Supporting Information

Surface-induced 2D/1D Hetero-structured Growth of ReS_2/CoS_2 for High Performance Electro-catalyst

Yuanwu Liu[1], Jing Li[1], Wentian Huang[1], Ying Zhang[1], Minjie Wang[1], Xingsen Gao[1], Xin Wang[2], Mingliang Jin[2], Zhipeng Hou[1], Guofu Zhou[2], Zhang Zhang[1,2]*, Junming Liu[1,3]*

1. Guangdong Provincial Key Laboratory of Quantum Engineering and Quantum Materials, Institute for Advanced Materials, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, P. R. China

2. National Center for International Research on Green Optoelectronics, South China Academy of Advanced Optoelectronics, South China Normal University, Guangzhou 510006, P. R. China

3. Laboratory of Solid State Microstructure, Nanjing University, Nanjing 210093, P. R. China

Corresponding Author

*E-mail: zzhang@scnu.edu.cn (Zhang Zhang)

*E-mail: houzp@m.scnu.edu.cn (Zhipeng Hou)

Calculation of lattice mismatch of ReS_2/CoS_2

The cell parameters of CoS_2 and ReS_2 are shown below: CoS_2 (JCPDS 41-1471; space group *Pa3*; a = 5.5376 Å), ReS_2 (JCPDS 52-0818; space group *P1*; a = 6.45 Å). According to the calculation formula of lattice mismatch degree of semiconductor heterojunction[1], the mismatch degree is 15.22%.

$$\delta = \frac{2|a_{CoS_2} - a_{ReS_2}|}{a_{CoS_2} + a_{ReS_2}} = 15.22\%$$

Supplementary figures

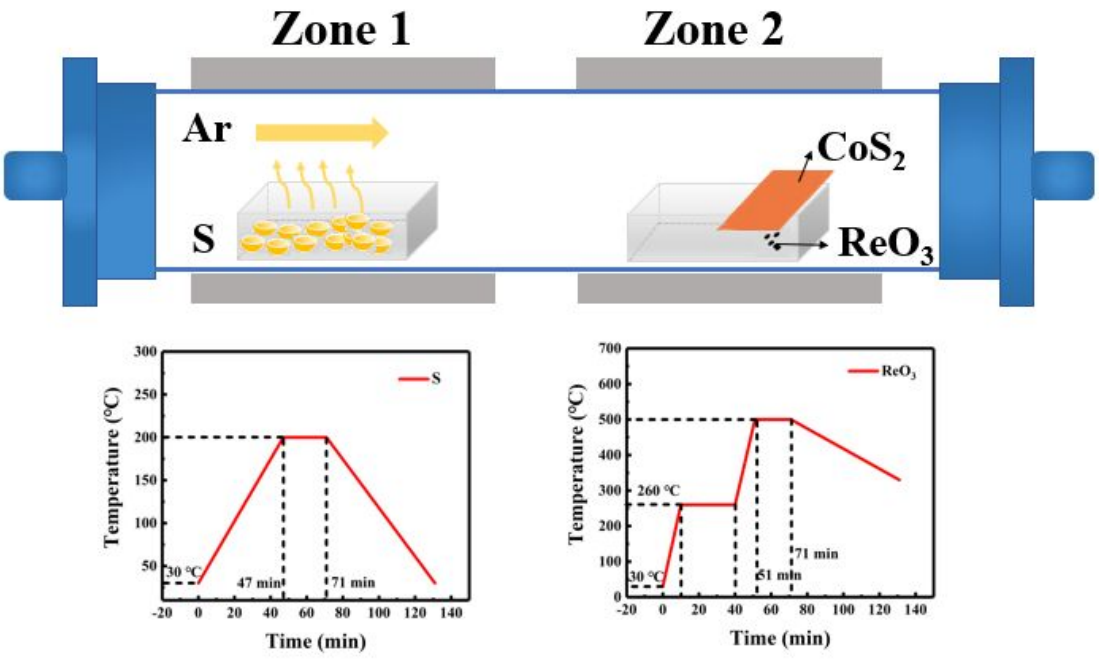

Figure S1. Schematic of the controlled synthesis of ReS_2 via CVD method.

