Activating MoS$_2$ with Super-High Nitrogen-Doping Concentration as Efficient Catalyst for Hydrogen Evolution Reaction

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Figure S1. High resolution XPS spectra of N 1s, Mo 3d, and S 2p of pristine MoS$_2$ and N-MoS$_2$ with different activation temperatures.
Figure S2. High resolution XPS spectra of N 1s, Mo 3d, and S 2p of pristine MoS$_2$ and N-MoS$_2$ with different activation times at 900 °C.
**Figure S3.** HR-TEM image of pristine MoS$_2$.

**Figure S4.** Raman spectra of pristine MoS$_2$ and N-MoS$_2$ treated at different activation temperatures.
Figure S5. Nitrogen adsorption-desorption isotherms and pore size distributions of pristine MoS$_2$ (a) and N-MoS$_2$-900-2 (b).
Figure S6. Electrochemical cyclic voltammograms of pristine MoS$_2$ and N-MoS$_2$ with different activation temperatures at different scan rates (4-50 mV).
Figure S7. Electrochemical impedance spectra of pristine MoS$_2$ and N-MoS$_2$ supported on FTO from 1000 kHz to 1 Hz.

Figure S8. Electrochemical cyclic voltammograms of N-MoS$_2$ with different activation times at different scan rates (4-50 mV).
Calculation of Electrochemical Active Surface Area (ECSA)

Firstly, we assume that the specific capacitance of a flat MoS$_2$ surface is $\sim 60 \mu$F cm$^{-2}$ for 1 cm$^2$ of real surface area.

The ECSA can be calculated from the following equation:

$$ A_{ECSA} = \frac{\text{Specific capacitance}}{60 \mu \text{F cm}^{-2} \text{ cm}^2_{ECSA}} $$

Table S1. Comparative results of surface area for our sample and other electrocatalysts

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific surface area ($S_{BET}$)/ m$^2$ g$^{-1}$</th>
<th>Loading Amount/µg</th>
<th>Geometric area</th>
<th>ECSA$<em>{mass}$/S$</em>{BE}$</th>
</tr>
</thead>
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<tr>
<th></th>
<th>Our Work</th>
<th>7.1</th>
<th>6.65</th>
<th>20</th>
<th>0.071</th>
<th>0.33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrathin MoS$_2$/graphene$^2$</td>
<td></td>
<td>245</td>
<td>285</td>
<td>50</td>
<td>0.196</td>
<td>0.44</td>
</tr>
<tr>
<td>Mo-N/C@MoS$_2$$^3$</td>
<td></td>
<td>519.5</td>
<td>225.80</td>
<td>—</td>
<td>0.196</td>
<td>&lt;0.41</td>
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<tr>
<td>MoSe$_2$-CoSe$_2$ Nanotubes$^4$</td>
<td></td>
<td>69.05</td>
<td>68.83</td>
<td>40</td>
<td>0.071</td>
<td>0.17</td>
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$^{\text{ECSA}}_{\text{mass}}$ is the value of ECSA per gram.

Calculation of Per Site Turn Over Frequency (TOF)$^{1, 5, 6}$

The number of electrochemically accessible surface sites on MoS$_2$ can be calculated via the following equation:

$$\frac{\text{# of surface sites (catalyst)}}{\text{cm}^2 \text{ geometric area}} = \frac{\text{# of surface sites (flat standard)}}{\text{cm}^2 \text{ geometric area}} \times \frac{C_{dl}}{60 \mu \text{F cm}^{-2}}$$

Active sites per cm$^2$ geometric area is $1.164 \times 10^{15}$ cm$^{-2}$$^2$ for the flat standard. Using the equation above, the number of surface active sites for N-MoS$_2$-900-2 corresponds to $7.75 \times 10^{15}$.

Then, the following equation is employed to estimate the per site TOF:

$$\text{TOF per site} = \frac{\text{# Total Hydrogen Turn Over}/\text{cm}^2 \text{ geometric area}}{\text{# Surface Sites (Catalyst)}/\text{cm}^2 \text{ geometric area}}$$
From the literature, the total number of hydrogen turn over events per geometric area at 1mA cm\(^{-2}\) is

\[
3.12 \times 10^{15} \frac{H_2}{s \ cm^2}
\]

Hence, the per site TOF of MoS\(_2\)-900-2 at the current density of 14 mA cm\(^{-2}\) is determined as follows:

\[
\text{TOF} = \left(3.12 \times 10^{15} \frac{H_2/s}{cm^2}\right) \times \left(\frac{14 \ mA}{cm^2}\right) \times \left(\frac{1 \ cm^2}{7.75 \times 10^{15} \text{ surface sites}}\right) = 5.6 \frac{H_2/s}{\text{surface site}}
\]

The TOF values for other samples can be calculated by same method.

**Table S2.** TOF values of N-MoS\(_2\) samples at a potential of 0.5 V

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<tbody>
<tr>
<td>TOF/H(_2) s(^{-1})</td>
<td>0.34</td>
<td>2.88</td>
<td>3.92</td>
<td>5.48</td>
<td>4.00</td>
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References


