Supplementary Information

Efficient hydrogen evolution reaction by molybdenum carbide and molybdenum nitride nanocatalysts synthesized via the urea glass route

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S1: Size Distribution and High Resolution Transmission Electron Micrographs (HRTEM) of Mo$_2$C and Mo$_2$N Nanoparticles

Figure S1: Particle size distribution of Mo$_2$C and Mo$_2$N nanoparticles synthesized in this work.
Figure S2: Representative high resolution TEM micrographs of (a-b) Mo$_2$C and (c) Mo$_2$N. The d-spacings measured are indicated in the respective TEM micrographs. The expected d-spacings of Mo$_2$C and Mo$_2$N as obtained from the ICDD-PDF4+ database are shown at the bottom right of the figure.
S2: Online Gas Chromatography (GC) for Quantifying Hydrogen Evolution

Experimental procedure:

A custom-made, gas-tight two compartment polytetrafluoroethylene cell was used for online gas chromatography.\(^1\) The cathodic compartment was filled with 32 ml electrolyte, leaving ~3 ml of headspace. Before each measurement, the electrolyte was saturated with N\(_2\) gas (Chemgas) for at least 30 minutes. All experiments were performed at 298 K. Using a mass flow controller (MC-100SCCM-D, Alicat Scientific), N\(_2\) was continuously pumped into the electrolyte at a flow rate of 20 sccm. The gas outlet of the cathodic compartment was connected to a gas chromatograph (GC-7890A, Agilent Technologies) for periodical sampling. A thermal conductivity detector (TCD) was used for detecting H\(_2\). The carrier gas for the TCD was N\(_2\).

A typical online GC experiment at a constant applied voltage spanned over 28.3 min. A gas aliquot (0.5 cm\(^3\)) was automatically injected into the GC every 4 minutes. The first injection was 240 seconds after the start of the HER. This is to ensure adequate flushing of the transfer line of atmospheric contaminants. Six gas aliquots were measured. The GC data collected in this work were translated to current efficiencies. It is assumed that the detected H\(_2\) gas originate solely from electrochemical reactions, and that two electrons are required to form one H\(_2\) molecule.

The current efficiency for HER using Mo\(_2\)C or Mo\(_2\)N is ~100%. We present here representative data of HER catalyzed by \(\alpha\)-Mo\(_2\)C nanoparticles in 1M KOH electrolyte (Figure S3 and Table S1).

![Figure S3](image)

Figure S3: (a) Chronoamperogram of Mo\(_2\)C recorded at -0.25 and -0.35 V respectively in N\(_2\)-saturated 1 M KOH. (b) A representative gas chromatogram of the gas products emitted during water electrolysis using Mo\(_2\)C catalyst. Only a single peak belonging to H\(_2\) gas was observed.
Table S1: Online GC measurements of gas products produced during HER using \( \alpha-\text{Mo}_2\text{C} \) catalyst.

<table>
<thead>
<tr>
<th>Voltage (V vs. RHE)</th>
<th>Average Current (mA)</th>
<th>Average H(_2) concentration (mol ppm)</th>
<th>Average current efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.25</td>
<td>-1.4</td>
<td>539.3</td>
<td>100.8</td>
</tr>
<tr>
<td>-0.35</td>
<td>-10.6</td>
<td>4052.4</td>
<td>98.3</td>
</tr>
</tbody>
</table>
S3: Calculations of Turnover Frequencies (TOF) of H₂ Production

S3.1 Calculation of TOF using the surface areas of the Mo₂C catalysts as determined by XRD data

The structural data of Mo₂C from the ICDD-PDF-4+ (ICDD 00-035-0787) database was used. Density of Mo₂C = 9.098 g cm⁻³. Average size of Mo₂C nanoparticle (as determined from the Scherrer equation) = 11 nm. The shapes of the nanoparticles are approximated to spherical.

