Supporting Information

Bimetallic Oxide $Fe_{1.89}Mo_{4.11}O_7$ Electrocatalyst with Highly Efficient Hydrogen Evolution Reaction Activity in Alkaline and Acidic Media

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Experimental Section

Chemicals

All chemical reagents were used as received without further purification.

Synthesis of precursors

Ferrimolybdate: The solution of $H_3[PMo_{12}O_{40}]\cdot XH_2O$, 1,10-phen, Fe_2O_3, NH_4VO_3, trea(triethylamine) and distilled water in a molar ratio of 1 : 1.5 : 1 : 0.5 : 2 : 1000 was stirred for 1h, and the pH value of solution was adjusted to 5.0 by 2 mol L^{-1} HCl solution. The mixture was then transferred into a Teflon-lined autoclave reactor (20 mL) at 175 ℃ for 5 days. The reactor was slowly cooled to room temperature. The resulted red-black block crystals were filtered, washed with water, and dried at room temperature. Anal. Calcd: C, 21.19; H, 1.17; N, 4.12; Fe, 4.12. Found: C, 21.74; H, 1.76; N, 4.01; Fe, 4.08. The crystal structure of ferrimolybdate was checked by single crystal X-ray diffractometer before it was used as precursor.

Polymolybdate: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 1,10-phen, H_3PO_4 and distilled water in a molar ratio of 1 : 0.05 : 0.1 : 2 : 1000 were mixed. The resulting suspension was stirred for 30min and then was transferred into a Teflon-lined autoclave reactor (20 mL). After heating at 170 ℃ for 3 days, the reactor was slowly cooled to room temperature. Yellow block crystals were filtered, washed with water, and dried at room temperature. Anal. Calcd: C, 18.31; H, 1.08; N, 3.55. Found: C, 18.28; H, 1.17; N, 3.56. The crystal structure of ferrimolybdate was checked by single crystal X-ray diffractometer before it was used as precursor.

Synthesis of MoO_2, Fe/MoO_2 and $Fe_{1.89}Mo_{4.11}O_7$/MoO_2

MoO_2: 0.5 g polymolybdates powder was homogeneously dispersed in a ceramic boat that was then put into a tube furnace. The sample was annealed under a continuous nitrogen flux of 10 sccm at 1000 ℃ for 1 hour, and then the ceramic boat was slowly cooled to room temperature. After the annealing was completed, the powders were collected. The heat-treated MoO_2 was then pre-leached in 0.5 M H_2SO_4 at 40 ℃ for 8 hours to remove unstable and inactive species from the catalyst, and thoroughly washed in de-ionized water. Finally, the catalyst was heat-treated again at nitrogen-gas atmosphere for 1 hour to get the final MoO_2.

Fe/MoO_2: 0.5 g polymolybdates and 0.533 g $Fe(NO_3)_3 \cdot 9H_2O$ were homogeneously mixed and then dispersed in a ceramic boat. Next, the samples were annealed in a tube furnace under a continuous nitrogen flux of 10 sccm at 1000 ℃ for 1 hour, and then the ceramic boat was slowly cooled to room temperature. The heat-treated Fe/MoO_2 was then pre-leached in 0.5 M H_2SO_4 at 40 ℃ for 8 hours to remove unstable and inactive species from the catalyst, and thoroughly washed in de-ionized water. Finally, the catalyst was heat-treated again in nitrogen-gas atmosphere for 1 hour to get the final Fe/MoO_2.

$Fe_{1.89}Mo_{4.11}O_7$/MoO_2: 0.5 g Ferrimolybdate powder was homogeneously dispersed in a ceramic boat that was then put into a tube furnace. The samples were annealed under a continuous nitrogen flux of 10 sccm at 1000 ℃ for 1 hour, and then the ceramic boat was slowly cooled to room temperature. After the annealing was completed, the powders were collected. The heat-treated $Fe_{1.89}Mo_{4.11}O_7$/MoO_2 was then pre-leached in 0.5 M H_2SO_4 at 40 ℃ for 8 hours to remove unstable and inactive species from the catalyst, and thoroughly washed in de-ionized water. Finally, the catalyst was heat-treated again in nitrogen-gas atmosphere for 1 hour to get the final $Fe_{1.89}Mo_{4.11}O_7$/MoO_2.

Characterization

Powder X-ray diffraction (XRD) measurement was performed on a Bruker D8 Focus Powder X-ray diffractometer using Cu Kα (λ = 0.15405 nm) radiation (40 kV, 40 mA). X-ray phototelectron spectra (XPS) was measured with VG ESCALAB MK (VK Company, UK) at room temperature by using a Al Kα X-ray source at 12 KV and 20 mA. The morphology of the nickel sulfide was analyzed by on a JSM-6701Feld-emission scanning electron microscope (FE-SEM) with 10KV and 10mA. Energy dispersive spectroscopy (EDS) data was collected with an ensemble measurement in the FE-SEM. Transmission electron microscope (TEM) was performed using a FEI Tecnai G2 S-Twin instrument with a field emission gun operating at 200 kV. Nitrogen adsorption measurements were performed on a Micromeritics ASAP 2020 adsorption analyzer. Specific surface areas were calculated by the Brunaure-Emmert-Teller method. Mass analysis of the generated gases was performed using an Ominstar-Thermostar GSD 320 system (Pfeiffer Vacuum) mass spectrometer, wherein argon gas was chosen as carrier gas. The electrochemical experiments were carried out with a ModuLab XM electrochemical workstation (Solartron Analytical, UK).

Electrochemical characterization

Electrochemical measurements were performed at room temperature in a standard three-electrode system. A platinum gauze electrode and a saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. The preparation of working electrode was described with the following procedures: 5 mg of catalyst powder was dispersed in diluted Nafion alcohol solution containing 1 mL ethanol and 50 μL Nafion, and then ultrasonicated for 2 h to obtain a homogeneous suspension. Next, the suspension was homogeneously loaded on a bare carbon paste and dried at room temperature. Potentials were referenced to a reversible hydrogen electrode (RHE): E(RHE) = E(SCE) + 0.242 + 0.059 ×

*p*H. Linear sweep voltammetry (LSV) was recorded in 1.0 M KOH and 0.5 M H_2SO_4 at a scan rate of 5 mV s^{-1} to obtain the polarization curves. The long-term stability tests were performed by continuous LSV scans at a sweep rate of 20 mV s^{-1}.

