

1 **Supporting Information**

2 **Self-supported iron-based bimetallic phosphide catalytic electrode for**
3 **efficient hydrogen evolution reaction at high current density**

4 Ziteng Zuo,^{a#} Xian Zhang,^{b#} Ouwen Peng,^a Lianwei Shan,^c Shengling Xiang,^a Qing
5 Lian,^a Ningxue Li,^a Guojun Mi,^a Abbas Amini^d and Chun Cheng^{a,e,*}

6 *^aDepartment of Materials Science and Engineering, Southern University of Science and*
7 *Technology, Shenzhen 518055, China*

8 *^bSchool of Resources and Environmental Engineering, Wuhan University of*
9 *Technology, Wenzhi Street 34, Wuhan 430070, China*

10 *^cSchool of Materials Science and Chemical Engineering, Harbin University of Science*
11 *and Technology, Harbin 150040, China*

12 *^dCenter for Infrastructure Engineering, Western Sydney University, Kingswood, New*
13 *South Wales 2751, Australia*

14 *^eGuangdong Provincial Key Laboratory of Energy Materials for Electric Power,*
15 *Southern University of Science and Technology, Shenzhen 518055, China*

16 *Email: chengc@sustech.edu.cn*

17 # These authors contribute equally.

18

19

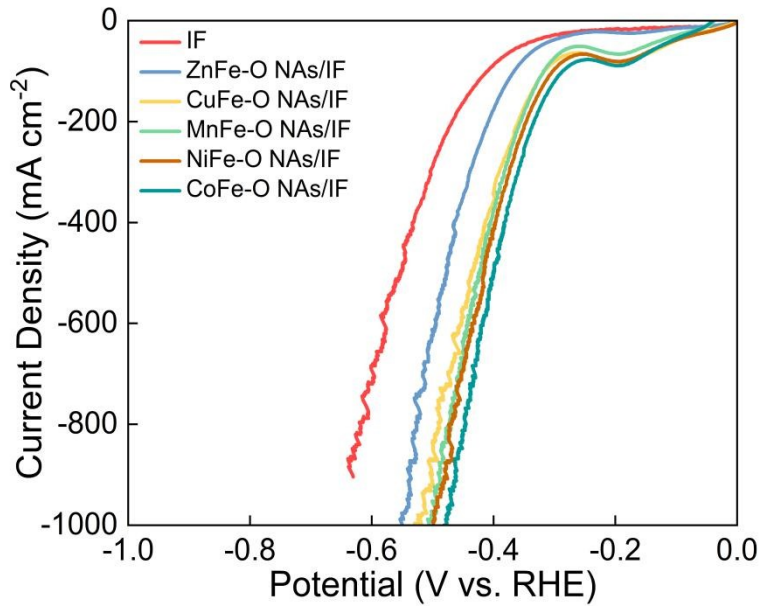
20

21

22

23

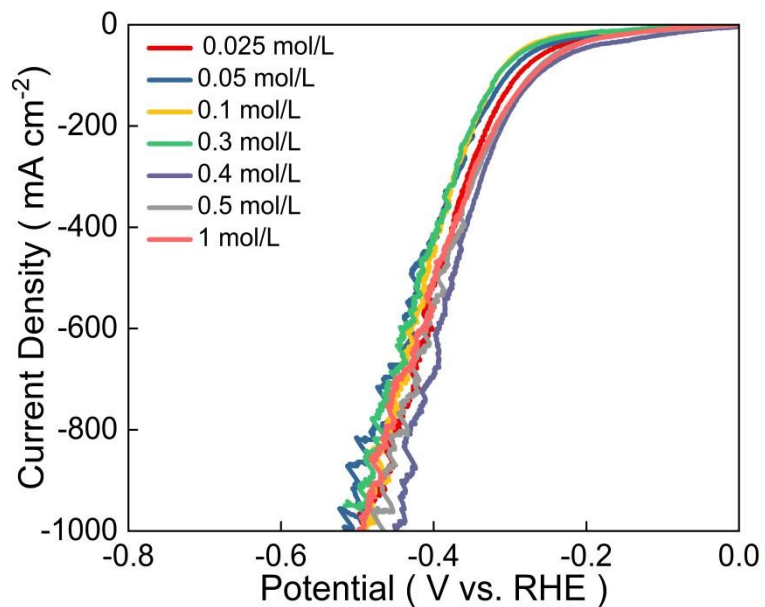
24



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

Fig. S1. LSV curves of electrodes soaked in different chloride solutions.
(CoCl₂ is chosen as the solution for soaking process)

Among various MFe-O NAs/IF samples prepared under similar conditions, CoFe-O NAs/IF shows the best HER catalytic performance, that is chosen as the nanoarray precursors for subsequent phosphorization.



