Supplementary Information

Low-Coordinated Cobalt Arrays for Efficient Hydrazine Electrooxidation

Qian Liu[a], Xiaobin Liao[b], Yuanhao Tang[a], Jianghao Wang[a], Xiangzhou Lv[a], Xuelei Pan[d], Ruihu Lu[b], Yan Zhao[b, c, *], Xin-Yao Yu[e, f, *], Hao Bin Wu[a, *]

[a]Institute for Composites Science Innovation (InCSI) and State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China

[b]State Key Laboratory of Silicate Materials for Architectures, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, P. R. China

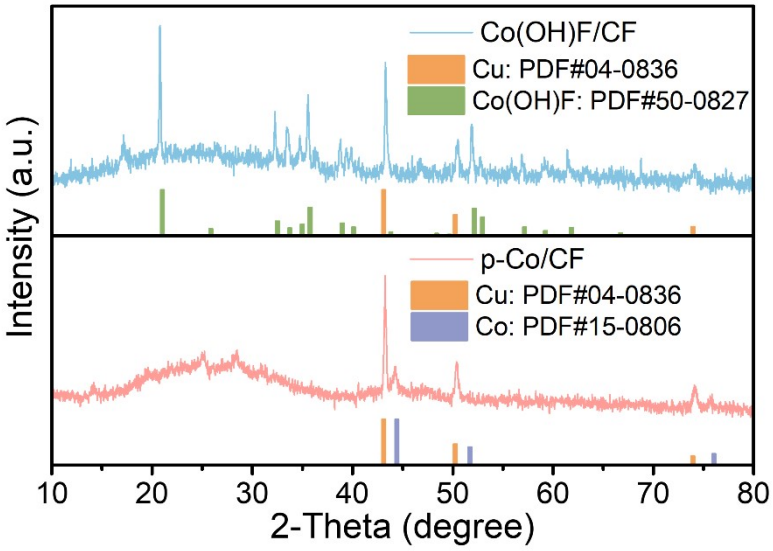
[c]The Institute of Technological Sciences, Wuhan University, Hubei, Wuhan 430072, P. R. China

[d]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, P. R. China

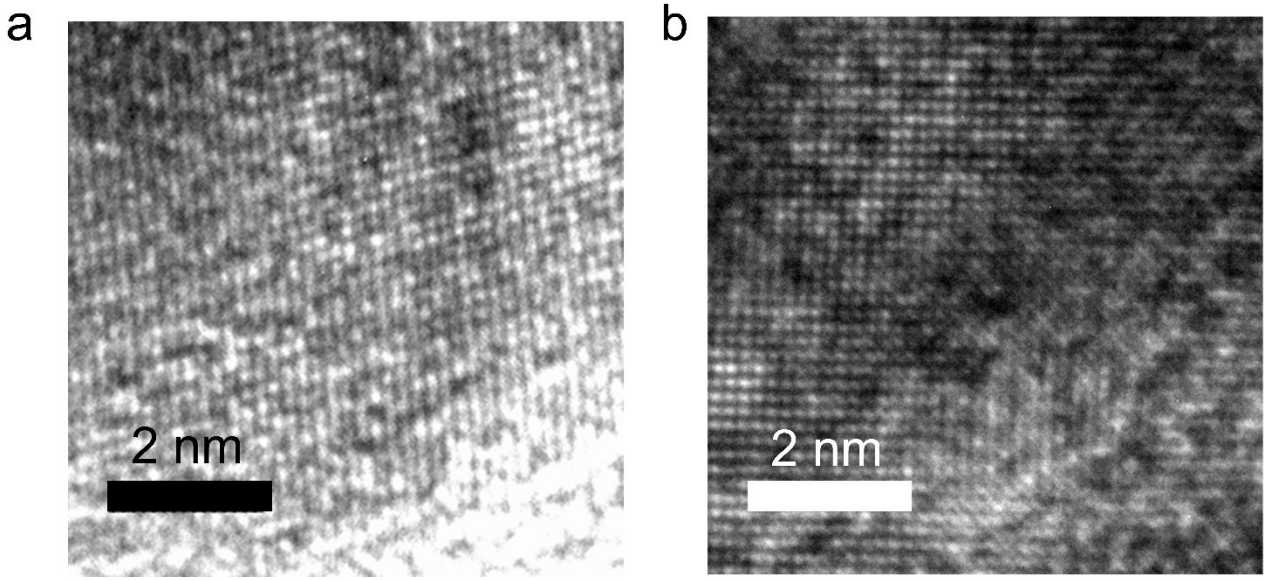
[e]Institutes of Physical Science and Information Technology, Key Laboratory of Structure and Functional Regulation of Hybrid Materials, Anhui University, Ministry of Education, Hefei 230601, P. R. China

[f]Energy Materials and Devices Key Lab of Anhui Province for Photoelectric Conversion, Anhui University, Hefei 230601, P. R. China

