Interfacial Engineering of Mo$_2$C-Mo$_3$C$_2$ Heteronanowires for High Performance Hydrogen Evolution Reaction

Lina Jia,a,b§ Chen Li,a§ Yaru Zhao,*b Bitao Liu,*a Shixiu Cao,a Dedan Mou,a Tao Han,a Gen Chen,*c Yue Lind

a Research Institute for New Materials Technology, Chongqing University of Arts and Sciences, Chongqing, 402160, China

b College of Physics and Optoelectronics Technology, Baoji University of Arts and Sciences, Baoji, 721016, China

c School of Materials Science and Engineering, Central South University, Changsha, 410083, China

d Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Anhui 230026, China.

§These authors contributed equally to this work.

* Corresponding author: bjwl_zyr@163.com; liubitao007@163.com; geenchen@gmail.com
1. Experimental Section

Materials. Ammonium heptamolybdatetetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O ≥ 99.0%), Hydrochloric acid (HCl (36.0%~38.0%)) were purchased from Chengdu Kelong Chemical Co. Ltd. was received from Alfa Aesar. Aniline (C₆H₅NH₂ ≥ 99.5%) were purchased from Tianjin Fuchen Chemical Reagents Factory.

Synthesis of MoOₓ-amine. 2.48 g ammonium heptamolybdatetetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O) was dissolved in 40 mL of distilled water in a three-necked flask. 3.28 mL of Aniline was added into the solution. Then the flask was heated to a temperature of 50 °C in thermostatic magnetic stirrer. In the next step, pre-prepared 1 M HCl solution was used to adjust the pH to 4.0. The reaction duration was 4 h. At the end of the reaction, the products were collected by centrifuge at 10000 r min⁻¹ and washed several times. Finally, the sample was dried in a freeze dryer for 12 h.

Synthesis of MoCₓ. 0.05 g precursor was put in the middle of the crucible. The crucible was transferred into the tubular furnace for carbonization at different temperature of 600 °C, 700 °C, 800 °C, 900 °C, respectively (denoted as MC-x, x = 600, 700, 800, 900 °C).

Synthesis of TG-DSC. 5-20 mg of Mo-MOF precursor is placed in the crucible and the samples were tested using a simultaneous thermal analysis (NETZSCH STA 449 F3). The test temperature was 1000 °C and the heating rate was 5 °C /min, which was in nitrogen and air, respectively.

Characterization. Test the sample TG-DSC curve using a simultaneous thermal analysis (NETZSCH STA 449 F3). The powder X-ray diffraction (XRD) patterns
were recorded by X-ray diffractometer using Cu Kα (Dandong TD-3500, 30 kV and 20 mA). The morphology and microstructures were characterized using a scanning electron microscope (SEM, Hitachi, SU-8010) and high-resolution transmission electron microscope (TEM/HRTEM, JEM-2100). The surface chemical compositions were recorded by an X-ray photoelectron spectroscopy (XPS, ESCA Lab MKII). Nitrogen adsorption-desorption isotherms were obtained through Brunauer-Emmett-Teller (BET) analysis on a BELSORP-MAX instrument.

**Electrochemical Measurement.** The electrochemical performance was tested by AUTOLAB PGSTAT302N (Methrohm) via three-electrode system at room temperature. The reference and counter electrodes were standard Ag/AgCl electrode and carbon rod, respectively. The Glassy carbon electrode (3.14×0.15 cm²) was used as the working electrode for HER catalysis. Linear sweep voltammetry (LSV) measurements were performed in 0.5 M H₂SO₄. Before HER tests, the electrolyte was deoxygenated with N₂ for at least 30 minutes to completely remove oxygen. Electrochemical impedance spectroscopy (EIS) was performed from the frequency of 0.001 Hz to 10 kHz at the open circuit potential or at other potentials. Long-term stability tests were executed using the chronopotentiometric method at the current density of 10 mA cm⁻² for 12 h and cyclic voltammogram (CV) at a scan rate of 50 mV s⁻¹ for 5000 times. The polarization curves were re-plotted as overpotential (η) vs. log current density (log j), and the Tafel slope (b) can be obtained according to the Tafel equation (η = a + blog(j)). Potentials were referenced to RHE according to the equation: E_{RHE} = 0.23 V + 0.059 × pH + E_{Ag/AgCl}. 
Cyclic voltammogram curves were performed with various scan rates. Electrochemical active surface area (ECSA) of catalysts were determined by electrochemical capacitance measurements with potential ranging from 0 to 0.2 V (vs. RHE) at the scan rates of 10, 20, 30, 50, 70 and 100 mV s$^{-1}$ to get the electrochemical capacitance. The capacitive currents were measured at a potential with no faradic processes, i.e. 0.16 V vs. RHE. The measured data were plotted with a function of scan rate, and a linear fitting determined the specific capacitance. Considering the specific capacitance of flat surface is usually measured in the range of 20-60 μF cm$^{-2}$. We assume specific capacitance as 40 μF cm$^{-2}$ for the following calculations of ECSA.

