## **Electronic Supplementary Information**

## **Experimental Section**

**Materials:**  $Co(NO_3)_2 \cdot 6H_2O$ ,  $NiCl_2 \cdot 6H_2O$ ,  $NH_4F$  and urea were purchased from Tianjin Fuchen Chemical Reagent Factory. S powder and Nafion (5 wt%) was purchased from Sigma Aldrich Chemical Reagent Co. Ltd. Pt/C (10 wt% Pt) was purchased from Alfa Aesar (China) Chemicals Co. Ltd. Carbon cloth (CC) was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. Typically, CC was cleaned by sonication sequentially in acetone, water and ethanol for 10 min each before use. The water used throughout all experiments was purified through a Millipore system. All the reagents and chemicals were used as received without further purification.

**Preparation of Co(OH)F/CC:** Precursor Co(OH)F/CC was prepared by a simple hydrothermal method. In a typical synthesis, 2 mmol Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 5 mmol NH<sub>4</sub>F, and 10 mmol urea were dissolved in 40 mL ultrapure water under magnetic stirring to form a uniform pink solution. The above solution and a piece of cleaned CC (2 cm  $\times$  3 cm) were transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 120 °C for 6 h. Then the autoclave cooled down naturally. The resulting precursor was taken out and washed with ultrapure water and dried at 60 °C for 2 h.

**Preparation of CoS<sub>2</sub>/CC:** To obtain CoS<sub>2</sub>/CC, the precursor Co(OH)F/CC and S powder (2 g) were placed at two separate positions in one porcelain boat with S powder at the upstream side of the furnace. Subsequently, the sample was heated at 400 °C for 1 h with a heating speed of 5 °C min<sup>-1</sup> under Ar. The furnace was then allowed to cool to room temperature in Ar.

**Preparation of Ni(OH)**<sub>2</sub>-CoS<sub>2</sub>/CC: The electrodeposition of Ni(OH)<sub>2</sub> on CoS<sub>2</sub>/CC nanowires was carried in a standard three electrode electrochemical cell (as-obtained CoS<sub>2</sub>/CC, working electrode; Pt foil, counter electrode; SCE, reference electrode). The electrolyte was an aqueous solution of 0.1 M NiCl<sub>2</sub>. The electrodeposition experiments were all carried out at a constant cathodic current density of 1 mA cm<sup>-2</sup> for different time, such as 150, 300, 600 and 900s. After the deposition, the obtained composite electrode was taken out, rinsed with deionized water and ethanol several times and dried at 60 °C in air. For comparison, the Ni(OH)<sub>2</sub> was directly

electrodeposited onto carbon cloth under the above mentioned electrodeposition condition.

**Characterizations:** The XRD patterns were obtained from a LabX XRD-6100 X-ray diffractometer with Cu K $\alpha$  radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM images were collected on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using Ni(OH)<sub>2</sub>-CoS<sub>2</sub>/CC as the working electrode, platinum wire as the counter electrode, and Hg/HgO as the reference electrode. The potentials reported in this work were corrected with ohmic potential drop (iR) losses arising from solution resistance and potentials were reported on a reversible hydrogen electrode (RHE) scale other than especially explained, using the following equation: E (RHE) = E (Hg/HgO) + (0.098 + 0.059 pH) - iR V, R was determined through fittingof AC impedance data to a modified Randles circuit. All experiments were carried out at room temperature (25 °C). The catalyst  $Ni(OH)_2$ -CoS<sub>2</sub>/CC we used for characteration and electrochemical measurements is the sample with deposition of Ni(OH)<sub>2</sub> for 600 s (Ni(OH)<sub>2</sub> loading: 0.6 mg cm<sup>-2</sup>, total loading: 1.8 mg cm<sup>-2</sup>) without further explaination.

**DFT calculations:** DFT calculations were performed using the Vienna ab initio simulation package (VASP).<sup>1-3</sup> The projector augmented wave (PAW) method of Blöchl<sup>4</sup> was used for the treatment of the core electrons. The exchange-correlation energy is described by the functional of Perderw, Burke, and Ernzerhof (PBE) and van der Waals (vdW) interactions were implemented via vdW-D3 functional in the VASP code.<sup>5,6</sup> A plane wave cutoff of 500 eV was chosen in all calculations, with the Monkhorst Pack (MP) grid9 of (3×3×1). The built model with vacuum layer of 15 Å in the perpendicular direction was applied. All geometry structures were allowed to be fully relaxed with the forces converged to less than 0.05 eV/Å and were optimized with a convergence criterion of 0.1 meV in energy.

