Supporting Information

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

Zhaomin Hao, a Shishuai Yang, a Jingyang Niu, a Zhiqiang Fang, a Liangliang Liu, b Qingsong Dong, a*, Shuyan Song, c and Yong Zhao, a*, b

a Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475004, Henan Province, P. R. China

b Key Lab for Special Functional Materials of Ministry of Education Collaborative Innovation Center of Nano Functional Materials and Applications, Henan University, Kaifeng, 475004, Henan Province, P. R. China

c State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China

* Correspondence authors: zmhao@henu.edu.cn, zhaoyong@henu.edu.cn
Experimental Section

Chemicals

Synthesis of precursors

Synthesis of MoO$_2$, Fe/MoO$_2$ and Fe$_{1.89}$Mo$_{4.11}$O$_7$/MoO$_2$

Characterization

Electrochemical characterization

Scheme S1 The synthesis route to prepare molybdenum-based nanomaterials

Figure S1 The thermogravimetric studies

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$_2$

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$_2$SO$_4$

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$_2$SO$_4$

Table S1 The HER performance of catalysts in this paper

Table S2 Comparison of HER performance for Fe$_{1.89}$Mo$_{4.11}$O$_7$/MoO$_2$ with other HER electrocatalysts

Figure S13 The exchange current density of Fe$_{1.89}$Mo$_{4.11}$O$_7$/MoO$_2$ catalyst 0.5 M H$_2$SO$_4$

Table S3 The HER performance of catalysts in this paper

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$_2$SO$_4$ 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$_5$O$_{14}$/Mo$_5$O$_{14}$-H and Mo$_9$O$_{23}$/Mo$_9$O$_{23}$-H
Experimental Section

Chemicals

All chemical reagents were used as received without further purification.

Synthesis of precursors

**Ferrimolybdate:** The solution of $\text{H}_3\text[PMo}_{12}\text{O}_{40}]\text{XH}_2\text{O}$, 1,10-phen, $\text{Fe}_2\text{O}_3$, $\text{NH}_4\text{VO}_3$, 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 °C 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:** ($\text{NH}_4$)$_6\text{Mo}_{7}\text{O}_{24}\cdot4\text{H}_2\text{O}$, 1,10-phen, $\text{H}_3\text{PO}_4$ 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 °C 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 °C 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$_2$SO$_4$ at 40 °C 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$_3$)$_3$∙9H$_2$O 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 °C 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$_2$SO$_4$ at 40 °C 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 °C 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$_2$SO$_4$ at 40 °C 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$_2$. 

4
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 Brunauer-Emmett-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): $E(RHE) = E(SCE) + 0.242 + 0.059 \times$
pH. Linear sweep voltammetry (LSV) was recorded in 1.0 M KOH and 0.5 M H₂SO₄ 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: CO₂ signals detected by mass spectrum during the thermal treatment of ferrimolybdate, polymolybdates and polymolybdates + Fe³⁺
Figure S2 The EDX elemental mapping images of Fe and Mo in Fe$_{1.89}$Mo$_{4.11}$O$_7$/MoO$_2$

![EDX Elemental Mapping Images](image)

Mo Lα1  Fe Kα1

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$_2$.

![FESEM Images](image)
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 $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7/\text{MoO}_2$ prepared with different annealing temperature.

![Polarization curves](image)

Figure S7 XRD patterns of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7/\text{MoO}_2$ prepared with different annealing temperature.

![XRD patterns](image)
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$_2$SO$_4$
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 $\text{H}_2\text{SO}_4$

![Tafel plots](image)

Figure S13 The exchange current density of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7/\text{MoO}_2$ catalyst