Total volume of Mo₂C particles present on the electrode = \((2 \times 10^{-5}) / (9.098) = 2.198 \times 10^{-6} \text{ cm}^3\)

Total number of Mo₂C nanoparticles present on the electrode
\[
= \left[\frac{2.198 \times 10^{-6}}{\left(\frac{4}{3}\pi(5.5 \text{ nm})^3\right)}\right]
\]
\[
= 3.15 \times 10^{12} \text{ particles}
\]

Surface area of 1 Mo₂C nanoparticle
\[
= (4\pi)(r^2)
\]
\[
= (4\pi)(5.5 \text{ nm})^2
\]
\[
= 3.80 \times 10^{-16} \text{ m}^2
\]

Hence, the total surface area of all the Mo₂C nanoparticles present
\[
= (3.80 \times 10^{-16} \text{ m}^2) \times (3.15 \times 10^{12})
\]
\[
= 1.197 \times 10^{-3} \text{ m}^2.
\]

The surface of the Mo₂C catalysts is assumed to be (100)- and Mo atom- terminated. The area per surface unit cell is = 602.8 pm × 519.7 pm = 3.13×10⁻¹⁹ m².² There are 3.5 Mo atoms in this cell.

Hence, the total number of surface Mo atoms present
\[
= \left[\frac{3.5}{(3.13 \times 10^{-19} \text{ m}^2)}\right] \times (1.197 \times 10^{-3} \text{ m}^2)
\]
\[
= 1.338 \times 10^{16} \text{ atoms}
\]

We assume that all the surface Mo atoms participate in the HER. Hence, the turnover frequency of H₂ production at \(\eta = 176 \text{ mV}\) (current density measured = 10 mA cm⁻², electrolyte = 1 M KOH).

\[
= \left[\frac{10 \text{ mA/cm}^2 \times 10^{-3} \times 0.196 \text{ cm}^2 \times (6.02 \times 10^{23})}{(96485.3 \text{ C/mol}) \times (2) \times (1.338 \times 10^{16})}\right]
\]
\[
= 0.5 \text{ s}^{-1}
\]

The factor \(\frac{1}{2}\) is derived by assuming that two electrons are required to form one H₂ molecule.
This TOF is a lower bound value, as it does not take into consideration agglomeration of the catalyst particles. Analogous calculations can be performed to obtain the TOFs occurring at other electrode potentials. These values are presented in Table 2.

**S3.2 Calculation of TOF using the surface areas of the Mo$_2$N catalysts as determined by XRD data**

The structural data of Mo$_2$N from the ICDD-PDF-4+ (ICDD 00-025-1366) database was used. Density of Mo$_2$N = 9.477 g cm$^{-3}$. Average size of Mo$_2$N nanoparticle (as determined from the Scherrer equation) = 16 nm. The shapes of the nanoparticles are approximated to spherical.

Total volume of Mo$_2$N particles present on the electrode = \( (2 \times 10^{-5}) / (9.477) = 2.110 \times 10^{-6} \text{ cm}^3 \)

Total number of Mo$_2$N nanoparticles present on the electrode
= \[ \frac{2.110 \times 10^{-6}}{(4/3)\pi (r^3)} \]
= \[ \frac{2.110 \times 10^{-6}}{(4/3)\pi (8 \text{ nm})^3} \]
= 9.84 \times 10^{11} \text{ particles}

Surface area of 1 Mo$_2$N nanoparticles
= \( 4\pi r^2 \)
= \( 4\pi (8 \text{ nm})^2 \)
= 8.04 \times 10^{-16} \text{ m}^2

Hence, the total surface area of all the Mo$_2$N nanoparticles present
= \( 8.04 \times 10^{-16} \text{ m}^2 \) \times \( 9.84 \times 10^{11} \)
= 7.91 \times 10^{-4} \text{ m}^2.

We assume that the surface of the Mo$_2$N catalysts consists of low index planes. The number of Mo atoms present is 1.09 \times 10^{15} \text{ Mo cm}^{-2}.^3

The total number of surface Mo atoms present
= \( 7.91 \times 10^{-4} \text{ m}^2 \) \times \( 1.09 \times 10^{15} \text{ Mo/cm}^2 \)
= 8.62 \times 10^{15} \text{ atoms}

We assume that all the surface Mo atoms participate in the HER. The turnover frequency of H$_2$ production at $\eta = 250 \text{ mV}$ (current density measured = -0.94 mA cm$^{-2}$, electrolyte = 1 M KOH).

