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 ($CoCl_2 \bullet 6H_2O$; $\geq 98\%$, Alfa Aesar), hydrated trisodium citrate (soft mold i.e. $Na_3C_6H_5O7.2H2O$; $\geq 99\%$, Alfa Aesar), sodium thiosulfate ($\geq 98\%$, Alfa Aesar) and ethanol ($\geq 99\%$, 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 M Ω).

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 20 range of 10 to 70 degrees using PANalytical's X'Pert Pro MPD wherein the X-ray source is Cu K α 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 K α radiation (hv = 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 Teflonembedded 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 μ m PINE instrument, USA) on the nylon polishing cloths (SM 407052, AKPOLISH). The working electrode was prepared by drop casting 20 μ l (50 μ g) of obtained sample slurry, which was prepared by dispersing the 1.25 mg of sample in 20 μ l 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 μ g) was employed to perform ORR in 0.1 M HClO₄ solution.

The electrochemical impedance was carried out to investigate the electrical properties of the facetcontrolled octahedral crystal of obtained cobalt sulfide. The impedance spectra was recorded in the 0.1M $HClO_4$ solution using 5mM K_4 [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 CoS_2 catalyst variants over Au electrode. Further, EQCM analysis was performed for each CoS_2 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 COS_2) 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 μ m × 1800 μ m area, with increment of 10 μ m in X-direction and 20 μ m in the Y-direction at a scanspeed of 20 μ m/s and 100 ms wait time in a 'Fast-comb' mode at a sample to tip distance of 12 μ m 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;

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

Where, E_{RHE} is the potential converted to RHE; $E_{Ag/AgCl}$ is the potential measured against the $E_{Ag/AgCl}$ reference electrode; $E^{o}_{Ag/AgCl}$ 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 HClO₄).



Figure S1. XRD pattern for octahedral CoS₂ 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. $[CoS_2 \text{ is marked with } (*) and Co_9S_8 as (#), dotted line represents the increase in peak intensity along particular {111} and {220} planes respectively].$



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 CoS₂ crystal.



Figure S7. EDS spectra of octahedral CoS₂ 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 HClO₄ electrolyte at 25 mV s⁻¹. Inset shows the zoomed part of CoS_2 in N_2 saturated 0.1 M HClO₄ solution.



Figure S9. RDE polarization curves for synthesized cobalt sulfide at various concentration of trisodium citrate (soft-mold) in O_2 -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			
Soft-mold concentration (mM)	<i>J_k</i> (mA cm ⁻²) at 0.7 V <i>vs</i> . RHE	j _d (mA cm ⁻²) at 0.0 V <i>vs</i> . RHE	E _{onset} (V vs. RHE) at -0.1 mA cm ⁻²
0	0.034	5.1	0.66
10	2.5	11	0.83
20	1.51	7.5	0.70
30	0.11	7.0	0.60



Figure S10. RDE polarization curves for synthesized cobalt sulfide at various concentration of cobalt chloride in O_2 -saturated 0.1 M HClO₄ electrolyte at 5 mV s⁻¹. CE: Pt mesh, RE: Ag/AgCl/3M KCl (potentials converted to RHE).

Table S2: ORR outcome upon varying Cobalt concentration			
Cobalt concentration (mM)	<i>J_k</i> (mA cm ⁻²) at 0.7 V <i>vs</i> . RHE	j _d (mA cm ⁻²) at 0.0 V <i>vs</i> . RHE	E _{onset} (V vs. RHE) at -0.1 mA cm ⁻²
5	2.5	11	0.83
10	0.51	8.7	0.77
15	1.16	7.5	0.74
20	0.09	3.1	0.70



Figure S11. RDE polarization curves for synthesized cobalt sulfide at various reaction time in O_2 -saturated 0.1 M HClO₄ 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				
Reaction time (h)	J _k (mA cm ⁻²) at 0.7 V <i>vs.</i> RHE	j _d (mA cm ⁻²) at 0.0 V <i>vs</i> . RHE	E _{onset} (V vs. RHE) at -0.1 mA cm ⁻²	
6	0.05	7.4	0.66	
8	0.18	7.0	0.71	
10	0.04	8.0	0.66	
12	2.5	11	0.83	
16	0.007	2.4	0.44	
20	0.006	1.2	0.38	



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 HClO₄ 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			
Reaction temperature (°C)	J _k (mA cm ⁻²) at 0.7 V <i>vs.</i> RHE	j _d (mA cm ⁻²) at 0.0 V <i>vs</i> . RHE	E _{onset} (V vs. RHE) at -0.1 mA cm ⁻²
200	2.5	11	0.83
220	0.11	9.7	0.70
240	0.025	8.2	0.65
260	0.01	4.2	0.62



Figure S13. Tafel plot for octahedral CoS₂ crystal and Pt/C derived from Figure 5f (manuscript).

