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Supporting Information for

Co_9S_8@N-, S-codoped Carbon Core-Shell Structured Nanowires: Constructing Fluffy Surface for High-Density Active Sites

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Experimental

Pre-treatment of carbon fiber paper (CFP)

A piece of CPF (1.0 cm × 1.5 cm) was firstly soaked in 0.1 M HNO_3 solution for 5 min, and then sonicated sequentially in acetone, water and ethanol for 30 min each to obtain the clean CFP.

Growth of cobalt chloride carbonate hydroxide nanowires on CFP ($CFP@Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$)

$Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$ nanowires were firstly grown on CFP via a hydrothermal route. In a typical preparation, one piece of clean CFP was floated on the surface of an aqueous solution (40 mL) containing 0.04 M $CoCl_2$ and 0.04 M $CO(NH_2)_2$, and the hydrothermal reaction was conducted at 120 °C for 6 hours.[1] After washed with deionized water and ethanol respectively, the $CFP@Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$ can be obtained.

Synthesis of $CFP@Co_3O_4$ and $CFP@Co_9S_8$

The $CFP@Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$ was transferred firstly to $CFP@Co_3O_4$ and then to $CFP@Co_9S_8$ by conducting suitable gaseous phase reactions in different circumstances. Particularly, pyrolysis of $CFP@Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$ in N_2 at 300 °C for 2 h produced $CFP@Co_3O_4$. For its further sulfurization, we placed two porcelain boats in a quartz tube as displayed in Figure S1, with the one located in the middle position filled with one piece of $CFP@Co_3O_4$, and the other one placed near the gas inlet added with thiourea (the mass of thiourea is 1.5 times that of loaded Co_3O_4). Then the furnace was heated to 350 °C at a heating rate of 2.0 °C min^{-1} and then maintained at the same temperature for 4 h in the presence of 5 % H_2/N_2 gas mixture, by which the final CFP@Co_9S_8 product can be made.

Synthesis of CFP@Co_3O_4@PDA, CFP@Co_9S_8@PDA, CFP@Co_3O_4@C and CFP@Co_9S_8@C

To coat PDA layer on the nanowire surface, the CFP@Co_3O_4 (or CFP@Co_9S_8) was soaked in 50 ml of Tris-HCl buffer solution (pH 8.5) containing 100 mg dopamine, which was then continuously stirred at 25 °C for 48 h. The achieved sample was washed with deionized water and ethanol.

The PDA layer was transferred into carbon coating through an annealing treatment. Particularly, to decrease the mass loss, melamine was additionally provided. As displayed in Figure S1, melamine with a mass being 1/5 the absolute mass of loaded Co_3O_4 (Co_9S_8) and 1 piece of CFP@Co_3O_4@PDA (or CFP@Co_9S_8@PDA) were loaded in two different porcelain boats respectively and placed inside a quartz tube. And the calcination was then conducted at 800 °C for 120 min.

Characterizations

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were conducted on a JEOL JSM-7800F microscope operated at 20 kV, and a FEI Tecnai G2 F20 S-TWIN microscope operated at 200 kV, respectively to acquire the morphologies and structures of the prepared materials. The crystal structures were confirmed using an automated X-ray diffraction equipment (XRD, PANalytical X' Pert PRO, Netherlands). X-ray photoelectron spectra (XPS) were recorded on a Thermal ESCALAB 250 XI.

Electrochemical tests

All electrochemical measurement data were collected on an electrochemical analyzer (CHI660D, CH Instruments, Shanghai, China) in a three-chamber electrochemical cell, with the prepared CFP supported catalysts (1.0 cm × 1.0 cm) used as the working electrodes, a graphite rod (10 mm diameter) as the counter electrode, and Hg/HgO (1.0 M KOH) as the reference electrode. The electrolyte (1.0 M KOH aqueous solution) was degassed by bubbling N_2 for at least 30 minutes before the electrochemical measurements.

