Supporting Information

Experimental section:

Carbon fiber paper was purchased from Fuel Cell Store *Inc. Ltd*. $CoCl_2 \cdot 6H_2O$. thiourea ($CS(NH_2)_2$), CH_3CH_2OH (~99 wt%), H_2SO_4 (~98 wt%) and HCl (~37 wt%) were purchased from Beijing Chemical Reagent *Co., Ltd*. All the reagents were of A. R. grade and used as received without further purification.

CoS_2/CFP electrode was synthesized by a simple solvothermal method. In a typical procedure, 0.238 g (1 mmol) $CoCl_2 \cdot 6H_2O$ (0.25, 0.5, 1.5 and 2 mmol $CoCl_2 \cdot 6H_2O$ with 5 times S source via hydrothermal synthesis for the control of mass loading) and 0.38 g (5 mmol) $CS(NH_2)_2$ (3 mmol $CS(NH_2)_2$ involed for other solvothermal reaction to synthesize CoS_2 micropyramid array) were dissolved in 36.0 mL distilled water (CoS_2 nanopyramid array) or absolute ethanol (CoS_2 film) and stirred to form a clear solution. Carbon fiber paper (4 cm × 1 cm) was carefully cleaned with plasma (using a YZD08-W3C Plasma Cleaner from Tangshan Yanzhao Institute of Technology) to ensure that the surface of carbon fiber paper was fully hydrophilic. The aqueous solution and carbon fiber paper were transferred to a 40-mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 180 °C for 12 hours, and then allowed to cool to room temperature within 15 min using cooling water. The final product was taken out from the autoclave and subsequently rinsed with distilled water, and dried at 60 °C for 30 minutes. The mass loading of the CoS_2 catalyst layer is determined by using a high precision microbalance (Mettler Toledo ML104, 0.1 mg resolution) to weigh 4 cm × 1 cm CoS_2/CFP electrode.

Scanning electron microscopy (SEM) images were taken on a Zeiss SUPRA55 scanning electron microscope with two accelerating voltages of 200 kV and 50 kV. High-resolution transmission electron microscope (HRTEM) images were obtained

on a JEOL 2010 High-resolution TEM system with operating at 200 kV. X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (Rigaku D/max 2500) at a scan rate of 10 (°)/min in the range from 5 to 90°. The Energy Dispersive X-ray Spectrometer (EDX) and mapping were used to examine the composition of the samples. X-ray photoelectron spectra (XPS) were carried out by using a model of ESCALAB 250 and LabRAM Aramis.

CoS_2 electrocatalysts are grown on carbon fiber paper as a binder-free cathode for HER. Electrochemically inert polyimide tape is employed to define the 1 cm^2 electrode area. All electrochemical measurements were performed on standard three-electrode setup under constant H_2 flow at room temperature. Electrochemical measurements (using a CHI 660E from Shanghai Chenghua Instrument Co., China) were conducted in an electrochemical cell using saturated calomel electrode (SCE, 0.262 V *vs*. reversible hydrogen electrode (RHE) in 0.5 M H_2SO_4 solution, pH=0) as the reference electrode, a 1 cm^2 Pt plate as the counter electrode and the sample as the working electrode. Prior to the test measurements, H_2 was bubbled through the electrolyte solution to eliminate the dissolved oxygen and to maintain a fixed Nernst potential for the H^+/H_2 redox couple. Linear sweep voltammetry with scan rate of 5 $mV \cdot s^{-1}$ was conducted in 0.5 M H_2SO_4 solution. AC impedance measurements were carried out in the same configuration at -0.1 V vs. RHE in the frequency range of 10^{-1} to 10^5 Hz with an AC voltage of 5 mV. The electrochemical double-layer capacitance (EDLC) measurements of CoS_2 electrodes were carried out by using cyclic voltammetry curves for two cycles between -0.05 and -0.15 V vs. SCE with scanning rates of 5, 10, 15, 20, 25 and 30 mV/s. The current densities at -0.1 V vs. SCE and the corresponding scanning rates were used to calculate the EDLC value (the slope of current density-scan rate plots), which served as an estimate of the effective electrochemically active surface area (ECSA) of the solid-liquid interface. The cycling stability of CoS_2 electrodes were carried out by using

cyclic voltammetry curves for 1000 and 2000 cycles between 0.2 and -0.3 V vs. RHE with scanning rate of 30 mV/s. The long-term stability of CoS_2 electrodes were carried out by using current-time curve with a time of 10 hours in a fixed potential. The same electrochemical measurements were conducted in 1.0 M potassium phosphate buffer solution (PBS, pH=7) and 1.0 M KOH solution (pH=14) using SCE as the reference electrode and a Pt plate as the counter electrode. Potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value of (0.262 + 0.059pH) V. All the potentials reported in our manuscript are against RHE.

Figures:

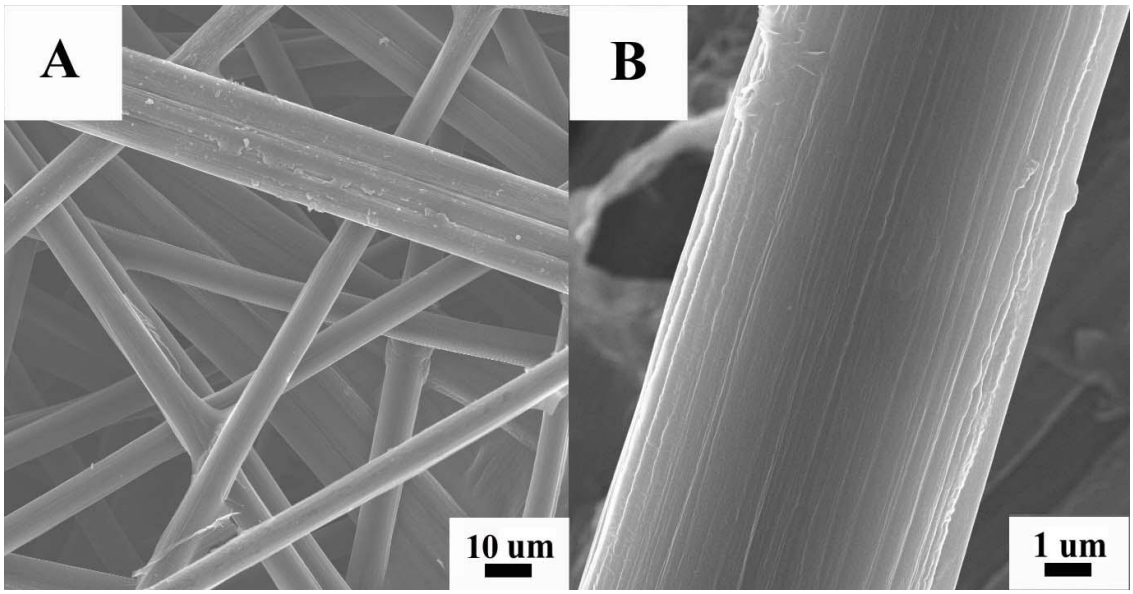

Figure S1: (A) Low-magnification and (B) high-magnification SEM images of pure 3D porous carbon fiber paper with simple cleanness.

Table S1. Comparison of mass loading for CoS_2 electrodes with different morphologies.

Sample	Mass loading of CoS_2 catalyst			Average mass loading (mg/cm^2)
CoS_2 micropyramid array	3.7 mg/4 cm^2	3.8 mg/4 cm^2	4.0 mg/4 cm^2	0.958
CoS_2 nanopyramid array	2.4 mg/4 cm^2	2.6 mg/4 cm^2	2.5 mg/4 cm^2	0.625
CoS_2 film	4.6 mg/4 cm^2	4.3 mg/4 cm^2	4.5 mg/4 cm^2	1.117

Table S2. Comparison of mass loading for CoS_2 NPA electrodes with different initial concentrations of raw materials.

$CoCl_2$ (mmol)	**Thiourea (mmol)**	**Mass loading of CoS_2 catalyst**			**Average mass loading (mg/cm^2)**
0.25	**1.25**	**2.0 mg/4 cm^2**	**1.8 mg/4 cm^2**	**1.8 mg/4 cm^2**	**0.467**
0.5	**2.5**	**2.3 mg/4 cm^2**	**2.4 mg/4 cm^2**	**2.4 mg/4 cm^2**	**0.592**
1	**5**	**2.4 mg/4 cm^2**	**2.6 mg/4 cm^2**	**2.5 mg/4 cm^2**	**0.625**
1.5	**7.5**	**3.8 mg/4 cm^2**	**3.9 mg/4 cm^2**	**3.9 mg/4 cm^2**	**0.967**
2	**10**	**3.9 mg/4 cm^2**	**4.2 mg/4 cm^2**	**4.3 mg/4 cm^2**	**1.033**

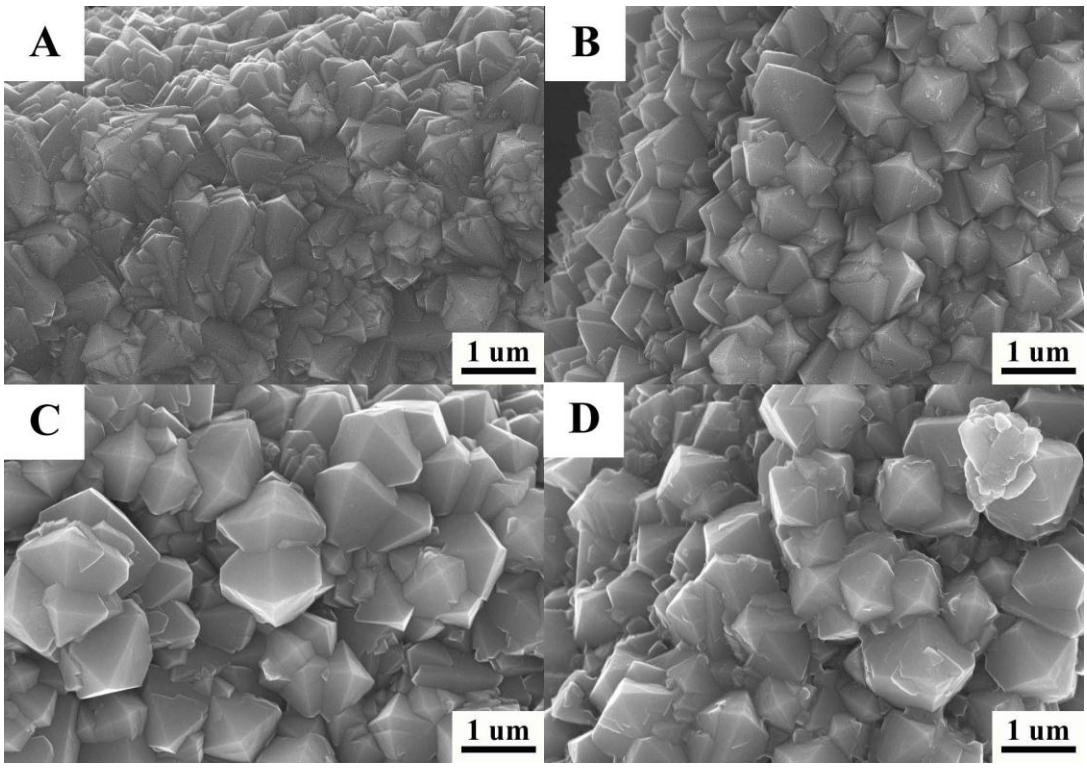

Figure S2: SEM images of CoS_2 NPA electrode with different mass loadings of (A) 0.467, (B) 0.592, (C) 0.967 and (D) 1.033 mg/cm^2.

