Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels. This journal is © The Royal Society of Chemistry 2017

1	Supplementary Information for Sustainable Energy & Fuels					
2						
3	Bi-functional composite electrocatalysts consisting of nanoscale (La, Ca) oxides and					
4	carbon nanotubes for long-term zinc-air fuel cell and rechargeable battery					
5						
6	Nengneng Xu ^a , Qi Nie ^a , Yanan Wei ^a , He Xu ^{a*} , Yu-Dong Wang ^b ,					
7	Xiao-Dong Zhou ^{b*} . Jinli Oiao ^{a*}					
8						
9	^a College of Environmental Science and Engineering. Donghua Universtiv. 2999 Ren'min					
10	North Road, Shanghai 201620, China					
11	^b Department of Chemical Engineering, Institute for Materials Research and Innovations,					
12	University of Louisiana at Lafavette, Lafavette, LA 70504, USA.					
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24 25						
25						
20						
28	*Corresponding author. Tel: +86-21-67792379. Fax: +86-21-67792159. E-mail:					
29	qiaojl@dhu.edu.cn; hexu@dhu.edu.cn, zhou@louisiana.edu					

1. Experimental Section 1

Materials and catalyst synthesis. A hydrothermal process was used to synthesize the raw 2 powders. In a typical process, 2 ml concentrated hydrochloric acid (37%) and 0.79 g 3 potassium permanganate were added to 50 ml deionized water to form a homogeneous 4 solution and then transferred into an autoclave, which was hydrothermally treated at 140 °C 5 for 12 hours. After cooling to ambient temperature, the resultant brown powders were washed 6 with ethanol and deionized water and then dried in air at 70 °C for 12 hours. Following this, a 7 certain amount of Ca(NO₃)₂ 4H₂O and La(NO₃)₂ 4H₂O were added to 15 ml of 1.3 mol 1⁻¹ 8 NH4OH. Then, 0.1 g of the as-prepared brown samples and 0.05 g carbon nanotubes 9 (diameter 30 - 50 nm, length ~15 μ m, purity > 95 wt%, Alpha Nano Technology Co. Ltd., 10 China) were dispersed in the above solution, where the mixture was decentralized for 1 hour 11 and then transferred into a 100 ml autoclave and hydrothermally treated at 150 °C for 6 hours. 12 The product were washed with deionized water and then dried in air at 60 °C for 6 hours. 13 Finally, the samples were calcined in air at 200 °C, 300 °C, 400 °C and 500 °C for 1, 3 and 5 14 hours, denoted as Composite-3h-200 °C, Composite-3h-300 °C, Composite-3h-500 °C, 15 composite-1h, composite-3h, and composite-5h. Their compositions are described as follows. 16 Table I summarizes the composition and the name of all specimens studied in this work. 17 18

-	0	
1	9	

Table S1. List of electrode composition studied in this work								
	Annealing time	CaO/La ₂ O ₃	CNT/(CaO/La ₂ O ₃ /MnO ₂)					
	temperature and							
Composite-3h-200 °C	3 hour, 200 °C	1	0.10					
Composite-3h-300 °C	3 hour, 300 °C	1	0.10					
Composite-3h-500 °C	3 hour, 500 °C	1	0.10					
Composite-1h	1 hour, 400 °C	1	0.10					
Composite-3h	3 hour, 400 °C	1	0.10					
Composite-5h	5 hour, 400 °C	1	0.10					
Composite-3h-CNT0	3 hour, 400 °C	1	0					
Composite-3h-CNT0.05	3 hour, 400 °C	1	0.05					
Composite-3h-CNT0.15	3 hour, 400 °C	1	0.15					
Composite-3h-CaO0	3 hour, 400 °C	0	0.10					
Composite-3h-CaO0.5	3 hour, 400 °C	0.5	0.10					

2

0.10

20

Composite-3h-CaO2

The role of CNT support and presence of CaO on the bi-functionality was studied by 21

3 hour, 400 °C

1 varying the mass fraction of CNTs and CaO in the composite electrode annealed for 3 hours 2 (e.g. composite-3h). Four ratios of CNTs to CaO/La₂O₃/MnO₂ were adopted, 0:1, 0.05:1, 3 0.1:1 and 0.15:1, which were named as, composite-3h-CNT0, composite-3h-CNT0.05, 4 composite-3h-CNT0.10 (equivalent to composite-3h), and composite-3h-CNT0.15, 5 respectively. The role of CaO was studied by changing the mass ratio of CaO/La₂O₃ with a 6 magnitude of 0:1, 0.5:1, 1:1 and 2:1, which are denoted as composite-3h-CaO0, composite-7 3h-CaO0.5, composite-3h-CaO1 (equivalent to composite-3h), and composite-3h-CaO2.

