

Supporting Information

Composition-Dependent Electrocatalytic Activity of Cobalt Sulfides for Triiodide Reduction in Dye-Sensitized Solar Cells

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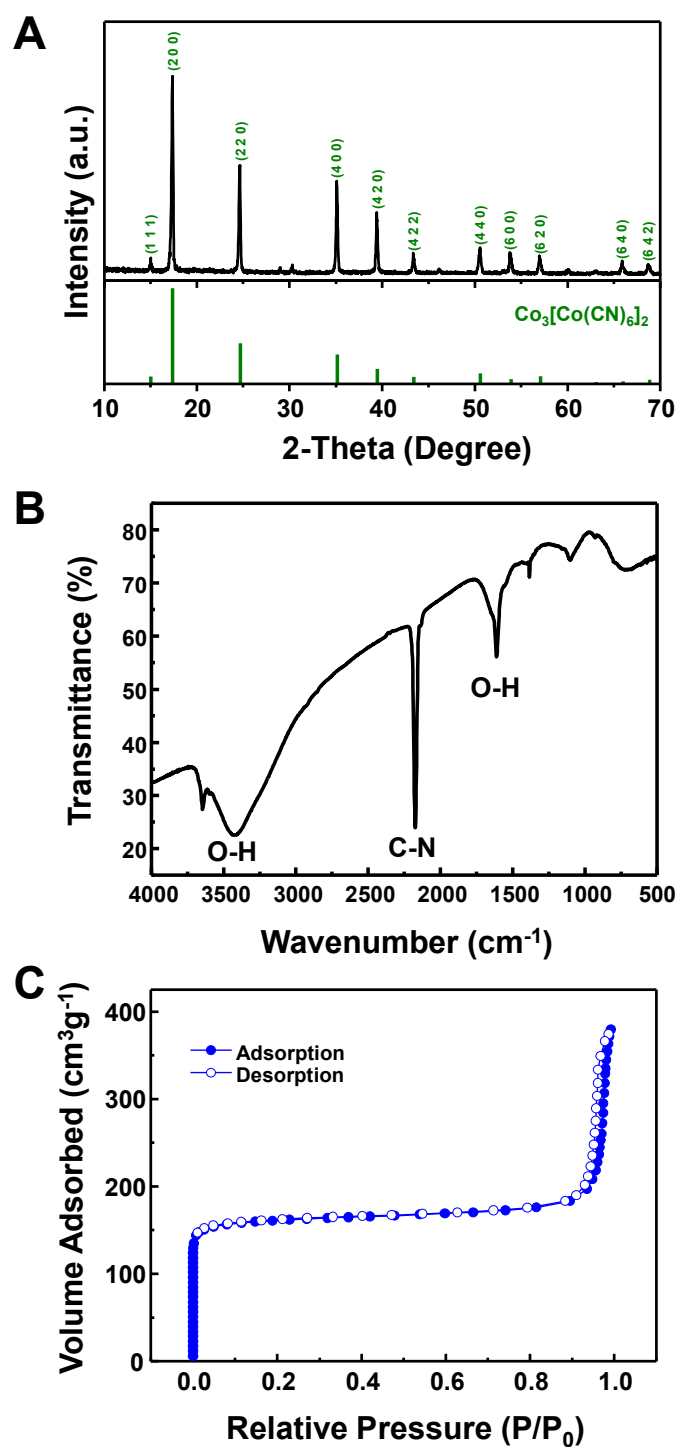


Figure S1. (A) XRD pattern, (B) FT-IR spectrum, and (C) N_2 physisorption isotherm of $\text{Co}_3[\text{Co}(\text{CN})_6]_2$.

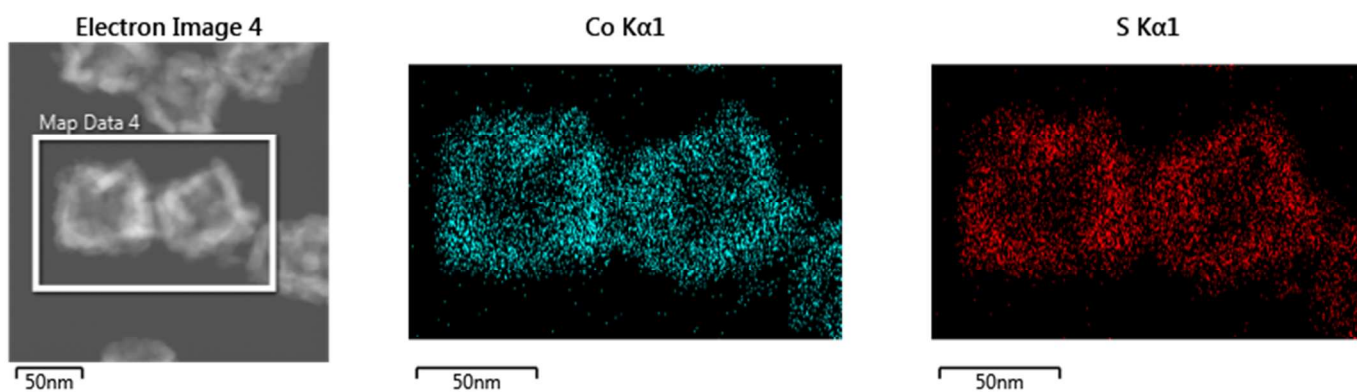


Figure S2. TEM-EDS mapping analysis of $\text{CoS}_x\text{-300}$.