For HER measurements, linear sweep voltammetry (LSV) curves of the electrocatalysts were recorded in O_2 saturated electrolyte solution at a scan rate of 10 mV s^{-1} in a potential window from 0.4 to –0.6 V vs. RHE. And the tafel slopes were then obtained from the LSV curves. CV data were collected in the potential range without a redox process from 0.2 to 0.3 V vs. RHE at changed scanning rates from 10 to 35 mV s^{-1} in 1.0 M KOH, by which the electrochemical surface areas (ECSAs) were estimated. And the durability test was carried out by multi-current steps at current density of 10 mA cm^{-2} for 30 h. The electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 100000 to 0.01 Hz in 1.0

M KOH aqueous solution at the potential of –0.2 V vs. RHE.

For OER measurements, the polarization curves were recorded in the potential range from 1.0 to 1.8 V vs. RHE at a scan rate of 1.0 mV s^{-1} in a O_2-saturated, 1.0 M KOH solution. And the tafel slopes were then obtained from the LSV curves. CV curves were scanned in the potential range without a redox process from 1.0 to 1.1 V vs. RHE at different scanning rates from 10 to 35 mV s^{-1} in 1.0 M KOH, by which the ECSAs were calculated. The durability test was carried out by multi-current steps at current density of 10 mA cm^{-2} for 30 h. EIS measurements were carried out in the frequency range from 100000 to 0.01 Hz in 1.0 M KOH at the potential of 0.2 V vs. RHE.

Results and Discussion

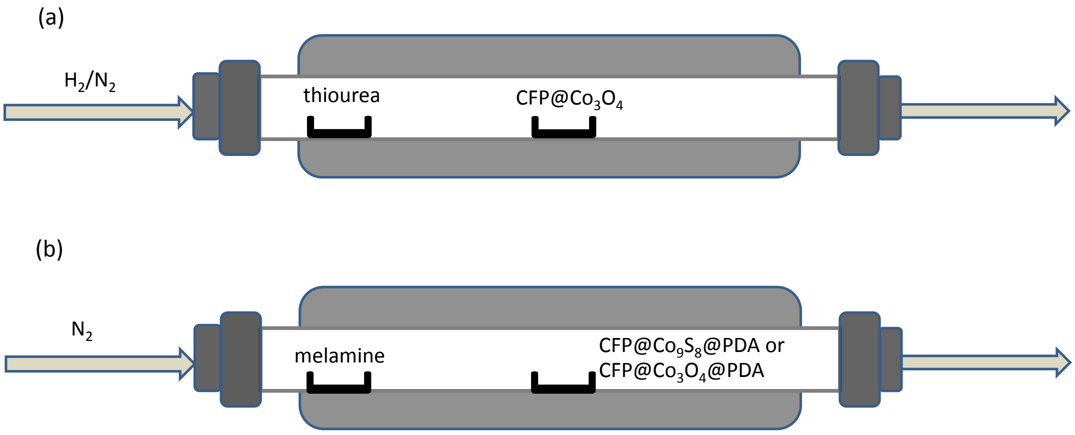

Figure S1. Schematic illustration of the sulfuration procedure of CFP@Co_3O_4 to CFP@Co_9S_8 (a), and the carbonization of PDA surface layer to C coating (b).

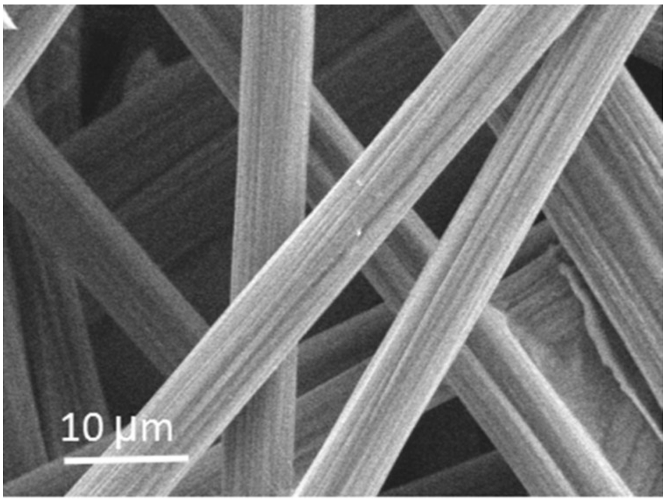

Figure S2. SEM images of the carbon fiber paper (CFP).