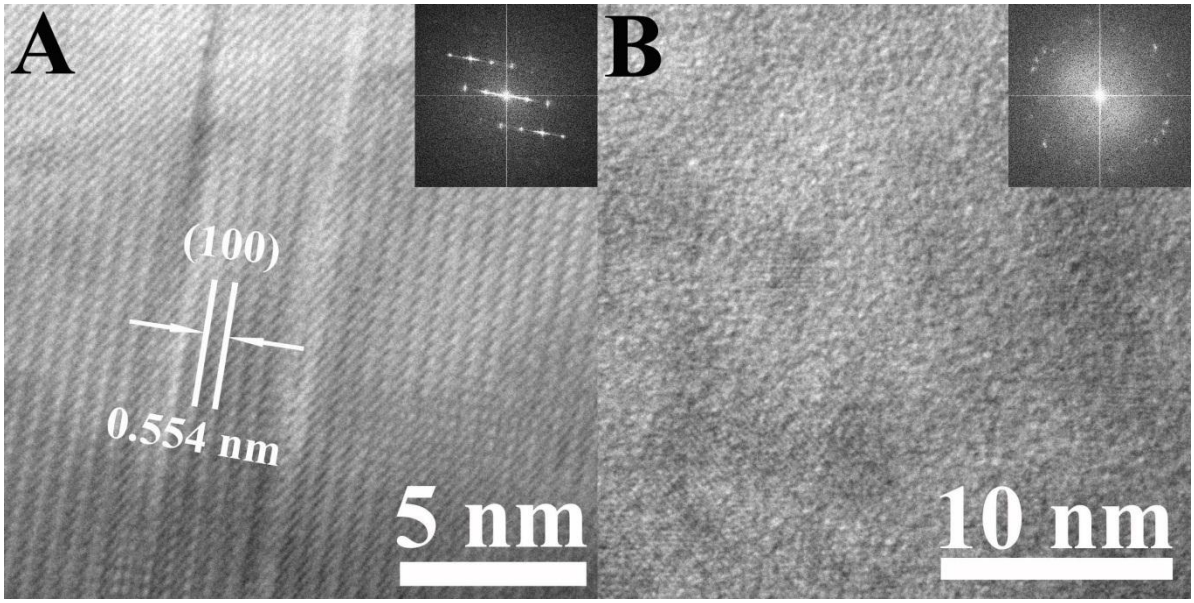

Figure S3: HRTEM images of the as-synthesized CoS_2 (A) micropyramid array and (B) film products. Inset: the corresponding fast Fourier transforms.

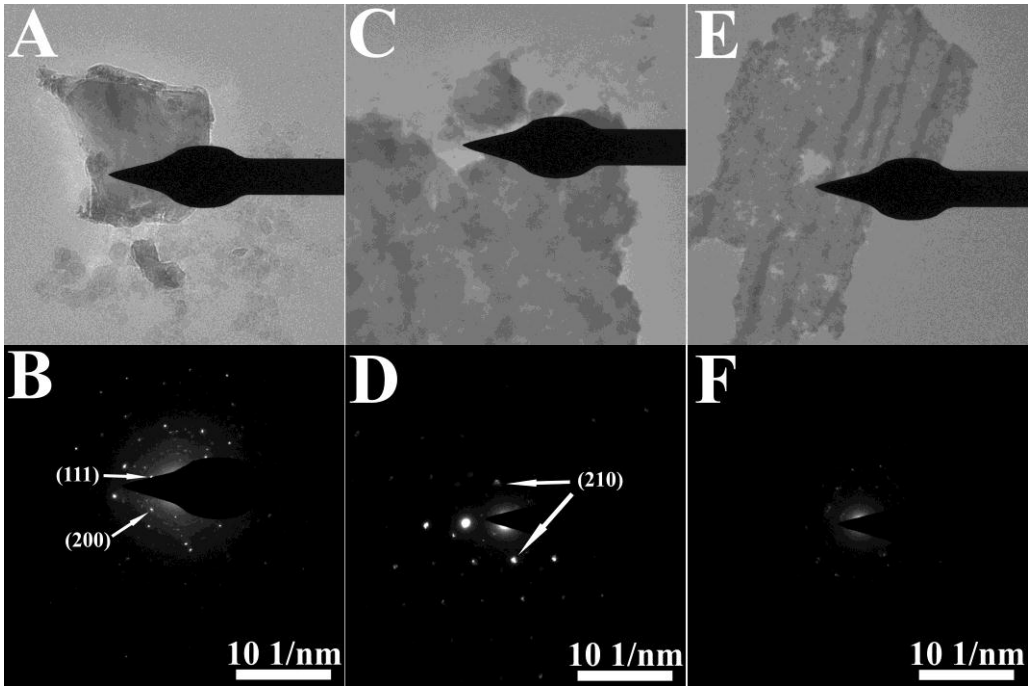

Figure S4: The TEM images and SAED patterns for the as-synthesized CoS_2 (A and B) nanopyramid array, (C and D) micropyramid array and (E and F) film products.