1

2 Fig. S2. LSV curves of CoFe-O NAs/IF prepared under different conditions.

3

(Other conditions are the same, optimized concentration is 0.4 M)

4

5

6

7

8

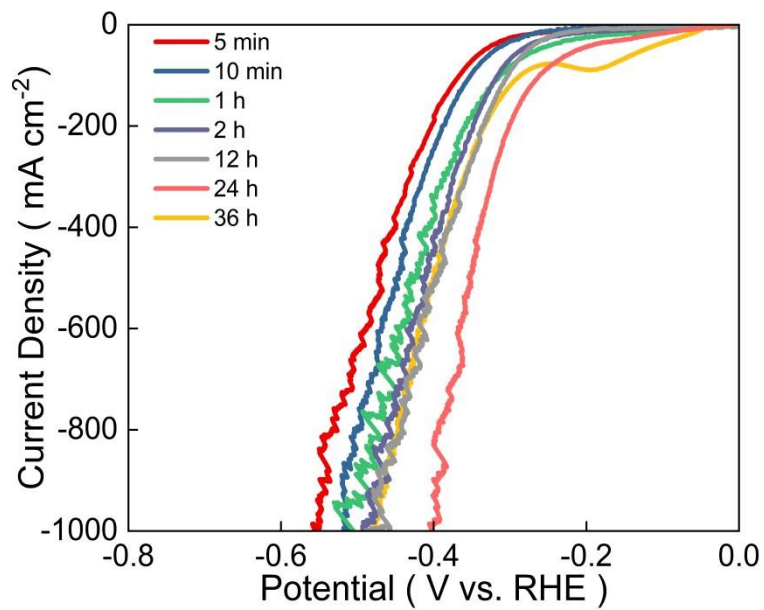
9

10

11

12

13



1

2 Fig. S3. LSV curves of CoFe-O NAs/IF prepared under different conditions.

3

(Other conditions are the same, optimized soaking time is 24 hours)

4

5

6

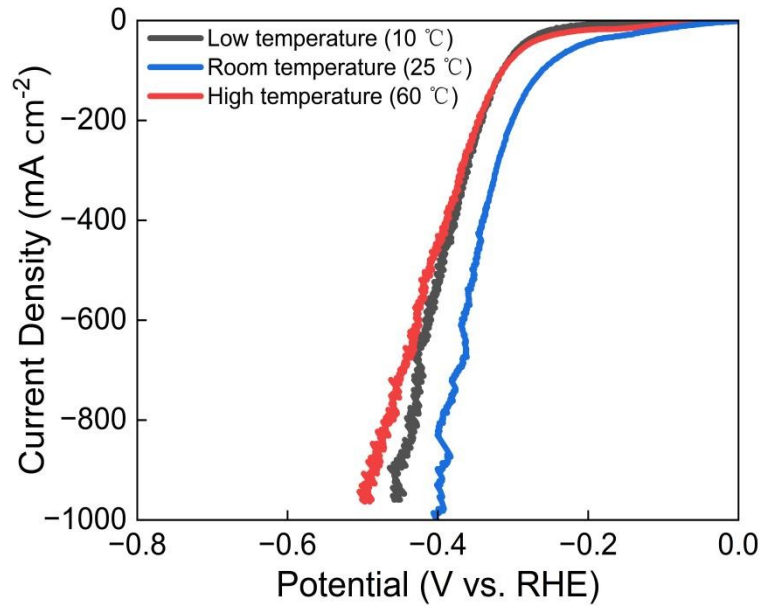
7

8

9

10

11



1

2 Fig. S4. LSV curves of CoFe-O NAs/IF prepared under different conditions.

3

4 (Other conditions are the same, optimized soaking temperature is room temperature)

5

6 According to the curves shown in **Figs. S2-S4**, the soaking conditions are optimized:

7 IF is soaked in 0.4 M CoCl₂ solution for 24 hours at room temperature.

8

9

10

11

12

13

14

15

16

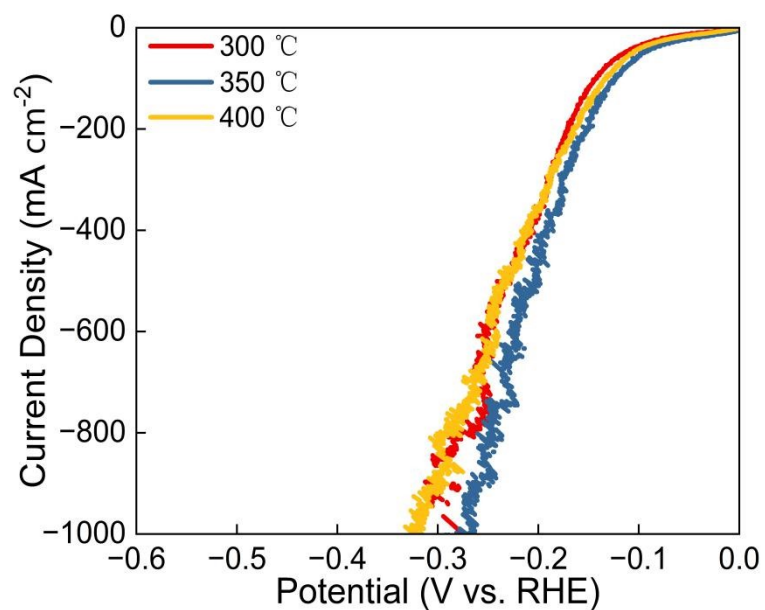
17

18

19

20

21



1

2

Fig. S5. LSV curves of CoFe-P NAs/IF prepared under different conditions.

