Facet-Controlled Morphology of Cobalt Disulfide towards Enhanced Oxygen Reduction

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Experimental Section

Materials

CoS$_2$ was synthesized by using hydrated cobalt chloride (CoCl$_2$•6H$_2$O; ≥ 98%, Alfa Aesar), hydrated trisodium citrate (soft mold i.e. Na$_3$C$_6$H$_5$O$_7$.2H$_2$O; ≥ 99%, Alfa Aesar), sodium thiosulfate (≥ 98%, Alfa Aesar) and ethanol (≥ 99%, Merck Millipore) of analytical grade without further purification and Pt/C (20%) was purchased from E-TEK. The requisite solutions were prepared using Millipore water (15 MΩ).

Synthesis of cobalt sulfide crystal.

Firstly, 50 ml of sodium citrate (10 mM) was taken in 250 ml conical flask followed by addition of 5 mM of cobalt chloride while stirring. After that 100 ml of 0.1 M, sodium thiosulfate was added to the above mixture and stirred for 1 h. The resulting mixture was transfer to Teflon lined hydrothermal reactor of capacity 100 ml and further treated at 200° C for 12 h. The obtained black precipitated product was retrieved by centrifugation after washing for multiples sets and solid product was dried overnight at 80 °C.

Characterization

The physical characterization of the as-synthesized samples was performed by employing powder X-ray diffraction (PXRD) measurements in the 2θ range of 10 to 70 degrees using PANalytical’s X’Pert Pro MPD wherein the X-ray source is Cu Kα radiation. The elemental composition was determined using energy dispersive X-ray measurements (EDX; Oxford, INCAx-act, 51-ADD0013) and further confirmed using X-ray photoelectron spectroscopy (XPS; PHI Versa Probe II Spectrometer) working at 15 kV and 35 mA under an ultrahigh vacuum (UHV; 7×10$^{-10}$ mbar pressure). The X-ray source used for sample analysis was a monochromatic Al Kα radiation ($h\nu = 1486.6$ eV). Fixed transmission mode with a pass energy of 376 eV was used to attain Co 2p, S 2p and C 2p spectra. FT-IR analysis was performed using a Bruker Tensor-27 spectrometer in the range of 400−4000 cm$^{-1}$, with a spectral resolution of 4 cm$^{-1}$ run by OPUS software. The morphology of the as synthesized variants were analyzed using scanning electron microscopic (SEM; JEOL, JSM-6610 LV) and field emission scanning electron microscopy (FE-SEM; ZEISS, ULTRA PLUS).

Electrochemical evaluation

Sample preparation and electrochemical investigation;

Electrochemical experiments were performed using Autolab 302N modular potentiostat/galvanostat controlled with Nova 1.11 software. All the measurements were carried out using single compartment glass cell consisting of three electrodes setup. The glassy carbon (GC, Ø3 mm) was taken as working
electrode, Pt mesh as counter electrode (CE) and Ag/Ag/Cl used as reference electrode (RE) respectively.
The RRDE measurement was analyzed for the facet-controlled octahedral cobalt sulfide using Teflon-
embedded glassy carbon Pt ring disk electrode (GC/Pt) by applying 1.4 V (vs. RHE) potential to the ring in
the 0.1 M HClO₄ solution. The RDE measurements were obtained for each sample by sweeping the
potential from 1.2 V to -0.1 V (vs. RHE) (diffusion limiting) in the oxygen saturated 0.1 M HClO₄ solution.
Prior to the use, working electrode was polished till mirror finishing by employing different grades of
alumina slurry (3, 0.3, 0.05 µm PINE instrument, USA) on the nylon polishing cloths (SM 407052,
AKPOLISH). The working electrode was prepared by drop casting 20 µl (50 µg) of obtained sample slurry,
which was prepared by dispersing the 1.25 mg of sample in 20 µl of isopropyl alcohol and 0.5 ml of water
followed by sonication for 30 minutes. The oxygen saturated electrolyte 0.1 M HClO₄ solution was used
to perform electrochemical measurement. The hydrodynamic experiment were carried out using speed
controlling unit (AFMSRCE, Pine Research Instrument Inc., USA) from 100 to 1300 rpm at a scan rate of 5
mV/s. For comparison with the state-of-art catalyst, Pt/C (20%) (50 µg) was employed to perform ORR in
0.1 M HClO₄ solution.

