

Supporting Information for
Boosting Electrocatalytic Oxygen Evolution over Prussian Blue
Analogs/Transition Metal Dichalcogenides Nanoboxes by Photo-
Induced Electron Transfer

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Experimental details

Synthesis of ZIF-67 nanocubes: The ZIF-67 nanocubes were synthesized according to a reference with a few modifications (Chem 2016, 1, 102-113). In a typical synthesis, 58.3 mg of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 2 mL of deionized water containing 1 mg of cetyltrimethylammonium bromide (CTAB). Then this solution was rapidly injected into 15 mL of aqueous solution containing 908 mg of 2-methylimidazole and stirred at room temperature for 20 min. The product was collected by centrifugation and washed by ethanol for several times.

Synthesis of ZIF-67@CoFe PBA nanocubes: 22 mg of ZIF-67 nanocubes was dispersed in 15 mL of ethanol by ultrasound. At the same time, 100 mg of $\text{K}_3[\text{Fe}(\text{CN})_6]$ was dissolved in 5 mL of H_2O to form a transparent solution. Then the $\text{K}_3[\text{Fe}(\text{CN})_6]$ aqueous solution was injected into the ZIF-67 solution rapidly with continuous stirring at room temperature for at least 3 h. Then, the product was collected by centrifugation and washed with water and ethanol three times.

Synthesis of CoS_2 nanoboxes: 22 mg of ZIF-67 nanocubes was dispersed in 15 mL of ethanol by ultrasound. At the same time, 100 mg of thioacetamide (TAA) was dissolved in 5 mL of ethanol, and then injected into the ZIF-67 solution rapidly. The mixture was further heated at 90 °C for 12 min. Finally, the product was collected by centrifugation and washed with water and ethanol three times.

Synthesis of CoFe PBA/ CoS_2 nanoboxes: The freshly prepared CoFe PBA nanocubes were dissolved into 15 mL of ethanol by ultrasound. Then, 5 mL of solution that dissolved with 100 mg of TAA was injected into above solution to form a homogeneous solution. After that, the mixture was then heated at 90 °C for 12 min. Finally, the product was collected by centrifugation and washed with water and ethanol three times. The CoFe PBA/ CoS_2 nanoboxes with different atomic ratios could be obtained by tuning the reaction times. For comparison, CoFe PBA/ CoS_2 -6 and CoFe PBA/ CoS_2 -30 were also prepared by changing the sulfurization time to 6 and 30 min, respectively, while keeping other conditions the same.

Synthesis of CoFe (II) PBA/ CoS_2 nanoboxes: The synthesis of CoFe (II) PBA/ CoS_2

nanoboxes was similar to that of CoFe PBA/CoS₂ nanoboxes just substituting the K₃[Fe(CN)₆] with K₄[Fe(CN)₆] while keeping other reaction condition the same.

Materials characterizations: UV–vis adsorption spectroscopic characterization was performed using Nanodrop-2000C spectrophotometer (Thermo Fisher Scientific Inc). The morphologies of each sample were characterized by transmission electron microscopy (TEM, JEM-2100, Japan) by drying a droplet of sample solutions on Cu-grids with carbon film. Scanning electron microscopic (SEM) images were acquired on silicon wafers by S-4800 (Japan). XPS spectra were obtained on a PHI 5000 VersaProbe (Japan). The binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. X-ray diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation at a low scanning speed of 0.2° per min. UV/Visible diffuse reflectance spectra (UV-DRS) of the powders were obtained for the dry pressed disk samples using a UV-3600 Plus Spectrophotometer (SHIMAZU, Japan).

OER Electrochemical tests: All electrochemical measurements were carried out using a CHI 760E instrument (Chen hua, China) at 25 °C. A working electrode was made by dropcasting 10 μL of the catalyst to cover a glassy carbon electrode (3 mm diameter). A graphite rod was used as the counter electrode and an Ag/AgCl electrode was used as the reference. All the measured potentials were converted to reversible hydrogen electrodes (RHE) according to Potential = E Ag/AgCl + 0.059 pH + 0.197. The electrolyte was 1 M KOH dissolved in water. LSV was recorded with the scan rates of 5 mV/s with and without light irradiation (150 W). The overpotential (η) was calculated according to the following formula: $\eta = E_{\text{RHE}} - 1.23 \text{ V}$. Linear sweep voltammetry (LSV) was recorded in 1.0 M KOH solution at a scan rate of 5 mV s⁻¹ to obtain the polarization curves. I-t curves were recorded at 1.6 V (vs RHE) with light on and off in the presence of 1M KOH. Tafel plots are recorded with the linear portions at low overpotential fitted to the Tafel equation ($\eta = b \log j + a$, where η is overpotential, j is the current density, and b is the Tafel slope). Electrochemical impedance spectroscopy (EIS) was recorded under the following conditions: amplitude 5 mV, frequency ranging from 100 to 0.1 Hz, and open circuit. Mott-

Schottky plots were derived from impedance-potential tests conducted at a frequency of 1000 Hz with light on and off. The current density was normalized to the geometrical area. All the electrochemical data were presented without iR correction. Cyclic voltammetry (CV) taken with various scan rates (10, 50, 100, 200 and 300 mV s^{-1}) in the presence of 1.0 M KOH has been collected in -0.05-0.05 V (vs. Ag/AgCl) and used to estimate the double-layer capacitance.

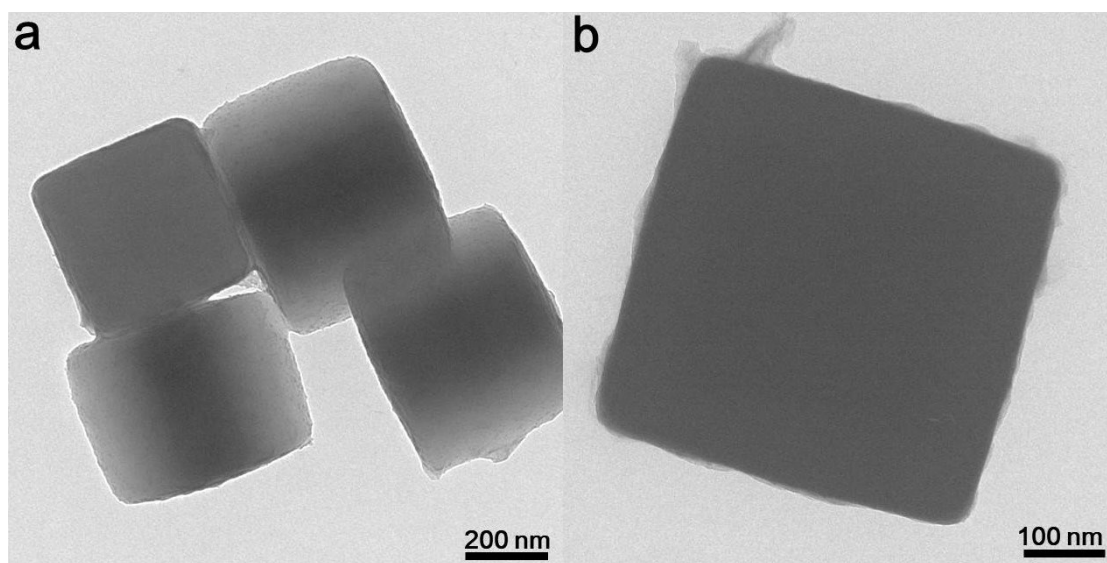


Figure S1 Representative TEM images of ZIF-67 nanocubes with different magnifications.