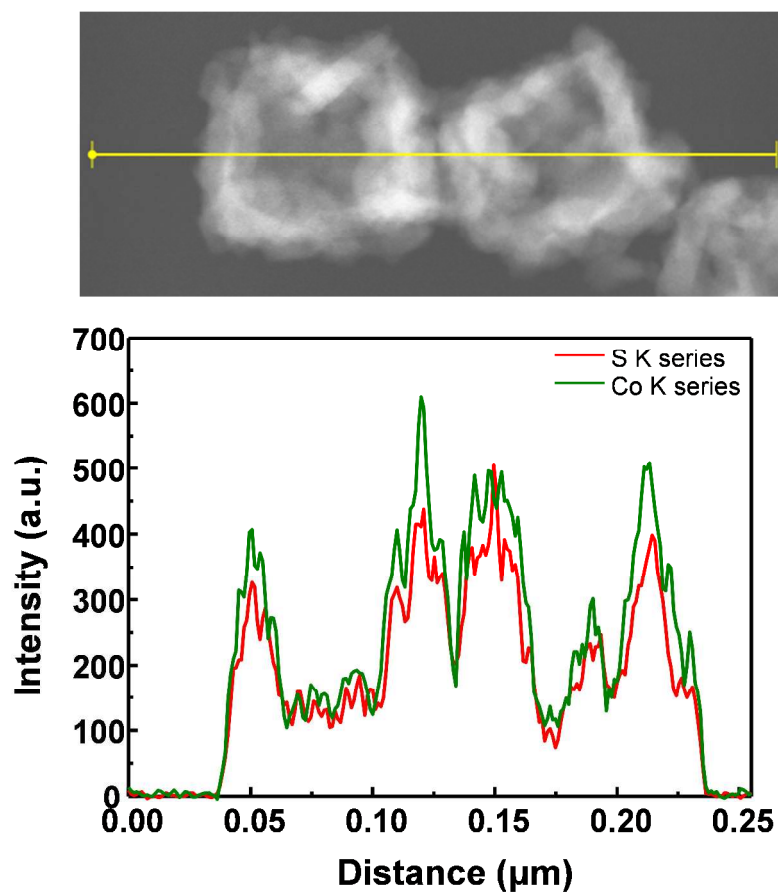


Figure S3. TEM-EDS line analysis of $\text{CoS}_x\text{-300}$.

