Supporting Information

Selenium doped Co-Fe mixed metal oxide decorated on g-C₃N₄ and MXenes as

bifunctional Oxygen electrocatalyst for rechargeable Zn-Air battery

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Figure S1. Photographic images of (a) SgCN, (b) CF/SgCN and (c) SeCF-MMO/ SgCN:MX powder.

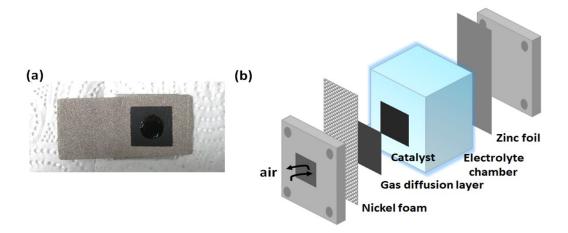


Figure S2. (a) Photographic image of electrocatalyst electrode and (b) schematic diagram of homemade zinc/air cell.

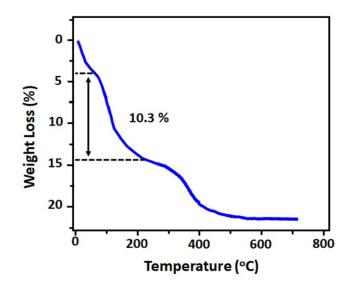


Figure S3. Thermogravimetric analysis for CoFe-LDH compound (CF sample).

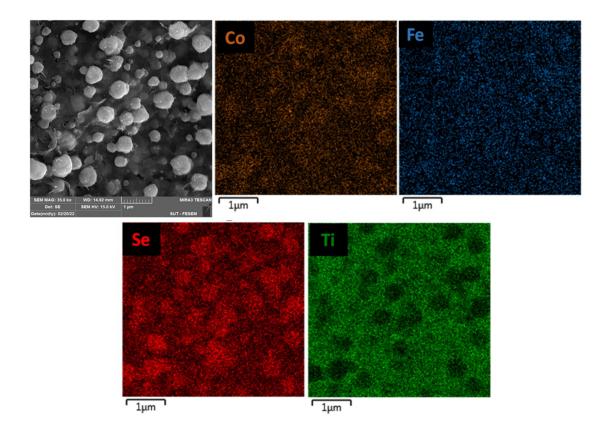


Figure S4. The Energy Dispersive Spectroscopy (EDS) mapping of Se-doped CoFe Mixed Metal Oxide/S-doped g-C₃N₄:Ti₃C₂T_x (SeCF-MMO/SgCN:MX) sample.

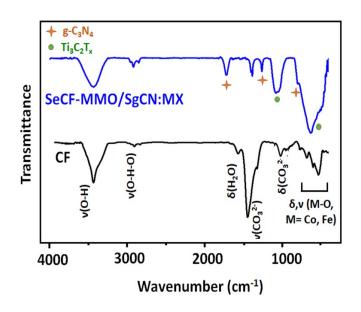


Figure S5. FT-IR spectra of CF and SeCF-MMO/SgCN:MX.

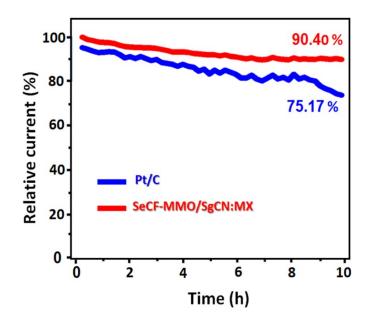


Figure S6. The ORR stability of Pt/C and SeCF-MMO/SgCN:MX samples.

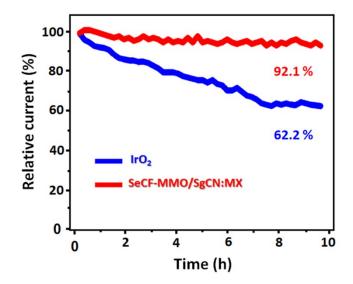


Figure S7. The OER stability of IrO₂ and SeCF-MMO/SgCN:MX samples.

