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Supporting Information

Hierarchical Co@C-N synthesized by confined pyrolysis of ionic liquid@metal-organic framework for aerobic oxidation of alcohols

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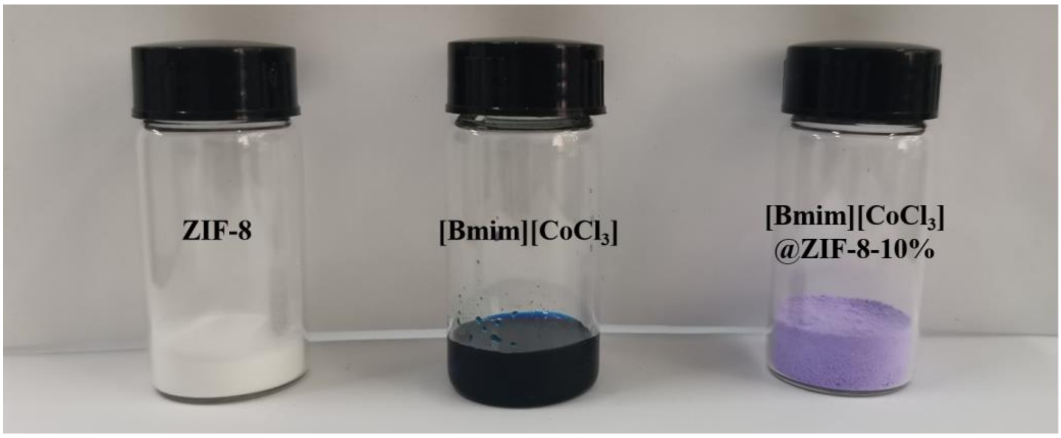


Figure S1. The photographs of ZIF-8, [Bmim][$CoCl_3$], and [Bmim][$CoCl_3$]@ZIF-8-10%.

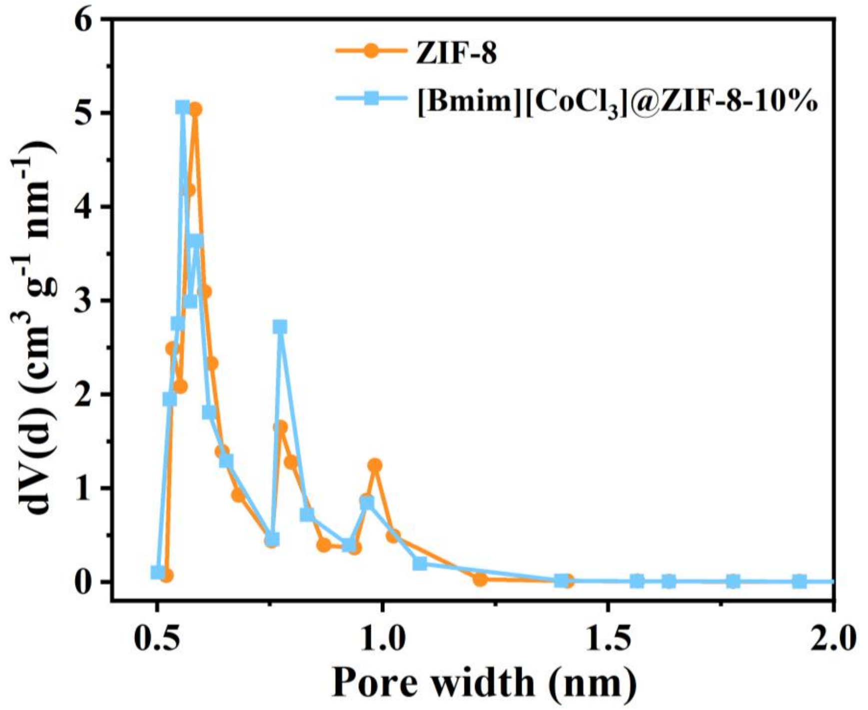


Figure S2. Pore size distributions of ZIF-8 and [Bmim][$CoCl_3$]@ZIF-8-10%.

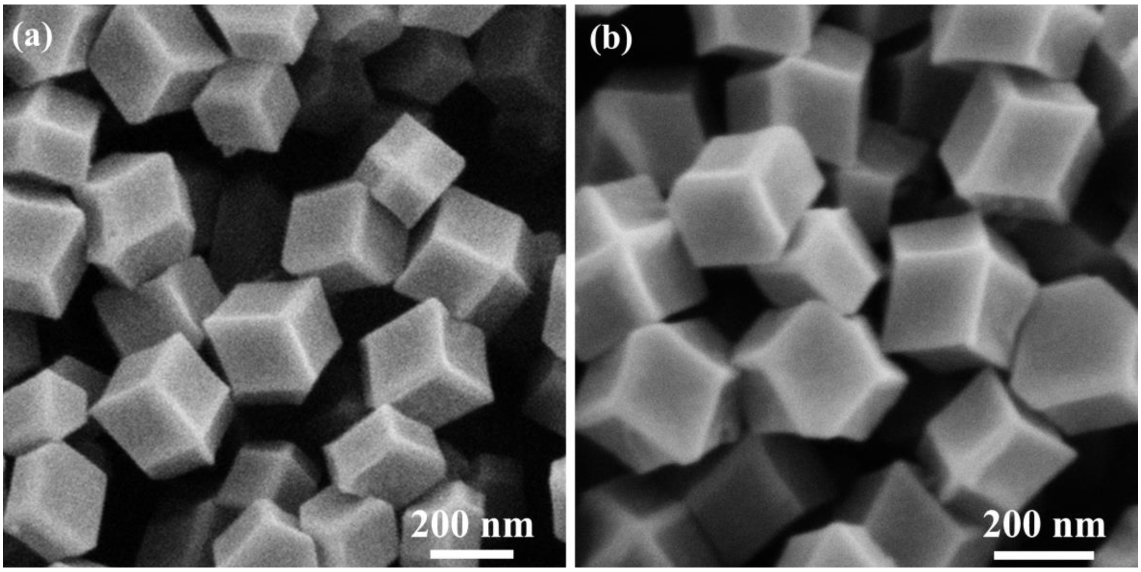


Figure S3. SEM images of ZIF-8 (a) and [Bmim][$CoCl_3$]@ZIF-8-10% (b).

