting of all the EXAFS data were set as 1.4-3.0 Å.

No. of atoms Interatomic ΔE₀ **Debye-Waller factor** R Atomic Sample distance (Å) (10-3×Å2) scatter (CN) (eV) factor Fe-O 3.00 $1.97{\pm}0.01$ 2.03 $7.80{\pm}2.25$ Fe₂O₃ 0.00002 Fe-O 3.00 2.11 ± 0.02 2.02 25.60±16.90 4.70±3.16 2.00 ± 0.21 3.32 8.5 ± 8.4 0.0004 h-NiMoFe, air Fe-O 4.44 ± 0.89 $2.02{\pm}0.04$ 5.10 Fe-O 2.47 h-NiMoFe, HER 0.0165 2.98 ± 0.09 Fe-Ni 4.44 ± 0.89 -9.48 16.20

Table S2. Structural parameters of h-NiMoFe and reference samples that are extracted from the Fe *K*-edge EXAFS fitting (S_0^2 =0.73).

Note: The background subtraction, merging, normalization, and fitting of the XAS data were performed by Demeter software package.¹¹ The k³-weighted EXAFS of Fe *K*-edge was Fourier transformed to R space using a hanning window (dk = 1.0 Å^{-1}) in k-space between 2.536 and 11.006 Å⁻¹. The amplitude-reduction factor S₀² was determined by fitting the experimental Fe₂O₃ powder data. The R-ranges for the fitting of the in-situ EXAFS data was set as 1.0–3.920 Å. The cathode potential is set as -0.28 V (vs RHE) for data collection of h-NiMoFe during HER, with a homemade electrochemical three-electrode cell (see details in Experimental Section).

| Catalasta | Els sturbets | Ove | Dof | | | |
|---------------------------------------|--------------|-----------------------------|--|------|-------------|--|
| Catalysts | Electrolyte | $j = 10 \text{ mA cm}^{-2}$ | $j = 10 \text{ mA cm}^{-2}$ $j = 100 \text{ mA cm}^{-2}$ $j = 1000 \text{ mA cm}^{-2}$ | | NUI. | |
| h-NiMoFe | 1.0 M KOH | 14 | 43 | 97 | This work | |
| MoS ₂ /Mo ₂ C | 1.0 M KOH | 87 | 149 | 220 | 12 | |
| NiCo ₂ P _x | 1.0 M KOH | 58 | 127 | N/A | 13 | |
| Co-Ex-MoS ₂ | 1.0 M KOH | 89 | N/A | N/A | 14 | |
| Ni ₂ P/NF | 1.0 M KOH | ~58 | ~136 | ~300 | 15 | |
| MoNi ₄ /MoO _{3-x} | 1.0 M KOH | 17 | 52 | ~155 | 16 | |
| FeP/Ni ₂ P | 1.0 M KOH | 14 | ~138 | ~265 | 17 | |
| Ru@C ₂ N | 1.0 M KOH | 17 | N/A (~50 mV @ $j = 30 \text{ mA cm}^{-2}$) | N/A | 18 | |
| Ru/np-MoS ₂ | 1.0 M KOH | 30 | N/A | N/A | 19 | |
| CF/VGSs/ MoS2/FeCoNiPx | 1.0 M KOH | 43 | ~125 | N/A | 20 | |
| NiMoO _x /NiMoS | 1.0 M KOH | 38 | 89 | 236 | 21 | |
| Ru/OMSNNC | 1.0 M KOH | 13 | N/A (~75 mV @ $j = 50 \text{ mA cm}^{-2}$) | N/A | 22 | |
| Ni-SN@C | 1.0 M KOH | 28 | ~144 | N/A | 23 | |
| Pt@mh-3D MXene | 1.0 M KOH | 27 | N/A | N/A | 24 | |
| Ru/WNO@C | 1.0 M KOH | 2 | ~56 | N/A | 25 | |

Table S3. A comparison of HER overpotentials of catalysts at 10 mA cm⁻² in this work with previously reported data.

