

Supplementary Information

Engineering Pyrite-type Bimetallic Ni-doped CoS₂ Nanoneedle Arrays over a Wide Compositional Range for Enhanced Oxygen and Hydrogen Electrocatalysis with Flexible Property

Guowei He¹, Wei Zhang¹, Yida Deng¹, Cheng Zhong^{1,2}, Wenbin Hu^{1,2} and Xiaopeng Han^{1,2,3,*}

¹ Tianjin Key Laboratory of Composite and Functional Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China

² Key Laboratory of Advanced Ceramics and Machining Technology (Ministry of Education), Tianjin University, Tianjin 300072, China.

³ Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

* Correspondence: xphan@tju.edu.cn

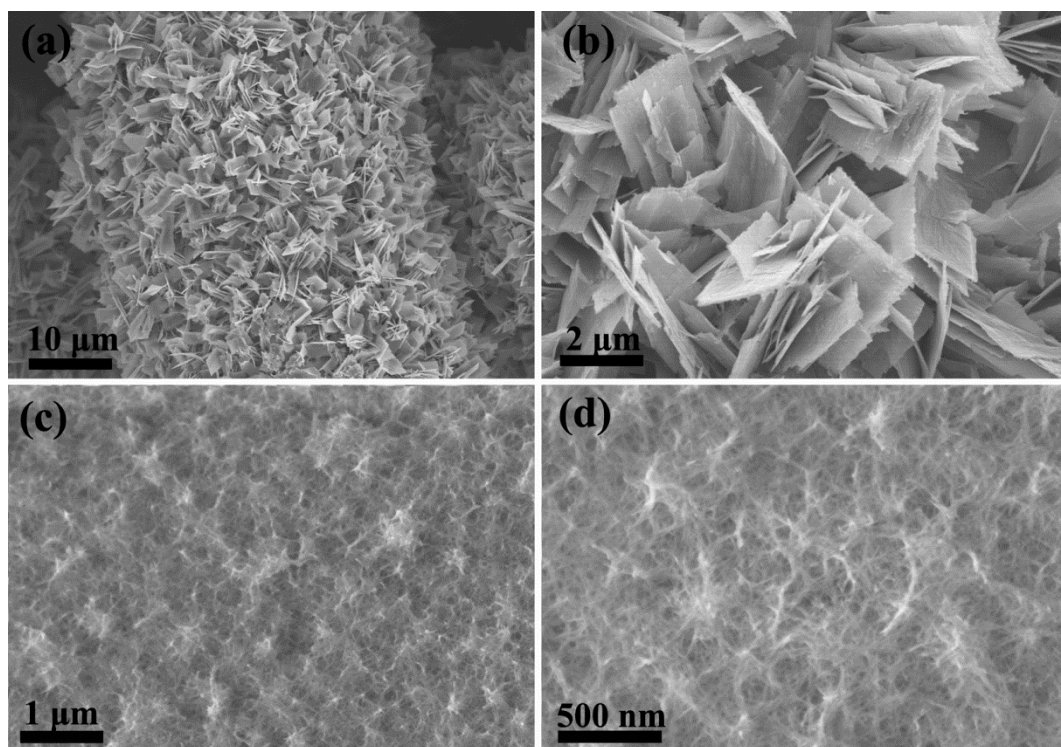


Figure S1. SEM images of synthesized bare $\text{Co}(\text{CO}_3)_{0.5}\text{OH}$ (a) and $\text{Ni}(\text{CO}_3)_{0.5}\text{OH}$ (b) precursors. It can be seen that completely different morphologies, i.e., nanoflakes and nanowire-aggregated products are observed for pure $\text{Co}(\text{CO}_3)_{0.5}\text{OH}$ and $\text{Ni}(\text{CO}_3)_{0.5}\text{OH}$ compared to the nanoneedles of Ni-Co carbonate hydroxide. Therefore, the Ni-doping has an important effect on the morphologies of final Ni-Co carbonate precursors.

