

Supporting Information

Macroporous Titanium Oxynitride Supported Bifunctional Oxygen Electrocatalyst for Zinc-air Batteries

Weixing Niu, Yani Guan, Yuhong Luo, Guihua Liu, Jingde Li *

Hebei Provincial Key Laboratory of Green Chemical Technology and High Efficient Energy Saving, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin, 300130, China

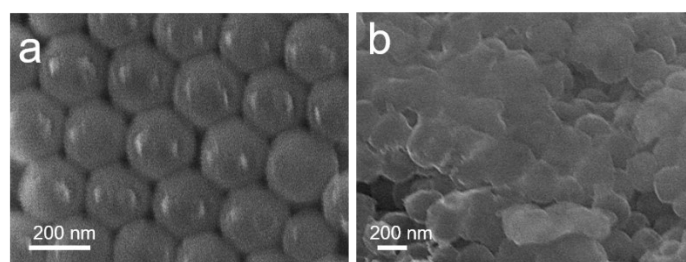


Figure S1. SEM images of a) PS template and b) PS@precursor.

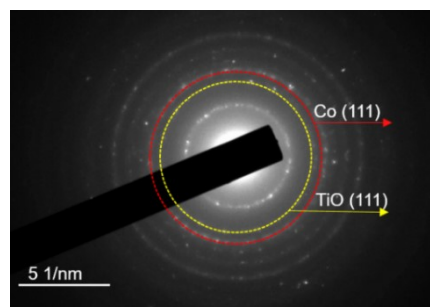


Figure S2. Selected area electron diffraction (SAED) of 3DOM Co-NSC@TiO_xN_y.

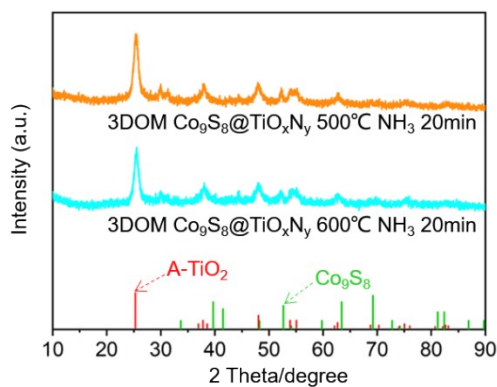


Figure S3. XRD patterns of various 3DOM composites under different temperatures.

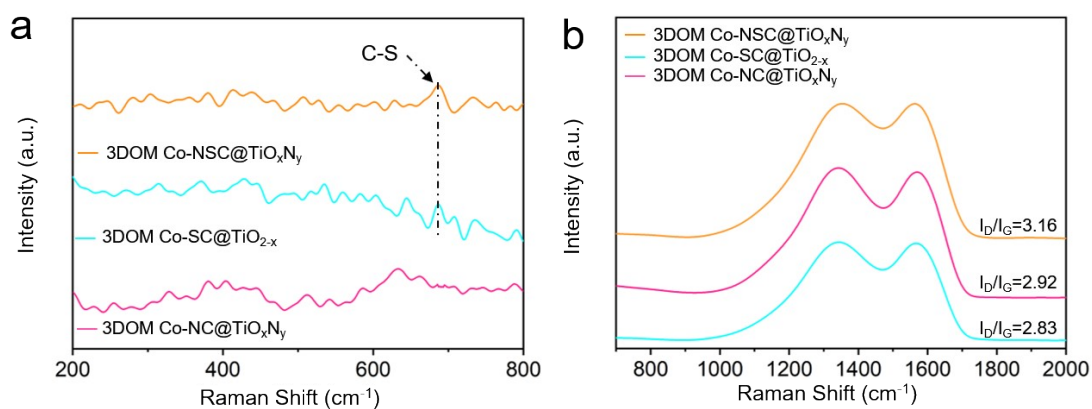


Figure S4. Raman spectra of 3DOM Co-NSC@TiO_xN_y, 3DOM Co-SC@TiO_{2-x} and 3DOM Co-NC@TiO_xN_y.

