In-situ Phase Transition Induced TM-MoC/Mo$_2$C (TM= Fe, Co, Ni, and Cu) Heterostructure Catalysts for Efficient Hydrogen Evolution

Jiancheng Li$^{a}$, Riyue Ge$^{a}$, Panpan Lan$^a$, Jack Yang$^b$, Jing Feng$^c$, Ying Li$^a$, Mingyuan Zhu$^a$, Sean Li$^b$, Bin Liu$^a$*, and Wenxian Li$^{a,b,**}$

$^a$ School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

$^b$ School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

$^c$ Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China

**Corresponding authors**

* E–mail: binliu@shu.edu.cn;

** E–mail: shuliwx@t.shu.edu.cn.

#These two authors contributed equally to this work.
Figure S1 (a) XRD pattern and (b,c) SEM images of Co-MoO$_3$
**Figure S2** XRD patterns of (a)Fe, (b)Cu, (c)Ni coupled samples.

**Figure S3** Carbon layer around the Co-MoC/Mo$_2$C-0.5
Figure S4 Low-wave Raman patterns of Co-MoC/Mo$_2$C-0.5, Co-Mo$_2$C-1 and Co-Mo$_2$C-2

Figure S5 Pore size distribution plots of pure MoC and Co-MoC/Mo$_2$C.
**Figure S6** XPS survey spectrum of Co-MoC/Mo$_2$C-0.5

**Table S1** Fitting parameters (peak position, peak area, and species percentage) for Mo 3d spectra taken on the Co-Mo$_x$C catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Peaks</th>
<th>Species</th>
<th>Area</th>
<th>Mo$^{2+}$ and Mo$^{3+}$ Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3d$_{5/2}$</td>
<td>3d$_{3/2}$</td>
<td>3d$_{5/2}$</td>
<td>3d$_{3/2}$</td>
</tr>
<tr>
<td>Mo$^{3+}$</td>
<td>228.7</td>
<td>231.8</td>
<td>46849</td>
<td>33463</td>
</tr>
<tr>
<td>MoC</td>
<td>229.9</td>
<td>234.1</td>
<td>22031</td>
<td>16947</td>
</tr>
<tr>
<td>Mo$^{6+}$</td>
<td>232.7</td>
<td>235.8</td>
<td>67968</td>
<td>45312</td>
</tr>
<tr>
<td>Co-MoC/Mo$_2$C-0.5</td>
<td>228.2</td>
<td>231.5</td>
<td>13145</td>
<td>8648</td>
</tr>
<tr>
<td>Mo$^{3+}$</td>
<td>229.1</td>
<td>232.1</td>
<td>7764</td>
<td>11413</td>
</tr>
<tr>
<td>Mo$^{4+}$</td>
<td>229.8</td>
<td>233.4</td>
<td>7681</td>
<td>5155</td>
</tr>
<tr>
<td>Mo$^{6+}$</td>
<td>232.8</td>
<td>236.2</td>
<td>11236</td>
<td>8025</td>
</tr>
<tr>
<td>Catalysts</td>
<td>Species</td>
<td>Peaks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>---------</td>
<td>---------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3d&lt;sub&gt;5/2&lt;/sub&gt;</td>
<td>3d&lt;sub&gt;3/2&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>Co-MoC/Mo&lt;sub&gt;2&lt;/sub&gt;C-0.5</td>
<td>Mo&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>228.2</td>
<td>231.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>229.1</td>
<td>232.1</td>
<td></td>
</tr>
<tr>
<td>Ni-MoC/Mo&lt;sub&gt;2&lt;/sub&gt;C-0.5</td>
<td>Mo&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>228.3</td>
<td>231.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>228.7</td>
<td>231.6</td>
<td></td>
</tr>
<tr>
<td>Fe-MoC/Mo&lt;sub&gt;2&lt;/sub&gt;C-0.5</td>
<td>Mo&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>228.9</td>
<td>232.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>229.5</td>
<td>232.4</td>
<td></td>
</tr>
<tr>
<td>Cu-MoC/Mo&lt;sub&gt;2&lt;/sub&gt;C-0.5</td>
<td>Mo&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>229.1</td>
<td>232.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mo&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>229.5</td>
<td>233.1</td>
<td></td>
</tr>
</tbody>
</table>

