Supplementary Materials for

Two-dimensional mineral hydrogel-derived single atoms-anchored heterostructures for ultrastable hydrogen evolution

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Supplementary Fig. 5 Concentration-dependent experiment SEM images of the FePMo composites obtained after self-assembly process with various molar ratios of Fe$^{3+}$ to PMo: 6:1 (a), 12:1 (b), 19:1 (c), 25:1 (d), 31:1 (e), and 37:1 (f).

A concentration-dependent experiment was carried out with various molar ratios of Fe$^{3+}$:
PMo (6:1, 12:1, 19:1, 25:1, 31:1, 37:1, and 60:1), and it can be clearly seen that some of these mixtures precipitated faster than others (Supplementary Fig. 3, 4). Specifically, precipitates of FePMoG were formed within minutes in lower molar ratio (6:1 and 12:1) mixtures of Fe\(^{3+}\): PMo and within several hours in higher molar ratio (19:1, 25:1, 31:1, and 37:1) mixtures of Fe\(^{3+}\): PMo; however, no precipitate was formed in the highest molar ratio (60:1) mixture of Fe\(^{3+}\): PMo.

As shown in Supplementary Fig. 4, 5a, when the ratio Fe\(^{3+}\)/PMo is as low as 6:1 forms a sphere-like shape with a diameter of about several hundred nanometers that is comprised of several spheres grown together. When the ratio is increased to 12:1, its morphology consists of uniform nanoparticles that are significantly smaller than that of the 6:1 (Supplementary Fig. 5b). When the ratio is increased again to 19:1, the morphology is totally different, as depicted in Supplementary Fig. 5c, it seems to form a nanosheet-like cluster, but it is like a rudiment of the whole nanosheet, and in some places, it appears to consist of many agminated nanoparticles covered by a thin film.

It's necessary to note that partially deposited on the bottom of the bottle and the upper liquid near to the solution surface became transparent. At a ratio of 25:1, Fe\(^{3+}\) and PMo obviously self-assembled into wrinkle-like nanosheets (Supplementary Fig. 5d). At a ratio of 31:1, they self-assembled into a wrinkle nanosheet (Supplementary Fig. 5e) with a significantly higher thickness than that of 25:1. At a ratio of 37:1, it took much longer to form precipitates, and the nanosheet was very large with vast wrinkles at the surface (Supplementary Fig. 5f).

Too high ratio led to overly lengthy assembly (when the molar ratio of Fe\(^{3+}\)/PMo was 50:1, not shown here, self-assembly took about seven days), and when the molar ratio of Fe\(^{3+}\)/PMo was as high as 60:1, the solution kept transparent. It can be concluded from this concentration-dependent experiment that the morphology of the FePMo composites is significantly dependent on the ratio of Fe\(^{3+}\) to POM, and the higher ratios of Fe\(^{3+}\)/PMo were associated with a longer self-assembly process.

Supplementary Table 1 Comparison of mineral hydrogel, porous framework and carbon substrate used for single atom-based catalyst production

| facile fabrication | Mineral hydrogel | Porous framework | Carbon |
|--------------------|-----------------|-----------------|--------|
| content | details | Score\(^{a}\) | details (e.g. Ref\(^{1}\)) | Score\(^{a}\) | details (e.g. Ref\(^{2}\)) | Score\(^{a}\) |
| instrument | centrifuge | 10 | oven, ice machine, heating agitator, glass reactor, freezer dryer, vacuum pump, filter, sonicator, centrifuge, tube furnace | 2 | glass beaker, heating agitator, oven, tube furnace, centrifuge, sonicator | 3 |
| procedure | standing, centrifugation | 10 | stirring, cooling, heating, vacuum filtration, freeze dry, conjugation, polymerization | 2 | stirring, drying, heating, noble metal deposition, sonication, heating and stirring | 3 |
|                      | sonication | centrifugation, drying |
|----------------------|------------|------------------------|
| template             | no need    | 10 no need             |
| purificatio n        | water wash | 10 washed with         |
|                      |            | degassed ethanol and   |
|                      |            | diethyl ether,         |
|                      |            | solvothermal           |
|                      |            | wash with organic      |
|                      |            | solvent                |
| reaction condition   | room       | 10 ice bath, heated at |
|                      | temperature| 120 °C, heated at      |
|                      |            | 300 °C                 |
| total access         | simple     | 100 complex synthetic  |
|                      | synthetic  | procedure, reaction    |
|                      | procedure, | conditions are complex |
|                      | equipment  | and numerous           |
|                      |            | 40 complex synthetic   |
|                      |            | procedure, reaction    |
|                      |            | conditions are complex |
|                      |            | and numerous           |
| green synthesis      | Fe(NO₃)₃·9H₂O, phosphomolybdic acid, NaCl, NaH₂PO₄, ethanol, deionized water | 10 CoCl₂·6H₂O, chloranilic acid, H₂SO₄, ethylenediamine, 1-methyl-2-pyrolidinone (NMP), anhydrous NMP, diethyl ether, ethanol, deionized water |
| yield (from raw material to final catalyst) | ~80% | 8 Synthesis of hexaaminobenzen e: ~39.69% conjugation: 50.89% polymerization: 90% | 1.5 carbonization: usually <30% |
| organic release      | none       | 10 isopropanol, NMP, anhydrous NMP, ethylenediamine, diethyl ether is easy to evaporate | 1 Organic waste during the high temperature pyrolysis |
| solvent              | deionized water | 10 isopropanol, NMP, ethylenediamine, diethyl ether | 1 ethylene glycol and ethanol mixture |
| Catalyst usage       | no         | 10 Some frame works preparation need catalyst, e.g. covalent organic framework | 3 CVD method to synthesize the carbon need grow the catalyst beforehand |
| recycle              | few kinds of | 10 Some organic | 5 the kind of |
| ions in liquid waste, easy to disposal | solvent can recycle but it is complicate to separate | organic solvent is less and easy to recycle, |
|---|---|---|
| total access | using common non-toxic inorganic salt, easy recycle | 100 | using multiple organic solution and some are toxic | 10 | using common non-toxic inorganic salt, easy recycle | 50 |