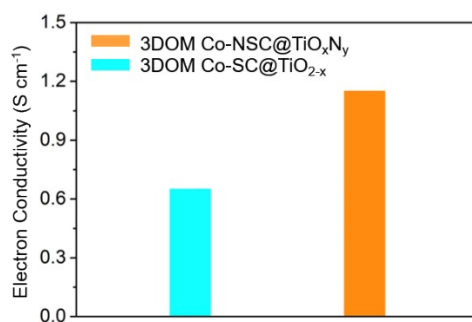


Figure S5. Electron conductivity of 3DOM composites.

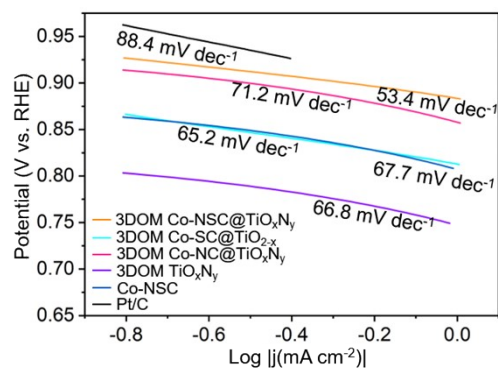


Figure S6. Tafel plots derived from Figure 4a) in the main text, respectively.

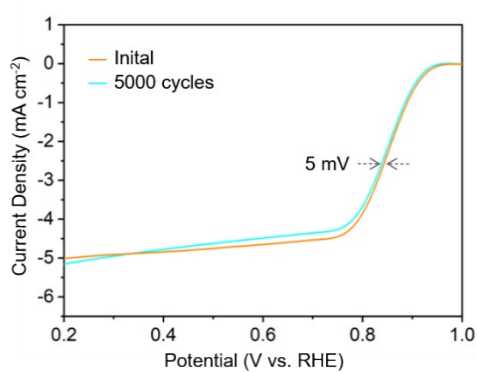


Figure S7. The ORR LSV curves of 3DOM Co-NSC@TiO_xN_y before and after 5000 cycles between 0.6 and 1.0 V at a scan rate of 100 mV s⁻¹.

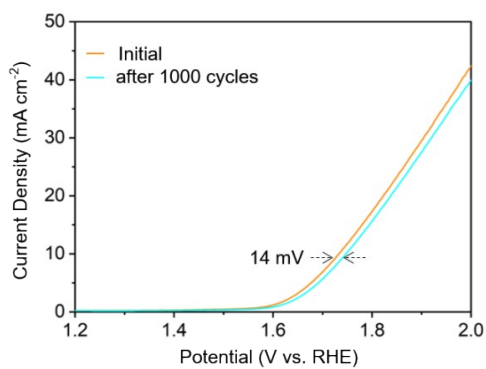


Figure S8. OER curves of 3DOM Co-NSC@TiO_xN_y before and after 1000 cycles.