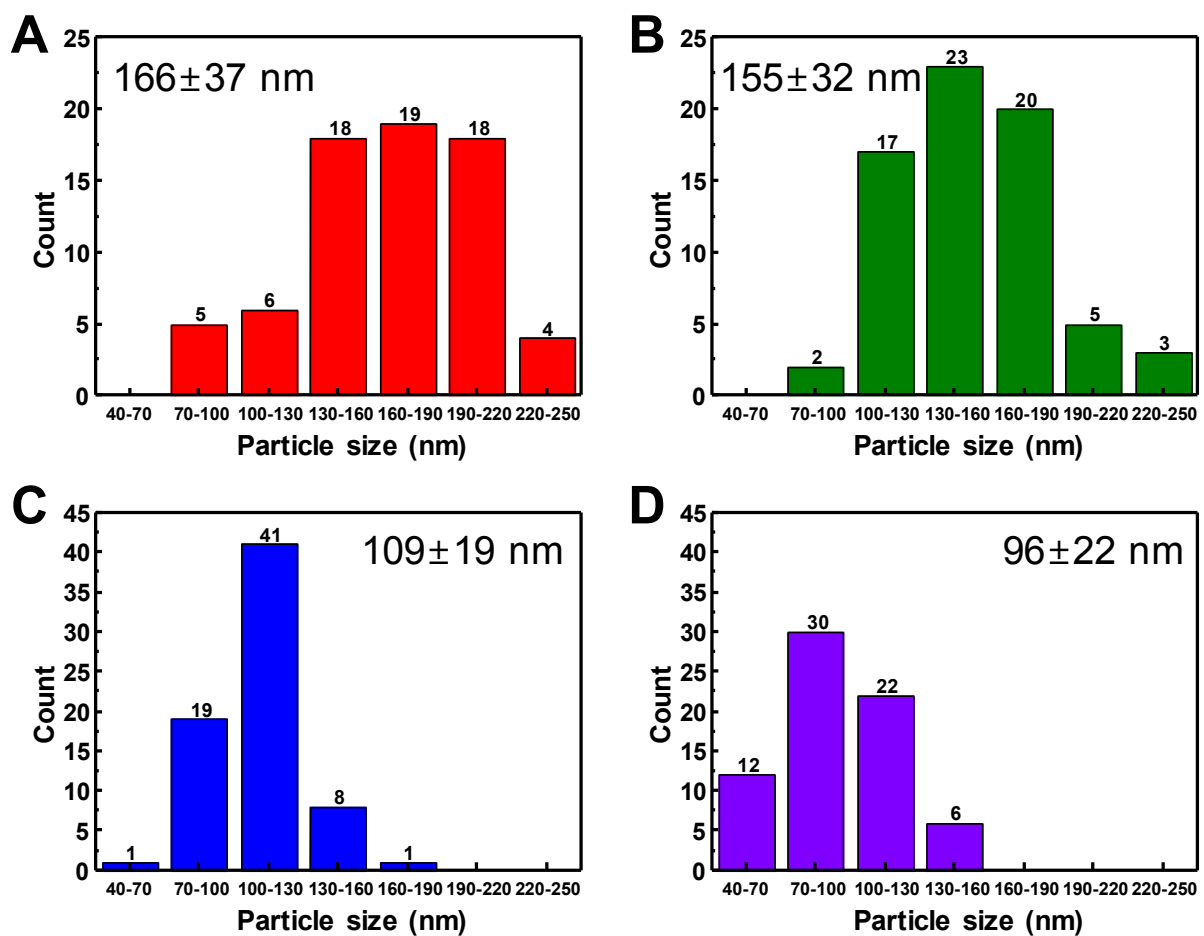


Figure S4. Particle size distribution of (A) $\text{Co}_3[\text{Co}(\text{CN})_6]_2$, (B) $\text{CoS}_x\text{-300}$, (C) $\text{CoS}_x\text{-350}$, and (D) $\text{CoS}_x\text{-400}$.

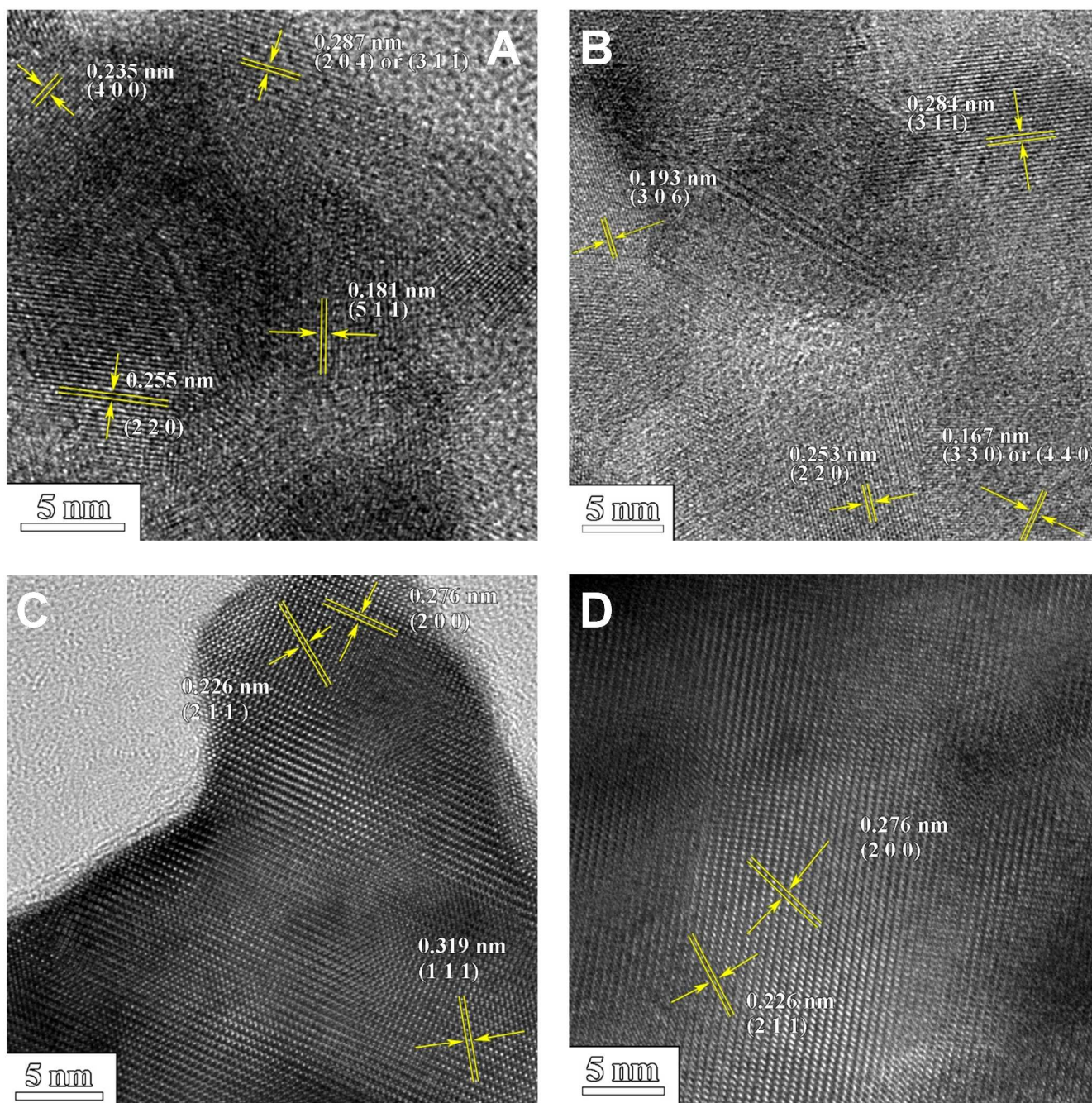


Figure S5. High-resolution TEM images of (A) CoS_x -300, (B) CoS_x -350 from a ruptured hollow nanocube, (C) CoS_x -350 from a deformed solid particle, and (D) CoS_x -400.