| time efficiency | precursor synthesis | 20 h | 8 | 64 h | 3 | 18 h | 8.5 |
|---|---|---|---|---|---|---|---|
| subsequent synthesis | 16.5 h | 9 | 81 h | 1 | 34 h | 3 |
| total access | no equipment needed, just few more cans can produce mineral hydrogel simultaneously | 100 | some MOF even need several week to prepare and purification | 20 | if use MOF and COF as carbon source, the synthetic time will increase greatly | 40 |

| morphological controlability | 1D Ref | 10 | Ref | 7 | 6 | Ref | 8,9 | 3 |
|---|---|---|---|---|---|---|---|---|
| 2D This work | 10 | Ref | 6,10 | 5 | Ref | 6,11 | 6 |
| 3D Ref | 10 | Ref | 12-14 | 9 | Ref | 15-19 | 9 |
| total access | easy to control the morphology | 100 | need to change a lot of reagents, reaction condition, even develop a new method | 60 | need to change a lot of reagents, reaction condition, even develop a new method, involving using the catalyst and using the porous framework to prepare | 35 |

| Organic free | raw material | yes | 10 | no | 0 | no, but using common organic solvent with low toxicity | 5 |
|---|---|---|---|---|---|---|---|
| products | yes | 10 | the intermediate products are organic | 1 | organic waste produced during the high temperature pyrolysis | 5 |
| total access | no organic species during the whole preparation process of mineral hydrogel | 100 | using a variety of and large amount organic solvents and some are toxic and complicate to prepare | 5 | the glucose and ethylene glycol is abundant and non-toxic | 50 |

| abundance | source of inorganic salts is rich and easy to process | 10 | the synthesis of some organic solvent is complex and their yield is low | 1 | noble metal salt is rare and expensive; the organic solvent used in easy to produce | 3 |
|---|---|---|---|---|---|---|
| total access | rich in raw materials and easy to prepare | 100 | using a variety of and large amount organic solvents | 5 | all regent except the noble metal salt is rich and | 60 |
and some are toxic and complicate to prepare  

| universal ity       | ion species | majority metal ion can be added in the mineral hydrogel | 9  | Ref\(^6\) can use multiple metal ion for conjugation. However, majority need special metal that can coordinate with linker, or absorb limited metal ion\(^{17,20}\) | 4  | many metal ions can be absorbed in the carbon or carbon precursor, the use of noble metal limit the universality | 6  |
|---------------------|-------------|--------------------------------------------------------|----|---------------------------------------------------------------------------------|----|---------------------------------------------------------------------------------|----|
| synthetic method    | simple, directly add other metal ion in the precursor solution | 10 | need to consider the coordinated property of the metal ions, or absorb ability of the framework | 3  | Need to consider the property of metal ion; the further deposition of noble metal is low efficiency | 3  |
| total access        | easy to add other metal ion and have large potential in prepare other metal single atom catalyst | 100 | can prepare other single atom catalyst but the efficiency and yield is low, synthetic method is complex | 30 | can prepare other single atom catalyst but the efficiency and yield is low, synthetic method is complex | 60 |
| Low cost (USD, per kg produced catalyst) | materials cost | 35.39 | 10 | 4779.64 | 2 | 8045.85 | 1 |
|                     | electricity consumption | 0.49 | 10 | 97.44 | 1 | 47.78 | 4 |
|                     | total access | only using abundant inorganic salts; simple preparation process; few instruments are used | 100 | need use many special organic solvent; rare in resources; complex production process; use many different instrument | 10 | the noble metal salt and some raw material is expensive; not rich in resources; need to use large amount of organic solvent, multiple preparation steps; some method didn’t use noble metal and the cost will reduce a lot\(^{21}\) | 70 |

\(^{a}\) These scores are based on the practical value, or complication degree, toxicity (in the range of 0-10); total access score of mineral hydrogel is normalized to 100; the details were refer to the example of 2D porous frame work and carbon.
Supplementary Fig. 6 Digital images of the time-dependent experiment of the FePMo nanosheets. The molar ratio of Fe$^{3+}$ to PMo reagents is 25:1.
Supplementary Fig. 7 SEM images of the time-dependent evolution of wrinkle-like FePMoG: 1h (a), 2 h (b), 4 h (c), 8 h (d), 16 h (e) and 24 h (f). The molar ratio of Fe$^{3+}$ to PMo reagents is 25:1; (g) schematic illustration of the FePMoG assemble process.
Supplementary Fig. 8 Optical photograph of the mineral hydrogels containing added ion species (~3 at.% of the sum of Fe and Mo atoms, the molar ratio of Fe³⁺/PMo is 25:1).

Supplementary Fig. 9 (a) XRD patterns, (b) FTIR spectra of the FePMoG with the molar ratio of Fe³⁺ to PMo reagents is 25:1.