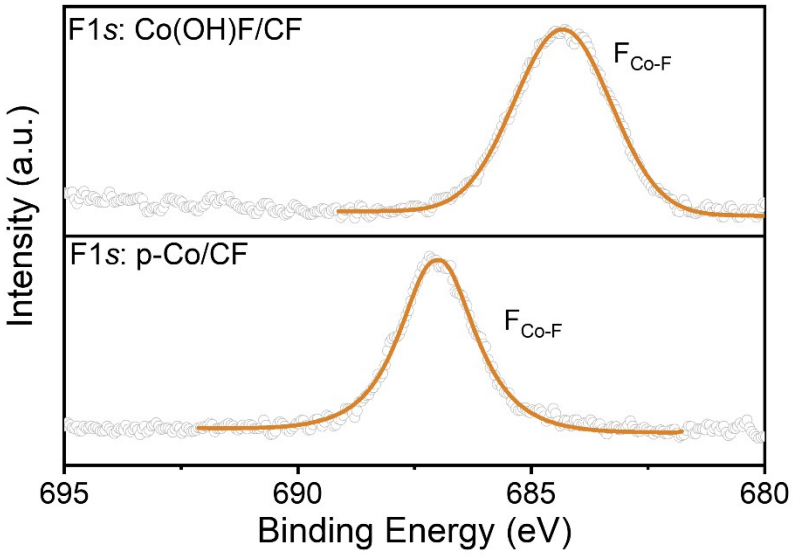
Email: yan2000@whut.edu.cn (Y. Zhao), yuxinyao@ahu.edu.cn (X.-Y. Yu), hbwu@zju.edu.cn (H. B. Wu)



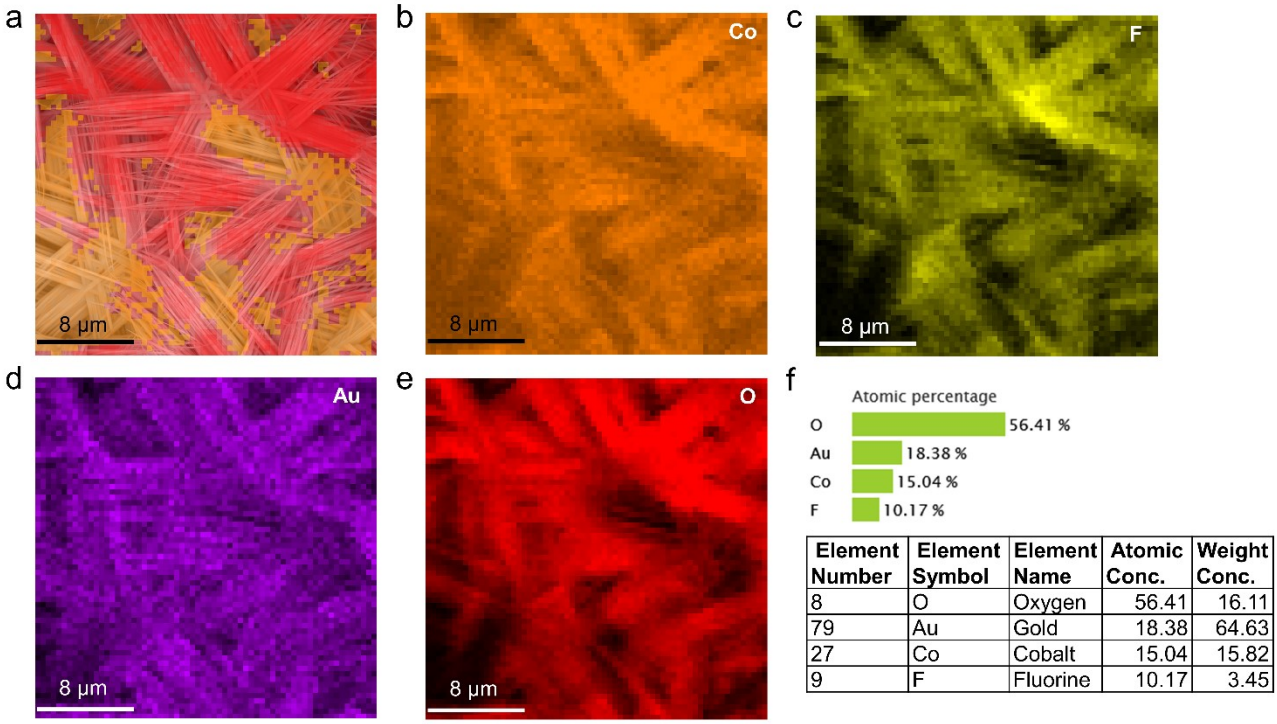
Supplementary Fig. 1, XRD patterns of Co(OH)F/CF and p-Co/CF.



Supplementary Fig. 2 Magnified HRTEM images of p-Co.

