Supporting information

Anion exchange reaction: an effective approach to prepare alloyed Co-Fe bimetallic disulfide for improving electrocatalytic activity

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Experimental

Reagents

Carbon cloth (CC) was purchased from CeTech Co., Ltd. Anhydrous cobalt chloride ($CoCl_2$, ≥98.0 %) and Nafion (5.0 wt.%) were purchased from Sigma-Aldrich. Potassium ferricyanide ($K_3[Fe(CN)_6]$, 99.5 wt.%) and urea ($CO(NH_2)_2$, 99 wt.%) were purchased from Sinopharm Group Chemical Reagent Co. Ltd. Pt/C (20 wt.% Pt on carbon) was purchased from Shanghai Macklin Biochemical Co., Ltd. All reagents are of analytical grade. All aqueous solutions were prepared in deionized (DI) water.

Synthesis of $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ nanoneedles on CC

The CC was ultrasonicated for 10 min with acetone, ethanol, and deionized water. Then, the CC was immersed in a mixed solution of concentrated sulfuric acid and concentrated nitric acid with volume ratio of 1:3, and ultrasonicated for 2 h. Finally, the cleaned CC was washed with deionized water for several times and dried in air before use. The $Co(CO_3)_{0.5}(OH) \cdot 0.11H_2O$ nanoneedles on CC (denoted as CCHH/CC)

was synthesized by a facile hydrothermal method. Typically, the CC is placed vertically into a volumetric flask with a capacity of 88 ml, which contains an aqueous solution of 0.1 M $CoCl_2$ and 3.12 wt.% urea. Then, the container is sealed and heated at 90 °C for 8 h.

Synthesis of $Co_2Fe(CN)_6 \cdot 2H_2O$ nanocrystal on CCHH/CC

The $Co_2Fe(CN)_6 \cdot 2H_2O$ was prepared with a slight modification of the method reported previously.[1] The $Co_2Fe(CN)_6 \cdot 2H_2O$ nanocrystals (denoted as CFNH) was prepared via a simple anion exchange reaction. The as-formed CCHH/CC was immersed into a 0.1 M $K_3[Fe(CN)_6]$ aqueous solution for anion exchange at 60 °C for 2 h. The resulted CFNH/CCHH/CC was collected washed with distilled water and then dried at 60 °C overnight in air.

Synthesis of $FeS_2/CoS_2/CC$

A tube furnace manufactured by Thermo Corporation of the United States (TF-55035KC-1) was used as an annealing apparatus for all the samples. The $FeS_2/CoS_2/CC$ composite were obtained through annealing CFNH/CCHH/CC in a hydrogen sulfide atmosphere (10% H_2S, 90% Ar) at 450 °C for 10 min. The same synthesis step was used for the preparation of CoS_2/CC composite, but the precursor was replaced with CCHH/CC.

Characterizations

Surface morphology of samples was characterized using scanning electron microscopy (SEM Hitachi S4800, Japan) and transmission electron microscopy (TEM, JEOL 2000). Powder X-ray diffraction (XRD) patterns were collected using an X'Pert

Pro MPD diffractometer (PANalytical) with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) was performed on a Perkin-Elmer Physical Electronics 5600 spectrometer using Al Kα radiation at 13 kV, and using the binding energy of C 1s at 284.6 eV as a reference.