The free energy was calculated using the equation:<sup>7</sup>

$$G = E + ZPE - TS$$

where *G*, *E*, *ZPE* and *TS* are the free energy, total energy from DFT calculations, zero point energy and entropic contributions (T was set to be 300K), respectively. *ZPE* could be derived after frequency calculation by:<sup>8</sup>

$$ZPE = \frac{1}{2} \sum hv_i$$

And the *TS* values of adsorbed species are calculated after obtaining the vibrational frequencies:<sup>9</sup>

$$TS_{v} = k_{B}T \left[ \sum_{K} \ln(\frac{1}{1 - e^{-hv/k_{B}T}}) + \sum_{K} \frac{hv}{k_{B}T} \frac{1}{(e^{hv/k_{B}T} - 1)} + 1 \right]$$

The energetics of every reaction step are provided in the Table S1.

**Table S1.** Thermodynamic data used in the free energy of formation calculations. CS and HS represent the clean surface and the heterostructured  $Ni(OH)_2$ -CoS<sub>2</sub>.

	ZPE(eV)	TS(eV)	E(eV)
CoS <sub>2</sub> -CS	0.00	0.00	-134.89
Ni(OH) <sub>2</sub> -CoS <sub>2</sub>	0.00	0.00	-341.30
H <sub>2</sub> O-CoS <sub>2</sub> -CS	0.61	0.48	-150.14
(HO-H) <sup>*</sup> -CoS <sub>2</sub> -CS	0.58	0.34	-150.10
H <sup>*</sup> -CoS <sub>2</sub> -CS	0.23	0.09	-138.75
H <sub>2</sub> O-CoS <sub>2</sub> -HS	0.67	0.33	-359.69
(HO-H) <sup>*</sup> -CoS <sub>2</sub> -HS	0.67	0.32	-358.03
H <sup>*</sup> -CoS <sub>2</sub> -HS	0.22	0.09	-349.31

The key reaction steps in alkaline HER:

(1)  $H_2O + e^- + cat \rightarrow H^*-cat + OH^-$  (Volmer step)

② 2H\*-cat →  $H_2$  ↑ (Tafel step)

③ H\*-cat + H<sub>2</sub>O + e<sup>-</sup> → cat + OH<sup>-</sup> + H<sub>2</sub> ↑ (Heyrovsky step)

The free energy for Step ① and ③ should be the same at equilibrium potential of HER. Under this assumption, one can avoid computation of the exact free energy of OH<sup>-</sup> in solutions by using computational hydrogen electrode<sup>.10</sup> Herein, four main stage are considered: initial state, activated water adsorption, H\* intermediates formation, H<sub>2</sub> formation<sup>11</sup>. The free energies (at the reduction potentials U<sub>0</sub>=0 V vs RHE) are calculated as:

$$\begin{split} G_{0} &= G_{cat-H_{2}O} \\ G_{1} &= G_{cat-(H-OH)^{*}} \\ G_{2} &= G_{cat-H^{*}} + G_{OH^{-}} \\ G_{3} &= G_{cat} + G_{OH^{-}} + \frac{1}{2}G_{H_{2}} \\ G_{3} &= G_{cat} + G_{OH^{-}} + \frac{1}{2}G_{H_{2}} \\ \end{split}$$



Fig. S1. XRD patterns of Co(OH)F/CC and CoS $_2$ /CC.



**Fig. S2.** SEM images of Co(OH)F/CC.



Fig. S3. SAED patterns of CoS<sub>2</sub>.



Fig. S4. EDX spectrum of  $Ni(OH)_2$ -CoS<sub>2</sub>.



Fig. S5. XPS spectra of  $CoS_2$  in the (a) Co 2p and (b) S 2p regions.



**Fig. S6.** High-magnification TEM images of  $Ni(OH)_2$ -CoS<sub>2</sub> nanowires with deposition of  $Ni(OH)_2$  layer for different time: (a) 150 s, (b) 300 s, (c) 600 s and (d) 900 s.



Fig. S7. LSV curves of  $Ni(OH)_2$ -CoS<sub>2</sub>/CC with different deposition time.



Fig. S8. Nyquist plots of  $CoS_2/CC$  and  $Ni(OH)_2$ - $CoS_2/CC$ .