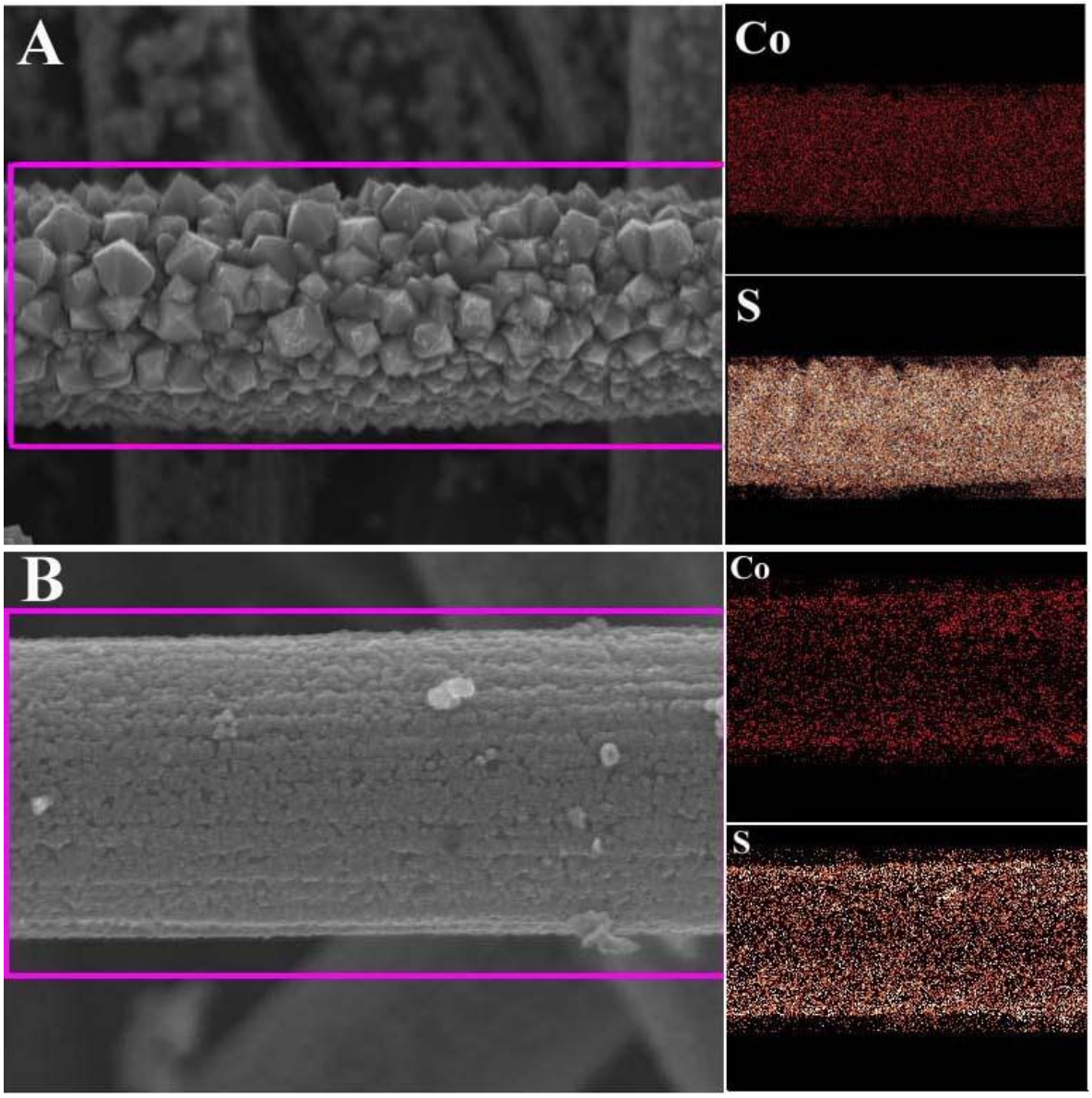

Figure S5: Elemental mappings of (A) CoS_2 micropyramid array and (B) CoS_2 film, red mapping: Co element, yellow mapping: S element.

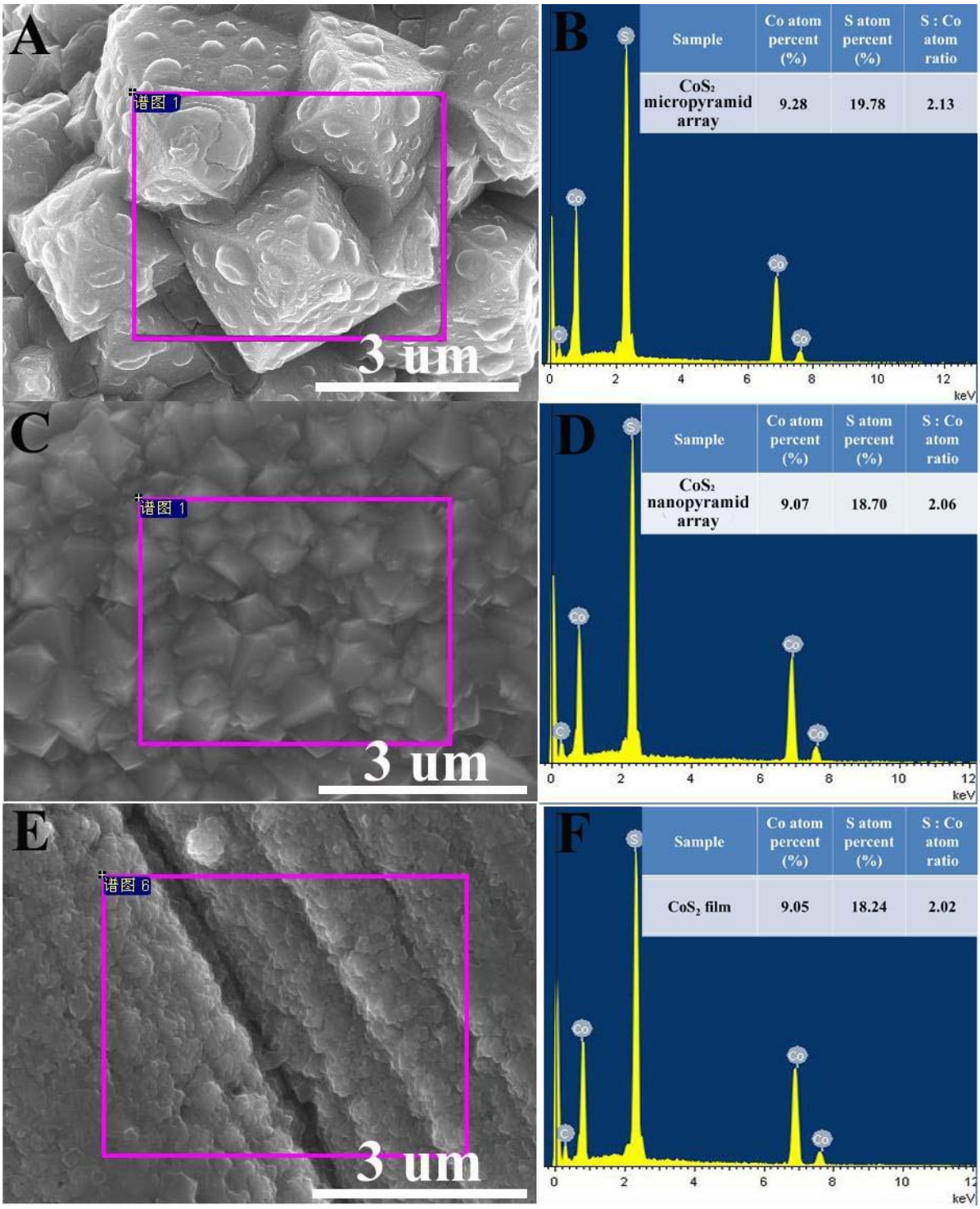

Figure S6: SEM images and EDX spectra of CoS_2 on carbon fiber paper with (A and B) micropyramid array, (C and D) nanopyramid array and (E and F) film. The inset is the corresponding atom percentage of different elements.