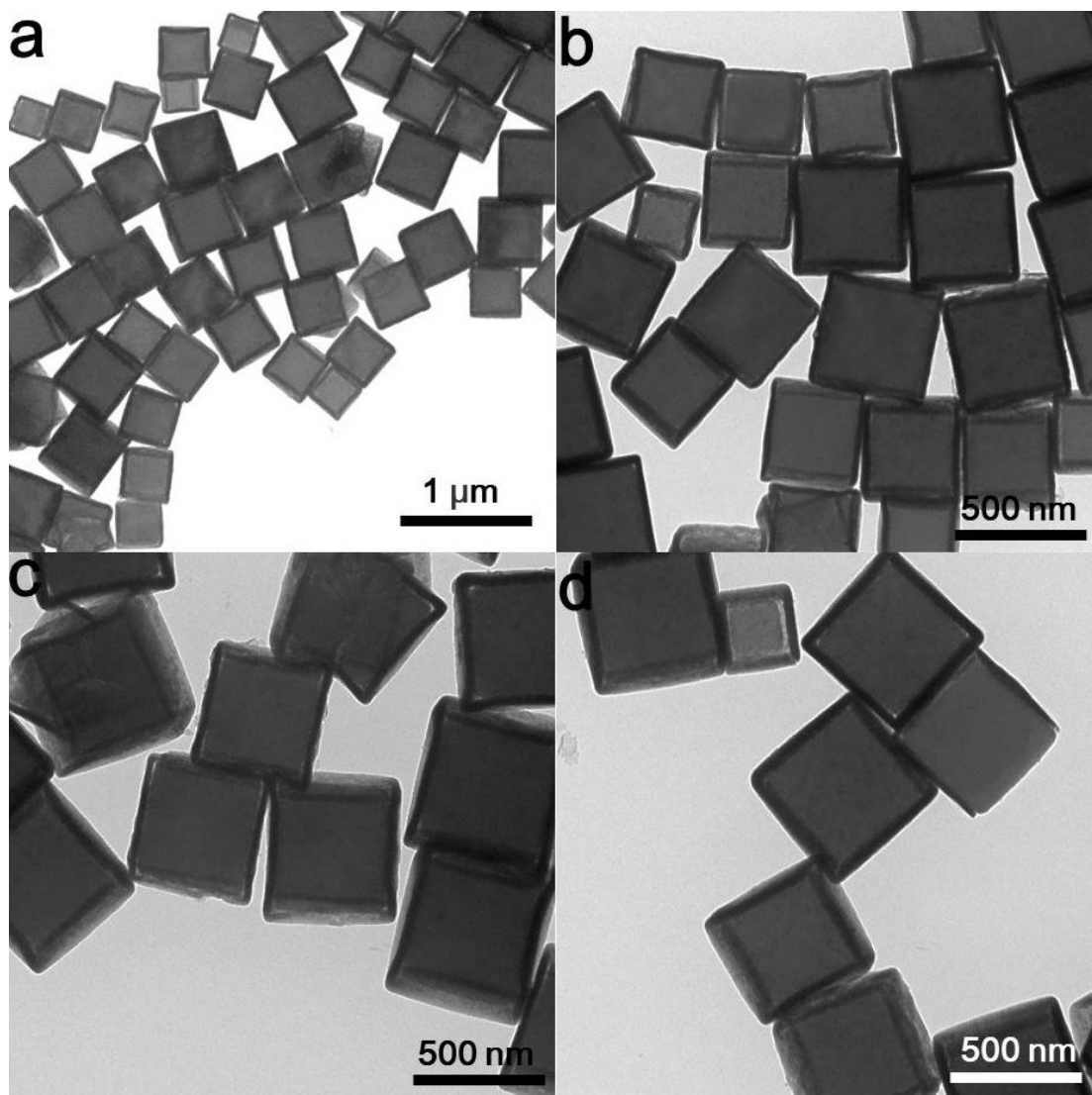


Figure S2 Representative TEM images of CoFe PBA cubes prepared by adding 50 mg of $K_3[Fe(CN)_6]$ for keeping reacting for 3h.

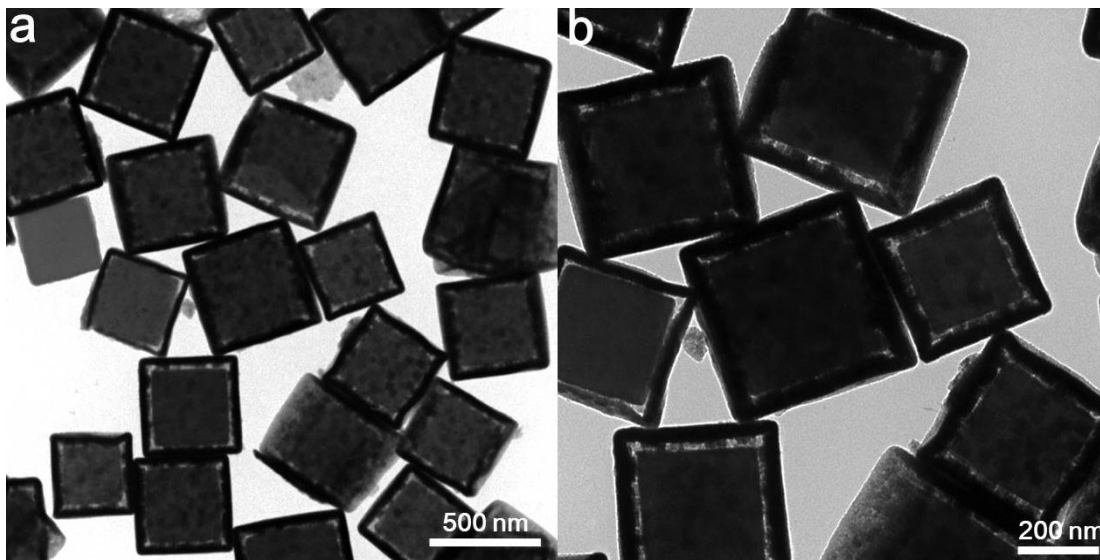


Figure S3 Representative TEM images of CoFe PBA cubes prepared by adding 100 mg of $K_3[Fe(CN)_6]$ for keeping reacting for 4 h.