The bands located at 1147 and 1126 cm⁻¹ represent asymmetric stretching vibrations ($\nu_{as}$) of P–Oₐ, and the band centred at 642 cm⁻¹ represents a $\delta$ (P–O) vibration. The bands at 1017 cm⁻¹ ($\nu_{as}$ (Mo–Oₐ)), 945 cm⁻¹ ($\nu_{as}$ (Mo–Oₐ)), and the triplet at 876 cm⁻¹ ($\nu_{as}$ (Mo–Oₐ–Mo)), 816 cm⁻¹ ($\nu_{as}$ (Mo–Oₐ–Mo)), and 760 cm⁻¹ ($\nu_{as}$ (Mo–Oₐ–Mo)) represent the interactions between Mo and various forms of O. The red and blue shifts in the vibrations of the Keggin structure result from the interaction between Fe³⁺ and PMo–heteropolyanions ²²-²⁴. In addition, the broad band at 1625 cm⁻¹ represents the asymmetric stretching mode of the OH coordinated to Fe³⁺, and the bands at 515 and 495 cm⁻¹ are due to an Fe–O–Mo vibration ²²,²³.
Supplementary Fig. 10 Mo 3d spectrum of FePMoG.

Supplementary Fig. 11 XRD patterns of samples obtained at different phosphorization temperatures.

The main phases at 27.95°, 32.17°, 43.15°, 57.48°, 64.93°, 67.86°, and 74.33° correspond to the (001), (100), (101), (110), (111), (102), and (201) crystal planes of MoP (JCPDS No. 24-0771), respectively. The diffraction peaks at 25.99°, 37.35°, and
53.46° represent the (011), (111), and (022) crystal planes of MoO$_2$ (JCPDS No. 78-1069), respectively. Other weak diffraction peaks at 23.90°, 34.64°, 41.68°, 47.20°, 48.91°, and 49.99° are ascribable to the (021), (111), (131), (112), (042), and (150) planes of MoP$_2$ (JCPDS No. 89-2678), respectively.

Supplementary Table 2 Chemical compositions of samples obtained at different phosphorization temperatures determined by XRD.

| Temperatures (°C) | FeP | MoO$_2$ | MoP | MoP$_2$ |
|------------------|-----|---------|-----|---------|
| 350              | ✓   | ✓       | —   | —       |
| 400              | ✓   | ✓       | ✓   | —       |
| 450              | ✓   | ✓       | ✓   | ✓       |
| 500              | —   | ✓       | ✓   | ✓       |
| 550              | —   | ✓       | ✓   | ✓       |
| 600              | —   | —       | ✓   | ✓       |
| 650              | —   | —       | ✓   | ✓       |
| 700              | —   | —       | ✓   | ✓       |
| 750              | —   | —       | ✓   | ✓       |

Supplementary Fig. 12 (a) Low magnification TEM image, (b) HRTEM image of bulk FeMoP-500.
Supplementary Fig. 13 (a) Low magnification TEM image, (b) High magnification bright-field TEM image, (c) Dark-field TEM image, (d) high-resolution TEM image, (e) SEAD pattern, (f) STEM image and the corresponding EDS elemental mapping of Fe (green), Mo (violet), P (orange) and O (cyan) of the FeMoP-450.
Supplementary Fig. 14 (a) Low magnification TEM image, (b) High magnification bright-field TEM image, (c) Dark-field TEM image, (d) high-resolution TEM image, (e) SEAD pattern, (f) STEM image and the corresponding EDS elemental mapping of Fe (green), Mo (violet), P (orange) and O (cyan) of the FeMoP-550.
Supplementary Fig. 15 (a) Nitrogen sorption isotherms, (b) pore size distributions of the FeMoP-450, Fe/SAs@Mo-based-HNSs and FeMoP-550 catalysts.

The Brunauer–Emmett–Teller (BET) surface area of the Fe/SAs@Mo-based-HNSs was found to be 89.6 m² g⁻¹, which is higher than that of FeMoP-450 and FeMoP-550 (81.7 m² g⁻¹ and 86.1 m² g⁻¹, respectively) and further demonstrates Fe/SAs@Mo-based-HNSs’ intrinsically porous structure (Supplementary Fig. 15). The pore-size distribution of the Fe/SAs@Mo-based-HNSs clearly indicates that they have many mesopores with diameters of 1.3–12 nm, which would provide numerous exposed active sites. The similar BET surface areas and pore-size distributions of FeMoP-450 and FeMoP-550 suggest that the phosphorisation temperature in the heterostructure-forming range has only a minor effect on the formation of a porous structure.

Supplementary Fig. 16 XPS spectrum of Fe/SAs@Mo-based-HNSs.
Supplementary Fig. 17 (a) The corresponding $k^2$-weighted FT-EXAFS spectra and fitting line of Fe/SAs@Mo-based-HNSs at Mo K-edge in the R spacing, Wavelet transforms for the $k^2$-weighted EXAFS signals at Mo K-edge of (b) Mo foil, (c) MoO$_2$, and (d) MoO$_3$.