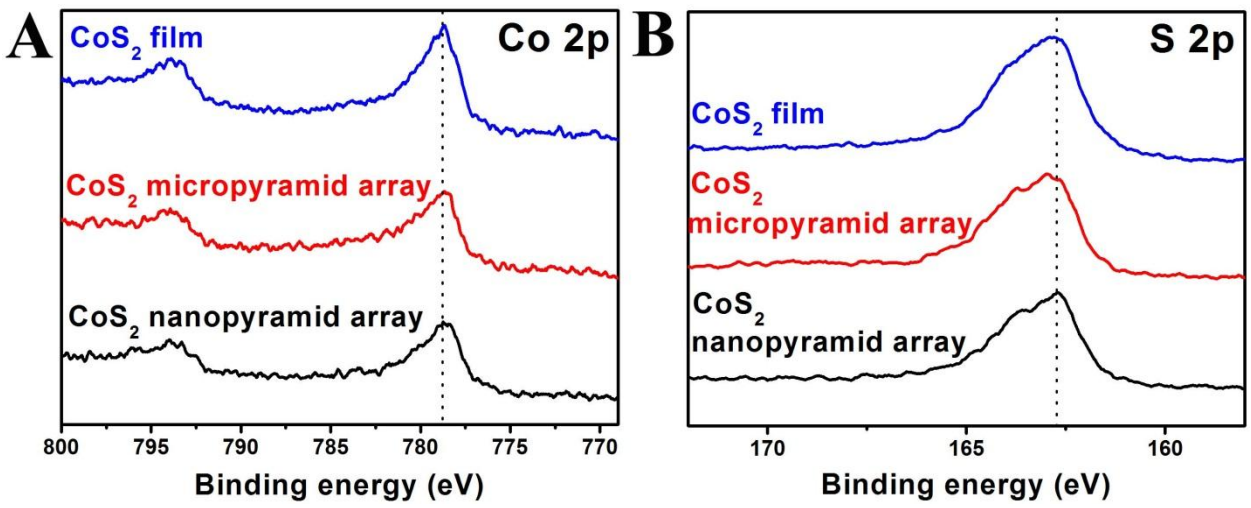

Figure S7: XPS spectra of the (A) Co 2p and (B) S 2p regions for as-synthesized CoS_2/CFP samples with micropyramid array, nanopyramid array and film.

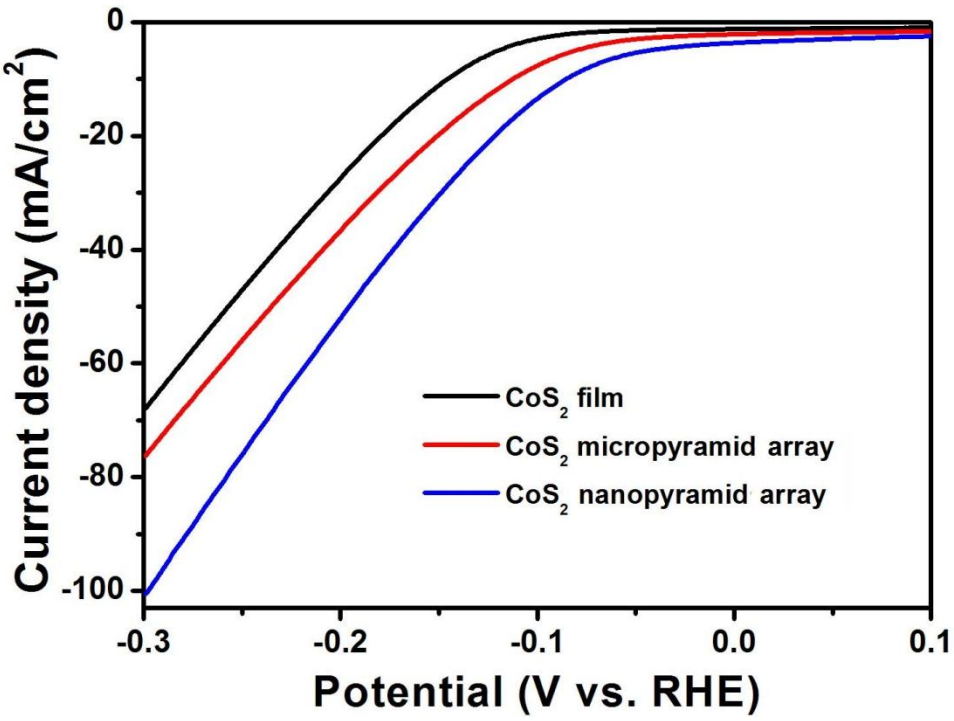

Figure S8: Polarization curves of CoS_2 electrodes with different morphologies. Scan rate: 5 mV/s.