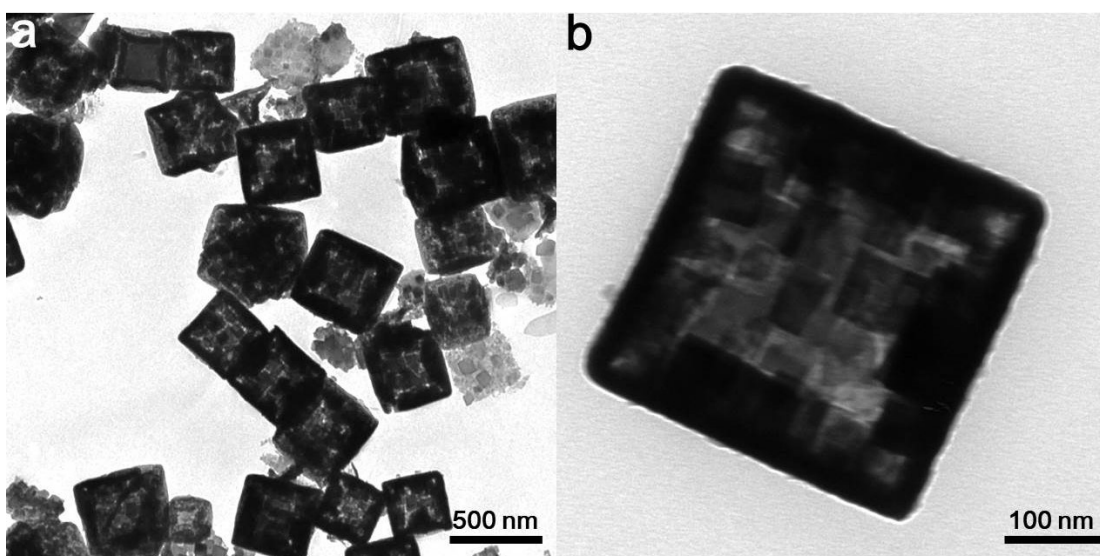


Figure S4 Representative TEM images of CoFe PBA cubes prepared by adding 100 mg of $K_3[Fe(CN)_6]$ for keeping reacting for 12 h.

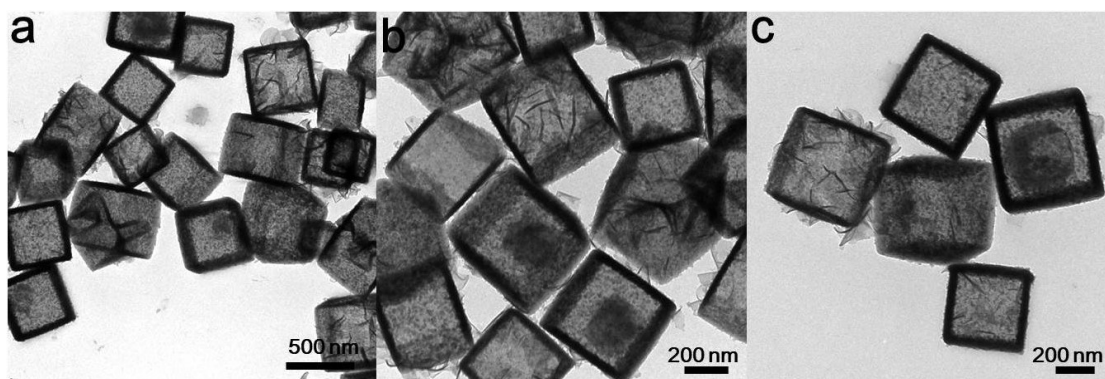


Figure S5 Representative TEM images of CoFe hydroxides prepared by hydrolyzing CoFe PBA.

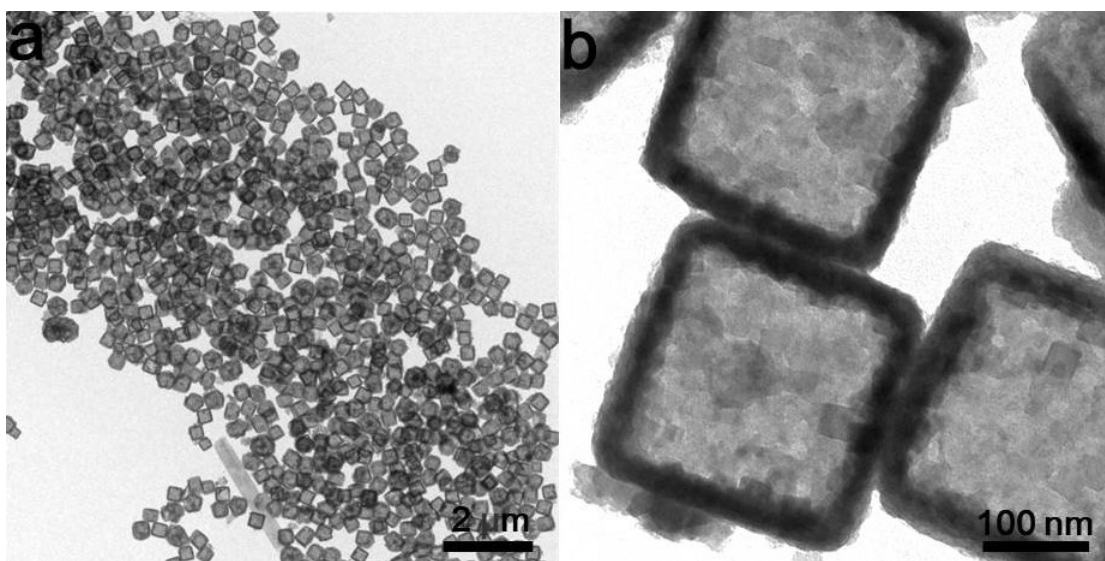


Figure S6 Additional TEM images of CoFe PBA/CoS₂-12 CNBs with different magnifications.

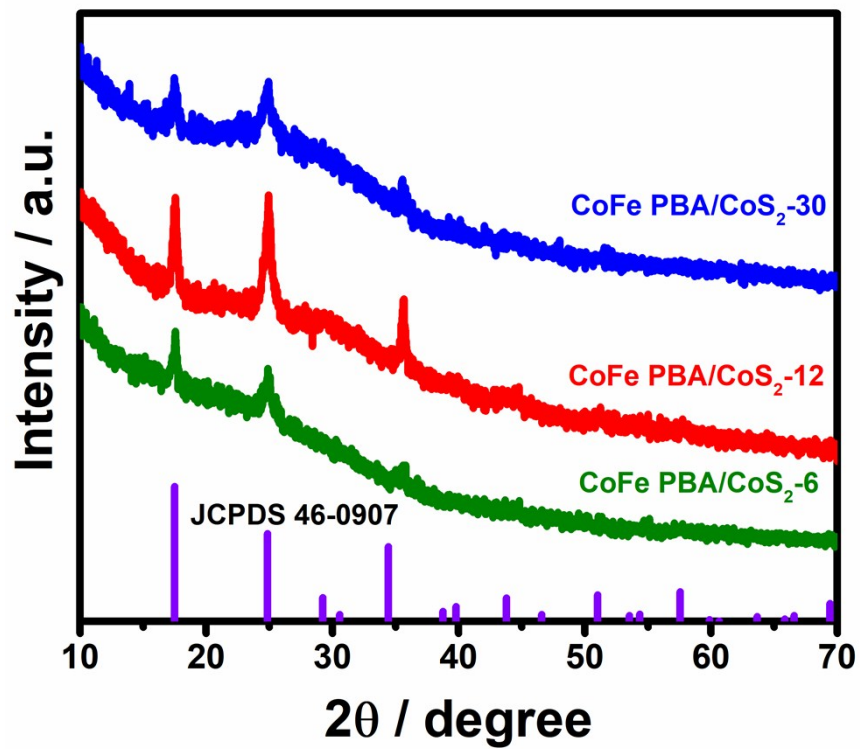


Figure S7 XRD patterns of CoFe PBA/CoS₂-6 CNBs, CoFe PBA/CoS₂-12 CNBs, and CoFe PBA/CoS₂-30 CNBs.