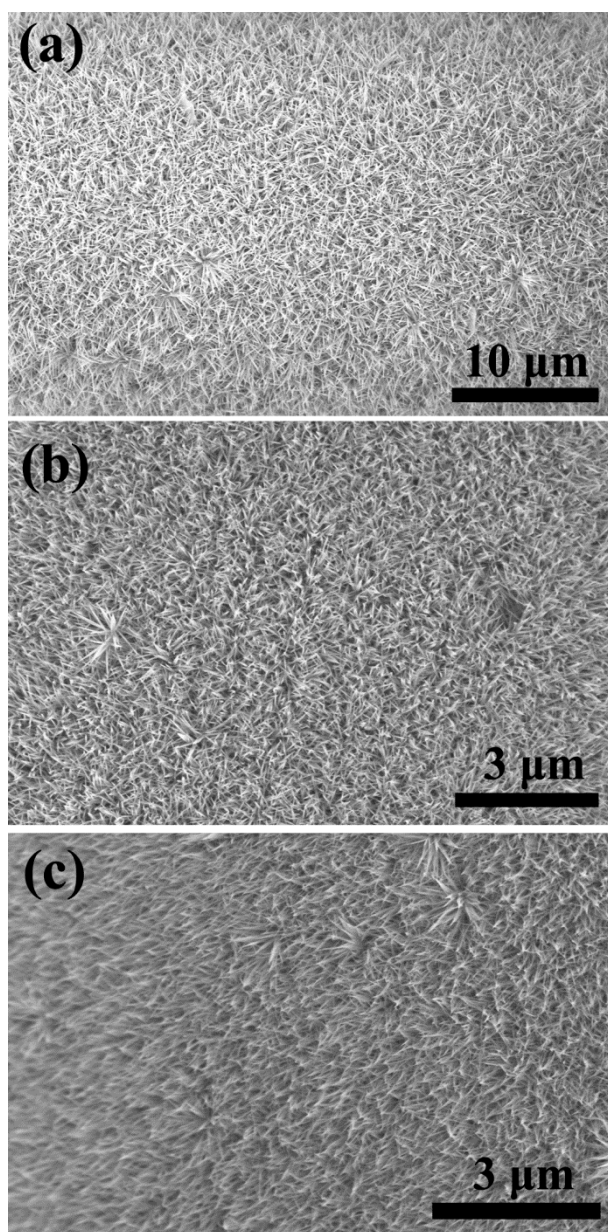


Figure S2. Low-magnification SEM images of prepared Ni-Co carbonate hydroxide precursors with Co/Ni ratios of 2:1 (a), 1:1 (b), and 1:2 (c), respectively. The SS substrate is covered densely and uniformly by the Ni-Co-carbonate hydroxide nanoneedle arrays on a larger scale size.