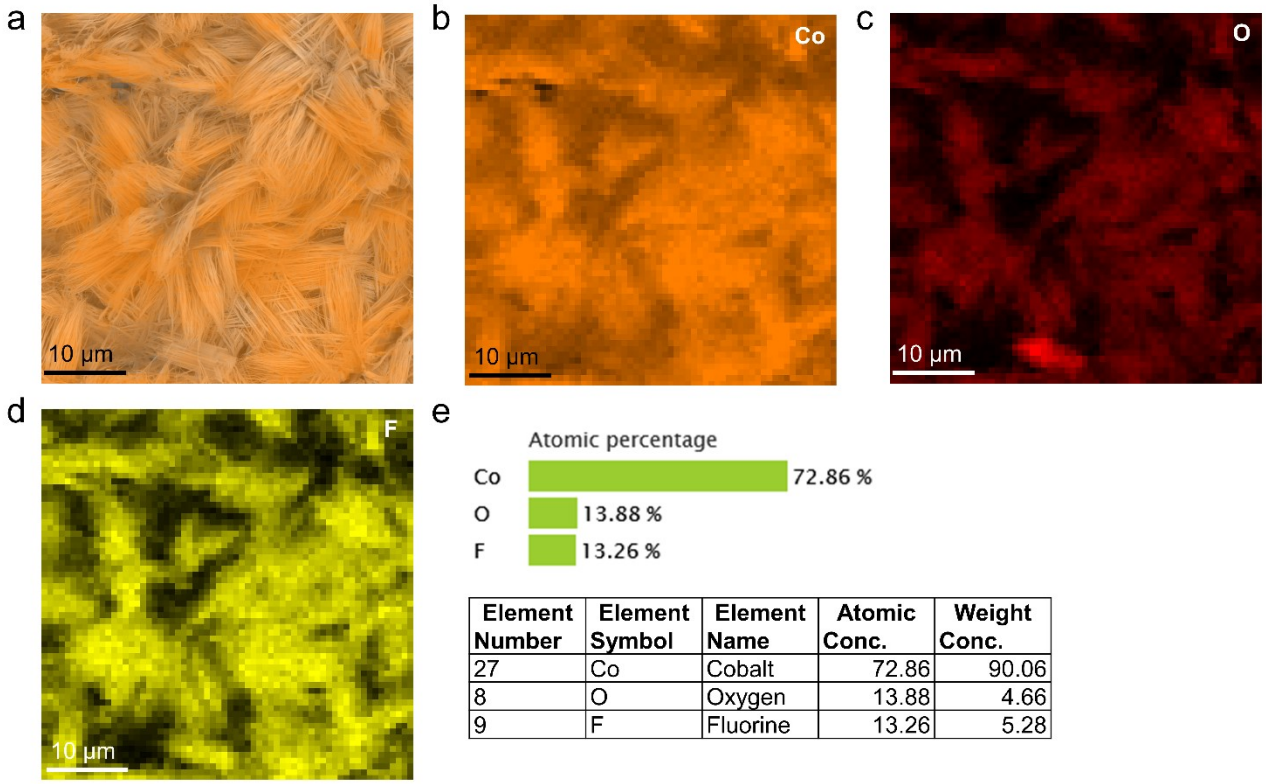


Supplementary Fig. 3, F 1*s* XPS spectra of Co(OH)F and p-Co/CF.



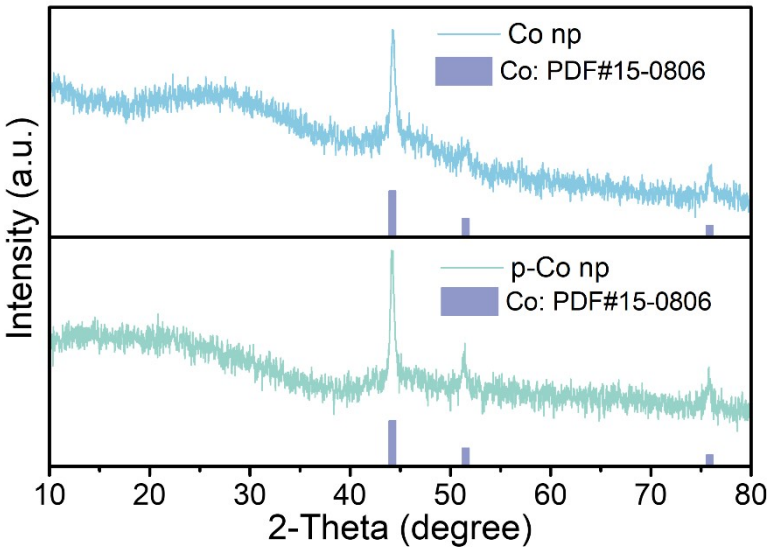
Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
8	O	Oxygen	56.41	16.11
79	Au	Gold	18.38	64.63
27	Co	Cobalt	15.04	15.82
9	F	Fluorine	10.17	3.45

Supplementary Fig. 4 a-e, Energy dispersive spectroscopy (EDS) mapping of Co(OH)F/CF; **f,** Element concentration of Co(OH)F/CF.

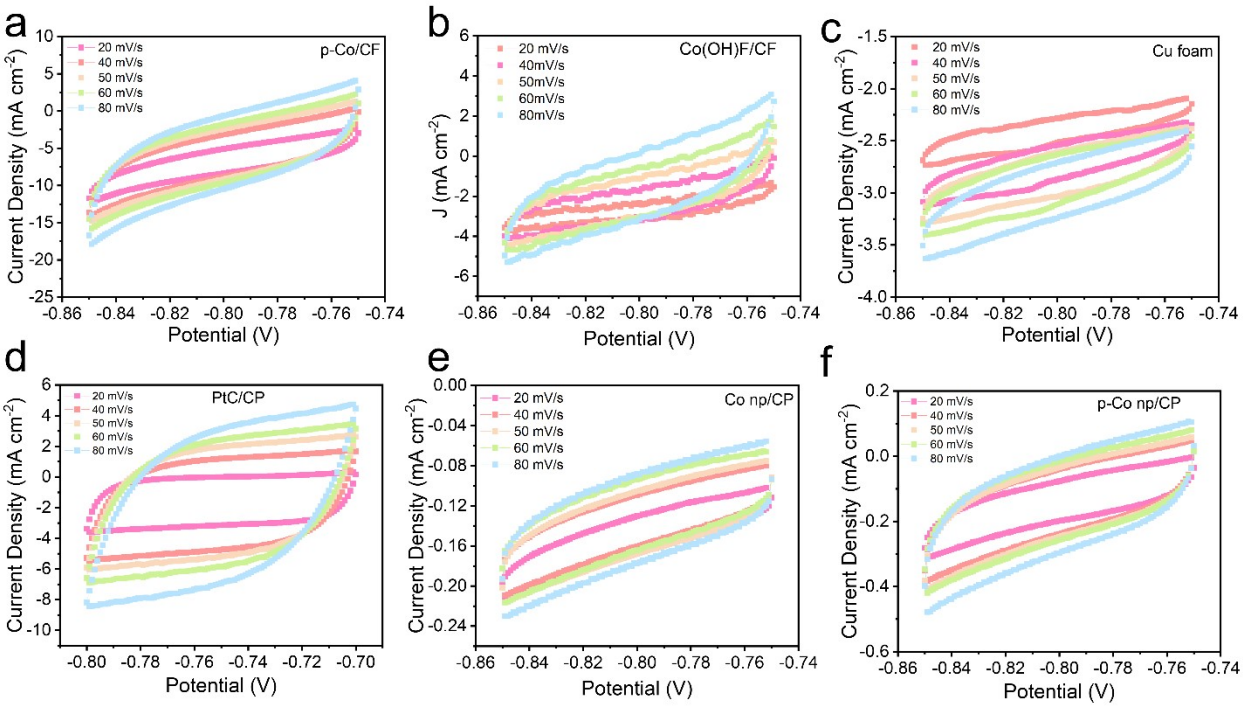


Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
27	Co	Cobalt	72.86	90.06
8	O	Oxygen	13.88	4.66
9	F	Fluorine	13.26	5.28

