

CoO-Co Heterojunction Covered with Carbon Enables Highly Efficient Integration of Hydrogen Evolution and 5-Hydroxymethylfurfural Oxidation

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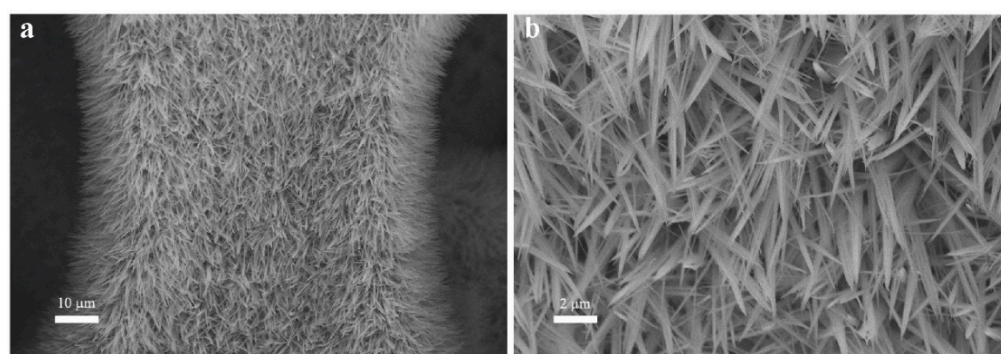


Figure S1. Typical SEM images of Co(OH)F/CF nanocones.

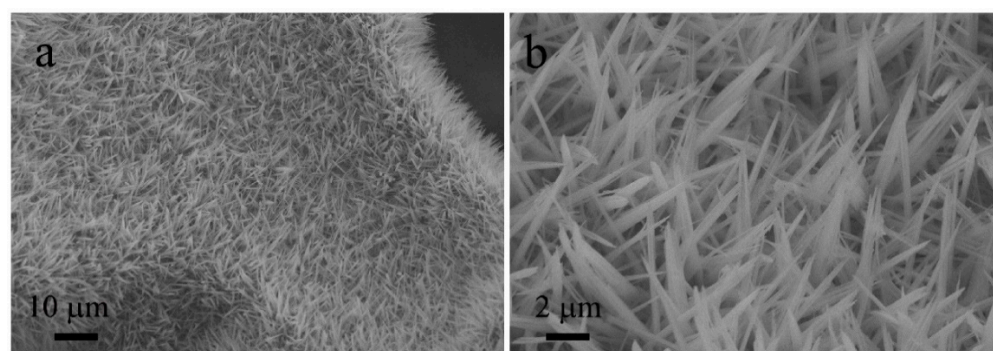


Figure S2. Typical SEM images of CoO/CF.

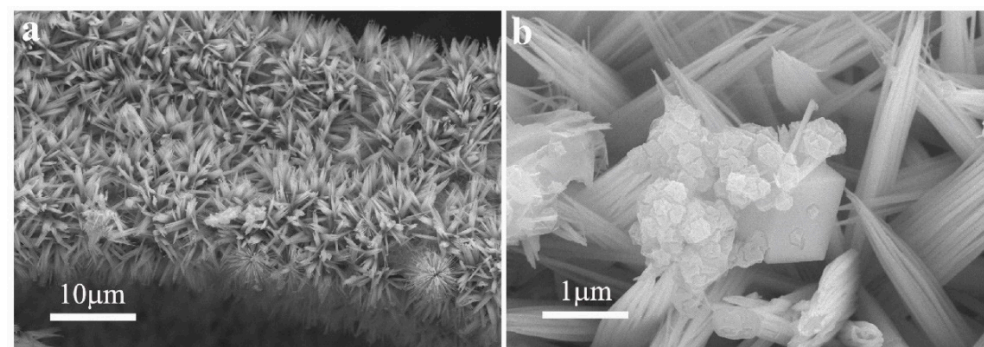


Figure S3. Typical SEM images of Co(OH)F@ZIF-67/CF.

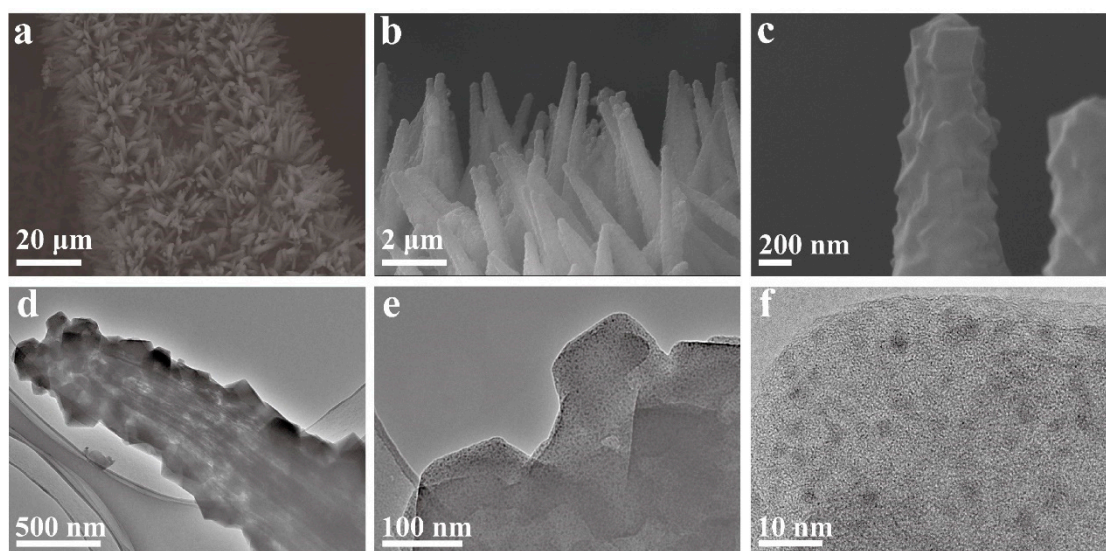


Figure S4. Typical SEM images (a-c), TEM images (d-e) and high-resolution TEM image of CoO@ZIF-67/CF.