Electrochemical measurements

The CHI660E electrochemical workstation (CH Instrument Co. Shanghai) was used for all electrochemical tests. Linear sweep voltammetry (LSV) was carried out with a typical three-electrode system in N_2-saturated 0.5 M H_2SO_4 at a scan rate of 5 mV s^{-1} at room temperature. The Pt foil and saturated calomel electrodes (SCE) were used as counter and reference electrodes, respectively. Electrochemically inert polyimide tape was employed to define 2 x 1 cm x 1 cm area of the working electrode, which was immersed in the solution. The potential measured against SCE was converted to the potential versus the RHE by adding a value of (0.242 + 0.059 pH) V. All linear sweep voltammetry tests were performed with 90% iR compensation. Electrochemical impedance spectroscopy (EIS) was performed at -0.2 V, and applying a scanning frequency from 100 kHz to 10 Hz.
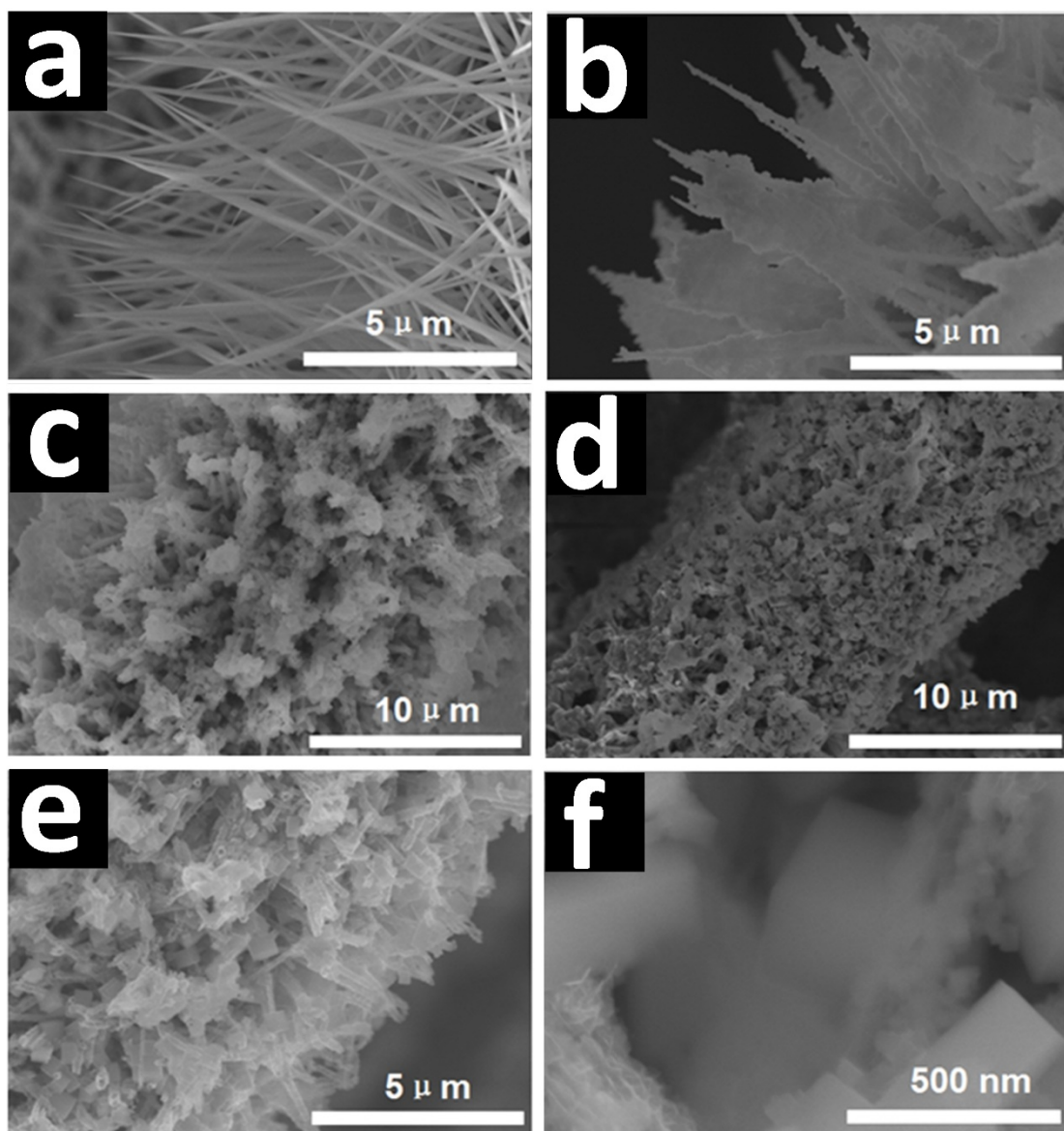
Fig. S1 SEM images of FeS$_2$/CoS$_2$/CC prepared by different anion exchange time of 0 h (a), 0.5 h (b), 1 h (c), 1.5 (d) and 2 h (e, f).
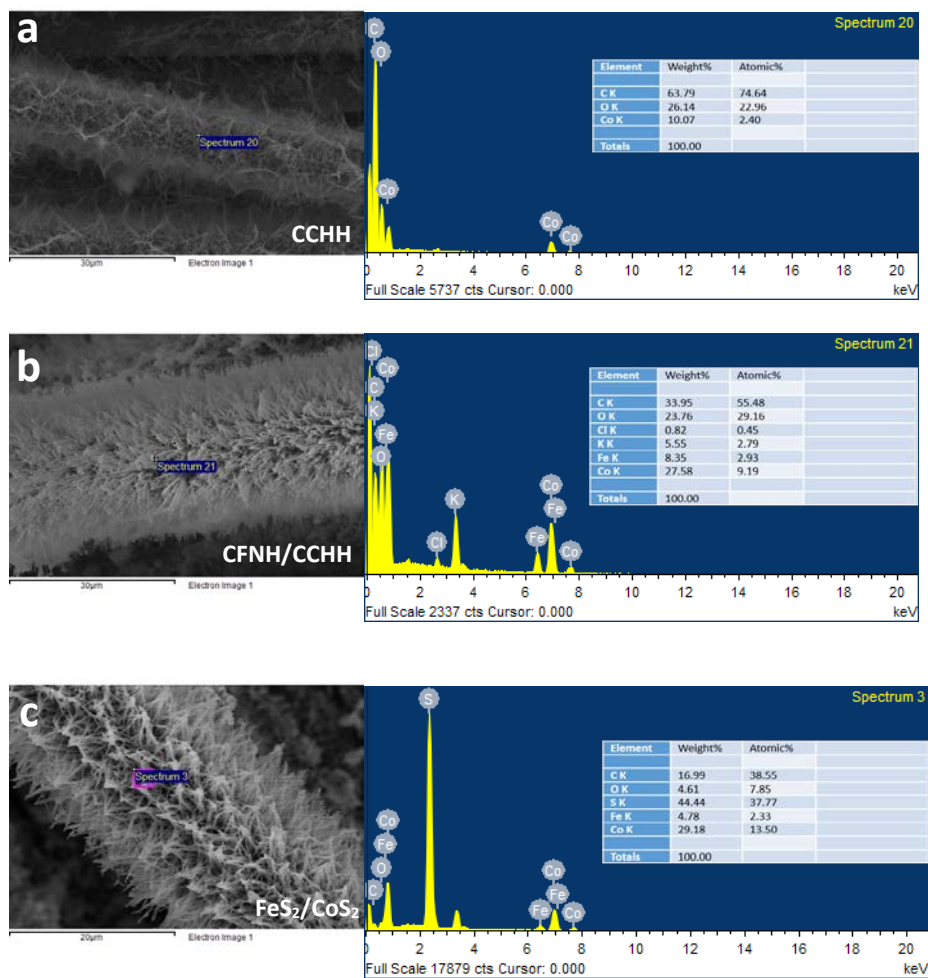
a — CCHH