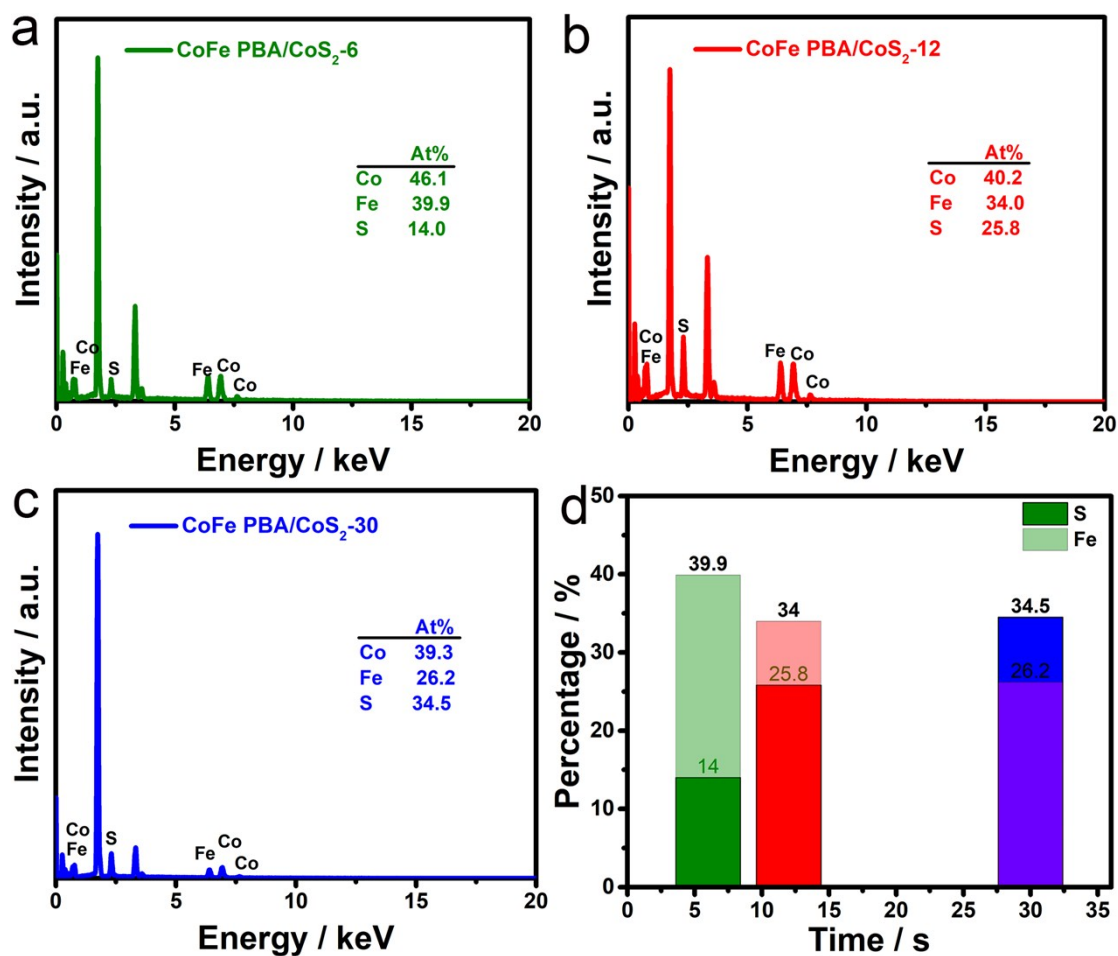


Figure S8 SEM-EDS spectra of (a) CoFe PBA/CoS₂-6 CNBs, (b) CoFe PBA/CoS₂-12 CNBs, and (c) CoFe PBA/CoS₂-30 CNBs. (d) The histogram for the percentage of Fe and S element in the CoFe PBA/CoS₂ over sulfurization time.

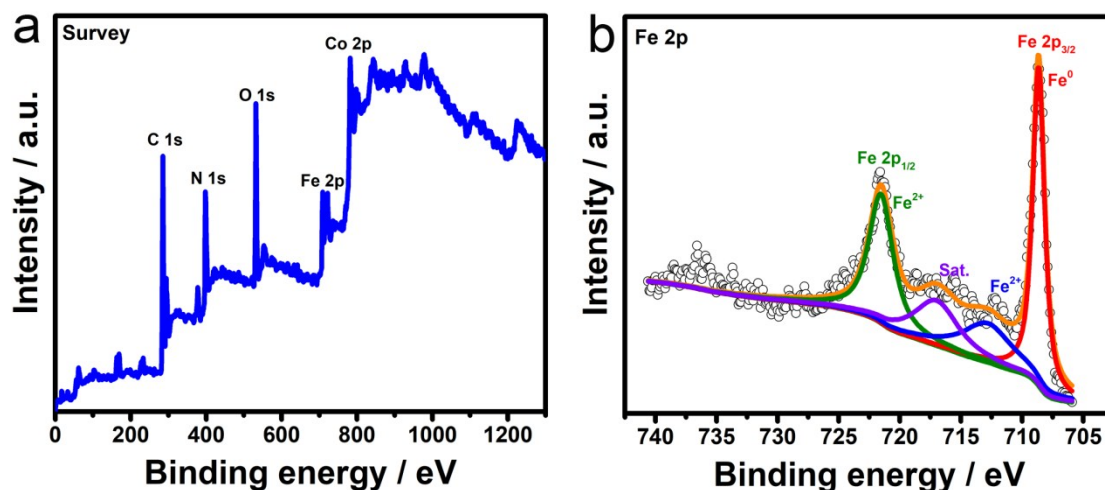


Figure S9 (a) XPS survey scan and (b) detailed Fe 2p XPS spectrum of CoFe PBA.

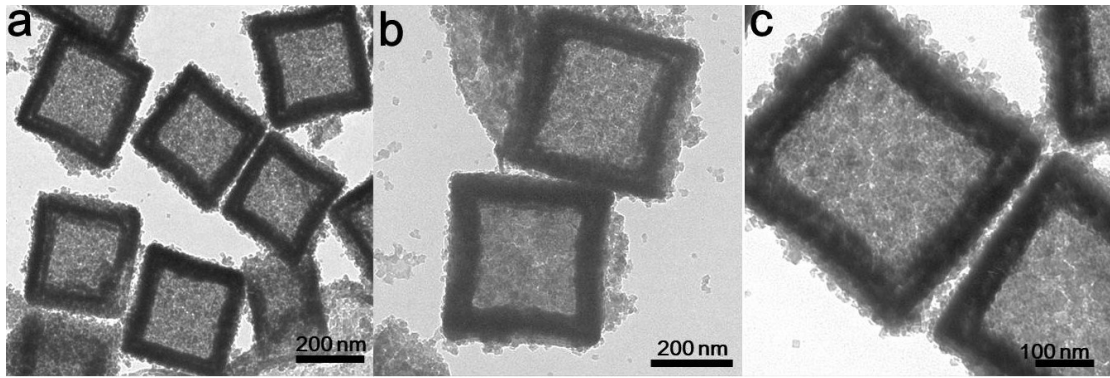


Figure S10 Representative TEM images of CoFe PBA/CoS₂-6 CNCs with different magnifications.