The electrochemical impedance was carried out to investigate the electrical properties of the facet-
controlled octahedral crystal of obtained cobalt sulfide. The impedance spectra was recorded in the 0.1M
HClO₄ solution using 5mM K₄[Fe(CN)₆] redox media. The impedance measurement was performed by
applying a DC potential of 320 mV over and above an AC perturbation of 10 mV for the various frequency
ranges from 0.1 Hz to 200 kHz in the logarithmic step.

**Electrochemical quartz crystal microbalance (EQCM):** The EQCM measurement was performed in a single
chamber electrochemical cell, which comprises of three-electrode having Au-coil as counter, Ag/AgCl/3M
KCl as reference and thin Au film deposited over 6 MHz AT-cut quartz crystal (Metrohm) was employed
as working electrode. The working electrode was prepared by drop casting thin film of CoS₂ catalyst
variants over Au electrode. Further, EQCM analysis was performed for each CoS₂ time variants towards
ORR in oxygen saturated 0.1 M HClO₄. The cyclic voltammetry experiments were performed at a scan rate
of 5 mV/s and simultaneously recording the change in frequency of the quartz crystal electrode w.r.t.
potential in the range of 1.1 to -0.2 V (vs. RHE). Further the obtained change in the frequency was
converted into the mass change during electro catalytic ORR using Sauerbrey’s equation;

$$\Delta m = -C_f \Delta f$$

Where, $C_f$ is the sensitivity factor of 6 MHz AT-cut quartz crystal whose theoretical value is 12.3 ng/Hz
cm².

**Scanning electrochemical microscopic studies**

The local electrocatalytic activity was studied using Scanning electron microscopic (SECM) technique. The
SECM measurement were conducted using Sensolytics Base SECM (Sensolytics, Bochum, Germany) with
stepper-motor-driven x-y-z stages and an additional three axis piezo-positioning system working in
conjunction with the bi-potentiostat (Autolab 204, Metrohm). The four-electrode setup was employed
wherein GC plate bearing catalyst spot (octahedral CoS₂) which acts as working electrode 1 (WE1), a Pt
microelectrode tip (Ø 10 µm) as WE2, Pt coil as counter electrode and Ag/AgCl/3M KCl as the reference
electrode respectively in 0.1 M HClO₄ electrolyte. The redox competition mode of SECM (RC-SECM) was
employed to test oxygen reduction ability of the prepared facet-controlled cobalt sulfide catalyst vs. Pt
microelectrode by polarizing the WE1 at 200 mV and the WE2 at 400 mV. Array scan was performed in a
1800 µm × 1800 µm area, with increment of 10 µm in X-direction and 20 µm in the Y-direction at a scan speed of 20 µm/s and 100 ms wait time in a ‘Fast-comb’ mode at a sample to tip distance of 12 µm using tilt-control. The data were collected and further analyzed by using Gwydion and Origin 8.5 software.

In order to convert the potential measured w.r.t. Ag/AgCl reference electrode to RHE following equation were employed:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E^o_{\text{Ag/AgCl}} + 0.059 \times \text{pH}$$

Where, $E_{\text{RHE}}$ is the potential converted to RHE; $E_{\text{Ag/AgCl}}$ is the potential measured against the $E_{\text{Ag/AgCl}}$ reference electrode; $E^o_{\text{Ag/AgCl}}$ is the standard electrode potential of Ag/AgCl/3M KCl reference electrode (+0.210 V for 3 M KCl) and pH is of the used electrolyte (1 for 0.1 M HClO$_4$).