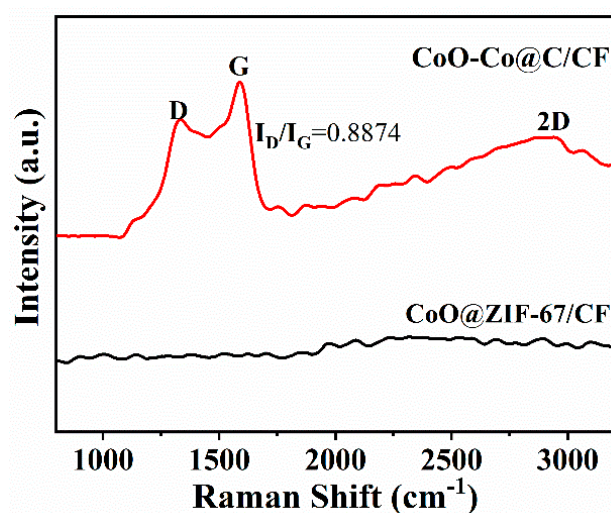


Figure S5. The Raman spectra of the CoO-Co@C/CF and CoO@ZIF-67/CF.

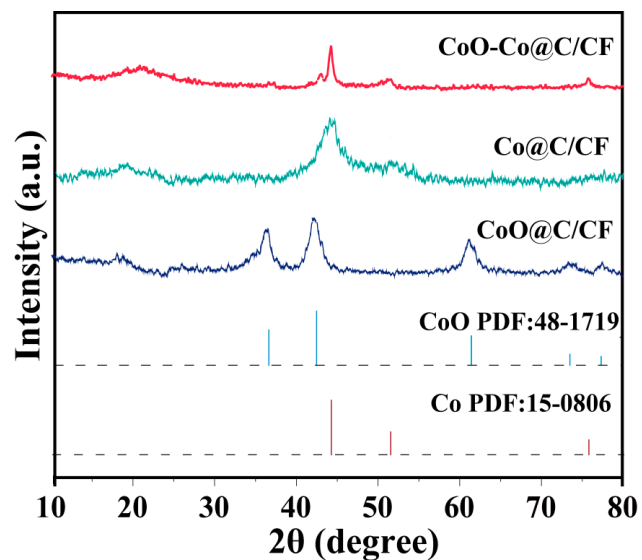


Figure S6. XRD patterns of CoO-Co@C/CF, CoO@C/CF and Co@C/CF.

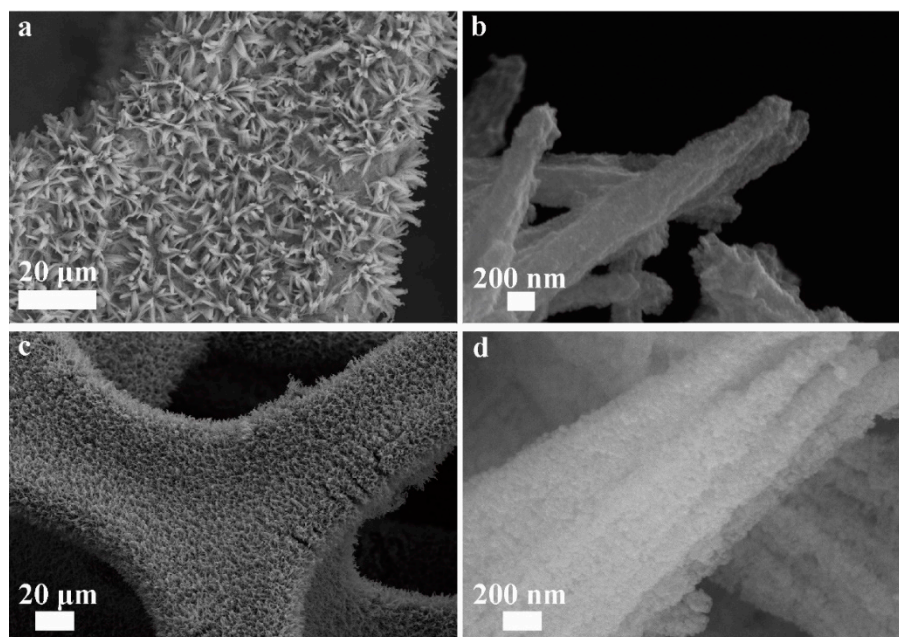


Figure S7. Typical SEM images of CoO@C/CF (a and b), Co@C/CF (c and d).