Scheme S1 The synthesis route to prepare molybdenum-based nanomaterials

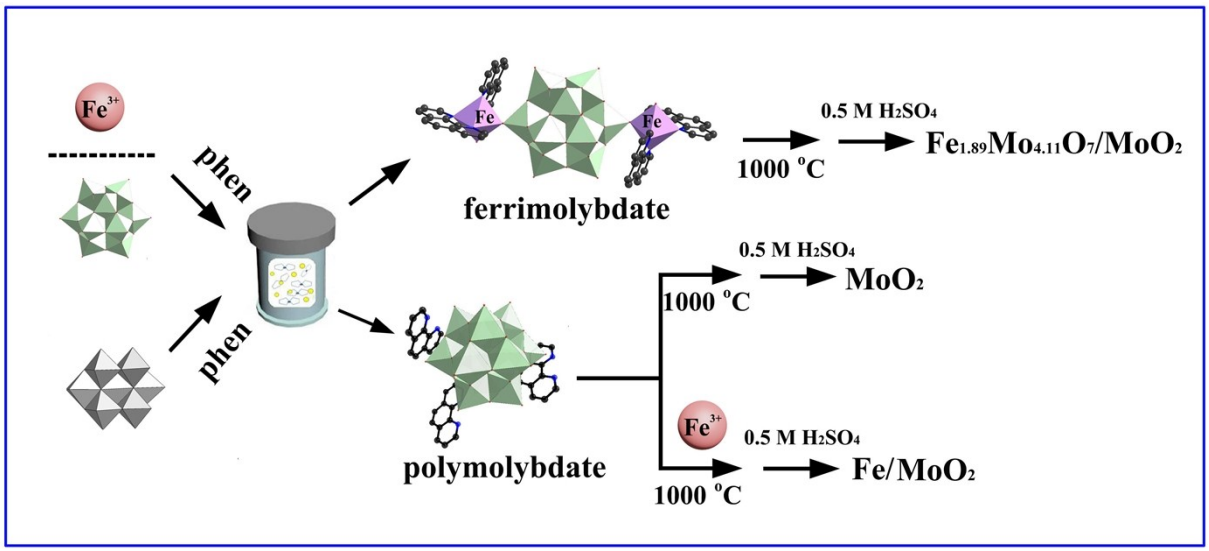


Figure S1 The thermogravimetric studies: CO_2 signals detected by mass spectrum during the thermal treatment of ferrimolybdate, polymolybdates and polymolybdates + Fe^{3+}

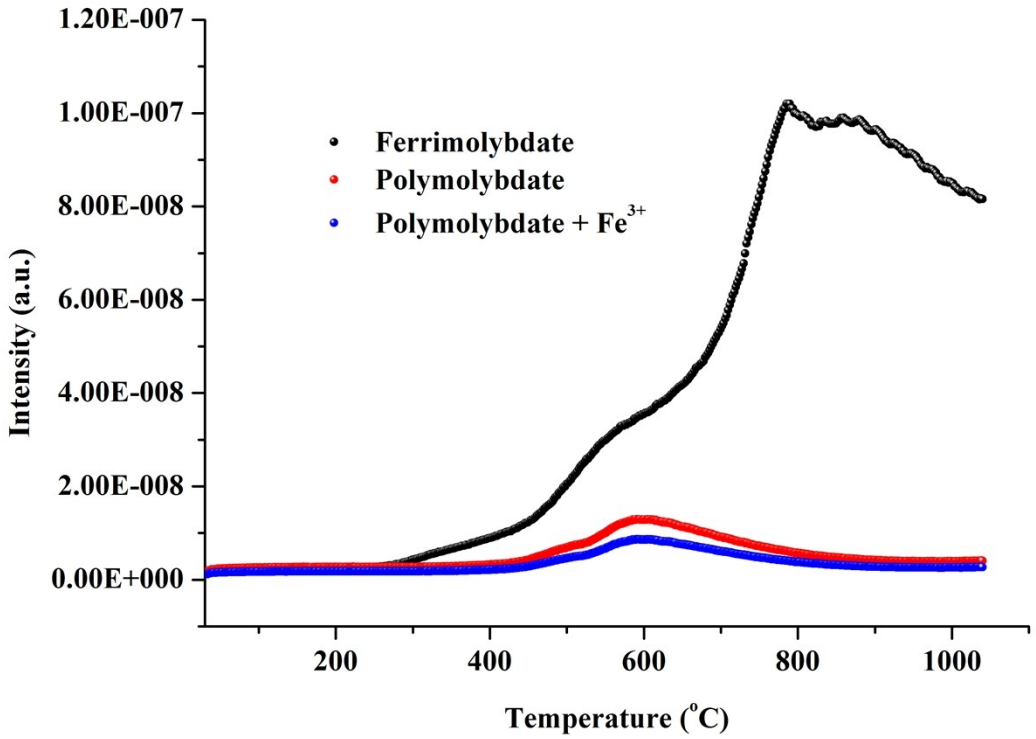


Figure S2 The EDX elemental mapping images of Fe and Mo in $Fe_{1.89}Mo_{4.11}O_7/MoO_2$

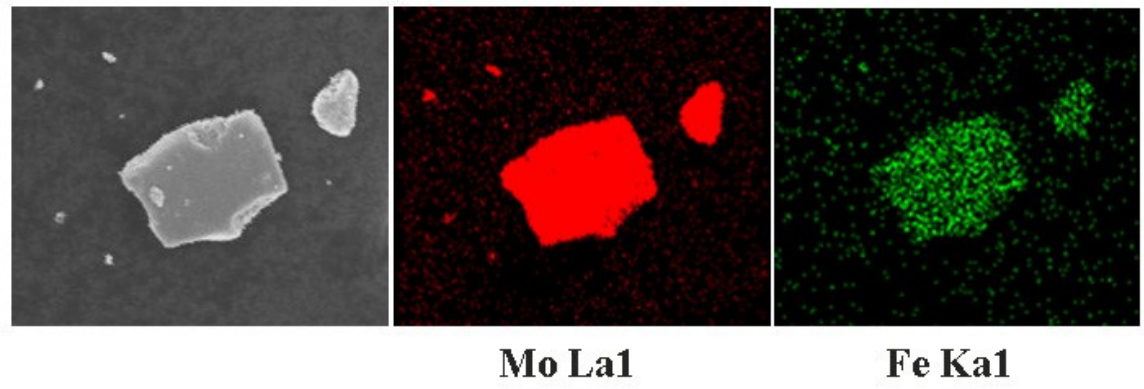


Figure S3 FESEM images of MoO_2 and Fe/MoO_2 for a) precursors of MoO_2, b) precursors of Fe/MoO_2, c) final products of MoO_2, d) final products of Fe/MoO_2.

