Supporting Information Available

Hot Electron of Au Nanorods Activates the Electrocatalysis of Hydrogen Evolution on MoS$_2$ Nanosheets

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Scheme S1. The synthetic procedure of Au–MoS₂ nanosheets.

Photograph S1. Dark-field electrochemical apparatus.
Figure S1. (A) SEM image of bulk MoS$_2$. (B) TEM image of ce–MoS$_2$. (C) Photograph of ce–MoS$_2$ solution after four weeks of storage under ambient temperature. (D) SEM image of Au rods.
Figure S2. The survey scans of XPS spectra for the samples and their corresponding calculated atomic concentrations of Mo, S, and Au.
**Figure S3.** (A) Polarization curves of Au−MoS$_2$ with (red) and without (black) 808 nm laser irradiation. Green line represents the electrochemical behavior of Au−MoS$_2$ in the dark immediately after one irradiation cycle. Blue line represents the electrochemical behavior upon sudden light-off test. (B) ce−MoS$_2$ with and without laser irradiation during electrochemical measurements. (C) HER activity of Au−MoS$_2$ with different wavelength irradiation or laser intensity. (D) HER activity of Au−MoS$_2$ with different Au loading.
**Figure S4.** Gas chromatography (GC) measurements of various samples shown in the figure. H$_2$ standard: pure H$_2$ collected from the gas cylinder; H$_2$-dark: gas collected from the working electrode in the dark; H$_2$-808: gas collected from the working electrode under 808 nm laser illumination. The electrolyzing was performed at $-0.23$ V vs RHE in a solution of 0.5 M sulfuric acid.

Three possible reaction steps suggested for the HER in acidic media:$^{13}$

\[
\begin{align*}
\text{H}_3\text{O}^+ + e^- + \text{catalyst} & \rightarrow \text{catalyst} - \text{H} + \text{H}_2\text{O} & \text{Volmer reaction} \quad \text{(S1)} \\
\text{H}_3\text{O}^+ + e^- + \text{catalyst} - \text{H} & \rightarrow \text{catalyst} + \text{H}_2 + \text{H}_2\text{O} & \text{Heyrovsky reaction} \quad \text{(S2)} \\
\text{catalyst} - \text{H} + \text{catalyst} - \text{H} & \rightarrow 2\text{catalyst} + \text{H}_2 & \text{Tafel reaction} \quad \text{(S3)}
\end{align*}
\]
Assessment of activation energy ($E_a$):

Figure S5. (A) HER activity of Au–MoS$_2$ under 808 nm laser excitation at different temperatures. (B) HER activity of ce–MoS$_2$ at different temperatures. (C) Arrhenius plots: semilogarithmic dependence of current density of ce–MoS$_2$ at various overpotentials plotted against inverse temperature. Overpotentials are taken from 300 to 400 mV at an interval of 25 mV. (D) Activation energy at the zero overpotential obtained through trend extrapolation.

Figure S5A and B are the original data directly obtained from experiments, which are used for further activation energy ($E_a$) calculation. The $E_a$ for ce–MoS$_2$ and Au–MoS$_2$ catalysts were calculated from the slope of the Arrhenius plot. An Arrhenius plot displays semilogarithmic
dependence of exchange current density plotted against inverse temperature. The Arrhenius equation given in the form:

\[ j = Ae^{-\frac{E_a}{RT}} \]  

(S4)
can be written equivalently as:

\[ \ln j = \ln A - (\frac{E_a}{R}) \frac{1}{T} \]  

(S5)

where \( A \) is pre-exponential factor, \( E_a \) is activation energy, \( R \) is gas constant and \( T \) is temperature (kelvin).