| Catalysts Electrolyte | | Current density at $\eta = 100 \text{ mV} (\text{mA cm}^{-2})$ | Ref. |
|--|--------------------------------------|--|-----------|
| h-NiMoFe | 1.0 M KOH | 1041 | This work |
| MoS ₂ /Mo ₂ C | 1.0 M KOH | 13.9 | 12 |
| NF/NiMoO-H ₂ | 1.0 M KOH | 300.4 | 26 |
| C-MoS ₂ | 1.0 M KOH | 45 | 27 |
| Ni(OH)2/MoS2 | 1.0 M KOH | 22.5 | 28 |
| NiCo ₂ P _x | 1.0 M KOH | 46.1 | 13 |
| Co-Ex-MoS ₂ | 1.0 M KOH | 12.3 | 14 |
| Ni ₂ P/NF | 1.0 M KOH | 30.8 | 15 |
| MoNi4/MoO _{3-x} | 1.0 M KOH | 373.8 | 16 |
| Co ₄ N-CeO ₂ /GP | 1.0 M KOH | 89.9 | 29 |
| FeP/Ni ₂ P | 1.0 M KOH | 51.3 | 17 |
| PtGa | 0.5 M H ₂ SO ₄ | 492.5 | 30 |
| NbS_2 | 0.5 M H ₂ SO ₄ | 5.3 | 31 |
| CoP | 0.5 M H ₂ SO ₄ | 3.6 | 32 |
| Pd,Ru-MoS _{2-x} OH _y | 0.5 M H ₂ SO ₄ | 64.2 | 33 |
| α-Mo ₂ B | 0.5 M H ₂ SO ₄ | 7.6 | 34 |
| Fe/GD | 0.5 M H ₂ SO ₄ | 32.7 | 35 |

Table S4. A comparison of the HER activity of the catalysts in this work with previously reported data.Data in H_2SO_4 are compared because acidic HER is thought to be more efficient than alkaline HER.

Table S5. Price of the scaling-up synthesized h-NiMoFe catalyst on a support with an area of 1.5 meter

 $\times 0.1$ meter.

| Materials | Suppliers | Price (US\$ kg ⁻¹) | Price of precursors (US\$ m ⁻²) | Total price of catalyst (US\$ m ⁻²) |
|------------------------------------|---|-----------------------------------|---|--|
| | Guangdong Guanghua Sci-Tech Co., Ltd | 43.72 | 23.06 | |
| Nickel (II) nitrate hexahydrate | Sigma-Aldrich Co., Ltd | 201.00 | 106.02 | |
| | Sinopharm Chemical Reagent Co. Ltd | 43.58 | 22.99 | |
| | Shanghai Aladdin Biochemical Technology Co., Ltd. | 48.01 | 24.72 | |
| Ammonium molybdate tetrahydrate | Sigma-Aldrich Co., Ltd | 178.80 | 92.06 | |
| | Sinopharm Chemical Reagent Co. Ltd | 40.50 | 20.85 | Suppliers in this work |
| | Shanghai Macklin Biochemical Co., Ltd | 15.17 | 4.04 | (w/o labor cost): 81.8 |
| Iron (III) nitrate nonahydrate | Sigma-Aldrich Co., Ltd | 145.60 | 38.78 | Other suppliers (with |
| | Sinopharm Chemical Reagent Co. Ltd | 15.00 | 3.99 | labor cost): 75.4 – 291.7 |
| | Linyi Gelon LIB Co., Ltd | 30 | 30 | |
| Ni foam | Kunshan Maipengchen Electronic Technology Co., Ltd | 48 | 48 | |
| | Kunshan Fangdou Electronic Technology Co., Ltd | 22.5 | 22.5 | _ |
| Labor cost | US\$ 600/month | N/A | 6.82 | |
| | US\$ 450/month | N/A | 5.11 | |

Note S1: For estimating labor cost, we assume that each worker can work for 22 days per month and 8 hours per working day. The labor cost per month uses the average wages in cities in central or south China. We assume that catalyst can synthesized on supports with an area of 5 m² (which is achievable in industry), and the time needed for each batch of catalyst is about 10 hours (*i.e.*, 6 hours for hydrothermal process, 2 hours for thermal reduction process, and 2 hours for intermediate steps). All the chemical prices shown here are those purchased in the lab scale.