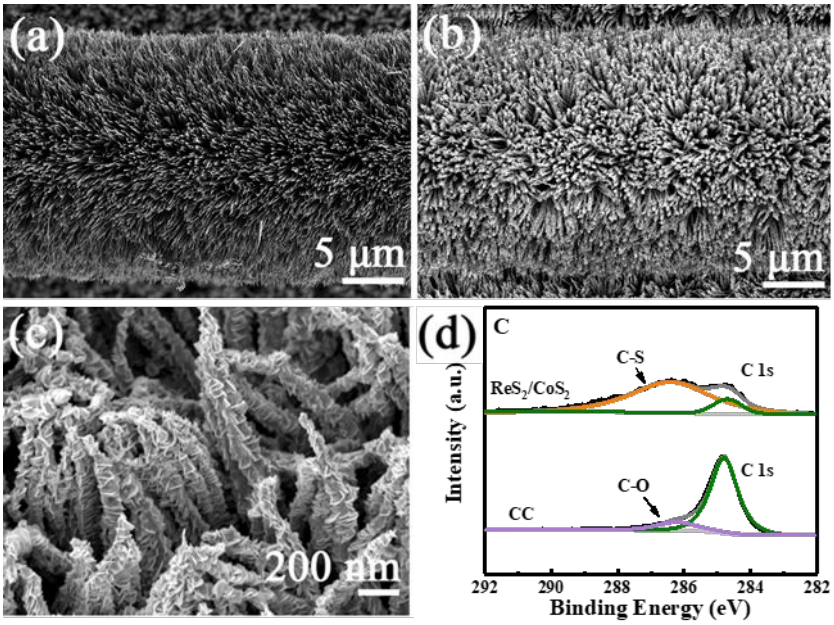

Figure S2. (a) Low-magnification SEM image of large scale CoS_2 nanowire arrays. (b) Low-magnification SEM image of ReS_2/CoS_2. (c) High-magnification SEM image of high density ReS_2 nanosheets distributed on CoS_2 nanowires. (d) High-resolution XPS spectrum of C 1s in ReS_2/CoS_2 and bare carbon cloth.

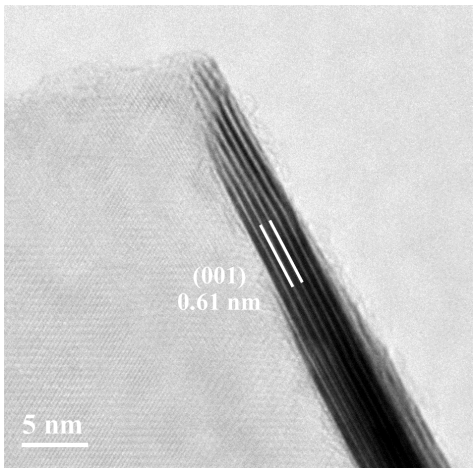

Figure S3. TEM image of a ReS_2 nanosheet.

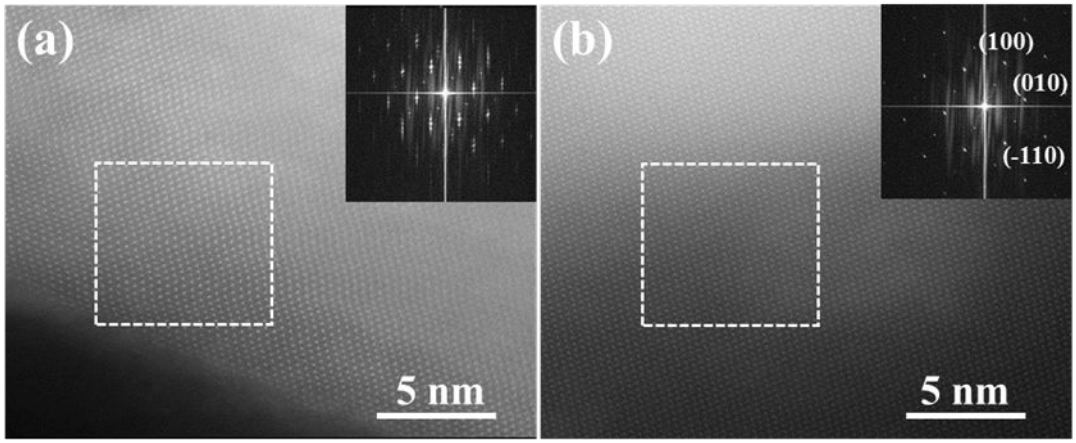

Figure S4. (a) STEM image of ReS_2 at the interface of ReS_2/CoS_2. (b) STEM image of ReS_2 away from the interface ReS_2/CoS_2. Inset in Figure a and b are corresponding FFT images.