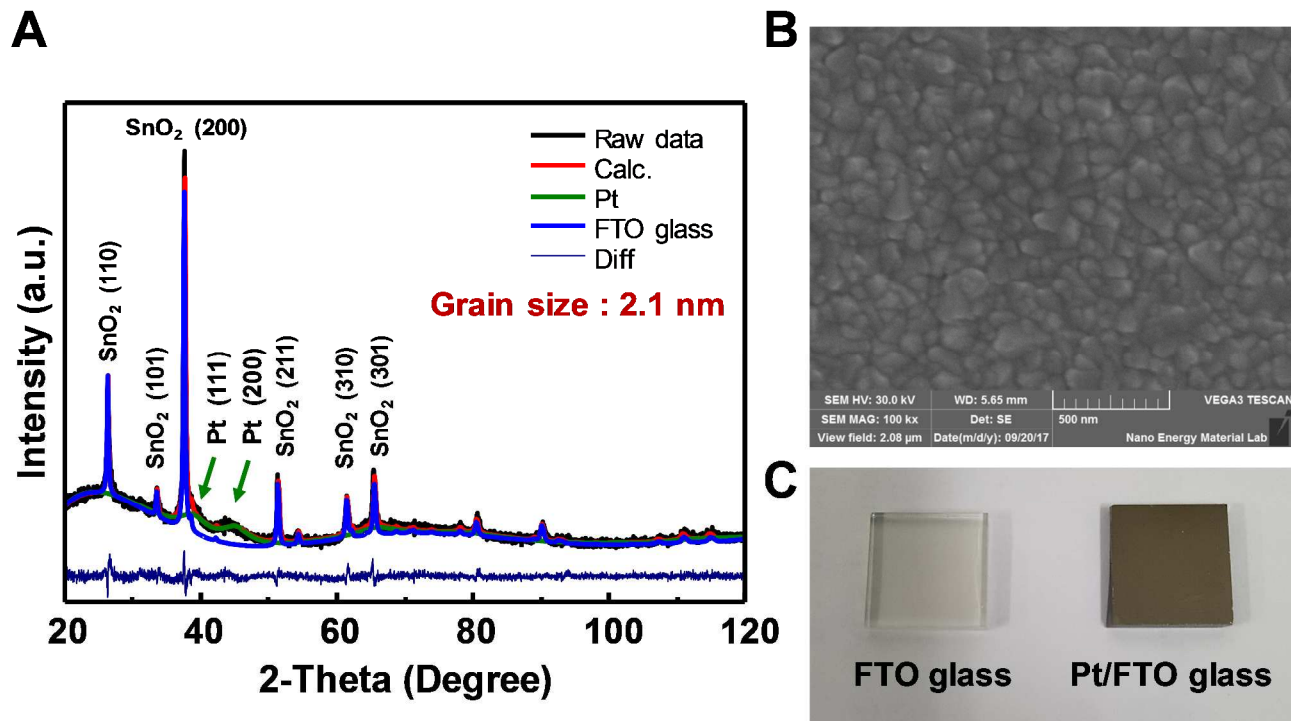


Figure S6. Characterization of Pt sputtered on FTO glass. (A) XRD diffraction pattern, (B) SEM image, and (C) photograph. Note that we tried in vain the direct visualization of Pt particles on FTO film by SEM for its morphology and particle size. Given the crystallite size calculated using the Scherrer equation is as small as 2.1 nm, it is beyond resolution limit. However, the photograph shows a clear difference in color after the Pt sputtering, which proves the deposition of Pt along with the XRD analysis.

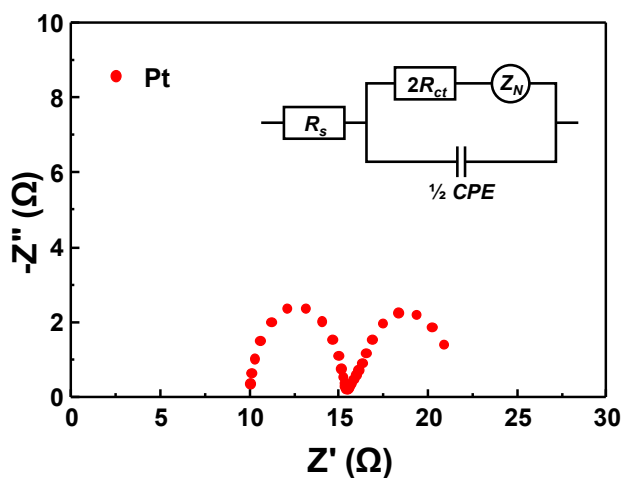


Figure S7. Nyquist plot (inset: equivalent circuit) of a symmetrical dummy cell made of Pt.