Figure S1. XRD pattern for octahedral CoS$_2$ catalyst.
Figure S2. FE-SEM images of cobalt sulfide at various cobalt concentrations (a) 5 mM and (b) 10 mM, SEM image at (c) 20 mM and (d) 30 mM with their corresponding (e) XRD patterns and (f) scatter plot representing ORR current density (at 0.0 V) along with onset potential (at -0.1 mA cm$^{-2}$) extracted from LSV in Figure S10 (SI). CE: Pt mesh, RE: Ag/AgCl/3M KCl (potentials converted to RHE).
Figure S3. SEM images of cobalt sulfide at various reaction time (a) 6h, (b) 8h, (c) 10h, (d) FE-SEM images at 12h and (e) 16h and (f) SEM images at 20h.
Figure S4. XRD pattern of cobalt sulfide at various reaction time from 6h to 20h. [CoS$_2$ is marked with (*) and Co$_9$S$_8$ as (#), dotted line represents the increase in peak intensity along particular {111} and {220} planes respectively].
Figure S5. (a) FT-IR spectra of octahedral CoS$_2$ crystal with zoomed portions denoting characteristics peaks for (b) carbonyl group originating from citrate and (c) Co-S bond.
Figure S6. (a-b) TEM and (c) HR-TEM images of octahedral CoS$_2$ crystal.
Figure S7. EDS spectra of octahedral CoS$_2$ crystal illustrating the presence of Cobalt, sulfur and carbon.
Figure S8. Cyclic voltammogram for octahedral CoS$_2$ crystal in both N$_2$ and O$_2$-saturated 0.1 M HClO$_4$ electrolyte at 25 mV s$^{-1}$. Inset shows the zoomed part of CoS$_2$ in N$_2$ saturated 0.1 M HClO$_4$ solution.
Figure S9. RDE polarization curves for synthesized cobalt sulfide at various concentration of trisodium citrate (soft-mold) in O₂-saturated 0.1 M HClO₄ electrolyte at 5 mV s⁻¹. CE: Pt mesh, RE: Ag/AgCl/3M KCl (potentials converted to RHE).
Figure S10. RDE polarization curves for synthesized cobalt sulfide at various concentration of cobalt chloride in O₂-saturated 0.1 M HClO₄ electrolyte at 5 mV s⁻¹. CE: Pt mesh, RE: Ag/AgCl/3M KCl (potentials converted to RHE).

Table S1: ORR outcome upon varying soft-mold concentration

<table>
<thead>
<tr>
<th>Soft-mold concentration (mM)</th>
<th>(J_k) (mA cm⁻²) at 0.7 V vs. RHE</th>
<th>(j_d) (mA cm⁻²) at 0.0 V vs. RHE</th>
<th>(E_{\text{onset}}) (V vs. RHE) at -0.1 mA cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.034</td>
<td>5.1</td>
<td>0.66</td>
</tr>
<tr>
<td>10</td>
<td>2.5</td>
<td>11</td>
<td>0.83</td>
</tr>
<tr>
<td>20</td>
<td>1.51</td>
<td>7.5</td>
<td>0.70</td>
</tr>
<tr>
<td>30</td>
<td>0.11</td>
<td>7.0</td>
<td>0.60</td>
</tr>
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</table>
Figure S11. RDE polarization curves for synthesized cobalt sulfide at various reaction time in O$_2$-saturated 0.1 M HClO$_4$ electrolyte at 5 mV s$^{-1}$. CE: Pt mesh, RE: Ag/AgCl/3M KCl (potentials converted to RHE).
Table S3: ORR outcome upon reaction time

<table>
<thead>
<tr>
<th>Reaction time (h)</th>
<th>$J_k$ (mA cm$^{-2}$) at 0.7 V vs. RHE</th>
<th>$J_d$ (mA cm$^{-2}$) at 0.0 V vs. RHE</th>
<th>$E_{onset}$ (V vs. RHE) at -0.1 mA cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.05</td>
<td>7.4</td>
<td>0.66</td>
</tr>
<tr>
<td>8</td>
<td>0.18</td>
<td>7.0</td>
<td>0.71</td>
</tr>
<tr>
<td>10</td>
<td>0.04</td>
<td>8.0</td>
<td>0.66</td>
</tr>
<tr>
<td>12</td>
<td>2.5</td>
<td>11</td>
<td>0.83</td>
</tr>
<tr>
<td>16</td>
<td>0.007</td>
<td>2.4</td>
<td>0.44</td>
</tr>
<tr>
<td>20</td>
<td>0.006</td>
<td>1.2</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Figure S12. (a) RDE polarization curves for synthesized cobalt sulfide at various synthesis temperature and (b) scatter plot representing ORR current density (at 0.0 V) along with onset potential (at -0.1 mA cm$^{-2}$) extracted from (a) in O$_2$-saturated 0.1 M HClO$_4$ electrolyte at 5 mV s$^{-1}$. CE: Pt mesh, RE: Ag/AgCl/3M KCl (potentials converted to RHE).
Table S4: ORR outcome upon reaction temperature variation

