

Supplementary Information

Co₂P nanowire arrays anchored on 3D porous reduced graphene oxide matrix embedded in nickel foam for high-efficiency hydrogen evolution reaction

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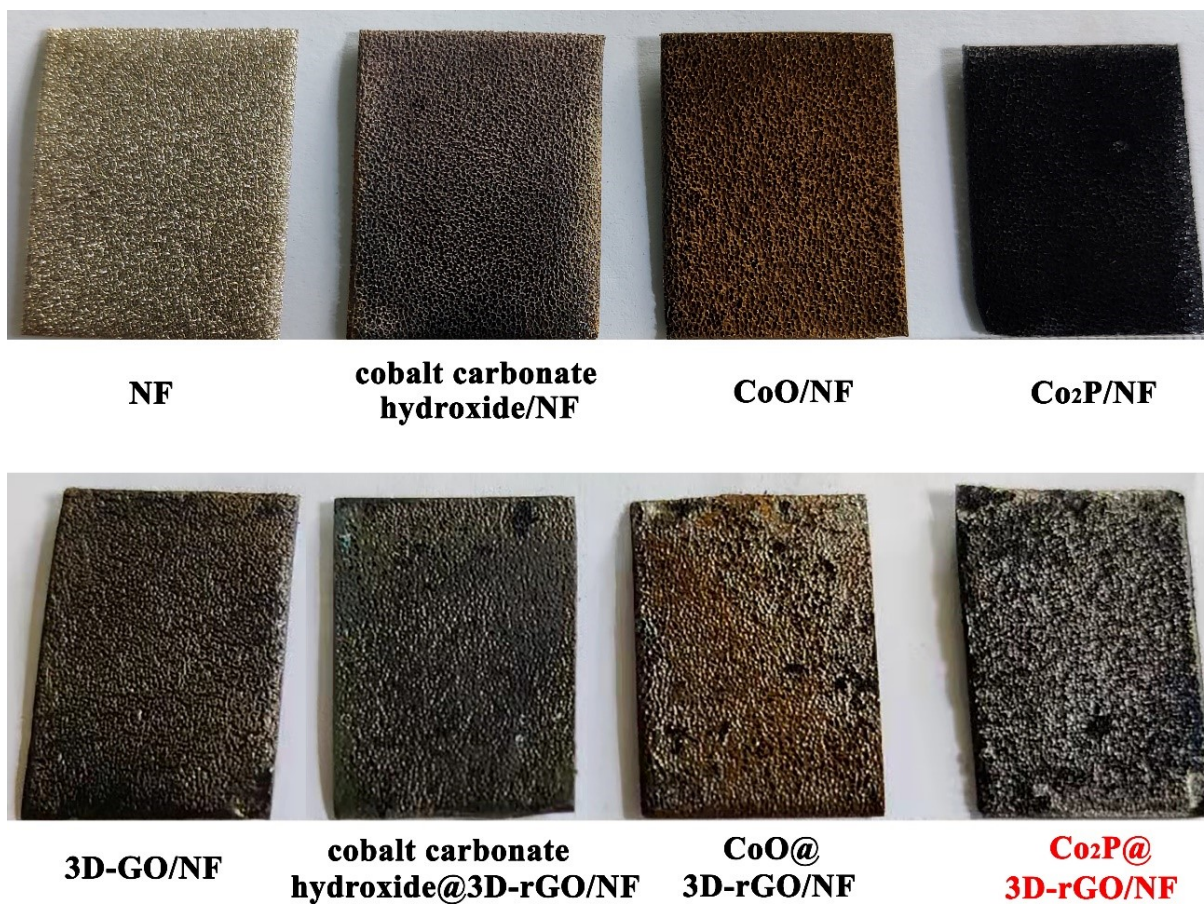


Fig. S1. Digital photographs of the samples during the preparation of Co₂P/NF and Co₂P@3D-rGO/NF.

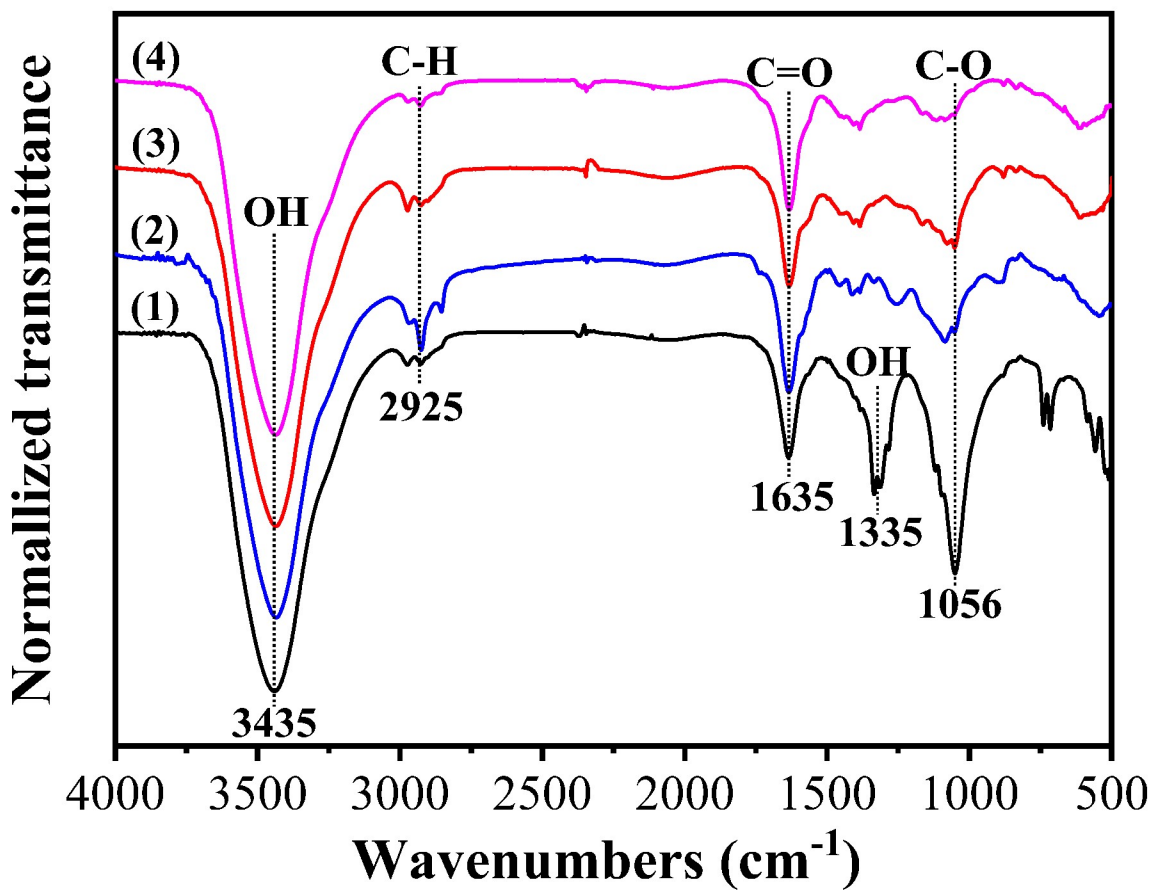


Fig. S2. FT-IR spectra of the samples: (1) 3D-GO obtained from 3D-GO/NF, (2) rGO powder prepared by the reduction of GO in HI acid, (3) Co_2P powder obtained from $\text{Co}_2\text{P}/\text{NF}$, and (4) $\text{Co}_2\text{P}@3\text{D-rGO}$ powder obtained from $\text{Co}_2\text{P}@3\text{D-rGO}/\text{NF}$.