S5. Morphology and structure characterization of ReS_2/CoP

As shown in Figure S5a, the crystal structures were investigated by X-ray diffraction (XRD). The characteristic peaks at 14.4°, 15.9°, 16.1°, 16.7°, 20.4°, 21.9° and 28.5° were ascribed to the (002), (010), (-110), (100), (-112), (003) and (110) of ReS_2 (PDF No. 89-0341). Other peaks were consistent with standard CoP, confirming that the composite was ReS_2/CoP[2]. High density 1D CoS_2 nanowires were uniformly distributed on the pure CC (Figure S3b). As displayed in Figure S3c, irregular ReS_2 nanosheets with a diameter of 200 nm are observed. However, the density of ReS_2 wasn't large and it was nearly grown at the tip of CoP nanowire. In Figure S3d, the element mapping of ReS_2/CoP manifested that the intimate contact between ReS_2 and CoP in ReS_2/CoP with uniform distribution of the S element. But S content wasn't high, indicating that S could only be replaced with a part of phosphorus in the same

time. All of these confirm that ReS_2/CoP was successfully synthesized.

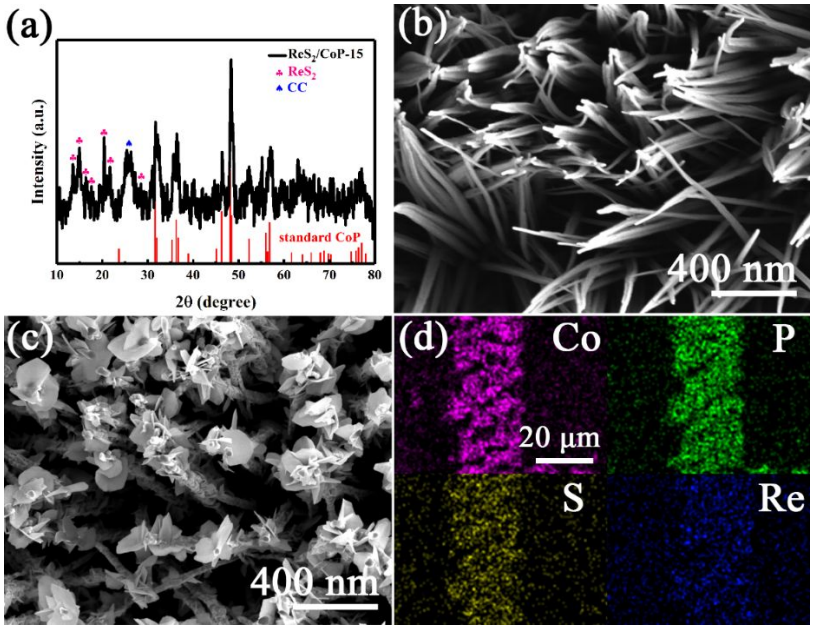

Figure S5. (a) XRD pattern of ReS_2/CoP. (b) SEM image of high-density CoP nanowires. (c) Low-magnification SEM image of ReS_2/CoP. (d) EDX elemental mapping images of Co, P, S and Re element distribution.

