## **Electronic supplementary information**

## Direct utilization of light energy to promote the power density of zinc-air batteries using $Co_3O_4$ (a) Cu<sub>x</sub>O air photocathodes with porous octahedral superstructures

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Fig. S1. XRD (a) and EDX (b) patterns of CuBTC (a) and ZIF67@CuBTC (a and b).



Fig. S2. SEM images of CuBTC (a and b) and ZIF67@CuBTC (c and d).



**Fig. S3.** UV-Vis-NIR spectra of the Cu<sub>x</sub>O and Co<sub>3</sub>O<sub>4</sub>@Cu<sub>x</sub>O samples.



**Fig. S4.** Tafel plots of OER (a) and ORR (b) for the  $Cu_xO$  and  $Co_3O_4@Cu_xO$  samples obtained under light on and off conditions, respectively.



Fig. S5. CV curves collected from the non-Faradaic regions of the  $Cu_xO$  (a) and  $Co_3O_4@Cu_xO$  (b) samples, respectively.



**Fig. S6.** Optical images of the building components of a ZAB cell: the air cathode (a, composed of water-proof membrane, nickel foam, and  $Co_3O_4@Cu_xO/PTFE/$  acetylene black film), and the Zn foil anode (b, with a punched hole for light passing through).



**Fig. S7.** The SEM image (a) and XRD pattern (b) of the  $Co_3O_4@Cu_xO$  sample after cycling test.



**Fig. S8.** A demonstration of a red LED lighted up by two connected ZAB cells (a), and power densities of the  $Co_3O_4@Cu_xO$ -based ZABs obtained with light on and off conditions, respectively. The power densities were calculated by the discharge current densities shown in Fig. 4c.



**Fig. S9.** Optimized atomic configurations of OOH\* adsorbed on  $Co_3O_4(311)$  (a), CuO(-111) (b), Cu<sub>2</sub>O(200) (c), and  $Co_3O_4$ @Cu<sub>x</sub>O heterojunction(d), respectively.



Fig. S10. Free energy diagrams at 0.68 V of OER processes on  $Cu_xO$  and  $Co_3O_4@Cu_xO$ , respectively.

Typ e	Cathode materials	Charge voltage /V		Current density	Light	Cycling /h	Capacity / mA h g <sup>-1</sup>	Power density	Ref.
		Dark Light /m	/mA cm <sup>-2</sup>	/%			/mW cm <sup>-2</sup>		
Photo-enhanced ZABs	Co <sub>3</sub> O <sub>4</sub> @Cu <sub>x</sub> O	1.837	1.748	0.1	31	160	759.1 2	76	This work
	α-Fe <sub>2</sub> O <sub>3</sub>	1.97	1.43	0.1	27.4	/	598.7	75.49	[1]
	BiVO <sub>4</sub>	1.96	1.20	0.1	38.8	/	538.5	69.24	[1]
	Co <sub>3</sub> O <sub>4</sub>	2.10	2.00	2	5.00	70	769	/	[2]
	NiCo <sub>2</sub> S <sub>4</sub>	1.97	1.92	2	2.54	12	734	/	[3]
	Ni <sub>2</sub> P <sub>5</sub> @NCNT	1.94	1.90	10	2.10	8.8	640	190	[4]
	PTTH	2.08	1.92	0.1	7.69	316	/	/	[5]
	CuO/ZnO	2.27	1.5	0.05	33.7	3	333.5	34.01	[6]
	$TiO_2 @In_2Se_3 @Ag_3P \\O_4$	/	0.64	0.1	/	210	/	13.1/	[7]
	g-C <sub>3</sub> N <sub>4</sub> -CuZIF-67	2.01	1.94	2	3.5	20	781.7	/	[8]
<b>Conventional ZABs</b>	Co <sub>2</sub> FeO <sub>4</sub> @NCNTs	2.32	/	50	/	100	/	90.68	[9]
	Co <sub>3</sub> O <sub>4-x</sub> @C	2.07	/	10	/	358	/	54.5	[10]
	Co@Co <sub>3</sub> O <sub>4</sub> @NAC	2.10	/	5	/	36	721	164	[11]
	Fe <sub>3</sub> C/Fe <sub>2</sub> O <sub>3</sub> @NGNs	2.11	/	10	/	40	722	139.8	[12]
	FeN <sub>x</sub> /C	2.08	/	5	/	84	/	36	[13]

**Table S1.** A comparison of the air cathode materials for ZABs with and without light enhancements.

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