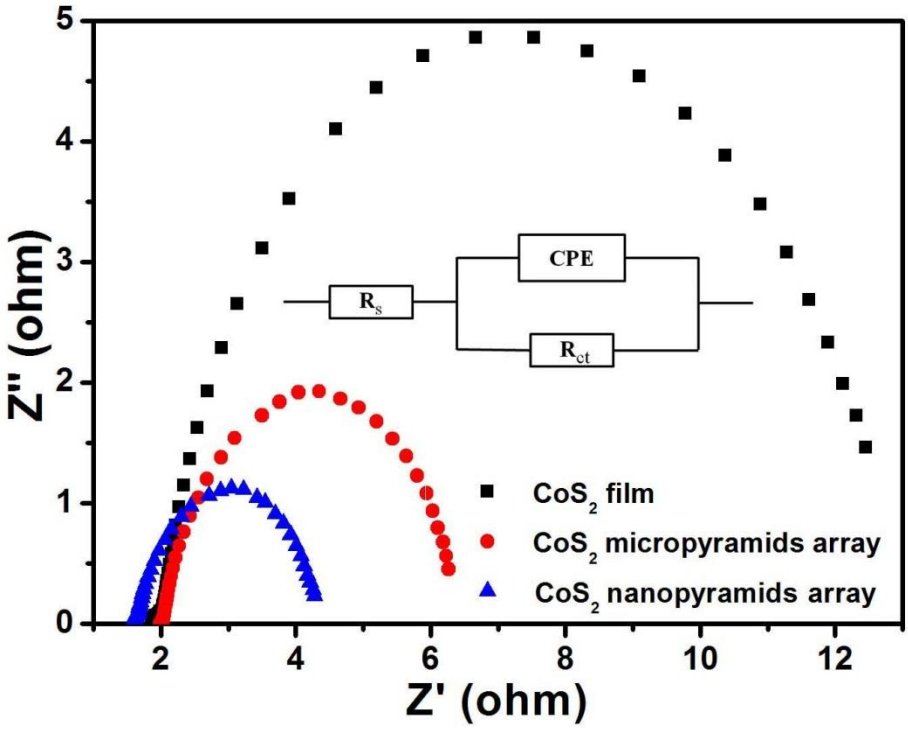

Figure S9: Nyquist plots of CoS_2 electrodes with different morphologies, and (inset) electrical equivalent circuit used to model the systems of all investigated samples.

Table S3. Comparison of solution resistances (R_s) and charge transfer resistances (R_{ct}) for CoS_2 electrodes with different morphologies.

Sample	R_s (Ω)	R_{ct} (Ω)
CoS_2 micropyramid array	**1.99**	**2.21**
CoS_2 nanopyramid array	**1.58**	**1.41**
CoS_2 film	**1.87**	**5.62**

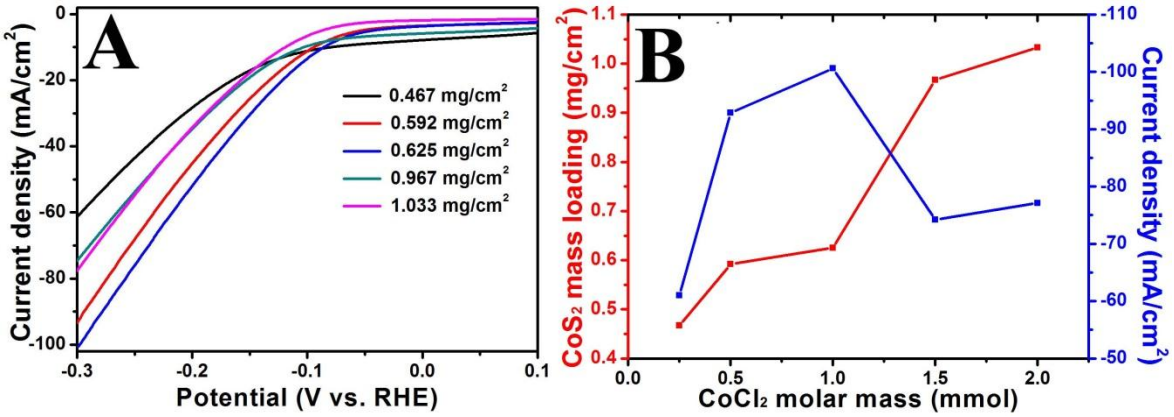

Figure S10: (A) Polarization curves of CoS_2 NPA electrodes with different mass loadings. Scan rate: 5 mV/s. (B) Curves plotting the dependence of CoS_2 mass loading and current density at -300 mV vs. RHE for different $CoCl_2$ concentrations.