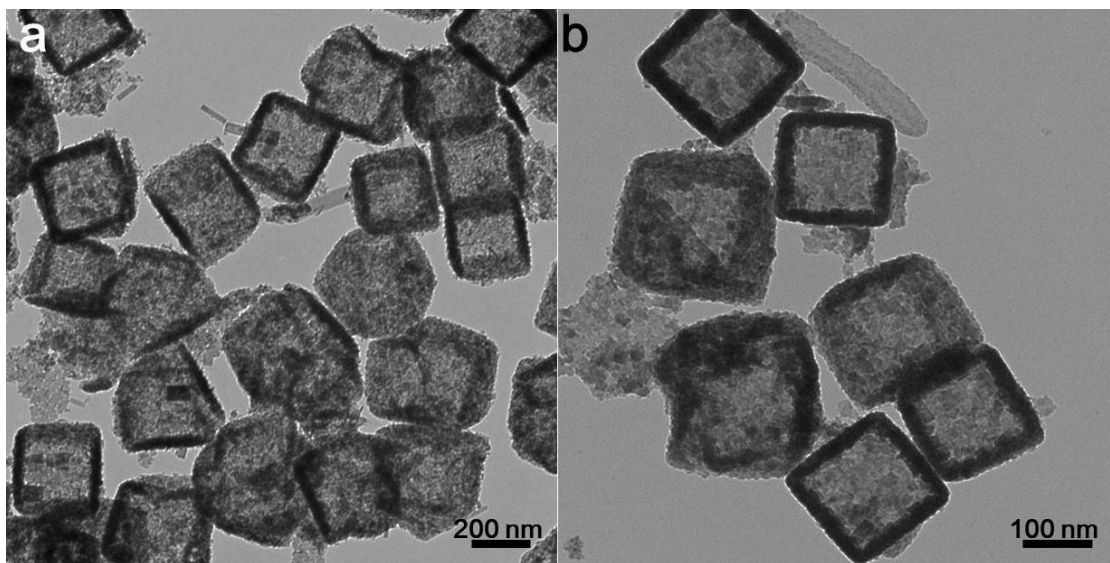


Figure S11 Representative TEM images of CoFe PBA/CoS₂-30 CNBs with different magnifications.

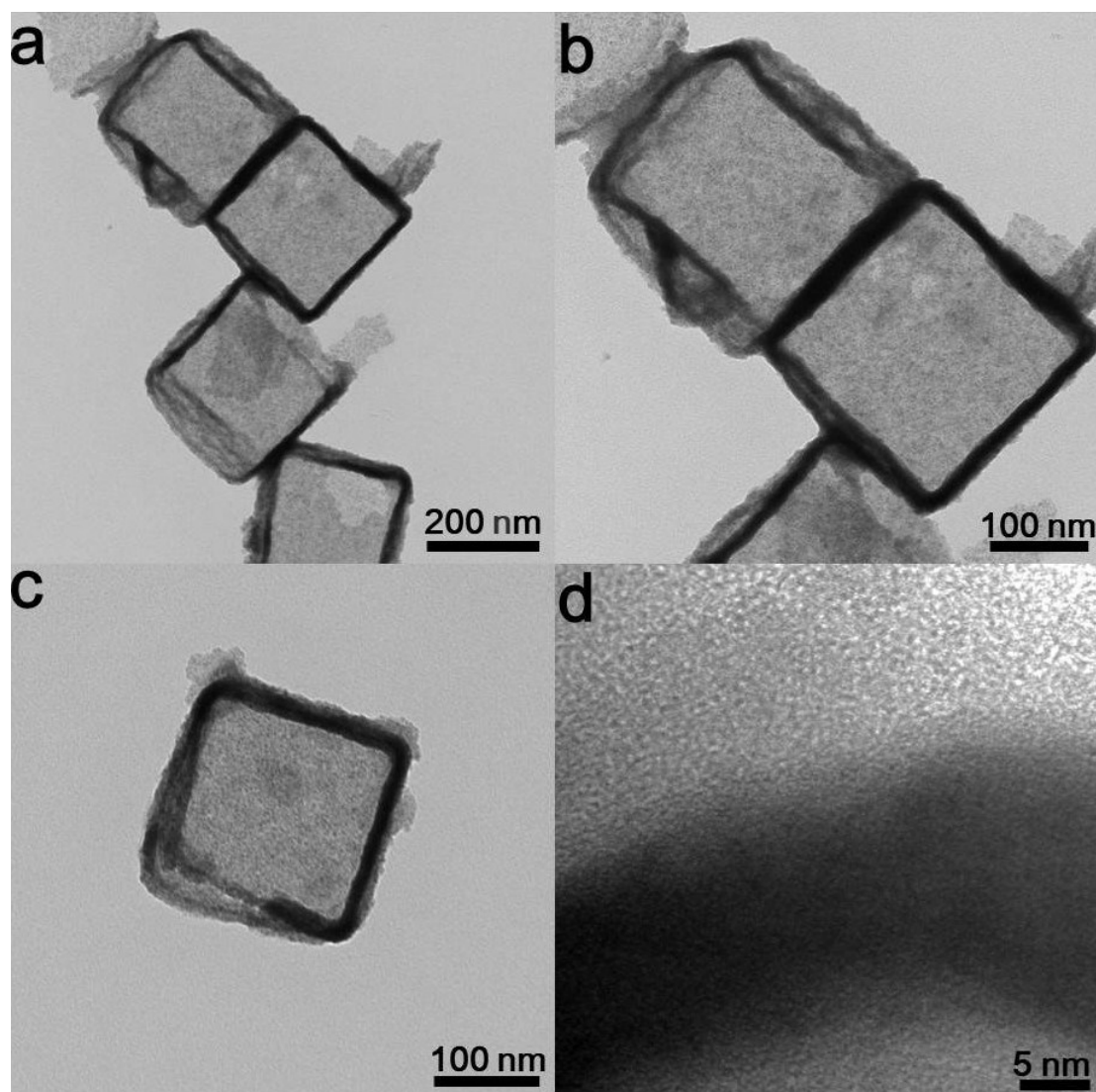


Figure S12 Representative TEM images of CoS₂ nanoboxes with different magnifications.

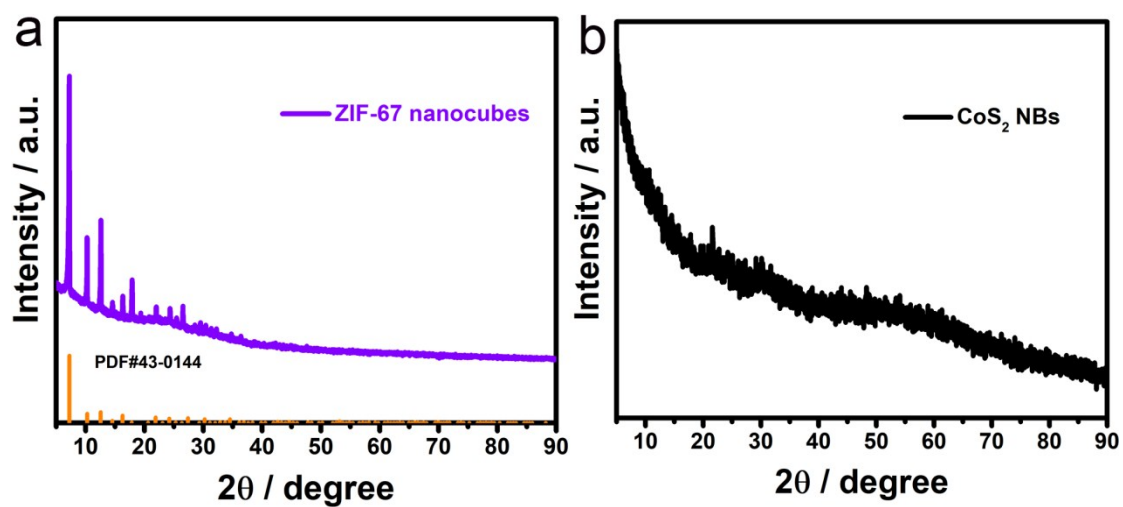


Figure S13 XRD patterns of (a) ZIF-67 nanocubes and (b) CoS₂ nanoboxes.