Table S1. The catalyst loadings on the CFP.

Samples	Weight (mg, based on 4.0 cm^2 of CFP)	Average (mg)	Loading (mg cm^{-2})
CFP	30	30	0
CFP@Co_9S_8	36.45	37.92	1.98
	37.02		
	39.58		
	38.63		
CFP@Co_9S_8@C	35.36	36.45	1.61
	36.04		
	36.98		
	37.42		

We weighted four different samples for CFP@Co_9S_8 and CFP@Co_9S_8@C here and got an average value for the final loading. Particularly, the CFP@Co_9S_8@C is slightly lighter than CFP@Co_9S_8, which probably is due to that reaction of Co_9S_8 and carbon released some volatile species.

Table S2. Comparison of OER activity of the fluffy structured CFP@Co_9S_8@C with literature results for Co based catalysts in basic solution.

Sample	Current collector	Electrolyte	Overpotential (mV) @10 mAcm $^{-2}$	Ref. No
CFP@Co_9S_8@C	carbon fiber paper	1.0 M KOH	287	This work
Co/Co_9S_8@SNGS	glassy carbon	0.1 M KOH	290	2
Co_9S_8@NOSC-900	glassy carbon	1.0 M KOH	340	3
Fe_3O_4@Co_9S_8/rGO	glassy carbon	1.0 M KOH	340	4
Co@N-C	carbon-fiber-woven cloths	0.1 M KOH	350	5
Co_3O_4	Ni foam	1.0 M KOH	310	6
N- Co_9S_8/G	glassy carbon	0.1 M KOH	280	7
β-CoOOH	thin films of cobalt oxides	1.0 M KOH	372	8
CoO-MoO_2	glassy carbon	1.0 M KOH	312	9
Fe–CoOH/G	glassy carbon	1.0 M KOH	330	10
Co_3O_4 /$NiCo_2O_4$	Ni foam	1.0 M KOH	340	11

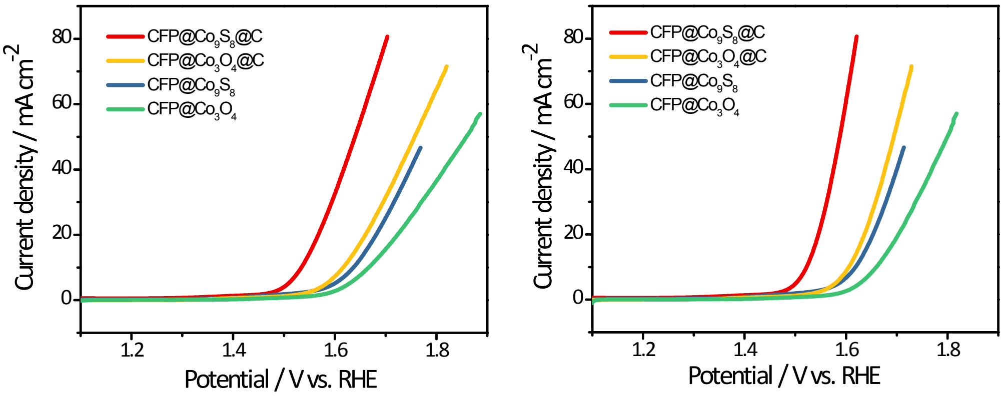

Figure S3. The polarization curves for the prepared nanowire materials before IR correction (left) and after IR correction (right).