Catalyst	<i>j</i> (mA cm <sup>-2</sup> )	η (mV)	Electrolyte	Ref.
Ni(OH) <sub>2</sub> -CoS <sub>2</sub> /CC	20	99	1.0 M KOH	This work
	50	152	1.0 M KOH	
Ni <sub>5</sub> P <sub>4</sub>	10	150	1.0 M KOH	12
CoOx@CN	10	232	1.0 M KOH	13
CoNi <sub>2</sub> S <sub>4</sub>	10	280	1.0 M KOH	14
Co <sub>9</sub> S <sub>8</sub> -Ni <sub>x</sub> S <sub>y</sub> /NF	10	160	1.0 M KOH	15
Co-P film	20	115	1.0 M KOH	16
Co-NRCNTs	20	>450	1.0 M KOH	17
Co-S/FTO	1	480	1.0 M KOH	18
Mo <sub>2</sub> C-C	10	149	1.0 M KOH	19
MoC <sub>x</sub> octahedrons	10	151	1.0 M KOH	20
WC-CNTs	10	150	1.0 M KOH	21
Ni/Mo <sub>2</sub> C-PC	10	179	1.0 M KOH	22
NiFe LDH/NF	10	209	1.0 M NaOH	23
Ni <sub>12</sub> P <sub>5</sub>	10	170	1.0 M KOH	24
CoS <sub>2</sub> NPA/CFP	20	290	1.0 M KOH	25
MoS <sub>2</sub> /Ni <sub>3</sub> S <sub>2</sub>	10	110	1.0 M KOH	26

**Table S2.** Comparison of HER performance of several recently reported highly active non-noble electrocatalysts.

## References

- 1 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter*, 1993, **48**, 13115–13118.
- 2 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter*, 1996, **54**, 11169–11186.
- 3 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
- 4 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
- 5 S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem., 2011, 32, 1456–1465.
- 6 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- 7 J. K. Norskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *Plos One*, 2005, **5**, 12154–12154.
- 8 J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, *J. Phys. Chem. B*, 2004, **108**, 17886–17892.
- 9 L. I. Bendavid and E. A. Carter, J. Phys. Chem. C, 2013, 117, 26048–26059.
- 10 Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, M. Jaroniec and S. Z. Qiao, J. Am. Chem. Soc., 2016, 138, 16174–16181.
- 11 J. Zhang, T. Wang, P. Liu, S. Liu, R. Dong, X. Zhuang, M. Chen and X. Feng, *Energy Environ. Sci.*, 2016, 9, 2789–2793.
- 12 M. Ledendecker, S. K. Calderon, C. Papp, H. P. Steinruck, M. Antonietti and M. Shalom, *Angew. Chem. Int. Ed.*, 2015, **54**, 12361–12365.
- H. Jing, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, J. Am. Chem. Soc., 2015, 137, 2688–2694.
- 14 D. Wang, X. Zhang, Z. Du, Z. Mo, Y. Wu, Q. Yang, Y. Zhang and Z. Wu, *Int. J. Hydrogen Energy*, 2017, **42**, 3043–3050.
- D. Ansovini, C. J. J. Lee, C. Chua, L. T. Ong, H. Tan, W. R. Webb, R. Rajab and
   Y. F. Lim, *J. Mater. Chem. A*, 2016, 4, 9744–9749.
- 16 N. Jiang, B. You, M. Sheng and Y. Sun, Angew. Chem. Int. Ed., 2015, 54, 1–5.
- 17 X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova and T. Asefa, *Angew. Chem. Int. Ed.*, 2014, **53**, 4372–4376.
- 18 Y. Sun, C. Liu, D. C. Grauer, J. Yano, J. R. Long, P. Yang and C. J. Chang, J. Am. Chem. Soc., 2013, 135, 17699–17702.

- 19 Z. Wu, J. Wang, R. Liu, K. Xia, C. Xuan, J. Guo, W. Lei and D. Wang, *Nano Energy*, 2017, **32**, 511–519.
- 20 H. Wu, B. Xia, L. Yu, X. Yu and X. Lou, *Nat. Commun.*, 2015, **6**, 6512.
- 21 X. Fan, H. Zhou and X. Guo, *ACS Nano*, 2015, **9**, 5125–5134.
- Z. Yu, Y. Duan, M. Gao, C. Lang, Y. Zheng and S. Yu, *Chem. Sci.*, 2017, 8, 968–973.
- J. Luo, J. H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N. G. Park, S. D.
   Tilley, H. Fan and M. Gratzel, *Science*, 2014, 345, 1593–1596.
- 24 P. W. Menezes, A. Indra, C. Das, C. Walter, C. Gobel, V. Gutkin, D. Schmeisser and M. Driess, ACS Catal., 2017, 7, 103–109.
- H. Zhang, Y. Li, G. Zhang, T. Xu, P. Wan and X. Sun, *J. Mater. Chem. A*, 2015, 3, 6303–6310.
- 26 J. Zhang, T. Wang, D. Pohl, B. Rellinghaus, R. Dong, S. Liu, X. Zhuang and X. Feng, Angew. Chem. Int. Ed., 2016, 55, 6702–6707.