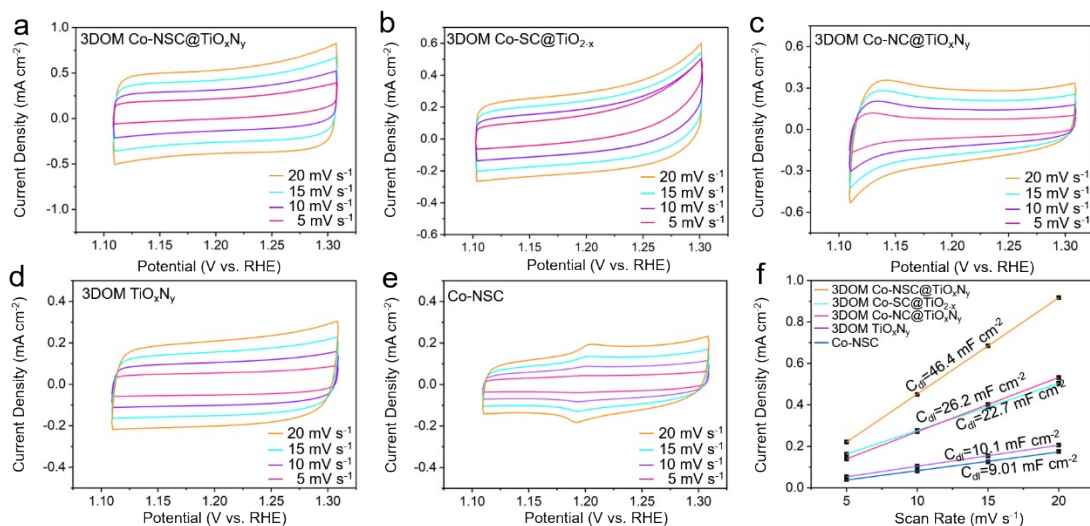


Figure S9. CV curves of various 3DOM composites at the double layer region at scan rates of 5, 10, 15, and 20 mV s⁻¹; f) Current density at the potential of 1.2 V, where no redox current peaks are observed, as a function of the scan rate derived from a-e), respectively.

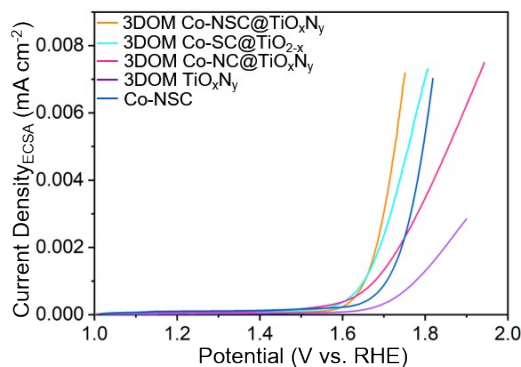


Figure S10. LSV curves of various 3DOM catalysts normalized by electrochemical active surface area.

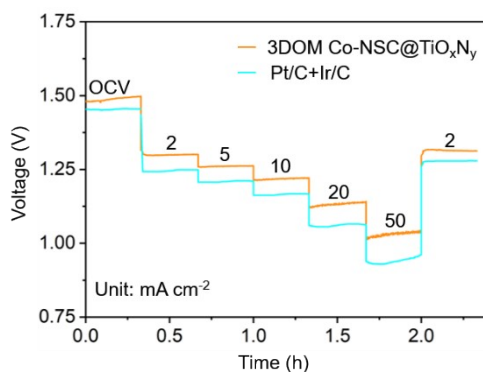


Figure S11. Discharge curves of the zinc-air battery assembled with 3DOM Co-NSC@TiO_xN_y at current densities of 2, 5, 10, 25, 50, 2 mA cm⁻² for 2 h.

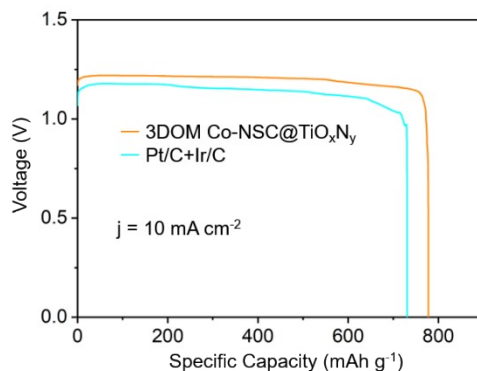


Figure S12. Discharge curve of primary zinc air battery with 3DOM Co-NSC@TiO_xN_y operated at 10 mA cm⁻².

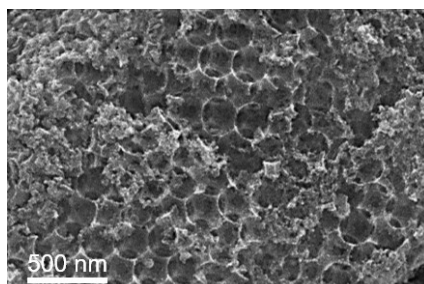


Figure S13. The SEM image of 3DOM Co-NSC@TiO_xN_y composite post 12 hours OER test at a constant potential of 1.67 V (vs. RHE).