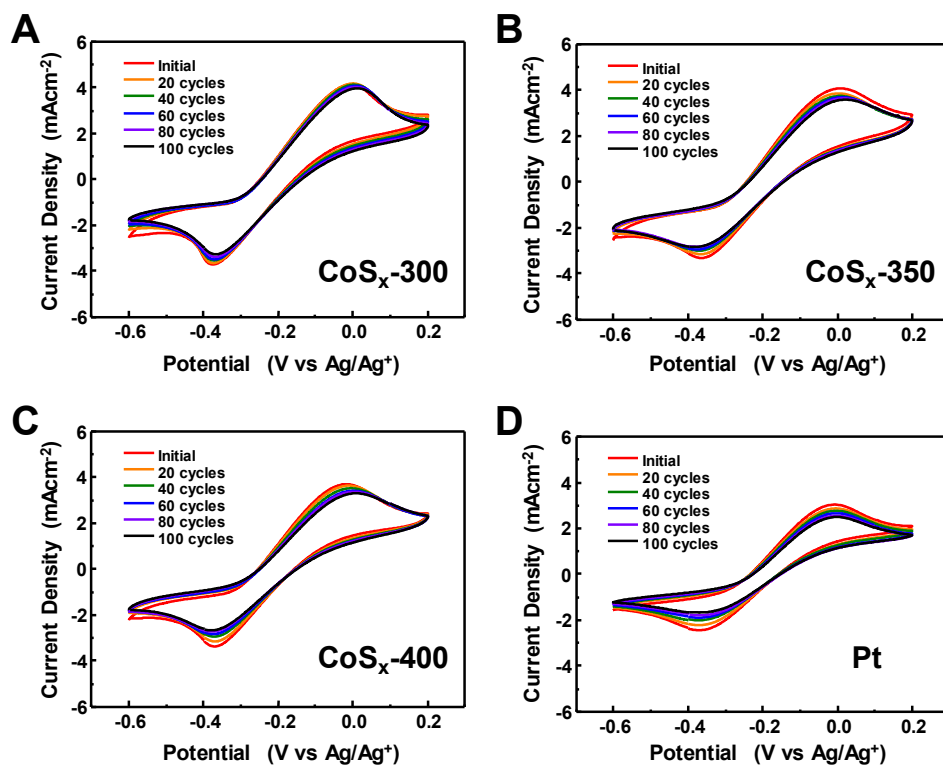


Figure S8. Cyclic voltammograms of CoS_x-300, CoS_x-350, CoS_x-400, and Pt over 100 cycles at a scan rate of 20 mVs^{-1} in an electrolyte containing 50 mM LiI, 10 mM I₂, and 500 mM LiClO₄ in acetonitrile with the Ag/Ag^+ quasi-reversible reference electrode and Pt mesh as the counter electrode.

Table S1. Comparison of PCEs of DSSCs Equipped with Various CoS_x CEs in the Literature.

CoS _x -based Electrocatalyst	V _{oc} (V)	J _{sc} (mAcm ⁻²)	FF	PCE (%)	Dye Used	Reference
NDG/CoS	0.71	20.38	0.74	10.71	N749	Ref. 1
CoS _x -300	0.72	16.9	0.69	8.49	N719	Current work
CoS ₂ on carbon nanocages	0.73	16.9	0.66	8.2	N719	Ref. 2
CoS nanoparticles	0.784	14.7	0.71	8.1	N719	Ref. 3
CoS on MWCNT/Ti	0.751	14.69	0.73	8.05	N719	Ref. 4
CoS nanorods	0.71	16.31	0.66	7.67	N719	Ref. 5
CoS on SnO ₂	0.76	15.6	0.63	7.5	N719	Ref. 6
CoS _{1.0365} nanorods	0.65	18.06	0.65	7.4	N719	Ref. 7
Mixed phase CoS	0.751	15.4	0.642	7.2	N719	Ref. 8
CNT@CoS _{1.097}	0.77	14.26	0.66	7.18	N719	Ref. 9
CoS/MWCNT	0.72	15.96	0.64	6.96	N719	Ref. 10
CoS ₂ spheres	0.71	14.62	0.64	6.78	N719	Ref. 11
CoS ₂ on graphene	0.73	15.12	0.60	6.55	N719	Ref. 12
CoS film	0.75	11.91	0.73	6.5	Z907Na	Ref. 13
CoS film	0.72	14.38	0.61	6.33	N719	Ref. 14