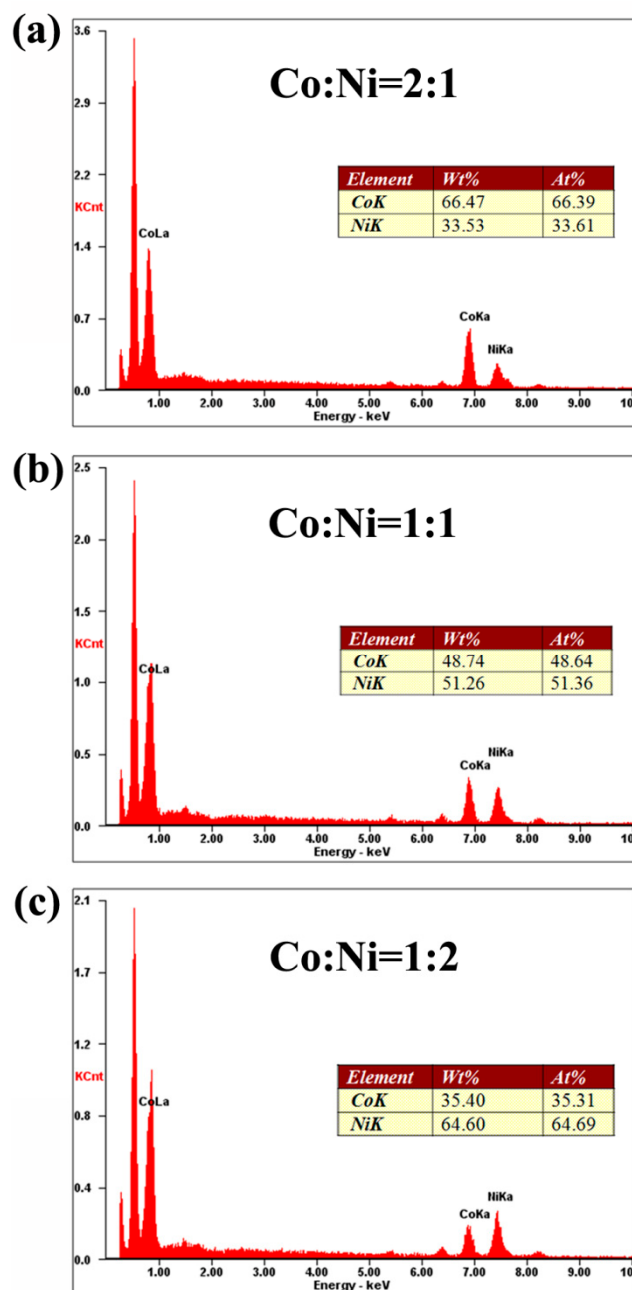


Figure S3. EDS spectra of prepared Ni-Co carbonate hydroxide precursors with Co/Ni ratios of 2:1 (a), 1:1 (b), and 1:2 (c), respectively. The results are in good accordance with the standard values.

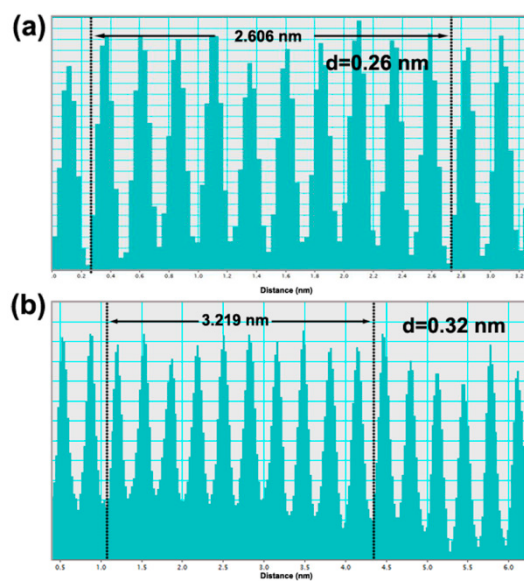


Figure S4. Intensity profiles from the selected area of HRTEM images of Ni-Co precursor and $\text{Ni}_x\text{Co}_{1-x}\text{S}_2$ samples with Ni:Co ratio of 1:2. The results here further confirmed the lattice distances of corresponding lattice planes.

