Engineering the surface structure of MoS$_2$ to preferentially expose active edge sites for electrocatalysis

Jakob Kibsgaard, † Zhebo Chen, † Benjamin N. Reneicke and Thomas F. Jaramillo*

Department of Chemical Engineering, Stanford University, Stanford, California 94305, USA

†These authors contributed equally to this work

*e-mail: jaramillo@stanford.edu

Thickness of DG Silica Films

Figure S1. Profilometry of 5 DG silica films after calcination using a Veeco Dektak 150 profilometer.

Since imaging of the silica template by SEM was not possible due to its non-conductive nature, the thickness of the DG silica films was measured using a Veeco Dektak 150 profilometer. The thickness of the film was measured by profiling the step height near the dip coating edge on a FTO support using a 12.5 μm tip on 5 different samples. Typical film thicknesses were approximately 300 nm using a dip coating speed of 1 mm/sec (Figure S1).
Charge Passed During Electrodeposition

The following coulombs were passed during deposition: 10 sec: 23 mC/cm², 20 sec: 50 mC/cm², 1 min: 131 mC/cm² (Figure S2), corresponding to ratios of 1.0x, 2.2x, and 5.8x, respectively (normalized to the 10 sec sample). The trend is in good agreement with the capacitance ratios measured by impedance (1.0x, 2.4x, and 4.3x, respectively).

Variation in the exact values is expected since the electrodeposited molybdenum bronze phase is highly unstable in the acidic electrodeposition solution, and is prone to rapid re-dissolution. Samples must be quickly removed after deposition, rinsed, and dried to maintain the film integrity. The charge passed during electrodeposition therefore provides an upper-bound estimate to the amount of material deposited. Assuming 3 Mo atoms per 11 electrons based on previous studies of the deposition mechanism,¹ and using a molar mass of 160.07 g/mol for MoS₂, we obtain mass loadings of approximately 10 μg/cm², 23 μg/cm², and 60 μg/cm² for the 10 sec, 20 sec, and 1 min samples, respectively.

Figure S2. Plot of charge passed during electrodeposition for 10 sec, 20 sec, and 1 min films.
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Figure S3. XPS of: (a) mixed-valent molybdenum bronze (Mo^{VI/IV}O_{3-x} (OH)_{x}); Mo 3d region.(b) and (c) DG MoS₂ film immediately following HF etching procedure. (b) Mo 3d and S2s region and (c) S 2p region. (d) and (e) DG MoS₂ film (1 min) after second sulphidization. (d) Mo 3d and S2s region and (e) S 2p region.
Aging of DG Silica template

The calcination of the DG silica template results in ~40% contraction along the [211] direction due to the template removal and silica condensation.\textsuperscript{2,3} We observe that upon aging the calcined DG silica templates experiences a small additional contraction which shifts the XRD peak positions towards larger 2θ as seen from Figure S4. The XRD peak positions of the DG MoS\textsubscript{2} samples thus shift to slightly larger values as a function of the age of the DG silica template.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{FigureS4.png}
\caption{Low angle XRD of an aging DG silica template.}
\end{figure}

UV-Vis-NIR Transmission Spectroscopy of DG MoS\textsubscript{2} Films

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{FigureS5.png}
\caption{UV-Vis-NIR transmission plot of DG MoS\textsubscript{2} thin films on FTO using a Cary 6000i spectrometer with baseline correction performed against a blank FTO substrate. Features at wavelengths > 1000 nm arise from Fabry-Perot interference fringes that result due to optical interactions with the high refractive index of the FTO substrate.}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
DG & 20 sec & 1 min & 10 sec & NW 8.2 \\
\hline
NW 10 sec & 1.3 & 1.6 & 1.0 & NW 8.2 \\
NW 20 sec & 2.6 & 3.4 & 2.2 & NW 8.2 \\
NW 1 min & 6.9 & 10 & 4.8 & NW 8.2 \\
\hline
\end{tabular}
\caption{Relative surface area vs. increased density of active sites for double-gyroid MoS\textsubscript{2} and core-shell MoO\textsubscript{3}-MoS\textsubscript{2} nanowires.}
\end{table}

Determination of Activity Enhancement of Double-Gyroid Structure

In order to evaluate and decouple the activity of the DG structure from contributions due to surface area vs. increased density of active sites per surface area, we employ a Tafel analysis of the j-V curves in conjunction with electrochemical impedance spectroscopy. First, we construct a Tafel plot of the various samples (iR-corrected for all losses) as shown below in Figure S6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{FigureS6.png}
\caption{Tafel plot of core-shell MoO\textsubscript{3}-MoS\textsubscript{2} nanowires and DG MoS\textsubscript{2} films (iR-corrected for all resistive losses) as shown below in Table S1.}
\end{figure}
SUPPLEMENTARY INFORMATION