| Catalysts | Materials | Suppliers | Price (US\$ m ⁻²) | Price per 1 m ² catalyst (US\$) |
|--------------------------------|--------------------------------------|---|-------------------------------|---|
| | h-NiMoFe catalyst | N/A | 47.8 - 236.9 | |
| h-NiMoFe (This work) | Ni foam | N/A | 22.5 - 48.0 | 75.4 – 291.7 |
| | Labor cost | N/A | 5.11 - 6.8 | |
| Pt/C | 10 wt% Pt/C powder | Sigma-Aldrich | 31,000 kg ⁻¹ | 310 (1 mg cm ⁻² , w/o support) |
| Pt black on carbon paper | Pt black | Fuel Cell Store | 13,500 m ⁻² | 13,500 |
| Pt black on carbon cloth | Pt black | Fuel Cell store | 9,100 m ⁻² | 9,100 |
| Pt commodity | Pt | Shanghai Gold Exchange | 27,000 kg ⁻¹ | N/A |
| Raney Ni on Ni foam support | >90% Ni <10% Al | Jiangsu Leini Metal Tech. Co., Ltd | 50 kg ⁻¹ | 60 (60 mg cm ⁻²) |
| MoS ₂ solid | MoS ₂ (30% solid content) | OKS 111, Germany | 470 kg ⁻¹ | 47 (10 mg cm ⁻² , w/o Mo support) |
| foil ³⁶ | Mo foil support | Luoyang Tuojing Refractory Metal Co., Ltd. | 613 m ⁻² | 613 |

Table S6. A comparison of the prices of catalysts in this work compared to commercial electrocatalysts.

| Catalysts (Cathode Anode) | Electrolyte | Current density at potential = 1.56 V (mA cm ⁻²) | Ref. |
|---|-------------|---|-----------|
| h-NiMoFe h-NiMoFe | 1.0 M KOH | 500 | This work |
| Co_4N - $CeO_2 \parallel Co_4N$ - CeO_2 | 1.0 M KOH | 35 | 29 |
| FeCoO _x -Vo-S CoP ₃ /Ni ₂ P-D | 1.0 M KOH | 23 | 37 |
| $V-CoP@a-CeO_2 \parallel V-CoP@a-CeO_2$ | 1.0 M KOH | 10 | 38 |
| $(Ru-Co)O_x \parallel (Ru-Co)O_x$ | 1.0 M KOH | 42 | 39 |
| Co ₃ Mo/Cu EO Co ₃ Mo/Cu | 1.0 M KOH | 40 | 40 |
| $Ni_{3}N\text{-}VN/NF\parallel Ni_{2}P\text{-}VP_{2}/NF$ | 1.0 M KOH | 15 | 41 |
| Fe-Ni@NC-CNTs Fe-Ni@NC-CNTs | 1.0 M KOH | 5 | 42 |
| FeP/Ni ₂ P FeP/Ni ₂ P | 1.0 M KOH | 51 | 43 |
| NiMo/Ni-P NiFe/Ni-P | 1.0 M KOH | 14 | 44 |
| $Ni_{11}(HPO_3)_8\text{-}(OH)_6 \parallel Ni_{11}(HPO_3)_8\text{-}(OH)_6$ | 1.0 M KOH | 8 | 45 |
| NC/CuCo/CuCoO _x NC/CuCo/CuCoO _x | 1.0 M KOH | 15 | 46 |

Table S7. A comparison of the performance of catalysts for overall water splitting in this work with

 previously reported data.