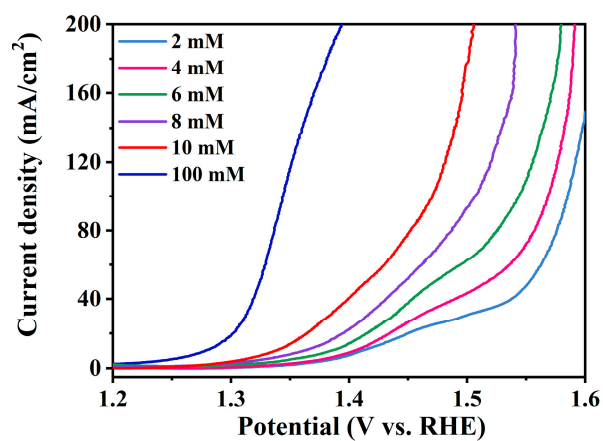


Figure S8. Polarization curves of HMFEOR over CoO-Co@C/CF in 1.0 M KOH with various concentrations of HMF (2, 4, 6, 8, 10 and 100 mM) at the scan rate of 5 mV·s⁻¹.

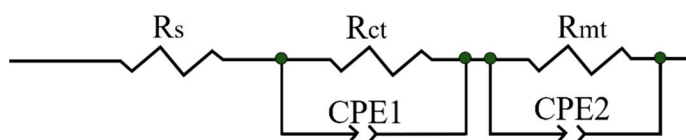


Figure S9. The equivalent circuit model of Nyquist plots.

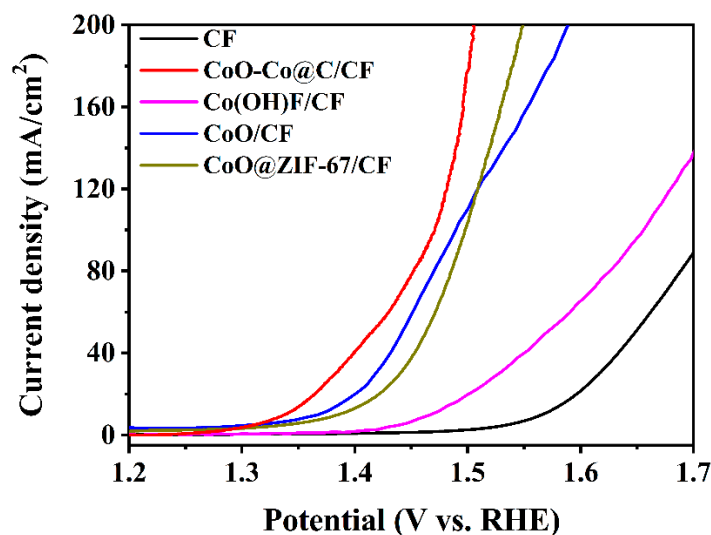


Figure S10. *iR*-compensated polarization curves of HMFEOR over CF, Co(OH)F/CF, CoO/CF, CoO@ZIF-67/CF, and Co-CoO@C/CF in 1.0 M KOH with 10 mM HMF at the scan rate of 5 mV·s⁻¹.

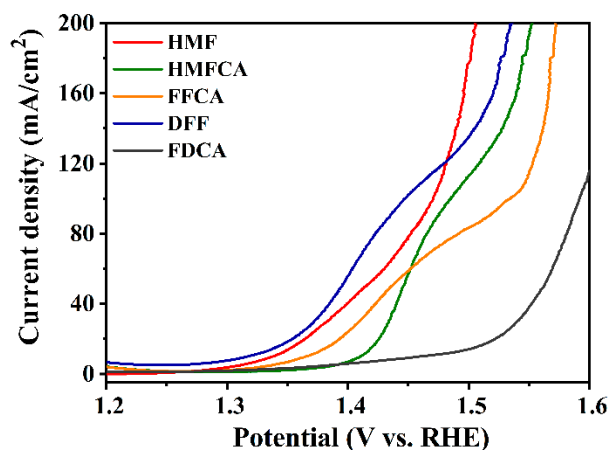


Figure S11. Polarization curves of CoO-Co@C/CF at a scan rate of 10 mV·s⁻¹ in 1.0 M of KOH with 10 mM various biomass substrates (HMF, HMFCA, FFCA, DFF or FDCA).

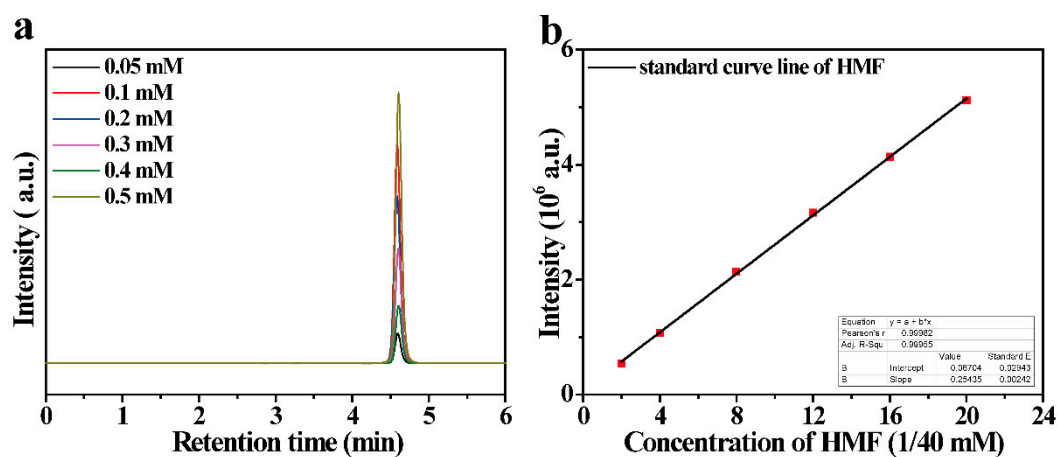


Figure S12. Measurements of HMF by HPLC and corresponding standard curve.