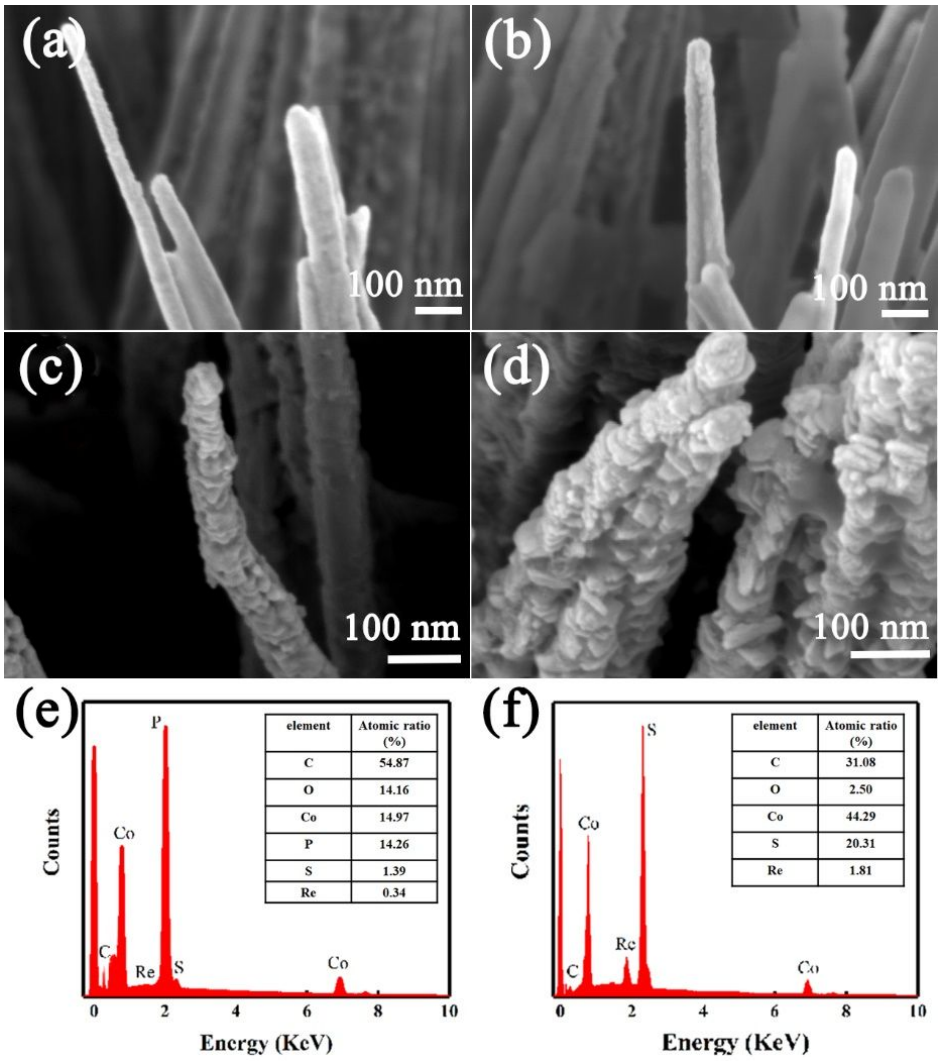

Figure S6. High-magnification SEM image of (a) CoP nanowires, (b) ReS_2/CoP-5, (c) CoS_2 nanowires and (d) ReS_2/CoS_2-5. (e, f) EDX spectra of ReS_2/CoP-5 and ReS_2/CoS_2-5, respectively. Insets in e and f are the atomic ratio of each element.

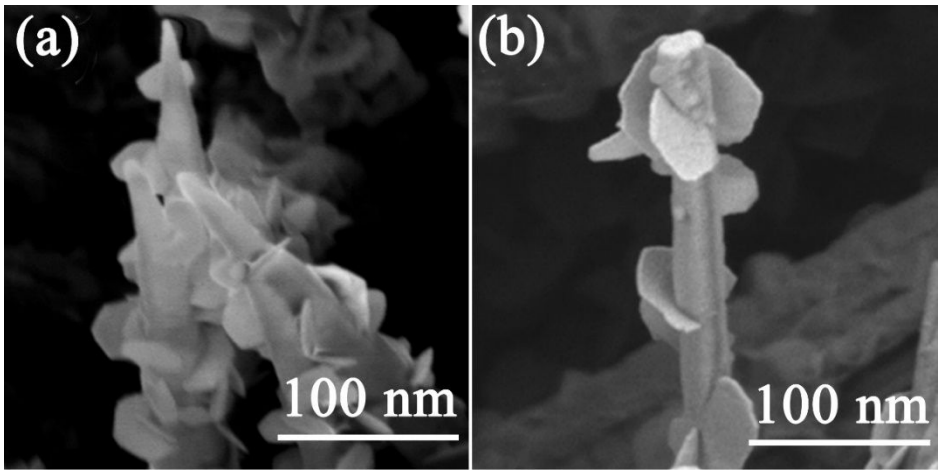

Figure S7. High-magnification SEM images of (a) ReS_2/CoS_2-10 and (b) ReS_2/CoP-10.