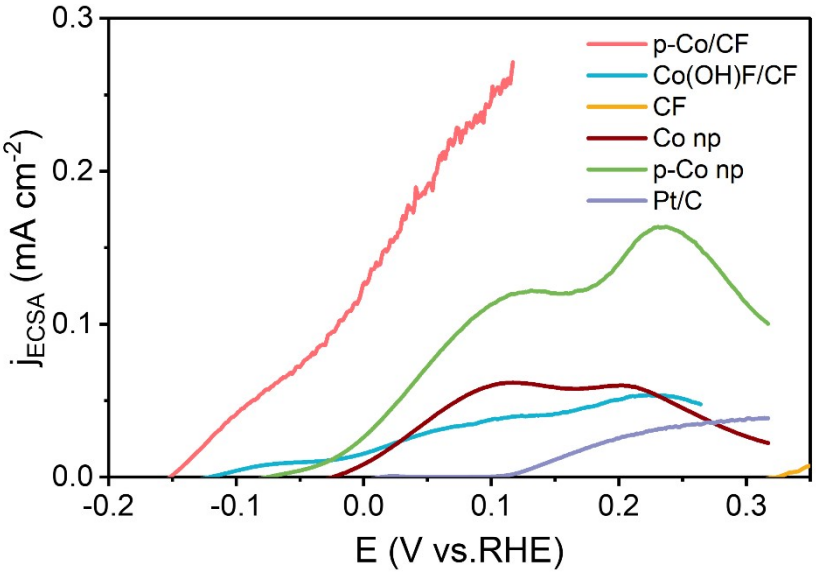
Supplementary Fig. 5 a-d, Energy dispersive spectroscopy (EDS) mapping of p-Co/CF; **e,** Element concentration of p-Co/CF.



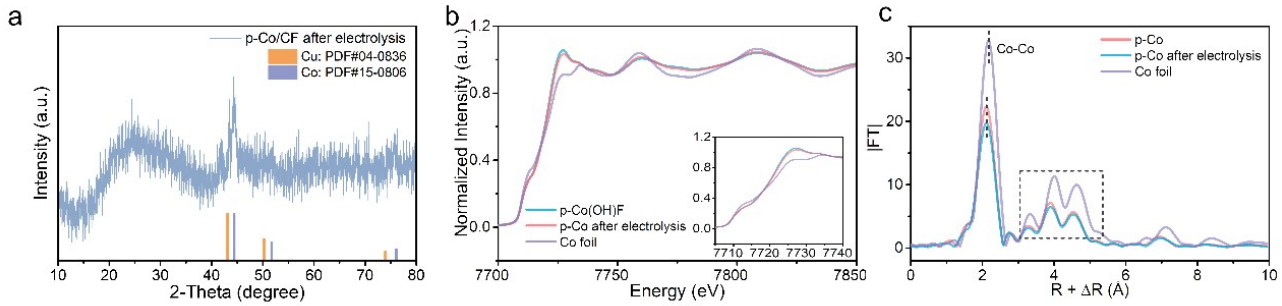
Supplementary Fig. 6, XRD patterns of Co nanoparticles (Co np) and p-Co nanoparticles (p-Co np).



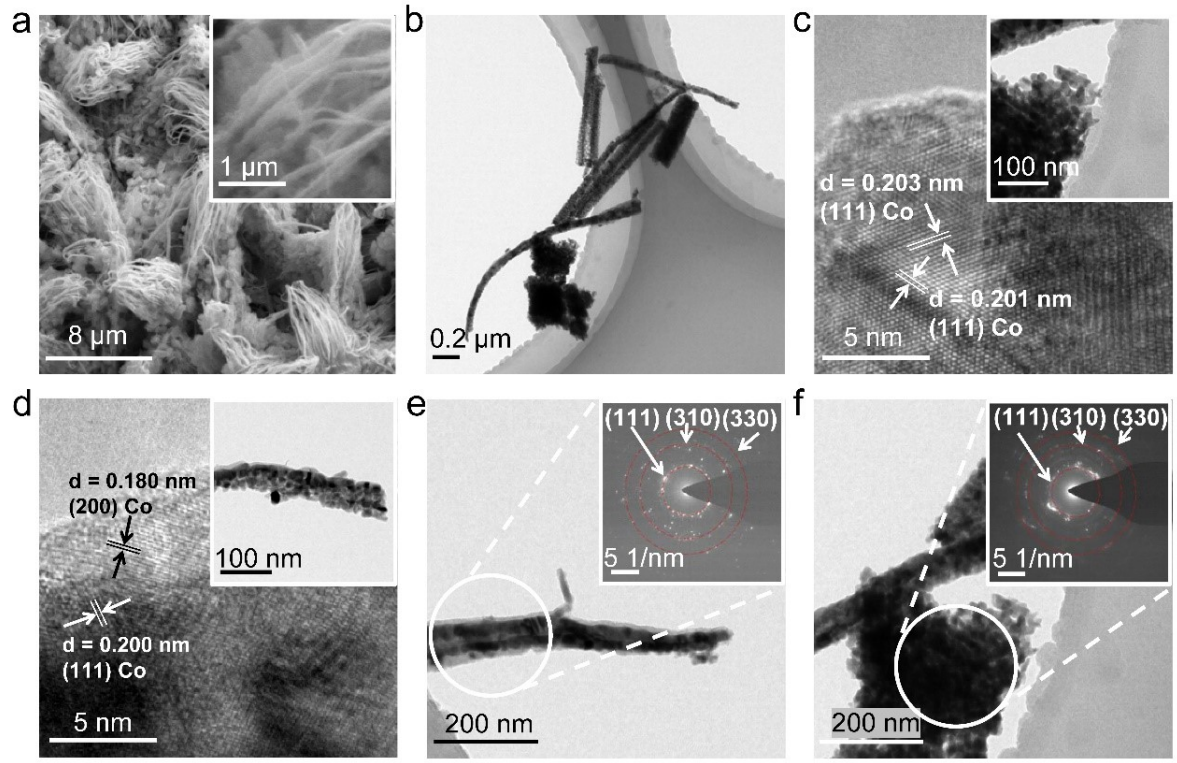
Supplementary Fig. 7 CV curves of **a,** p-Co/CF, **b,** Co(OH)F/CF, and **c,** Cu foam, **d,** PtC/CP, **e,** Co np/CP, **f,** p-Co np/CP at different scan rates.