3

(Other conditions are the same, optimized phosphorization temperature is 350 °C)

4

5

6

7

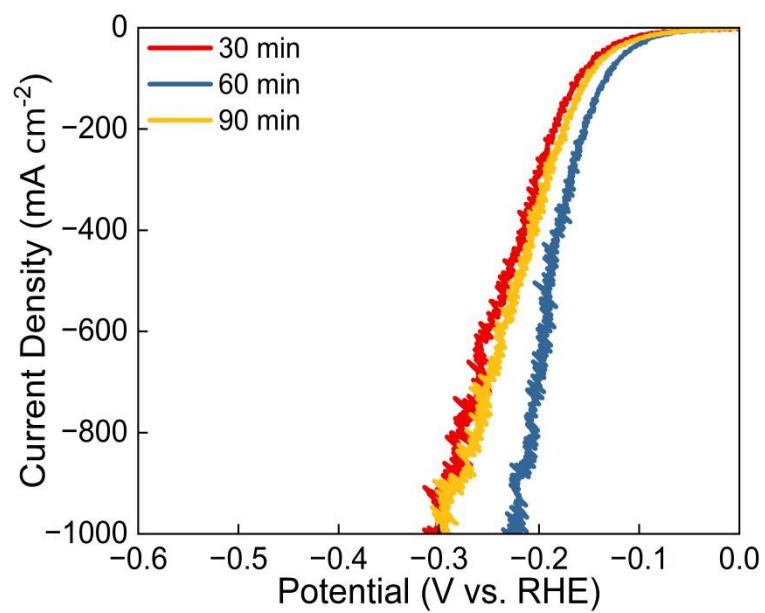
8

9

10

11

12



1

2 Fig. S6. LSV curves of CoFe-P NAs/IF prepared under different conditions.

3 (Other conditions are the same, optimized phosphorization time is 60 minutes)

4

5

6

7

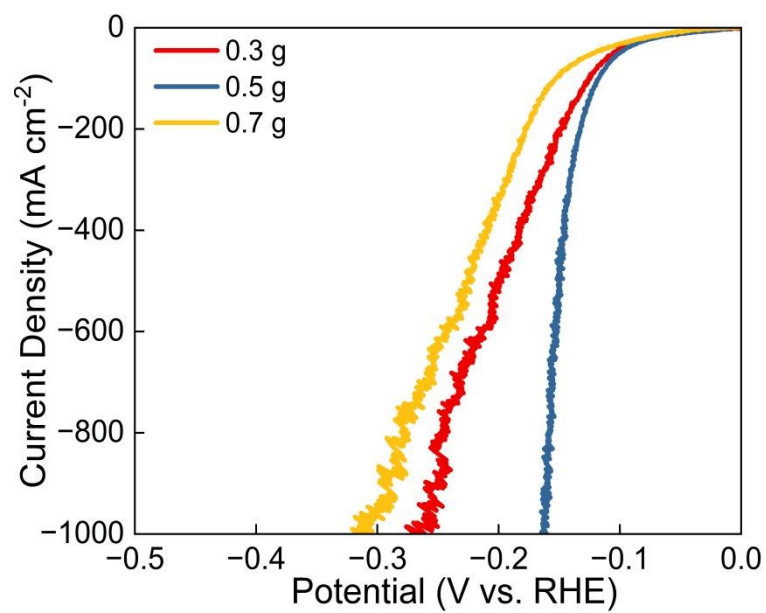
8

9

10

11

12



1

2 Fig. S7. LSV curves of CoFe-P NAs/IF prepared under different conditions.

3

(Other conditions are the same, optimized mass of NaH₂PO₂ is 0.5 g)

