Electronic Supplementary Information (ESI)

## Bifunctional Electrocatalysts of MOF-Derived Co-N/C on Bamboo-Like MnO

## Nanowires for High-Performance Liquid and Solid-State Zn-Air Batteries

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Fig. S1 (a) SEM and (b) TEM images of hollow MnO<sub>2</sub>. (c) SEM and (d) TEM images of MnO<sub>2</sub>@ZIF-67.



Fig. S2 XRD patterns for various samples.



Fig. S3 SEM images of Co-N/C derived from ZIF-67.



Fig. S4 (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distribution curve for MnO@Co-N/C.



Fig. S5 CV curves in O<sub>2</sub>-saturated (solid lines) or N<sub>2</sub>-saturated (dashed line) in 0.1 M KOH at 5 mV s<sup>-1</sup>.



Fig. S6 Kinetic current density at 0.85 V for various catalysts.

 Table S1. Comparison of the ORR and OER performance of MnO@Co-N/C against previously

 reported bifunctional catalyst in 0.1M KOH solution.

Catalysts	E <sub>ORR1/2</sub> /V half-wave potential	E <sub>OER</sub> /V i=10 mA cm <sup>-2</sup>		Reference
MnO@Co-N/C	0.83	1.76	0.93	This work
<i>c</i> -CoMn₂/C	0.85	1.80	0.95	1
NPMC-1000	0.85	1.90	1.05	2
3DOM Co <sub>3</sub> O <sub>4</sub>	0.64	1.67	1.00	3
ZnCoNC-0.1	0.84	1.75	0.91	4
Co <sub>2</sub> P@CoNPG-900	0.81	1.73	0.92	5
RuO <sub>2</sub>	0.29	1.64	1.27	6
Pt/C	0.9	1.90	1.0	6



Fig. S7 Tafel plots calculated from OER curves.



Fig. S8 XPS of Co2p and Mn2p before and after OER.



Fig. S9 XRD patterns of MnO@Co-N/C obtained at 600, 700, and 800 °C.



Fig. S10 LSV curves of MnO@Co-N/C prepared at different temperatures.



Fig. S11 EIS of MnO@Co-N/C prepared at different temperatures loaded on glass-carbon electrodes.



Fig. S12 TEM image of MnO@Co-N/C-800.



Fig. S13 LSV curves of MnO@Co-N/C before and after  $0.5 \text{ M H}_2\text{SO}_4$  treatment.



Video S1 The video of a mini fan driven by two Zn-air batteries (Double click the picture to watch the video).



Fig. S14 The photograph of the PVA gel electrolyte.



Fig. S15 Open circuit potential of a liquid Zn-air battery with MnO@Co-N/C catalysts.

Table S2. Cv	vcle performance	of rechargeable Zn-air	batteries with variou	s catalysts.
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	Peak power	Cycling		
catalyst	density (mW cm <sup>-2</sup> )	conditions	Cycling performance	Reference
		(mA cm <sup>-2</sup> )		
MnO@Co-N/C	130.3	5	20 min per cycle for 1900	This work
			Cycles (633 h)	
		10	2 h per cycle for 89 cycles	This work
			(178 h)	
Co3O4/N-rGO	-	3	20 min per cycle for 75	7
			cycles (25 h)	
Fe <sub>0.5</sub> Co <sub>0.5</sub> O <sub>x</sub> /NrGO	86	10	2 h per cycle for 60	8
			cycles (120 h)	
$Co_3FeS_{1.5}(OH)_6$	113.1	2	20 min per cycle for 108	9
			cycles (36 h)	
Co <sub>3</sub> O <sub>4</sub> /N-CNTAs	-	5	10 min per cycle for100	10
			cycles (16.7 h)	
Co-N <sub>x</sub> -C	152	2	20 min per cycle for 180	11
			cycles (60 h)	
CoS <sub>x</sub> @PCN/rGO	-	10	6.6 min per cycle for 394	12
			cycles (43.8 h)	
NPMC-1000	55	2	10 min per cycle for 180	13
			cycles (30 h)	
RuO <sub>2</sub> -coated	-	4	20 min per cycle for 100	14
MCNAs			cycles (34 h)	
C-MOF-C2-900	105	10	20 min per cycle for 90	15
			cycles (30 h)	
S-GNS/NiCo <sub>2</sub> S <sub>4</sub>	216.3	10	40 min per cycle for 150	16
			cycles (100 h)	

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