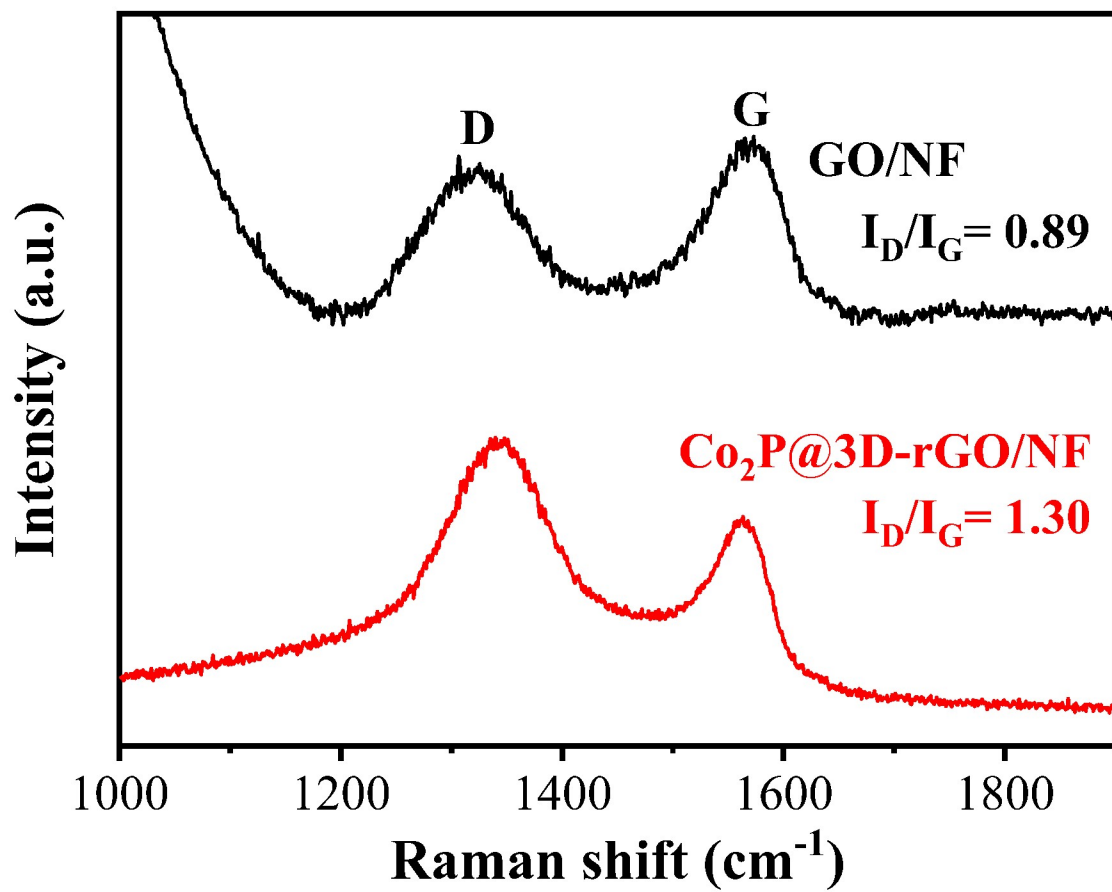


Fig. S3. Raman spectra of GO/NF and Co₂P@3D-rGO/NF.

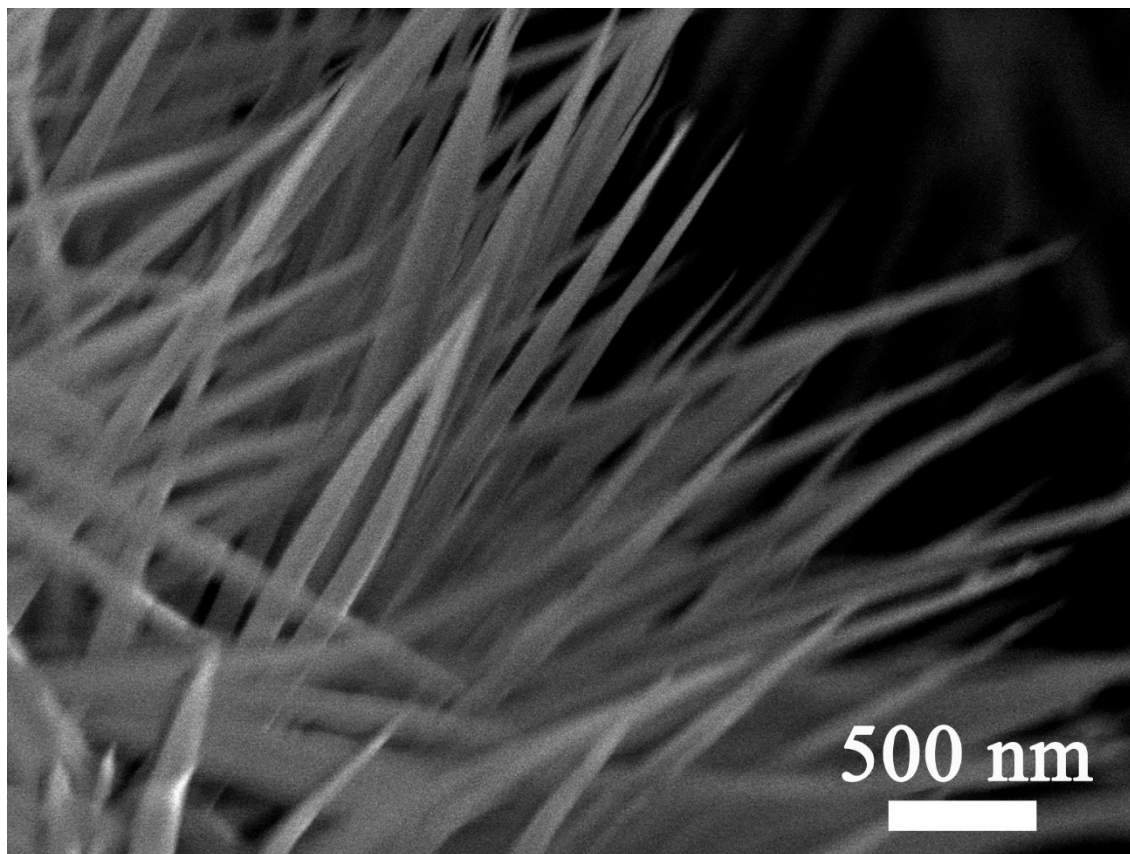


Fig. S4. FESEM image of $\text{Co}(\text{CO}_3)_{0.5}(\text{OH})_{0.11} \cdot \text{H}_2\text{O} @ 3\text{D-GO/NF}$.