CoS ₂ nanotubes	0.804	11.58	0.658	6.13	N719	Ref. 15
CoS film	0.73	14.17	0.59	6.01	N719	Ref. 16
CoS on graphene	0.67	12.91	0.64	5.54	N719	Ref. 17
CoS ₂ on RGO	0.67	12.87	0.63	5.43	Z907Na	Ref. 18
CoS ₂ nanoflake	0.747	10.13	0.688	5.20	N719	Ref. 19
CoS on graphene	0.72	12.8	0.36	3.42	N719	Ref. 20

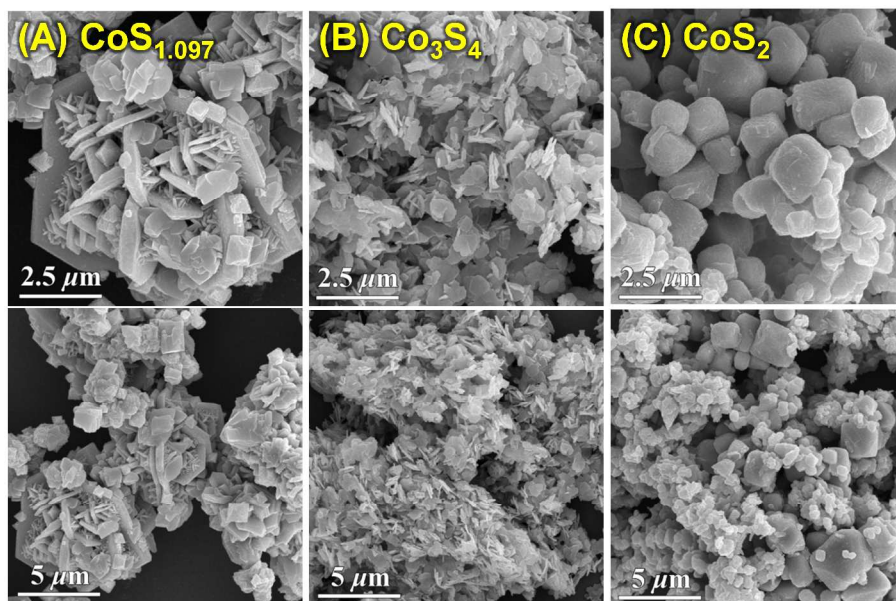


Figure S9. SEM images of (A) CoS_{1.097} (BET surface area: 1.28 m²g⁻¹), (B) Co₃S₄ (BET surface area: 6.98 m²g⁻¹), and (C) CoS₂ (BET surface area: 1.66 m²g⁻¹). CoS_{1.097} was prepared as described in Ref. 9, and Co₃S₄ was prepared by sulfidizing Co₃O₄ under a H₂S gas flow at 400 °C,²¹ and CoS₂ was purchased from Alfa Aesar (#13114).