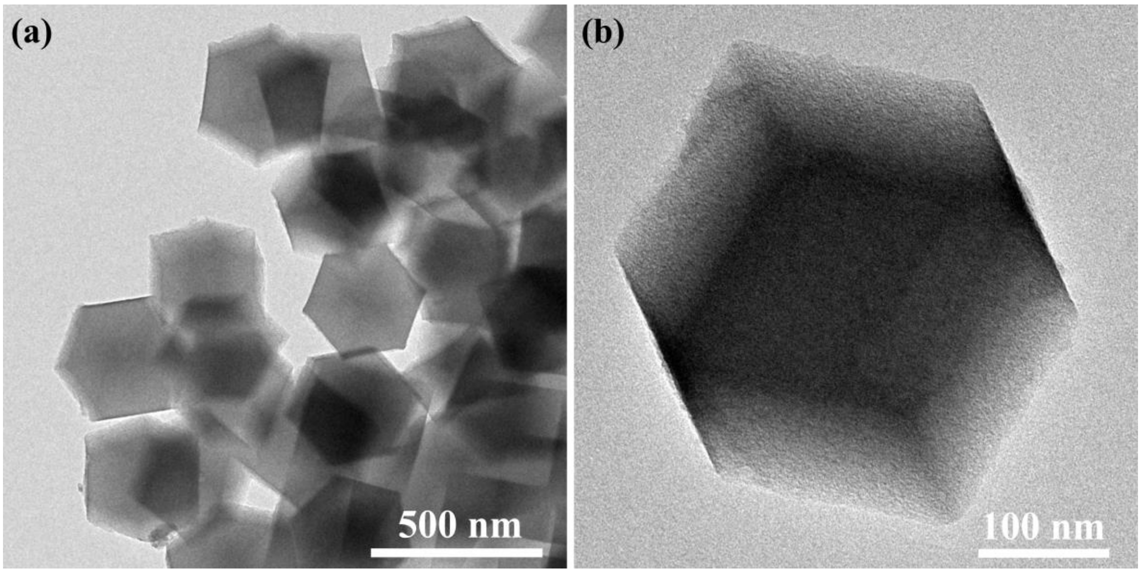


Figure S4. TEM images of C-N-900.

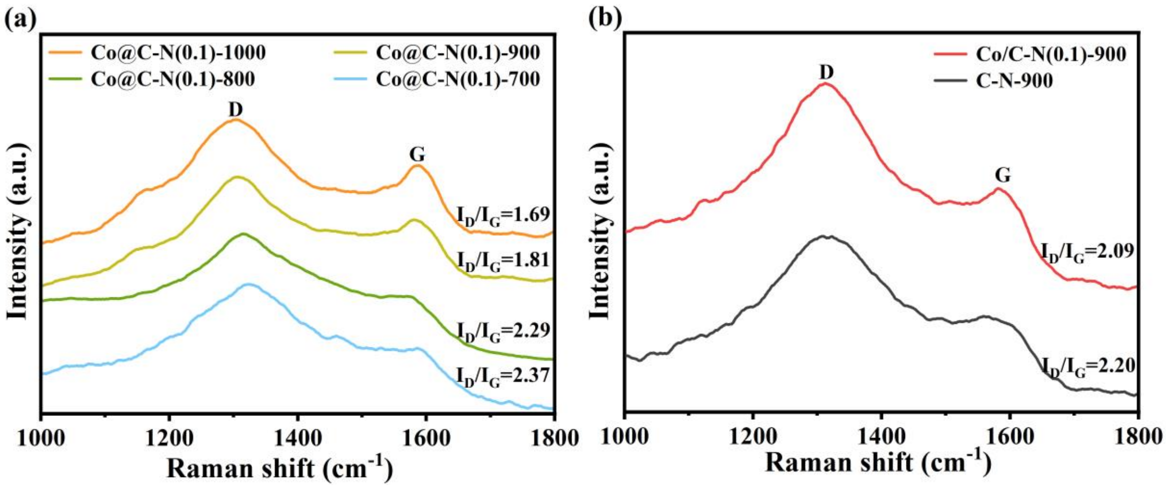


Figure S5. Raman spectra of Co@C-N(0.1)-T, C-N-900, and Co/C-N(0.1)-900.

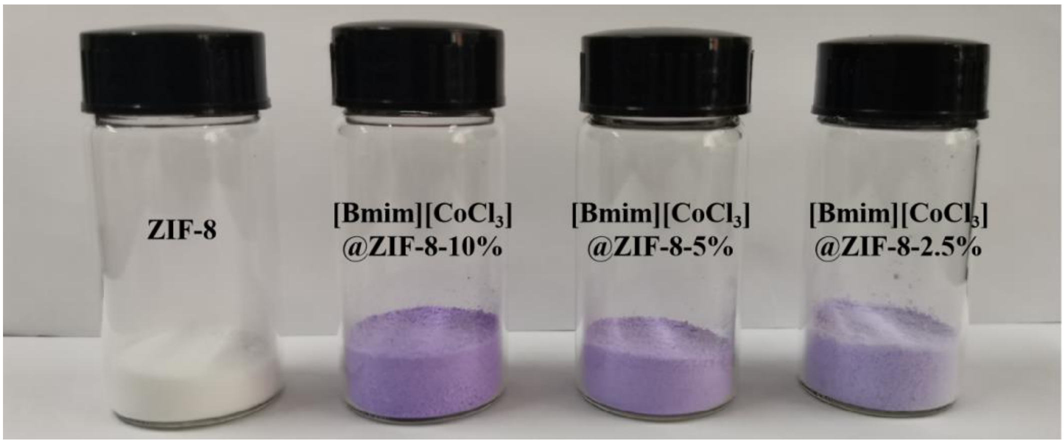


Figure S6. The photographs of the as-prepared ZIF-8 and [Bmim][$CoCl_3$]@ZIF-8-x materials in this work.

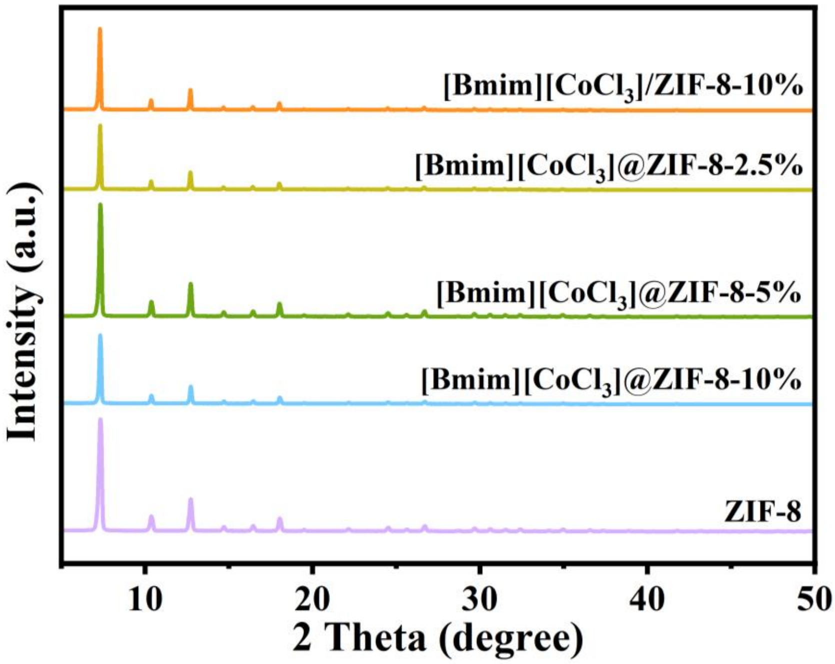


Figure S7. XRD patterns of ZIF-8, [Bmim][$CoCl_3$]@ZIF-8-x, and [Bmim][$CoCl_3$]/ZIF-8-10%.

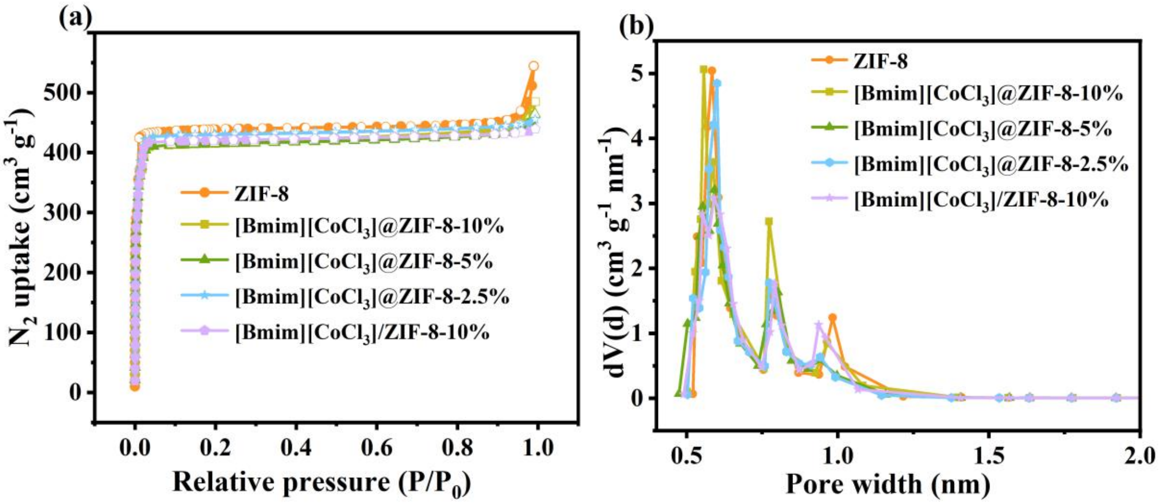


Figure S8. (a) N_2 adsorption isotherms and (b) pore size distributions of ZIF-8, [Bmim][$CoCl_3$]@ZIF-8-x, and [Bmim][$CoCl_3$]/ZIF-8-10%.

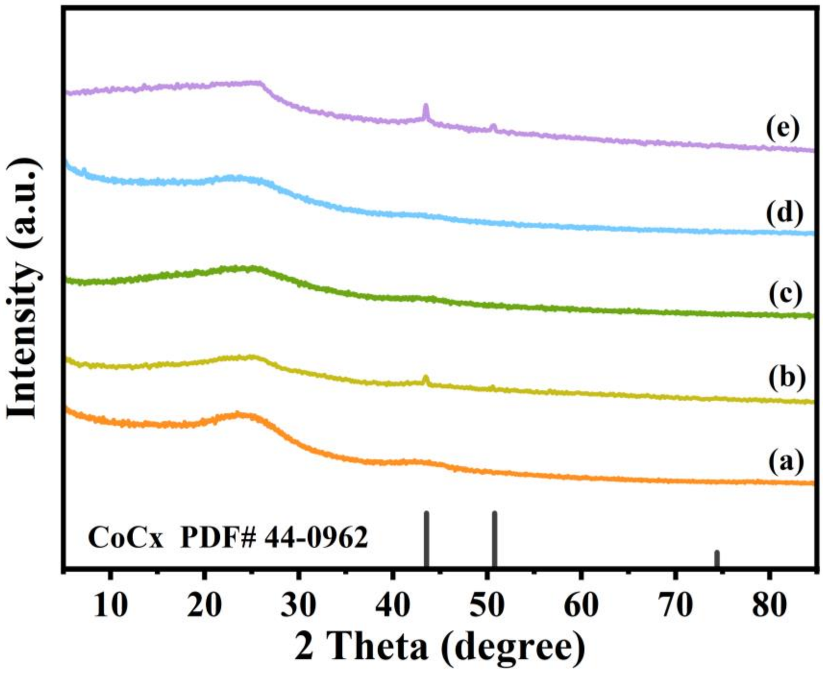


Figure S9. XRD patterns of (a) C-N-900, (b) Co@C-N(0.1)-900, (c) Co@C-N(0.05)-900, (d) Co@C-N(0.025)-900, and (e) Co/C-N(0.1)-900.

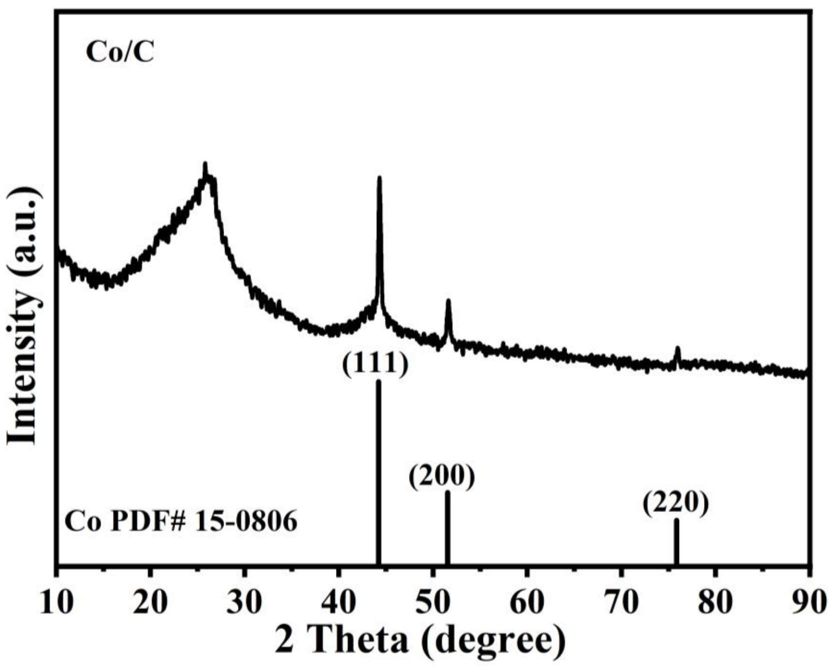


Figure S10. XRD patterns of Co/C.

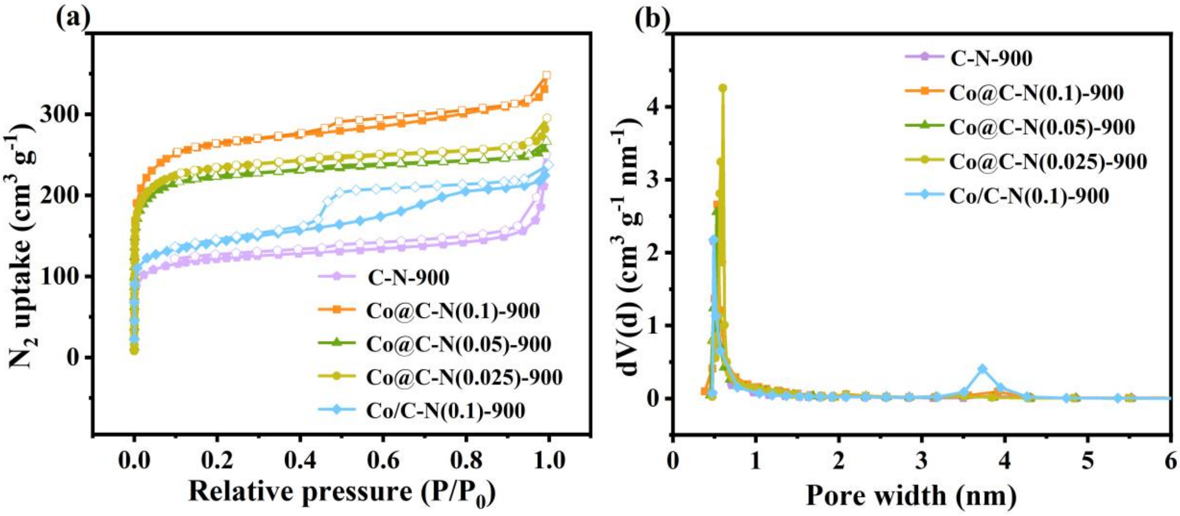


Figure S11. (a) N_2 adsorption isotherms and (b) pore size distributions of C-N-900, Co@C-N(x)-900, and Co/C-N(0.1)-900.

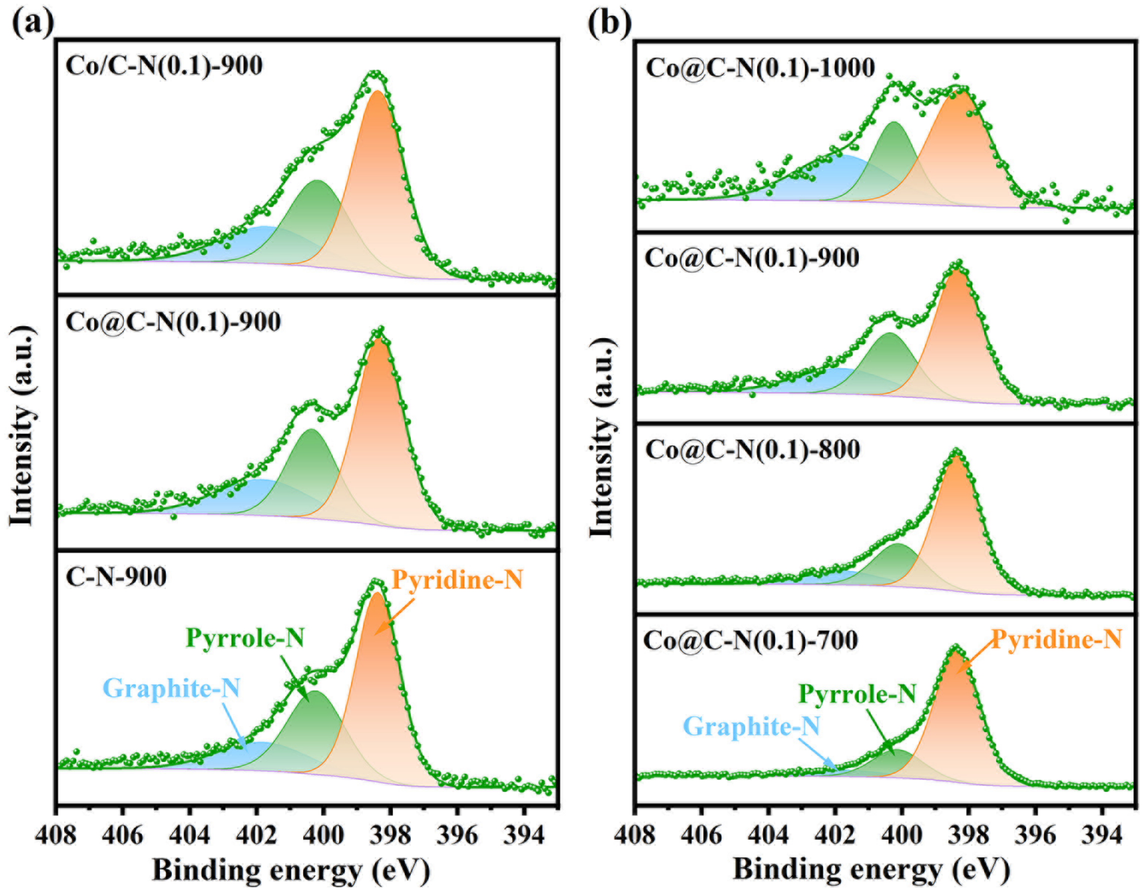


Figure S12. N 1s XPS spectra of C-N-900, Co@C-N(0.1)-T, and Co/C-N(0.1)-900.

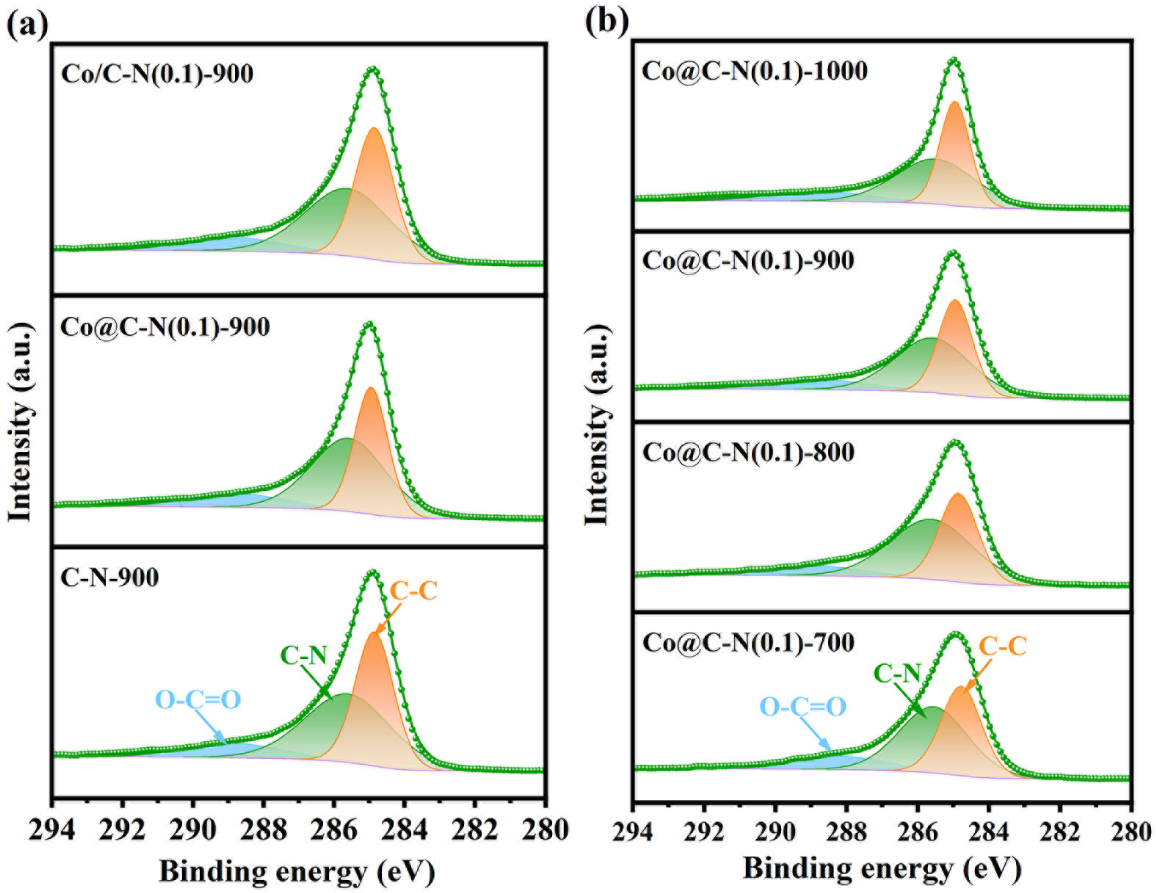


Figure S13. C 1s XPS spectra of C-N-900, Co@C-N(0.1)-T, and Co/C-N(0.1)-900.

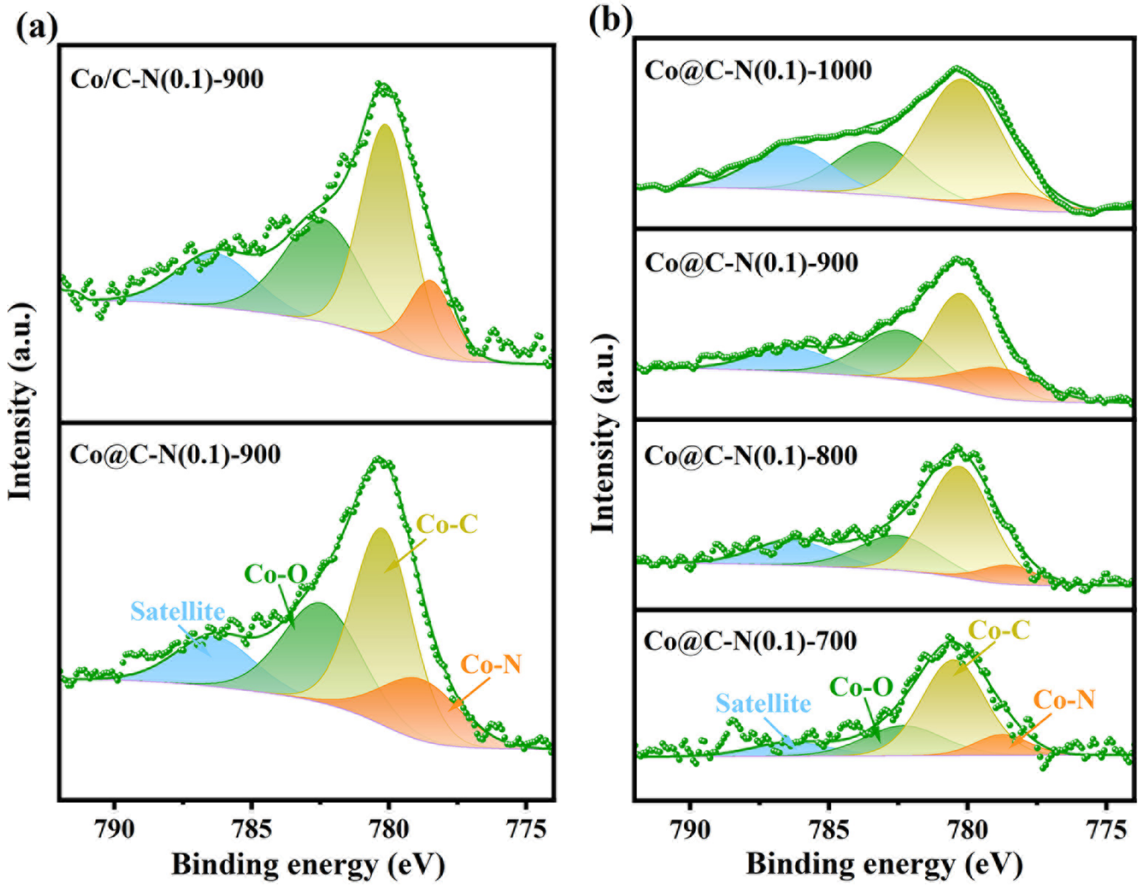


Figure S14. Co $2p_{3/2}$ XPS spectra of Co@C-N(0.1)-T and Co/C-N(0.1)-900.