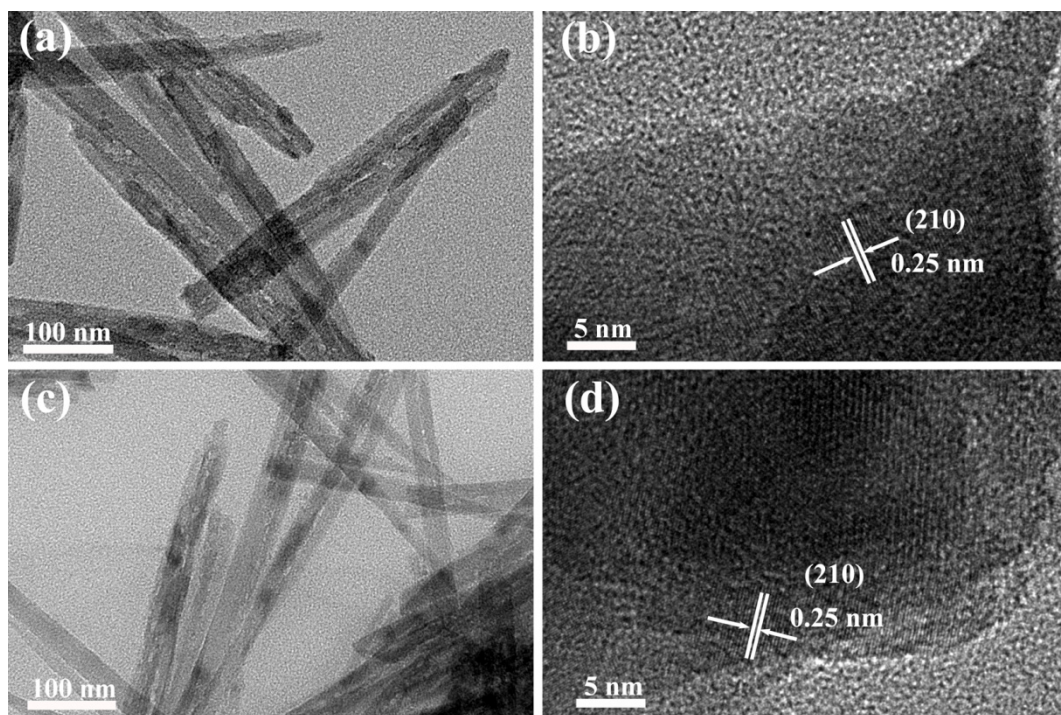


Figure S5. TEM and HRTEM images of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_2$ (a, b) and $\text{Ni}_{0.67}\text{Co}_{0.33}\text{S}_2$ (c, d) nanoneedles.

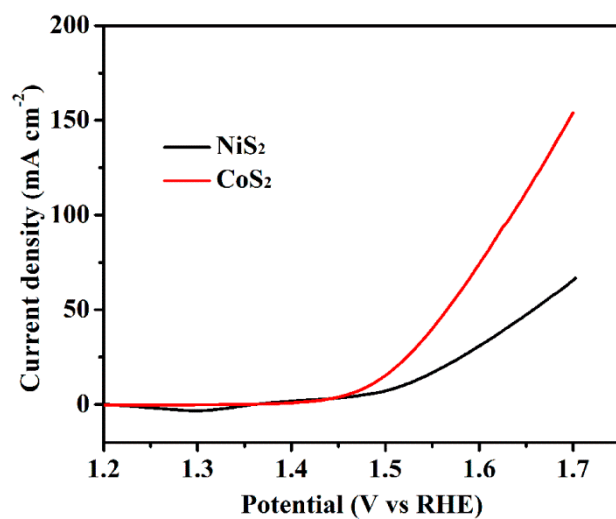


Figure S6. OER performance of monometallic CoS₂ and NiS₂.