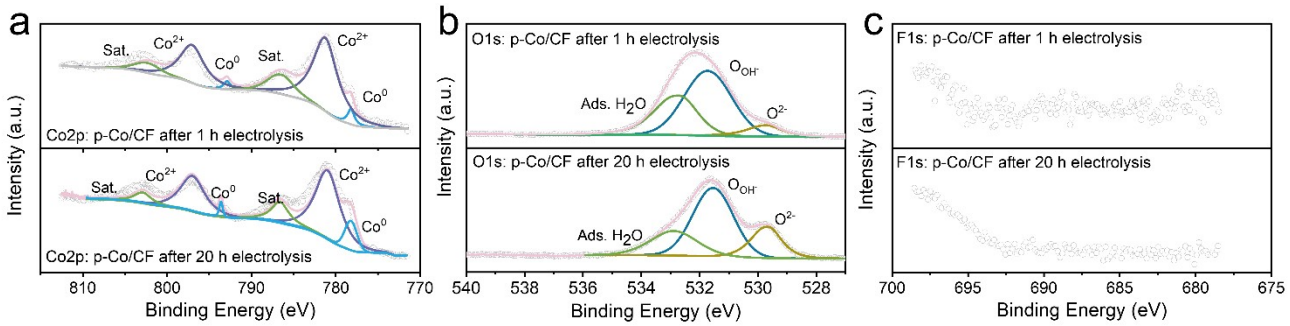
Supplementary Fig. 8 ECSA normalized polarization curves in 1 M KOH with 0.05 M N_2H_4.



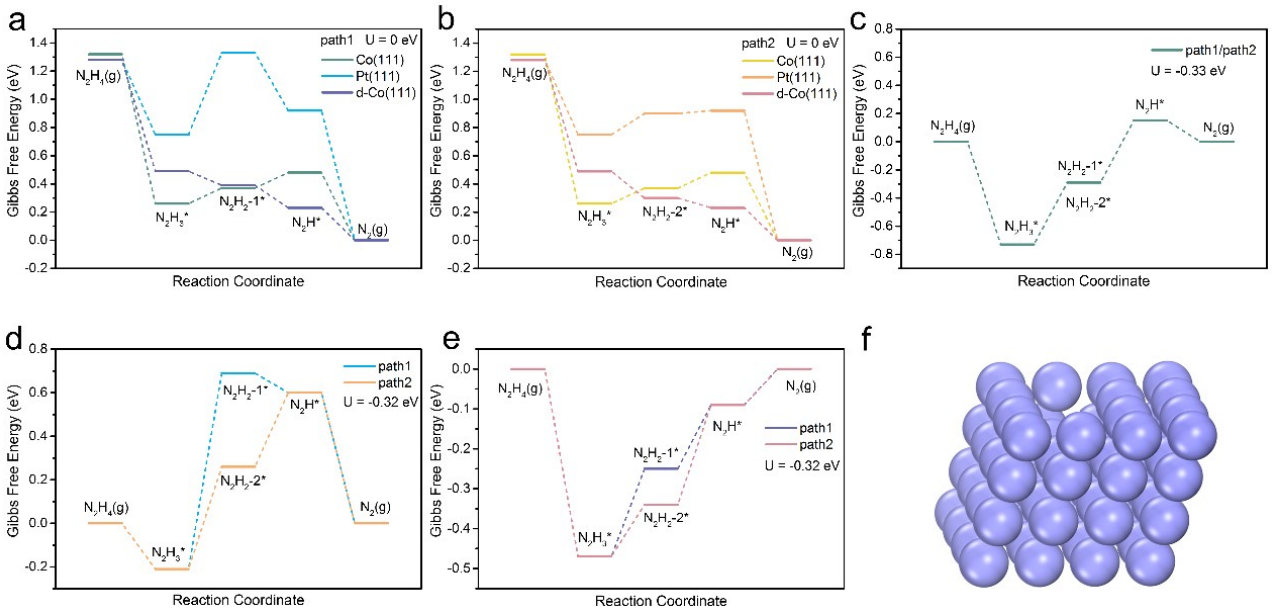
Supplementary Fig. 9 a, XRD pattern of p-Co(OH)F after electrolysis. **b,** Normalized Co K-edge spectra. **c,** Fourier-transform spectra from EXAFS.