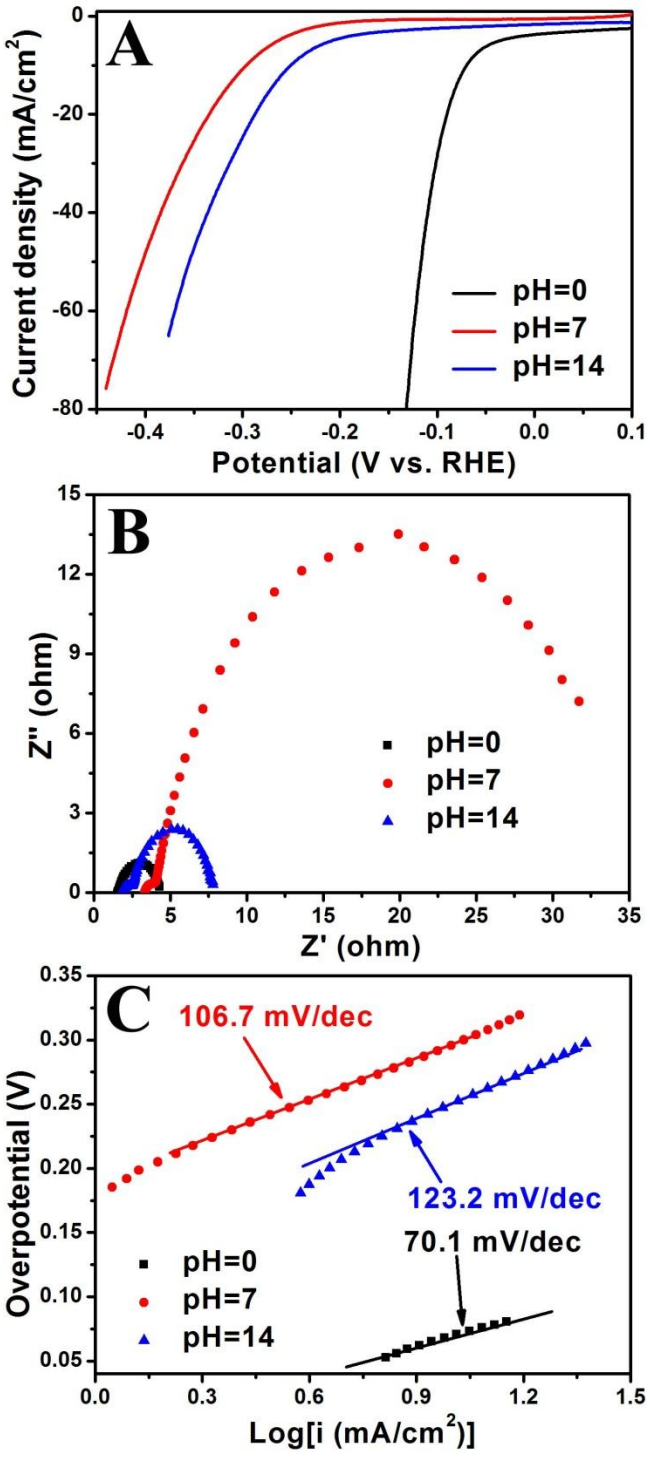

Figure S11: (A) Polarization curves, (B) Nyquist plots and (C) Tafel plots of CoS_2 nanopyramid array in different pH-value electrolytes.

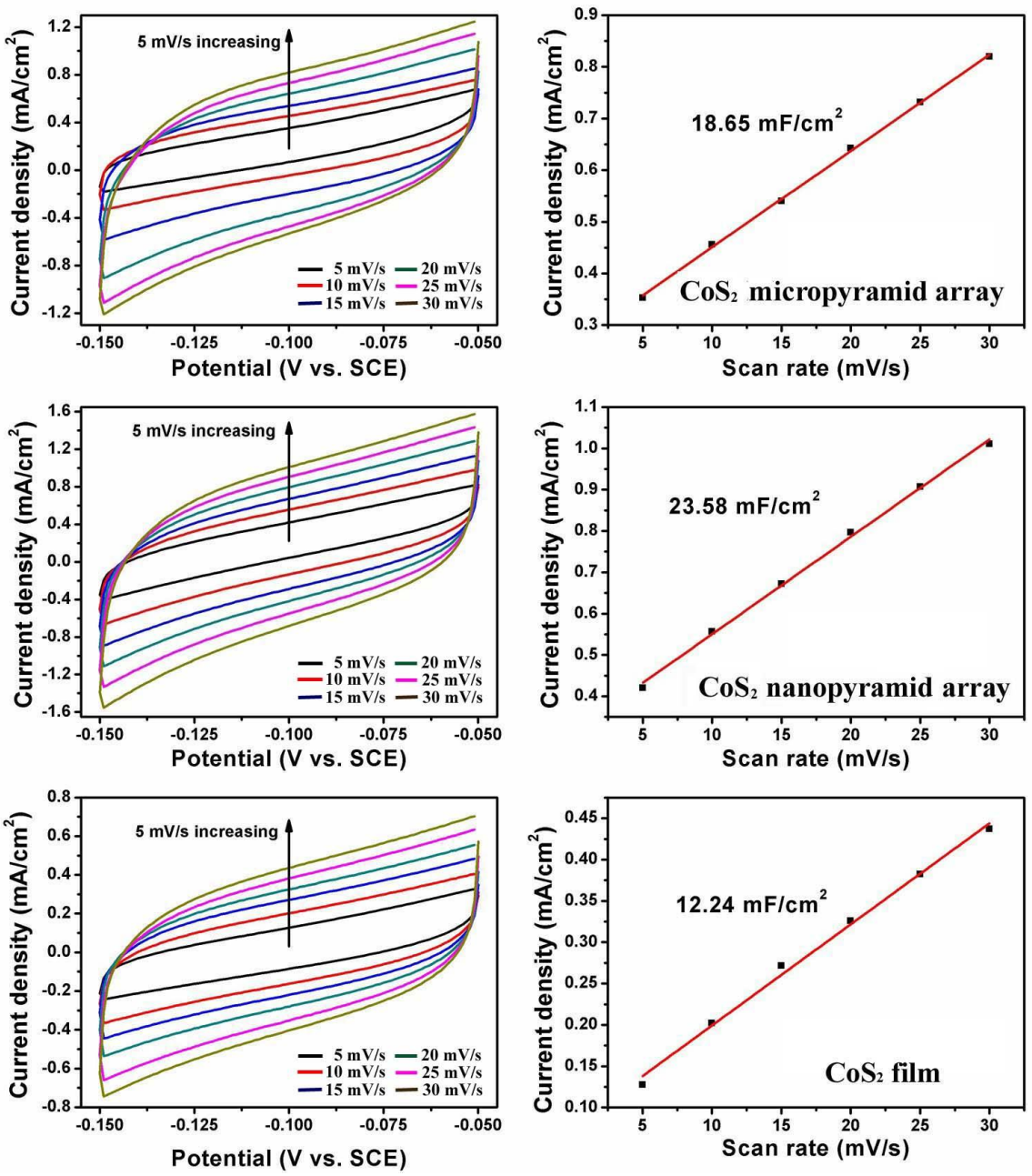

Figure S12: Electrochemical double-layer capacitance (EDLC) measurements of CoS_2 electrodes with different morphologies and the corresponding current density-scan rates curves. The current densities at -0.1 V vs. SCE were used to calculate the EDLC.

Table S4. Comparison of EDLC and relative surface area for CoS_2 electrodes with different morphologies

Sample	EDLC (mF/cm^2)	Relative surface area
CoS_2 micropyramid array	**18.65**	**0.79**
CoS_2 nanopyramid array	**23.58**	**1**
CoS_2 film	**12.24**	**0.52**