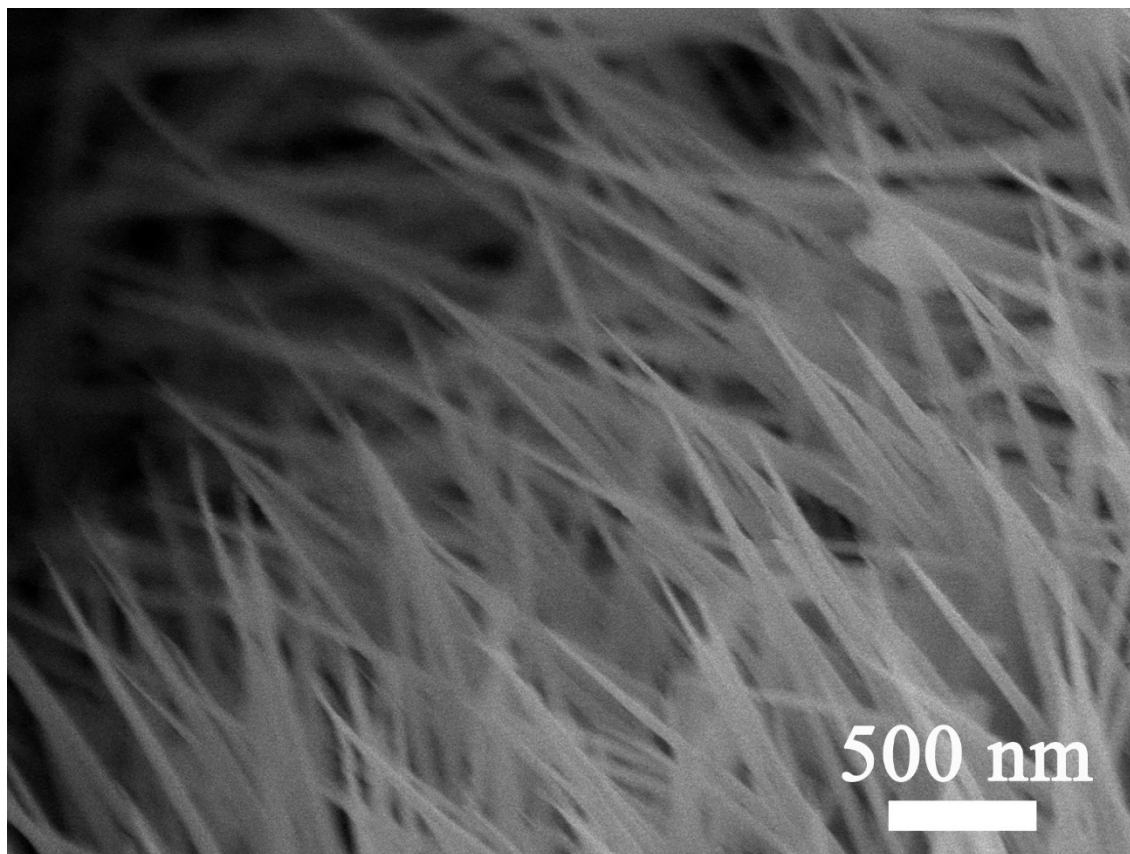


Fig. S5. FESEM image of CoO@3D-GO/NF.