Spectrum 20

Element	Weight%	Atomic%
C K	63.79	74.64
O K	26.14	22.96
Co K	10.07	2.40
Totals	100.00	

Full Scale 5737 cts Cursor: 0.000

b — CFNH/CCHH

Spectrum 21

Element	Weight%	Atomic%
C K	33.95	55.48
O K	23.76	29.16
Cl K	0.82	0.45
K K	5.55	2.79
Fe K	8.35	2.93
Co K	27.58	9.19
Totals	100.00	

Full Scale 2337 cts Cursor: 0.000

c — FeS$_2$/CoS$_2$

Spectrum 3

Element	Weight%	Atomic%
C K	16.99	38.55
O K	4.61	7.85
S K	44.44	37.77
Fe K	4.78	2.33
Co K	29.18	13.50
Totals	100.00	

Full Scale 17879 cts Cursor: 0.000

Fig. S2 SEM images and corresponding EDX results of the products in different steps. (a) Co(CO$_3$)$_{0.5}$(OH)·0.11H$_2$O/CC (CCHH) obtained by hydrothermal treatment, (b) CCHH after ion exchange for 2 h in 0.1 M K$_3$[Fe(CN)$_6$] solution, and (c) the resultant FeS$_2$/CoS$_2$/CC.
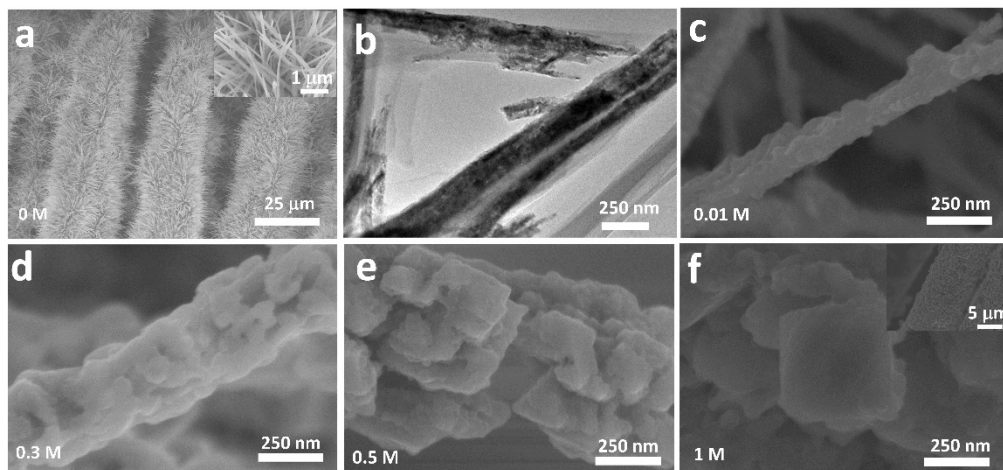
Fig.S3 The morphology of the samples treated with different concentration of K$_3$[Fe(CN)$_6$]. (a) SEM and (b) TEM images of the sample without K$_3$[Fe(CN)$_6$] treatment (CoS$_2$/CC). Inset in (a) is the enlarged SEM image. SEM images of the samples treated with (c) 0.01 M, (d) 0.3 M, (e) 0.5 M and (f) 1 M K$_3$[Fe(CN)$_6$], respectively. Inset in (f) is the SEM image in less magnification.
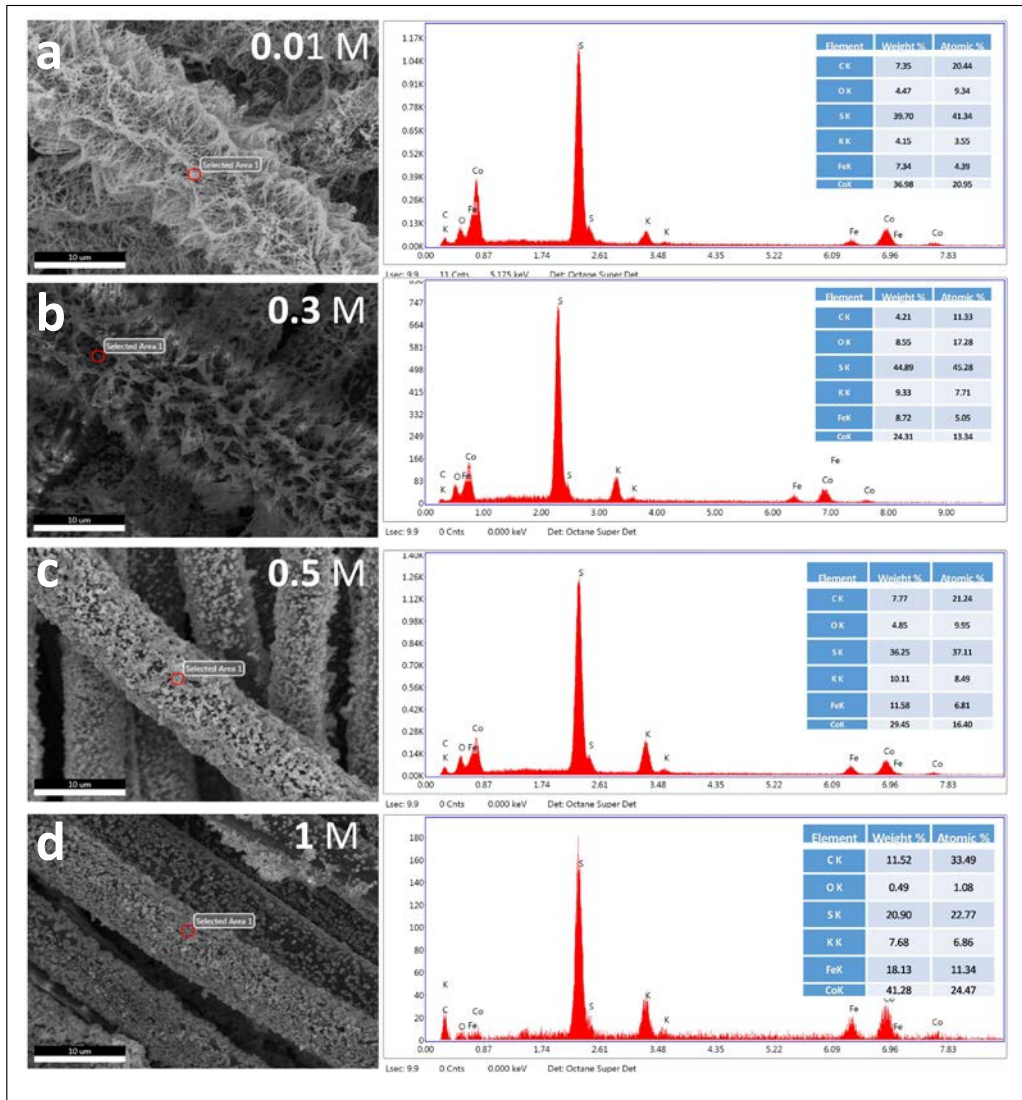
Fig.S4 SEM images and corresponding EDX results of the samples treated with different concentration of $K_3[Fe(CN)_6]$. (a) 0.01 M, (b) 0.3 M, (c) 0.5 M and (d) 1 M $K_3[Fe(CN)_6]$, respectively.
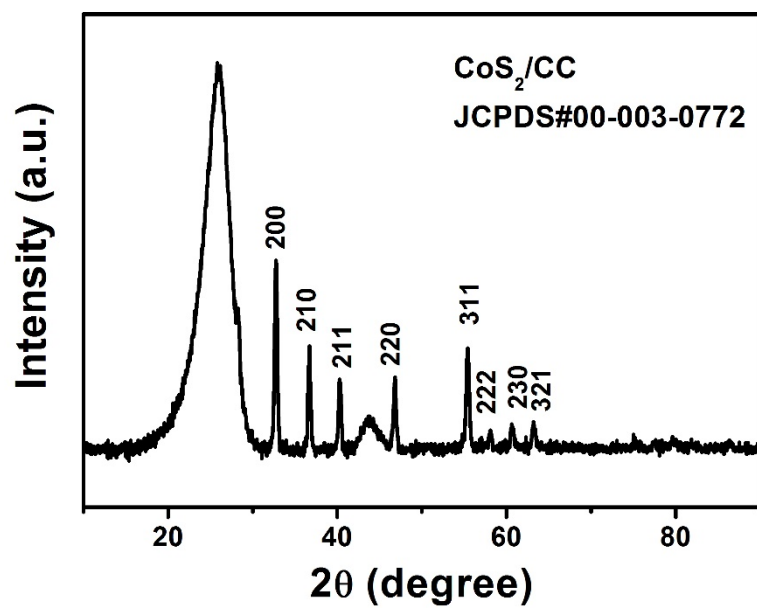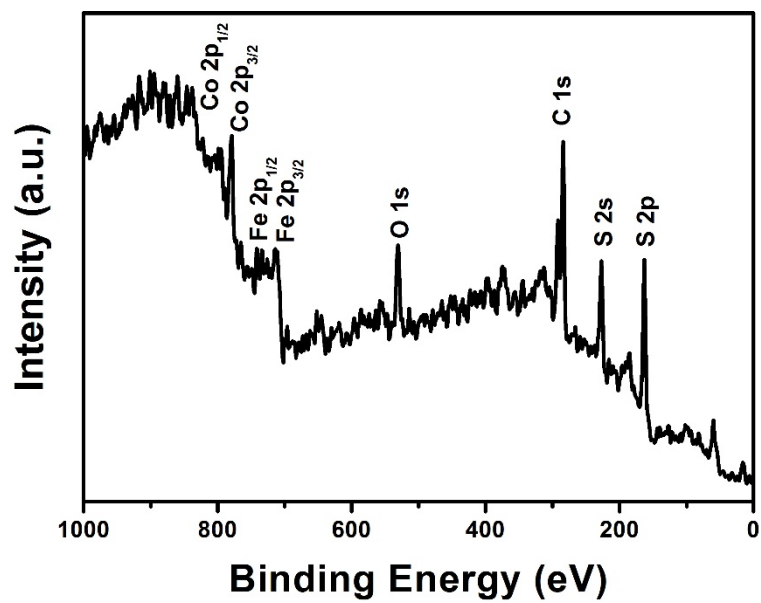
Fig. S5 XRD pattern of CoS$_2$/CC.