Supplementary Table 3 EXAFS fitting parameters at the Mo K-edge for various samples ($S^2_0=0.94$)

| Shell   | CN | R(Å)   | $\sigma^2$ | $\Delta E_0$  | R factor |
|---------|----|--------|------------|---------------|----------|
| Mo foil |     |        |            |               |          |
| Mo-Mo   | 8  | 2.72±0.01 | 0.0039     | 4.1±0.6       | 0.0022   |
| Mo-Mo   | 6  | 3.14±0.01 | 0.0040     |               |          |
| Fe/SAs@Mo-based HNSs |     |        |            |               |          |
| Mo-O    | 0.5±0.2 | 1.99±0.03 | 0.0033     | 2.6±1.3       | 0.0118   |
| Mo-P    | 3.0±0.2 | 2.44±0.01 | 0.0048     |               |          |
| Mo-O    | 2.5±0.2 | 3.20±0.01 | 0.0035     |               |          |

$^a$N: coordination numbers; $^b$R: bond distance; $^c$σ: Debye-Waller factors; $^d$ Δ$E_0$: the inner potential correction. R factor: goodness of fit.

In the FT-EXAFS spectra and fitting line at Mo K-edge, the peaks at 1.45, 1.95 and 2.93 Å, which could be attributed to Mo-O, Mo-P and Mo-O bonds, respectively. Comparing with Mo foil, no apparent peaks (2.72 and 3.14 Å) for Mo-Mo bonds are detected in both Fe/SAs@Mo-based-HNSs, confirming the absence of Mo nanoparticles.
Supplementary Fig. 18 (a) The corresponding $k^2$-weighted FT-EXAFS spectra and fitting line of Fe/SAs@Mo-based-HNSs at Fe K-edge in the R spacing, Wavelet transforms for the $k^2$-weighted EXAFS signals at Fe K-edge of (b) Fe foil, (c) Fe$_2$O$_4$, and (d) Fe$_3$O$_4$.

Supplementary Table 4 EXAFS fitting parameters at the Fe K-edge for various samples ($S_0^2=0.94$)

| Shell         | CN | R(Å)      | $\sigma^2$ | $\Delta E_0$ | R factor |
|---------------|----|-----------|------------|--------------|----------|
| Fe foil       |    |           |            |              |          |
| Fe-Fe         | 8  | 2.47±0.01 | 0.0052     | 7.1±1.1      | 0.0040   |
| Fe-Fe         | 6  | 2.85±0.01 | 0.0069     | 7.1±1.1      | 0.0040   |
| Fe/SAs@Mo-based HNSs | 5.9±0.3  | 1.98±0.01 | 0.0054     | -6.3±1.6    | 0.0059   |

$^aN$: coordination numbers; $^bR$: bond distance; $^c\sigma^2$: Debye-Waller factors; $^d\Delta E_0$: the inner potential correction. $R$ factor: goodness of fit.
Supplementary Fig. 19 O 1s XPS spectra of Fe/SAs@Mo-based-HNSs.

Supplementary Table 5 Elemental compositions for FePMoG, FeMoP-450, Fe/SAs@Mo-based-HNSs, FeMoP-550 and tested FeMoP-500 determined by XPS.

| Samples               | Fe (at%) | Mo (at%) | P (at%) | O (at%) | r<sub>Fe/Mo</sub> |
|-----------------------|----------|----------|---------|---------|-------------------|
| FePMoG                | 7.8      | 16.9     | 0.4     | 74.9    | 0.461             |
| FeMoP-450             | 4.5      | 18.8     | 8.1     | 68.6    | 0.239             |
| Fe/SAs@Mo-based HNSs  | 4.6      | 20.7     | 10.4    | 64.3    | 0.222             |
| FeMoP-550             | 1.0      | 17.3     | 19.8    | 61.9    | 0.058             |
| Tested FeMoP-500      | 4.1      | 19.2     | 10.2    | 66.5    | 0.213             |

r<sub>Fe/Mo</sub> is the atomic ratio of Fe to Mo
**Supplementary Table 6** Elemental compositions for FePMoG, FeMoP-450, Fe/SAs@Mo-based-HNSs and FeMoP-550 determined by TEM EDS.

| Samples                  | Fe (at%) | Mo (at%) | P (at%) | O (at%) | Fe/Mo |
|--------------------------|----------|----------|---------|---------|-------|
| FePMoG                   | 8.28     | 15.56    | 0.51    | 75.65   | 0.532 |
| FeMoP-450                | 5.3      | 19.7     | 8.9     | 66.1    | 0.269 |
| Fe/SAs@Mo-based HNSs     | 5.1      | 21.4     | 11.3    | 62.2    | 0.238 |
| FeMoP-550                | 1.4      | 18.2     | 21.9    | 58.5    | 0.077 |

$r_{\text{Fe/Mo}}$ is the atomic ratio of Fe to Mo.

**Supplementary Table 7** Elemental compositions for FePMoG, FeMoP-450, Fe/SAs@Mo-based-HNSs and FeMoP-550 determined by ICP-OES.

| Samples                  | Fe (mg/kg) | Mo (mg/kg) | P (mg/kg) | O (mg/kg) | Fe/Mo |
|--------------------------|------------|------------|-----------|-----------|-------|
| FePMoG                   | 146725.83  | 481927.19  | /         | /         | 0.523 |
| FeMoP-450                | 70586.59   | 431511.55  | /         | /         | 0.281 |
| Fe/SAs@Mo-based HNSs     | 62367.61   | 420141.41  | /         | /         | 0.255 |
| FeMoP-550                | 22122.89   | 447094.81  | /         | /         | 0.085 |

$r_{\text{Fe/Mo}}$ is the atomic ratio of Fe to Mo.
Supplementary Fig. 20 Spectroscopy of FeMoP-550 at Fe K-edge: (a) Fe K-edge XANES spectra; (b) corresponding $k^3$-weighted FT of EXAFS spectra; (c) the corresponding $k^3$-weighted FT-EXAFS spectra and fitting line in the R spacing; and (d) wavelet transforms for $k^3$-weighted EXAFS signals.