Table S1. Electrochemical analysis of DG MoS2 films and Core-Shell MoO3-MoS2 nanowires based on exchange current density.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$j_0$ [A/cm$^2$]</th>
<th>Total Enhancement relative to NW</th>
<th>Double-layer Capacitance ($C_{dl}$) [mF/cm$^2$]</th>
<th>Surface Area relative to NW</th>
<th># of Active Sites per Surface Area relative to NW</th>
</tr>
</thead>
<tbody>
<tr>
<td>NW</td>
<td>$8.2 \times 10^{-8}$</td>
<td>1</td>
<td>2.2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>DG 10 sec</td>
<td>$1.3 \times 10^{-7}$</td>
<td>1.6</td>
<td>1.1</td>
<td>0.5</td>
<td>3.1</td>
</tr>
<tr>
<td>DG 20 sec</td>
<td>$2.6 \times 10^{-7}$</td>
<td>3.2</td>
<td>2.7</td>
<td>1.2</td>
<td>2.6</td>
</tr>
<tr>
<td>DG 1 min</td>
<td>$6.9 \times 10^{-7}$</td>
<td>8.4</td>
<td>4.8</td>
<td>2.2</td>
<td>3.9</td>
</tr>
</tbody>
</table>

The total relative activity is proportional to the total relative number of active sites, which can be further decoupled as contributions from the relative surface area and the relative density of active sites per surface area:

$$j \propto \left( \frac{\text{Active Sites}}{\text{Surface Area}} \right)$$

To obtain the relative surface area of the samples, we employ electrochemical impedance spectroscopy at open circuit potential and at low frequencies (~10 Hz) using a R-C equivalent circuit to determine the double-layer capacitance ($C_{dl}$). For the core-shell MoO3-MoS2 nanowires, we obtain a $C_{dl}$ of 2.2 mF/cm$^2$. As a reference for comparison, a flat sample of Mo prepared by sputter deposition and sulphidized into MoS2 yielded a $C_{dl}$ of ~60 µF/cm$^2$, which is close to the range of expected values for a flat electrode (typically tens of µF/cm$^2$). The NWs therefore have a measured roughness factor (RF, total sample surface area relative to geometric planar surface area) of ~37. This is a good match with the theoretical roughness factor of the nanowires based on their geometry (approximate dimensions of 50 nm diameter, 2 µm length, $10^{10}$/cm$^2$ density), which should yield RF ~30 assuming a cylindrical rod morphology. We measure $C_{dl}$ of 1.1 mF/cm$^2$, 2.7 mF/cm$^2$, and 4.8 mF/cm$^2$ for the 10 sec, 20 sec, and 1 min DG samples, respectively. These correspond to RFs of 19, 45, and 80.

A theoretical RF for the DG phase can be estimated numerically from 3D reconstructions of the film. The parameters used to construct the 3D model were optimized by comparing simulated TEM from the model with experimental TEM images of the DG MoS2 structure. The 3D model and simulated TEM images was modelled using the following equation for the electron density $\rho(x,y,z)$ of double-gyroid MoS2:

$$\rho(x,y,z) = \begin{cases} 
\sin \left( \frac{2\pi x}{a} \right) \cos \left( \frac{2\pi y}{a} \right) + & \sqrt{2} \sin \left( \frac{2\pi w}{a} \right) \\
1 & \text{for} \\
\sin \left( \frac{2\pi y}{a} \right) \cos \left( \frac{2\pi z}{a} \right) + & \sqrt{2} \sin \left( \frac{2\pi x}{a} \right) \\
\sin \left( \frac{2\pi z}{a} \right) \cos \left( \frac{2\pi x}{a} \right) & \text{0 otherwise}
\end{cases}$$

where $a$ is the lattice constant of the uncontracted cubic structure and $w$ is the pore size. The resulting model defined by this equation was rotated and uniaxially contracted to account for the 40% contraction along the [211] direction of the DG silica template from calcination. Figure S7a shows a TEM image of the [311] projection of the DG MoS2 structure and Figure S7b shows the simulated TEM image and model constructed to fit the experimental image ($a = 18$ nm and $w = 3$ nm) as shown from the linescans in Fig. S7c.
Figure S7. (a) TEM image of [311] projection of the DG MoS$_2$ structure. (b) Simulated TEM image and model of the DG MoS$_2$ constructed to fit the experimental image in (a). (c) Comparison of linescans as indicated by the arrows in (a) and (b).

The mesopore surface area was calculated numerically from this 3D model to be $5.4 \times 10^6$ cm$^2$ / cm$^3$ which are similar to the values found by Urade et al.$^2$. Using film thicknesses of 50 nm, 150 nm, and 250 nm, this model gives theoretical RF values of 27, 81 and 134, respectively.