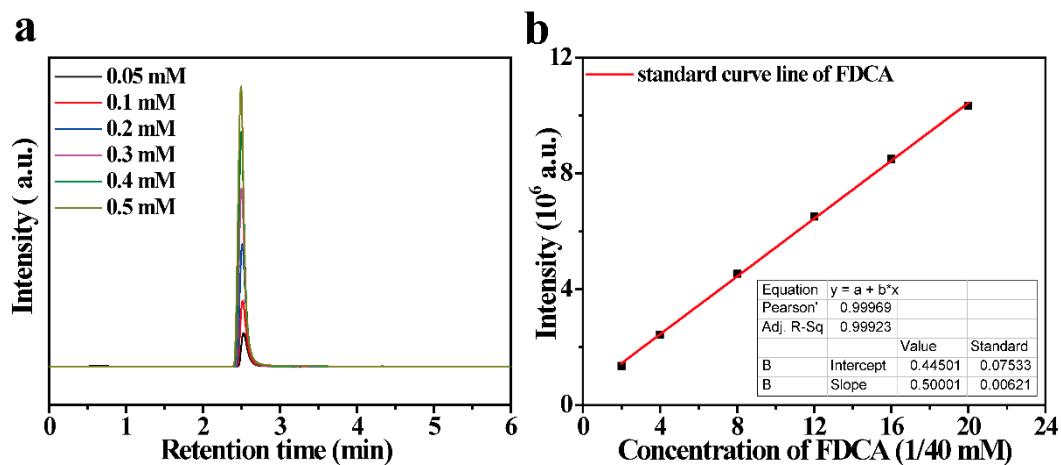


Figure S13. Measurements of FDCA by HPLC and corresponding standard curve.

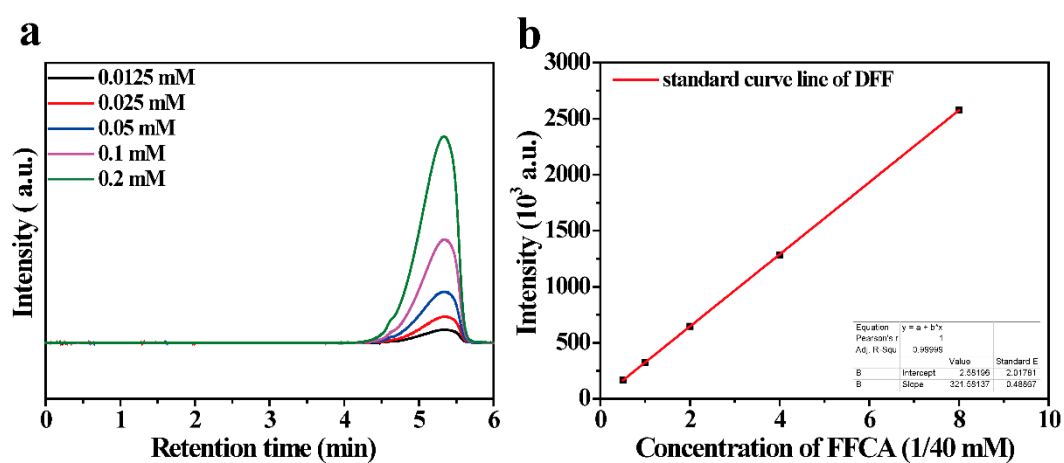


Figure S14. Measurements of DFF by HPLC and corresponding standard curve.

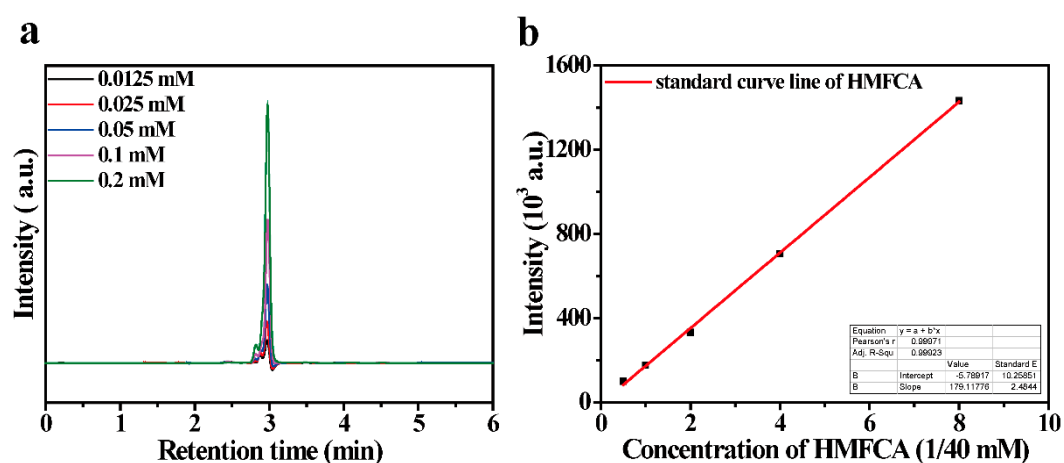


Figure S15. Measurements of HMFA by HPLC and corresponding standard curve.

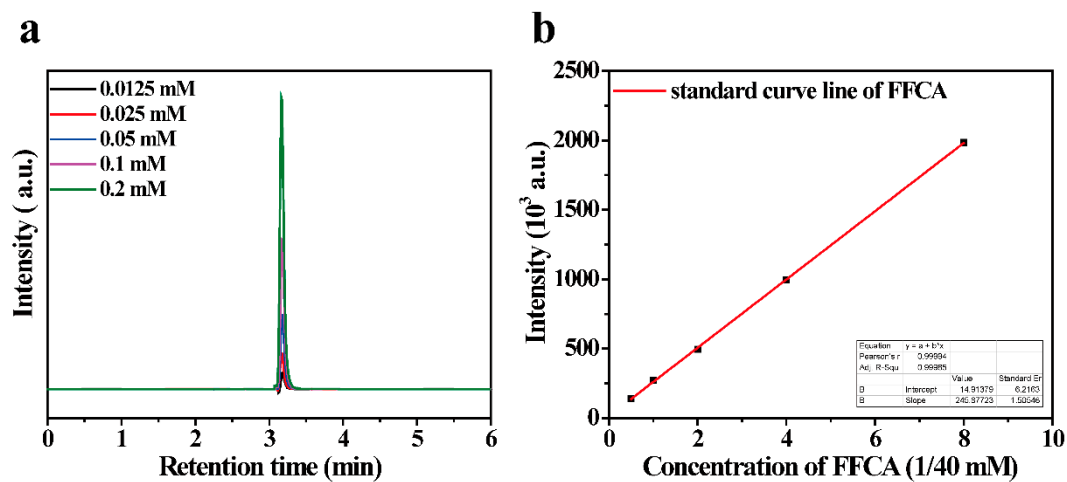


Figure S16. Measurements of FFCA by HPLC and corresponding standard curve.

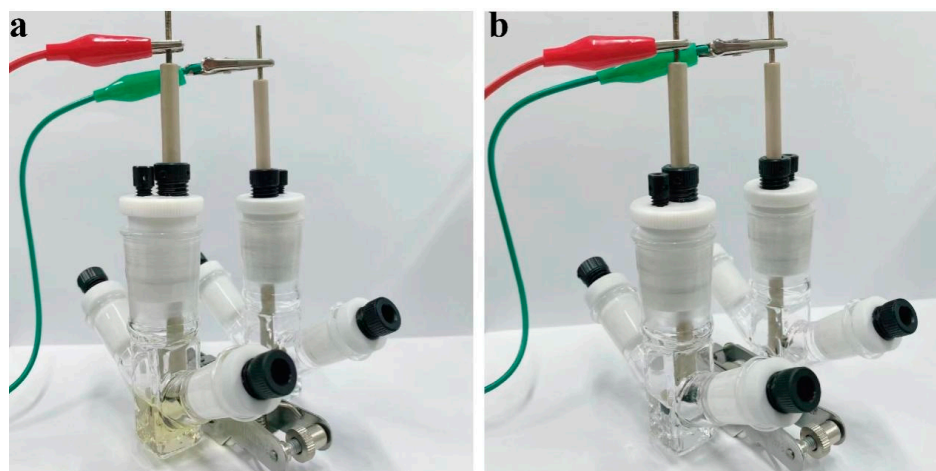


Figure S17. The photographs of H-type cell (the right side: HMFEOR cell and the left side: HER cell) before (a) and after (b) HMFEOR (Charge: 58 C, a potential of 1.37 V vs. RHE for 2.4 h).