Supplementary Table 8 EXAFS fitting parameters at the Fe K-edge for various samples ($S_0^2=0.74$)

| shell     | CN | R(Å)      | $\sigma^2$ | $\Delta E_0$ | R factor |
|-----------|----|-----------|------------|--------------|----------|
| Fe foil   |    |           |            |              |          |
| Fe-Fe     | 8  | 2.47±0.01 | 0.0049     | 6.5±1.2      | 0.0066   |
| Fe-Fe     | 6  | 2.85±0.01 | 0.0060     |              |          |
| FeMoP-550 |    |           |            |              |          |
| Fe-O      | 6.3±0.2 | 1.98±0.01 | 0.0045    | -2.4±1.1     | 0.0039   |

$^a$N: coordination numbers; $^b$R: bond distance; $^c$σ²: Debye-Waller factors; $^d$Δ$E_0$: the inner potential correction. $R$ factor: goodness of fit.
Supplementary Table 9 Comparison of HER performance in 1 M KOH for FeMoP-T catalysts.

| Samples                     | $\eta_{10}$ (mV) | Tafel slope (mV dec$^{-1}$) |
|-----------------------------|------------------|-----------------------------|
| FeMoP-350                   | 242.7            | 104.1                       |
| FeMoP-400                   | 214.4            | 90.5                        |
| FeMoP-450                   | 97.0             | 57.6                        |
| Fe/SAs@Mo-based-HNSs (FeMoP-500) | 38.5             | 35.6                        |
| FeMoP-550                   | 104.3            | 60.4                        |
| FeMoP-600                   | 143.1            | 84.7                        |
| FeMoP-650                   | 222.3            | 88.9                        |
| FeMoP-700                   | 236.4            | 86.1                        |
| FeMoP-750                   | 305.4            | 122.6                       |
| Bulk FeMoP-500              | 257.1            | 89.3                        |

Supplementary Fig. 22 Polarization curves of three independent Fe/SAs@Mo-based-HNSs prepared from different batches in 1 M KOH with iR correction.
Supplementary Fig. 23 Cyclic voltammograms in the region of 0-0.1 V vs. RHE at various scan rates for (a) FeMoP-450, (b) Fe/SAs@Mo-based-HNSs, (c) FeMoP-550, and (d) Bulk FeMoP-500.

Supplementary Table 10 Amount of hydrogen production for samples at a constant current density of 10 mA/cm².

| Time (min) | Bulk FeMoP-500 (μmol) | 20% Pt/C (μmol) | Fe/SAs@Mo-based-HNSs (μmol) |
|-----------|------------------------|------------------|-----------------------------|
| 15        | 11.77 ± 0.60           | 20.40 ± 1.08     | 21.93 ± 1.06                |
| 30        | 23.20 ± 0.64           | 40.39 ± 0.89     | 44.89 ± 0.79                |
| 45        | 35.45 ± 1.05           | 60.59 ± 0.61     | 68.64 ± 0.81                |
| 60        | 47.08 ± 0.47           | 80.82 ± 0.54     | 88.80 ± 0.56                |
| 75        | 59.31 ± 0.46           | 101.16 ± 0.64    | 113.24 ± 0.78               |
| 90        | 71.99 ± 0.62           | 121.44 ± 0.88    | 134.22 ± 0.68               |
| 105       | 83.67 ± 0.31           | 140.92 ± 0.39    | 158.44 ± 0.78               |
| 120       | 94.77 ± 0.52           | 162.06 ± 0.47    | 179.46 ± 0.70               |

* This value is the average of three different electrode test results.
Supplementary Fig. 24 Polarisation curves of Fe/SAs@Mo-based-HNSs before and after 500 h test at a scan rate of 5 mV s$^{-1}$ with potential error (iR) correction.

Supplementary Fig. 25 (a) Low magnification TEM image, (b) High magnification TEM image, (c) high-resolution TEM image, (d) STEM image and the corresponding EDS elemental mapping of Fe (green), Mo (violet), P (orange) and O (cyan) of the Fe/SAs@Mo-based-HNSs after 500 h test.
Supplementary Fig. 26 XRD pattern of the Fe/SAs@Mo-based-HNSs after 500 h test (blue curve). The peaks indexed with mark * derived from the carbon paper as the sample load on the carbon paper.

Supplementary Fig. 27 (a) Mo 3d, (b) Fe 2p spectrum, (c) P 2p spectrum, and (d) O 1s spectrum of the Fe/SAs@Mo-based-HNSs after 500 h test.

Supplementary Table 11 ICP-OES results of the Fe/SAs@Mo-based-HNSs after stability test for 500h at 20 mA cm$^{-2}$ current density.

|                | Fe    | Mo    | P     |
|----------------|-------|-------|-------|
| Concentration (mmol/L) | 0.014 | 0.009 | 0.012 |
| Limit of reporting (mmol/L) | 0.010 | 0.0058 | 0.030 |
*The lowest concentration of a substance that can be reliably reported by ICP-OES.

