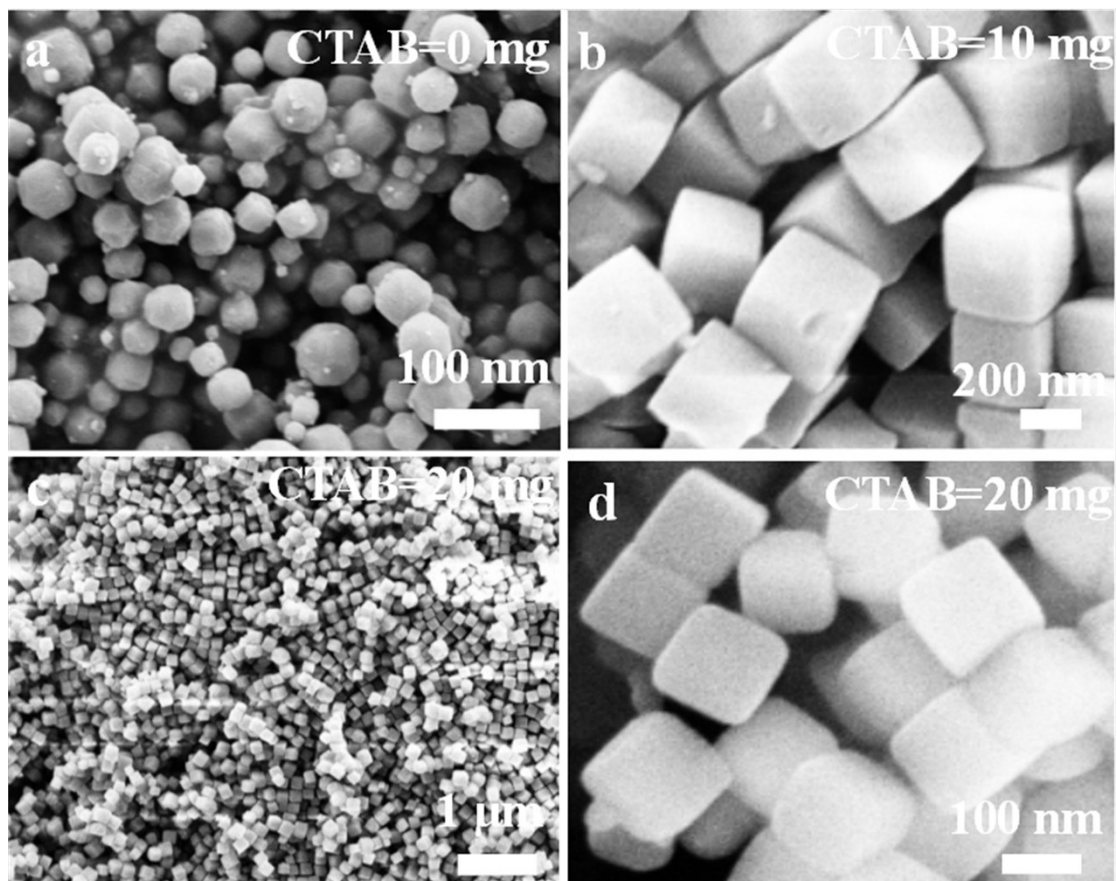


## Supporting Information

### **Electrospun ZIF Derived cavity porous carbon nanofibers as freestanding cathode for lithium-oxygen batteries with ultralow overpotential**

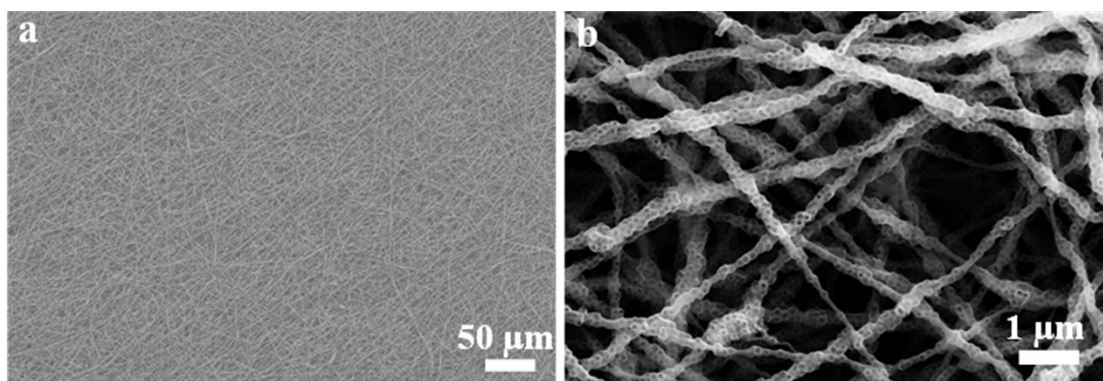
*School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China; Beijing Key Laboratory of Resource-oriented Treatment of Industrial pollutants, Beijing 100083, China*