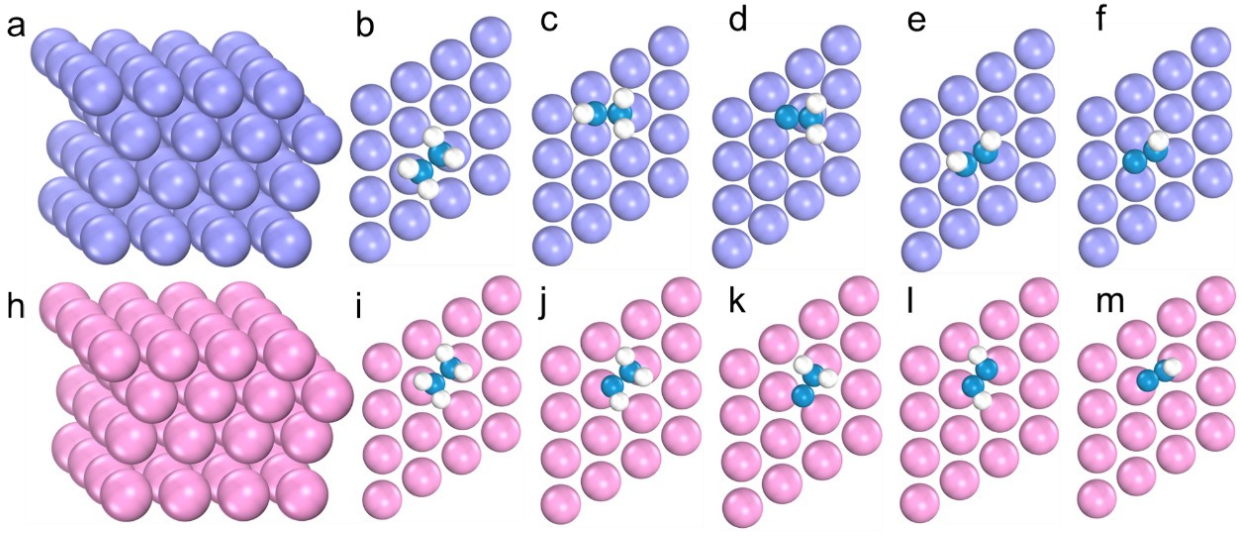
Supplementary Fig. 10 a, FESEM image of p-Co after electrolysis. **b**, TEM image of p-Co after electrolysis. **c,** HRTEM image of cubic structure of p-Co after electrolysis. **d,** HRTEM image of nanoneedle structure of p-Co after electrolysis. **e,** TEM image and SAED pattern of nanoneedle structure of p-Co after electrolysis. **f,** TEM image and SAED pattern of cubic structure of p-Co after electrolysis.



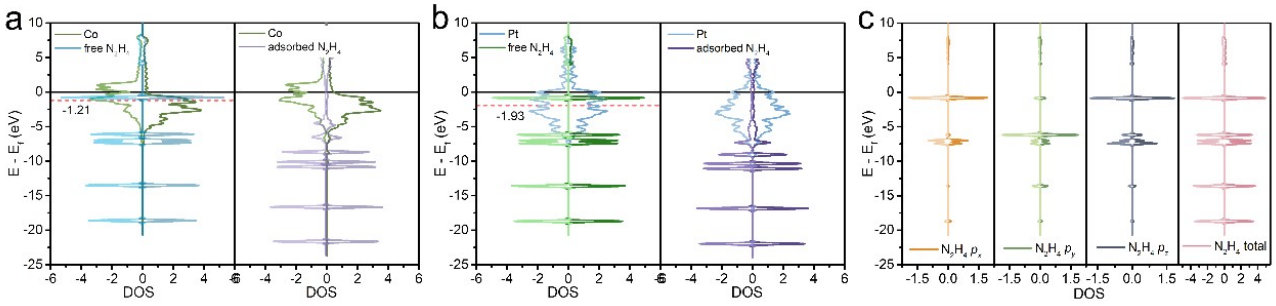
Supplementary Fig. 11 a, Co 2p XPS of p-Co/CF after 1h and 20 h chronopotentiometry test, **b,** O 1s XPS of p-Co/CF after 1h and 20 h chronopotentiometry test, **c,** F 1s XPS of p-Co/CF after 1h and 20 h chronopotentiometry test.



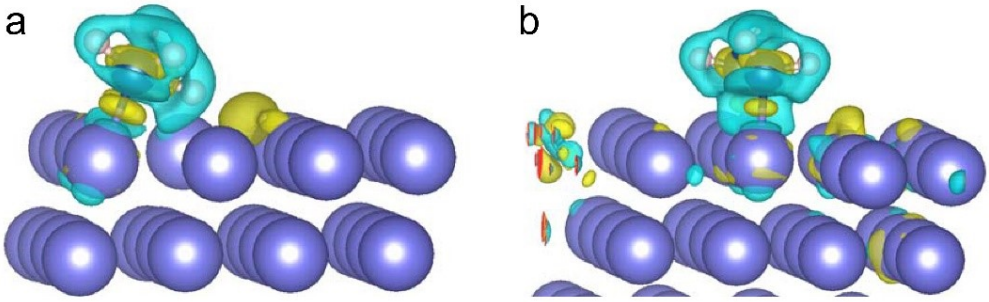
Supplementary Fig. 12 a-e, Gibbs free energy diagram of HzOR. **a b,** At zero cell potential[1] (U = 0 eV). **c-e,** At the equilibrium potential (U = Ueq). **f,** Computational model for d-Co.