References

- 1. G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, 6, 15-50.
- 2. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
- 3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.
- 4. J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23.
- F. Yang, Y. Luo, Q. Yu, Z. Zhang, S. Zhang, Z. Liu, W. Ren, H. M. Cheng, J. Li and B. Liu, *Adv. Funct. Mater.*, 2021, DOI: 10.1002/adfm.202010367.
- W. Li, X. Gao, D. Xiong, F. Wei, W.-G. Song, J. Xu and L. Liu, *Adv. Energy Mater.*, 2017, 7, 1602579.
- R. Zhang, X. Wang, S. Yu, T. Wen, X. Zhu, F. Yang, X. Sun, X. Wang and W. Hu, *Adv Mater*, 2017, 29, 1605502.
- J. Kibsgaard, C. Tsai, K. Chan, J. D. Benck, J. K. Nørskov, F. Abild-Pedersen and T. F. Jaramillo, *Energy Environ. Sci.*, 2015, 8, 3022-3029.
- Y. Duan, Z. Y. Yu, S. J. Hu, X. S. Zheng, C. T. Zhang, H. H. Ding, B. C. Hu, Q. Q. Fu, Z. L.
 Yu, X. Zheng, J. F. Zhu, M. R. Gao and S. H. Yu, *Angew. Chem. Int. Ed.*, 2019, 58, 15772.
- 10. F. Dury, E. M. Gaigneaux and P. Ruiz, *Applied Catalysis A: General*, 2003, 242, 187-203.
- 11. B. R. M. Newville, Journal of Synchrotron Radiation, 2005, 12, 537-541.
- 12. Y. Luo, L. Tang, U. Khan, Q. Yu, H.-M. Cheng, X. Zou and B. Liu, *Nat. Commun.*, 2019, **10**, 269.
- R. Zhang, X. Wang, S. Yu, T. Wen, X. Zhu, F. Yang, X. Sun, X. Wang and W. Hu, *Adv. Mater.*, 2017, 29, 1605502.
- Y. Luo, X. Li, X. Cai, X. Zou, F. Kang, H. M. Cheng and B. Liu, ACS Nano, 2018, 12, 4565-4573.
- X. Yu, Z. Y. Yu, X. L. Zhang, Y. R. Zheng, Y. Duan, Q. Gao, R. Wu, B. Sun, M. R. Gao, G. Wang and S. H. Yu, *J. Am. Chem. Soc.*, 2019, 141, 7537-7543.
- Y.-Y. Chen, Y. Zhang, X. Zhang, T. Tang, H. Luo, S. Niu, Z.-H. Dai, L.-J. Wan and J.-S. Hu, *Adv. Mater.*, 2017, 29, 1703311.
- 17. F. Yu, H. Zhou, Y. Huang, J. Sun, F. Qin, J. Bao, W. A. Goddard, S. Chen and Z. Ren, Nat.

Commun., 2018, 9, 2551.

- J. Mahmood, F. Li, S.-M. Jung, M. S. Okyay, I. Ahmad, S.-J. Kim, N. Park, H. Y. Jeong and J.-B. Baek, *Nat. Nanotechnol.*, 2017, **12**, 441-446.
- K. Jiang, M. Luo, Z. X. Liu, M. Peng, D. C. Chen, Y. R. Lu, T. S. Chan, F. M. F. de Groot and Y. W. Tan, *Nat. Commun.*, 2021, **12**, 1687.
- X. X. Ji, Y. H. Lin, J. Zeng, Z. H. Ren, Z. J. Lin, Y. B. Mu, Y. J. Qiu and J. Yu, *Nat. Commun.*, 2021, **12**, 1380.
- P. L. Zhai, Y. X. Zhang, Y. Z. Wu, J. F. Gao, B. Zhang, S. Y. Cao, Y. T. Zhang, Z. W. Li, L. C. Sun and J. G. Hou, *Nat. Commun.*, 2020, 11, 5462.
- Y. L. Wu, X. F. Li, Y. S. Wei, Z. M. Fu, W. B. Wei, X. T. Wu, Q. L. Zhu and Q. Xu, *Adv. Mater.*, 2021, 33, 2006965.
- H. Y. Jin, X. S. Wang, C. Tang, A. Vasileff, L. Q. Li, A. Slattery and S. Z. Qiao, *Adv. Mater.*, 2021, 33, 2007508.
- L. Xiu, W. Pei, S. Zhou, Z. Wang, P. Yang, J. Zhao and J. Qiu, *Adv. Funct. Mater.*, 2020, 1910028, 1910028.
- 25. L.-N. Zhang, Z.-L. Lang, Y.-H. Wang, H.-Q. Tan, H.-Y. Zang, Z.-H. Kang and Y.-G. Li, *Energy Environ. Sci.*, 2019, **12**, 2569-2580.
- Z.-Y. Yu, C.-C. Lang, M.-R. Gao, Y. Chen, Q.-Q. Fu, Y. Duan and S.-H. Yu, *Energy Environ*. Sci., 2018, 11, 1890-1897.
- Y. Zang, S. Niu, Y. Wu, X. Zheng, J. Cai, J. Ye, Y. Xie, Y. Liu, J. Zhou, J. Zhu, X. Liu, G. Wang and Y. Qian, *Nat. Commun.*, 2019, 10, 1217.
- B. Zhang, J. Liu, J. Wang, Y. Ruan, X. Ji, K. Xu, C. Chen, H. Wan, L. Miao and J. Jiang, *Nano Energy*, 2017, 37, 74-80.
- 29. H. Sun, C. Tian, G. Fan, J. Qi, Z. Liu, Z. Yan, F. Cheng, J. Chen, C.-P. Li and M. Du, *Adv. Funct. Mater.*, 2020, **30**, 1910596.
- 30. Q. Yang, G. Li, K. Manna, F. Fan, C. Felser and Y. Sun, *Adv. Mater.*, 2020, **32**, e1908518.
- J. Yang, A. R. Mohmad, Y. Wang, R. Fullon, X. Song, F. Zhao, I. Bozkurt, M. Augustin, E. J. G. Santos, H. S. Shin, W. Zhang, D. Voiry, H. Y. Jeong and M. Chhowalla, *Nat. Mater.*, 2019, 18, 1309-1314.
- 32. L. A. King, M. A. Hubert, C. Capuano, J. Manco, N. Danilovic, E. Valle, T. R. Hellstern, K.