Corresponding author: [congjuli@126.com](mailto:congjuli@126.com)

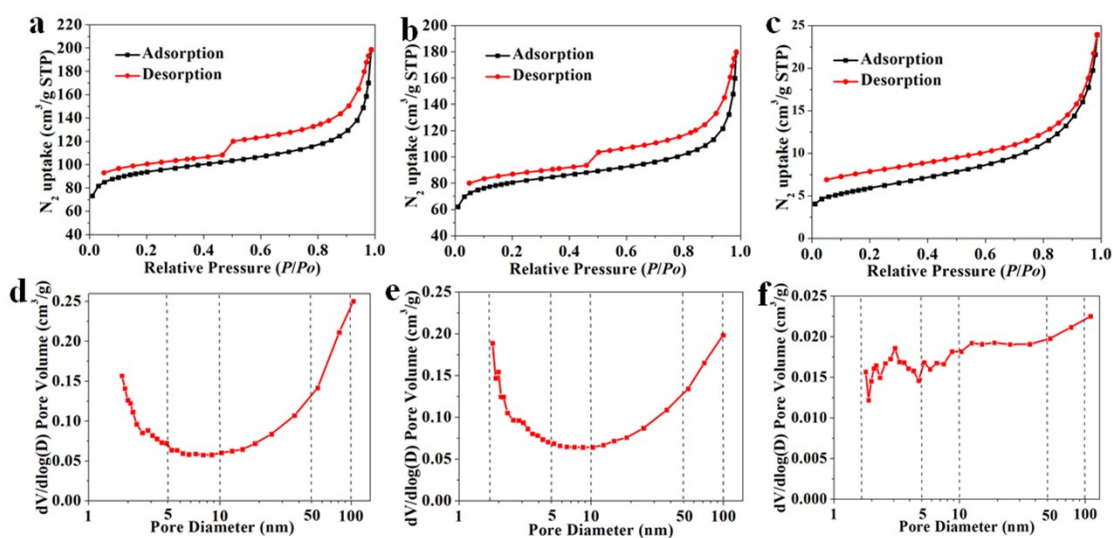


**Fig. S1.** SEM images of (a, b) pure ZIF-8 and cubic ZIF-8 prepared with CTAB contents of 0, 10 mg and (c-d) pure cubic ZIF-8 prepared with CTAB contents of 20 mg at different magnifications.

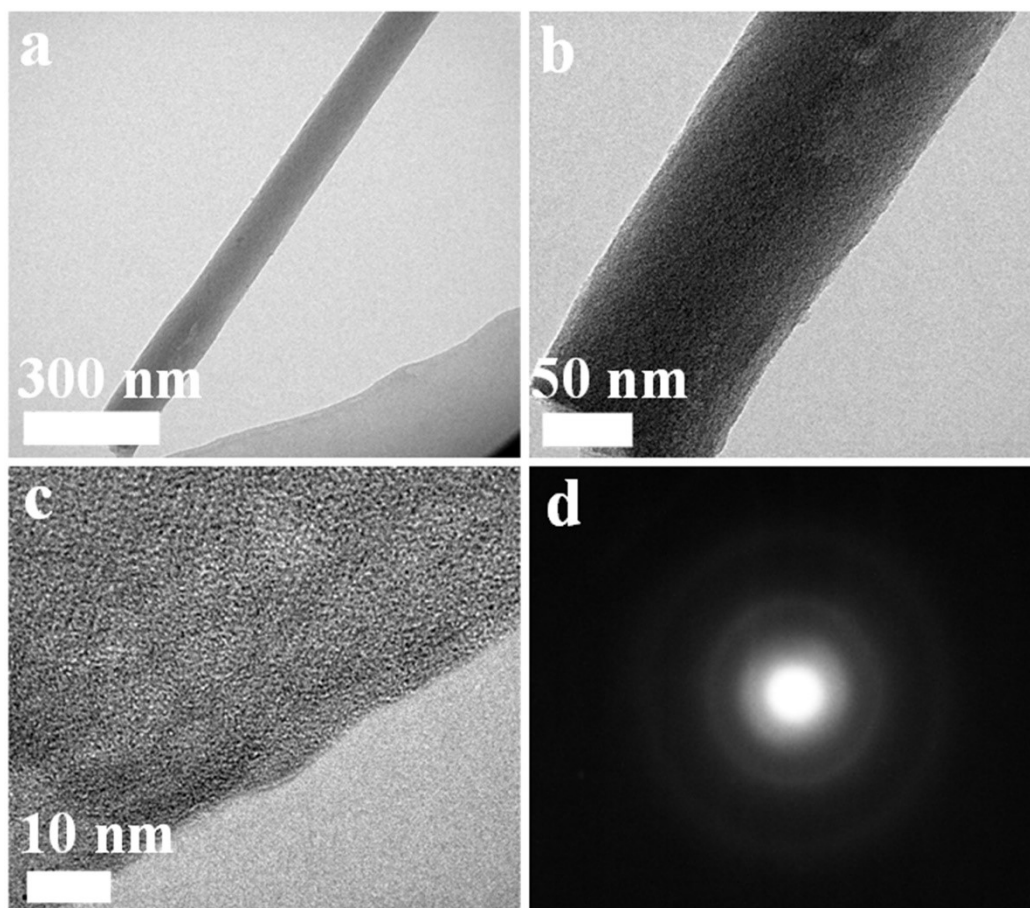
The average sizes are determined as 380 and 150 nm for the cubic ZIF-8 when the added CTAB amounts are 10 and 20 mg, respectively. The more CTAB added, the faster the nucleation speed and the smaller the size.