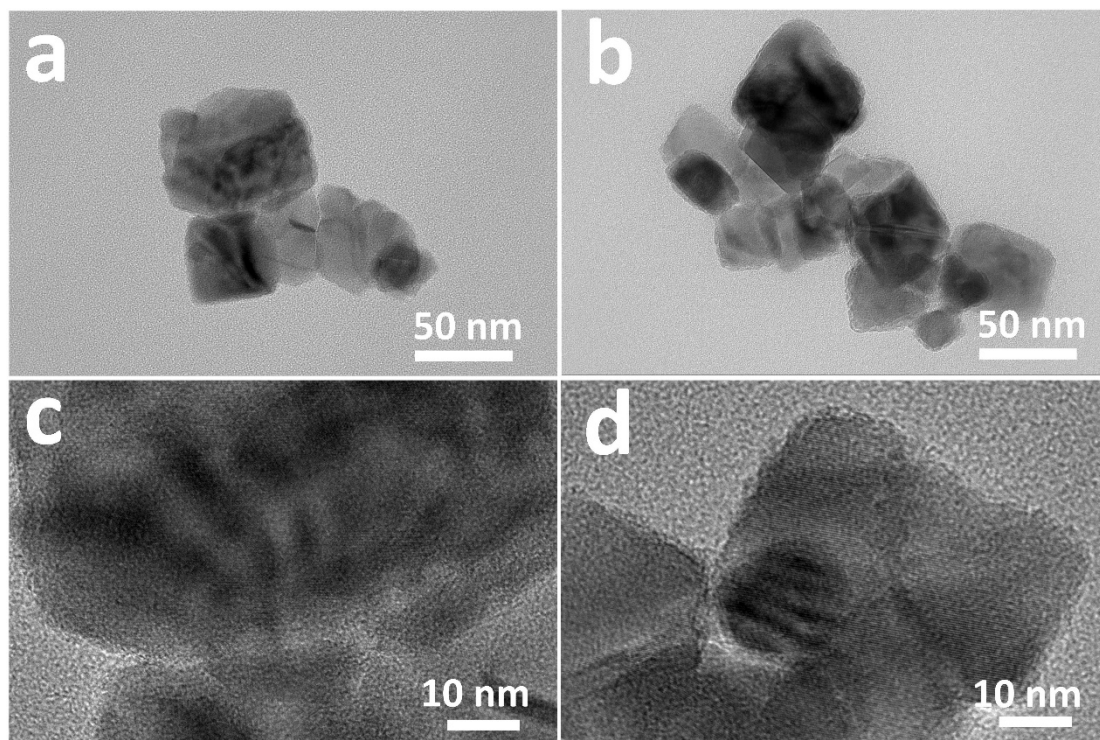**Fig. S6** XPS survey spectrum of FeS$_2$/CoS$_2$/CC.