**Calculations methods.** Calculations were carried out using the GPAW code with projector augmented wave functions on a real space grid and PAW pseudopotentials [1]. The PBE functional was used for the exchange–correlation contribution. The Mo$_2$C/Mo$_3$C$_2$ crystal structure was copied from The Materials Project [2], and imported to The Atomic Simulation Environment (ASE) [3]. Bulk lattice constants were converged to $a=b=3.011$ Å and $c=4.771$ Å for Mo$_2$C, $a=b=3.013$ Å and $c=14.637$ Å for Mo$_3$C$_2$. The clean Mo$_2$C/Mo$_3$C$_2$ (101) surface, and the unit cell p(2 × 3) is used for these models. Several defect sites for Mo were conderated and the most stable defect site was used for the HER reaction calculation. A Monkhorst–Pack 36 sampling of Gamma k-points was used for the large (101) surfaces. The dipoles across the unit cells were all less than 0.10 V. The slabs were relaxed using the Broyden–Fletcher–Goldfarb–Shanno algorithm within ASE until the forces were below 0.02 eV
Å⁻¹. A recalculation was later carried out with double the k-point sampling for the most interesting slabs and adsorbate configurations. The resulting differences in adsorption energies did not exceed 0.02 eV, which is below the accuracy usually attributed to DFT. The transition states were calculated using the double-ended surface walking method with Lasp software [4].

The free adsorption energies are found from calculated potential energies by correcting for the gas phase entropy \( S = -S_0(H_2) \) and the difference in zero-point energy \( \Delta ZPE \) using the equation

\[
\Delta G(H^*) = \Delta E(H^*) + \Delta ZPE - T\Delta S
\]

where \( \Delta E(H^*) \), and \( \Delta ZPE \) and \( \Delta S \) are the binding energy, zero-point energy change, and entropy change of \( H^* \) adsorption, respectively. The correction for ZPE and entropy makes an addition of 0.24 eV to the adsorption energy of a hydrogen atom [5, 6].
2. Figures

Figure S1. XRD pattern of MoO$_x$-amine precursors.

Figure S2. SEM images with different magnifications of MoO$_x$-amine precursors.
Figure S3. (a) Nitrogen adsorption-desorption isotherms; (b-d) pore size map of MC-700, MC-800 and MC-900.

Figure S4. TEM images with different magnification and selected area electron diffraction (SAED) pattern of MC-600.
**Figure S5.** (a-c) TEM images MC-700 (Insert: grain size distribution of MC-700).

**Figure S6.** TEM images MC-800.
**Figure S7.** TEM images MC-900.

**Figure S8.** The total EDS elemental mappings of (a) MC-800, and (b) MC-900.
Figure S9. XPS high-resolution spectra for Mo 3p of the MC-800 and MC-900.

Figure S10. XRD patterns of the catalyst after HER process.
Figure S11. HRTEM images of the catalyst after HER process.

Figure S12. Electrochemical cyclic voltammetry curves of (a) MC-700, (b) MC-800, (c) MC-900 in 0.5 M H₂SO₄. The different scan rates are 10, 20, 30, 50, 70 and 100 mV s⁻¹, respectively.
Figure S13. The top view structures of the clean (101) surface of Mo$_2$C and Mo$_2$C composite with carbon, as well as the atomic H adsorption structures on these models.
Table S1. Comparison of the HER performance of other MoC\textsubscript{x} -based HER electrocatalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Onset overpotential (mV at 1 mA cm\textsuperscript{-2})</th>
<th>Tafel slope (mV dec\textsuperscript{-1})</th>
<th>Overpotential (mV at 10 mA cm\textsuperscript{-2})</th>
<th>Catalysis condition</th>
<th>Loading (mg cm\textsuperscript{-2})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo\textsubscript{2}C-Mo\textsubscript{3}C\textsubscript{2}</td>
<td>61</td>
<td>64</td>
<td>134</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.84</td>
<td>This work</td>
</tr>
<tr>
<td>HNWs</td>
<td>33</td>
<td>64</td>
<td>116</td>
<td>1 M KOH</td>
<td>1.4</td>
<td>7</td>
</tr>
<tr>
<td>Mo\textsubscript{2}C</td>
<td>100</td>
<td>56</td>
<td>210</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>1 M KOH</td>
<td>8</td>
</tr>
<tr>
<td>Mo\textsubscript{2}C NWs</td>
<td>160</td>
<td>55.8</td>
<td>200</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.357</td>
<td>1</td>
</tr>
<tr>
<td>Mo\textsubscript{2}C NPs</td>
<td>160</td>
<td>56</td>
<td>198</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>1 M KOH</td>
<td>9</td>
</tr>
<tr>
<td>MoCx nano-octahedrons</td>
<td>87</td>
<td>53</td>
<td>142</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.8</td>
<td>10</td>
</tr>
<tr>
<td>(\beta)-Mo\textsubscript{2}C</td>
<td>-</td>
<td>120</td>
<td>205</td>
<td>0.1 M HClO\textsubscript{4}</td>
<td>0.28</td>
<td>11</td>
</tr>
<tr>
<td>Mo\textsubscript{2}C@N-CNFs</td>
<td>102</td>
<td>70</td>
<td>195</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.255</td>
<td>12</td>
</tr>
<tr>
<td>Mo\textsubscript{2}C/C</td>
<td>-</td>
<td>75.1</td>
<td>135</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.84</td>
<td>13</td>
</tr>
<tr>
<td>Mo\textsubscript{2}C@C NPs</td>
<td>-</td>
<td>110</td>
<td>160</td>
<td>0.05 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.25</td>
<td>14</td>
</tr>
</tbody>
</table>

Reference