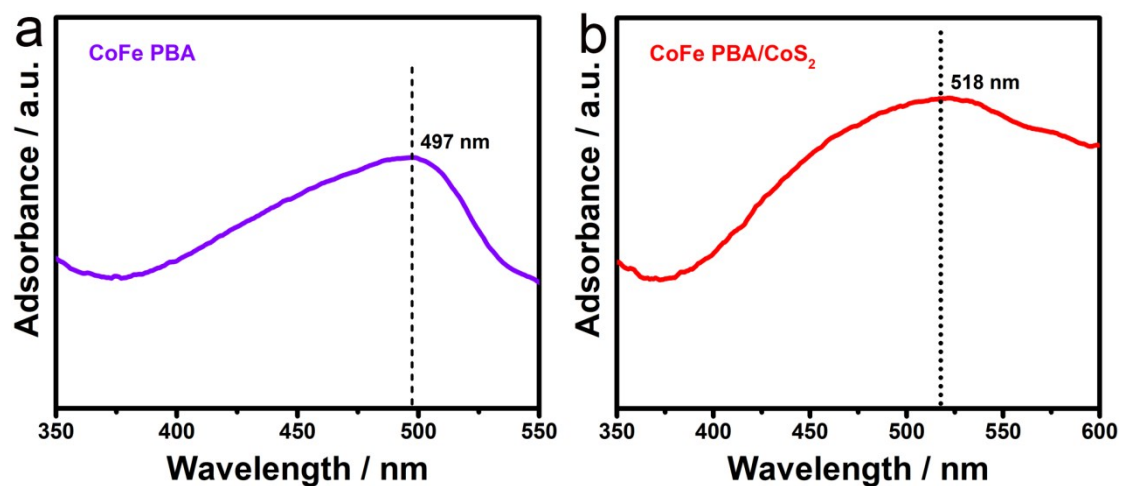


Figure S14 UV-vis spectra of (a) CoFe PBA and (b) CoFe PBA/CoS₂ CNBs.

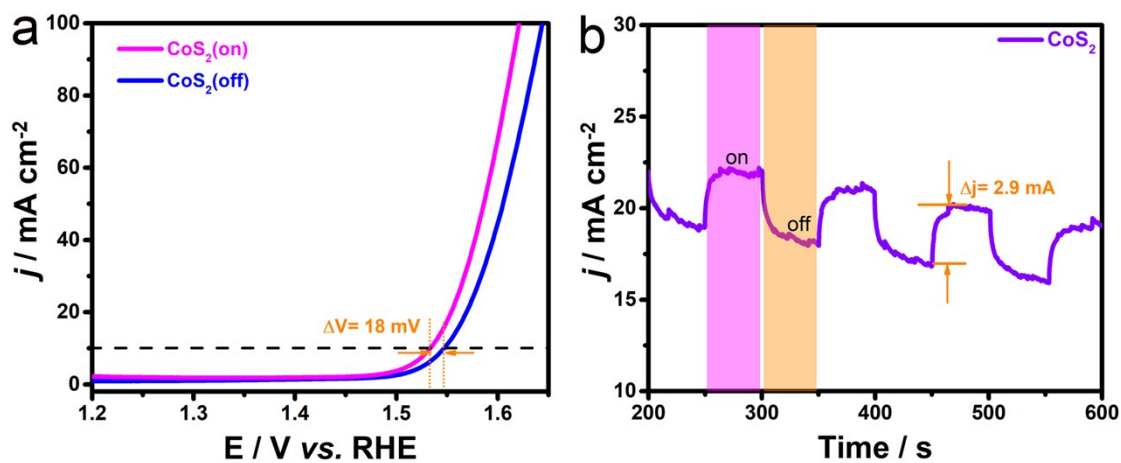


Figure S15 (a) LSV polarization curves and (b) I-t curve of CoS₂ nanoboxes in the absence or presence of light irradiation (potential=1.6 V).

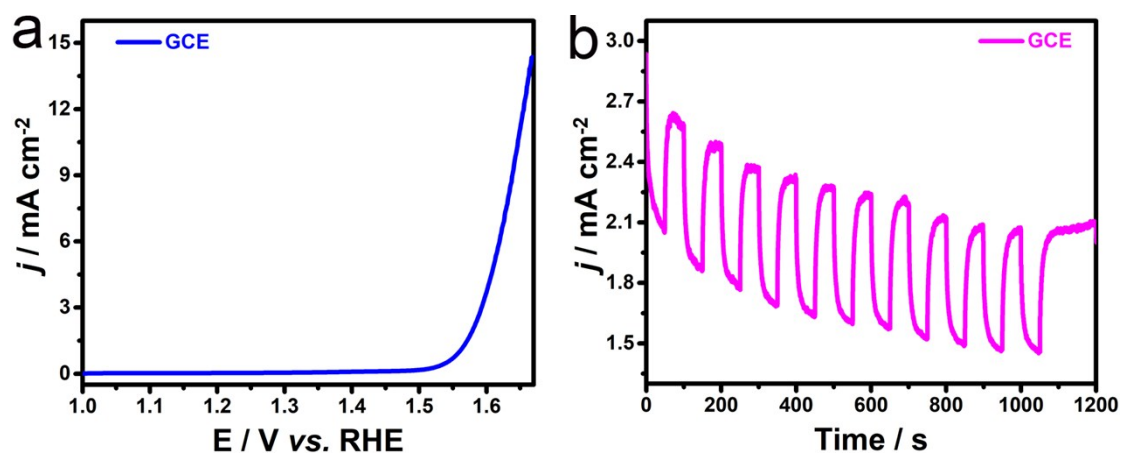


Figure 16 (a) LSV polarization curves of and (b) I-t curve of pure GCE in the absence or presence of light irradiation (potential=1.6 V).