**Table S2** Fitting parameters of peak position for Mo<sup>2+</sup> and Mo<sup>3+</sup> spectra taken on the Co-MoC/Mo<sub>2</sub>C-0.5, Ni-MoC/Mo<sub>2</sub>C-0.5, Fe-MoC/Mo<sub>2</sub>C-0.5, and Cu-MoC/Mo<sub>2</sub>C-0.5 catalysts.
Figure S7: Ni 2p spectra of Ni-MoC/Mo$_2$C-0.5

Figure S8: Cu 2p spectra of Cu-MoC/Mo$_2$C-1
Figure S9. Fe 2p spectra of Fe-MoC/Mo₂C-0.5

Figure S10. LSV of Co doped samples in (a) 0.5 M H₂SO₄ and (b) 1 M KOH
Figure S11 LSV of Fe doped samples in (a) 0.5 M H$_2$SO$_4$ and (b) 1 M KOH

Figure S12 LSV of Cu doped samples in (a) 0.5 M H$_2$SO$_4$ and (b) 1 M KOH
**Figure S13** LSV of Ni doped samples in (a) 0.5 M $\text{H}_2\text{SO}_4$ and (b) 1 M KOH

**Table S3** HER activity comparison of recently published Mo-based catalysts in 0.5 M $\text{H}_2\text{SO}_4$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\eta_{10}$</th>
<th>Tafel slope</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Mo$_2$C (1:2)-NCNFs</td>
<td>143</td>
<td>57.8</td>
<td>[1]</td>
</tr>
<tr>
<td>MoC–Mo$_2$C-31.4</td>
<td>126</td>
<td>43</td>
<td>[2]</td>
</tr>
<tr>
<td>Mo$_2$C-carbon sphere</td>
<td>164</td>
<td>85</td>
<td>[3]</td>
</tr>
<tr>
<td>Mo$_2$C-0.4</td>
<td>155</td>
<td>53</td>
<td>[4]</td>
</tr>
<tr>
<td>Mo$_3$N–Mo$_2$C/HGr-3</td>
<td>157</td>
<td>55</td>
<td>[5]</td>
</tr>
<tr>
<td>Co-NC@Mo$_2$C</td>
<td>143</td>
<td>60</td>
<td>[6]</td>
</tr>
<tr>
<td>MoCx/C</td>
<td>135</td>
<td>62</td>
<td>[7]</td>
</tr>
<tr>
<td>Mo$_2$C–GNR</td>
<td>152</td>
<td>65</td>
<td>[8]</td>
</tr>
<tr>
<td>Mo$_2$C@SNC</td>
<td>146</td>
<td>83</td>
<td>[9]</td>
</tr>
</tbody>
</table>

**Table S4** Comparison of Catalytic Performance of Different HER Electrocatalysts in 0.5 M $\text{H}_2\text{SO}_4$
<table>
<thead>
<tr>
<th>Electro catalyst</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>$j_0$ (mA cm$^{-2}$)</th>
<th>$C_{dl}$ (mF cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoC</td>
<td>171</td>
<td>77</td>
<td>0.14</td>
<td>3.1</td>
</tr>
<tr>
<td>Co-MoC/Mo$_2$C-0.5</td>
<td>114</td>
<td>54</td>
<td>0.22</td>
<td>17.9</td>
</tr>
<tr>
<td>Fe-MoC/Mo$_2$C-0.5</td>
<td>138</td>
<td>80</td>
<td>0.2</td>
<td>8.9</td>
</tr>
<tr>
<td>Cu-MoC/Mo$_2$C-1</td>
<td>156</td>
<td>78</td>
<td>0.16</td>
<td>4.4</td>
</tr>
<tr>
<td>Ni-MoC/Mo$_2$C-0.5</td>
<td>124</td>
<td>53</td>
<td>0.18</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Figure S14 Equivalent circuit model of the TM-MoC/Mo$_2$C heterostructure catalysts in 0.5 M H$_2$SO$_4$. $R_s$: the electrolyte resistance, $C_{dl}$: double layer capacitance, $R_{et}$: charge transfer resistance.
Figure S15 Cyclic voltammetry curves in a non-faradaic potential region under different scan rates of (a) MoC, (b) Co-MoC/Mo$_2$C-0.5, (c) Fe-MoC/Mo$_2$C-0.5, (d) Cu-MoC/Mo$_2$C-1, (e) Ni-MoC/Mo$_2$C-0.5
Table S5 Comparison of Catalytic Performance of Different HER Electrocatalysts in 1 M KOH