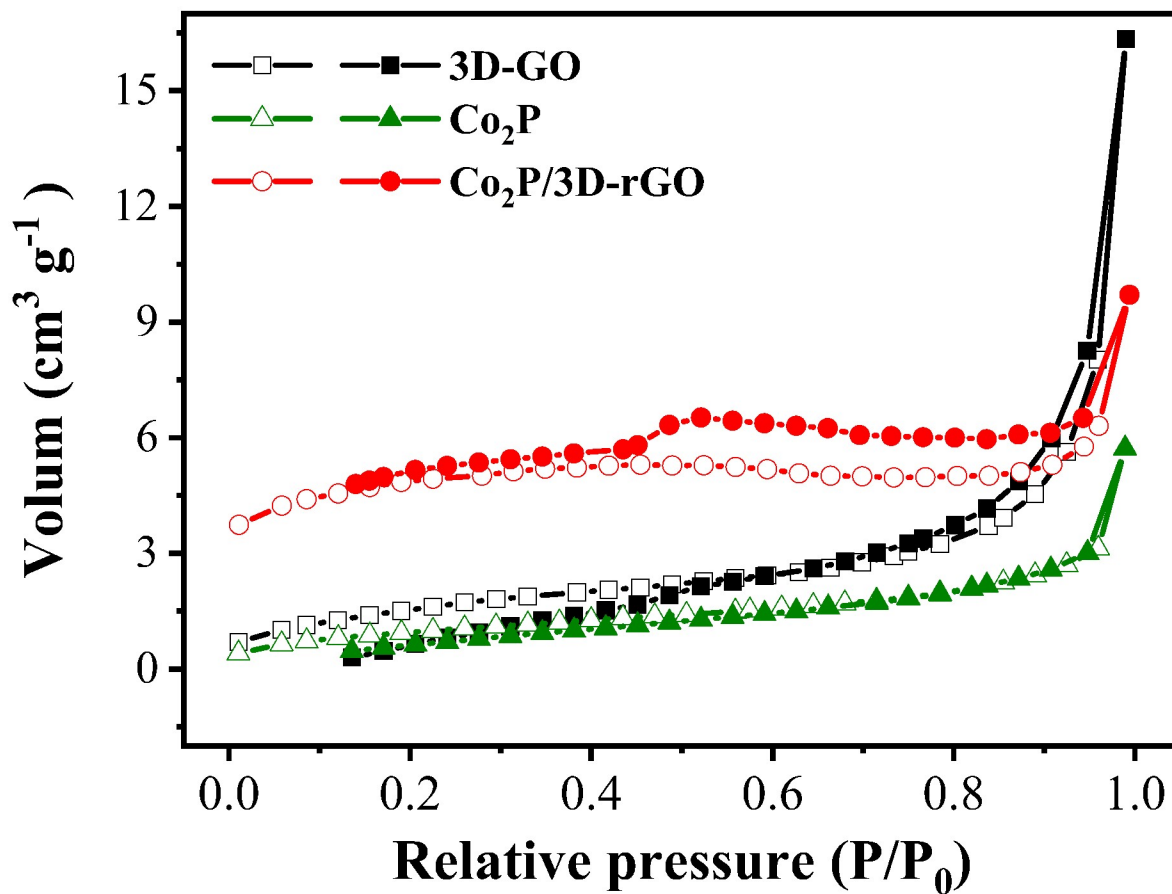


Fig. S6. N₂ adsorption-desorption isotherms of 3D-GO, Co₂P, and Co₂P@3D-rGO powders scraped from 3D-GO/NF, Co₂P/NF and Co₂P@3D-rGO/NF, respectively.

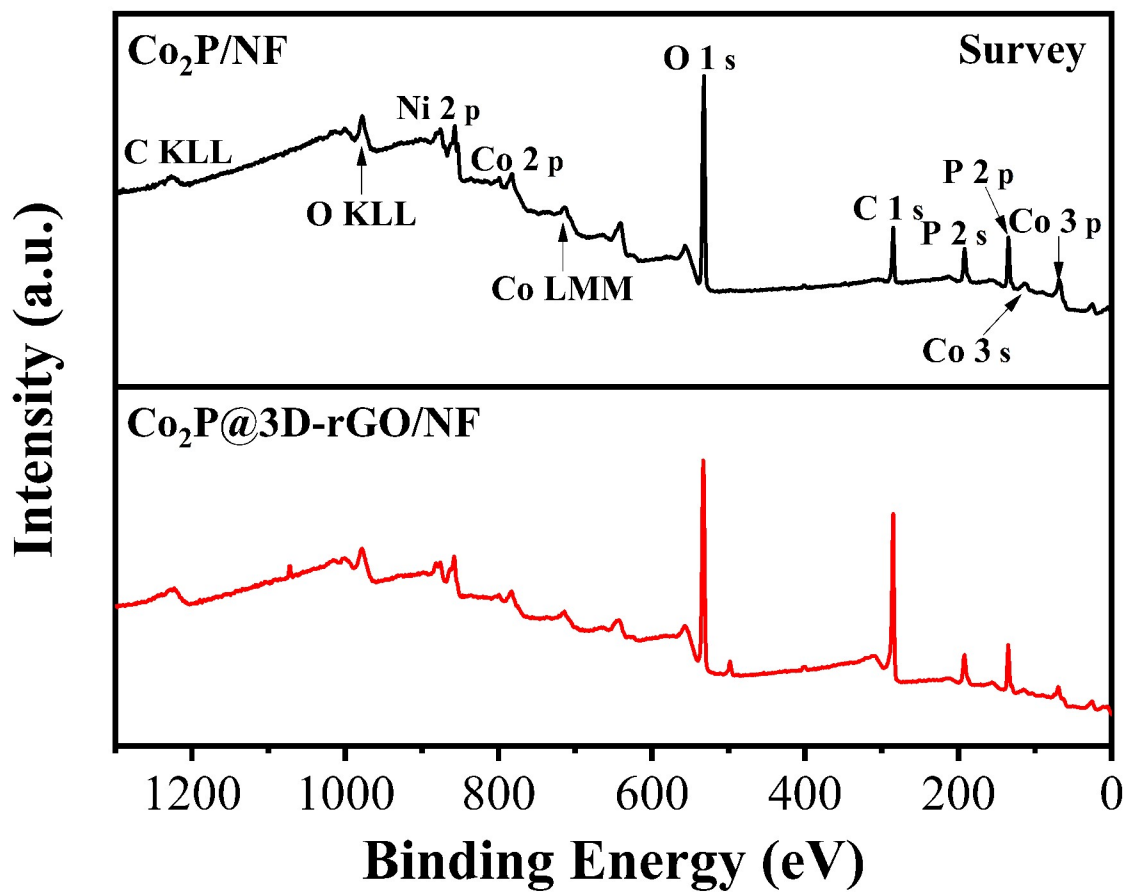


Fig. S7. XPS full survey spectra of Co₂P/NF and Co₂P@3D-rGO/NF.

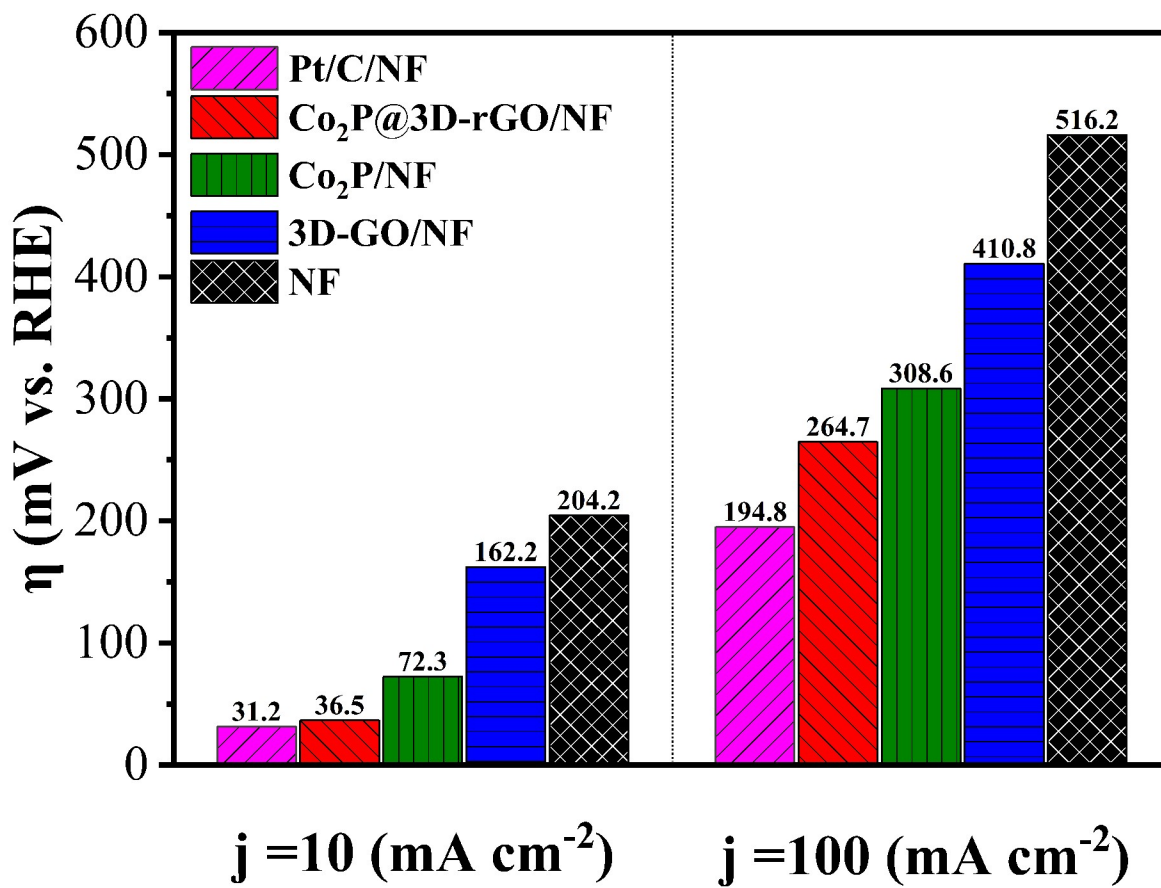


Fig. S8. HER overpotentials of the electrodes.

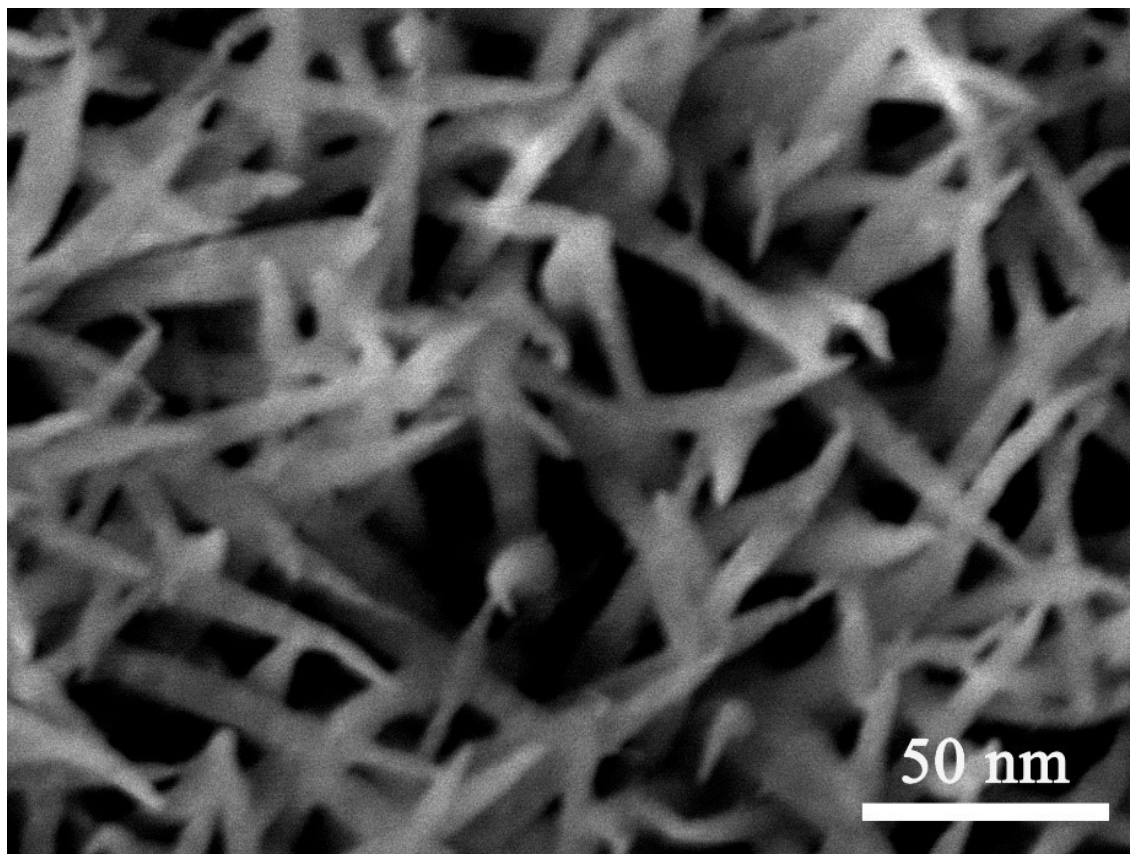


Fig. S9. FESEM image of $\text{Co}_2\text{P}@3\text{D-rGO/NF}$ after the LSV test.