Sample	Mass ratio %		Relative atomic ratio	
	Co	Fe	Co	Fe
$[Co_{0.75}Fe_{0.25}(OH)_2](CO_3^{2-})_{0.125}.0.64H_2O$	76.01	24.02	0.75	0.25

Table S1. Elemental ratios calculated by ICP (Inductively Coupled Plasma) analysis for CoFe-LDH compound.

Table S2. Comparison electrocatalysts behavior of previously electrocatalyst reported and this

work.

Catalyst	Onset potential (V	Half potential (V vs	Limiting current density	Ref
	vs RHE)	RHE)	(mA cm ⁻²)	
AC-HC	0.92	0.77	Large	[1]
CNT/Ag1/CNF	0.874	0.724	-5.1	[2]
Fe-N-C/HPCS@CNT		0.873	6.01	[3]
Pt _{1.1} Fe _{8.8} NiPF	1.0	0.87		[4]
Co@IC/MoC@PC	1.034	0.875	5.89	[5]
Ag/Ag ₂ O @MCOF(Co)	0.87	0.76	-4.8	[6]
FeCo SAs@Co/N-GC		0.88	6.70	[7]
-		Pt/C (0.84)		
Co _{0.25} Ni _{0.75} @NCNT30	0.94	0.84		[8]
FeCo/N-CNTs@CC	0.87	0.78	5.63	[9]
MnCoNi-C-D	0.91	0.82		[10]
V-Co ₃ O ₄		0.821		[11]
CoWO ₄ /WS ₂ @C-N	1.15	0.87		[12]
NiCo ₂ O ₄ /N-G	0.90	0.72	5.27	[13]
FeCO@NS-CA	0.97	0.87	5.81	[14]
Co ₃ O ₄ /NEGF	0.94	0.80		[15]
ZnCoFe-NC	0.95	0.878		[16]
MnCoNi-C-D	0.91	0.82		[10]
FeCo/Co ₂ P@NPCF	0.85	0.79		[17]
Co/N@CNTs@CNMF800	0.99	0.86		[18]
BFC-FC-0.2	1.03	0.9		[19]
	Pt/C (1.02)	Pt/C (0.89)		
Co@NCNTA-700	0.973	0.861		[20]
$(Cu, Co)_3 oS_3 @CNT-C_3 N_4$	0.8			[21]
NiO/NiCo ₂ O ₄	0.89	0.73	4.77	[22]
N-C/Co-1	0.94	0.86		

NiCo ₂ S ₄ /RGO0.02		0.78		[23]
Fe20@N/HCSs		0.85	5.75	[24]
Co3HITP2	0.91	0.8	5.52	[25]
NF@Co _{3-x} Ni _x O ₄	0.91	0.8	1.4	[26]
ONPC	0.95	0.79	5.8	[27]
IOSHs-NSC-Co ₉ S ₈		0.82	5.35	[28]
PtFe-DCNT	0.95	0.84	5.3	[29]
MNG-CoFe	0.98	-	-	[30]
Mn ₃ O ₄ /O-CNTs	0.92	0.85		[31]
NiFe ₂ O ₄ /FeNi ₂ S ₄ HNSs	0.715			[32]
FeN _x -embedded PNC	0.997	0.86		[33]
CoO-NSC-800		0.74	5.5	[34]
Co-N, B-CSs		0.83	5.66	[35]
Co ₂ P@CNF	0.915	0.803	5.27	[36]
CuCoO _x /FeOOH	0.89	0.78	5.3	[37]
Co ₉ S ₈ /CD@NSC		0.84		[38]
Mn/Co-N-C0.02-800	0.90	0.80	5.3	[39]
3D Co-N-C NN	1.05		6.3	[40]
	Pt/C (1.04)		Pt/C (5.6) pt loading of	
			28.2 wt.%)	
NiO/CoN PINWs	0.89	0.68		[41]
	Pt (0.95)	Pt (0.78)		
SeCF-MMO/SgCN:MX	1.04	0.8	6.01	This
				work

References

- [1] J. Feng, R. Tang, X. Wang, and T. Meng, "Biomass-Derived Activated Carbon Sheets with Tunable Oxygen Functional Groups and Pore Volume for High-Performance Oxygen Reduction and Zn–Air Batteries," ACS Applied Energy Materials, vol. 4, no. 5, pp. 5230-5236, 2021.
- [2] S. Li *et al.*, "A Tough Flexible Cellulose Nanofiber Air Cathode for Oxygen Reduction Reaction with Silver Nanoparticles and Carbon Nanotubes in Rechargeable Zinc-Air Batteries," *Energy & Fuels*, vol. 35, no. 10, pp. 9017-9028, 2021.
- [3] F. Fan *et al.*, "Anchoring Fe–N–C Sites on Hierarchically Porous Carbon Sphere and CNT Interpenetrated Nanostructures as Efficient Cathodes for Zinc–Air Batteries," *ACS Applied Materials & Interfaces*, vol. 13, no. 35, pp. 41609-41618, 2021.
- [4] G. Wang, J. Chang, S. Koul, A. Kushima, and Y. Yang, "CO₂ Bubble-Assisted Pt Exposure in PtFeNi Porous Film for High-Performance Zinc-Air Battery," *Journal of the American Chemical Society*, vol. 143, no. 30, pp. 11595-11601, 2021.
- [5] L. Zhang *et al.*, "Co/MoC Nanoparticles Embedded in Carbon Nanoboxes as Robust Trifunctional Electrocatalysts for a Zn–Air Battery and Water Electrocatalysis," *ACS nano*, vol. 15, no. 8, pp. 13399-13414, 2021.
- [6] M. Wang *et al.*, "Efficient Ag/Ag₂O-Doped Cobalt Metallo-Covalent Organic Framework Electrocatalysts for Rechargeable Zinc-Air Battery," *ACS Sustainable Chemistry & Engineering*, vol. 9, no. 17, pp. 5872-5883, 2021.
- [7] N. K. Wagh, D.-H. Kim, S.-H. Kim, S. S. Shinde, and J.-H. Lee, "Heuristic Iron–Cobalt-Mediated Robust pH-Universal Oxygen Bifunctional Lusters for Reversible Aqueous and Flexible Solid-State Zn–Air Cells," ACS nano, vol. 15, no. 9, pp. 14683-14696, 2021.