8 **Characterization.** The morphology and structure of the as-synthesized samples were 9 characterized by using an FEI Sirion 200 field-emission scanning electron microscope (SEM) 10 operating at 5 kV and high-resolution transmission electron microscopy (TEM, Hitachi JEM-11 2100F) at 200 kV. The x-ray diffraction (XRD) patterns of catalyst samples were collected on 12 a Philips PW3830 x-ray diffractometer using Cu K α radiation ($\lambda = 0.15406$ nm) with a 13 current of 40 mA and voltage of 40 kV. The intensity data were collected at 25 °C from 5° to 14 80° with a scan rate of 1.20° min⁻¹.

Electrode preparation and measurements. To prepare a catalyst ink, 5 mg of the 15 catalyst was ultrasonically dispersed into 1 mL ethanol and 8 μ L 5 wt% Nafion[®] solution to 16 form a homogeneous ink. Then, 4 μ L of the ink was deposited onto a glassy carbon rotating 17 disk electrode (RDE) and dried at room temperature. The catalyst loading was 0.1 mg cm⁻². 18 The initial electrochemical measurements were conducted in a standard three-electrode 19 electrochemical cell at room temperature. The working electrode was immersed in a glass cell 20 containing 0.1 M KOH aqueous electrolyte. A platinum rod and a saturated calomel electrode 21 were used as the counter and reference electrodes. Electrochemical activity was studied using 22 linear sweep voltammetry (LSV) employing a rotating disk electrode (RDE). In an O₂-23 saturated electrolyte solution, the bi-functional catalyst activities were evaluated at a potential 24 from -1 to 0.7 V vs SCE. The rotation rate of the RDE and the potential scan rate were 25 controlled at 1600 rpm and 5 mV s⁻¹. Baseline catalysts were examined for the purpose of 26 comparison, including 20 wt% Pt/C (Johnson Matthey), IrO₂/C (Johnson Matthey), CNTs and 27 the corresponding composite catalysts. For more quantitative analyze using Koutecky-Levich 28

1 theory, the electrode was rotated at several other rates, e.g. 100, 400, 900 and 1600 rpm.

Battery fabrication and measurement. A home-made ZAB was used to study the 2 performance of the air electrode comprised of the aforementioned catalysts. A 20 mg of 3 catalyst was dispersed in 10 ml of ethanol and 40 µL of 5 wt% Nafion® solution. The air 4 electrode was prepared by spraying the catalyst slurry onto a gas diffusion layer (Toray TGP-5 H-090, 2 cm \times 2 cm) to achieve a loading of 2 mg cm⁻². A clean zinc plate (thickness: 0.8 6 mm, Shengshida Metal Mater. Co. Ltd., China) was used as the anode, and the electrolyte 7 was a 6 M KOH solution. The polarization curve and power density were obtained by using a 8 galvanodynamic method (a current density ranging from 0 to 1000 mA cm⁻²). For the long-9 term studies, the cell OCV and the power density were measured during a continuous power 10 11 generation mode, where a total of 30 pieces of zinc plates was replaced including the electrolyte. And the charge-discharge cycling experiments were operated through the 12 recurrent galvanic pulse method. 13



Fig. S1 XPS spectrum of composite-3h obtained before (a, c and e) and after (b, d and f) full-1



3 region and (e) (f) Ca 2p region.