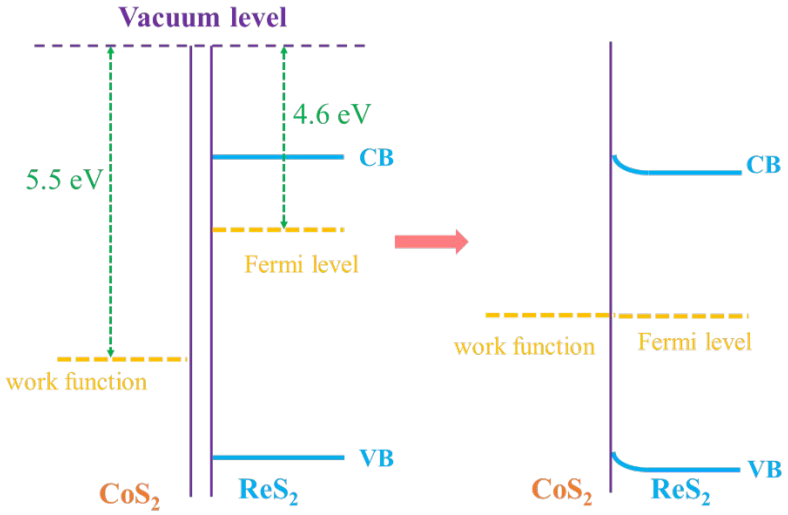

Figure S8. Band alignment diagram between CoS_2 and ReS_2.

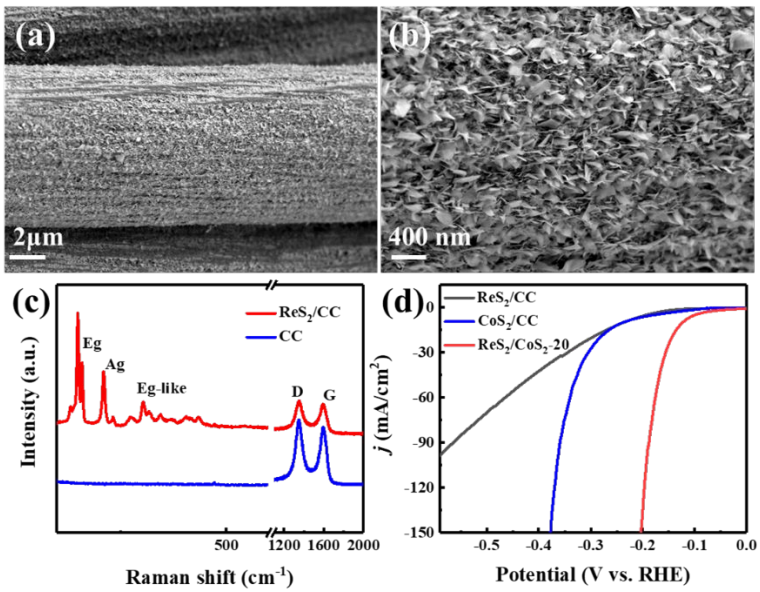

Figure S9. (a, b) SEM images of ReS_2/CC. (c) Raman spectrum of ReS_2/CC and CC. (d) HER polarization curves of ReS_2/CC, CoS_2/CC and ReS_2/CoS_2-20.