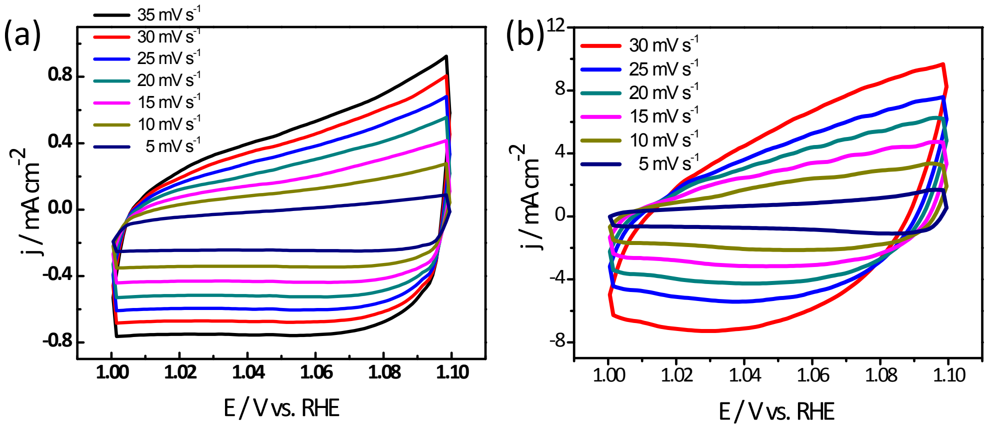

Figure S4. CVs of CFP@Co_3O_4@C (a) and CFP@Co_9S_8@C (b) electrodes in the double layer capacitance charging region at different scan rates in 1.0 M KOH aqueous electrolyte.

