Supplementary Information (SI) for New Journal of Chemistry.

Construction of N-doped hierarchically porous carbon catalysts with CoFe alloy via spatial and chemical anchor confinement for oxygen catalytic reaction

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Table S1 the ICP-OES results of FeCo@CN catalyst

Samples	**Co@NC**	**$Fe_{0.21}Co_{1}$@NC**	**$Fe_{0.46}Co_{1}$@NC**	**$Fe_{1.30}Co_{1}$@NC**	**Fe@NC**
Weight ratio of ZIF-67/FePc-NH_2 in precursors	100:0	75:25	1:1	25:75	0:100
Co wt%	14.82	12.63	3.78	1.72	0
Fe wt%	0	2.63	1.76	2.24	2.89
Fe/Co ratio	/	0.21:1	0.46:1	1.30:1	/

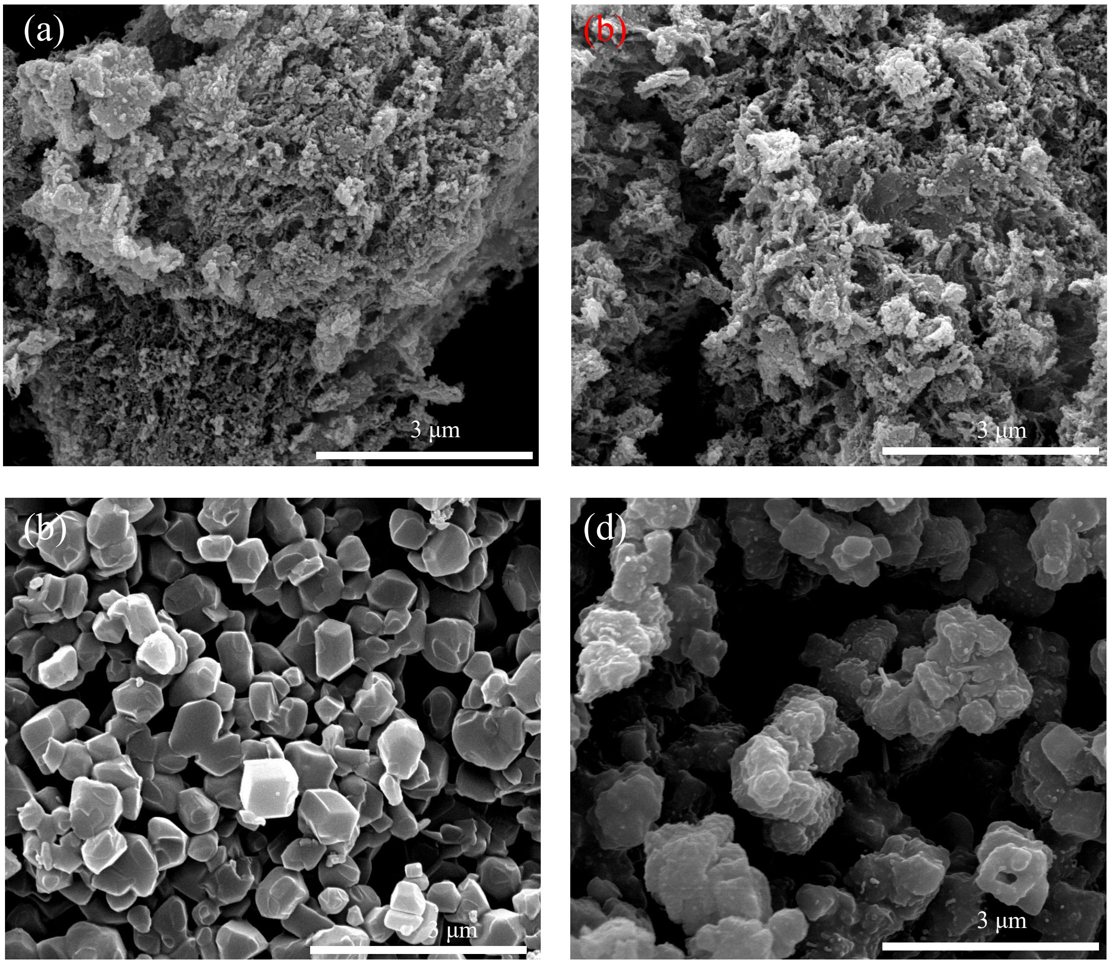

Figure S1. The SEM images of as-prepared catalysts (a) $Fe_{0.21}Co_1$@NC, (b)$Fe_{0.46}Co_1$@NC, (c)ZIF-67 and (d) Co@NC.