Fig. S2 (a) ORR and OER polarization curves of composite-3h, the commercial 20%Pt/C and IrO₂/C. (b) ORR and OER polarization curves of composite-3h, composite-3h-CNT0, pure MnO₂, pure La₂O₃/MnO₂ and pure CNTs catalysts. (c) RDE curves with composite-3h nanocomposite catalyst loaded on a glassy carbon substrate in an oxygen-saturated 0.1 M KOH electrolyte at various rotation rates. (d) the corresponding Koutecky–Levich plots obtained from Fig. S1c at different potentials.



Fig. S3 (a) ORR and OER polarization curves of composite-3h-200°C, composite-3h-300°C composite-3h and composite-3h-500°C nanocomposite catalysts. (b) ORR and OER polarization curves of composite-1h, composite-3h and composite-5h nanocomposite catalysts. (c) ORR and OER polarization curves of composite-3h-CaO0, composite-3h-CaO0, composite-3h-CaO0.5, composite-3h and composite-3h-CaO2 nanocomposite catalysts. (d) ORR and OER polarization curves of composite-3h-CNT0.05, composite-3h and composite-3h and composite-3h-CNT0, composite-3h-CNT0.05, composite-3h and composite-3h and composite-3h-CNT0.15 nanocomposite catalysts.



Fig. S4 (a) Typical discharge curves of zinc-air fuel cell with commercial 20% Pt/C and 14 composite-3h as the air cathode under a continuous discharging process until the complete 15 consumption of zinc plate at 6 M KOH, (Inset: long-time discharge curve). (b) Charge and 16 discharge polarization (V-i) curves of the rechargeable Zn-air battery using the commercial 17 20%Pt/C, IrO₂/C cathode. and composite-3h the 18 as



Sample	ORR: E _{half}	OER: E(V)	$\Delta E/V$	Reference
	(V)	at $j=1 \text{ mA cm}^{-2}$	$(E_{OER}-E_{ORR})$	
Pt/C	0.85	1.71	0.86	This work
IrO ₂ /C	0.60	1.57	0.97	This work
CNTs	0.54	1.73	1.19	This work
MnO ₂	0.78	1.65	0.87	This work
La ₂ O ₃ /MnO ₂	0.49	1.71	1.22	This work
Composite-3h-200 °C	0.83	1.62	0.79	This work
Composite-3h-300 °C	0.84	1.62	0.78	This work
Composite-3h-500 °C	0.41	1.73	1.32	This work
Composite-1h	0.35	1.71	1.36	This work
Composite-3h	0.83	1.6	0.77	This work
Composite-5h	0.61	1.66	1.05	This work
Composite-3h-CNT0	0.65	1.66	1.1	This work
Composite-3h-CNT0.05	0.54	1.63	1.09	This work
Composite-3h-CNT0.15	0.67	1.67	1	This work
Composite-3h-CaO0	0.52	1.65	1.13	This work
Composite-3h-CaO0.5	0.83	1.62	0.79	This work
Composite-3h-CaO2	0.64	1.66	1.02	This work
FCO/HrGOS	0.77	1.61	0.84	1
CoFe ₂ O ₄ /rGO	0.78	1.57	0.79	2
CaMnO ₃ microsphere	0.76	1.9	1.14	3
CaMn ₃ O ₆	0.77	1.85	1.08	3
FMC-3	0.80	1.59	0.79	4
La2O3/Co3O4/MnO2-CNTs	0.84	1.59	0.76	5

Table S2 Comparison of bifunctional oxygen electrochemical activities of different
electrocatalysts in this work and literatures.

1 References

- 2 1 W. N. Yan, Z. R. Yang, W. Y. Bian and R. Z. Yang, Carbon 2015, 92, 74-83.
- 3 2 W. Y. Bian, Z. R. Yang, P. Strasser and R. Z. Yang, J. Power Sources, 2014, 250, 196-203.
- 4 3 X. P. Han, T. R. Zhang, J. Du, F. Y. Cheng and J. Chen, Chem. Sci., 4 (2013) 368-376.
- 5 4 N. N. Xu, X. M. Li, H. R. Li, Y. N. Wei and J. L. Qiao, Science Bulletin, 2017, 62, 12166 1226.
- 7 5 N. N. Xu, J. L. Qiao, X. Zhang., C. Y. Ma, S. S. Jian, Y. Y. Liu and P.C. Pei, Applied
- 8 Energy, 2016, 175, 495-504.