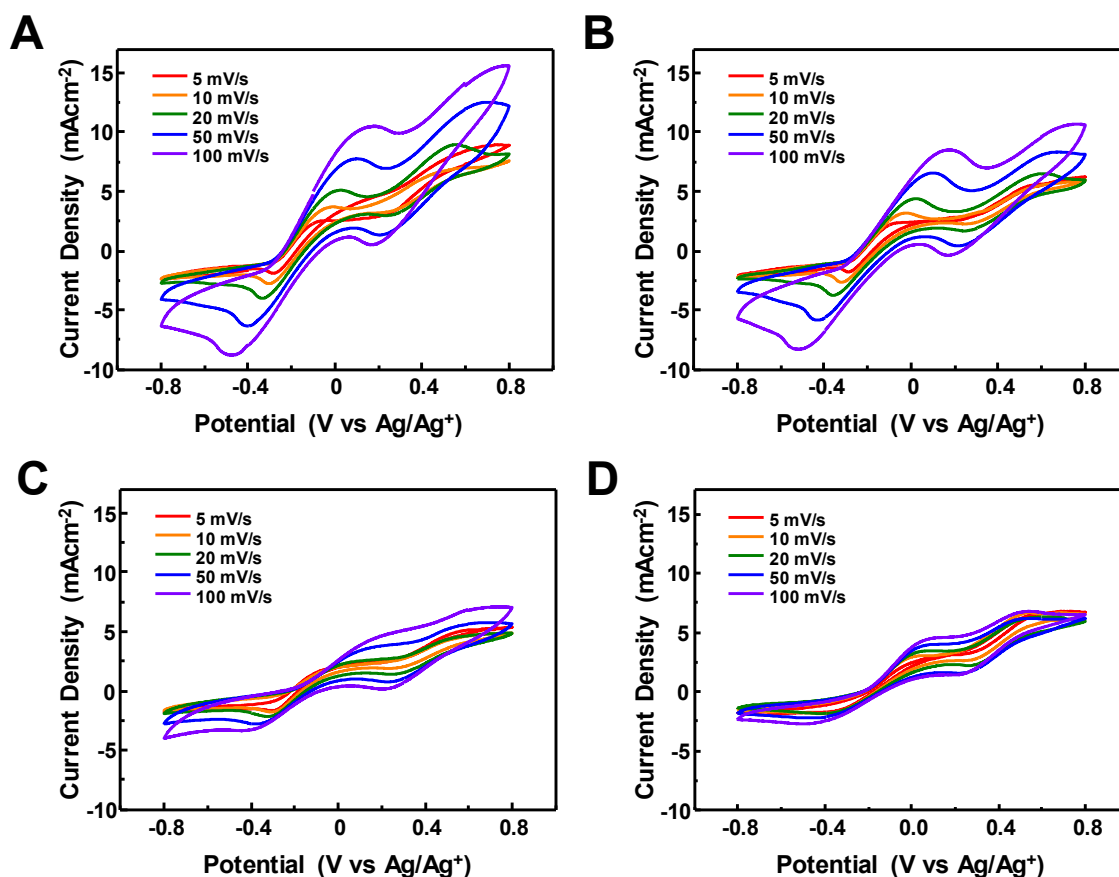
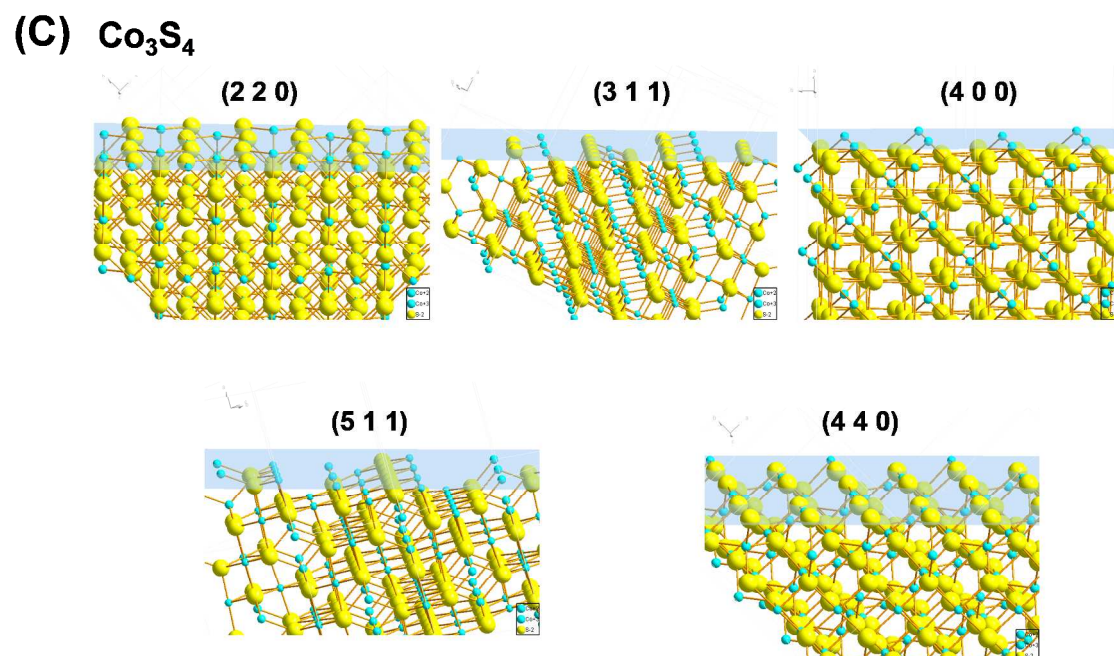
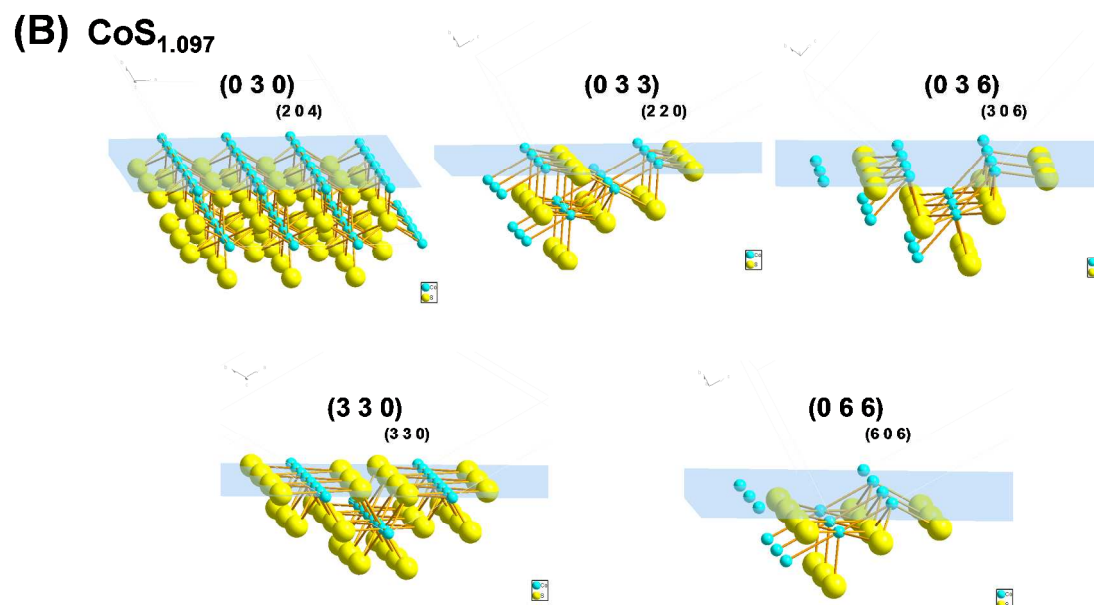
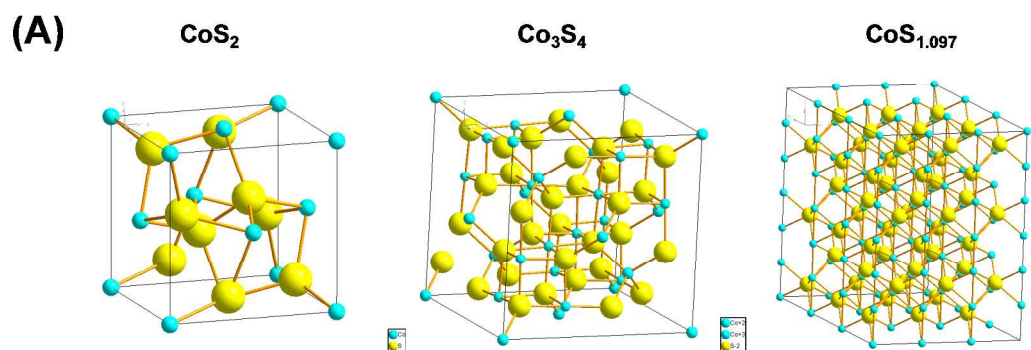