Table S2 Summary of the key performance indicators, including, E_{onset}(defined the potential at the 5% of J_L), $E_{1/2}$, and J_L, of prepared samples.

Samples	**E_{onset} (vs. RHE)**	**$E_{1/2}$ (vs. RHE)**	**J_L (mA cm^{-2})**	**OER $E_{J=10\ mA/cm2}$ (vs. RHE)**
Co@NC	0.90	0.81	5.37	1.70
$Fe_{0.21}Co_1$@NC	0.97	0.84	5.71	1.67
$Fe_{0.46}Co_1$@NC	1.04	0.86	5.68	1.62
$Fe_{1.30}Co_1$@NC	1.08	0.87	5.39	1.69
Fe@NC	0.94	0.84	5.91	1.70

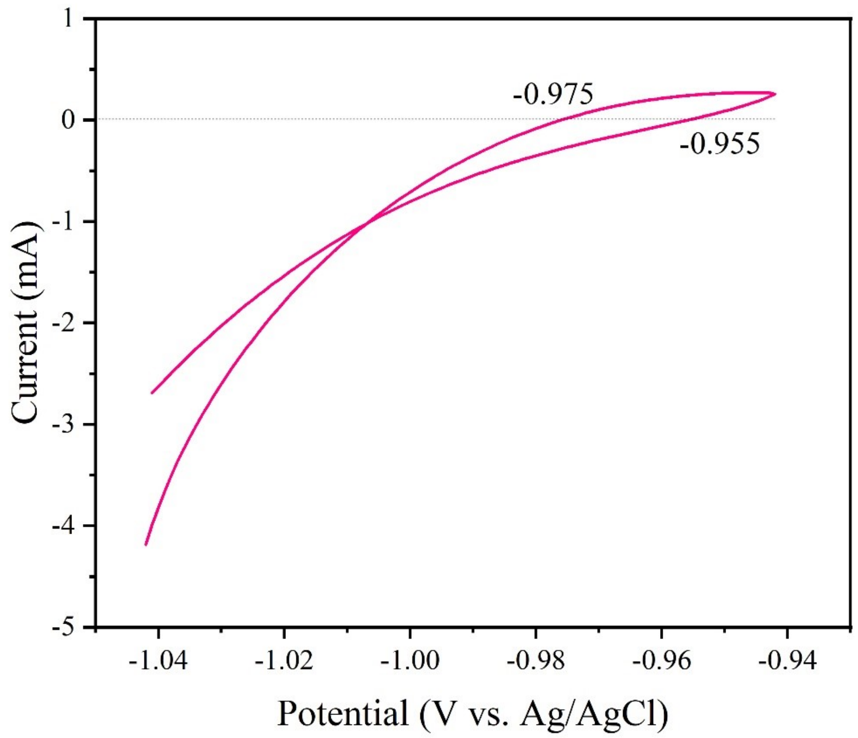

Fig.S1 (a) the CV curves of Ag/AgCl electrode calibration in 0.1M KOH.