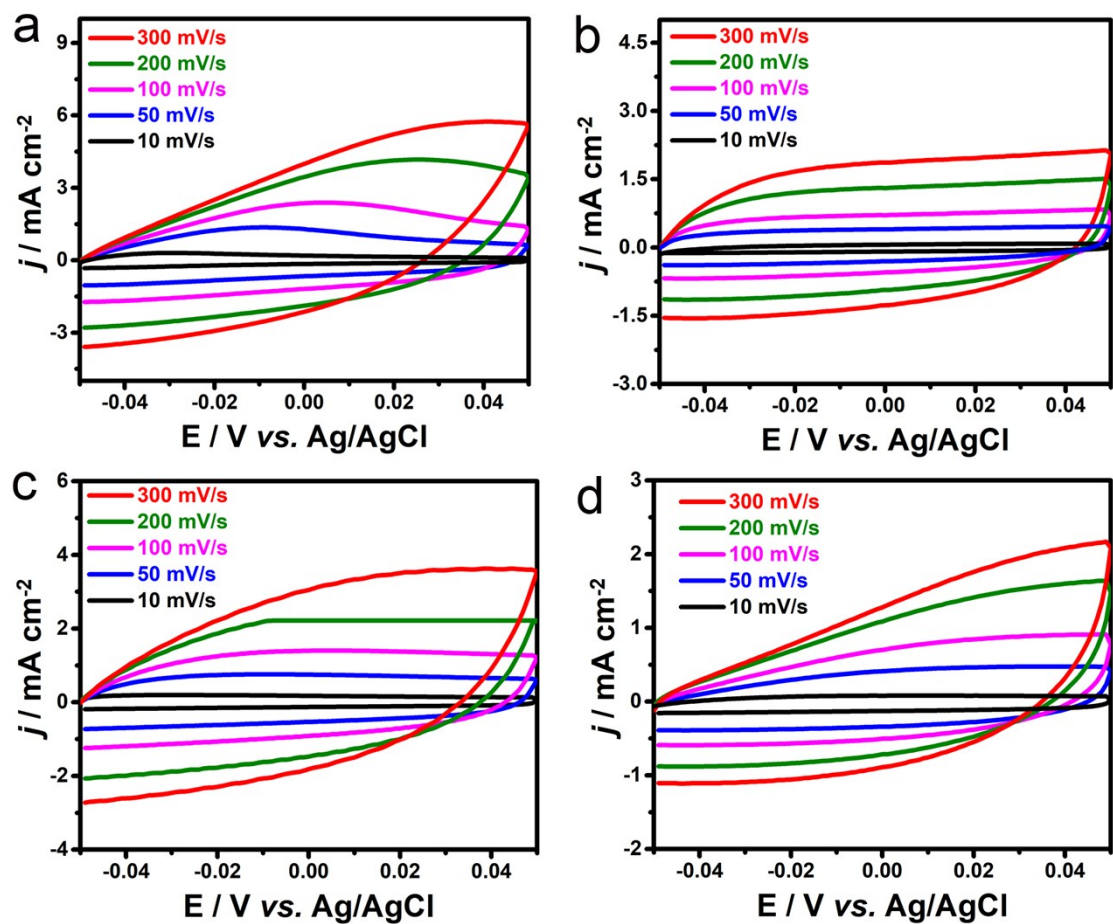


Figure S17 CV curves of (a) CoFe PBA, (b) CoFe PBA/CoS₂-6 CNBs, (c) CoFe PBA/CoS₂-12 CNBs, and (d) CoFe PBA/CoS₂-30 CNBs in 1 M KOH solution with different scan rates.

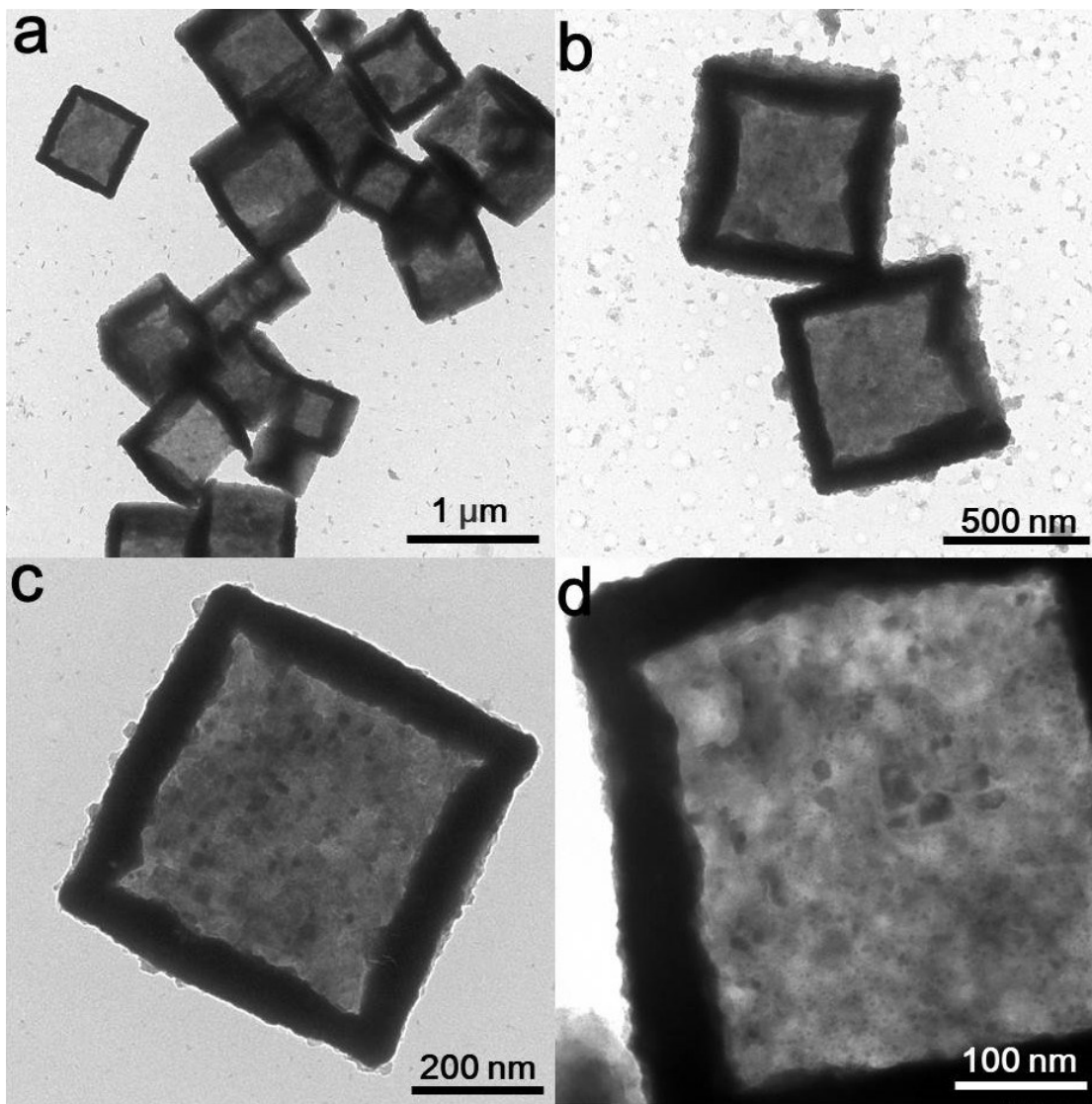


Figure S18 Representative TEM images of CoFe(II) PBA/CoS₂ CNBs with different magnifications.