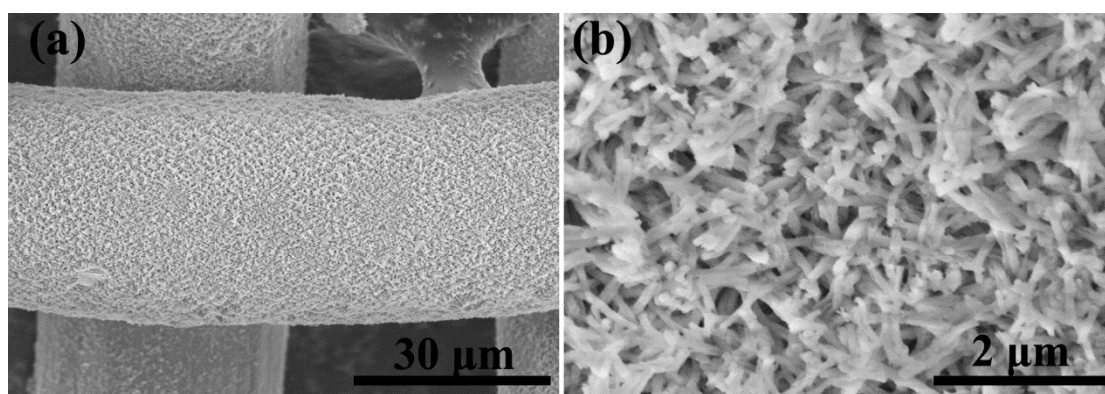


Figure S7. SEM images of Ni-Co-S NN after OER polarization for 15,000 s.

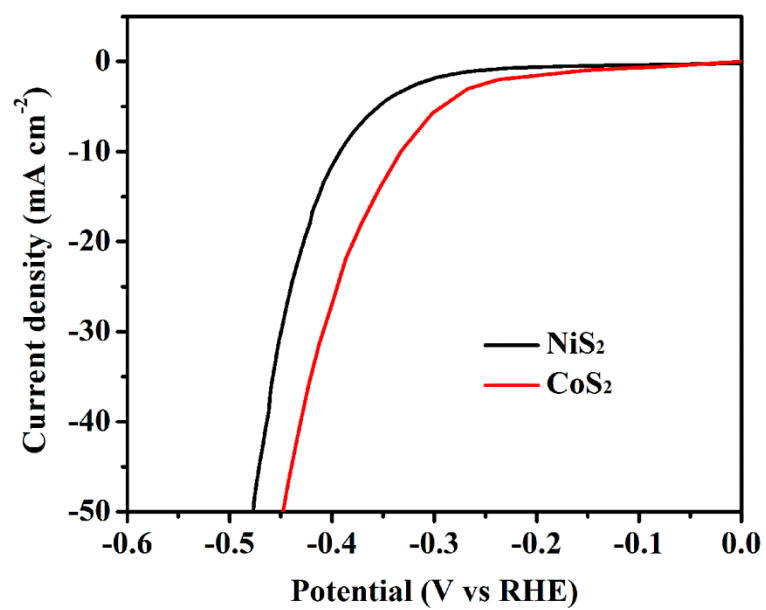


Figure S8. HER performance of monometallic CoS₂ and NiS₂.