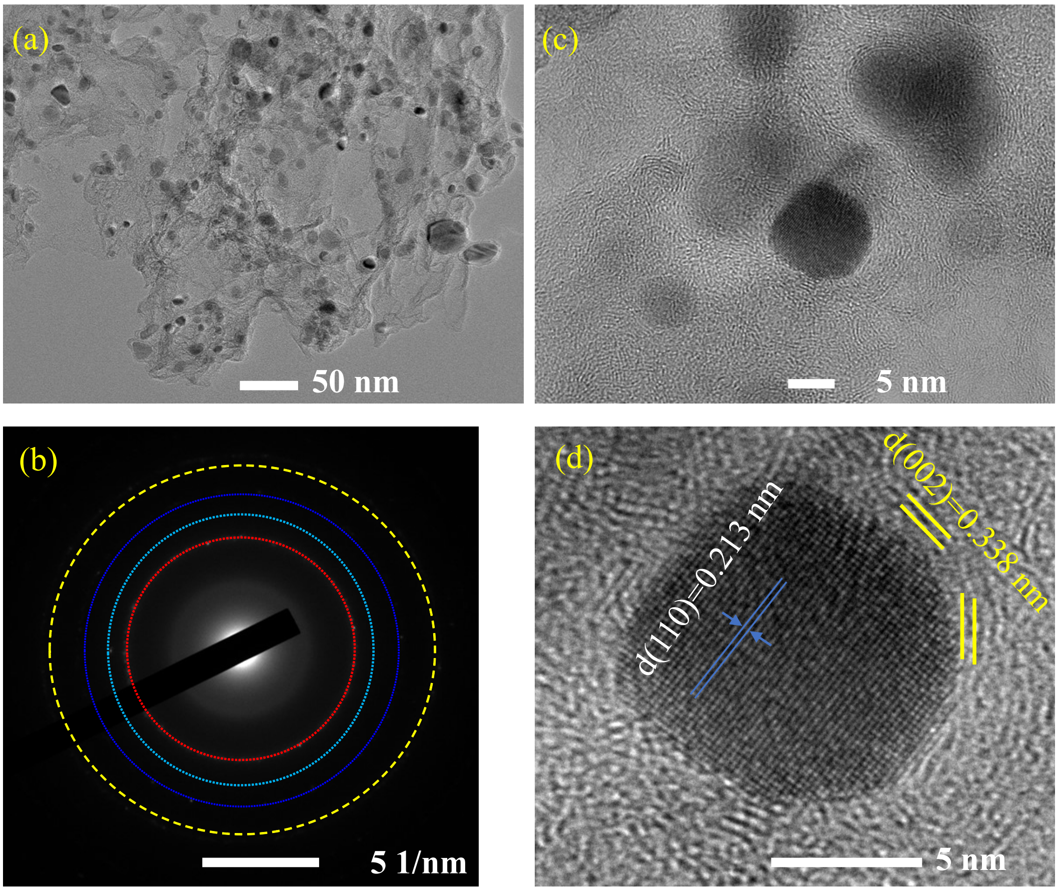

Fig.S2 (a) TEM image of $Fe_{0.46}Co_1$@NC. (b) SEAD pattern of $Fe_{0.46}Co_1$@NC, (c) and (d) High-resolution TEM images of $Fe_{0.46}Co_1$@NC. The catalyst of $Fe_{0.46}Co_1$@NC was subjected a 3000 cycles of CV testing before TEM test.

The catalyst $Fe_{0.43}Co_1$@NC, after 3000 cycles of CV testing, was characterized by HR-TEM. The results revealed that the metal alloy nanoparticles were uniformly dispersed on the porous carbon support, with the majority of the metal nanoparticles ranging in size from 10 to 20 nm. SAED patterns showed diffraction rings corresponding to the (002), (110), (200), and (211) crystal planes. Further magnification of the TEM images revealed distinct lattice fringes within the metal nanoparticles, with an interplanar spacing of 0.213 nm, corresponding to the (110) plane of the FeCo alloy. Additionally, lattice fringes with a spacing of 0.338 nm were observed at the periphery, attributed to the (002) plane of graphitic carbon. The results indicate that after prolonged ORR testing, no significant changes were observed in the structural composition of the catalyst, demonstrating its excellent structural stability

Table S3. The comparison of $E_{1/2}$ and potential of OER at 10 mA cm^{-2} of $Fe_{0.43}Co_1$@NC with reported transition-metal-based bifunctional oxygen catalysts.