= \[ \frac{(0.94 \text{ mA/cm}^2) \times (10^{-3}) \times (0.196 \text{ cm}^2) \times (6.02 \times 10^{23})}{(96485.3 \text{ C/mol}) \times (2) \times (8.62 \times 10^{15})} \]
= 0.07 \text{ s}^{-1}
This TOF is a lower bound value, as it does not take into consideration agglomeration of the catalyst particles. Analogous calculations can be performed to obtain the TOFs occurring at other electrode potentials. These values are presented in Table 2

**S3.3 Calculation of TOF using BET surface area**

We give a sample calculation for the TOF of H\textsubscript{2} production by Mo\textsubscript{2}C in 1 M KOH. The overpotential is \(\eta= 176\) mV, which gives a current density of 10 mA/cm\textsuperscript{2}. The surface area of Mo\textsubscript{2}C was determined by BET measurements to be 9.1 m\textsuperscript{2} g\textsuperscript{-1}. The surface of the Mo\textsubscript{2}C catalysts is assumed to be (100)- and Mo atom terminated. The area per surface unit cell is \(= 602.8\) pm \(\times 519.7\) pm \(= 3.13\times10^{-19}\) m\textsuperscript{2}. There are 3.5 Mo atoms in this cell.

Hence, the total number of surface Mo atoms present

\[
= [3.5 / (3.13\times10^{-19}\text{ m}^2)] \times (2\times10^{-5}\text{ g}) \times (9.1\text{ m}^2\text{ g}^{-1})
\]

\[
= 2.04 \times 10^{15}\text{ atoms}
\]

We assume that all the Mo sites are involved in the HER process. The factor \(\frac{1}{2}\) is derived by assuming that two electrons are required to form one H\textsubscript{2} molecule.

Turnover frequency of H\textsubscript{2} production at \(\eta= 176\) mV (measured current density = 10 mA cm\textsuperscript{2})

\[
= [(10\text{ mA/cm}^2) (10^{-3}) (0.196\text{ cm}^2) (6.02 \times 10^{23})] / [(96485.3\text{ C/mol}) (2) (2.04 \times 10^{15})]
\]

\[
= 3\text{ s}^{-1}
\]

The TOF calculated here is higher than that determined in S3.1. This is because the surface area of Mo\textsubscript{2}C as determined by the BET method is lower than that determined by XRD and TEM data. This can be attributed to agglomeration of the catalysts powder which reduces the effective surface areas that can be probed by N\textsubscript{2} sorption (the BET method). Analogous calculations and findings can be made for the TOFs of Mo\textsubscript{2}N.

*In this work, we shall use the more conservative TOF values as determined in S3.1-3.2 for comparison with other works.*
Figure S4: (a) Two-time constant model and (b) Nyquist plot of the Mo$_2$C electrode at $\eta = 200$ mV with amplitude of 5 mV in 1 M KOH solution.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Tafel slope from LSV (mV dec(^{-1}))</th>
<th>Tafel slope from EIS (mV dec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Mo(_2)C</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>1 M KOH</td>
<td>58</td>
<td>57</td>
</tr>
<tr>
<td>γ-Mo(_2)N</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>100</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>1 M KOH</td>
<td>108</td>
<td>126</td>
</tr>
</tbody>
</table>

Table S2: Tafel slopes of the as-synthesized Mo compounds.
Figure S5 (a) Nyquist and (b) corresponding Bode plots of the Mo$_2$C recorded at selected overpotentials in N$_2$-saturated 0.5 M H$_2$SO$_4$ solution.

Figure S6: Plots of log ($R_{ct}^{-1}$) vs overpotential for the Mo$_2$C (square), and Mo$_2$N (circle) catalysts in N$_2$-saturated 0.5 M H$_2$SO$_4$ (solid) and N$_2$-saturated 1 M KOH (open).
References