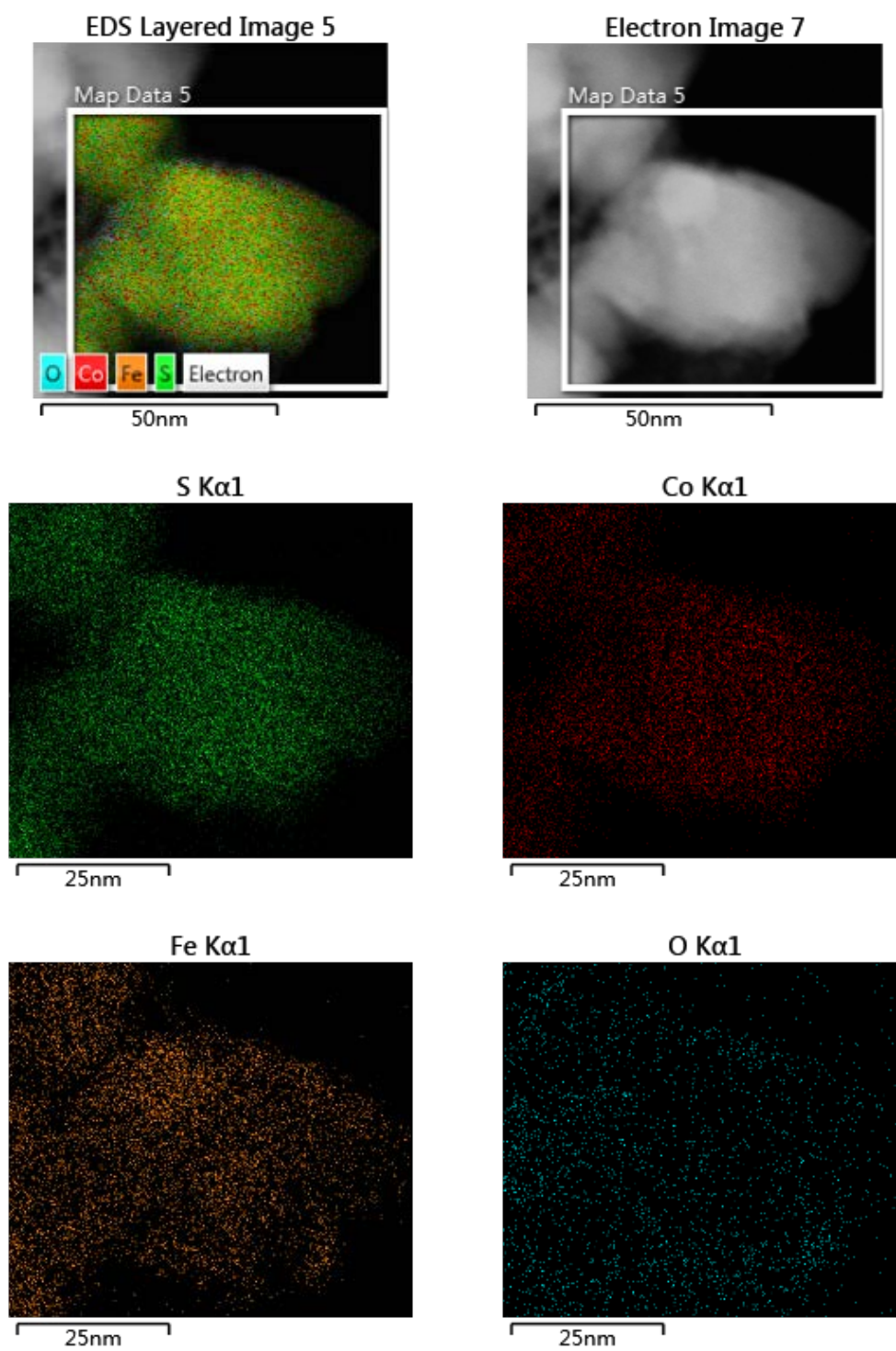**Fig. S7** Additional TEM and HR-TEM image of FeS$_2$/CoS$_2$/CC.