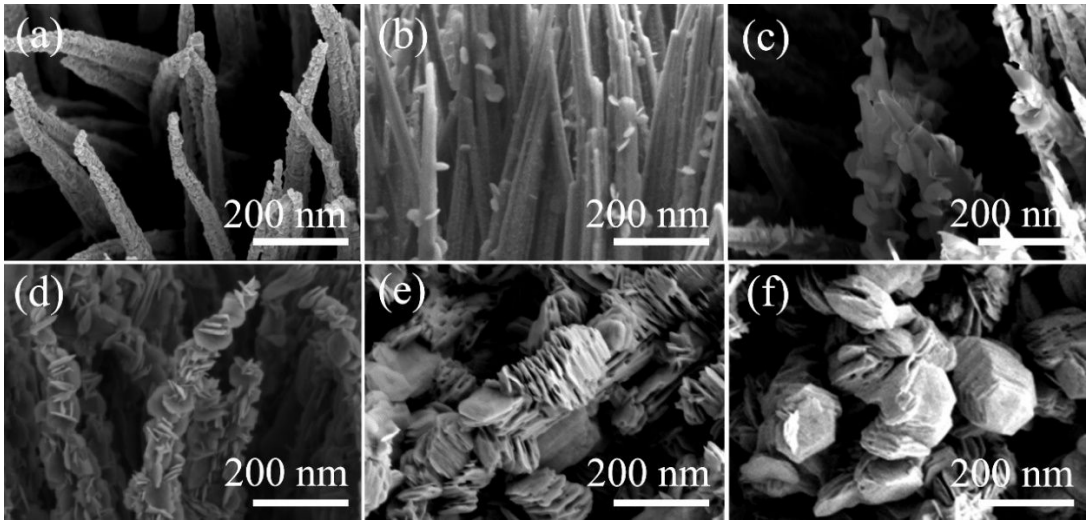

Figure S10. SEM image of ReS_2 with different growth time (a) 0 min, (b) 10 min, (c) 15 min, (d) 20 min and (e) 25 min on CoS_2 nanowires. (f) high-magnification SEM image in c.

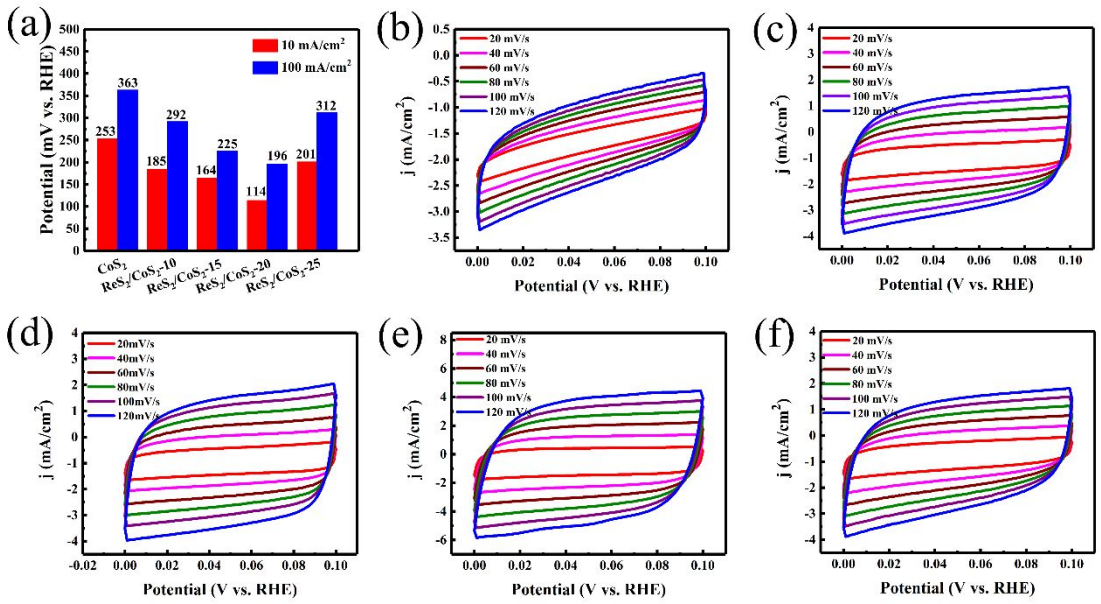

Figure S11. (a) The overpotential of CoS_2, ReS_2/CoS_2-10, ReS_2/CoS_2-15, ReS_2/CoS_2-20 and ReS_2/CoS_2-25 at 10 mA/cm^2 and 100 mA/cm^2, respectively. (b) CoS_2, (c) ReS_2/CoS_2-10, (d) ReS_2/CoS_2-15, (e)ReS_2/CoS_2-20 and (f) ReS_2/CoS_2-25 are the CV curves at different scan rates.