<table>
<thead>
<tr>
<th>Reaction temperature (°C)</th>
<th>( J_k ) (mA cm(^{-2})) at 0.7 V vs. RHE</th>
<th>( j_d ) (mA cm(^{-2})) at 0.0 V vs. RHE</th>
<th>( E_{\text{onset}} ) (V vs. RHE) at -0.1 mA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.5</td>
<td>11</td>
<td>0.83</td>
</tr>
<tr>
<td>220</td>
<td>0.11</td>
<td>9.7</td>
<td>0.70</td>
</tr>
<tr>
<td>240</td>
<td>0.025</td>
<td>8.2</td>
<td>0.65</td>
</tr>
<tr>
<td>260</td>
<td>0.01</td>
<td>4.2</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Figure S13. Tafel plot for octahedral CoS\(_2\) crystal and Pt/C derived from Figure 5f (manuscript).
Table S5: ORR performance of Cobalt sulfide-based electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Synthetic approach</th>
<th>$E_{\text{onset}}$ (V vs. RHE)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$_{1-x}$S/RGO</td>
<td>Treated at 500 °C in Ar</td>
<td>0.80</td>
<td>$^1$</td>
</tr>
<tr>
<td>CoS$_2$/RGO</td>
<td>Hydrothermal at 180 °C</td>
<td>-</td>
<td>$^1$</td>
</tr>
<tr>
<td>CoS$_2$/CG</td>
<td>Hydrothermal at 400 °C</td>
<td>0.78</td>
<td>$^2$</td>
</tr>
<tr>
<td>CoS$_2$/C</td>
<td>Hydrothermal at 150 °C</td>
<td>0.78</td>
<td>$^3$</td>
</tr>
<tr>
<td>CoS/NSGA.</td>
<td>Multi-steps</td>
<td>-</td>
<td>$^4$</td>
</tr>
<tr>
<td>Co$_9$S$_8$/NHCS</td>
<td>Calcination at 900 °C followed by etching with HCl</td>
<td>-</td>
<td>$^5$</td>
</tr>
<tr>
<td>Cobalt sulfide over N and S doped rGO</td>
<td>Calcination at 600 °C</td>
<td>0.79</td>
<td>$^6$</td>
</tr>
<tr>
<td>Octahedral CoS$_2$</td>
<td>Hydrothermal at 200 °C</td>
<td>0.83</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Table S5: ORR outcome and mass change upon adsorption-desorption during EQCM analysis

<table>
<thead>
<tr>
<th>Time variants</th>
<th>$i$ (mA) at 0.0 V vs. RHE</th>
<th>$\Delta m$ (ng cm$^{-2}$) at 0.0 V vs. RHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.031</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
<td>0.047</td>
<td>14</td>
</tr>
<tr>
<td>10</td>
<td>0.07</td>
<td>15</td>
</tr>
<tr>
<td>12</td>
<td>0.3</td>
<td>25</td>
</tr>
<tr>
<td>16</td>
<td>0.008</td>
<td>4</td>
</tr>
<tr>
<td>20</td>
<td>0.004</td>
<td>1</td>
</tr>
</tbody>
</table>
**Table 6 Elemental analysis in CoS\(_2\) catalyst**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Carbon (%)</th>
<th>Sulphur (%)</th>
<th>Hydrogen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHNS</td>
<td>7.6</td>
<td>48.6</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**Figure S14.** RRDE polarization curves for (a) octahedral CoS\(_2\), (b) for Pt/C in O\(_2\)-saturated 0.1 M HClO\(_4\) electrolyte at 5 mV s\(^{-1}\) and different rotation rates, (c) bar diagram represents the respective peroxide formation for both CoS\(_2\) (red) and Pt/C (green) along with number of electrons (n) transferred during the electrocatalytic conversion of oxygen to water. CE: Pt mesh, RE: Ag/AgCl/3M KCl (potentials converted to RHE).
Koutecky-Levich Analysis:

The linear sweep voltammogram recorded by performing rotating disk electrode (RDE) measurements at various rotation rate ranging from 100 to 1300 rpm for both octahedral CoS$_2$ and Pt/C. The obtained polarization curve was further utilized to construct the K-L plot and also to calculate the number of electron transfer during the electrocatalytic reaction. The number of electrons were evaluated for both CoS$_2$ and Pt/C using using Koutecky-Levich equation$^1$:

$$\frac{1}{j} = \frac{1}{j_d} + \frac{1}{j_k} = \frac{1}{B\sqrt{\omega}} + \frac{1}{j_k}$$  \hspace{1cm} (1)

Where, \(j\) represents the measured current density, \(j_d\) for diffusion limited current density and \(j_k\) is the kinetic current density. Whereas, \(\omega\) is the angular rotation rate of the electrode where \(B\) can be defined as$^1$:

$$B = 0.62 n F A D^{2/3} \gamma^{-1/6} C$$  \hspace{1cm} (2)

Where, \(n\) is the number of electrons, \(F\) is the Faraday constant (96500 C/mol), \(A\) is the area of the electrode (here, 0.0707 cm$^2$), \(D\) is the oxygen diffusion coefficient (1.93 x 10$^{-5}$ cm$^2$s$^{-1}$), \(\gamma\) is the kinematic viscosity of the electrolyte (0.01 cm$^2$s$^{-1}$) and \(C\) is the bulk concentration of oxygen in the electrolyte medium (1.2x10$^{-3}$ mol L$^{-1}$).