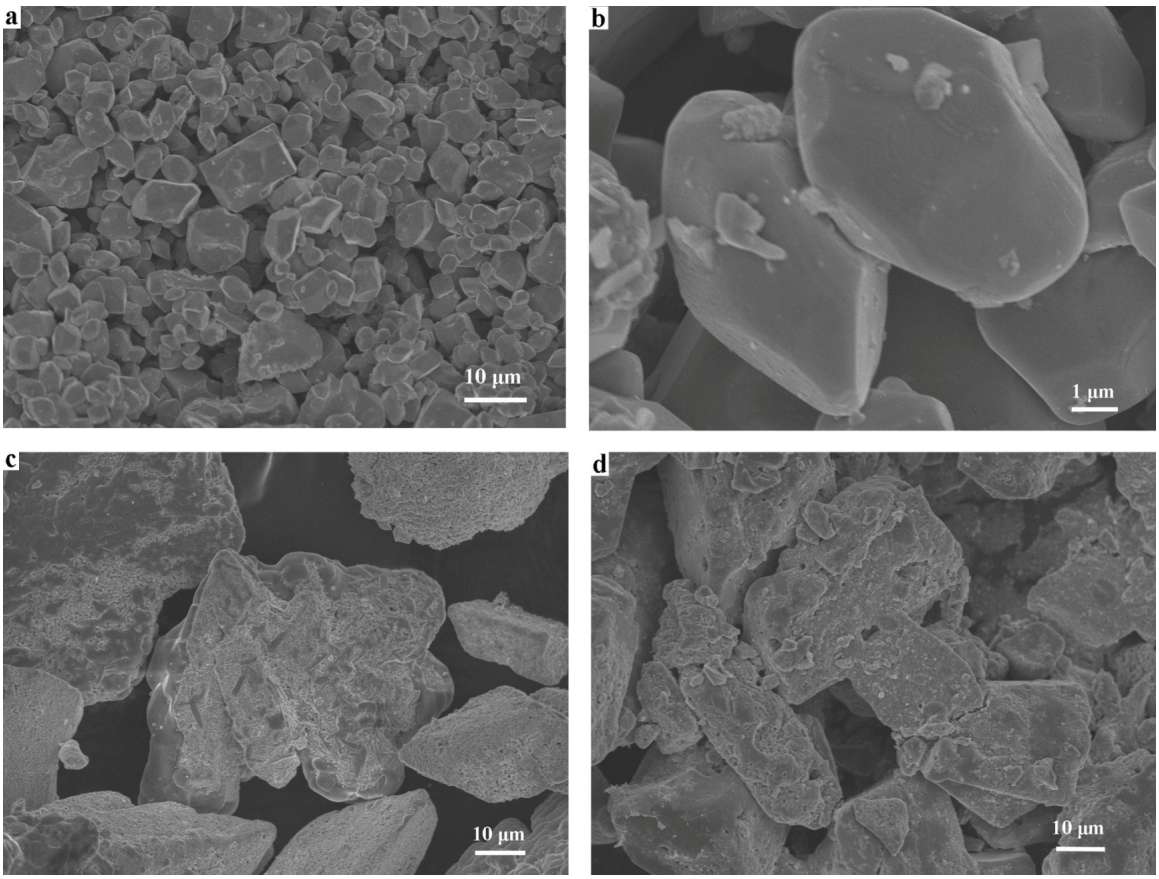


Figure S4 HRTEM image of $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ sample.

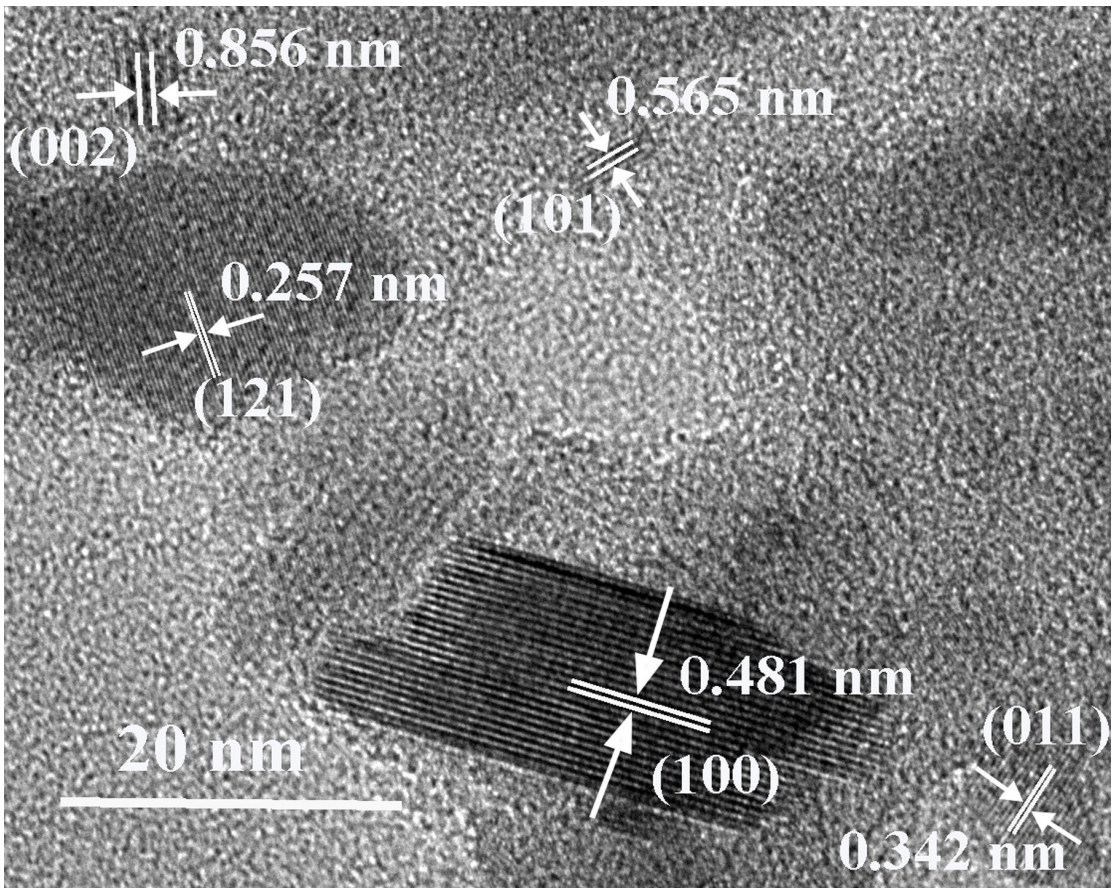


Figure S5 Polarization curves of $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ with different loadings.

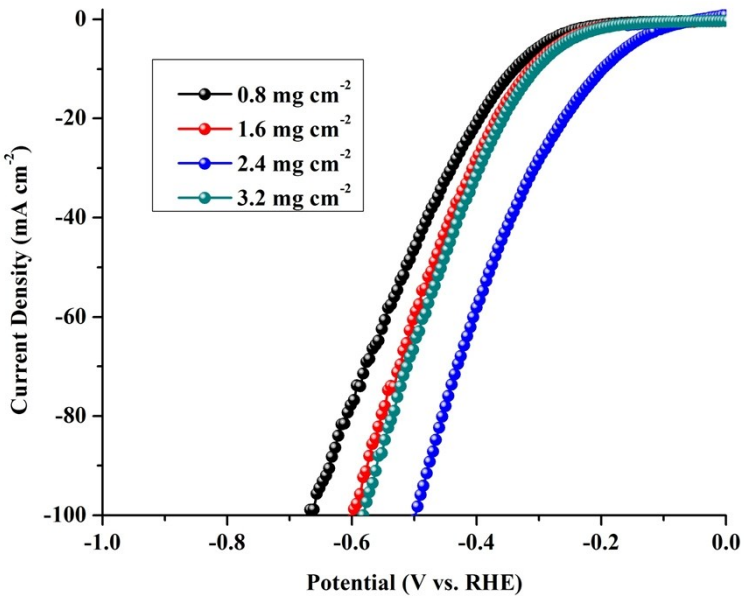


Figure S6 Polarization curves of $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ prepared with different annealing temperature.