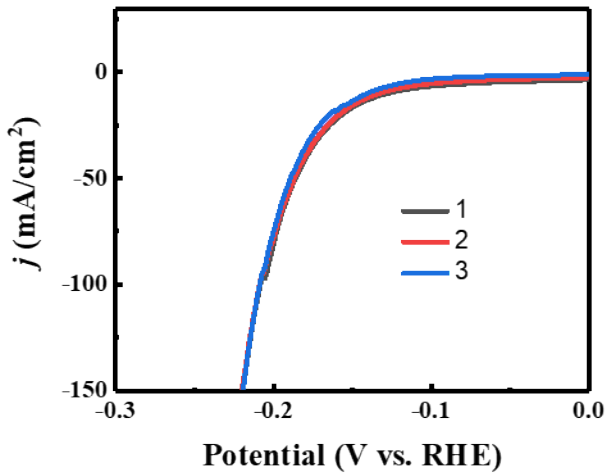

Figure S12. HER polarization curves of different batches of ReS_2/CoS_2-20.

Table S1. Electrochemical performances of Pt/C.

samples	η(mV vs RHE) for j=10 mA/cm²	Tafel slope (mV/dec)	Refs
Pt/C	50	34	3
Pt/C	48	44	10
Pt/C	62	33	8
Pt/C	33	30	11
Pt/C	78	42	12
Pt/C	49	42	13
Pt/C	28	43	This work

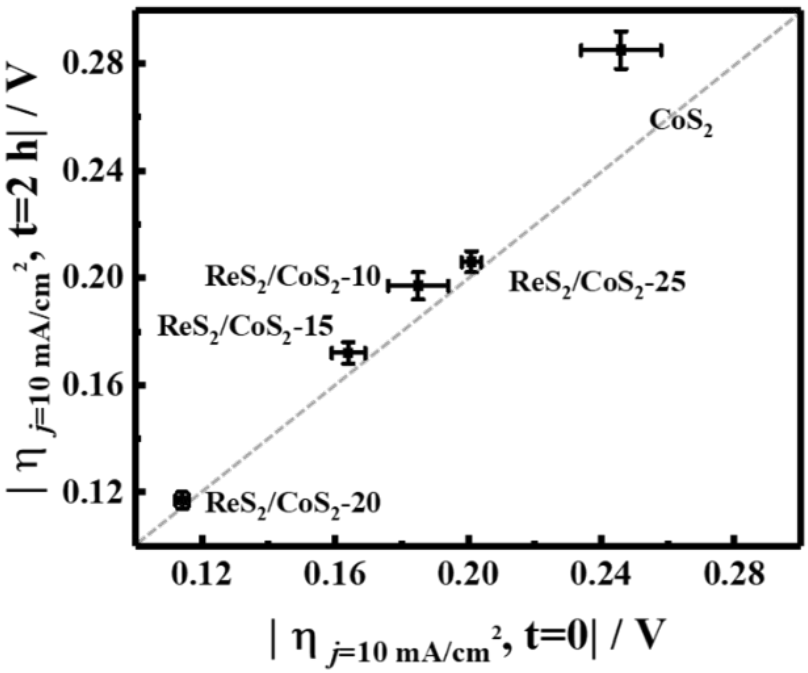

Figure S13. Plots of catalytic activity, stability, and electrochemically-active surface area for HER electrocatalysts in acidic solutions. The x-axis is the overpotential required to achieve 10 mA cm^{-2} per geometric area at time t = 0. The y-axis is the overpotential required to achieve 10 mA cm^{-2} per geometric area at time t = 2 h. The diagonal dashed line is the expected response for a stable catalyst that does not change in activity during 2 h constant polarization.

Table S2. Electrochemical performances of CoS_2-based and ReS_2-based catalysts.

samples	η(mV vs RHE) for j=10 mA/cm^2	Tafel slope (mV/dec)	Refs
$CoS_{2x}Se_{2(1-x)}$ nanowire array	129.5	68.7	3
CoS_2-C@MoS_2	173	67	4
$MoO_2/MoS_2/CoS_2$	123	133	5
V_{Re}-ReS_2	147	69	6
Sunflower-shaped ReS_2	270	76	7
NiS_2/CoS_2/C	165	72	8
Li-vertical ReS_2@Au	201	84	9
ReS_2/CoS_2	114	63.7	This work

References

(1) Jacques, A.; Diologent, F.; Bastie, P. In Situ Measurement of the Lattice Parameter Mismatch of a Nickel-Base Single-Crystalline Superalloy under Variable Stress. *Mater. Sci. Eng. A* **2004**, *1*, 387–389.