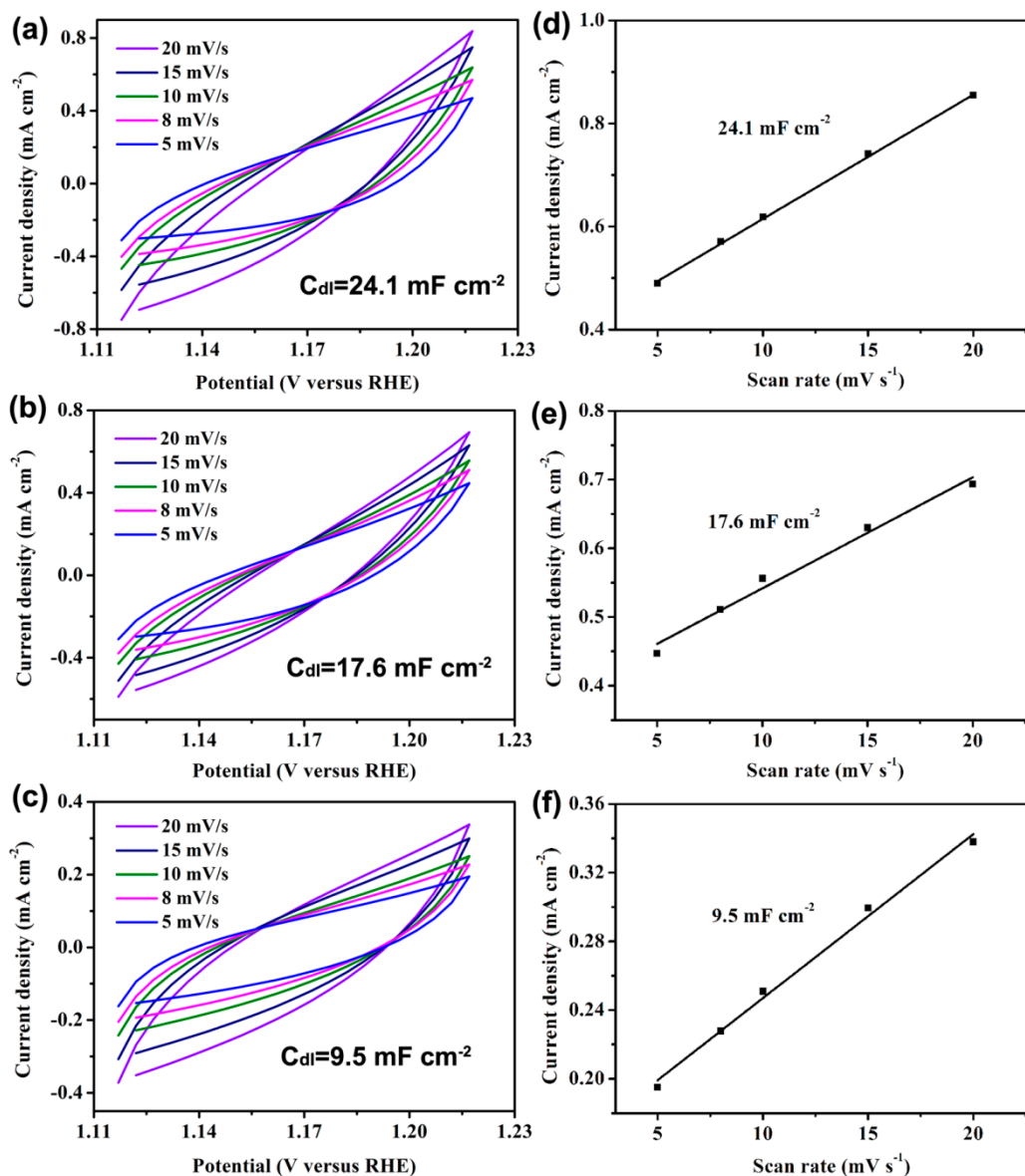


Figure S9. Cycle voltammograms of (a) $\text{Ni}_{0.33}\text{Co}_{0.67}\text{S}_2$, (b) $\text{Ni}_{0.5}\text{Co}_{0.5}\text{S}_2$, and (c) $\text{Ni}_{0.67}\text{Co}_{0.33}\text{S}_2$ from 1.12 to 1.22 V vs RHE in 1.0 M KOH at scan rates of 5, 8, 10, 15, 20 mV s^{-1} . (d-f) The corresponding fitted linear relationship of the capacitive current density versus scan rates.

Table S1. 2 θ degree of selected crystal planes in prepared samples.

Sample	(200)	(210)	(211)	(220)	(311)
CoS ₂	32.5	36.4	40.0	46.5	55.2
Ni _{0.33} Co _{0.67} S ₂	32.4	36.1	39.7	46.1	54.6
Ni _{0.5} Co _{0.5} S ₂	32.0	36.0	39.6	46.0	54.5
Ni _{0.67} Co _{0.33} S ₂	31.7	35.6	39.2	45.5	54.0
NiS ₂	31.5	35.4	38.9	45.2	53.5

Table S2. Comparison of OER performances of Ni_{0.33}Co_{0.67}S₂ NN/SS with other reported non-noble metal OER electrocatalysts in 1.0 M KOH.