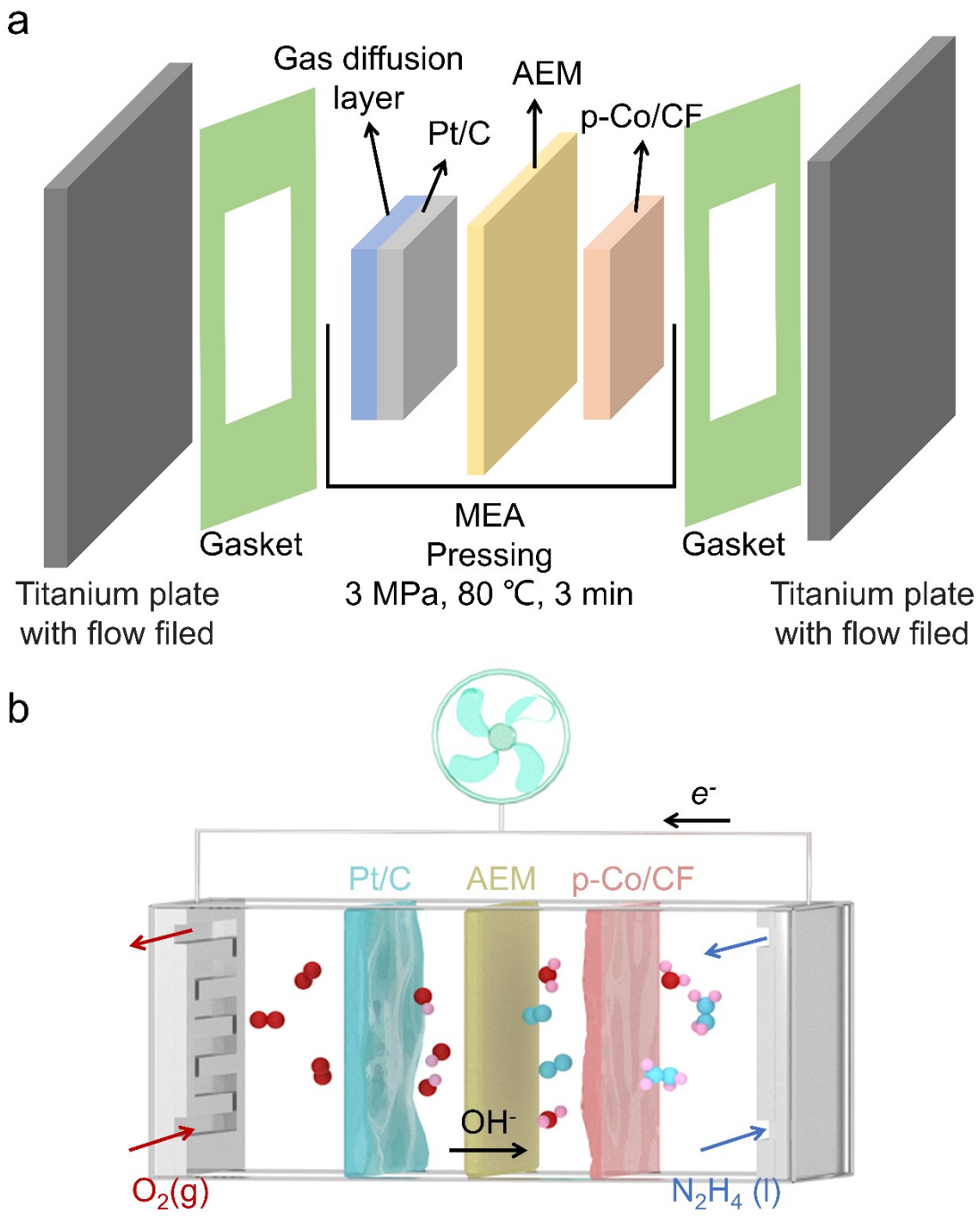
Supplementary Fig. 13 a-f, Computational model of Co(111) and different adsorption configurations of intermediate species. **h-m,** Computational model of Pt(111) and different adsorption configurations of intermediate species.



Supplementary Fig. 14 a, b DOS for Co(111) and Pt(111) surfaces before and after hydrazine adsorption. **c,** PDOS and total DOS for free hydrazine molecule.



Supplementary Fig. 15 Differential charge density of N_2H_4 adsorbed on **a,** d-Co(111) and **b,** Co(111). Cyan and yellow represent charge depletion and accumulation, respectively.



Supplementary Fig. 16 Schematic diagrams of **a,** MEA set up and **b,** device operation.

Supplementary Table 1 Fitted Parameters of Co K-Edge EXAFS Curves for p-Co.

Sample	Path	N	R (Å)	σ^2 (10^{-3} Å^2)	ΔE_0 (eV)
Co foil theoretical	Co-Co	12.0	2.51	--	--
p-Co	Co-Co	9.2	2.49	6.479	-5.2

Supplementary Table 2 Comparison of HzOR onset potential (potential at 1 mA cm-1) and Tafel slope with other catalysts.