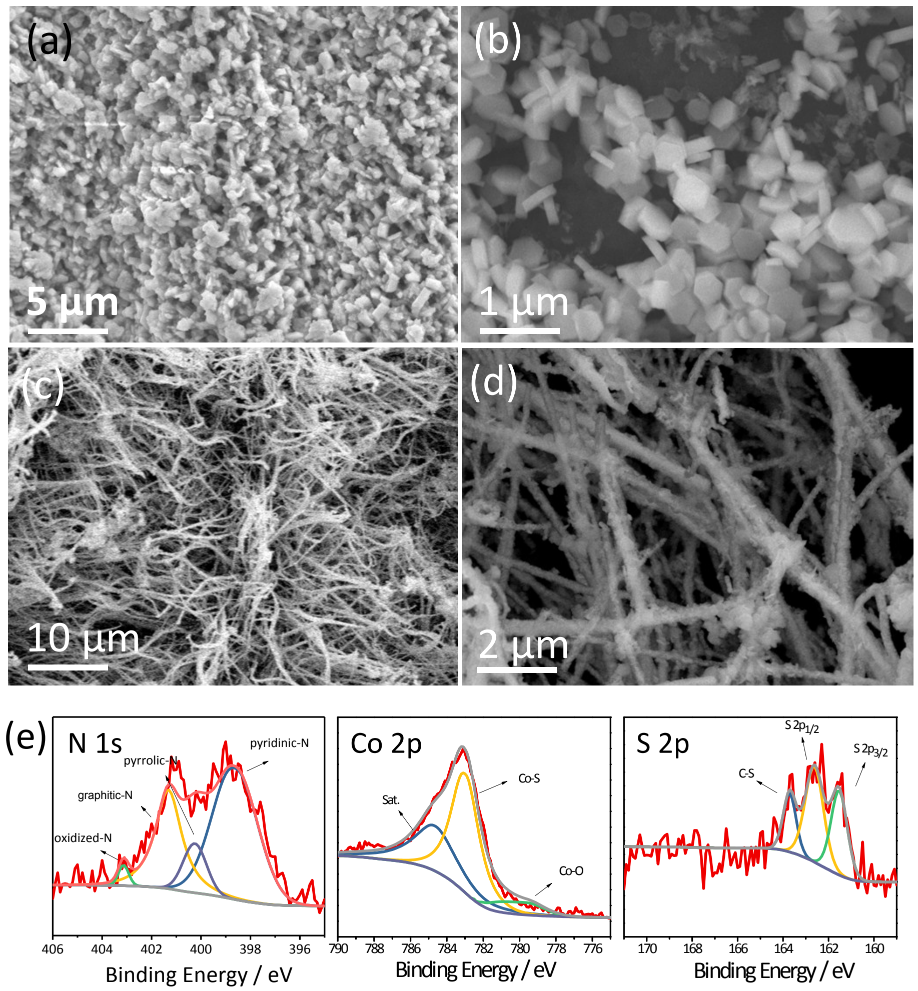

Figure S5. (a, b) FESEM images of the CFP@Co_9S_8 after 1.0 h of OER tests in 1.0 M KOH electrolyte solution. (c, d) FESEM images and (e) XPS spectra of the CFP@Co_9S_8@C after 30 h of OER tests in 1.0 M KOH electrolyte solution.

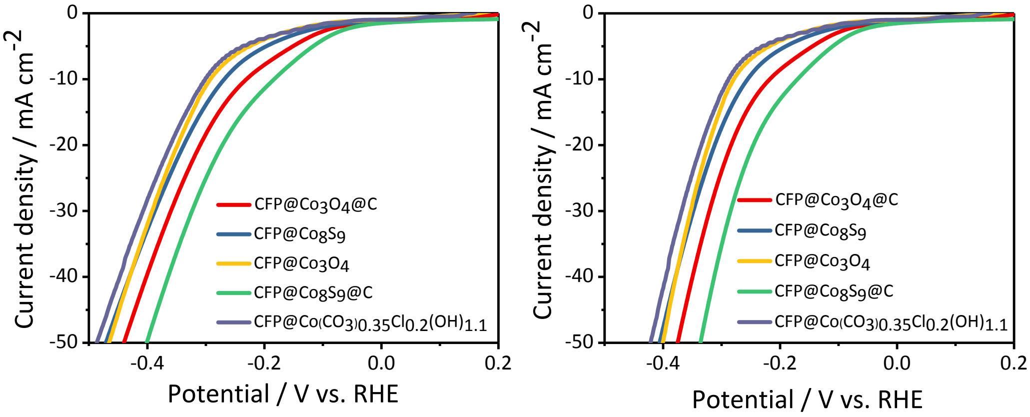

Figure S6. The polarization curves for the prepared nanowire materials before IR correction (left) and after IR correction (right).

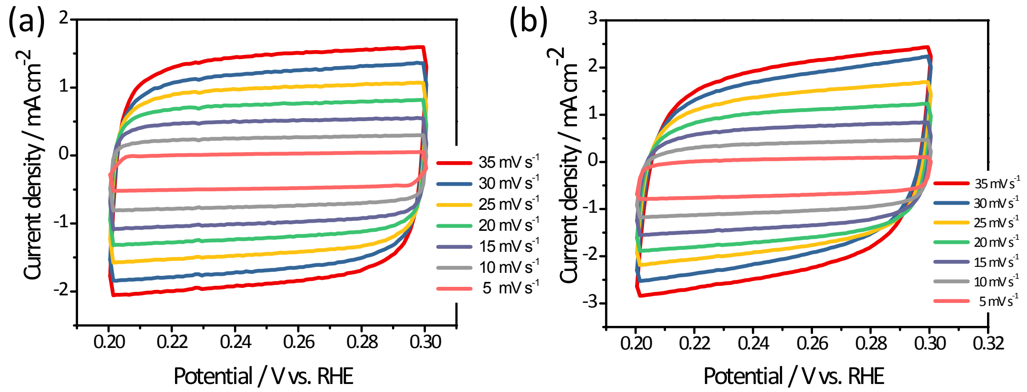

Figure S7. CVs of CFP@Co_3O_4@C (a) and CFP@Co_9S_8@C (b) electrodes in the double layer capacitance charging region at different scan rates in 1.0 M KOH aqueous electrolyte.