Further, in order to calculate the electrons \((n)\) transferred during electrocatalytic reduction of oxygen a plot between \(1/j\) vs. \(1/\sqrt{\omega}\) was constructed as shown in Figure 5f-inset (manuscript). The slope of this K-L plot gives \(1/B\) which is further used to calculate the potential dependent transfer of electrons which found to be 3.8 for CoS$_2$ and 4 for Pt/C at 0.2 V which confirming CoS$_2$ exhibit 4 electron transfer pathway.

Rotating ring-disk Analysis:

The rotating ring-disk electrode measurements we performed in oxygen saturated 0.1 M HClO$_4$ solution in the potential range of 1.2 V to 0.0 V at a scan rate of 5 mV/s. The obtained RRDE polarization curve shown in Figure S14, SI shows a half wave potential 0.83 V and 0.61 V for Pt/C and CoS$_2$ respectively. Further quantitative estimation of H$_2$O$_2$ formation and the number of electrons transferred during the electrocatalytic reduction of oxygen were evaluated. The number of transferred electrons were calculated using the following equation;

$$n = 4I_d \left[ I_d + \left(\frac{I_r}{N}\right) \right]$$

Where \(I_d\) and \(I_r\) represents the disk and ring current collected during ORR. Whereas, \(N\) stands for collection efficiency of ring determined to 0.38 by performing RRDE analysis in Fe$^{2+/3+}$ redox medium. The percentage of peroxide formation was also evaluated using the following equation;

$$\% \text{ H}_2\text{O}_2 = 200 \times \left( \frac{I_r/N}{I_d + (I_r/N)} \right)$$

The potential dependent \(n\) were evaluated by putting all the desired values in the above equation for CoS$_2$ catalyst and the obtained graph is shown in Figure S14, SI.
Figure S15. Fitted Nyquist plot for octahedral CoS\textsubscript{2} catalysts in 5 mM K\textsubscript{4}[Fe(CN)\textsubscript{6}] prepared in 100 mM KCl electrolyte at 0.32V.

➢ Electrochemical surface area analysis:

Electrochemical active surface area (ECSA) was determined by evaluating double-layer capacitance measurements. Cyclic voltammograms were recorded at various scan rates ranging from 10 to 320 mV s\textsuperscript{-1} in a non-faradaic potential range i.e. 0.1 to -0.1 V (vs. Ag/AgCl) in 0.1 M HClO\textsubscript{4} electrolyte. The obtained response was therefore attributed to have origin only in the capacitance behavior of the electrocatalytic system. A plot between the average current density \([(I_a+I_c)/2]]; where ‘I\textsubscript{a}’ denotes anodic current and ‘I\textsubscript{c}’ is for cathodic current at 0 V (vs. Ag/AgCl)] vs. the scan rate results in a linear graph, the slope of which gives double-layer pseudo-capacitance \(C_{\text{dl}} = 2 \times 10^{-4} \text{ F cm}^{-2}\). Subsequently dividing this \(C_{\text{dl}}\) with specific capacitance for a planar surface \((40 \times 10^{-6} \text{ F cm}^{-2})\) yields ECSA to be 28.4 cm\textsuperscript{2}. Normalizing ECSA with the catalyst loading (50 µg over Ø 3 mm GC) gave a very high specific electrochemical surface area (SESA) of 56.8 m\textsuperscript{2} g\textsuperscript{-1} which is strikingly at par with Pt/C (20%) having 58.9 m\textsuperscript{2} g\textsuperscript{-1} SESA\textsuperscript{8}. 
Figure S16. (a) Cyclic voltammograms obtained for octahedral CoS$_2$ in the non-faradic potential region in 0.1 M HClO$_4$ electrolyte at various scan rates ranging from 10 to 320 mV s$^{-1}$ and its corresponding (b) absolute current versus scan rate plot. CE: Pt mesh; RE: Ag/AgCl/3 M KCl.

References