Catalyst	Onset potential (V)	Tafel slope (mV dec^{-1})	Stability (h)	*C* (N_2H_4) (M)	*E* (at 0.2 A cm^{-2}) (V)
This work	-0.15	8.83	29	0.05	-0.068
Co_3Ta/C[2]	-0.1	56.9	3.3	0.2	--
Co/$LaCoO_x$@ N-C[3]	-0.17	80	20	0.1	--
Ni-Zn/rGO[4]	0	33.5	10	0.5	0.14
PW-Co_3N/NF[5]	-0.05	14	10	0.1	0.025
Ni-Co/NF[6]	-0.16	14.5	10	0.5	-0.01
V-Ni_3N[7]	0.002	31	10	0.1	0.07
P-$CoCO_3$/CF[8]	-0.055	27.78	18	0.3	-0.025
NiCo-$MoNi_4$/NF[9]	-0.05	37.9	40	0.1	0.11
Ni NCNAs[10]	-0.026	32.6	20	0.3	--
A-Ru-KB[11]	-0.01	12.9	20	0.1	--
Ni-Zn[12]	-0.05	44.58	10	0.1	--
RP-CPM[13]	-0.1	47.6	20	0.3	--
Ni_3N-Co_3N PNAs/NF[14]	-0.1	21.6	40	0.1	--

Supplementary Table 3 The free-energy change (eV) of each elementary reaction for alternating pathway (path1) of HzOR on the surfaces at U = 0 V.

	Co(111)	Pt(111)	d-Co(111)
ΔG_1	-1.06	-0.53	-0.79
ΔG_2	0.11	0.58	-0.1
ΔG_3	0.11	-0.41	-0.16
ΔG_4	-0.48	-0.92	-0.23
ΔG_{total}	-1.32	-1.28	-1.28

Supplementary Table 4 The free-energy change (eV) of each elementary reaction for distal pathway (path2) of HzOR on the surfaces at U = 0 V.

	Co(111)	Pt(111)	d-Co(111)
ΔG_1	-1.06	-0.53	-0.79
ΔG_2	0.11	0.15	-0.19
ΔG_3	0.11	0.02	-0.07
ΔG_4	-0.48	-0.92	-0.23
ΔG_{total}	-1.32	-1.28	-1.28

Supplementary Table 5 The adsorption energies of intermediates on d-Co(111), Co(111) and Pt(111).

Eads	N_2H_4*	N_2H_3*	N_2H_2* (path 1)	N_2H_2* (path 2)	N_2H*
Co(111)	-1.34	-2.63	-2.24	-3.82	-2.36
Pt(111)	-1.63	-2.28	-1.43	-3.46	-2.12
d-Co(111)	-1.86	-2.49	-2.37	-4.05	-2.77

Supplementary Table 6 Performance comparison of homemade DHzFCs.

Catalyst	OCV (V)	P_{max} (mW cm^{-2})	J (A cm^{-2})	C (N_2H_4) (M)	Temp. (°C)
This work	1.1	185.9	0.36	1.5	25
PW-Co_3N/NF[5]	0.98	46.3	0.1	0.5	25
Nanostructured -Cu film[15]	1	160.8	0.4	6.25	80
Ni_3N-Co_3N PNAs/NF[14]	1	60.3	0.14	0.5	25
RP-CPM[13]	1.01	64.77	0.175	0.5	25

Supplementary References

1. G. Tomaschun and T. Kluner, *Phys. Chem. Chem. Phys.*, 2019, **21**, 18227-18239.
2. G. Feng, L. An, B. Li, Y. Zuo, J. Song, F. Ning, N. Jiang, X. Cheng, Y. Zhang and D. Xia, *Nat. Commun.*, 2019, **10**, 4514.
3. L. Gao, J. Xie, S. Liu, S. Lou, Z. Wei, X. Zhu and B. Tang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 24701-24709.
4. Z. Feng, H. Zhang, B. Gao, P. Lu, D. Li and P. Xing, *Int. J. Hydrogen Energy*, 2020, **45**, 19335-19343.
5. Y. Liu, J. Zhang, Y. Li, Q. Qian, Z. Li, Y. Zhu and G. Zhang, *Nat. Commun.*, 2020, **11**, 1853.
6. P.-P. Tang, X. Lin, H. Yin, D.-X. Zhang, H. Wen, J.-J. Wang and P. Wang, *ACS Sustainable Chem. Eng.*, 2020, **8**, 16583-16590.
7. J. Zhang, Y. Liu, J. Li, X. Jin, Y. Li, Q. Qian, Y. Wang, A. El-Harairy, Z. Li, Y. Zhu, H. Zhang, M. Cheng, S. Zeng and G. Zhang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 3881-3890.
8. F. Liu, H. Li, Y. Li, Q. Cao, X. Geng, C. Gu, W. Sun and J. Wang, *Sustainable Energy Fuels*, 2021, **5**, 2257-2265.
9. Q. Qian, Y. Li, Y. Liu, Y. Guo, Z. Li, Y. Zhu and G. Zhang, *Chem. Eng. J.*, 2021, **414**, 128818.
10. Y. Li, J. Li, Q. Qian, X. Jin, Y. Liu, Z. Li, Y. Zhu, Y. Guo and G. Zhang, *Small*, 2021, **17**, 2008148.
11. F. He, N. Xia, Y. Zheng, Y. Zhang, H. Fan, D. Ma, Q. Liu and X. Hu, *ACS Appl. Mater. Interfaces*, 2021, **13**, 8488–8496.
12. H. Zhang, Z. Feng, L. Wang, D. Li and P. Xing, *Nanotechnol.*, 2020, **31**, 365701.
13. Q. Q. Yapeng Li; Jihua Zhang; Yi Liu, Ziyun Li, Yin Zhu, Genqiang Zhang, *Sci. Adv.*, 2020, **6**, 4197.
14. Y. Xie, Q. Qian, J. Zhang, J. Li, Y. Li, X. Jin, Y. Zhu, Y. Liu, Z. Li, A. El-Harairy, C. Xiao and G. Zhang, *Angew Chem Int Ed Engl*, 2020, **60**, 5984-5993.
15. Z. Lu, M. Sun, T. Xu, Y. Li, W. Xu, Z. Chang, Y. Ding, X. Sun and L. Jiang, *Adv. Mater.*, 2015, **27**, 2361-2366.