4

5

6

7

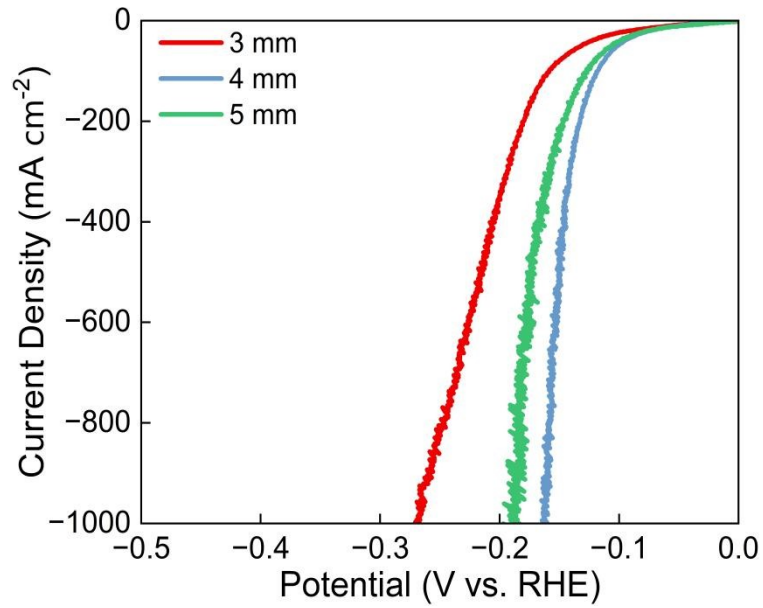
8

9

10

11

12



1

2 Fig. S8. LSV curves of CoFe-P NAs/IF prepared under different conditions.

3

(Other conditions are the same, optimized thickness of IF is 4 mm)

4

5 According to the curves shown in **Figs. S5-S8**, the chemical vapor deposition

6 conditions are optimized: CoFe-O NAs/IF (thickness of IF is 4 mm) is phosphorized at

7 350 °C for 60 minutes, while 0.5 g NaH₂PO₂ acts as the source of P.

8

9

10

11

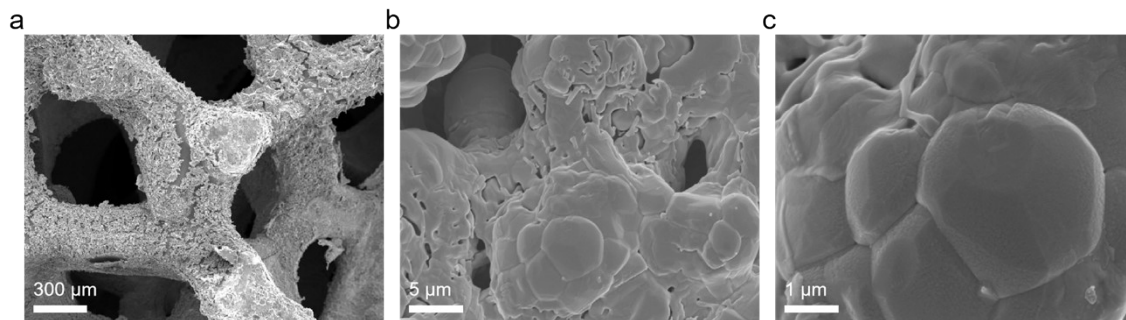
12

13

14

15

16



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21

Fig. S9. SEM images of IF.

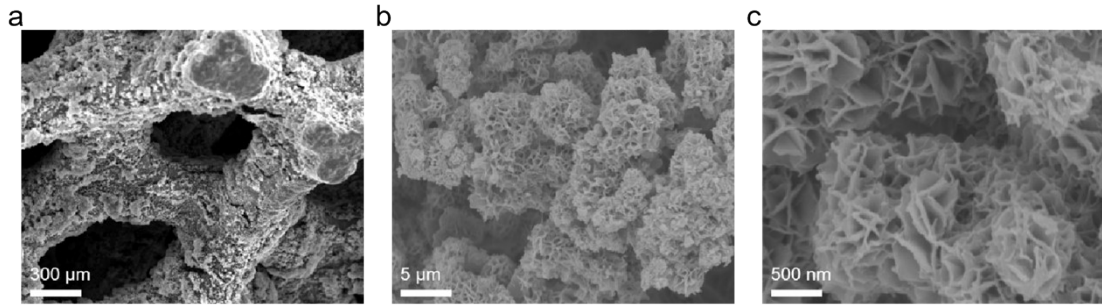


Fig. S10. SEM images of CoFe-O NAs/IF.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31

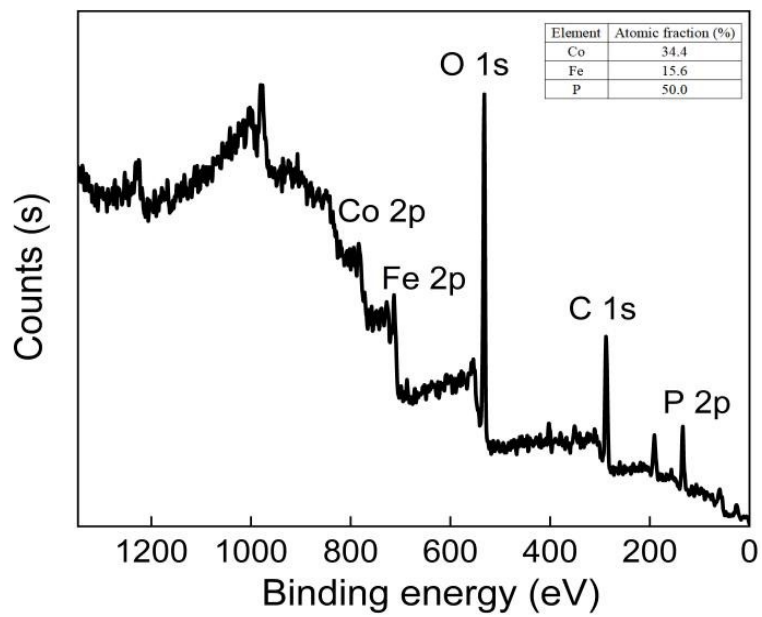


Fig. S11. XPS survey scan of CoFe-P NAs/IF.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