Table S1 The performance of recently published catalysts for zinc air batteries.

Catalyst	0.1M KOH		Power density (mW cm ⁻²)	Long term cycling		Ref.
	E _{1/2} (V)	η ₁₀ (mV)				
Co@Co ₃ O ₄ -1000	0.80	370	64	10mA cm ⁻²	200h	1
Co@NGC-NSs	0.82	360	52	5mA cm ⁻²	36h	2
Ni-Co-S/NSC	0.81	309	137	10mA cm ⁻²	180h	3
CoO _x @CoN _y /NCNF	0.81	460	80	10mA cm ⁻²	50h	4
Co/S/N-800	0.83	361	76	5mA cm ⁻²	48h	5
CMS/NCNF	0.84	565	-	10mA cm ⁻²	100h	6

(3D) Co-N-C	0.83	470	138	10mA cm ⁻²	16h	7
Ni ₃ Fe/Co-N-C	0.83	310	72	10mA cm ⁻²	60h	8
CoP/NP-HPC	0.83	590	186	2mA cm ⁻²	80h	9
N-CoSe ₂ /3D-MXenx	0.79	310	130	10mA cm ⁻²	167h	10
Co-NSC@TiO _x N _y	0.84	440	123	10mA cm ⁻²	300h	This work

Reference

- [1] Z. Guo, F. Wang, Y. Xia, J. Li, A. G. Tamirat, Y. Liu, L. Wang, Y. Wang and Y. Xia, *J. Mater. Chem. A*, 2018, **6**, 1443-1453.
- [2] P. Thakur, M. Yeddala, K. Alam, S. Pal, P. Sen and T. N. Narayanan, *ACS Appl. Energy Mater.*, 2020, **3**, 7813-7824.
- [3] Z. Wu, H. Wu, T. Niu, S. Wang, G. Fu, W. Jin and T. Ma, *ACS Sustain. Chem. Eng.*, 2020, **8**, 9226-9234.
- [4] K. R. Yoon, C. K. Hwang, S. H. Kim, J. W. Jung, J. E. Chae, J. Kim, K. A. Lee, A. Lim, S. H. Cho, J. P. Singh, J. M. Kim, K. Shin, B. M. Moon, H. S. Park, H. J. Kim, K. H. Chae, H. C. Ham, I. D. Kim and J. Y. Kim, *ACS Nano*, 2021, **15**, 11218-11230.
- [5] N. Jia, J. Liu, Y. Gao, P. Chen, X. Chen, Z. An, X. Li and Y. Chen, *ChemSusChem*, 2019, **12**, 3390-3400.
- [6] Y. Wang, J. Fu, Y. Zhang, M. Li, F. M. Hassan, G. Li and Z. Chen, *Nanoscale*, 2017, **9**, 15865-15872.
- [7] R. Wang, J. Cao, S. Cai, X. Yan, J. Li, W. M. Yourey, W. Tong and H. Tang, *ACS Appl. Energy Mater.*, 2018, **1**, 1060-1068.
- [8] J. Tan, T. Thomas, J. Liu, L. Yang, L. Pan, R. Cao, H. Shen, J. Wang, J. Liu and M. Yang, *Chem. Eng. J.*, 2020, **395**, 125151.
- [9] Y. Wang, M. Wu, J. Li, H. Huang and J. Qiao, *J. Mater. Chem. A*, 2020, **8**, 19043-19049.
- [10] Z. Zeng, G. Fu, H. Bin Yang, Y. Yan, J. Chen, Z. Yu, J. Gao, L. Y. Gan, B. Liu and P. Chen, *ACS Mater. Lett.*, 2019, **1**, 432-439.