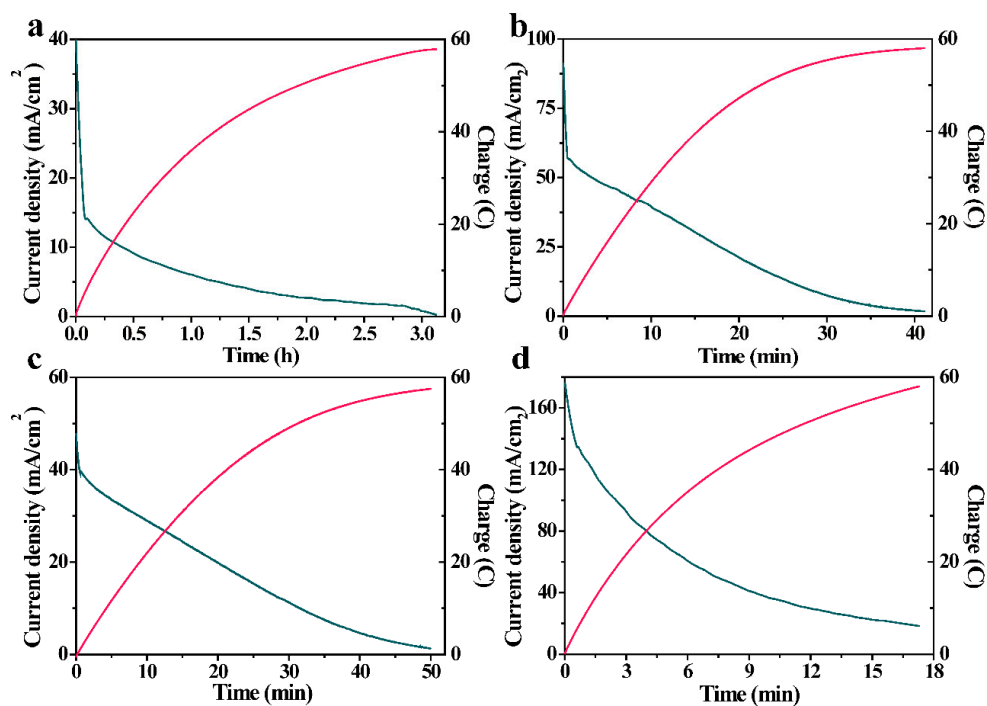


Figure S18. I-t curve for CoO-Co@C/CF at various constant potential in 1.0 M KOH with 10 mM HMF by passing the charge of 58 C, the constant potential is 1.34 V vs. RHE (a), 1.42 V vs. RHE (b), 1.47 V vs. RHE (c), 1.52 V vs. RHE (d), respectively.

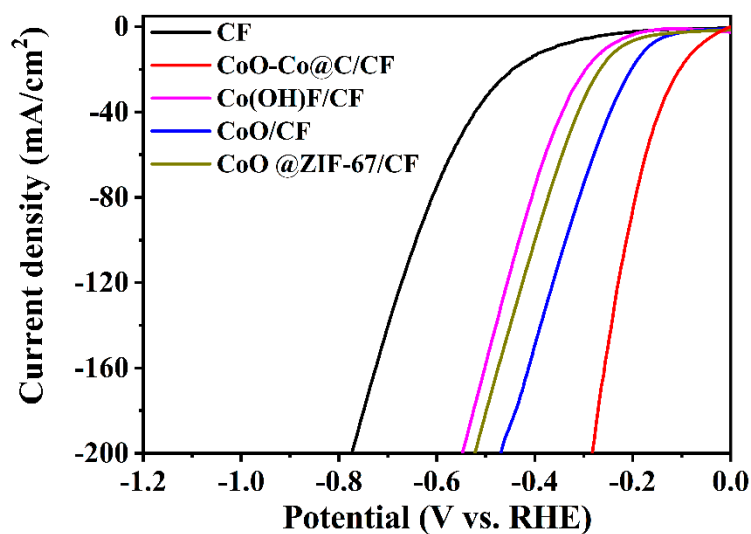


Figure S19. *iR*-compensated polarization curves of HER over CoO-Co@C/CF, CF, Co(OH)F/CF, CoO/CF, and CoO@ZIF-67/CF in 1.0 M KOH at a scan rate of 5 mV·s⁻¹.

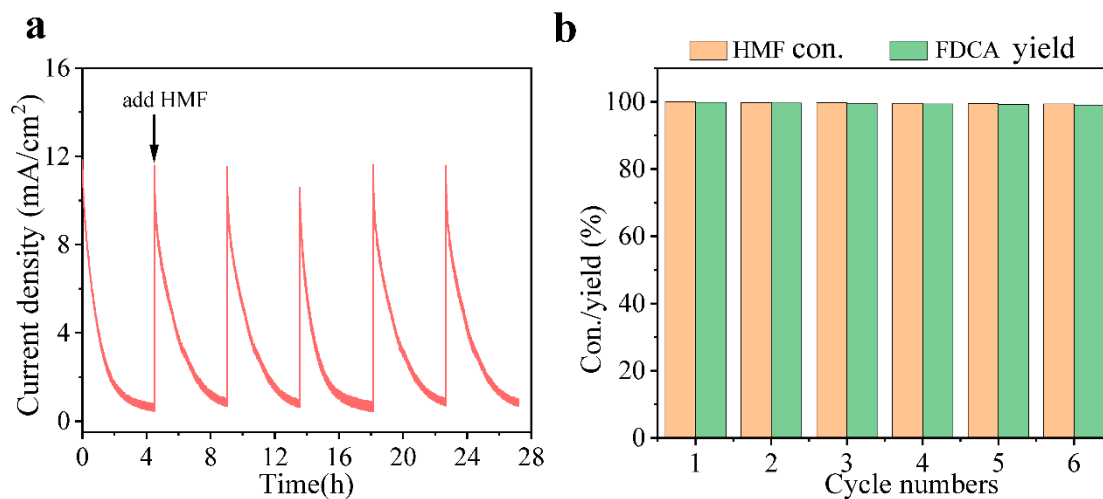


Figure S20. The stability test of CoO-Co@C/CF || CoO-Co@C/CF system in 1.0 M KOH with the intermittent addition of 10 mM HMF at voltage of 1.45 V, I-t curves of 6 cycles (a) and the corresponding HMF conversion and FDCA yield (b).