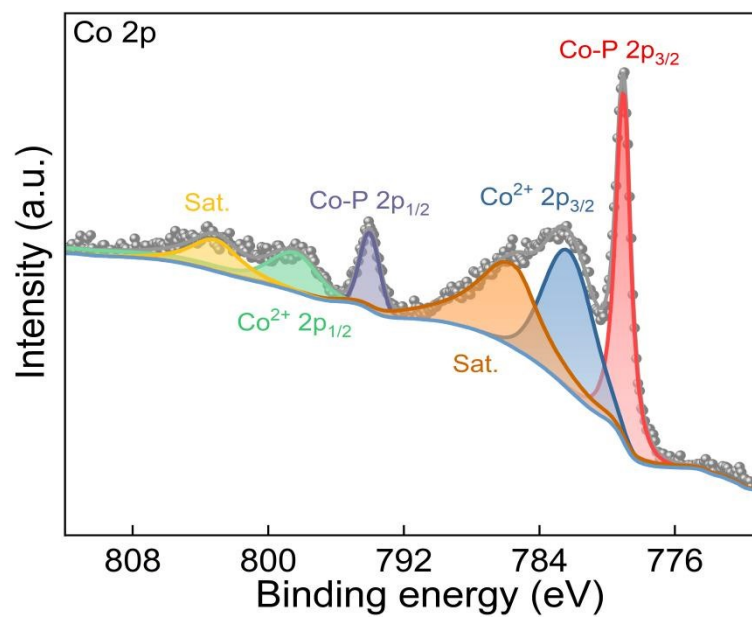
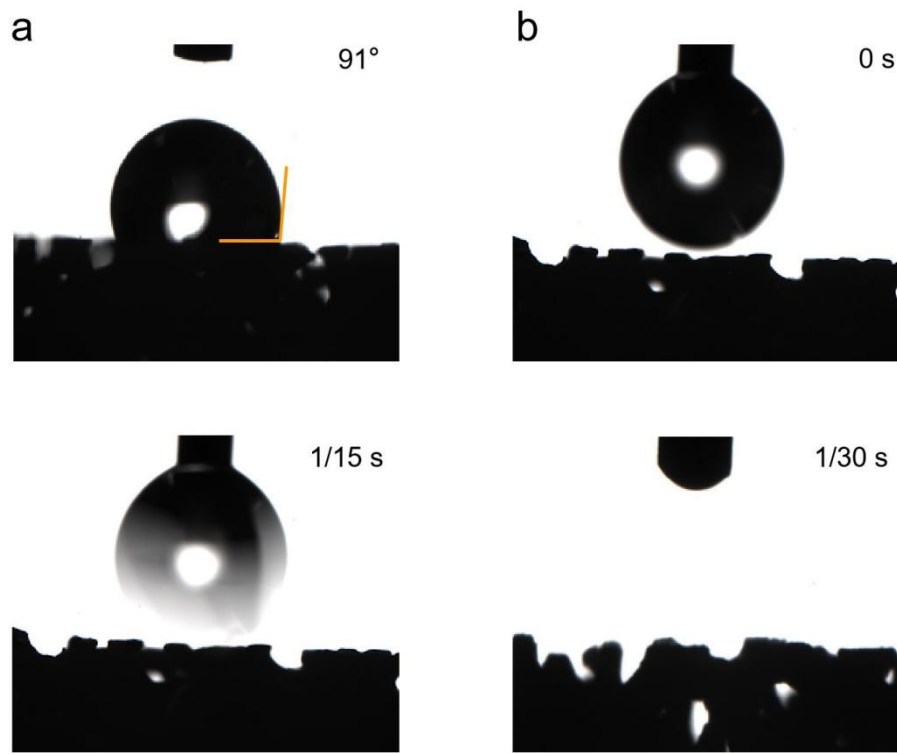


Fig. S12. High resolution Co 2p XPS spectrum of CoFe-P NAs/IF.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21



1
2
3
4
5
6
7
8
9
10
11
12
13

Fig. S13. Advancing contact angles of (a) IF and (b) CoFe-P NAs/IF.