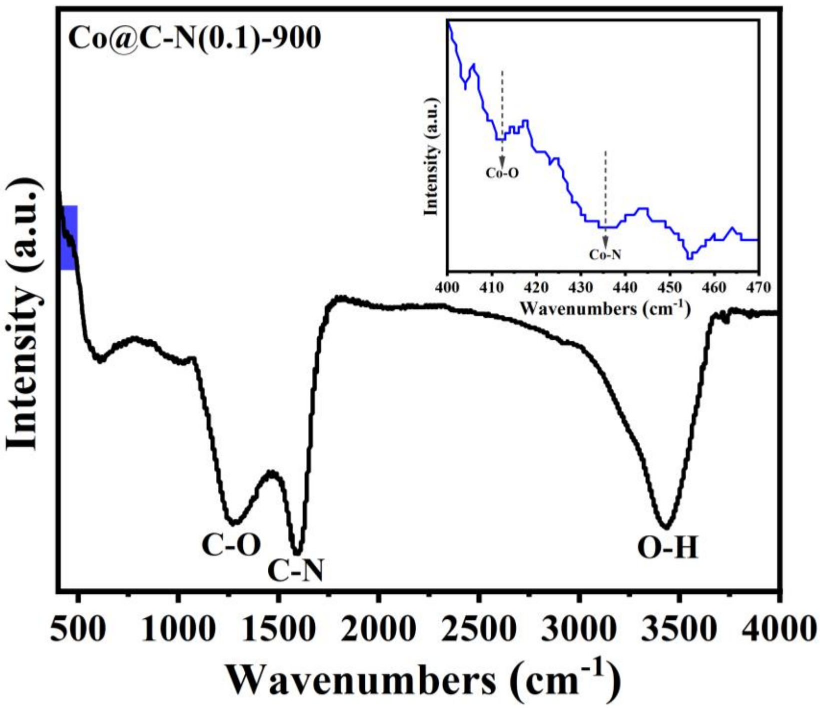


Figure S15. FTIR spectrum of Co@C-N(0.1)-900.

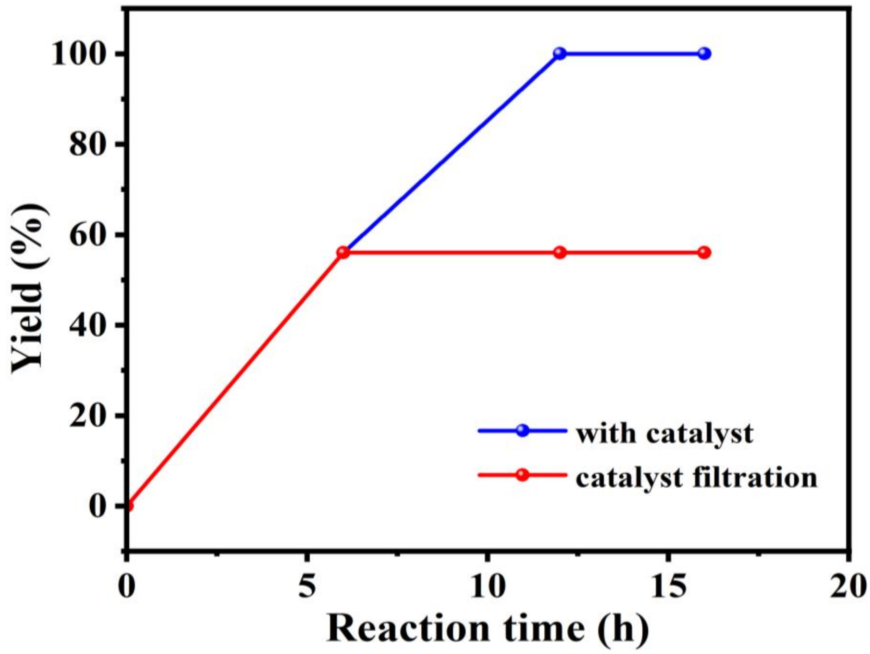


Figure S16. Heterogeneity test of Co@C-N(0.1)-900 for the oxidation of benzyl alcohol.

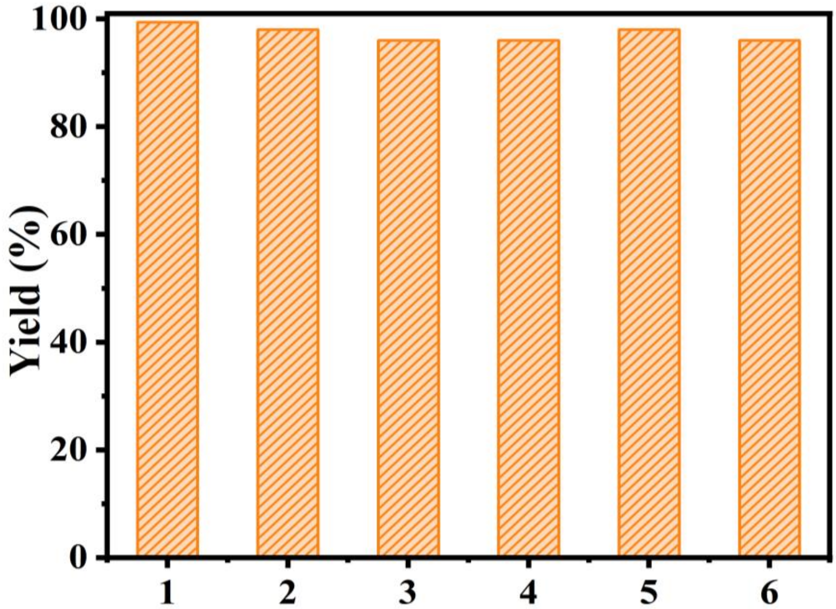


Figure S17. Reusability of Co@C-N(0.1)-900 in the aerobic oxidation of benzyl alcohol.