- [8] A. Kundu, A. Samanta, and C. R. Raj, "Hierarchical Hollow MOF-Derived Bamboo-like N-doped Carbon Nanotube-Encapsulated Co_{0.25}Ni_{0.75} Alloy: An Efficient Bifunctional Oxygen Electrocatalyst for Zinc–Air Battery," ACS Applied Materials & Interfaces, 2021.
- [9] Z. Li *et al.*, "Highly Nitrogen-Doped Carbon Nanotube Nanoarrays as Self-supported Bifunctional Electrocatalysts for Rechargeable and Flexible Zinc-Air Batteries," *ACS Sustainable Chemistry & Engineering*, vol. 9, no. 12, pp. 4498-4508, 2021.
- [10] X. Wang, J. Zhang, D. Ma, X. Feng, L. Wang, and B. Wang, "Metal–Organic Framework-Derived Trimetallic Nanocomposites as Efficient Bifunctional Oxygen Catalysts for Zinc–Air Batteries," ACS Applied Materials & Interfaces, vol. 13, no. 28, pp. 33209-33217, 2021.
- [11] Y. Rao, S. Chen, Q. Yue, and Y. Kang, "Optimizing the Spin States of Mesoporous Co₃O₄ Nanorods through Vanadium Doping for Long-Lasting and Flexible Rechargeable Zn–Air Batteries," ACS Catalysis, vol. 11, pp. 8097-8103, 2021.
- [12] D. Yin *et al.*, "Polyoxometalate@ ZIF Induced CoWO₄/WS₂@CN Nanoflower as a Highly Efficient Catalyst for Zn–Air Batteries," *ACS Applied Energy Materials*, vol. 4, no. 7, pp. 6892-6902, 2021.
- [13] Y. Ma et al., "Synthesis of Ultrasmall NiCo₂O₄ Nanoparticle-Decorated N-Doped Graphene Nanosheets as an Effective Catalyst for Zn–Air Batteries," *Energy & Fuels*, vol. 35, no. 17, pp. 14188-14196, 2021.
- [14] H. Pang *et al.*, "Wood-Derived Bimetallic and Heteroatomic Hierarchically Porous Carbon Aerogel for Rechargeable Flow Zn–Air Batteries," *ACS Applied Materials & Interfaces*, vol. 13, no. 33, pp. 39458-39469, 2021.
- [15] N. Manna, S. K. Singh, G. P. Kharabe, A. Torris, and S. Kurungot, "Zinc–Air Batteries Catalyzed Using Co₃O₄ Nanorod-Supported N-Doped Entangled Graphene for Oxygen Reduction Reaction," ACS Applied Energy Materials, vol. 4, no. 5, pp. 4570-4580, 2021.
- [16] G. Li *et al.*, "Zn, Co, and Fe Tridoped N–C Core–Shell Nanocages as the High-Efficiency Oxygen Reduction Reaction Electrocatalyst in Zinc–Air Batteries," *ACS Applied Materials & Interfaces*, 2021.
- [17] Q. Shi et al., "High-Performance Trifunctional Electrocatalysts Based on FeCo/Co₂P Hybrid Nanoparticles for Zinc–Air Battery and Self-Powered Overall Water Splitting," Advanced Energy Materials, vol. 10, no. 10, p. 1903854, 2020.
- [18] T. Liu, J. Mou, Z. Wu, C. Lv, J. Huang, and M. Liu, "A facile and scalable strategy for fabrication of superior bifunctional freestanding air electrodes for flexible zinc–air batteries," *Advanced Functional Materials*, vol. 30, no. 36, p. 2003407, 2020.
- [19] Z. Pei *et al.*, "A Flexible Rechargeable Zinc–Air Battery with Excellent Low-Temperature Adaptability," *Angewandte Chemie*, vol. 132, no. 12, pp. 4823-4829, 2020.
- [20] L. Liu *et al.*, "Cobalt-encapsulated nitrogen-doped carbon nanotube arrays for flexible zinc–air batteries," *Small Methods*, vol. 4, no. 1, p. 1900571, 2020.
- [21] X. Wang *et al.*, "Cu/S-Occupation Bifunctional Oxygen Catalysts for Advanced Rechargeable Zinc– Air Batteries," *ACS Applied Materials & Interfaces*, vol. 12, no. 47, pp. 52836-52844, 2020.
- [22] Y. Li *et al.*, "Dual interface engineering of NiO/NiCo₂O₄/CoO heterojunction within graphene networks for high-performance lithium storage," *Electrochimica Acta*, p. 138536, 2021.
- [23] Y. Liang, Q. Gong, X. Sun, N. Xu, P. Gong, and J. Qiao, "Rational fabrication of thin-layered NiCo₂S₄ loaded graphene as bifunctional non-oxide catalyst for rechargeable zinc-air batteries," *Electrochimica Acta*, vol. 342, p. 136108, 2020.
- [24] B. Wang *et al.*, "Space-Confined Yolk-Shell Construction of Fe₃O₄ Nanoparticles Inside N-Doped Hollow Mesoporous Carbon Spheres as Bifunctional Electrocatalysts for Long-Term Rechargeable Zinc–Air Batteries," *Advanced Functional Materials*, vol. 30, no. 51, p. 2005834, 2020.