Fig. S8 Additional STEM image and corresponding EDX mapping of Co, Fe, S, and O elements in FeS$_2$/CoS$_2$ nanocarystals..
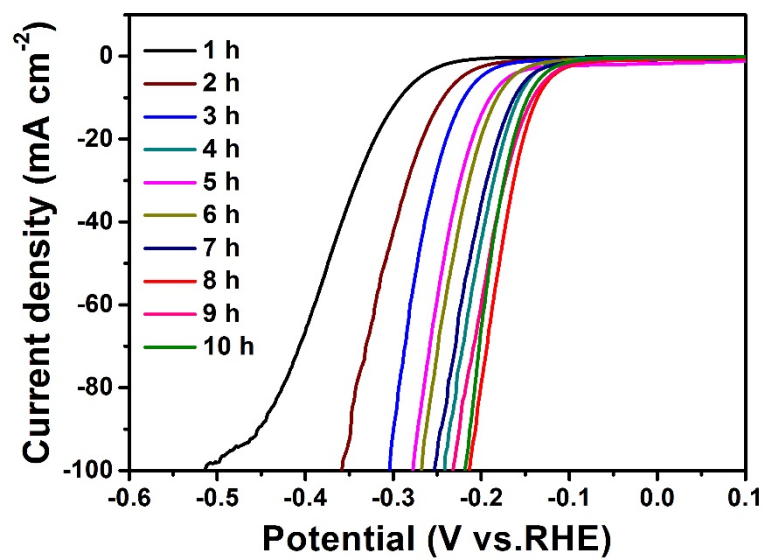
Fig. S9 Polarization curves of FeS$_2$/CoS$_2$/CC prepared with different hydrothermal time in the first step.
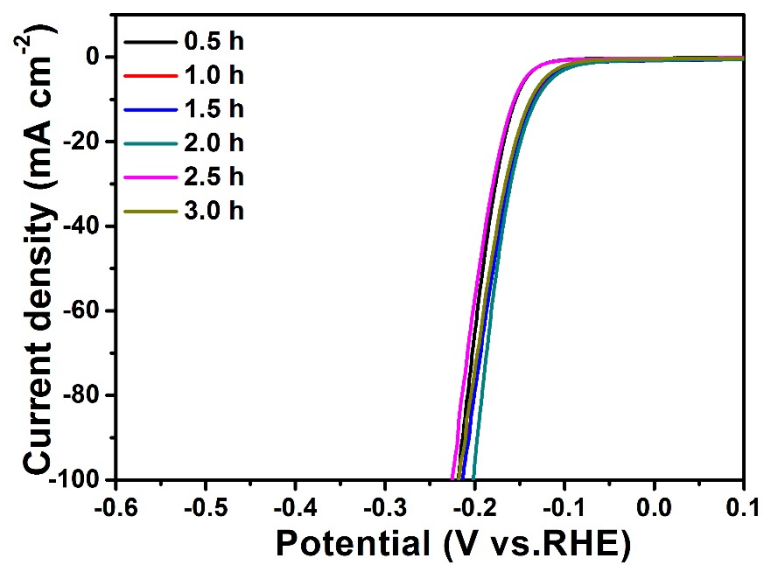
Fig. S10 Polarization curves of $FeS_2/CoS_2/CC$ prepared with different anion exchange time in second-step.
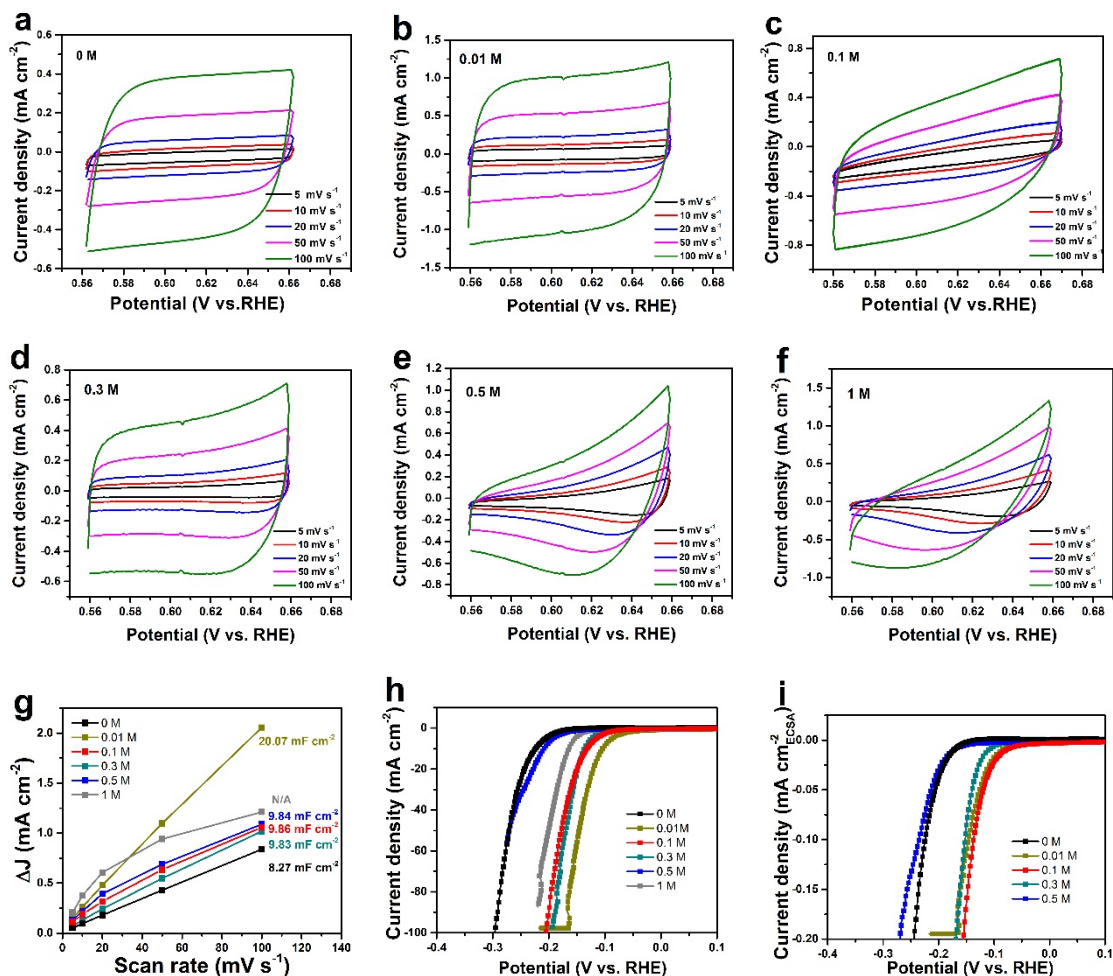
Fig.S11 Cyclic voltammograms (CVs) of samples treated with (a) 0 M, (b) 0.01 M, (c) 0.1 M, (d) 0.3 M, (e) 0.5 M and (f) 1 M $K_3[Fe(CN)_6]$, respectively. (g) The calculated values of the double layer capacitance (C_{dl}). HER polarization curves of the samples in N_2-saturated 0.5 M H_2SO_4 normalized by geometric area (h) and ECSA (i), respectively.