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>$j_0$ (mA cm$^{-2}$)</th>
<th>$C_{dl}$ (mF cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoC</td>
<td>120</td>
<td>63</td>
<td>0.20</td>
<td>5.5</td>
</tr>
<tr>
<td>Co-MoC/Mo$_2$C-0.5</td>
<td>82</td>
<td>53</td>
<td>0.44</td>
<td>15.2</td>
</tr>
<tr>
<td>Fe-MoC/Mo$_2$C-0.5</td>
<td>97</td>
<td>56</td>
<td>0.29</td>
<td>8.1</td>
</tr>
<tr>
<td>Cu-MoC/Mo$_2$C-1</td>
<td>106</td>
<td>50</td>
<td>0.21</td>
<td>9.9</td>
</tr>
<tr>
<td>Ni-MoC/Mo$_2$C-0.5</td>
<td>107</td>
<td>40</td>
<td>0.14</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Table S6 HER activity comparison of recently published Mo-based catalysts in 1 M KOH

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\eta_{10}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_2$N–Mo$_2$C/HGr-3</td>
<td>154</td>
<td>68</td>
<td>[5]</td>
</tr>
<tr>
<td>Co-NC@Mo$_2$C</td>
<td>99</td>
<td>66</td>
<td>[6]</td>
</tr>
<tr>
<td>MoC$_x$/C</td>
<td>150</td>
<td>99</td>
<td>[7]</td>
</tr>
<tr>
<td>Mo$_2$C–GNR</td>
<td>121</td>
<td>54</td>
<td>[8]</td>
</tr>
<tr>
<td>Co/β-Mo$_2$C@N-CNTs</td>
<td>170</td>
<td>92</td>
<td>[10]</td>
</tr>
<tr>
<td>h-Mo$_2$C/MoO$_2$</td>
<td>92</td>
<td>56.6</td>
<td>[11]</td>
</tr>
</tbody>
</table>
Figure S16 Cyclic voltammetry curves in a non-faradaic potential region under different scan rates of (a) MoC, (b) Co-MoC/Mo$_2$C-0.5, (c) Fe-MoC/Mo$_2$C-0.5, (d) Cu-MoC/Mo$_2$C-1, (e) Ni-MoC/Mo$_2$C-0.5
**Figure S17** Equivalent circuit model of the TM-MoC/Mo$_2$C heterostructure catalysts in 1 M KOH. $R_s$: the electrolyte resistance, $C_{dl}$: double layer capacitance, $R_{ct}$: charge transfer resistance.

**Figure S18** I–t curve at the current density of Co-MoC/Mo$_2$C-0.5 in both 0.5 M H$_2$SO$_4$ and 1 M KOH.
Figure S19 XRD patterns of the Co-MoC/Mo$_2$C-0.5 catalyst before and after 20 h durability test. The results show that the Co-MoC/Mo$_2$C-0.5 catalyst has a highly stability.

Figure S20 SEM images of Co-MoC/Mo$_2$C-0.5 catalyst (a) before and (b) after 20 h durability test.
Figure S21 TEM images of Co-MoC/Mo$_2$C-0.5 catalyst after 20 h durability test. The almost unchanged TEM images of the Co-MoC/Mo$_2$C-0.5 electrode before and after the stability test shows that the catalyst has super stability.

Reference: