

Supplementary Information

Thermally induced nanostructuring for the synthesis of core/shell-structured CoO/CoS_x electrocatalyst

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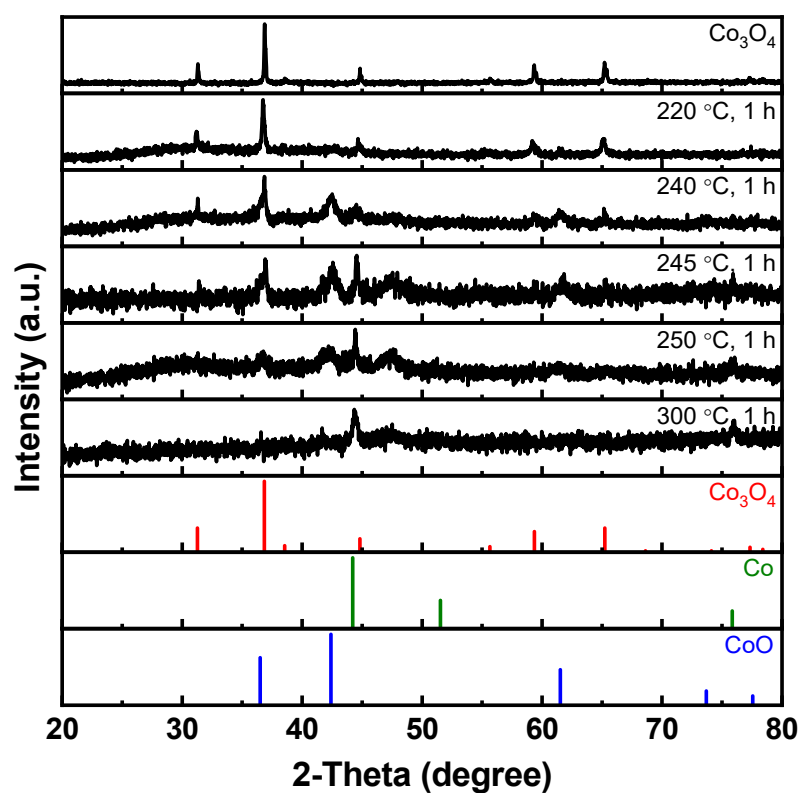


Fig. S1 XRD patterns of intermediates obtained during a hot H_2 treatment of Co_3O_4 at various temperatures for 1 h.

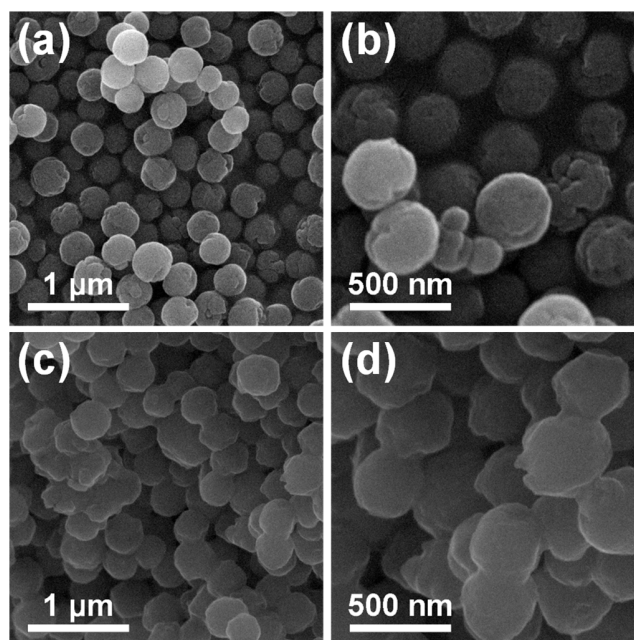


Fig. S2 SEM images of Co_3O_4 (a,b) before and (c,d) after a hot H_2 treatment at 300 °C for 1 h.

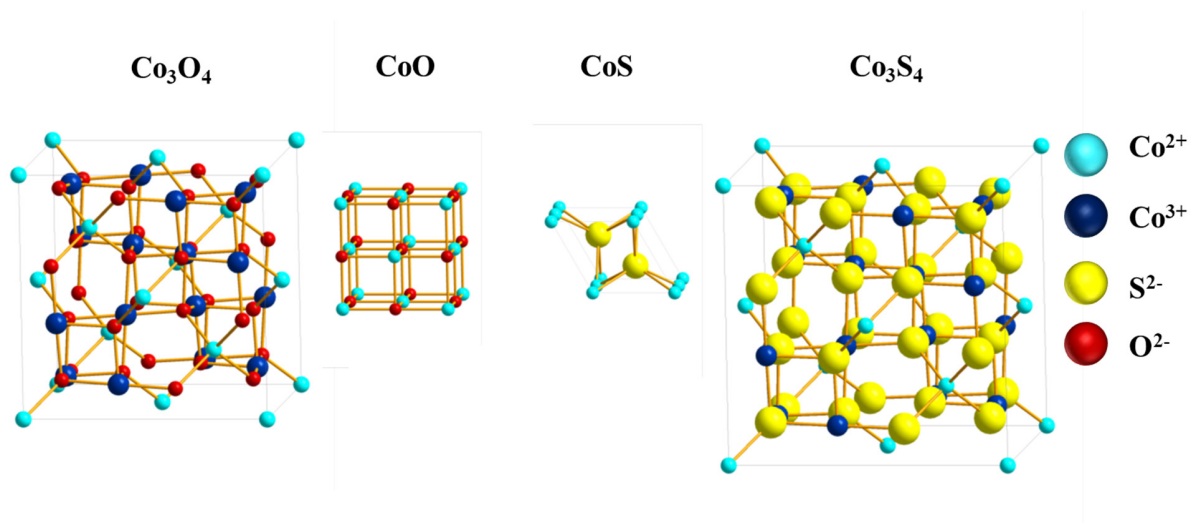
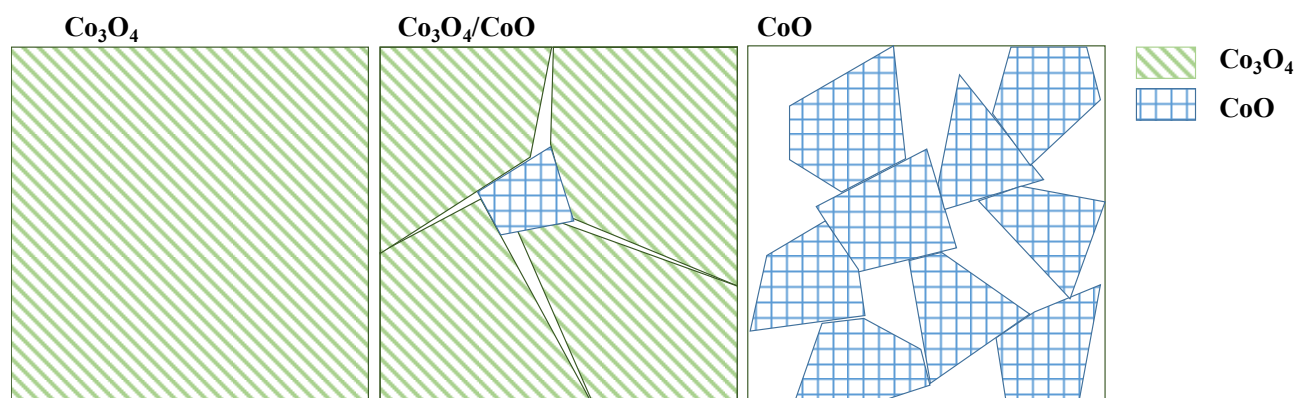


Fig. S3 The crystal structure of cobalt oxides and cobalt sulfides.

Scheme S1 Schematic representation of the grain fracture of Co_3O_4 and the formation of mesoporous CoO with smaller crystallites from bulk Co_3O_4 under a reducing environment of hot NH_3 .



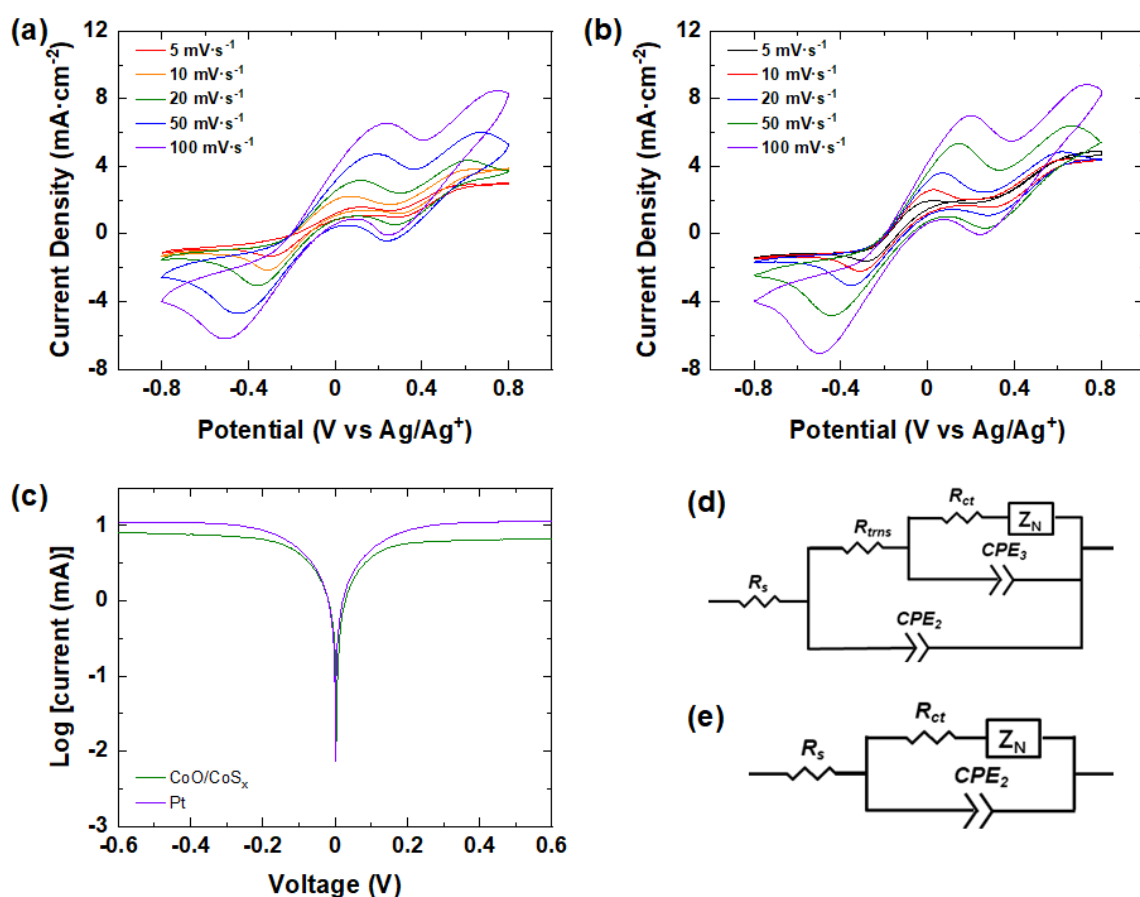


Fig. S4 Cyclic voltammograms of (a) CoO/CoS_x and (b) Pt electrodes at various scan rates. (c) Tafel polarization curves of CoO/CoS_x and Pt counter electrodes. Equivalent circuits used for fitting the Nyquist plots of (d) CoO/CoS_x and (e) Pt counter electrodes. R_s is the equivalent series resistance, R_{ct} is the charge transfer resistance, Z_N is the Nernst diffusion impedance, R_{trns} is the electron transport resistance in the carbon layer, and CPE_2 and CPE_3 are the constant phase elements associated with resistances.

Table S1 Various resistance values extracted from fitting the Nyquist plots of CoO/CoS_x and Pt electrodes. EIS was carried out with symmetric dummy cells.

Counter Electrode	R_s ($\Omega \cdot \text{cm}^2$)	R_{trns} ($\Omega \cdot \text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	Z_N ($\Omega \cdot \text{cm}^2$)
CoO/CoS _x	3.30	0.57	0.91	1.35
Pt	3.31	-	0.97	1.32

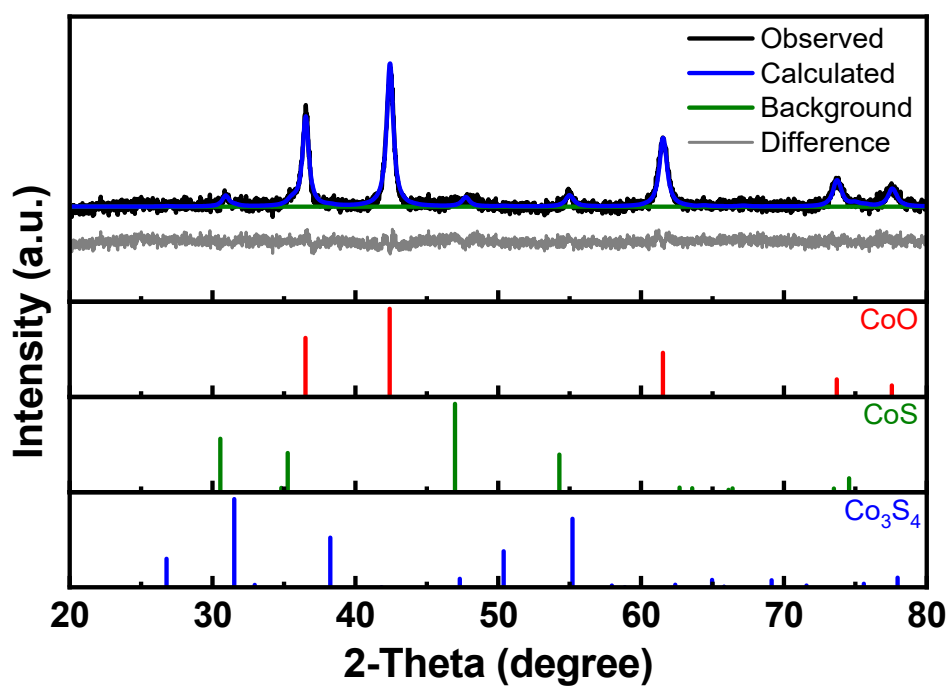


Fig. S5 XRD pattern of CoO/CoS_x and Rietveld refinement result that determines the composition of each component (CoO: 86.2%, CoS: 11.9%, and Co₃S₄: 1.9%).

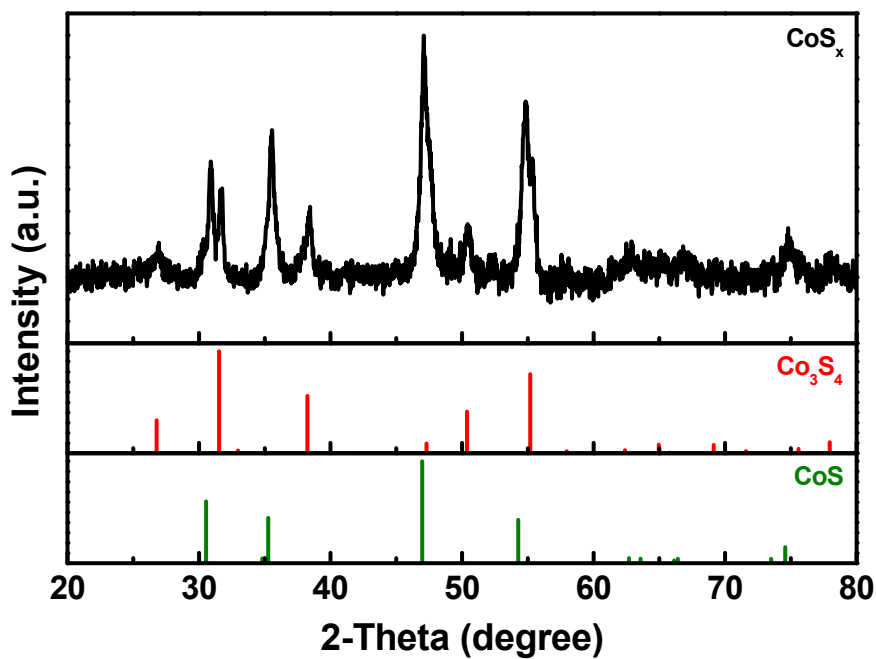


Fig. S6 XRD pattern of CoS_x obtained at 300 °C for 1 h. The compositional percentages of CoS and Co_3S_4 determined by Rietveld refinement were 76.5 and 23.5%, respectively.

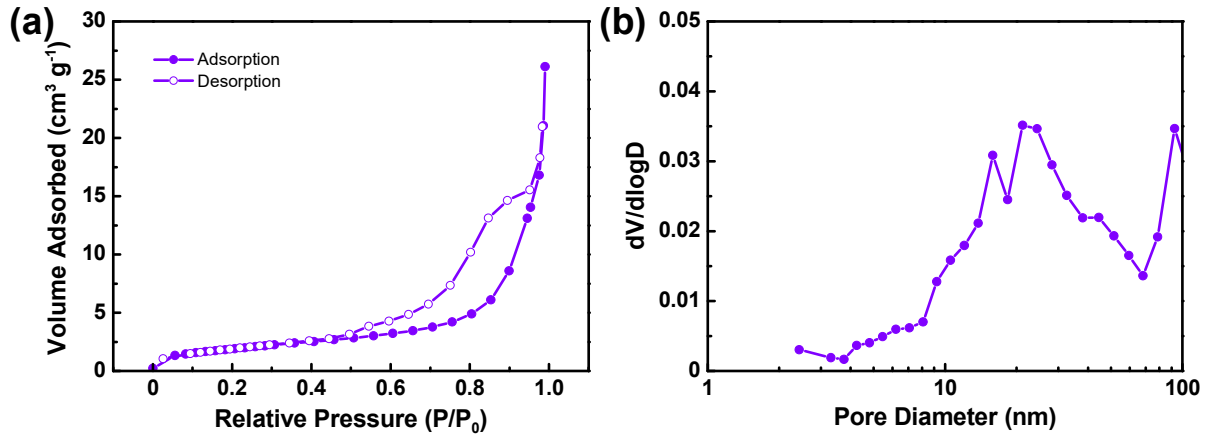


Fig. S7 (a) N_2 physisorption isotherms and (b) pore size distributions of CoS_x . The BET surface area was $7.34 \text{ m}^2 \cdot \text{g}^{-1}$ and the total pore volume was $0.047 \text{ cm}^3 \cdot \text{g}^{-1}$.

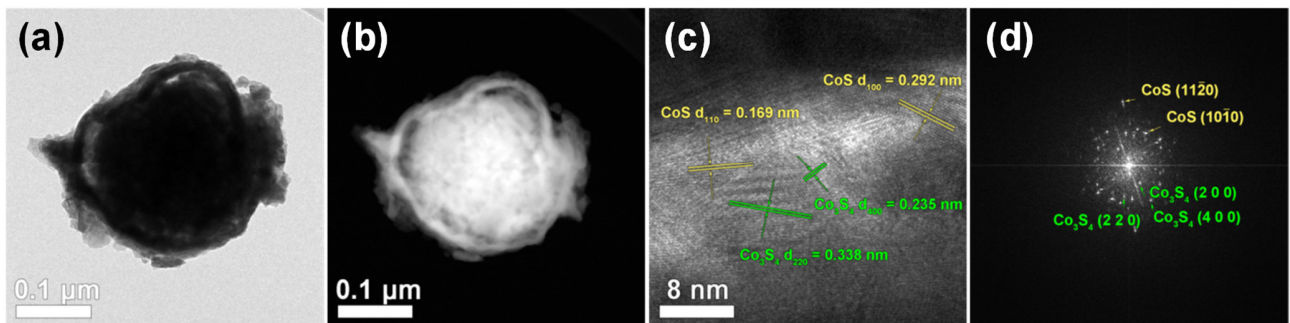


Fig. S8 (a-c) TEM images and (d) FFT patterns of CoS_x .

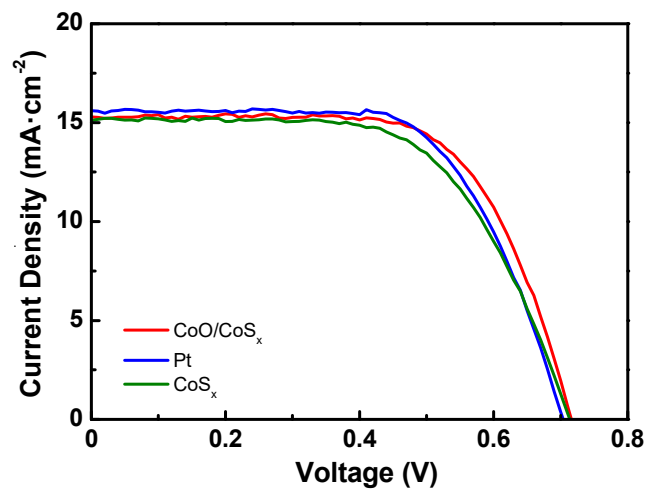


Fig. S9 J – V curve of DSSCs assembled with various CEs made of CoO/CoS_x, Pt, and CoS_x.

Table S2 J – V parameters of DSSCs fabricated with the above CEs.

CE	J_{sc} (mA·cm ²)	V_{oc} (V)	FF	PCE (%)
CoO/CoS _x	15.5 ± 0.3	0.73 ± 0.01	0.66 ± 0.02	7.27 ± 0.06
Pt	15.9 ± 0.2	0.70 ± 0.01	0.65 ± 0.01	7.12 ± 0.05
CoS _x	15.1 ± 0.5	0.71 ± 0.02	0.62 ± 0.03	6.73 ± 0.16

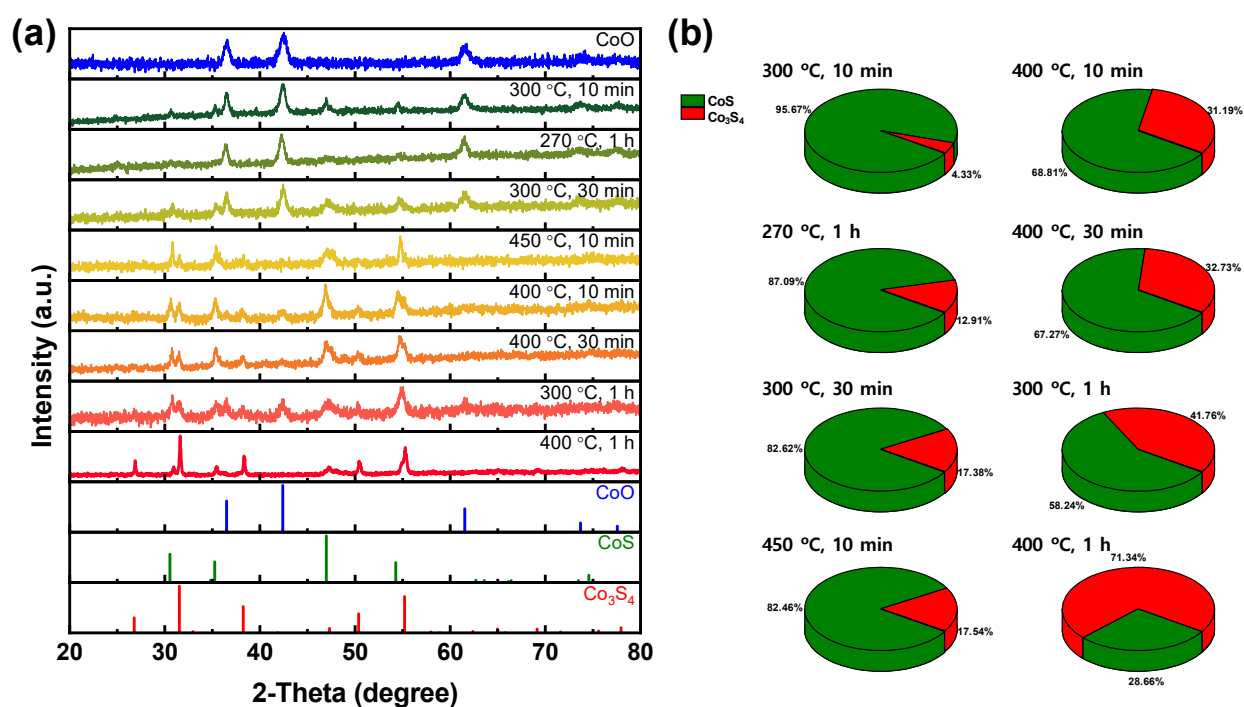


Fig. S10 (a) XRD patterns of CoO/CoS_x obtained at various reaction conditions and (b) CoS and Co₃S₄ composition ratios determined by Rietveld refinement.

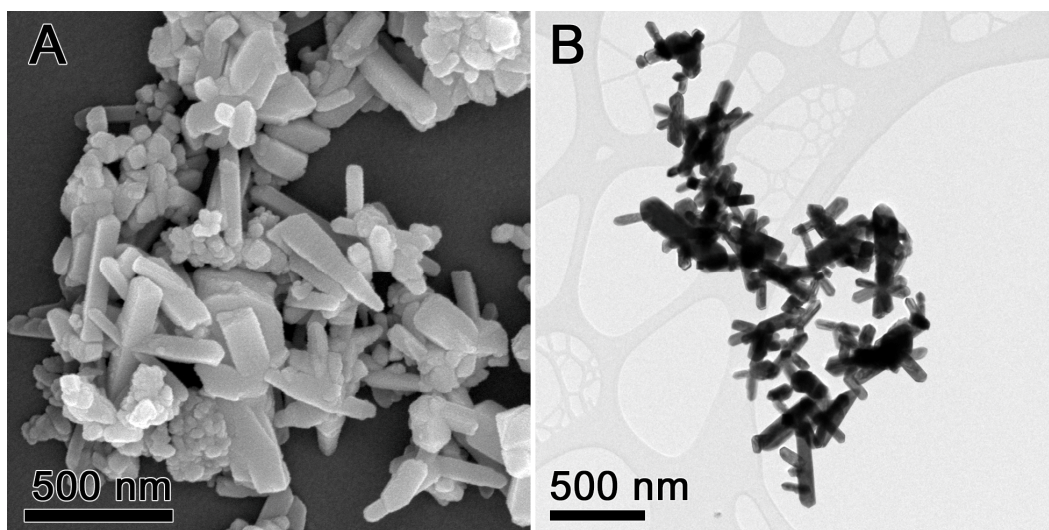


Fig. S11 (a) SEM and (b) TEM images of commercially available IrO₂.

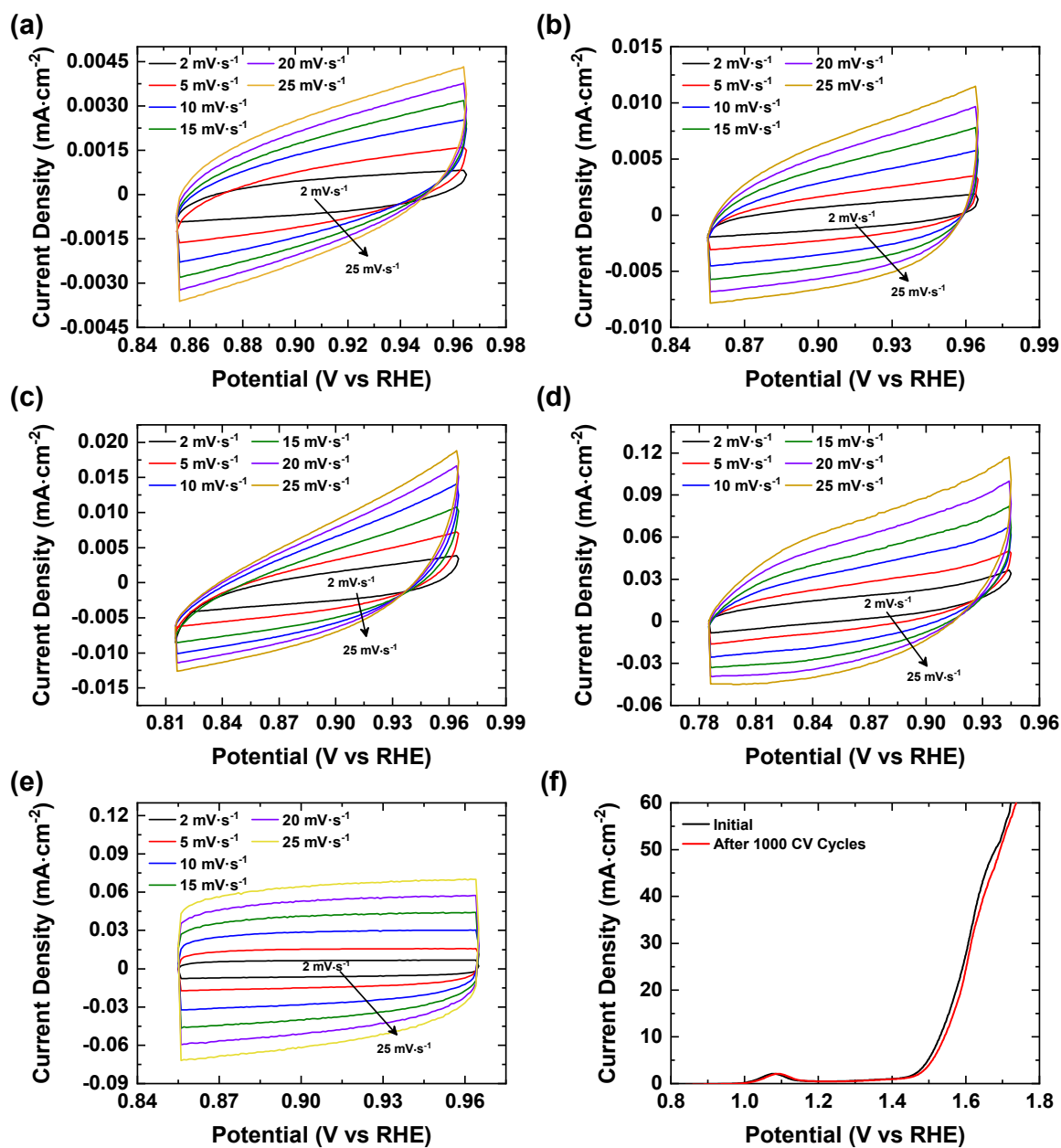


Fig. S12 Cyclic voltammograms of (a) Bare GC, (b) Co_3O_4 , (c) CoO , (d) CoO/CoS_x , and (e) IrO_2 electrodes in 0.1 M KOH at various scan rates to determine the electrochemical double layer capacitance (C_{dl}). (f) Linear scan voltammograms of CoO/CoS_x as an electrocatalyst for OER before and after 1000 CV scans, demonstrating excellent stability of CoO/CoS_x .

Table S3 The ECSA calculations of each catalyst.

Sample	Slope ($\text{mF}\cdot\text{cm}^{-2}$)	C_{dl} ($\text{mF}\cdot\text{cm}^{-2}$)	R_f	ECSA (cm^2)
Bare GC	0.154	0.077	-	-
Co_3O_4	0.427	0.214	2.77	0.54
CoO	0.458	0.229	2.98	0.58
CoO/CoS _x	3.7	1.85	23.99	4.70
IrO_2	4.85	2.425	31.45	6.16

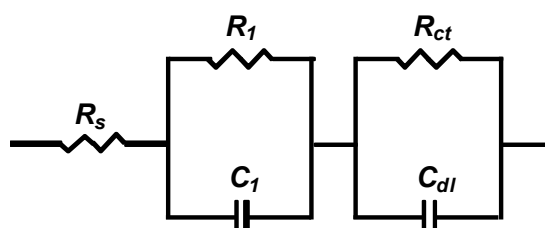


Fig. S13 Equivalent circuit used for fitting the impedance spectra of OER electrocatalysts. R_s represents the solution resistance. R_1 and C_1 denote the diffusion/adsorption of reaction intermediates due to slow diffusion through the reaction interface in the porous electrode. R_2 and C_{dl} are ascribed to the charge transfer resistance the capacitance associated with OER, respectively.

Table S4 Various resistance values extracted by fitting the equivalent circuit in Fig. S5 to the Nyquist plots of various cobalt oxides and IrO_2 when employed as OER electrocatalysts.

Catalyst	R_s ($\Omega\cdot\text{cm}^2$)	R_1 ($\Omega\cdot\text{cm}^2$)	R_{ct} ($\Omega\cdot\text{cm}^2$)
Co_3O_4	2.30	111.82	952.36
CoO	1.19	0.97	185.24
CoO/CoS _x	1.87	0.38	21.77
IrO_2	2.11	1.77	40.68

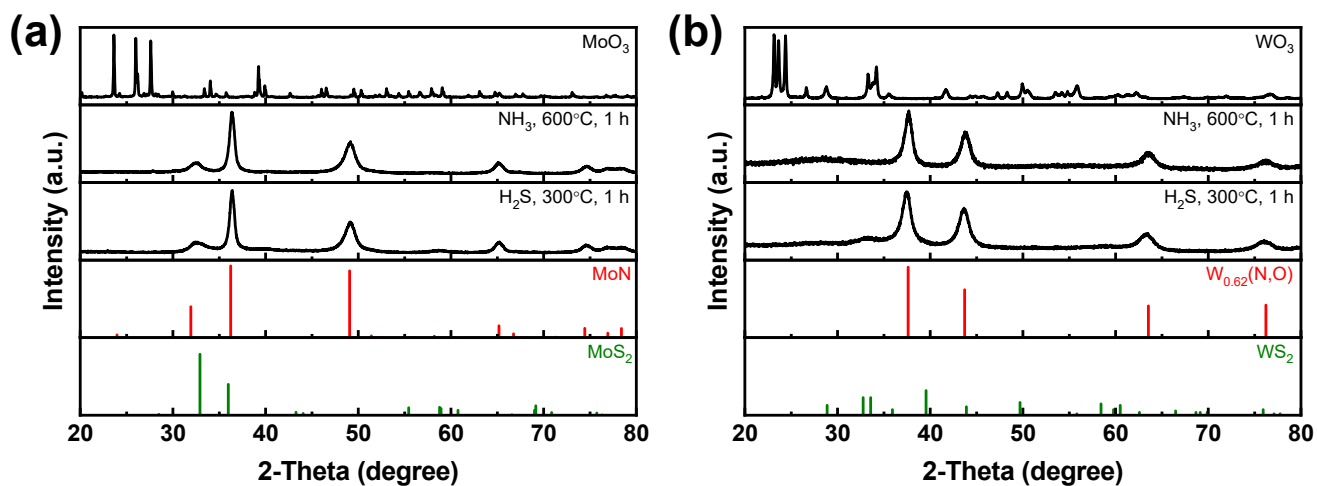


Fig. S14 XRD patterns taken during the synthesis of (a) nanostructured MoN/MoS₂ and (b) nanostructured W_{0.62}(N,O)/WS₂.

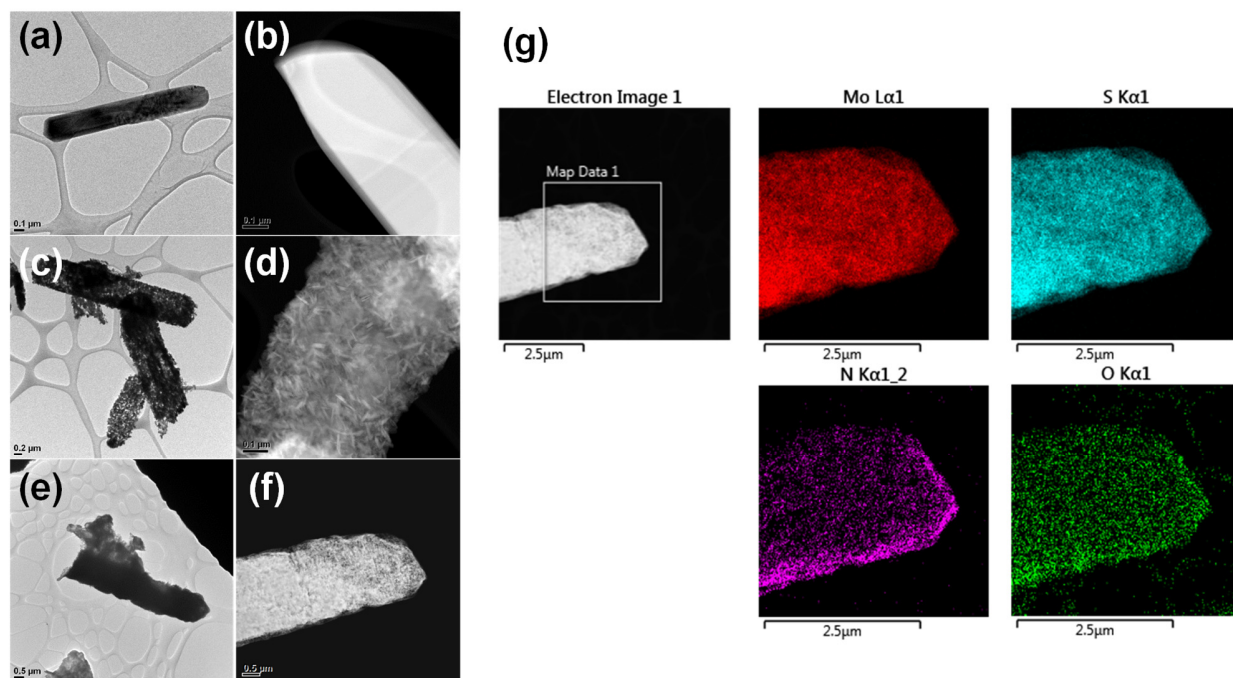


Fig. S15 TEM images of taken during the synthesis of nanostructured MoN/MoS₂: (a,b) MoO₃, (c,d) MoN, (e,f) MoN/MoS₂, and (g) STEM-EDS mapping analysis results of MoN/MoS₂.

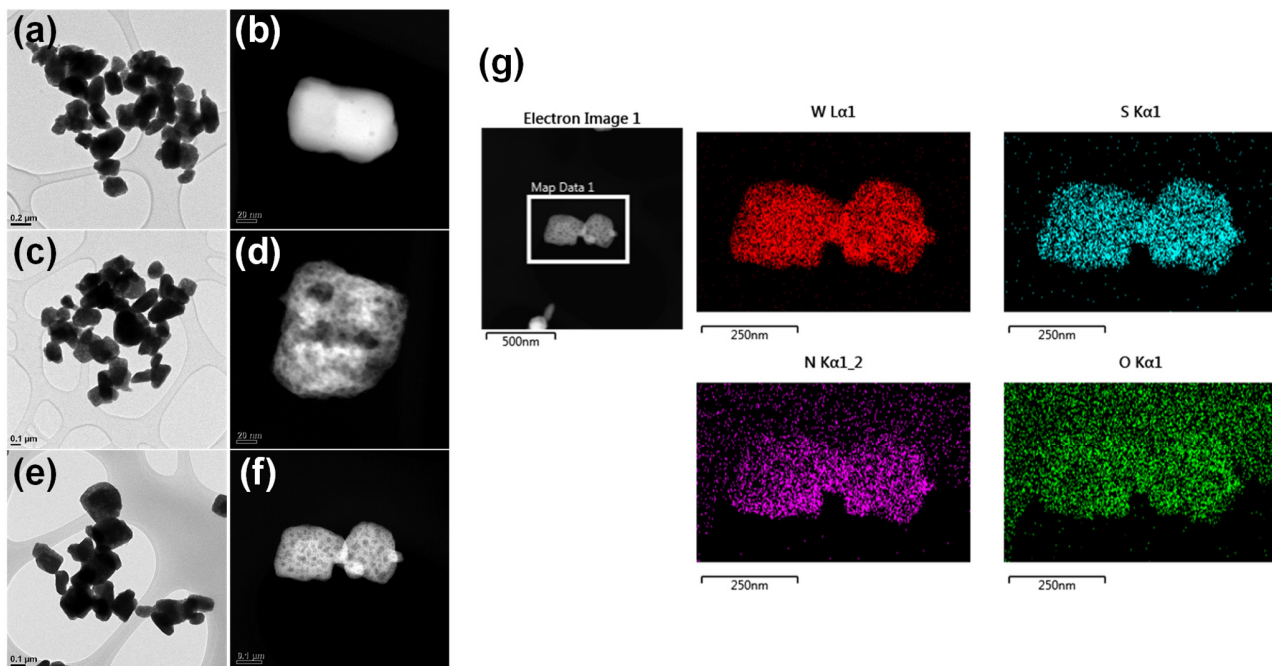


Fig. S16 TEM images of taken during the synthesis of nanostructured $W_{0.62}(N,O)/WS_2$: (a,b) WO_3 , (c,d) $W_{0.62}(N,O)$, (e,f) $W_{0.62}(N,O)/WS_2$, and (g) STEM-EDS mapping analysis results of $W_{0.62}(N,O)/WS_2$.