Supplementary Table 12 Comparison of HER performance in 1 M KOH for Fe/SAs@Mo-based-HNSs and previous reported catalysts.

| Electrocatlysts                  | Overpotential (at 10 mA cm\(^2\)) | Tafel slope (mV dec\(^{-1}\)) | Loading (mg cm\(^{-2}\)) | \(C_\text{a}\) (mF cm\(^{-2}\)) | Stability (h) | Ref. |
|----------------------------------|----------------------------------|-------------------------------|---------------------------|-------------------------------|---------------|------|
| **Mo-based**                     |                                  |                               |                           |                               |               |      |
| Fe/SAs@Mo-based-HNSs             | 39.5                             | 47.8                          | 0.67                       | 40.3                          | 600           |      |
| Mo\(_2\)C/Mo\(_2\)N/C-850       | 60                               | 55                            | 0.38                       | 22.5                          | 16.6          | [25] |
| MoP@NCHSa-900                    | 92                               | 62                            | 0.39                       | ~130                          | 12            | [26] |
| FLiNPC@MoP-NC                    | 69                               | 52                            | ~5                        | 55.3                          | 50            | [27] |
| MoP NA/CC                       | 80                               | 83                            | ~2.5                       | 4.02                          | 46            | [28] |
| MoP/SNG-20                      | 49                               | 31                            | 0.4-0.5                    | 20.5                          | 20            | [29] |
| **Fe-based**                     |                                  |                               |                           |                               |               |      |
| Ni-Fe/P/TiN/CC-1                 | 75                               | 73                            | N/A                       | 33.7                          | 10            | [30] |
| NiFe LDH-NS@DG10                 | 300                              | 110                           | 0.283                     | 4.3                           | 5.6           | [31] |
| FePSe@/NC                        | 118.5                            | 88                            | 0.212                     | 3.03                          | 24            | [32] |
| rGO-few layer FePSe\(_3\)       | 155                              | 37                            | 0.15                      | 5.9                           | 40            | [33] |
| FeNi\(_2\)N/NG                   | ~90                              | 83.1                          | 2                        | 33.3                          | 22            | [34] |
| **Heterostructure**              |                                  |                               |                           |                               |               |      |
| Mo\(_2\)N-Mo\(_2\)C/HGr         | 154                              | 68                            | 0.337                     | 33                            | 50            | [35] |
| MoP/NiP/NF                       | 75                               | 100.2                         | N/A                       | 4.78*                         | 24            | [36] |
| 1T-2H MoS\(_2\)                 | ~290                             | 65                            | 0.28                      | 2.41                          | 28            | [37] |
| MoS\(_2\)/NiS\(_2\)             | 110                              | 83.1                          | ~7                        | 15.6                          | 10            | [38] |
| Ni(OH)\(_2\)/MoS\(_2\)          | 80                               | 60                            | 4                         | 735                           | 17            | [39] |
| CoSe/MoS\(_2\)                   | 218                              | 76                            | 0.204                     | 4.3                           | N/A           | [40] |
| HF-MoSP-900                      | 119                              | 85                            | 0.07065                   | 45.3                          | 30            | [41] |
| ES-WC/Wo:C                       | 75                               | 59                            | 0.075                     | 97.8                          | 20            | [42] |
| W/WoC@NPC-2                      | 82                               | 84.6                          | 0.283                     | 4.52                          | 10            | [43] |
| WC/WoC@C NWs                     | 56                               | 52                            | 0.34                      | 61                            | 45            | [44] |
| CoP/NiCoP/NC                     | 75                               | 59                            | 0.318                     | ~19                           | 85            | [45] |
| CoP/NiCoP NTs                    | 133                              | 88                            | 2                        | N/A                           | 24            | [46] |
| CoP-CoMo                         | 198                              | 95                            | 1.12                      | N/A                           | 10            | [47] |
| CoP/CoWO\(_4\)                  | 81                               | 47                            | N/A                       | 21.72                         | 16            | [48] |
| Ni(OH)\(_2\)-NiS/TM             | ~62                              | 86                            | 3.2                       | 7.25                          | 25            | [49] |
| NiCoS\(_2\)/NiS\(_2\)/Ni         | 119                              | 105.2                         | N/A                       | 113.5                         | 24            | [50] |
| Ni/NiP\(_3\)                     | 130                              | 58.5                          | N/A                       | 23.1                          | 24            | [51] |