0.5 M $\text{H}_2\text{SO}_4$
Table S1 The HER performance of catalysts in this paper

<table>
<thead>
<tr>
<th>Samples</th>
<th>Electrolyte</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>η (mV) at 10 mA cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon paste</td>
<td>1 M KOH</td>
<td>232</td>
<td>514</td>
</tr>
<tr>
<td></td>
<td>0.5 M H₂SO₄</td>
<td>180</td>
<td>321</td>
</tr>
<tr>
<td>20% Pt/C</td>
<td>1 M KOH</td>
<td>27</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td>0.5 M H₂SO₄</td>
<td>22</td>
<td>33</td>
</tr>
<tr>
<td>MoO₂</td>
<td>1 M KOH</td>
<td>205</td>
<td>431</td>
</tr>
<tr>
<td></td>
<td>0.5 M H₂SO₄</td>
<td>162</td>
<td>318</td>
</tr>
<tr>
<td>Fe/MoO₂</td>
<td>1 M KOH</td>
<td>194</td>
<td>322</td>
</tr>
<tr>
<td></td>
<td>0.5 M H₂SO₄</td>
<td>128</td>
<td>194</td>
</tr>
<tr>
<td>Fe₈Mo₄.1O₇MoO₂</td>
<td>1 M KOH</td>
<td>79</td>
<td>197</td>
</tr>
<tr>
<td></td>
<td>0.5 M H₂SO₄</td>
<td>47</td>
<td>125</td>
</tr>
</tbody>
</table>
Table S2 Comparison of HER performance for Fe_{1.89}Mo_{4.11}O_7/MoO_2 with other HER electrocatalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>Electrolyte</th>
<th>Onset $\eta$ (mV)</th>
<th>Tafel slope (mV dec^{-1})</th>
<th>$\eta$ (mV) at 10 mA cm^{-2}</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double-gyroid MoS_2/PTO</td>
<td>0.5 M H_2SO_4</td>
<td>200 – 150</td>
<td>50</td>
<td>240</td>
<td><em>Nat. Mater.</em> 2012, 11, 963</td>
</tr>
<tr>
<td>MoS_2/CoSe_2 hybrid Exfoliated metallic MoS_2 nanosheets</td>
<td>0.5 M H_2SO_4</td>
<td>11</td>
<td>36</td>
<td>68</td>
<td><em>Nat. Commun.</em> 2015, 6, 5982</td>
</tr>
<tr>
<td>MoO_2-MoS_2</td>
<td>0.5 M H_2SO_4</td>
<td>200</td>
<td>50 – 60</td>
<td>250</td>
<td><em>Nano Lett.</em> 2011, 11, 4168</td>
</tr>
<tr>
<td>NiMoN_x/C</td>
<td>0.1 M HClO_4</td>
<td>78</td>
<td>35.9</td>
<td>170</td>
<td><em>J. Am. Chem. Soc.</em> 2011, 133, 7296</td>
</tr>
<tr>
<td>MoS_2/RGO</td>
<td>0.5 M H_2SO_4</td>
<td>100</td>
<td>41</td>
<td>140</td>
<td><em>Adv. Funct. Mater.</em> 2015, 26, 8537</td>
</tr>
<tr>
<td>MoO_2/MoSe_2</td>
<td>0.5 M H_2SO_4</td>
<td>63</td>
<td>49.1</td>
<td>181</td>
<td><em>Adv. Mater.</em> 2016, 28, 9831</td>
</tr>
<tr>
<td>MoSe_2/Mo</td>
<td>0.5 M H_2SO_4</td>
<td>89</td>
<td>34.7</td>
<td>166</td>
<td><em>Adv. Mater.</em> 2016, 18, 197</td>
</tr>
<tr>
<td>Co–Mo–S_x</td>
<td>0.1 M KOH</td>
<td>&gt;200</td>
<td></td>
<td></td>
<td><em>Nat. Mater.</em> 2016, 13, 197</td>
</tr>
<tr>
<td></td>
<td>0.1 M HClO_4</td>
<td>&gt;200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_{1.89}Mo_{4.11}O_7/MoO_2</td>
<td>1 M KOH</td>
<td>70</td>
<td>79</td>
<td>197</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>0.5 M H_2SO_4</td>
<td>40</td>
<td>47</td>
<td>125</td>
<td></td>
</tr>
</tbody>
</table>
Figure S14 Polarization curves of Fe$_{1.89}$Mo$_{4.11}$O$_7$/MoO$_2$ after continuous potential sweeps at 20 mV s$^{-1}$

![Polarization curves](image1)

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

![Time-dependent current density curves](image2)
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$_2$SO$_4$ 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$_7$. 

![HRTEM images](image1.png)  

![DFT calculation](image2.png)
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$_5$O$_{14}$/Mo$_5$O$_{14}$-H and Mo$_8$O$_{23}$/Mo$_8$O$_{23}$-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$_5$O$_{14}$ and Mo$_8$O$_{23}$. All adsorption sites were based on Mo for comparison, and all initial structures and optimized intermediates were listed as following.