Catalyst	Electrode	Loading (mg cm ⁻²)	Current density (mA cm ⁻²)	Overpotential (mV)	References
Ni _{0.33} Co _{0.67} S ₂ NN/SS	Stainless steel	1.2	10 50	247 286	This work
Ni(OH) ₂ /O-MWCNTs	Glassy carbon	0.54	10 50	~310 ~340	Adv. Energy Mater. 2016, 6, 1600516.
CoO _x -ZIF	Glassy carbon	0.2	10 50	~290 ~320	Adv. Funct. Mater. 2017, 27, 1702546.
Zn _{0.76} Co _{0.24} S/CoS ₂ nanowires	Ti mesh	1.0	20 50	~330 ~370	Electrochim. Acta 2016, 190, 360.
Zn-Co-S nanoneedle arrays	Carbon fiber paper	0.60	10 50	320 391	ACS Appl. Mater. Interfaces 2017, 9, 12574.
Co-P film	Copper foil	2.71	10 50	345 395	Angew. Chem., Int. Ed. 2015, 54, 6251.
CoFePO nanowires	Nickel foam	2.187	10 50	274.5 ~360	ACS Nano 2016, 10, 8738.
Co ₃ O ₄ /N-rmGO	Glassy carbon	1.00	10	310	Nat. Mater. 2011, 10, 780.
NiFe@N-doped carbon	Ti foil	3.00	10 50	297 340	Adv. Energy Mater. 2017, 7, 1700220.
NiCo ₂ S ₄ NW/NF	Nickel foam		10 50	260 ~340	Adv. Funct. Mater. 2016, 26, 4661.
FeB ₂	Glassy carbon	0.2	10 50	296 360	Adv. Energy Mater. 2017, 7, 1700513.
Fe-doped NiO	Gold electrode		10 40	297 ~320	ACS Nano 2015, 9, 5180.

Table S3. Comparison of overall water-splitting Performances of Ni_{0.33}Co_{0.67}S₂ NN/SS with other reported non-noble metal electrocatalysts in 1.0 M KOH.

Sample	Loading amount	Current density (mA cm ⁻²)	Potential (V)	Reference
Ni _{0.33} Co _{0.67} S ₂ NN/SS	1.2 mg cm ⁻²	10	1.67	This work
Zn-Co-S NN/CFP	0.6 mg cm ⁻²	10	1.71	ACS Appl. Mater. Interfaces 2017, 9, 12574.
a-CoSe/Ti	3.8 mg cm ⁻²	10	1.65	Chem. Commun., 2015, 51, 16683.
Co _{0.85} Se/NiFe-LDH/graphene foil	4.0 mg cm ⁻²	10	1.67	Energy Environ. Sci., 2016, 9, 478.
Ni ₃ S ₂ /Nickel foam	1.6 mg cm ⁻²	13	1.76	J. Am. Chem. Soc. 2015, 137, 14023.
Co-S/carbon Tubes/carbon paper	~0.32 mg cm ⁻²	10	1.743	ACS Nano, 2016, 10, 2342.
Ni/NiS/Nickel foam	11 mg cm ⁻²	1.7	1.61	Adv. Func. Mater. 2016, 26, 3314.
Co1Mn1CH/NF	~5.6 mg cm ⁻²	10	1.68	J. Am. Chem. Soc. 2017, 139, 8320.
Zn _{0.76} Co _{0.24} S/CoS ₂ nanowires	1.0 mg cm ⁻²	10	1.66	Electrochim. Acta 2016, 190, 360.
NiCo ₂ O ₄ Ni _{0.33} Co _{0.67} S ₂	0.3 mg cm ⁻²	10	~1.72	Adv. Energy Mater. 2015, 5, 1402031.
Ni-P@CFP		20	1.73	Adv. Energy Mater. 2016, 26, 4067.