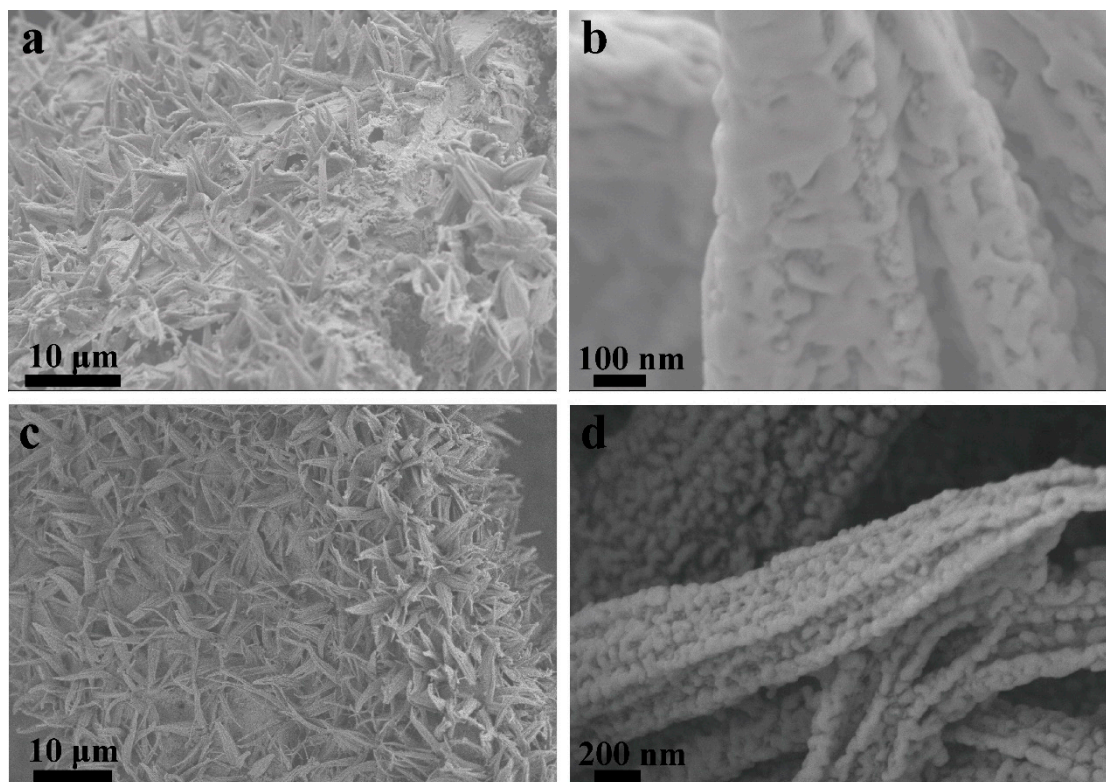


Figure S21. SEM images of CoO-Co@C/CF after HMFEOR (a-b) and HER (c-d).

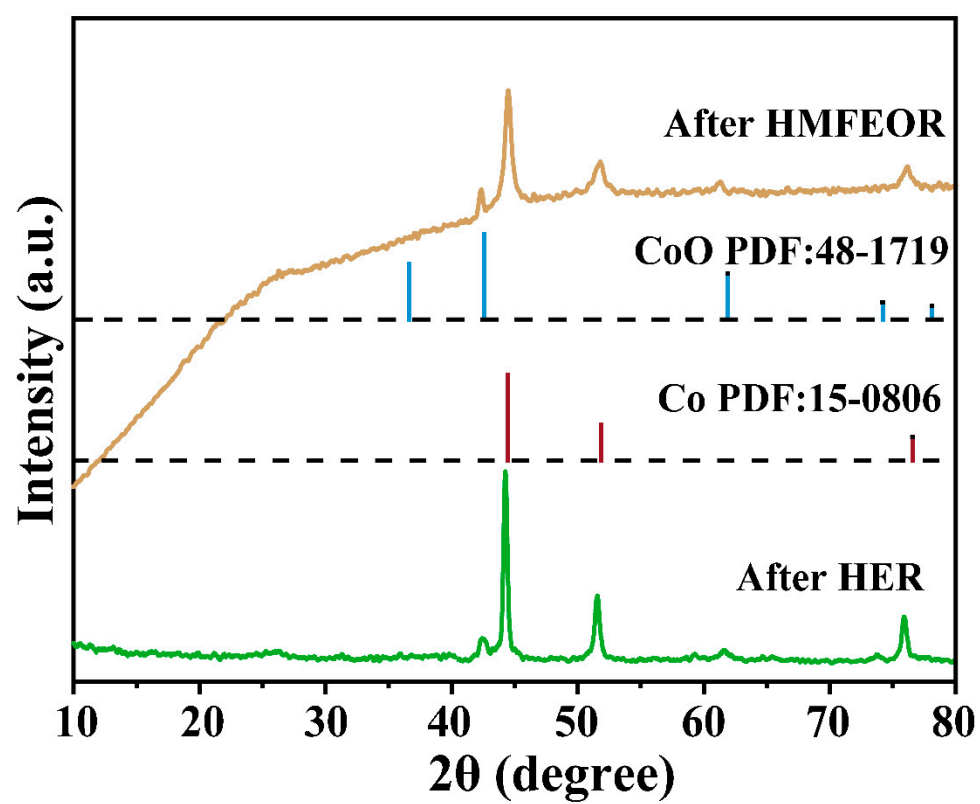


Figure S22. XRD patterns of CoO-Co@C/CF after HMFEOR and HER.

Table S1. Parameters obtained by fitting the Nyquist plots of CoO-Co@C/CF, CoO@C/CF and Co@C/CF measured in 1.0 M KOH with 10 mM HMF based on **Figure S9**.

Catalyst	R_{ct} (Ω)	
	HMFEOR (1.34 V vs. RHE)	HER (80 mV vs. RHE)
Co@C/CF	5.13	5.2
CoO@C/CF	39.7	38.3
Co-CoO@C/CF	58.1	26.4

Table S2. Comparison of HMFEOR performance for CoO-Co@C/CF with recently reported electrocatalysts.