1 **Estimation of Electrochemical Active Surface Area.**

2 The electrochemical double-layer capacitance (C_{dl}) is calculated to estimate the
3 electrochemical surface area (ECSA) through cyclic voltammetry (CV) measurement
4 at different scan rates. By plotting current density differences ($\Delta j = |j_a - j_c|/2$) against the
5 CV scan rates, the C_{dl} values can be calculated. The C_{dl} can be converted to an ECSA
6 using the specific capacitance value for a flat standard with 1 cm² of real surface area.
7 The specific capacitance for a flat surface is generally found to be within the range
8 of 20-60 $\mu\text{F cm}^{-2}$.¹ In the calculation of turnover frequency, 40 $\mu\text{F cm}^{-2}$ is used for
9 calculations. The ECSA can be calculated from the following equation:

$$A_{ECSA} = \frac{C_{dl \text{ of electrode (mF cm}^{-2}\text{)}}}{40 \mu\text{F cm}^{-2} \text{ per cm}_{ECSA}^2}$$

10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

26 **Turnover frequency calculation.**

1 The turnover frequency (TOF) is calculated from the following equation:

$$2 \quad TOF = \frac{\# \text{ of total hydrogen turnovers/cm}^2 \text{ geometric area}}{\# \text{ of active sites/cm}^2 \text{ geometric area}}$$

3 The total number of hydrogen turnovers is obtained from the corresponding current

4 density of:

$$5 \quad \begin{aligned} \#_{H_2} &= \left(j \frac{mA}{cm^2} \right) \left(\frac{1 C s^{-1}}{1000 mA} \right) \left(\frac{1 mol e^{-}}{96485.3 C} \right) \left(\frac{1 mol H_2}{2 mol e^{-}} \right) \left(\frac{6.022 \times 10^{23} H_2 \text{ molecules}}{1 mol H_2} \right) = 3 \\ &\text{per } \frac{mA}{cm^2} \end{aligned}$$

6 As the exact hydrogen binding site is not known, we estimate the number of active sites

7 as the number of surface sites (including the whole atoms as the postulated active sites)

8 from the roughness factor together with the unit cell and simulated models in DFT

9 calculations.

10 The number of surface sites per real surface area:

$$11 \quad \#_{Active Sites}^{IF} = \left(\frac{2 \text{ atoms/unit cell}}{23.4 \text{ \AA}^3/\text{unit cell}} \right)^{\frac{2}{3}} = 1.940 \times 10^{15} \text{ atoms cm}_{real}^{-2}$$

12

$$13 \quad \#_{Active Sites}^{FeP} = \left(\frac{4 \text{ atoms/unit cell}}{93.2 \text{ \AA}^3/\text{unit cell}} \right)^{\frac{2}{3}} = 1.226 \times 10^{15} \text{ atoms cm}_{real}^{-2}$$

14

$$15 \quad \#_{Active Sites}^{CoFe-P} = \left(\frac{205 \text{ atoms/unit cell}}{4847.7 \text{ \AA}^3/\text{unit cell}} \right)^{\frac{2}{3}} = 1.214 \times 10^{15} \text{ atoms cm}_{real}^{-2}$$

16 Finally, the plot of current density can be converted to a TOF plot based on the

17 following equation:

$$TOF = \frac{(3.12 \times 10^{15} \frac{H_2 \text{ molecule } s^{-1}}{cm^2} \text{ per } \frac{mA}{cm^2}) \times |j|}{\#_{Active Sites} \times A_{ECSA}}$$

1

2

1 **Comparison of HER performances of CoFe-P NAs/IF (this work) with other**
 2 **electrodes.**

3 Table S1. Comparison of different HER electrodes.

Catalysts	Overpotential at	Overpotential at	Overpotential at	Overpotential at
	10 mA cm⁻²	100 mA cm⁻²	500 mA cm⁻²	1000 mA cm⁻²
CoFe-P NAs/IF (This work)	40 mV	108 mV	151 mV	162 mV
MoS ₂ /Ni ₃ S ₂ NW-NF ²	70 mV	137 mV	182 mV	200 mV
MoS ₂ /Mo ₂ C-Ti foil ³	—	—	191 mV	220 mV
Co-B-P/NF ⁴	42 mV	—	—	165 mV
NiCoP/NF ⁵	55 mV	122 mV	171 mV	193 mV
Co ₂ P–Ni ₁₂ P ₅ /NF ⁶	37 mV	109 mV	173 mV	219 mV
CoFeOH/CoFeP/IF ⁷	—	114.9 mV	194.9 mV	221.8 mV
P-Fe ₃ O ₄ /IF ⁸	—	138 mV	220 mV	240 mV
F-Co ₂ P/Fe ₂ P/IF ⁹	—	151.8 mV	229.8 mV	260.5 mV