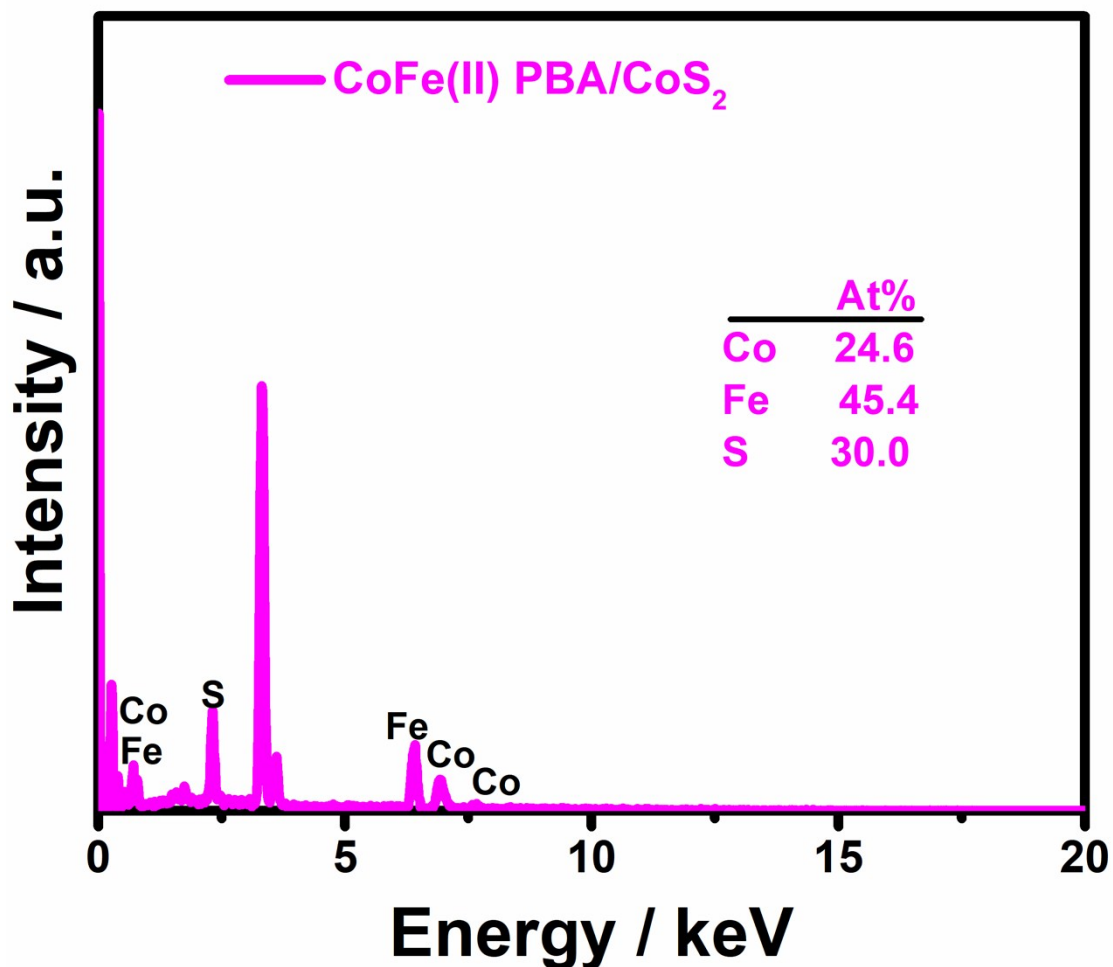


Figure S19 SEM-EDS spectrum of CoFe(II) PBA/CoS₂ CNBs.

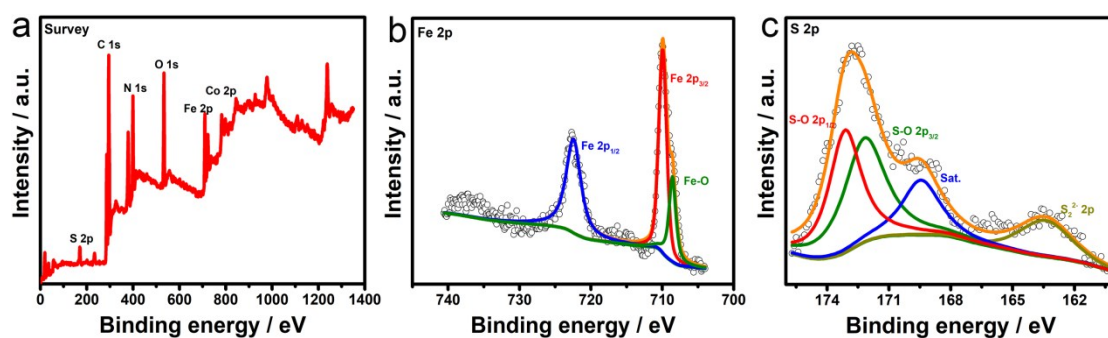


Figure S20 (a) XPS survey scan and (b) detailed Fe 2p, (c) S 2p XPS spectra of CoFe(II) PBA/CoS₂ CNBs.

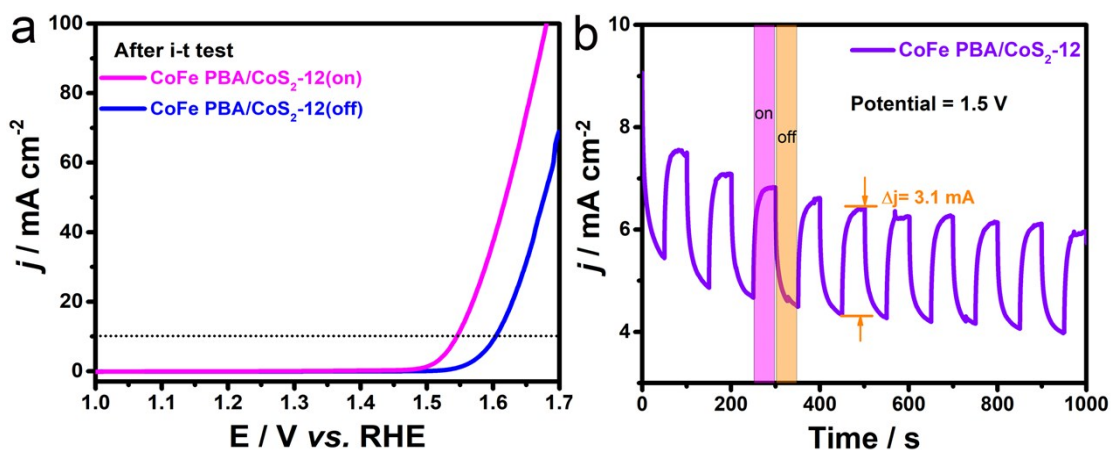


Figure S21 (a) LSV polarization curves of and (b) I-t curve of CoFe PBA/CoS₂ nanoboxes in the absence or presence of light irradiation (potential=1.5 V).

Based on LSV polarization curves CoFe PBA/CoS₂ nanoboxes in the absence or presence of light irradiation after the long-term I-t test, it is clearly observed that the the OER activity of CoFe PBA/CoS₂ CNBs is significantly improved (Figure S21), presenting a much lower overpotential and much higher current increase rate than that under dark. Specifically, the overpotential of CoFe PBA/CoS₂ CNBs at 10 mA cm⁻² related to that under dark is negatively shifted by more than 50 mV, further confirming the excellent photoelectrocatalytic OER activity and long-term stability. Moreover, I-t curve of CoFe PBA/CoS₂ nanoboxes at the potential of 1.5 V was also performed to study their photo-induced current effect. As seen, the CoFe PBA/CoS₂ CNBs displayed the prompt current responses to on-off irradiation cycles with a Δj of 3.1 mA cm⁻² at 1.5 V, further confirming the excellent photoelectrocatalytic activity at low potential.