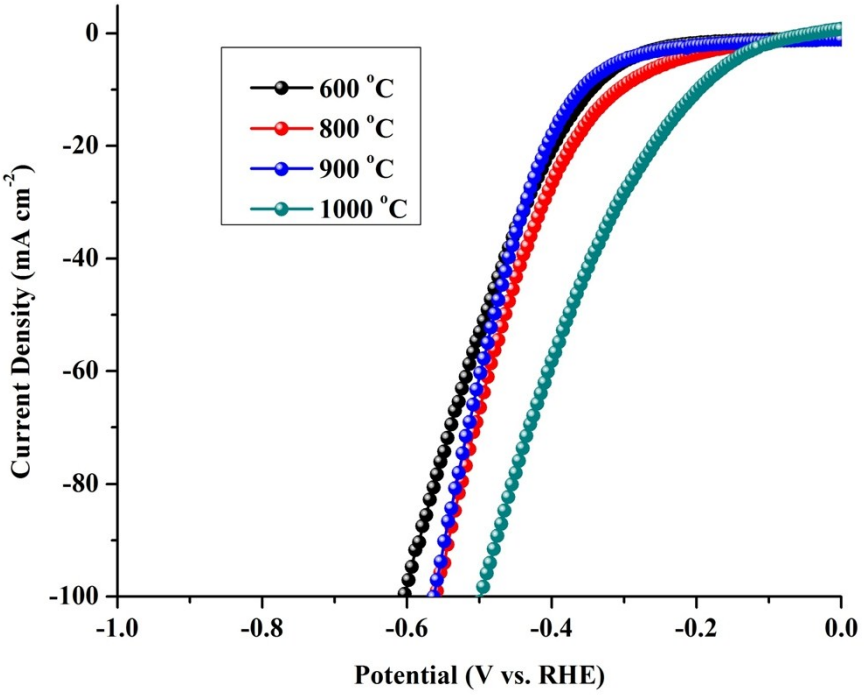


Figure S7 XRD patterns of $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ prepared with different annealing temperature.

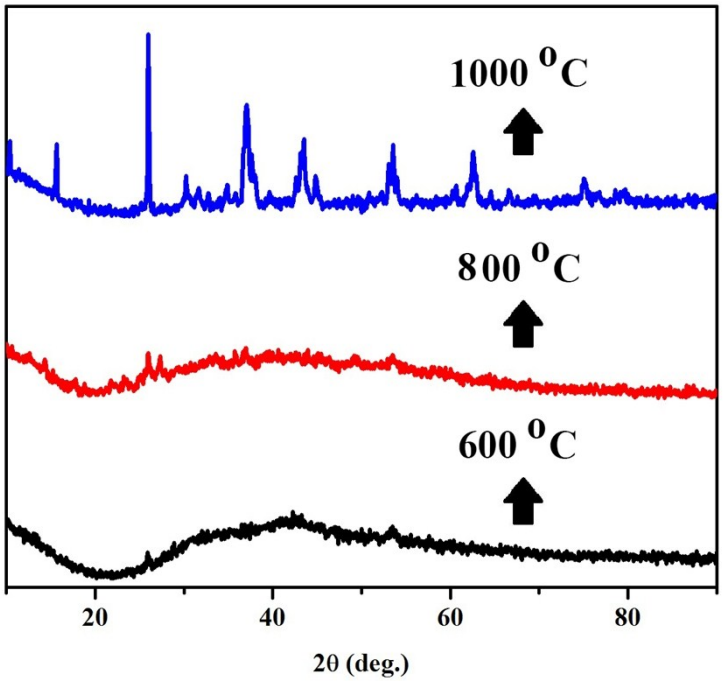


Figure S8 The onset potential of $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ catalyst in 1 M KOH

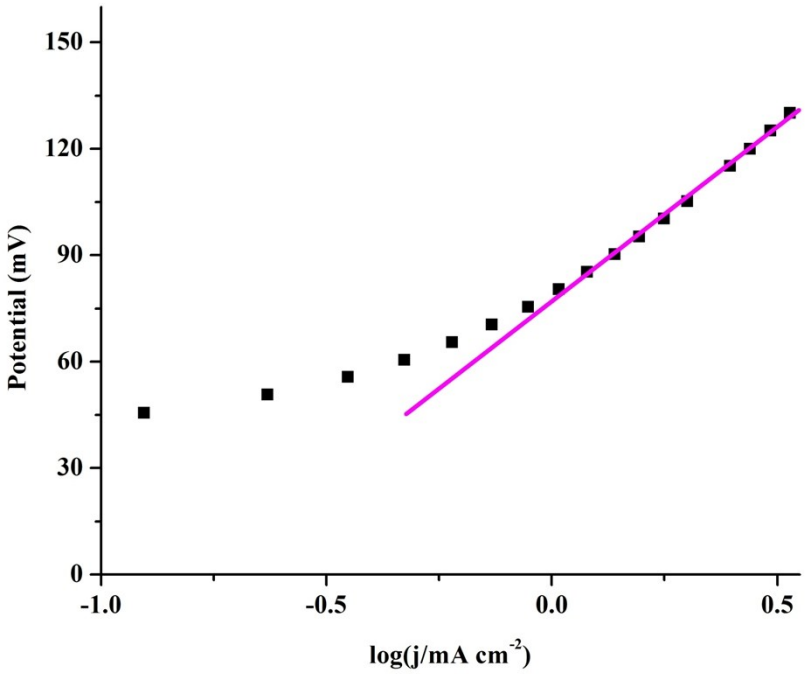


Figure S9 The onset potential of $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ catalyst in 0.5 M H_2SO_4