4

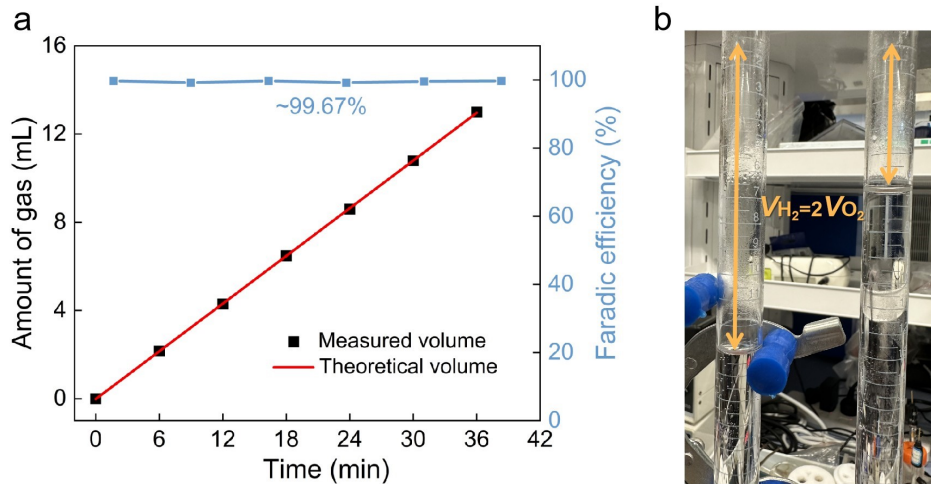
5

6

7

8

9



1

2 Fig. S14. (a) Measurement of Faradic efficiency of CoFe-P NAs/IF||CoFe-P NAs/IF.

3

(b) Optical image of Hoffman apparatus setup.¹⁰

4

5

6

7

8

9

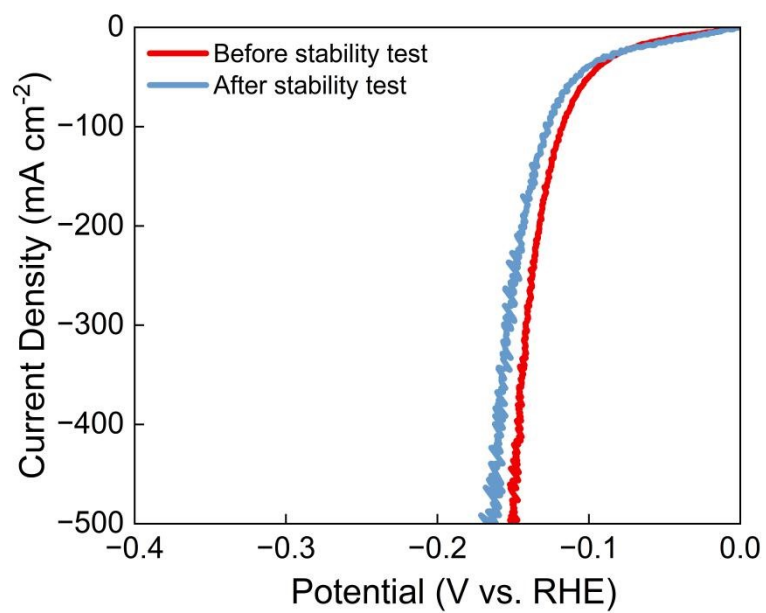
10

11

12

13

14



1

2

Fig. S15. LSV curves of CoFe-P NAs/IF before and after stability test.

3

4

5

6

7

8

9

10

11

12

13

14

15

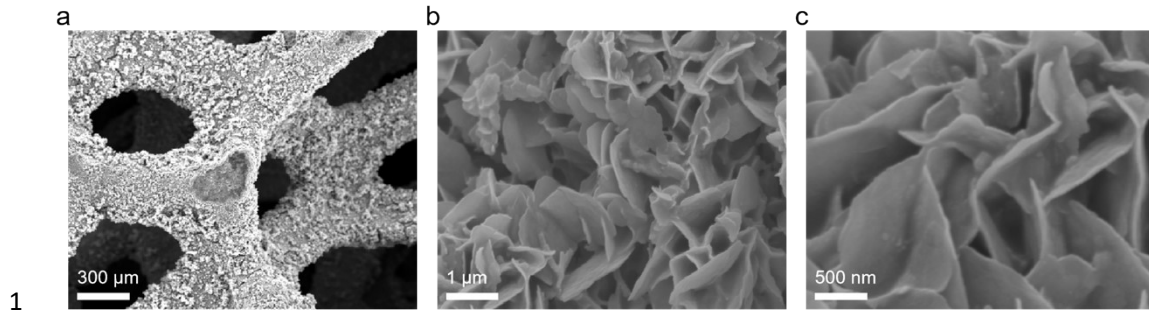


Fig. S16. SEM images of CoFe-P NAs/IF after stability test.