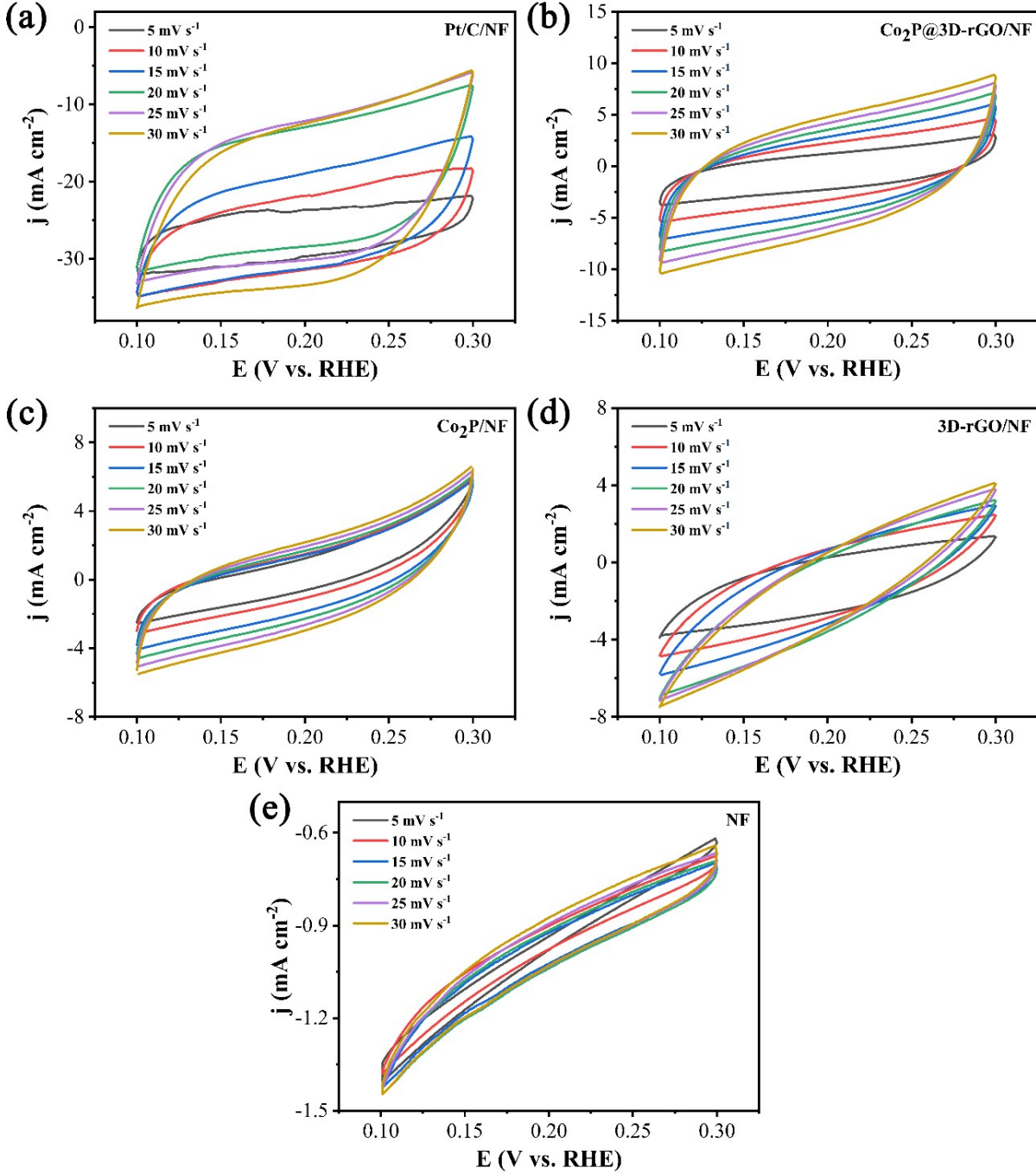


Fig. S10. Cyclic voltammety curves of the electrodes: (a) Pt/C/NF, (b) $\text{Co}_2\text{P}@3\text{D-rGO}/\text{NF}$, (c) $\text{Co}_2\text{P}/\text{NF}$, (d) 3D-rGO/NF, and (e) NF in a potential window (0.10 - 0.30 V vs. RHE) at various scan rates in 1.0 M KOH solution.

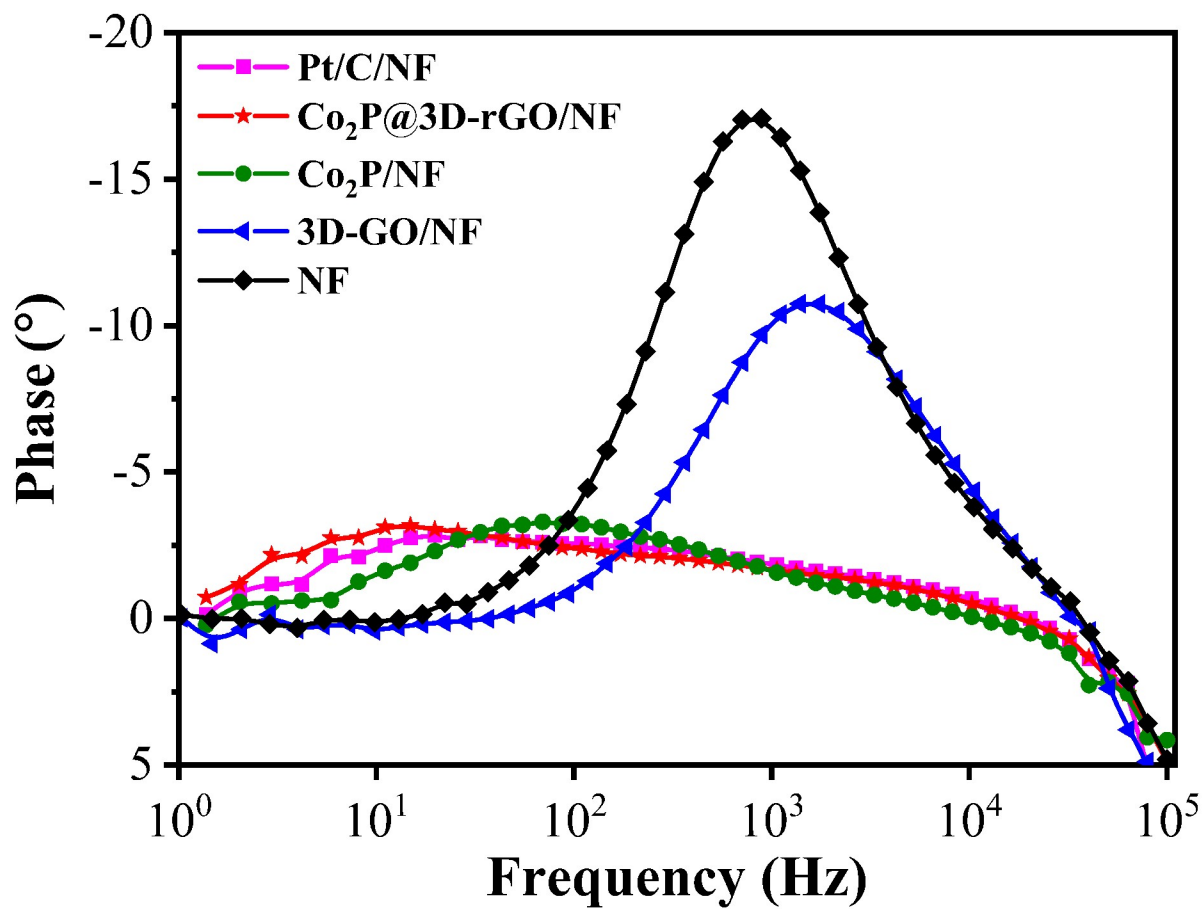


Fig. S11. Bode-phase plots of the electrodes.