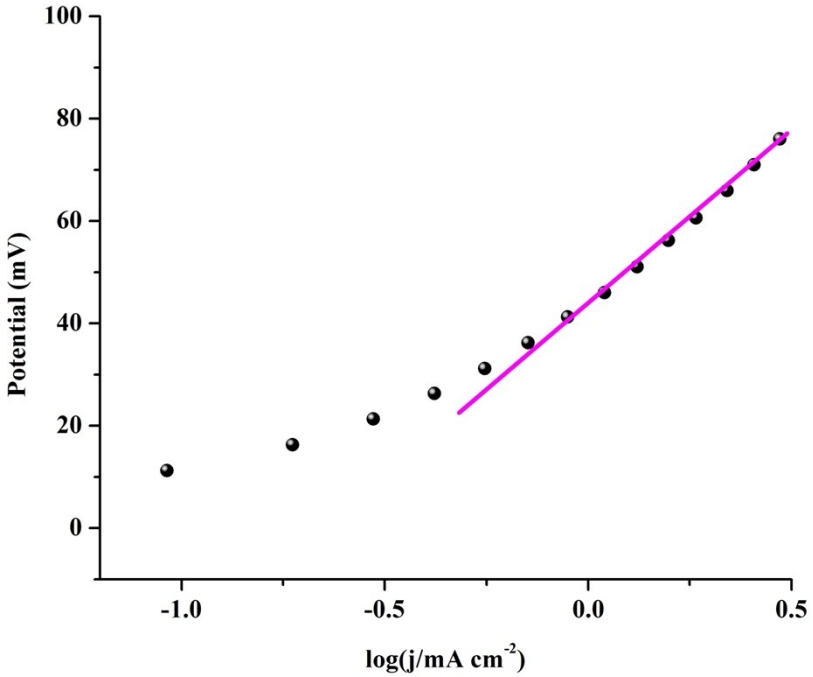


Figure S10 The Tafel plots in 1 M KOH

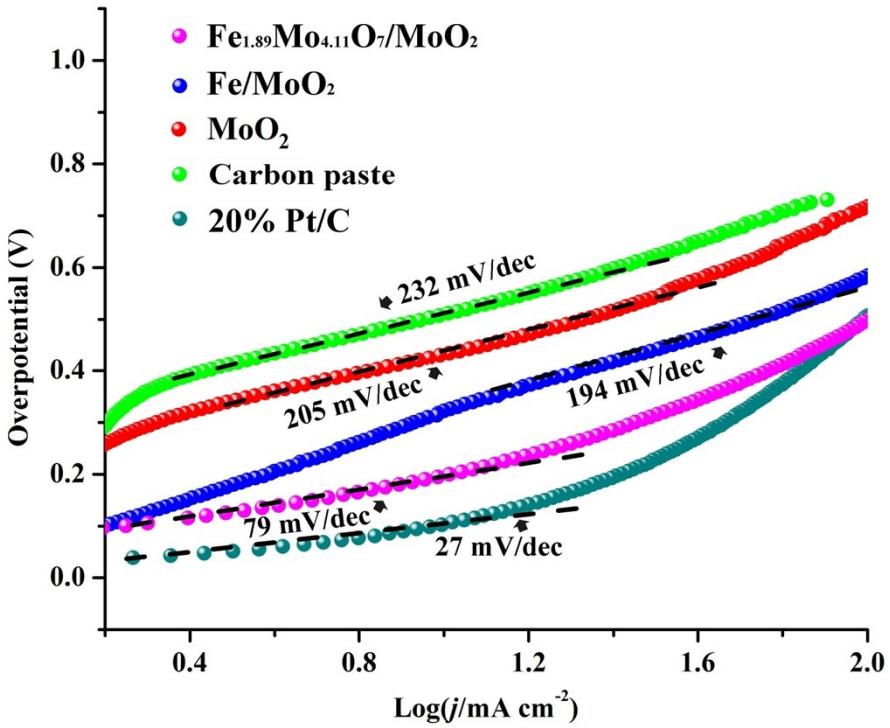


Figure S11 The exchange current density of $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ catalyst in 1 M KOH

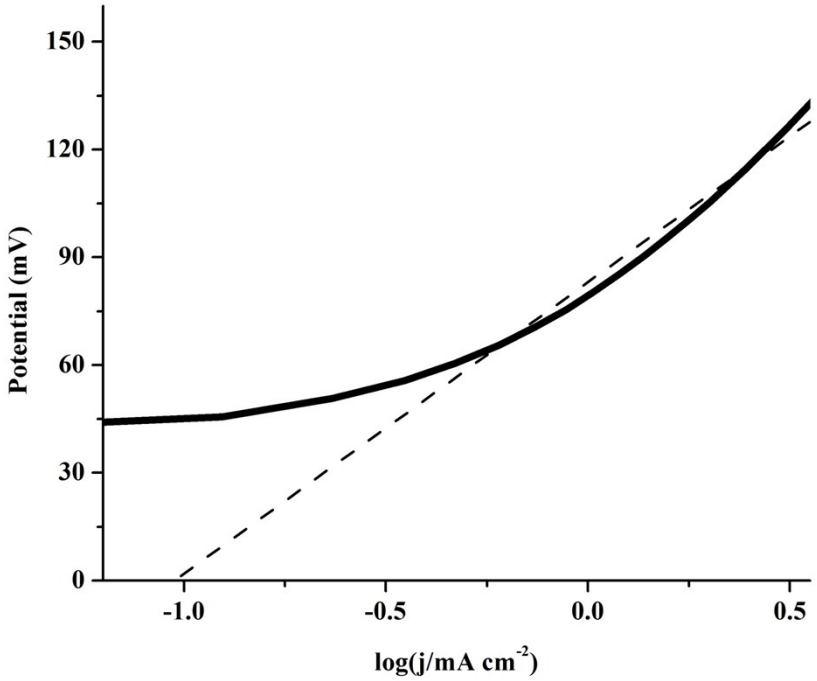


Figure S12 The Tafel plots in 0.5 M H_2SO_4

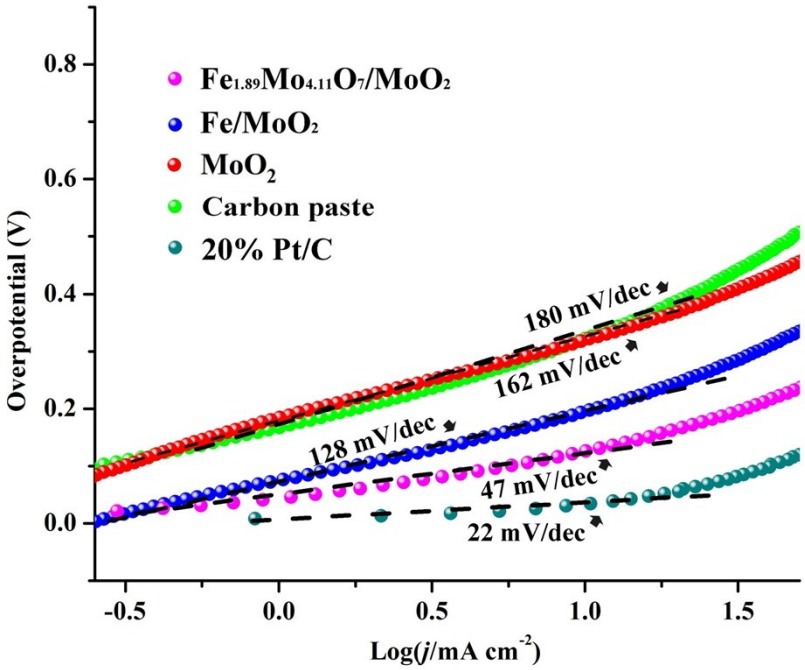


Figure S13 The exchange current density of $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ catalyst 0.5 M H_2SO_4