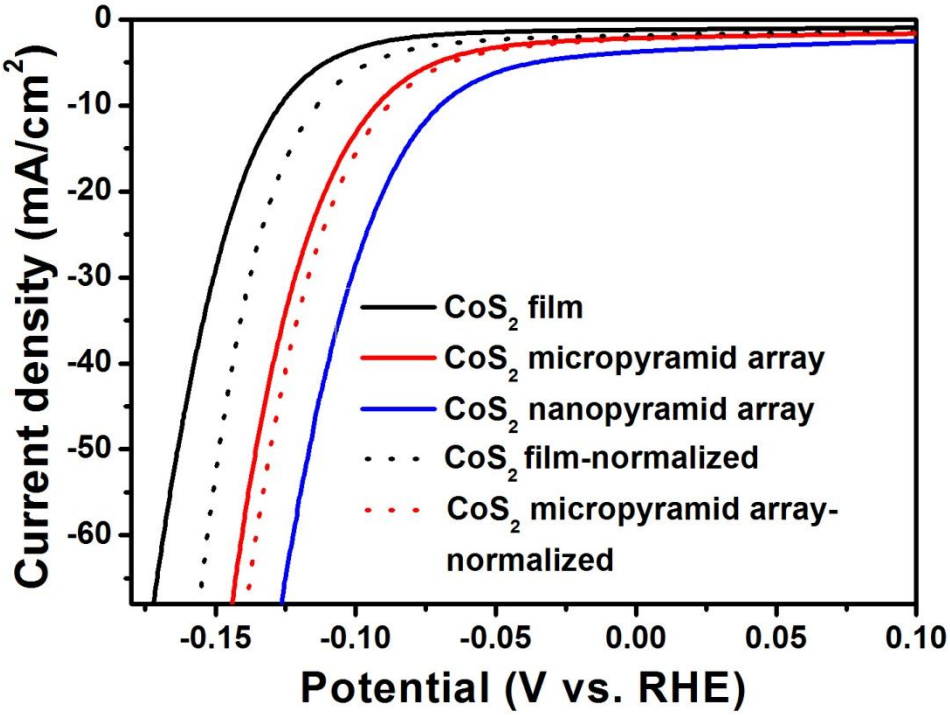

Figure S13: IR-corrected and relative surface area-normalized polarization curves of CoS_2 electrodes with different morphologies. Scan rate: 5 mV/s.

Table S5. Comparison of HER performances in 0.5 M H_2SO_4 solution for CoS_2 nanopyramids electrodes with other HER electrocatalysts

Electrocatalyst	Mass loading of catalyst (mg/cm^2)	Onset potential (mV)	Overpotential at -10 mA/cm^2 (mV)	Overpotential at -100 mA/cm^2 (mV)
CoS_2 nanopyramids/3D CFP, our work	**0.625**	**61**	**70**	**140**
$CoSe_2$ nanoparticles/3D CFP, ref. 3	**2.5**	**89**	**137**	**181**
CoS_2 nanowires/graphite, ref. 5	**1.7**	**75**	**145**	**205**
CoS_2 nanosheets/RGO-CNT, ref. 7	**1.15**	**100**	**142**	**178**
CoS_2 nanopyramids/Ti foil, ref. 9	**N/A**	**81**	**193**	**276**

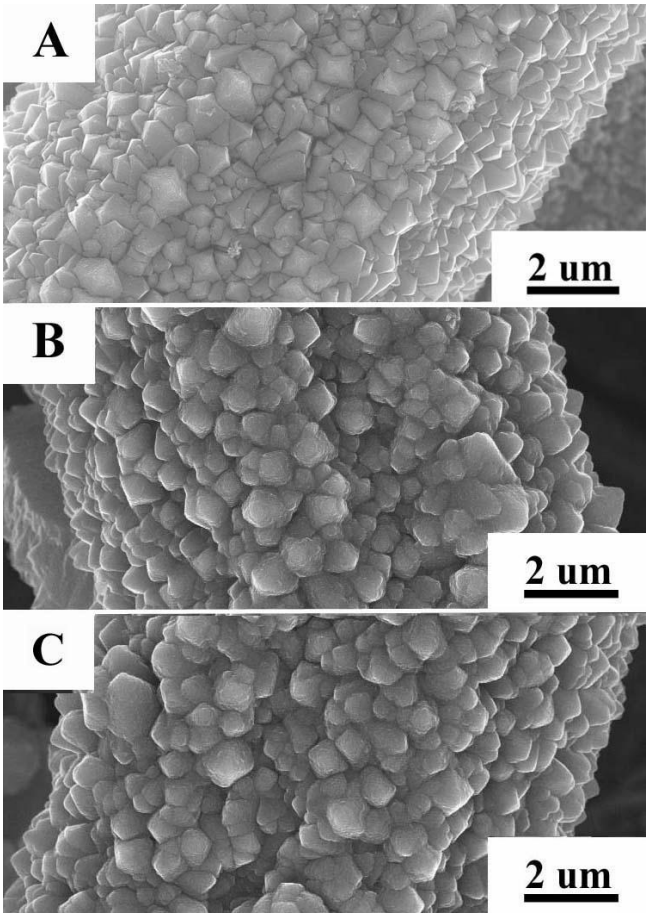

Figure S14: SEM images of CoS_2 NPA electrode (A) initially and after (B) 1000 and (C) 2000 CV cycles durability test.

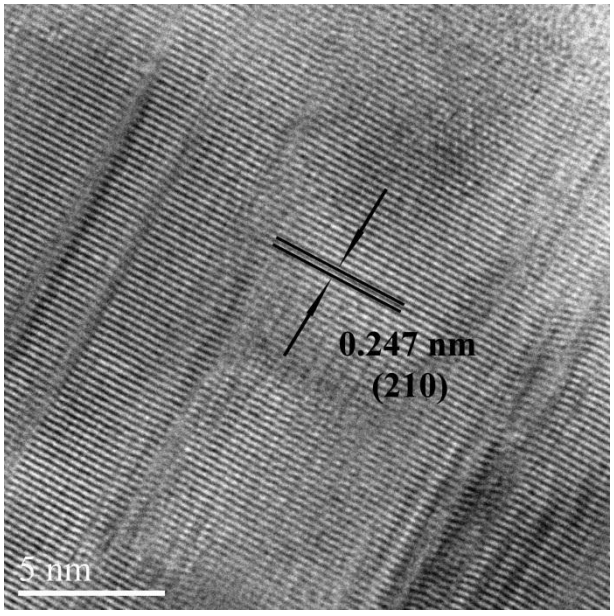

Figure S15: HRTEM image of the CoS_2 NPA electrode after 2000 CV cycles durability test.