Figure S10. Cyclic voltammograms of (A) $\text{CoS}_{1.097}$, (B) Co_3S_4 , (C) CoS_2 and (D) Pt at various scan rates in an electrolyte containing 50 mM LiI, 10 mM I_2 , and 500 mM LiClO_4 in acetonitrile with the Ag/Ag^+ quasi-reversible reference electrode and Pt mesh as the counter electrode.

Table S2. XPS fitting results of $\text{CoS}_{1.097}$, Co_3S_4 , and CoS_2 .

Catalysts	Co-S (atomic weight%)	Co-S with surface-adsorbed hydroxide species (atomic weight%)	Co-O bonds associated with CoO (atomic weight%)	Co-O bonds associated with $\text{Co}(\text{OH})_x$ (atomic weight%)
$\text{CoS}_{1.097}$	42.9	30.8	2.4	23.9
Co_3S_4	54.2	28.1	1.3	16.4
CoS_2	3.0	18.1	35.1	43.8



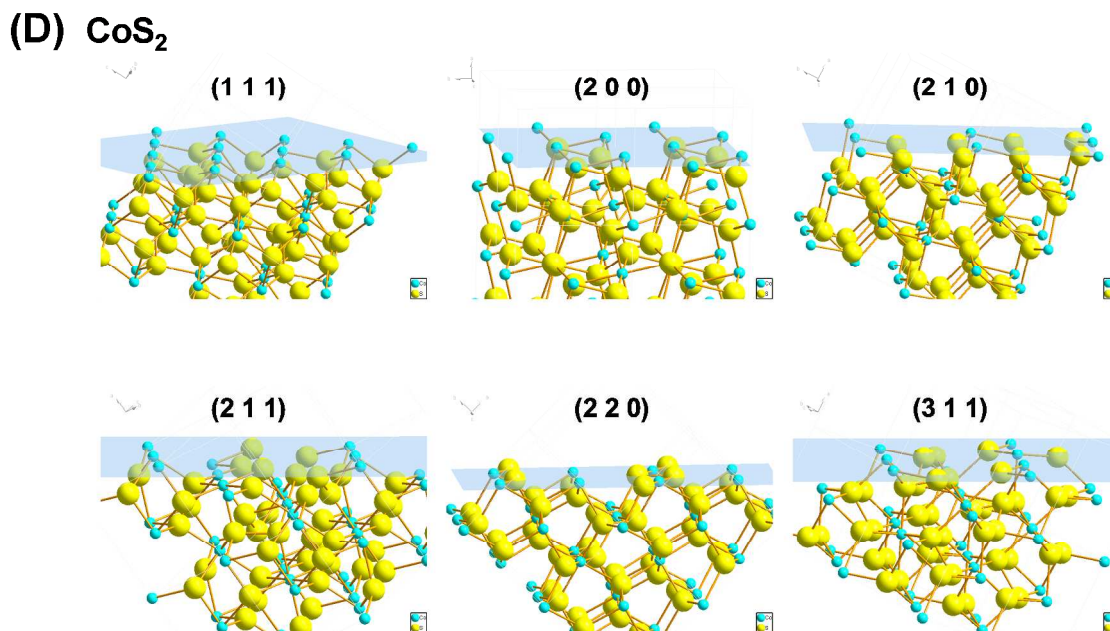


Figure S11. (A) Crystal structure of CoS_{1.097}, Co₃S₄, and CoS₂. Schematic illustrations of major crystal facets that could be found in (B) CoS_{1.097}, (C) Co₃S₄, (D) CoS₂.

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