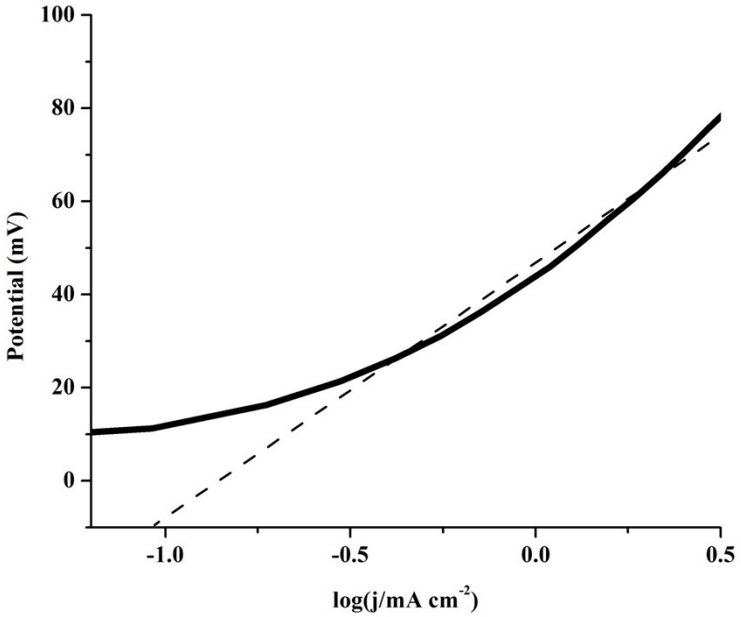


Table S1 The HER performance of catalysts in this paper

Samples	Electrolyte	Tafel slope ($mV\ dec^{-1}$)	η (mV) at 10 $mA\ cm^{-2}$
Cabon paste	1 M KOH	232	514
	0.5 M H_2SO_4	180	321
20% Pt/C	1 M KOH	27	103
	0.5 M H_2SO_4	22	33
MoO_2	1 M KOH	205	431
	0.5 M H_2SO_4	162	318
Fe/MoO_2	1 M KOH	194	322
	0.5 M H_2SO_4	128	194
$Fe_{1.89}Mo_{4.11}O_7/MoO_2$	1 M KOH	79	197
	0.5 M H_2SO_4	47	125

Table S2 Comparison of HER performance for $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ with other HER electrocatalysts

Samples	Electrolyte	Onset η (mV)	Tafel slope (mV dec^{-1})	η (mV) at 10 mA cm^{-2}	Ref.
Double-gyroid MoS_2/FTO	0.5 M H_2SO_4	200 –150	50	240	*Nat. Mater.* **2012**, *11*, 963
MoS_2/$CoSe_2$ hybrid	0.5 M H_2SO_4	11	36	68	*Nat. Commun.* **2015**, *6*, 5982
Exfoliated metallic MoS_2 nanosheets	0.1 M H_2SO_4	135	43	187	*Nat. Mater.* **2013**, *12*, 850.
MoO_3-MoS_2	0.5 M H_2SO_4	200	50-60	250	*Nano Lett.* **2011**, ***11***, 4168
$NiMoN_x$/C	0.1 M $HClO_4$	78	35.9	170	*Angew. Chem. Int. Ed.* **2012**, *51*, 6131
MoS_2/RGO	0.5 M H_2SO_4	100	41	140	*J. Am. Chem. Soc.* **2011**, *133*, 7296.
MoO_2/$MoSe_2$	0.5 M H_2SO_4	63	49.1	181	*Adv. Funct. Mater.* **2016**, *26*, 8537
$MoSe_2$/Mo	0.5 M H_2SO_4	89	34.7	166	*Adv. Mater.* **2016**, *28*, 9831.
Co–Mo–S_x	0.1 M KOH			>200	*Nat. Mater.* **2016**, *15*, 197
	0.1 M $HClO_4$			>200	
$Fe_{1.89}Mo_{4.11}O_7$/ MoO_2	1 M KOH	70	79	197	This work
	0.5 M H_2SO_4	40	47	125	

Figure S14 Polarization curves of $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ after continuous potential sweeps at 20 mV s^{-1}

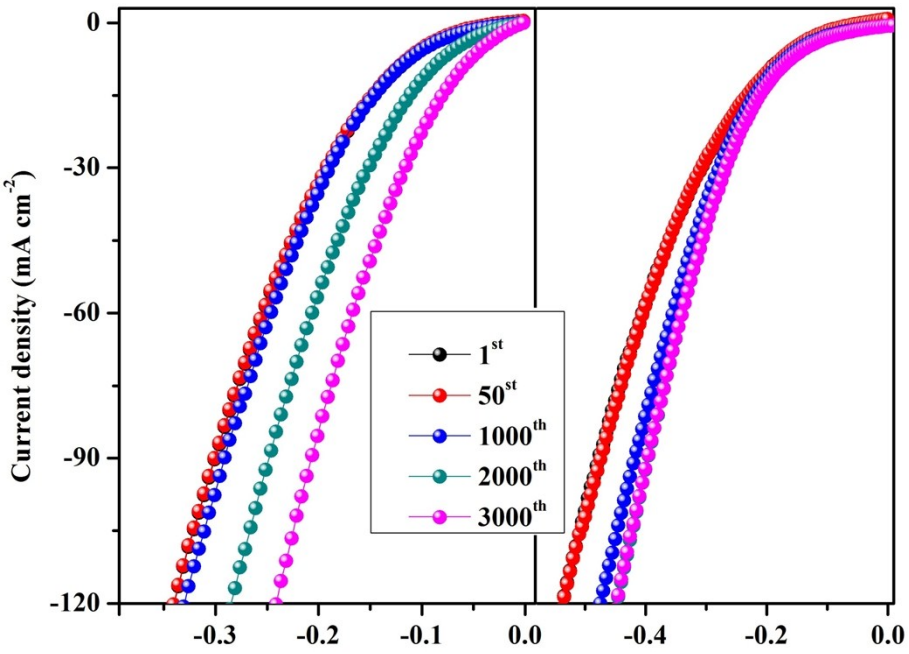


Figure S15 Time-dependent current density curves (carbon as a counter electrode) of the $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ in 1 M KOH