(2) Tian, J.; Chen, J.; Liu, J.; Tian, Q.; Chen, P. Graphene Quantum Dot Engineered Nickel-Cobalt Phosphide as Highly Efficient Bifunctional Catalyst for Overall Water Splitting. *Nano Energy* **2018**, *48*, 284–291.

(3) Liu, K.; Wang, F.; Xu, K.; Shifa, T. A.; Cheng, Z.; Zhan, X.; He, J. $CoS_{2x}Se_{2(1-x)}$ Nanowire Array: An Efficient Ternary Electrocatalyst for the Hydrogen Evolution Reaction. *Nanoscale* **2016**, *8*, 4699–4704.

(4) Zhu, Y.; Song, L.; Song, N.; Li, M.; Wang, C.; Lu, X. Bifunctional and Efficient CoS_2-C@MoS_2 Core-Shell Nanofiber Electrocatalyst for Water Splitting. *ACS Sustain. Chem. Eng.* **2019**, *7*, 2899–2905.

(5) Wang, Y.; Zhu, Y.; Afshar, S.; Woo, M. W.; Tang, J.; Williams, T.; Kong, B.;

Zhao, D.; Wang, H.; Selomulya, C. One-Dimensional CoS_2-MoS_2 Nano-Flakes Decorated MoO_2 Sub-Micro-Wires for Synergistically Enhanced Hydrogen Evolution. *Nanoscale* **2019**, *11*, 3500–3505.

(6) Zhou, Y.; Song, E.; Zhou, J.; Lin, J.; Ma, R.; Wang, Y.; Qiu, W.; Shen, R.; Suenaga,K.; Liu, Q. Auto-Optimizing Hydrogen Evolution Catalytic Activity of ReS_2 through Intrinsic Charge Engineering. *ACS Nano* **2018**, *12*, 4486–4493.

(7) Huang, J.; Gao, H.; Xia, Y.; Sun, Y.; Xiong, J.; Li, Y.; Cong, S.; Guo, J.; Du, S.; Zou, G. Enhanced Photoelectrochemical Performance of Defect-Rich ReS_2 Nanosheets in Visible-Light Assisted Hydrogen Generation. *Nano Energy* **2018**, *46*, 305–313.

(8) Xin, W.; Jiang, W. J.; Lian, Y.; Li, H.; Hong, S.; Xu, S.; Yan, H.; Hu, J. S. NiS_2 Nano dotted Carnation-like CoS_2 for Enhanced Electrocatalytic Water Splitting. *Chem. Commun.* **2019**, *55*, 3781–3784.

(9) Gao, J.; Li, L.; Tan, J.; Sun, H.; Li, B.; Idrobo, J. C.; Singh, C. V.; Lu, T.-M.; Koratkar, N. Vertically Oriented Arrays of ReS_2 Nanosheets for Electrochemical Energy Storage and Electrocatalysis. *Nano Lett.* **2016**, *16*, 3780–3787.

(10) Zhang, H.; Li, Y.; Xu, T.; Wang, J.; Huo, Z.; Wan, P.; Sun, X. Amorphous Co-Doped MoS_2 Nanosheet Coated Metallic CoS_2 Nano cubes as an Excellent Electrocatalyst for Hydrogen Evolution. *J. Mater. Chem. A* **2015**, *3*, 15020–

15023.

(11) Zhang, J.; Liu, Y.; Sun, C.; Xi, P.; Peng, S.; Gao, D.; Xue, D. Accelerated Hydrogen Evolution Reaction in CoS_2 by Transition-Metal Doping. *ACS Energy Lett.* **2018**, *3*, 779–786.

(12) Zhang, Q.; Ye, C.; Li, X. L.; Deng, Y. H.; Tao, B. X.; Xiao, W.; Li, L. J.; Li, N. B.; Luo, H. Q. Self-Interconnected Porous Networks of NiCo Disulfide as Efficient Bifunctional Electrocatalysts for Overall Water Splitting. *ACS Appl. Mater. Interfaces* **2018**, *10*, 27723–27733.

(13) Wen, L.; Sun, Y.; Zhang, C.; Yu, J.; Li, X.; Lyu, X. Cu-Doped CoP Nanorod Arrays : Efficient and Durable Hydrogen Evolution Reaction Electrocatalysts at All PH Values. *ACS Appl. Energy Mater.* **2018**, *1*, 3835-3842.