**Assessment of turnover frequency (TOF):**

**Figure S6.** (A) Process illustrating the underpotential deposition of Cu adatoms at the defects of MoS\(_2\) nanosheets used to calculate the number of active sites for HER.\(^1\) (B) Cyclic voltammogram of ce-MoS\(_2\). Oxidation current starting from 0.75 V vs RHE attributable to the
transitions from MoS$_2$→MoO$_3$ and cathodic current due to the evolution of hydrogen are observed. (C) Cyclic voltammograms of ce–MoS$_2$ and GC in 0.1 M H$_2$SO$_4$ in the presence of cupric sulfate (CuSO$_4$, 2 mM). $I_A$ and $I_C$ peaks correspond to the stripping and bulk deposition of Cu, respectively. $II_A$ and $II_C$ broad peaks are assigned to the underpotential processes of Cu adatoms.

In ref. 1, Voiry et al. have demonstrated that at a particular potential the same quantity of copper adatoms as hydrogen adatoms is deposited on the surface of the electrode at the active sites. Thus, the number of active sites can be calculated by applying underpotential deposition (UPD) of copper (schematic diagram shown in Figure S6A). From Figure S6B, we come to a conclusion that the scanning potential value in UPD experiment can only reach as high as 0.75 V, since higher potential will result in oxidation of MoS$_2$ to MoO$_3$. It is shown that compared to glassy carbon (GC), copper ions can be electrochemically reduced on ce-MoS$_2$ at higher potentials (underpotential deposition, UPD) than its thermodynamic potential (Figure S6C). From the quantity of charges generated during the Cu adatoms stripping for the peak centered at 566 mV vs RHE, it can be calculated that 3.98×10$^{14}$ mol of Cu adatoms (Q$_{Cu}$/96500/2) have been deposited. From this, an active site density 5.63×10$^{15}$ sites/cm$^2$ (n$_{Cu}$/A$_{electrode}$) is obtained for hydrogen adsorption on ce–MoS$_2$.

**Conversion of measured current to H$_2$ turnover (assuming 100% Faradaic efficiency):**

$$ (j \, \text{mA/cm}^2) \left( \frac{1 \, \text{A}}{1000 \, \text{mA}} \right) \left( \frac{1 \, \text{C/s}}{1 \, \text{A}} \right) \left( \frac{6.241 \times 10^{18} \, \text{e}^-}{1 \, \text{C}} \right) \left( \frac{1 \, \text{H}_2}{2 \, \text{e}^-} \right) = (3.12 \times 10^{15} \, \text{H}_2/\text{s/cm}^2) \text{ per } \frac{\text{mA}}{\text{cm}^2} $$

**TOF at 300 mV:**

ce–MoS$_2$:

$$ 2.17 \times \frac{\text{mA}}{\text{cm}^2} \times (3.12 \times 10^{15} \, \text{H}_2/\text{s/cm}^2) = 6.77 \times 10^{15} \, \text{H}_2/\text{s/cm}^2 $$
\[
\left( \frac{6.77 \times 10^{15} \text{ H}_2/\text{s}}{\text{cm}^2} \right) \left( \frac{\text{cm}^2}{5.63 \times 10^{15} \text{ Mo}} \right) = 1.2 \frac{\text{H}_2/\text{s}}{\text{Mo}}
\]

Au–MoS\textsubscript{2}:

\[
7.33 \times \frac{\text{mA}}{\text{cm}^2} (3.12 \times 10^{15} \frac{\text{H}_2/\text{s}}{\text{cm}^2}) = 2.27 \times 10^{16} \frac{\text{H}_2/\text{s}}{\text{cm}^2}
\]

\[
\left( 2.27 \times 10^{16} \frac{\text{H}_2/\text{s}}{\text{cm}^2} \right) \left( \frac{\text{cm}^2}{5.63 \times 10^{15} \text{ Mo}} \right) = 4 \frac{\text{H}_2/\text{s}}{\text{Mo}}
\]