| NiP-NiSe\(_2\)/CC                | 66                               | 72.6                          | 9.2                       | 31                            | 12            | [52] |
| **Single atoms**                 |                                  |                               |                           |                               |               |      |
| Pt\(_3\)/N-C                     | 46                               | 36.8                          | 0.25                      | N/A                           | 20            | [53] |
| Fe/NiC                           | 111.1                            | 86.1                          | ~0.3                      | N/A                           | 20            | [54] |
| Pt@Fe-N-C                        | 108                              | ~50                           | 0.4                       | N/A                           | 20            | [55] |
| Co\(_2\)/N-C                     | 247                              | 75                            | 2                        | N/A                           | N/A           | [56] |
| Ru-MoS\(_2\)/CC                  | 41                               | 114                           | 12.446                    | N/A                           | 20            | [57] |
| Pt/PCCM                          | 139                              | 73.6                          | 21.23                     | 51.09                         | 5             | [58] |
| Co1/PCN                          | 89                               | 59                            | 0.5                       | N/A                           | 24            | [59] |
| Mo/Ni\(_2\)C                     | 132                              | 90                            | 0.408                     | N/A                           | N/A           | [60] |
| E-Co SAs                         | 59                               | 105                           | 0.4                       | N/A                           | 500           | [61] |
| **2D nanosheets**                |                                  |                               |                           |                               |               |      |
| WS\(_2\)/rGO                     | ~250                             | 58                            | 0.4                       | N/A                           | N/A           | [62] |
| Material                  | Specific Capacity | Mass Activity | Selectivity | Stability | Notes               |
|---------------------------|-------------------|---------------|-------------|-----------|---------------------|
| CoB/CoSe₂                 | 320               | 76            | 0.4         | 36.2      | 30 [63]             |
| MoP@Ni₃P/NF               | 45                | 56            | N/A         | 7.7       | 35 [64]             |
| Co₃P NS/CNTs              | 68                | 57            | 0.272       | 3.2       | 24 [65]             |
| Ni-BDT-A                  | 80                | 70            | N/A         | 59.2      | N/A [66]            |
| **Noble-metal-based**     |                   |               |             |           |                     |
| 4H/fcc Au-Ru-2 NWs        | 50                | 30.8          | 0.08        | N/A N/A   | N/A [67]            |
| 20% Pt/Ni(HCO₃)₂          | 27                | 45            | 0.204       | 2.58      | 30.5 [68]           |
| Pr-Co(OH)₂/CC             | 32                | 70            | 6.9         | 68        | 20 [69]             |
| w-Au@MoS₂                 | 120               | 52.9          | N/A         | N/A       | 10 [70]             |
| Ni@Ni₃P-Ru                | 31                | 41            | 0.283       | N/A       | 11 [71]             |
| Pt-Pt-S                   | 71                | 31            | ~0.02       | N/A       | 2 [72]              |
| **Multiple metal-based**  |                   |               |             |           |                     |
| VN@Ni₃N–Ni₆/CC            | 57                | 40            | N/A         | 31.86     | 40 [73]             |
| Co₃Ni₃P NTs               | 129               | ~460          | 0.19        | 52        | 20 [74]             |
| P-Co₃Mo₃C/Co/CNF          | 81                | 64            | 0.43        | 35        | 40 [75]             |
| Ni–P/MoS₂                 | 140               | 64            | N/A         | 3.5       | 10 [76]             |
| TiO₂ NDs/Co NSNTs-CFs     | ~90               | 62            | N/A         | 71.1      | 100 [77]            |
| MoS₂(NiS)MoO₃             | 91                | 54.5          | N/A         | 45.12     | 20 [78]             |
| Co₃S₄@MoS₂                | 136               | 74            | 0.283       | 62        | 10 [79]             |
| Cu NDs/Ni₃S₂ NTs-CFs      | 128               | 76.2          | N/A         | 62.37     | 32 [80]             |
| Cu@Co₃S₄/CF               | 270               | 61            | N/A         | N/A       | 200 [81]            |
| np-(Co₃S₄Fe₁₅₋ₓ)P         | ~70               | 40            | 1           | N/A       | 50 [82]             |
| 2D-MoS₂/Co(OH)₂           | 128               | 76            | 0.285       | 0.91      | 20 [83]             |
| NiS₂/MoS₂ HNW             | 204               | 65            | 0.2         | 5.6       | 6 [84]              |
| H-CeO₂ₓ/Ni₃P@NC           | 123               | 60            | 0.35        | 21.76     | 27 [85]             |
| **carbon-free**           |                   |               |             |           |                     |
| MoP/NF                    | 114               | 54.6          | N/A         | 52.1      | 20 [86]             |
| MoP NSAs/Mo               | 106               | 55            | ~1          | 73        | 36 [87]             |
| Ni₃P NPs                  | 140               | ~30           | 1           | N/A       | 200 [88]            |
| FeP NAs/CC                | 58                | 146           | 1.5         | 60        | 20 [89]             |
| Co/Co₃O₄ NS               | ~55               | 44            | 0.85        | N/A       | 2 [90]              |
| CoP/CC                    | 67                | 51            | 0.92        | N/A       | 22.2 [91]           |