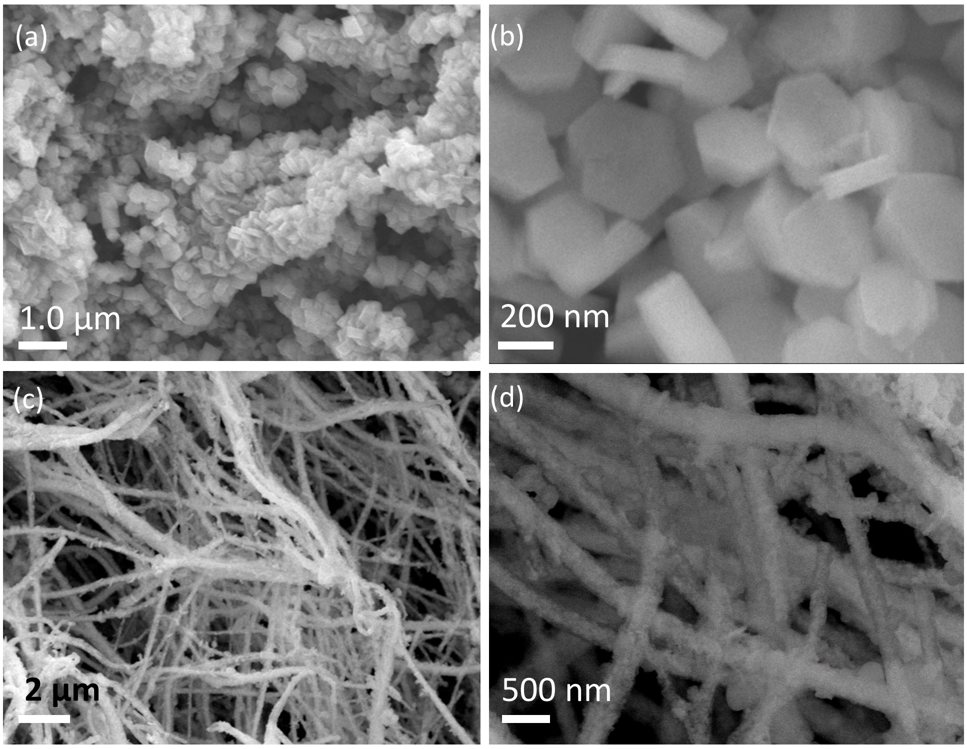

Figure S8. (a, b) FESEM images of the CFP@Co_9S_8 after 1.0 h of HER tests in 1.0 M KOH electrolyte solution. (c, d) FESEM images of the CFP@Co_9S_8@C after 30 h of HER tests in 1.0 M KOH electrolyte solution.