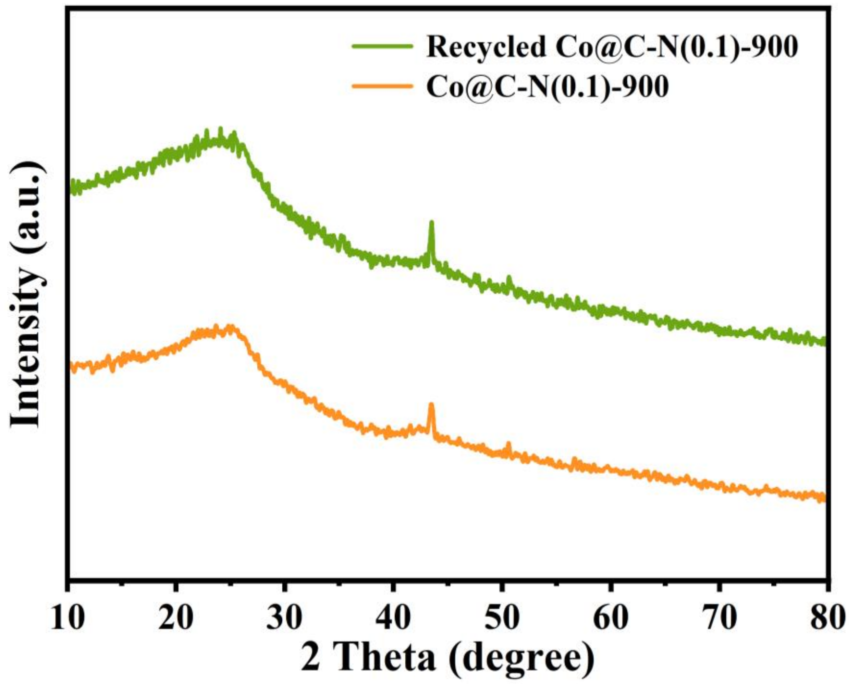


Figure S18. XRD patterns of Co@C-N(0.1)-900 and recycled Co@C-N(0.1)-900.

Table S1. Surface areas and pore volumes of the samples.

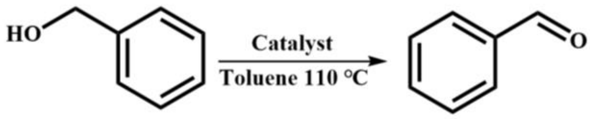
Samples	S_{BET} (m^2 g^{-1})	$S_{Langmuir}$ (m^2 g^{-1})	V_{pore} (cm^3 g^{-1})
ZIF-8	1424	1922	0.75
[Bmim][$CoCl_3$]@ZIF-8-10%	1213	1798	0.73
[Bmim][$CoCl_3$]@ZIF-8-5%	1246	1801	0.71
[Bmim][$CoCl_3$]@ZIF-8-2.5%	1287	1874	0.70
[Bmim][$CoCl_3$]/ZIF-8-10%	1219	1842	0.68
Co@C-N(0.1)-700	353	524	0.37
Co@C-N(0.1)-800	536	785	0.34
Co@C-N(0.1)-900	824	1202	0.52
Co@C-N(0.1)-1000	480	719	0.43
C-N-900	381	564	0.36
Co@C-N(0.05)-900	698	1009	0.40
Co@C-N(0.025)-900	731	1066	0.44
Co/C-N(0.1)-900	454	680	0.35

Table S2. Co content of samples.

Samples	Content (wt%)[a]
Co@C-N(0.1)-700	1.8
Co@C-N(0.1)-800	3.9
Co@C-N(0.1)-900	4.1
Co@C-N(0.1)-1000	5.5
Co@C-N(0.05)-900	1.2
Co@C-N(0.025)-900	0.7

[a] Measured by ICP-OES.

Table S3. Oxidation of benzyl alcohol catalyzed by various catalysts[a].



Entry	Catalysts	$Co-N_x$ content (%)[b]	Yield (%)[c]
1	-	-	0
2	C-N-900	-	47
3	Co@C-N(0.1)-700	10.6	45
4	Co@C-N(0.1)-800	8.4	81
5	Co@C-N(0.1)-900	27.7	**>99**
6	Co@C-N(0.1)-1000	20.6	68
7	Co/C-N(0.1)-900	12.6	70

[a] Reaction conditions: benzyl alcohol (0.1 mmol), catalyst (10.5 mmol % Co), toluene (1 mL), air, 110 °C and 12 h.

[b] Measured by XPS.

[c] Yield was determined by GC-FID.

Table S4. Comparison of reaction results in oxidation of benzyl alcohol to benzaldehyde over different catalysts.

Entry	Reaction conditions	Conv. (%)	Sel. (%)	Ref.
1	Co-N-C/700, O_2, toluene, 100 °C, 36 h	92	100	New J. Chem., 2018, 42, 15871.
2	Co@C-N(1)-800, air, water, 110 °C, 4 h	>99	>99	ACS Catal., 2018, 8, 1417.
3	Co/C-N700, air, water, 110 °C, 65 h	92	99	Green Chem., 2016, 18, 1061.
4	Co@NC (800-2h), O_2, EtOH, 80 °C, 30 h	99	96	RSC Adv., 2017, 7, 1498.
5	Fe-N-C, O_2, water, 80 °C, 8 h	77	90	ChemSusChem, 2017, 10, 359-362.
6	Co-NG-750, O_2, DMF, 130 °C, 5 h	95	92	Appl. Catal. A, 2017, 543, 61-66.
7	Cu(bdc)(ted)$_{0.5}$, O_2, DMF, 90 °C, 8 h	82	82	RSC Adv., 2016, 6, 72433.
8	Pd_3Cl/TNT, O_2, toluene, 30 °C, 26 h	99	100	Adv. Synth. Catal., 2018, 360, 4731- 4743.
9	Co@C-N(0.1)-900, air, toulene, 110 °C, 12 h	>99	>99	**This work**