Catalysts	Oxidation potential (V)	Conversion (%)	Selectivity (%)	FE (%)	Reference
NiCo ₂ O ₄ /NF	1.36 (onset)	99.6	90.8	80	[50]
NiCo ₂ O ₄	1.50 (20 mA/cm ²)	90.8	90.8	87.5	[50]
CoNW/NF	1.311 (10 mA/cm ²)	100	96.82	/	[51]
CuNi(OH) ₂	1.45 (4.6 mA/cm ²)	>99	93.3	93	[52]
Ni(OH) ₂ /NiOOH	1.34 (onset)	99.8	96.0	96.0	[53]
NiSe@NiOx	1.35 (onset)	99	98	98	[54]
Ni ₃ N@C	1.36 (20 mA/cm ²)	/	98	99	[55]
CoNiFe LDH	1.55 (20 mA/cm ²)	84.9	84.9	90	[21]
NiS _x /Ni ₂ P	1.346 (20 mA/cm ²)	98.5	98.5	95.1	[56]
Co ₉ S ₈ -Ni ₃ S ₂ @NSOC	1.330 (10 mA/cm ²)	99.5	98.8	98.6	[57]
om-Co ₃ O ₄	1.45 (20 mA/cm ²)	>99.8	>99.8	>99.8	[58]
NiCo ₂ O ₄ -CFP	1.43 (50 mA/cm ²)	98.4	94.3	89.6	[59]
Cu _{0.5} Co _{2.5} O ₄	1.55 (20 mA/cm ²)	90	93	91	[60]
CoO@C/CF	1.37 (10 mA/cm ²)	90	84	82	This work
Co@C/CF	1.38 (10 mA/cm ²)	80	74	72	This work
CoO-Co@C/CF	1.34 (10 mA/cm ²)	100	99.4	99.4	This work

Table S3. Comparison of the HER performance for CoO-Co@C/CF with recently reported Co-based electrocatalysts in 1 M KOH electrolyte.

Catalysts	Potential (mV) at 10 mA cm ⁻²	Reference
CoOx@CN	232	[61]
CoO@Co/N-rGO	237	[62]
Co@NG	200	[62]
Co@CFNG@NF	212	[63]
Co@NC/CFP	178	[64]
Co@N-CS/N-HCP@CC	66	[65]
CoNi@NC	142	[66]
CoNi@NC-NCNTs	85	[67]
Co@NC/CNT	203	[68]
Co/CoO@NC@CC	152	[69]
Cu _{0.5} Co _{2.5} O ₄	103	[60]
CuCo ₂ O ₄	144	[60]
Co ₃ O ₄	180	[60]
Cu _x S@NiCo-LDH	107	[24]
Co ₃ O ₄ /NF	105	[70]
NiCo ₂ S ₄	345	[71]
CoNiBDC/CC	135	[72]
Co(OH) ₂ @P-NiCo-LDH	226	[73]
NiCo ₂ O ₄ /NiCoP	198	[74]
CoO@C/CF	190	This work
Co@C/CF	94	This work
CoO-Co@C/CF	69	This work

Table S4. Comparison of H₂O-HMF paired electrolysis on CoO-Co@C/CF with recently reported electrocatalysts in alkaline electrolyte.

Electrode Assembly	Anodic Reaction	Cell performance	Reference
Ni ₃ S ₂ /NF Ni ₃ S ₂ /NF	HMF oxidation	1.58 V (50 mA/cm ²) 1.64 V (100 mA/cm ²)	[41]
Ni ₂ P/NF Ni ₂ P/NF	HMF oxidation	1.5 V (50 mA/cm ²) 1.63 V (100 mA/cm ²)	[17]
NC@CuCo ₂ N _x /CF NC@CuCo ₂ N _x /CF	Benzyl Alcohol	1.56 V (10 mA/cm ²)	[75]
NiMoO-Ar/NF NiMoO-H ₂ /NF	Urea oxidation	1.48 V (50 mA/cm ²) 1.55 V (100 mA/cm ²)	[76]
NiSe/NF CoP	Amine oxidation	1.44 V (10 mA/cm ²)	[77]
Co(OH)F/NF CoP/NF	Urea oxidation	1.42 V (20 mA/cm ²)	[78]
CoNW/NF CoNW/NF	HMF oxidation	1.504 V (10 mA/cm ²)	[51]
Ni _{0.33} Co _{0.67} (OH) ₂ /NF Ni _{0.33} Co _{0.67} (OH) ₂ /NF	Methanol oxidation	1.65 V (50 mA/cm ²) 1.75 V (100 mA/cm ²)	[79]
Cu _x S@Ni _{0.75} Co _{0.25} OmHn Cu _x S@Ni _{0.75} Co _{0.25} OmHn	HMF oxidation	1.49 V (50 mA/cm ²) 1.58 V (100 mA/cm ²)	[24]
MoO ₂ -FeP@C MoO ₂ -FeP@C	HMF oxidation	1.486 V (10 mA/cm ²)	[80]
CoO@C/CF	HMF oxidation	1.502 V (10 mA/cm ²)	This work
Co@C/CF	HMF oxidation	1.552 V (10 mA/cm ²)	This work
CoO-Co@C/CF	HMF oxidation	1.448 V (10 mA/cm ²)	This work

Reference

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