Heterostructures Engineering of Co doped MoS₂ coupling with Mo₂CTₓ MXene for Enhanced Hydrogen Evolution in Alkaline Media

Junmei Liang, Chaoying Ding, Jiapeng Liu, Tao Chen, WenChao Peng, Yang Li, Fengbao Zhang and Xiaobin Fan*

School of Chemical Engineering and Technology, State Key Laboratory of Chemical Engineering, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, China

E-mail: xiaobinfan@tju.edu.cn
Figure S1 a) HRTEM image of pristine MoS$_2$; b) elemental mapping showing the uniform distribution of F and O elements in Co-MoS$_2$/Mo$_2$CT$_x$ nanohybrids.

The following simplified reactions occurs when the exfoliation of M$_{n+1}$AX$_n$ phase by HF solution, the as-obtained pristine MXene are chemically terminated with oxygen-containing and/or fluoride functional groups. Thus, the negatively charged terminal groups (–F and –O) can be detected by elemental mapping.

\[
M_{n+1}AX_n + 3HF = AF_3 + M_{n+1}X_n + 1.5H_2 \quad (1)
\]

\[
M_{n+1}X_n + 2H_2O = M_{n+1}X_n(OH)_2 + H_2 \quad (2)
\]

\[
M_{n+1}X_n + 2HF = M_{n+1}X_nF_2 + H_2 \quad (3)
\]
The SEM images of pure MoS$_2$ and Co-MoS$_2$/Mo$_2$CT$_x$ nanohybrids have been shown in Figure S2. The pure MoS$_2$ in Figure S2a shows the large bulk morphology, while the Co-MoS$_2$/Mo$_2$CT$_x$ nanohybrid in Figure S2b exhibits dispersed MoS$_2$ particles attached on the surface of Mo$_2$CT$_x$ MXene. This result further confirms the Mo$_2$CT$_x$ MXene can prevent MoS$_2$ particles from agglomeration during preparation progress. The corresponding modification is also made in original manuscript.
Figure S3  a) XRD patterns of Mo₂CTₓ MXene by HF etching without annealing in Ar atmosphere and pristine Mo₂Ga₂C; b) XRD pattern of Co-Mo₂CTₓ sample.
Figure S4 XPS spectrum of S 2p in Co-MoS$_2$/Mo$_2$CT$_x$ hybrid.
Figure S5 Cyclic voltammograms for different materials at the different rates range from 20 to 200 mV s\(^{-1}\).

To evaluate the electrochemically active surface area (ECSA), a series of cyclic voltammetry (CV) measurements were performed at different scan rates varying from 20 to 200 mV s\(^{-1}\) in the region from 0.05 to 0.25 V to determine the double-layer capacitance (\(C_{dl}\)). For comparison, the CV at different scan rates of Co-MoS\(_2\)/Mo\(_2\)Ga\(_2\)C catalyst was performed. The results are shown in Figure S5.
Figure S6 XRD patterns of Co-MoS$_2$/Mo$_2$CT$_x$ catalyst before and after stability test.
Figure S7 TEM image of Co-MoS₂/Mo₂CT₅ after stability test.
Figure S8  a) Polarization curves of Co-MoS$_2$/Mo$_2$CT$_x$ in 1M KOH, 0.5 M H$_2$SO$_4$ and 1M PBS electrolytes and b) the corresponding Tafel plots.