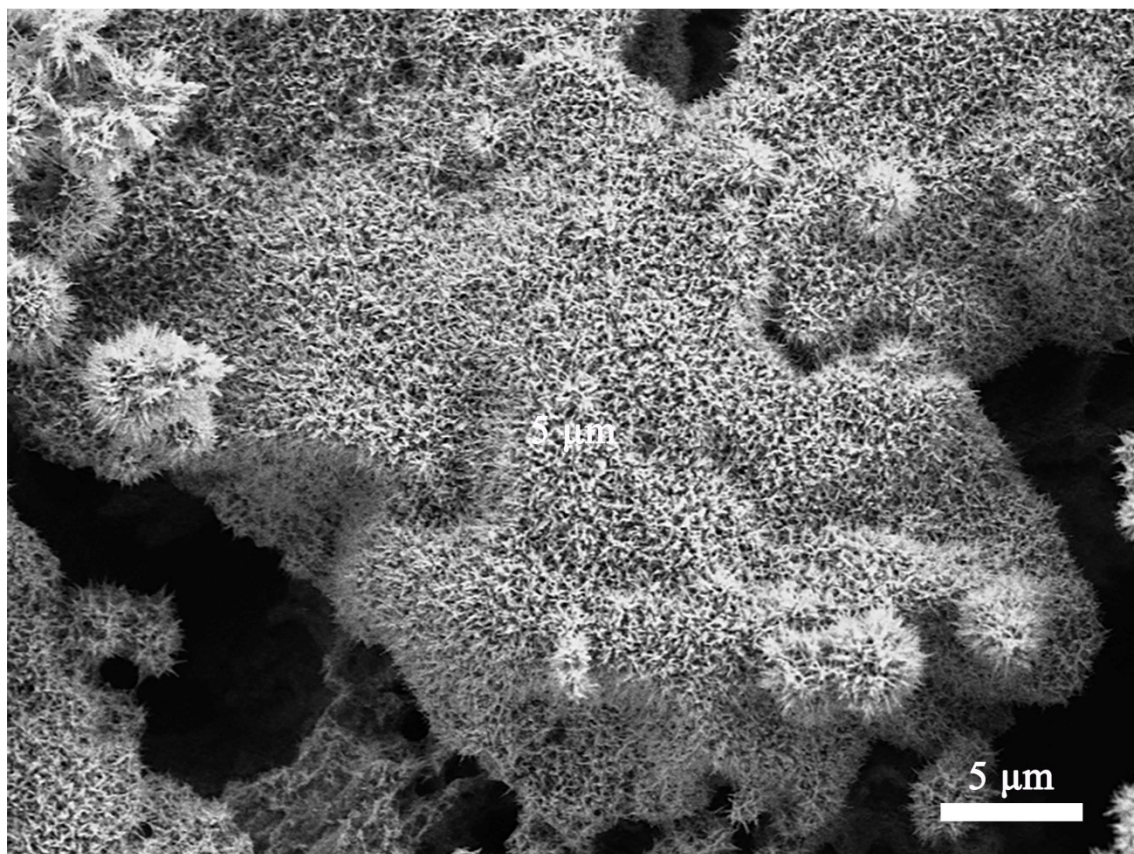


Fig. S12. FESEM image of Co₂P@3D-rGO/NF after 2000 CV sweeps.

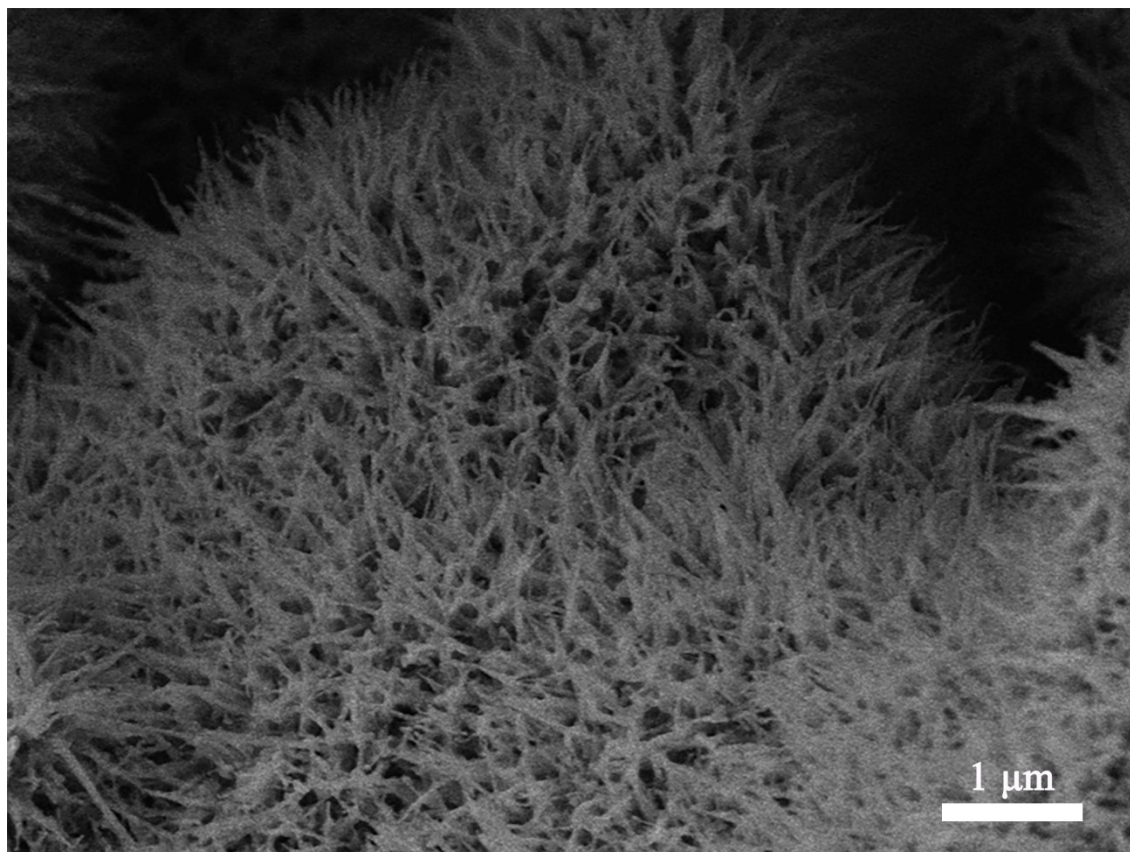


Fig. S13. FESEM image of Co₂P@3D-rGO/NF after 20 h of chronoamperometry test.

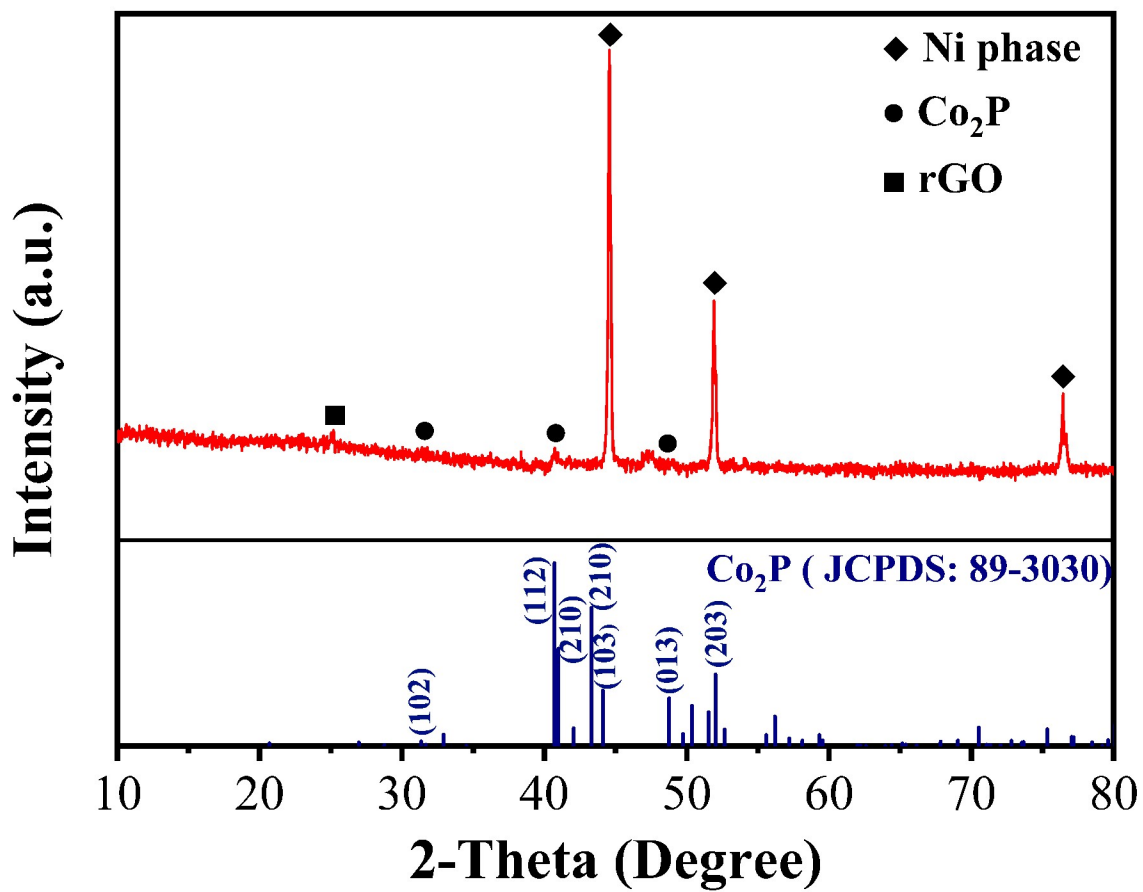


Fig. S14. XRD pattern of Co₂P@3D-rGO/NF after 20 h of chronoamperometry test.

Table S1 The pore properties of 3D-GO, Co₂P, and Co₂P@3D-rGO powders scraped from 3D-GO/NF, Co₂P/NF, and Co₂P@3D-rGO/NF, respectively.

Pore properties	3D-GO	Co ₂ P	Co ₂ P@3D-rGO
BET surface area (m ² g ⁻¹)	15.7	3.6	6.0
BJH Adsorption Pore volume (cm ³ g ⁻¹)	0.0096	0.0088	0.0255
BJH Desorption Pore volume (cm ³ g ⁻¹)	0.0097	0.0087	0.0247
BJH Adsorption pore size (nm)	7.5	10.2	16.8
BJH Desorption pore size (nm)	6.2	10.6	15.9

Table S2 HER activities of nanocomposite electrocatalysts associated with Co₂P.

Electrocatalysts	Electrolyte	$\eta(\text{mV})@j$ ($\text{mA}\cdot\text{cm}^{-2}$)	Tafel Slope ($\text{mV}\cdot\text{dec}^{-1}$)	Reference
CoP/Co ₉ S ₈ -Cu	1 M KOH	118@10	66.75	Ref ¹
CoP@FeCoP/NC YSMPs	1 M KOH	141@10	56.34	Ref ²
Co ₂ P/CoWO ₄ /NF	1 M KOH	81@10	79	Ref ³
Co ₂ P/NPSC-800	1 M KOH	173@10	106.52	Ref ⁴
Co ₂ P NRs	1 M KOH	151@10	--	Ref ⁵
Co ₂ P/NPSC-800	1 M KOH	173@20	106.52	Ref ⁶
Co/CoN/Co ₂ P-NPC	1 M KOH	99@10	51	Ref ⁷
CoP/Co ₂ P hybrids	1 M KOH	103@10	61.2	Ref ⁸
Co ₂ P NPs	1 M KOH	131@10	36	Ref ⁹
Co ₂ P/CoP branched	1 M KOH	87@10	76.8	Ref ¹⁰
Co ₂ P/CNTs	1 M KOH	132@10	103	Ref ¹¹
Fe-Co ₂ P BNRs	1 M KOH	156@10	90	Ref ¹²
Co₂P@3D-rGO/NF	1 M KOH	36.5@10	55.5	This work

References:

1. Y. Pan, Y. Q. Liu, Y. Lin and C. G. Liu, *ACS Appl. Mater. Interfaces*, 2016, **8**, 13890-13901.
2. J. H. Shi, F. Qiu, W. B. Yuan, M. M. Guo and Z. H. Lu, *Chem Eng J*, 2021, **403**, 126312.
3. K. Y. Tao, H. M. Dan, Y. Hai, L. Liu and Y. Gong, *Electrochim Acta*, 2019, **328**, 135123.
4. X. W. Sun, H. Liu, G. R. Xu, J. Bai and C. P. Li, *Int J Hydrogen Energ*, 2021, **46**, 1560-1568.
5. Z. P. Huang, Z. Z. Chen, Z. B. Chen, C. C. Lv, M. G. Humphrey and C. Zhang, *Nano Energy*, 2014, **9**, 373-382.
6. Y. Li, M. N. Cui, T. J. Li, Y. Shen, Z. J. Si and H. G. Wang, *Int J Hydrogen Energ*, 2020, **45**, 16540-16549.
7. L. Hu, Y. W. Hu, R. Liu, Y. C. Mao, M. S. Balogun and Y. X. Tong, *Int J Hydrogen Energ*, 2019, **44**, 11402-11410.
8. L. Y. Chen, Y. Y. Zhang, H. F. Wang, Y. X. Wang, D. Z. Li and C. Y. Duan, *Nanoscale*, 2018, **10**, 21019-21024.
9. X. Y. Wang, C. H. Liu, C. Wu, X. M. Tian, K. Wang, W. L. Pei and Q. Wang, *Electrochim. Acta*, 2020, **330**, 135191.
10. M. J. Song, Y. He, M. M. Zhang, X. R. Zheng, Y. Wang, J. F. Zhang, X. P. Han, C. Zhong, W. B. Hu and Y. D. Deng, *J. Power Sources*, 2018, **402**, 345-352.
11. D. Das and K. K. Nanda, *Nano Energy*, 2016, **30**, 303-311.
12. Y. Lin, K. A. Sun, X. M. Chen, C. Chen, Y. Pan, X. Y. Li and J. Zhang, *J Energy Chem*, 2021, **55**, 92-101.