The specific capacitance can be converted into an ECSA using the specific capacitance value for a flat standard with 1 cm^2 of real surface area. The specific capacitance for a flat surface is generally found to be in the range of 20-60 $\mu F\ cm^{-2}$. 40 $\mu F\ cm^{-2}$ is assumed for a flat surface in the following calculations of TOF.

$$\text{Area}_{ECSA}^{\text{FeS}_2/\text{CoS}_2/\text{CC}} = \frac{9.86 \ mFcm^{-2}}{40 \ \mu Fcm^{-2} \ per \ cm_{ECSA}^2} = 246.5 \ cm_{ECSA}^2$$

$$\text{Area}_{ECSA}^{\text{CoS}_2/\text{CC}} = \frac{8.27 \ mFcm^{-2}}{40 \ \mu Fcm^{-2} \ per \ cm_{ECSA}^2} = 206.8 \ cm_{ECSA}^2$$

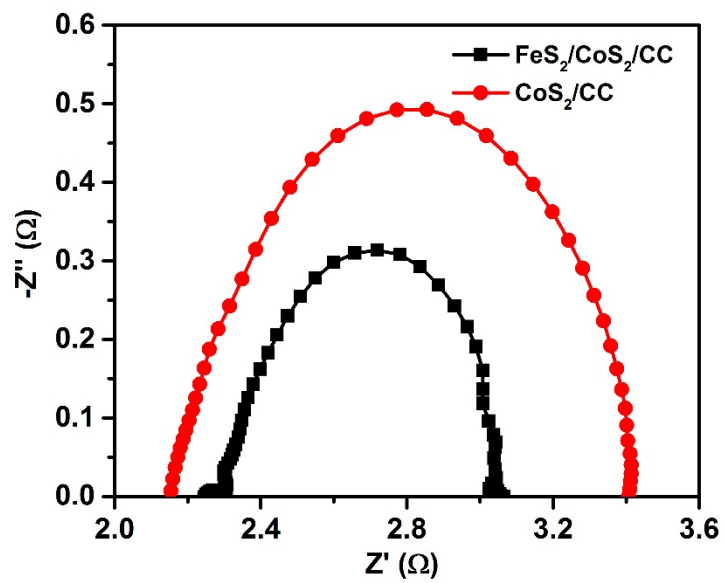**Fig. S12** Nyquist plots of (a) CoS$_2$/CC and (b) FeS$_2$/CoS$_2$/CC at -200 mV (vs. RHE).

Table.S1 The atomic concentration of the elements in the $FeS_2/CoS_2/CC$.

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Atomic Concentration of FeS₂/CoS₂/CC  by XPS
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  C1s     O1s     S2p     Fe2p    Co2p

 55.76   13.26   23.34    3.95    3.69
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Table.S2 The lattice spacing parameters of the cubic pyrite phase crystal.

Spot#	d-Spacing (nm)	Rec. Pos. (1/nm)	Degrees to Spot 1	Facet
1	0.2778	3.6	0	(200)
2	0.1964	5.093	36.75	(220)
3	0.3154	3.171	80.26	(111)
4	0.2268	4.409	135.1	(211)

Table.S3 Comparison of HER performance of $FeS_2/CoS_2/CC$ in acid media with recently well-developed HER electrocatalysts.

Catalyst	Mass loading (mg cm^{-2})	C_{dl} (mF cm^{-2})	Tafel slope (mV decade^{-1})	Current Density (j, mA cm^{-2})	Overpotential at the corresponding j (η mV)	Reference
CoS_2-MoS_2/CNTs	~0.35	/	67	80	240	[2]
NiP-MoS_2	/	/	76	40	250	[3]
Zn-Co-S/TM	1.0	28.58	164	20	238	[4]
CoS_2/GO-5%	/	/	285	100	350	[5]
MoS_2/CoS_2/CC	18.6	7.04	73.4	100	240	[6]
CoS_2 Pyramid/Ti	/	3.42±0.09	~72	~65	~260	[7]
Ag_2S/CuS	12.06	/	75	10	200	[8]
NiCu-P	65	/	37	10	226	[9]
$(Fe_{0.48}Co_{0.52})S_2$	/	3.74	47.5	10	196	[10]
FeCo@N-graphene	0.285	/	74	10	262	[11]
MoS_2-WS_2 Heterostructures	/	/	72	10	129	[12]
Ti_3C_2 NFs	0.3	21	97	10	169	[13]
M-MoS_2 nanopetals	0.1	10.05	44	10	210	[14]
MoP/CNT	1	54	51.6	10	114	[15]
				50	~200	
FeS_2/CoS_2/CC	0.91	9.86	57	100	205	This work

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