*Obtained from the figures in the reference.
Supplementary Table 13 The H$_2$O adsorption energy, adsorption site and the bonding distance between active site and O atom in H$_2$O.

| Catalyst       | Adsorption energy (eV) | Adsorption site | Mo/Fe-O bonding distance |
|---------------|------------------------|-----------------|-------------------------|
| MoP           | -0.64                  | Mo top          | 2.334 Å                 |
| MoP$_2$       | -0.62                  | Mo top          | 2.410 Å                 |
| MoO$_2$       | -0.79                  | Mo top          | 2.284 Å                 |
| MoP/MoP$_2$   | -0.99                  | Mo top          | 2.187 Å                 |
| MoP/MoO$_2$   | -0.88                  | Mo top          | 2.439 Å                 |
| MoP$_2$/MoO$_2$| -0.94                 | Mo top          | 2.410 Å                 |
| Fe@MoO$_2$-1  | -0.92                  | Fe top          | 2.027 Å                 |
| Fe@MoO$_2$-2  | -0.36                  | Fe top          | 2.271 Å                 |

Supplementary Table S13 lists the H$_2$O adsorption energies, active adsorption sites, and the bonding distance between the O atoms of H$_2$O and atoms in electrocatalytic active sites for all of the models. It can be seen that the H$_2$O adsorption ability of single-phase models is inversely proportional to the Mo–O bonding distance, which is consistent with H$_2$O adsorption abilities varying with Mo–O and Fe–O bonding distances in heterostructured interface models and monoatomic dispersed Fe models. Intriguingly, even though the Mo–O bonding distances for MoP/MoO$_2$ and MoP$_2$/MoO$_2$ (2.439 Å and 2.410 Å, respectively) are larger than those for MoP, MoP$_2$, and MoO$_2$ (2.334 Å, 2.410 Å, and 2.284 Å, respectively), the H$_2$O adsorption ability of heterostructured interfaces is higher than that of the single phase. This demonstrates that heterostructured interfaces in Fe SAs@Mo-based HNSs effectively promote the transfer of electrons from active sites to H$_2$O molecules, and thus improve these compounds’ H$_2$O adsorption ability.
Supplementary Fig. 28 Partial density of states (PDOS) of MoP, MoP₂, MoO₂, MoP/MoP₂, MoP/MoO₂, MoP₂/MoO₂, Fe@MoO₂-1 and Fe@MoO₂-2 after H₂O adsorption at surface sites. The black dashed lines at the energy of zero indicate the Fermi level (Eₘₚ).

To further explore the strength of bonding between H₂O molecules and active sites, we determined the partial density of states (PDOS) curves of Mo/Fe active sites and O atoms in H₂O molecules (Supplementary Fig. 28). As can be seen, the intensities of interaction between the electrons in the s-, p-, d-orbitals of Mo/Fe and the s-, p-orbitals of O are rather different, which accounts for the variation in the H₂O adsorption ability of different models. The PDOS peak overlap of Mo and O orbitals is most extensive in MoO₂ in the single-phase models, whereas it is most extensive in MoP/MoP₂ in the heterostructured interface models. In addition, the PDOS peaks of O perfectly overlap with that of Fe in Fe@MoO₂-1 but not in Fe@MoO₂-2, which accounts for the significant difference in these species’ H₂O adsorption ability. These physical insights explain the variation in the electron-transfer ability of different structures, and thus highlight the microstructures that are critical for efficient H₂O adsorption.
Supplementary Fig. 29 Free energy diagrams of reaction coordinate for water dissociation on the surfaces of single-phase models (MoP, MoP$_2$ and MoO$_2$), heterostructured interface models (MoP/MoP$_2$, MoP/MoO$_2$ and MoP$_2$/MoO$_2$), monoatomic dispersed Fe onto MoO$_2$ surface models (Fe@MoO$_2$-1 and Fe@MoO$_2$-2) and Pt(111).
Supplementary Fig. 30 The representative atomic configurations after H adsorption at the surface sites of MoP, MoP$_2$ and MoO$_2$ with corresponding $\Delta G_{H*}$.

Supplementary Fig. 31 DFT results of 2D electron density differences after adsorption of H* onto the active sites in the single-phase models. Red and blue represent the depletion and accumulation of electrons with the unit of e/Å$^3$, respectively.
In the single-phase models (Supplementary Fig. 30), it can be seen that electron transfer between H* and Mo is too weak at the Mo top of MoP, given its $\Delta G_{\text{H*}}$ value of 0.31 eV. A stronger depletion of electrons in Mo occurs at the Mo–Mo bridge than that at the Mo top, which improves H* adsorption at the surface of MoP; however, this interaction is too strong, resulting in an unsuitable $\Delta G_{\text{H*}}$ value (-0.35 eV). The electron-transfer ability of the Mo top of MoP₂ is similar to that of MoP, which results in a similarly unsuitable $\Delta G_{\text{H*}}$ value (0.37 eV). The Mo–P bridge in MoP₂ shows a slightly stronger interaction with H*, owing to additional electron transfer from P to H*, and thus its $\Delta G_{\text{H*}}$ value is slightly better (0.30 eV) than those of the Mo–Mo bridge and the Mo top of MoP. Compared with <MoP (Mo top)> and <MoO₂ (Mo top)>, the ability of Mo to transfer electrons to H* is much stronger in MoO₂; however, it is too strong, as it results in a $\Delta G_{\text{H*}}$ value of -0.48 eV. While in the heterostructured interface models (Figure 5e), the electron transfer from the MoP/MoP₂ interface to H* is too high, leading to a $\Delta G_{\text{H*}}$ value of -0.37 eV; in contrast, the electron transfer from the MoP/MoO₂ interface to H* is much lower, leading to a better (i.e., closer to zero) $\Delta G_{\text{H*}}$ value (0.22 eV).

Supplementary Fig. 32 The d-orbital partial density of states (d-PDOS) of three single-phase and two heterostructured interface models with H adsorption onto Mo top. The solid lines marked with digits show the position of d-band centers and the dashed line indicate Fermi level ($E_F$). The corresponding $\Delta G_{\text{H*}}$ values for the models are also indicated.

To ensure the comparability of d-band centres in active sites, we examined only the same Mo
top sites in single-phase and heterostructured interface models: thus, MoP/MoO$_2$ and MoP$_2$/MoO$_2$ interface models with optimal $\Delta G_{\text{H}*}$ values were compared with the single-phase models.

Supplementary Table 14 The $\Delta G_{\text{H}*}$ and $d$-band centers of three single-phase and two heterostructured interface models with H adsorption onto Mo top.

|                | MoP$_2$ | MoP | MoP/MoO$_2$ | MoP$_2$/MoO$_2$ | MoO$_2$ |
|----------------|---------|-----|-------------|-----------------|---------|
| $\Delta G_{\text{H}*}$ (eV) | 0.37    | 0.31| 0.22        | 0.04            | -0.48   |
| $d$-band center | -1.40   | -1.23| -1.13       | -0.99           | -0.75   |

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