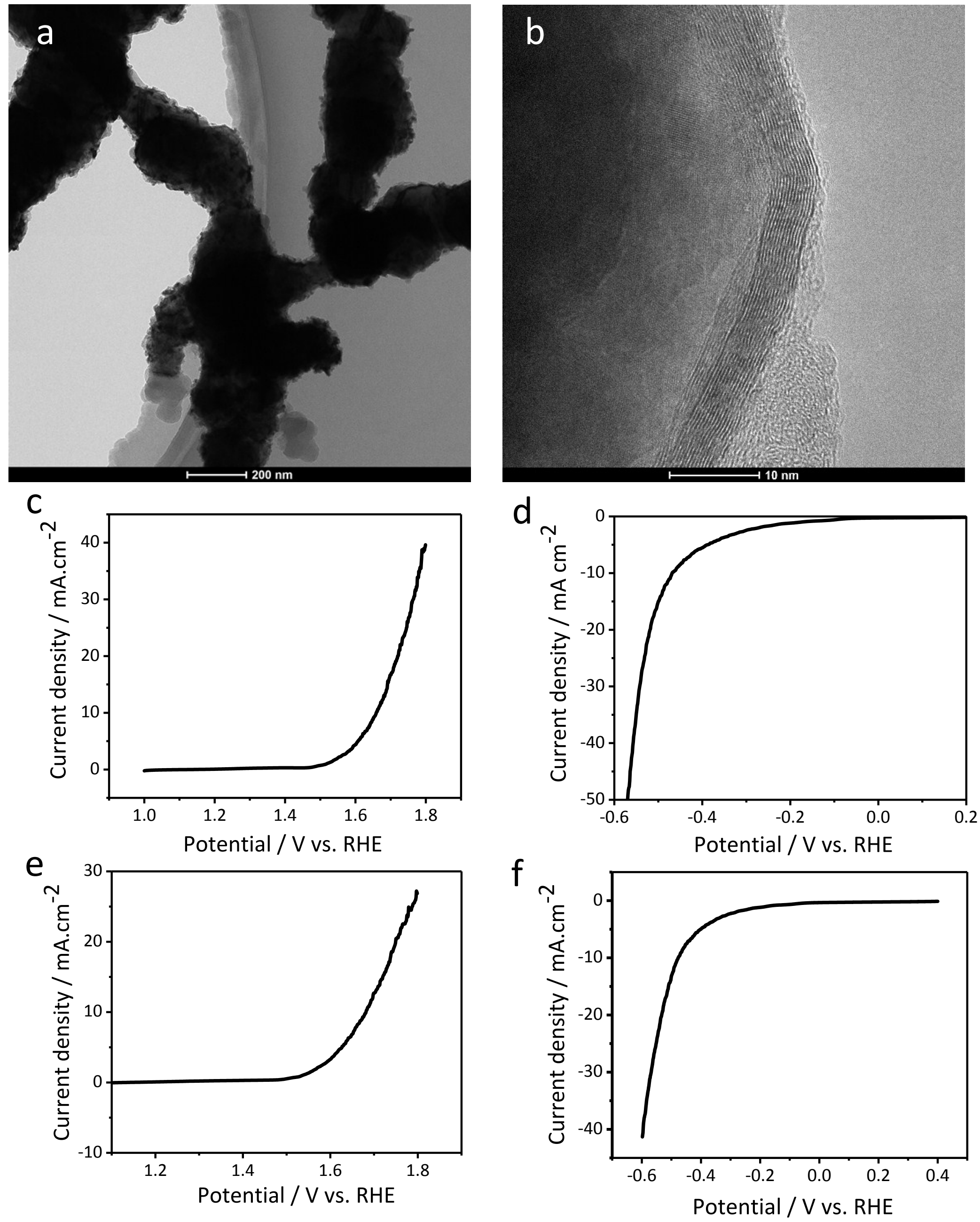

Figure S9. (a, b) TEM images of CFP@Co_3O_4@C; (c, d) LSV curves for the CFP@C obtained by dissolving the Co_3O_4 core in an acid solution. Etching method: Soaking the CFP@Co_3O_4@C in a 1.0 M H_2SO_4 solution at 60 °C for 12 h; (e, f) The LSV curves for the prepared powder product of N, S-coped carbon. Preparation method: 100 mg dopamine was added into 50 ml of Tris-HCl buffer solution (pH 8.5) and continuously stirred at 25 °C for 48 h to get polymerized dopamine. The achieved product was washed with deionized water and ethanol, and dried at 60 °C in vacuum, which was then subject to sequent sulfuration and carbonization via a procedure as that applied to the nanowire catalysts. We then loaded the powder onto the CFP at a loading of 1.6 mg cm^{-2} to test its activity.

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