Ayers and T. F. Jaramillo, Nat. Nanotechnol., 2019, 14, 1071-1074.

- Z. Luo, H. Zhang, Y. Yang, X. Wang, Y. Li, Z. Jin, Z. Jiang, C. Liu, W. Xing and J. Ge, *Nat. Commun.*, 2020, 11, 1116.
- Y. Chen, G. Yu, W. Chen, Y. Liu, G. D. Li, P. Zhu, Q. Tao, Q. Li, J. Liu, X. Shen, H. Li, X. Huang, D. Wang, T. Asefa and X. Zou, *J. Am. Chem. Soc.*, 2017, 139, 12370-12373.
- Y. Xue, B. Huang, Y. Yi, Y. Guo, Z. Zuo, Y. Li, Z. Jia, H. Liu and Y. Li, *Nat. Commun.*, 2018, 9, 1460.
- D. Kiriya, P. Lobaccaro, H. Y. Nyein, P. Taheri, M. Hettick, H. Shiraki, C. M. Sutter-Fella, P. Zhao, W. Gao, R. Maboudian, J. W. Ager and A. Javey, *Nano Lett.*, 2016, 16, 4047-4053.
- L. Zhuang, Y. Jia, H. Liu, Z. Li, M. Li, L. Zhang, X. Wang, D. Yang, Z. Zhu and X. Yao, *Angew. Chem. Int. Ed.*, 2020, **59**, 2-9.
- 38. L. Yang, R. Liu and L. Jiao, Adv. Funct. Mater., 2020, 30, 1909618.
- 39. C. Wang and L. Qi, Angew. Chem. Int. Ed., 2020, 59, 17219-17224.
- 40. H. Shi, Y.-T. Zhou, R.-Q. Yao, W.-B. Wan, X. Ge, W. Zhang, Z. Wen, X.-Y. Lang, W.-T. Zheng and Q. Jiang, *Nat. Commun.*, 2020, **11**, 2940.
- H. Yan, Y. Xie, A. Wu, Z. Cai, L. Wang, C. Tian, X. Zhang and H. Fu, *Adv. Mater.*, 2019, 31, e1901174.
- 42. X. Zhao, P. Pachfule, S. Li, J. R. J. Simke, J. Schmidt and A. Thomas, *Angew. Chem. Int. Ed.*, 2018, **57**, 8921-8926.
- 43. F. Yu, H. Zhou, Y. Huang, J. Sun, F. Qin, J. Bao, W. A. Goddardiii, S. Chen and Z. Ren, *Nat. Commun.*, 2018, **9**, 2551.
- 44. A. Sahasrabudhe, H. Dixit, R. Majee and S. Bhattacharyya, *Nat. Commun.*, 2018, 9, 2014.
- P. W. Menezes, C. Panda, S. Loos, F. Bunschei-Bruns, C. Walter, M. Schwarze, X. Deng, H. Dau and M. Driess, *Energy Environ. Sci.*, 2018, 11, 1287-1298.
- 46. J. Hou, Y. Sun, Y. Wu, S. Cao and L. Sun, Adv. Funct. Mater., 2018, 28, 1704447.