Catalysts	**ORR**		**OER**	**Ref.**
	$E_{1/2}$ (V vs. RHE)	J_L (mA/cm^2)*	$E_{J=10\ mA/cm2}$ (V)	
$Fe_{0.43}Co_1$@NC	0.84	5.8	1.62	This work
RuCoOx@Co/N-CNT	0.79	6.2	1.58	J. Mater. Chem. A, 2020, 8, 1229-1237[1]
Mn_3O_4@CS/CP	0.80	4.78	1.52	Chemelectrochem, 2019, 6, 359-368[2]
Co@NCNT	0.85	4.70	1.55	J. Mater. Chem. A, 2018, 6, 15523-15529[3]
FeCo-NPC-1100	0.79	4.90	1.60	J. Mater. Chem. A, 2019, 7, 19355-19363[4]
FeNi-NC	0.83	4.84	1.61	Energy Storage Materials, 2018, 12, 277-283[5]
ZIF-67@NPC-2	0.82	4.94	1.64	Appl. Catal. B 2017, 205, 55–67[6]
Fe@N-C-700	0.83	6.15	1.71	Nano Energy 2015, 13, 387 –396[7]
3D Co-N-C NN-800	0.9	6.3	1.7	ACS Appl. Energy Mater. 2018, 1, 1060–1068[8]
Fe/Co-N/Sx-C	0.836	5.44	1.53	Inorg. Chem. Front., 2023, 10, 1826[9]
$Co/Co_2N_{0.67}$	0.878	5.02	1.56	J. Colloid Interface Sci, 2026, 702, 138938.[10]
CoNi-NCNT	0.81	4.58	1.52	J. Colloid Interface Sci., 2025, 683, 631-640[11]
$Co\text{-}ZIF_{1.5}/10CNF_2$	0.85	3.65	1.62	J. Colloid Interface Sci., 2023, 630, 140-149[12]
CoNi@GO	0.87	5.30	1.57	J. Alloys Compd. 2024, 971, 172735[13]
Fe/Ni@NSC	0.87	5.37	1.55	Fuel, 2026, 406, 137050[14]
VS-FeCo/Fe-CoS/NSC	0.85	5.87	1.56	J. Power Sources, 2025, 625, 235653.[15]
HNPC-900	0.85	6.3	1.62	Appl. Catal. B, 2023, 339, 123088[16]
$A\text{-}MnO_2$/NSPC-2	0.87	5.4	1.51	Adv. Mater.2024, 36(18),2312868[17]
CrFeCoNiCu	0.87	5.00	1.54	Colloids Surf. A Physicochem. Eng. Asp., 2025, 709, 136106[18]
CoOx@NC-800	0.89	5.18	1.59	ACS Appl. Mater. Interfaces. 2023, 15(33), 39448-39460[19]
Co_4N/PNC-920	0.86	6.05	1.58	Appl. Surf. Sci. 2025, 679, 161212[20]

FeCoNi@Mn_2AlO_4-850	0.79	5.2	0.77	J. Alloys Compd. 2024, 1004, 175802[21]

* Some of the data were estimated from figures in the literature, rather than from the exact values mentioned in the text.

Table S4. Summary of the Zn-air battery performance assembled by $Fe_{0.43}Co_1$@NC catalyst compared with other TMs-based catalysts.

Catalysts	OCP	Maximum power density (mW/cm^2)	Discharge-charge cycle life (hours)	Ref.
$Fe_{0.43}Co_1$@NC	1.46	168.4	65	This work
Co_9S_8/P@CS	1.34	69.75	350	Chem. Eng. J., 2020, 381, 122683[22]
Co@NCNT	1.48	159.8	150	J. Mater. Chem. A, 2018, 6, 15523-15529[3]
FeCo-NPC-1100	1.48	92	35	J. Mater. Chem. A, 2019, 7, 19355-19363[4]
FeNi-NC	0.83	/	23	Energy Storage Materials, 2018, 12, 277-283[5]
CoNi@GO	1.34	260	240	J. Alloys Compd. 2024, 971, 172735[13]
Fe/Ni@NSC	1.47	172.59	370	Fuel, 2026, 406, 137050[14]
VS-FeCo/Fe-CoS/NSC	1.63	164.68	120	J. Power Sources, 2025, 625, 235653.[15]
HNPC-900	1.37	120	300	Appl. Catal. B, 2023, 339, 123088[16]
A-MnO_2/NSPC-2	1.52	181	270	Adv. Mater.2024, 36(18), 2312868 [17]
CoOx@NC-800	1.46	121.09	200	ACS Appl. Mater. Interfaces. 2023, 15(33), 39448-39460[19]
Co_4N/PNC-920	1.46	170.7	260	Appl. Surf. Sci. 2025, 679, 161212[20]

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