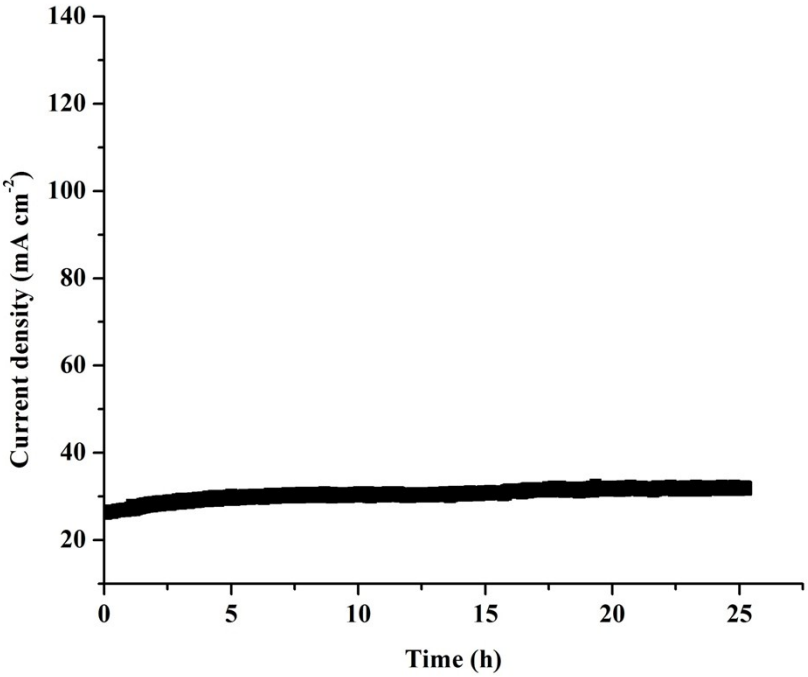


Figure S16 The HRTEM images for $Fe_{1.89}Mo_{4.11}O_7/MoO_2$ in 1 M KOH and 0.5 M H_2SO_4 after 3000 potential sweeps

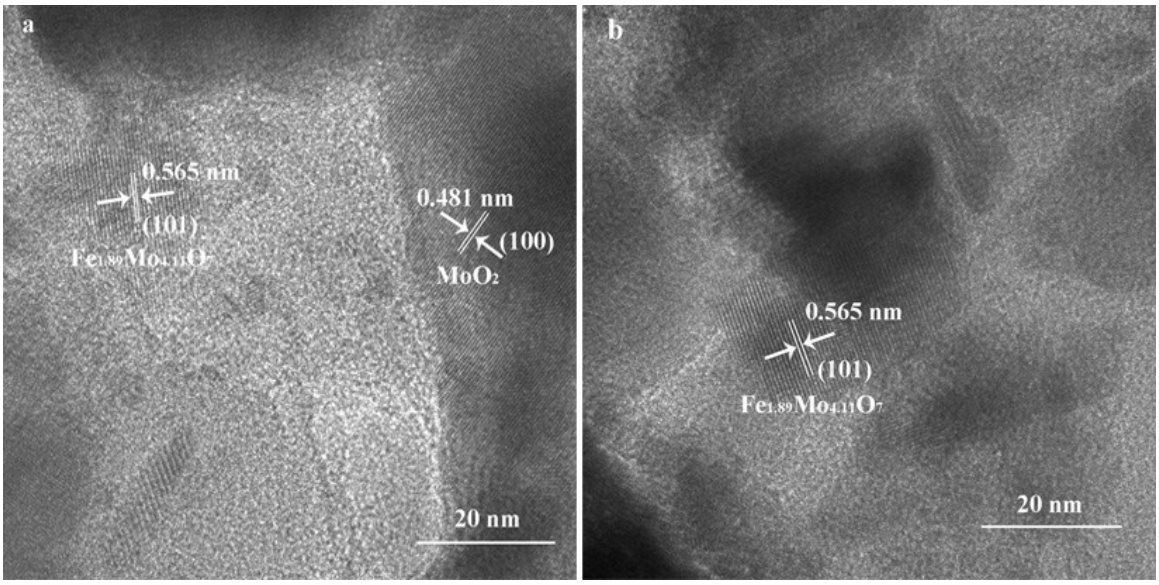


Figure S17 The DFT calculation of metal-hydrogen bond strength based on Mo and Fe element in $Fe_{1.89}Mo_{4.11}O_7$.