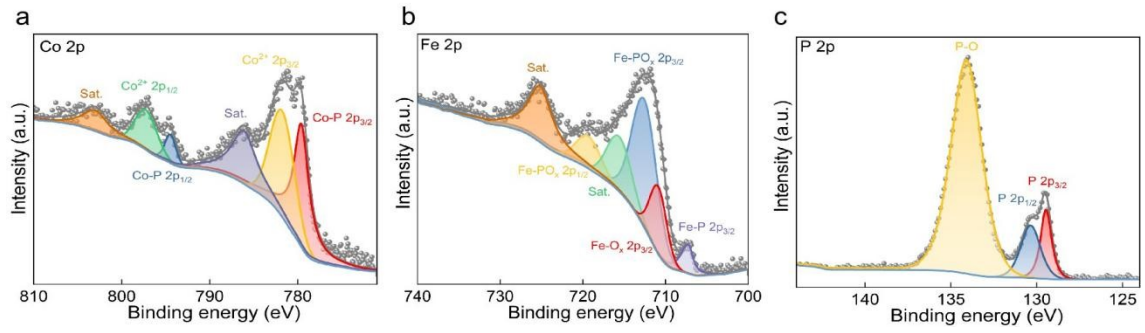
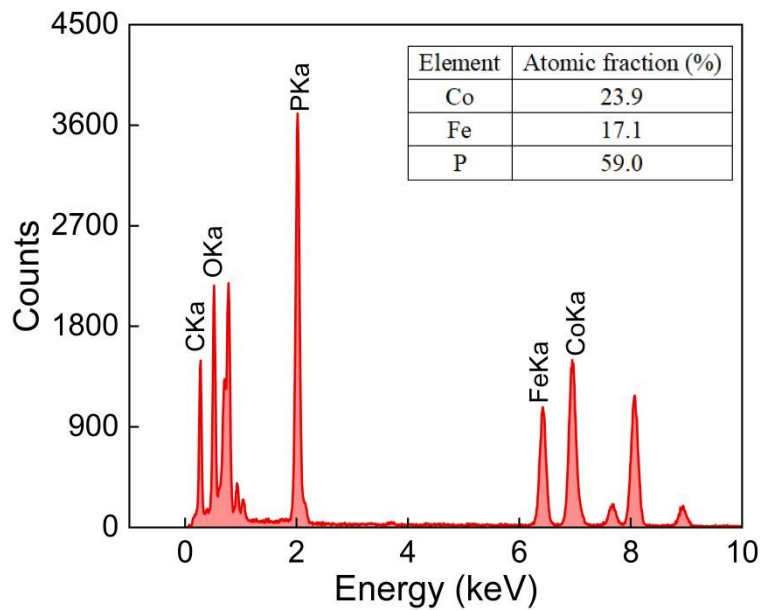


Fig. S17. XPS spectra of CoFe-P NAs/IF after stability test. (a) Co 2p.
(b) Fe 2p. (c) P 2p.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21

Fig. S18. EDX spectrum of CoFe-P NAs/IF and atomic fractions of the constituent elements.

The atomic ratio of Co:Fe in CoFe-P NAs/IF is approximately 1.4:1, which is consistent with the values in Fig. S11 basically. Some differences arise from the distinction of investigation depth between XPS and EDX. The investigation depth of XPS is about 2-4 nm, while that of EDX is around 1-3 μm , so it is understandable that the data obtained from these two methods exists some differences.

1 References

- 2 1 M. Jin, X. Zhang, R. Shi, Q. Lian, S. Niu, O. Peng, Q. Wang and C. Cheng, *Appl.*
3 *Catal. B - Environ.*, 2021, **296**, 120350.
- 4 2 S. Xue, Z. Liu, C. Ma, H. M. Cheng and W. Ren, *Sci. Bull.*, 2020, **65**, 123.
- 5 3 Y. Luo, L. Tang, U. Khan, Q. Yu, H. M. Cheng, X. Zou and B. Liu, *Nat. Commun.*,
6 2019, **10**, 269.
- 7 4 H. Sun, X. Xu, Z. Yan, X. Chen, L. Jiao, F. Cheng and J. Chen, *J. Mater. Chem. A*,
8 2018, **6**, 22062.
- 9 5 L. Li, W. Zou, Q. Ye, Q. Li, Q. Feng, J. Wei, X. Xu and F. Wang, *J. Power. Sources*,
10 2021, **516**, 230657.
- 11 6 L. Guo, X. Liu, Z. He, Z. Chen, Z. Zhang, L. Pan, Z. Huang, X. Zhang, Y. Fang and
12 J. J. Zou, *ACS Sustain. Chem. Eng.*, 2022, **10**, 9956.
- 13 7 X. Y. Zhang, F. L. Wang, J. Y. Fu, Y. N. Zhen, B. Dong, Y. N. Zhou, H. J. Liu, D. P.
14 Liu, C. G. Liu and Y. M. Chai, *J. Power. Sources*, 2021, **507**, 230279.
- 15 8 J. Zhang, X. Shang, H. Ren, J. Chi, H. Fu, B. Dong, C. Liu and Y. Chai, *Adv. Mater.*,
16 2019, **31**, 1905107.
- 17 9 X. Y. Zhang, Y. R. Zhu, Y. Chen, S. Y. Dou, X. Y. Chen, B. Dong, B. Y. Guo, D. P.
18 Liu, C. G. Liu and Y. M. Chai, *Chem. Eng. J.*, 2020, **399**, 125831.
- 19 10 X. Yu, Z. Yu, X. Zhang, Y. Zheng, Y. Duan, Q. Gao, R. Wu, B. Sun, M. Gao, G.
20 Wang and S. Yu, *J. Am. Chem. Soc.*, 2019, **141**, 7537.

21