1 Supplementary Information for

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3	Superior Stability of Bifunctional Oxygen Electrode for Primary, Rechargeable					
4	and Flexible Zn-Air Batteries					
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30 Experimental Section

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Materials and catalyst preparation: MnO₂ catalyst samples: the catalysts were 32 prepared by a combined facial hydrothermal self-assembled process along with the 33 calcination treatment. In a typical synthesis of MnO₂ nanotubes as precursors: 0.79g 34 KMnO₄ and 2 mL concentrated HCl (37%) were added to 50 mL deionized (D.I.) 35 water to form a precursor solution, then transferred into a 100 mL Teflon-lined 36 37 stainless steel autoclave, which was sealed and hydrothermally treated at 140°C for 12 hours. After cooled down to the room temperature, the brown MnO₂ nanotube as 38 precursors samples were collected and washed with ethanol and D.I. water, then dried 39 in air at 70°C for 24 hours to remove the solvents. (the the brown MnO₂ nanotube as 40 precursors product was further calcined in air at 350°C for 3 hours to obtain the MnO₂ 41 catalyst samples.) 42

NiCo₂O₄-CNTs hybrid nanocatalyst materials: 0.2 g Co(NO₃)₂ 4H₂O and 0.2 g 43 Ni(Ac)₂ 4H₂O were dissolved in 15 mL of 1.3 mol L⁻¹ ammonia solution at first. 44 Afterwards, 0.06g CNTs were dispersed in the above solution by ultrasonication for 1 45 hour. This mixture was then transferred into a 100 mL autoclave, which was sealed 46 and maintained at 160°C for 6 hours. The resulting product was separated by 47 centrifugation, washed with deionized water, dried at 60°C for 6 hours, and then 48 49 calcined in air at 350°C for 1 hour. The obtained catalyst samples are then expressed as NiCo₂O₄-CNTs, respectively, in this paper. 50

51 Ni₂O₃@MnO₂-CNTs hybrid nanocatalyst materials: at first, 0.20 g Ni(AC)₂ 4H₂O was homogeneously dissolved in 30 mL of 1.3 mol L⁻¹ ammonia solution. 52 Then, 0.20 g as-prepared MnO₂ nanotubes and and 0.06 g CNTs were dispersed in the 53 above solution, sonicated for 0.5 hour to form a uniform mixture. This mixture was 54 55 then transferred into a 100 mL autoclave, which was sealed and maintained at 160°C for 10 hours. The resulting product was separated by centrifugation, washed with D.I. 56 water, and then dried at 60°C for 6 hours. Finally, the resulting product was further 57 calcined in air at 350°C for 3 hours to obtain the target catalyst samples. The resulted 58 powder was denoted as Ni₂O₃@MnO₂-CNTs. 59

Co₂O₃@MnO₂-CNTs hybrid nanocatalyst materials: at first, 0.20 g Co(AC)₂ 4H₂O 60 was homogeneously dissolved in 30 mL of 1.3 mol L⁻¹ ammonia solution. Then, 0.20 61 g as-prepared MnO₂ nanotubes and and 0.06g CNTs were dispersed in the above 62 solution, sonicated for 0.5 hour to form a uniform mixture. This mixture was then 63 transferred into a 100 mL autoclave, which was sealed and maintained at 160°C for 10 64 hours. The resulting product was separated by centrifugation, washed with D.I. water, 65 and then dried at 60°C for 6 hours. Finally, the resulting product was further calcined 66 in air at 350°C for 3 hours to obtain the target catalyst samples. The resulted powder 67 was denoted as Co₂O₃@MnO₂-CNTs. 68

69 NiCo₂O₄/MnO₂-CNTs-1 and NiCo₂O₄/MnO₂-CNTs-5: at first, 0.20 g Ni(AC)₂ 4H₂O and 0.20 g Co(NO₃)₂ 6H₂O was homogeneously dissolved in 30mL of 1.3 mol 70 L^{-1} ammonia solution. Then, 0.10 g as-prepared MnO₂ nanotubes and 0.06 g CNTs 71 72 were dispersed in the above solution, sonicated for 0.5 hour to form a uniform mixture. This mixture was then transferred into a 100 mL autoclave, which was sealed 73 and maintained at 160°C for 10 hours. The resulting product was separated by 74 centrifugation, washed with D.I. water, and then dried at 60°C for 6 hours. Finally, the 75 resulting product was further calcined in air at 350°C for 1 and 5 hours to obtain the 76 target catalyst samples. The resulted powder was denoted as NiCo₂O₄/MnO₂-CNTs-1 77 and NiCo₂O₄/MnO₂-CNTs-5 this 78 in paper.



Fig. S1 (a) SEM image of NiCo₂O₄@MnO₂-CNTs-3 (inset: enlarged view of SEM image (a) marked with the red colored dotted line); (b) Nitrogen adsorption-desorption isotherms of the NiCo₂O₄@MnO₂-CNT-3 hybrid nanomaterials; (c) the pore-size distributions of the NiCo₂O₄@MnO₂-CNT-3 hybrid nanomaterials.



Fig. S2 TEM images of (a) MnO_2 ; (b) $NiCo_2O_4$ -CNTs; (c) $Ni_2O_3@MnO_2$ -CNTs; (d) $Co_2O_3@MnO_2$ -CNTs; (e) $NiCo_2O_4@MnO_2$ -CNTs-1; (f) $NiCo_2O_4@MnO_2$ -CNTs-5.



Fig. S3 Cycling data at 20 mA cm⁻² in cycle periods of 5 minutes per cycle of the bielectrode Zn-air battery using (a) MnO_2 ; (b) $NiCo_2O_4$ -CNTs; (c) Ni_2O_3 @ MnO_2 -CNTs; (d) Co_2O_3 @ MnO_2 -CNTs; (e) $NiCo_2O_4$ @ MnO_2 -CNTs-1; (f) $NiCo_2O_4$ @ MnO_2 -CNTs-5 hybrid catalysts as cathode catalyst, with zinc plate with a thickness of 0.5 mm as the anode.

Air catalyst used	Cycling conditions and stability	Voltage	Reference	
5	, , ,	polarization / V		
NiCo ₂ O ₄ @MnO ₂ -CNTs-1	20 mA/cm^2 , 10 min per cycle	1.5	This work	
	period for 49 hours			
	20 A = 2 10 F	0.77	TTI · 1	
$N1CO_2O_4(a)MnO_2$ -CN IS-3	20 mA/cm ² , 10 min per cycle	0.77	I his work	
	period for 380 hours			
NiCo2O4@MnO2-CNTs-5	20 mA/cm^2 10 min per cycle	1 48	This work	
	period for 51 hours			
		1.5	TT1 · 1	
Pt/C	20 mA/cm^2 , 10 min per cycle	1.5	This work	
	period for 6 hours			
MnO ₂	20 mÅ/cm^2 10 min per cycle	19	This work	
1.11.02	poriod for 11 hours			
		1.45	TT1 · 1	
$N_1Co_2O_4$ -CNTS	20 mA/cm^2 , 10 min per cycle	1.45	This work	
	period for 13.5 hours			
$Ni_2O_2@MnO_2-CNTs$	20 mA/cm^2 10 min per cycle	14		
	pariod for 45 hours	1.1	This work	
$Co_2O_3(a)MnO_2$ -CNTs	20 mA/cm^2 , 10 min per cycle			
	period for 55 hours	1.3	This work	
	1			
NCNT/CoO NIO NICo	$20 + \frac{1}{2} +$	0.07	F 1 3	
Incini/CoO-IniO-IniCo	20 mA/cm^2 , 10 min per cycle	0.87	[1]	
	period for 16.5 hours			
	15 mA/cm^2 20 min per cycle			
$Co(OH)_2$ –N-rGO	period for 50 hours	1.2	[2]	
$[(a-MnO_2)_2-(LaN_1O_3)_3]_{40\%}$	20 mA/cm^2 , 10 min per cycle	0.85	[3]	
/(CNT) _{60%}	period for 12.5 hours	0.85	[-]	
· ·	8 mA/cm^2 , 10 min per cycle		5.43	
MnO. NCNT	neriod for 6 hours	1.7	[4]	

Table S1: Stability of rechargeable Zn-air batteries with several key parameters extracted from literatures.

Air catalyst used	electrolyte	Peak power density (mW cm ⁻ ²)	Cycling conditions and stability	Voltage polarization / V	Reference
NiCo ₂ O ₄ @MnO ₂ -CNTs-3	Tokuyama A901	85.9	3 mA/cm ² , 10 min per cycle period for 90 hours	1.125	This work
Co ₃ O ₄ /MnO ₂ -CNTs	Tokuyama A901	62	5 mA/cm^2 , 10 min per cycle period for 4 hours	0.875	[5]
La ₂ O ₃ /Co ₃ O ₄ /MnO ₂ -CNTs	Tokuyama A901	32	5 mA/cm^2 , 10 min per cycle period for 2 hours	1.75	[6]
Fe/N/C-900	0.1M KOH- based GGPE	/	/	/	[7]
Co ₄ N/CNW/CC	hydrogel polymer electrolyte	/	5 mA/cm ² , 20 min per cycle period for 12 hours	2.2	[8]
Co ₃ O ₄ nanoparticles	Conductive QAFCGO Membrane	52	1 mA/cm ² , 20 min per cycle period for 10 hours	0.85	[9]
LaNiO ₃ /NCNT	porous- gelled PVA electrolyte membrane	56.1	250 A/L ¹ , 20 min per cycle period for 40 hours	1.0	[10]

Table S2: The flexible rechargeable Zn-air batteries with several key parameters extracted from literatures.

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- 106