The HER performance of Co-MoS$_2$/Mo$_2$CT$_x$ electrode in acid and neutral media were evaluated and the results are compared in Figure S8. The Co-MoS$_2$/Mo$_2$CT$_x$ electrocatalyst exhibits the small overpotentials of 218 and 286 mV at current density of 10 mA cm$^{-2}$ in acid and neutral media, respectively. Accordingly, the Tafel slopes are 94 and 128 mV dec$^{-1}$ in acid and basic media. The results suggest the great potential of all pH hydrogen evolution for Co-MoS$_2$/Mo$_2$CT$_x$ hybrids. In addition, the Co-MoS$_2$/Mo$_2$CT$_x$ electrocatalyst exhibits much better alkaline HER activity than acidic HER activity, suggesting the enhanced HER activity of Co-MoS$_2$/Mo$_2$CT$_x$ catalyst in alkaline media is mainly attributed to the initially accelerated water dissociation, rather than the hydrogen adsorption properties.
Figure S9 a) Polarization curves of Co-MoS$_2$/Mo$_2$Ga$_2$C catalyst at a scan rate of 5 mV s$^{-1}$ in 1 M KOH; b) Tafel plots of Co-MoS$_2$/Mo$_2$Ga$_2$C catalyst; c) EIS spectrum of Co-MoS$_2$/Mo$_2$Ga$_2$C catalyst at $\eta = 200$ mV; d) capacitive current at 0.15 V as a function of scan rates (20 to 200 mV s$^{-1}$) for Co-MoS$_2$/Mo$_2$Ga$_2$C catalyst.

In view of the effect of etching by HF solution, the HER performance of Co-MoS$_2$/Mo$_2$Ga$_2$C catalyst was evaluated, and the results are shown in Figure S9. It suggests Co-MoS$_2$/Mo$_2$Ga$_2$C exhibits lower HER activity than Co-MoS$_2$/Mo$_2$CT$_x$ catalyst.
Figure S10 a) Polarization curves, b) Tafel plots, c) EIS spectra and d) capacitive current at 0.15 V as a function of scan rates (20 to 200 mV s\(^{-1}\)) of Co-MoS\(_2\)/Mo\(_2\)CT\(_x\) catalyst at different ATTM/Mo\(_2\)CT\(_x\) mass ratios.

The HER performance of Co-MoS\(_2\)/Mo\(_2\)CT\(_x\) strongly depends on ATTM/Mo\(_2\)CT\(_x\) mass ratios. The ATTM/Mo\(_2\)CT\(_x\) MXene mass ratio of 3:1 described in manuscript displays higher HER activity than ATTM/Mo\(_2\)CT\(_x\) MXene mass ratio of 1:1 and 1:3.
Table S1 A comparison of Co-MoS$_2$/Mo$_2$CT$_x$ electrocatalyst with recently reported non-noble metal catalysts in HER performance (1M KOH).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Overpotential at $j = 10$ mA cm$^{-2}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>References</th>
<th>Cites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-MoS$_2$/Mo$_2$CT$_x$</td>
<td>112</td>
<td>82</td>
<td>This work</td>
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<tr>
<td>Ni/Mo$_2$C-PC</td>
<td>179</td>
<td>101</td>
<td><em>Chem. Sci.</em>, 2017, 8, 968</td>
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<td>MoS$_2$/Ti$_3$C$_x$-MXene@C</td>
<td>135</td>
<td>45</td>
<td><em>Adv. Mater.</em>, 2017, 29, 1607017</td>
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<td>Mo$_2$C-C</td>
<td>149</td>
<td>66</td>
<td><em>Nano Energy</em>, 2017, 32, 511–519</td>
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<td>Cu@NiFe LDH</td>
<td>116</td>
<td>58.9</td>
<td><em>Energy Environ. Sci.</em>, 2017, 10, 1820</td>
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<td>MoSSe</td>
<td>140</td>
<td>40</td>
<td><em>Adv. Mater.</em>, 2018, 30, 1705509</td>
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<td>NC@CuCo$_2$N$_x$/CF</td>
<td>105</td>
<td>76</td>
<td><em>Adv. Funct. Mater.</em>, 2017, 27, 1704169</td>
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<td>Ti$_2$CT$_x$ nanosheets</td>
<td>170</td>
<td>100</td>
<td><em>Nano Energy</em>, 2018, 47, 512–518</td>
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<td>NiCu@C-1</td>
<td>74</td>
<td>94.5</td>
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<td>CoP@NC-NG</td>
<td>155</td>
<td>68.6</td>
<td><em>Small</em>, 2017, 14, 702895</td>
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<td>R-MoS$_2$@NF</td>
<td>71</td>
<td>100</td>
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<td>SWCNTs/MoSe$_2$</td>
<td>170</td>
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<td><em>Adv. Energy Mater.</em>, 2018, 8, 1703212</td>
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Supplementary References