- [25] Y. Lian *et al.*, "Unpaired 3d electrons on atomically dispersed cobalt centres in coordination polymers regulate both oxygen reduction reaction (ORR) activity and selectivity for use in zinc–air batteries," *Angewandte Chemie International Edition*, vol. 59, no. 1, pp. 286-294, 2020.
- [26] M. Wu, G. Zhang, N. Chen, W. Chen, J. Qiao, and S. Sun, "A self-supported electrode as a highperformance binder-and carbon-free cathode for rechargeable hybrid zinc batteries," *Energy Storage Materials,* vol. 24, pp. 272-280, 2020.
- [27] Y. Wang *et al.*, "Direct Conversion of Biomass into Compact Air Electrode with Atomically Dispersed Oxygen and Nitrogen Coordinated Copper Species for Flexible Zinc–Air Batteries," *ACS Applied Energy Materials,* vol. 2, no. 12, pp. 8659-8666, 2019.
- [28] K. Tang, C. Yuan, Y. Xiong, H. Hu, and M. Wu, "Inverse-opal-structured hybrids of N, S-codopedcarbon-confined Co₉S₈ nanoparticles as bifunctional oxygen electrocatalyst for on-chip all-solidstate rechargeable Zn-air batteries," *Applied Catalysis B: Environmental*, vol. 260, p. 118209, 2020.
- [29] S. Zeng *et al.*, "PtFe alloy nanoparticles confined on carbon nanotube networks as air cathodes for flexible and wearable energy devices," *ACS Applied Nano Materials*, vol. 2, no. 12, pp. 7870-7879, 2019.
- [30] W. Niu and Y. Yang, "Amorphous MOF introduced N-doped graphene: An efficient and versatile electrocatalyst for Zinc–air battery and water splitting," ACS Applied Energy Materials, vol. 1, no. 6, pp. 2440-2445, 2018.
- [31] L. Li *et al.*, "Anchoring Mn₃O₄ nanoparticles on oxygen functionalized carbon nanotubes as bifunctional catalyst for rechargeable zinc-air battery," *ACS Applied Energy Materials*, vol. 1, no. 3, pp. 963-969, 2018.
- [32] L. An *et al.*, "Heterostructure-promoted oxygen electrocatalysis enables rechargeable zinc–air battery with neutral aqueous electrolyte," *Journal of the American Chemical Society*, vol. 140, no. 50, pp. 17624-17631, 2018.
- [33] L. Ma *et al.*, "Single-site active iron-based bifunctional oxygen catalyst for a compressible and rechargeable zinc–air battery," *ACS nano*, vol. 12, no. 2, pp. 1949-1958, 2018.
- [34] S. Chen, S. Chen, B. Zhang, and J. Zhang, "Bifunctional Oxygen Electrocatalysis of N, S-Codoped Porous Carbon with Interspersed Hollow CoO Nanoparticles for Rechargeable Zn–Air Batteries," *ACS applied materials & interfaces,* vol. 11, no. 18, pp. 16720-16728, 2019.
- [35] Y. Guo *et al.*, "Carbon nanosheets containing discrete Co-N_x-B_y-C active sites for efficient oxygen electrocatalysis and rechargeable Zn–Air Batteries," *ACS nano*, vol. 12, no. 2, pp. 1894-1901, 2018.
- [36] J. Gao et al., "Co₂P@N,P-codoped carbon nanofiber as a free-standing air electrode for Zn–Air batteries: synergy effects of CoNx satellite shells," ACS applied materials & interfaces, vol. 11, no. 10, pp. 10364-10372, 2019.
- [37] M. Kuang *et al.*, "CuCoO_x/FeOOH Core–shell nanowires as an efficient bifunctional oxygen evolution and reduction catalyst," *ACS Energy Letters*, vol. 2, no. 10, pp. 2498-2505, 2017.
- [38] P. Zhang *et al.*, "Efficient oxygen electrocatalyst for Zn–air batteries: carbon dots and Co₉S₈ nanoparticles in a N, S-codoped carbon matrix," *ACS applied materials & interfaces*, vol. 11, no. 15, pp. 14085-14094, 2019.
- [39] L. Wei, L. Qiu, Y. Liu, J. Zhang, D. Yuan, and L. Wang, "Mn-doped Co–N–C dodecahedron as a bifunctional electrocatalyst for highly efficient Zn–air batteries," ACS Sustainable Chemistry & Engineering, vol. 7, no. 16, pp. 14180-14188, 2019.
- [40] R. Wang *et al.*, "MOF@ Cellulose Derived Co–N–C Nanowire Network as an Advanced Reversible Oxygen Electrocatalyst for Rechargeable Zinc–Air Batteries," *ACS Applied Energy Materials*, vol. 1, no. 3, pp. 1060-1068, 2018.
- [41] J. Yin *et al.*, "NiO/CoN porous nanowires as efficient bifunctional catalysts for Zn–air batteries," *ACS nano*, vol. 11, no. 2, pp. 2275-2283, 2017.