Table S5: ORR performance of Cobalt sulfide-based electrocatalysts.			
Catalyst	st Synthetic approach		Ref.
Co _{1-x} S/RGO	Treated at 500 °C in Ar	0.80	1
CoS₂/RGO	Hydrothermal at 180 °C	-	1
CoS ₂ /CG	Hydrothermal at 400 °C	0.78	2
CoS ₂ /C	Hydrothermal at 150 °C	0.78	3
CoS/NSGA.	Multi-steps	-	4
Co ₉ S ₈ /NHCS	Calcination at 900 °C followed by etching with HCl	-	5
Cobalt sulfide over N and S doped rGO	Calcination at 600 °C	0.79	6
Octahedral CoS ₂	Hydrothermal at 200 °C	0.83	Present work

Table S5: ORR outcome and mass change upon adsorption- desorption during EQCM analysis			
Time variants	i (mA)	<i>∆m</i> (ng cm ⁻²)	
	at 0.0 V <i>vs.</i> RHE	at 0.0 V <i>vs.</i> RHE	
6	0.031	12	
8	0.047	14	
10	0.07	15	
12	0.3	25	
16	0.008	4	
20	0.004	1	

Table 6 Elemental analysis in CoS ₂ catalyst				
TechniqueCarbon (%)Sulphur (%)Hydrogen				
CHNS	7.6	48.6	0.8	



Figure S14. RRDE polarization curves for (a) octahedral CoS_2 , (b) for Pt/C in O_2 -saturated 0.1 M HClO₄ 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 perfroming rotating disk electrode (RDE) masurements at various rotation rate ranging form 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 equation¹:

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

Where, 'j' represents the measured current density, ' j_d ' for diffusion limited current density and ' j_k ' is the kinetic current density. Whereas, ' ω ' is the angular rotation rate of the electrode where 'B' can be defined as¹:

$$B = 0.62 n F A D^{2/3} \gamma^{-1/6} C$$
⁽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 cm²), 'D' is the oxygen diffusion coefficient (1.93 x 10^{-5} cm²s⁻¹), ' γ ' is the kinematic viscosity of the electrolyte (0.01 cm²s⁻¹) and 'C' is the bulk concentration of oxygen in the electrolyte medium (1.2×10⁻³ mol L⁻¹).

Further, in order to calculate the electrons (*n*) transferred duirng 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 CoS₂ and 4 for Pt/C at 0.2 V which confirming CoS2 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 CoS₂ respectively. Further quantitative estimation of H_2O_2 formation and the number of electrons transferred during the electroatalytic 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;

%
$$H_2O_2 = 200 \text{ x} (I_r/N)/[I_d + (I_r/N)]$$

The potential dependent 'n' were evaluted 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_2 catalysts in 5 mM K₄[Fe(CN)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⁻¹ in a non-faradaic potential range *i.e.* 0.1 to -0.1 V (*vs.* Ag/AgCl) in 0.1 M HClO₄ 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_a' denotes anodic current and 'I_c' is for cathodic current at 0 V (*vs.* (*vs.* Ag/AgCl))] *vs.* the scan rate results in a linear graph, the slope of which gives double-layer pseudo-capacitance (C_{dl} = 2 × 10⁻⁴ F cm⁻²). Subsequently dividing this C_{dl} with specific capacitance for a planar surface (40 × 10⁻⁶ F cm⁻²)⁷ yields ECSA to be 28.4 cm². 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 m² g⁻¹ which is strikingly at par with Pt/C (20%) having 58.9 m² g⁻¹ SESA⁸.



Figure S16. (a) Cyclic voltammograms obtained for octahedral CoS_2 in the non-faradic potential region in 0.1 M HClO₄ 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.

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