These values agree well with the RF values from the double-layer capacitance since the thickness values from which the theoretical RF values are calculated represent rough approximations due to the inherent surface roughness of the FTO substrate itself, which is on the order of tens of nanometres (Figure S8). Consequently, we can see that the DG films possess 2-4x the # of active sites per surface area compared to the NW structure. As a result, even the thinnest film (10 sec, ~50 nm) has a higher overall activity compared to the NW even though it has half the surface area.

Bubble Formation on DG vs. NW

In contrast to the vertically oriented NW morphology, the DG film is a highly tortuous morphology that can better trap bubbles and exclude surface area from contact with the electrolyte. This consequently blocks more active sites within the DG structure during H$_2$ evolution. Furthermore, the density of nanowires ($10^{10}$ cm$^{-2}$) is low and individual wires are spaced much farther apart (tens of nm) than domains of MoS$_2$ in the DG structure (few nm). Therefore, compared to bubbles growing at the tips of the NWs, the much higher MoS$_2$/liquid ratio presented by the topmost surface of the DG film allows the bubbles to anchor stronger to the surface, enabling them to grow larger in size.

Figure S8. Atomic force microscopy of TEC8 FTO surface performed using a Veeco Digital Instruments NanoScope IIIa Scanning Probe microscope and a KTEK TETRA18/Au tip.

Figure S9. Schematic of bubble formation on nanowires (left) vs. double-gyroid (right).
Setup of Electrochemical Cell

Figure S10. Illustration of the three electrode compression cell used for electrochemical testing. Allen bolts pass through four holes at the circumference and are secured with nuts. The electrolyte is sparged with 99.999% H₂.

Figure S11. Comparison of MoS₂ activity in N₂ and H₂ sparged 0.5 M H₂SO₄ electrolyte, taken at 50 mV/s (not iR-corrected).
Long-term stability of DG MoS$_2$ Films in Air

The 10 sec, 20 sec, and 1 min DG MoS$_2$ films were left in air over a period of 4 months. XPS/XRD measurements were performed on these films, followed by resulphidization in 10%/90% H$_2$S/H$_2$ to revert any oxide back into a sulphide (Figures S12 and S13). The resulphidized films were then analysed using XPS/XRD (Figures S12 and S13), and reassessed for electrochemical activity using cyclic voltammetry (Figure S14).

Figure S12. XPS of DG MoS$_2$ films after 4 months of exposure to air (a and b), and following resulphidization in 10%/90% H$_2$S/H$_2$ (c and d).
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Figure S12. XPS of DG MoS$_2$ films after 4 months of exposure to air (a and b), and following resulphidization in 10%/90% H$_2$S/H$_2$ (c and d).

Figure S13. XRD of DG MoS$_2$ films after 4 months of exposure to air (a), and following resulphidization in 10%/90% H$_2$S/H$_2$ (b).

Figure S14. Initial electrochemical activity of DG MoS$_2$ (1 min) (dark blue) and after 4 months (light blue) following resulphidization in 10%/90% H$_2$S/H$_2$.

Comparison of Activity for Molybdenum Sulphide Catalysts

Figure S15. Tafel plot comparing various molybdenum sulphide catalysts, including nanoclusters synthesized in UHV,$^6$ core-shell MoO$_3$-MoS$_2$ nanowires,$^7$ amorphous MoS$_{x},$ $^8$ and MoS$_2$/reduced graphene oxide (RGO).$^9$
**Table S2.** Comparison of catalyst loading, exchange current density, and Tafel slope between DG MoS$_2$ vs. amorphous MoS$_x$ and MoS$_2$/RGO catalysts as provided in a previous reference. The exchange current density for the MoS$_2$/RGO was determined from the Tafel plot in Figure S15. Catalyst loadings for DG MoS$_2$ were estimated based on charge passed during electrodeposition (Figure S2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst loading [μg/cm$^2$]</th>
<th>$j_0$ [A/cm$^2$]</th>
<th>Tafel slope [mV/decade]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous MoS$_x$</td>
<td>9</td>
<td>0.4-1.5×10$^{-7}$</td>
<td>40</td>
</tr>
<tr>
<td>MoS$_2$/RGO</td>
<td>285</td>
<td>5.1×10$^{-6}$</td>
<td>41</td>
</tr>
<tr>
<td>DG 10 sec</td>
<td>10</td>
<td>1.3×10$^{-7}$</td>
<td>50</td>
</tr>
<tr>
<td>DG 20 sec</td>
<td>23</td>
<td>2.6×10$^{-7}$</td>
<td>50</td>
</tr>
<tr>
<td>DG 1 min</td>
<td>60</td>
<td>6.9×10$^{-7}$</td>
<td>50</td>
</tr>
</tbody>
</table>

**References**