808 nm laser excited Au–MoS\textsubscript{2}:

\[
16.07 \times \frac{\text{mA}}{\text{cm}^2} (3.12 \times 10^{15} \frac{\text{H}_2/\text{s}}{\text{cm}^2}) = 4.98 \times 10^{16} \frac{\text{H}_2/\text{s}}{\text{cm}^2}
\]

\[
\left( 4.98 \times 10^{16} \frac{\text{H}_2/\text{s}}{\text{cm}^2} \right) \left( \frac{\text{cm}^2}{5.63 \times 10^{15} \text{ Mo}} \right) = 8.76 \frac{\text{H}_2/\text{s}}{\text{Mo}}
\]
**Table S1.** HER activities of MoS$_2$–based catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Onset potential/ V</th>
<th>Tafel slope/ mV dec$^{-1}$</th>
<th>$\eta$/mV</th>
<th>TOF/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce–MoS$_2$ (in this work)</td>
<td>−0.26</td>
<td>94</td>
<td>300</td>
<td>1.2</td>
</tr>
<tr>
<td>Au–MoS$_2$ (in this work)</td>
<td>−0.22</td>
<td>86</td>
<td>300</td>
<td>4</td>
</tr>
<tr>
<td>Irradiated Au–MoS$_2$ (in this work)</td>
<td>−0.16</td>
<td>71</td>
<td>300</td>
<td>8.76</td>
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<tr>
<td>[Mo$_3$S$_4$]$^{4+}$ cubanes / HOPG</td>
<td>−0.20</td>
<td>120</td>
<td>200~300</td>
<td>1~5</td>
</tr>
<tr>
<td>Amorphous MoS$_3$$^4$</td>
<td>−0.15</td>
<td>60</td>
<td>200</td>
<td>0.3</td>
</tr>
<tr>
<td>MoS$_2$ Particles$^5$</td>
<td>−0.16</td>
<td>82</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Defect–Rich MoS$_2$ sheets$^6$</td>
<td>−0.12</td>
<td>50</td>
<td>300</td>
<td>0.725</td>
</tr>
<tr>
<td>Amorphous MoS$_3$–CV film$^7$</td>
<td>−0.16</td>
<td>40</td>
<td>220/240</td>
<td>0.8/2</td>
</tr>
<tr>
<td>double–gyroid MoS$_2$$^8$</td>
<td>−0.15~−0.20</td>
<td>50</td>
<td>200</td>
<td>1</td>
</tr>
<tr>
<td>MoO$_3$–MoS$_2$ nanowires$^9$</td>
<td>−0.15~−0.20</td>
<td>50~60</td>
<td>272</td>
<td>4</td>
</tr>
<tr>
<td>Ce–MoS$_2$ nanosheets$^{10}$</td>
<td>−0.17</td>
<td>54</td>
<td>N/A</td>
<td>N/A</td>
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<tr>
<td>MoS$_2$ nanosheets$^{11}$</td>
<td>−0.15</td>
<td>45</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>MoS$_x$/Graphene$^{12}$</td>
<td>−0.11</td>
<td>43</td>
<td>N/A</td>
<td>N/A</td>
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<td>MoS$_2$/RGO$^{13}$</td>
<td>−0.10</td>
<td>41</td>
<td>200</td>
<td>0.1</td>
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<tr>
<td>[Mo$<em>3$S$</em>{13}$]$^{2−}$ clusters / HOPG$^{2}$</td>
<td>−0.10</td>
<td>40</td>
<td>200</td>
<td>3</td>
</tr>
</tbody>
</table>
**Figure S7.** UV−vis spectrum of Au rods with SPR band centered at ~650 nm.

**Figure S8.** SPR scattering spectra of Au rods in Au/ITO and Au−MoS$_2$/ITO under open circuit condition in 0.1 M KCl solution. The SPR scattering of Au rods deposited on ITO (Au/ITO) is located at ~660 nm. After MoS$_2$ nanosheets are *in-situ* immobilized on the Au/ITO (Au−MoS$_2$/ITO), the SPR scattering of Au rods shows a red-shift of ~18 nm, directly indicating that
hot electron is exactly transferred from Au rods to MoS$_2$ nanosheets even at open circuit potential.

**Figure S9.** The $i$–$t$ curves of Au/ITO and Au–MoS$_2$/ITO at $-0.23$ V vs RHE in 0.1 M KCl solution.

**Figure S10.** Polarization curves of Au–MoS$_2$ under 808 nm laser irradiation with EtOH as hole scavenger, bulk MoS$_2$ and commercial Pt/C.
References and Notes