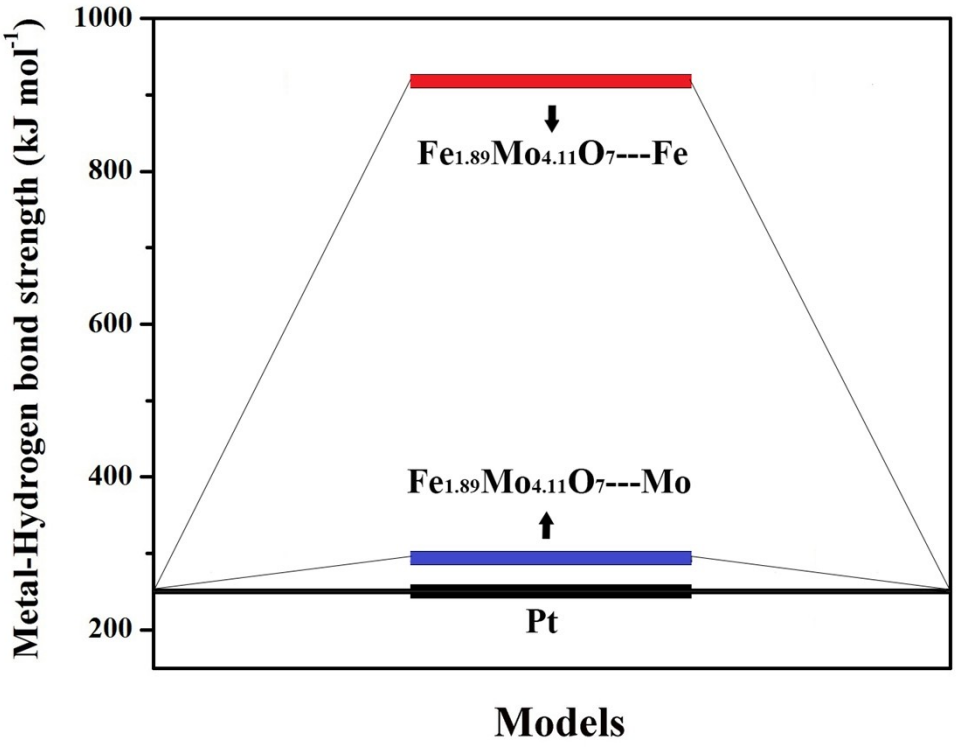
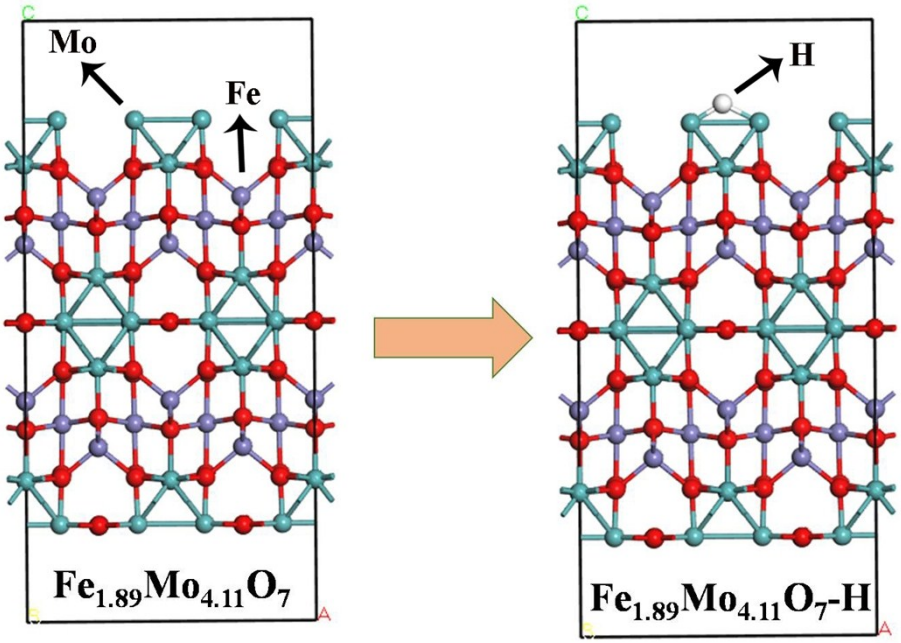
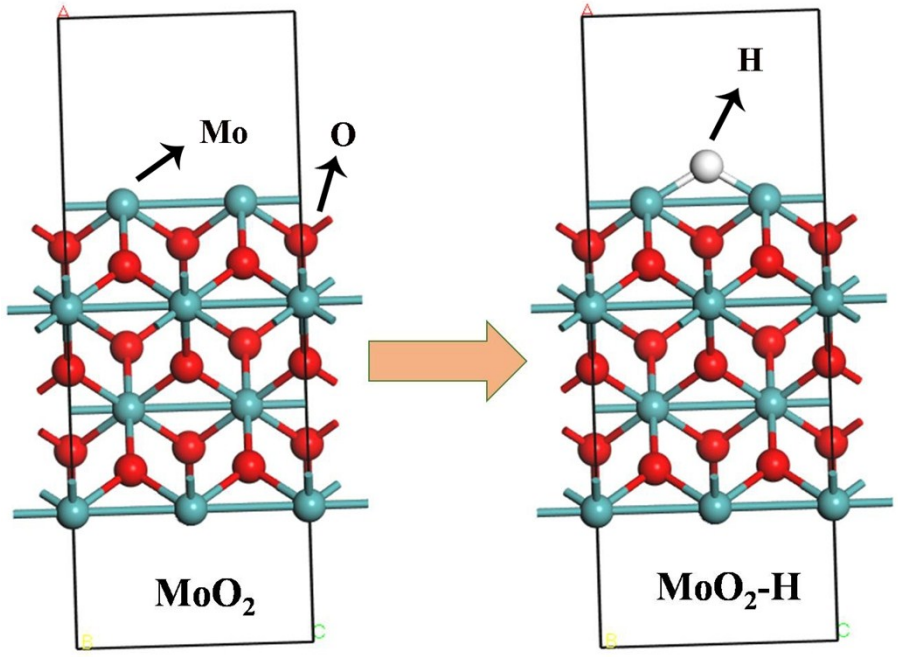
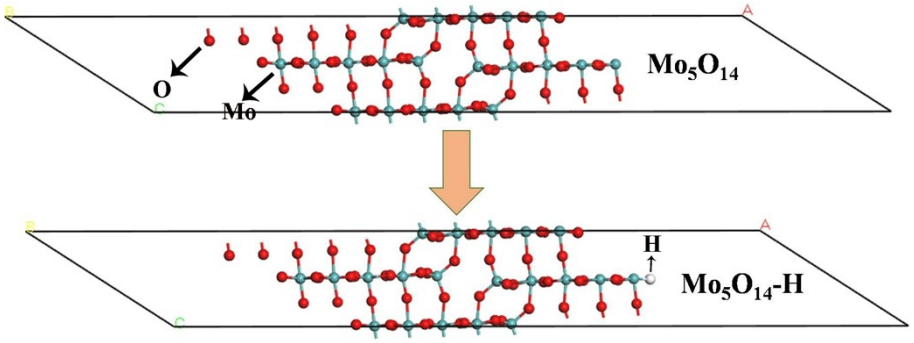


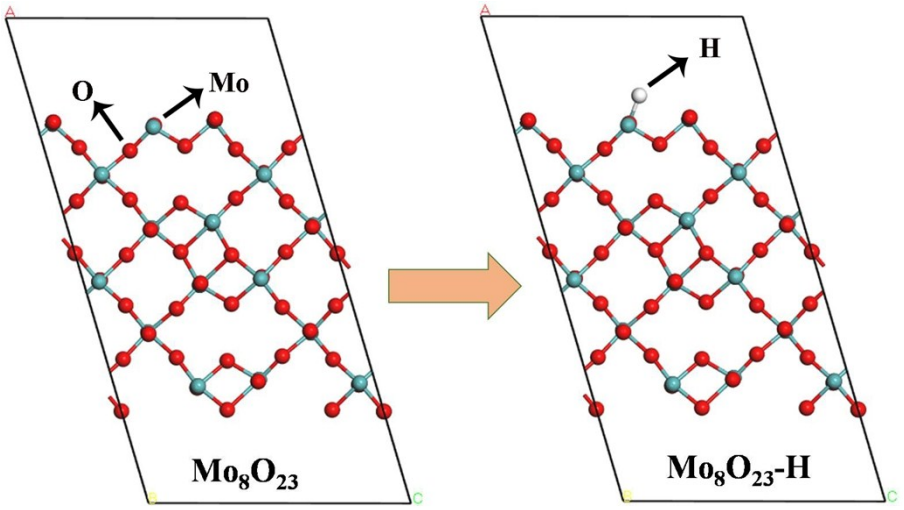
Figure S18 Optimized structure of $Fe_{1.89}Mo_{4.11}O_7$/$Fe_{1.89}Mo_{4.11}O_7$-H, MoO_2 /MoO_2-H, Mo_5O_{14}/Mo_5O_{14}-H and Mo_8O_{23}/Mo_8O_{23}-H.

We perform DFT calculation using the Vienna Ab Initio Simulation Package (VASP), the Perdew-Becke-Ernzerhof (PBE) is used for the exchange-correlation functional. The cut-off energies for plane waves is 450 eV, providing a convergence of 10^{-4} eV in total energy and 0.02 eV/Å in Hellmann Feynman force on each atom. The metal-hydrogen bond strength in $Fe_{1.89}Mo_{4.11}O_7$ is calculated to state the Mo active sites with MoO_2, Mo_5O_{14} and Mo_8O_{23}. All adsorption sites were based on Mo for comparison, and all initial structures and optimized intermediates were listed as following.




Mo
O
MoO2
H
MoO2-H


O
Mo
Mo5O14
H
Mo5O14-H


O
Mo
Mo8O23
H
Mo8O23-H