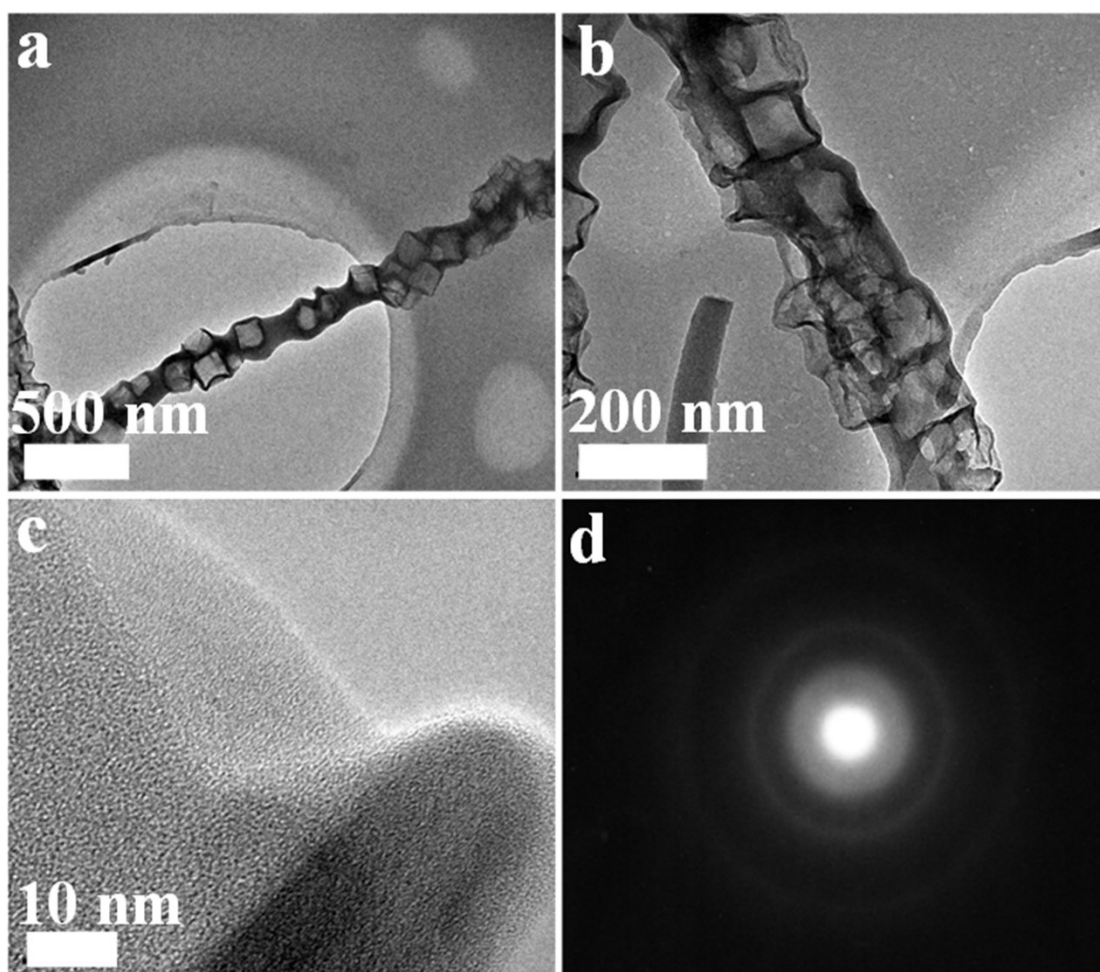
**Fig. S2.** FE-SEM images of Zn/CoNC@CPCFs, respectively (different magnification).



**Fig. S3.** Nitrogen adsorption isotherms and pore size distribution curves of Zn/CoNC@CPCFs (a, d), ZnNC@CPCFs (b, e) and CoNC@CFs (c, f).



**Fig. S4.** TEM image (a-c) and HRTEM image (d, inset of corresponding SAED pattern) of CoNC@CFs.



**Fig. S5.** TEM image (a-c) and HRTEM image (d, inset of corresponding SAED pattern) of ZnNC@CPCFs.

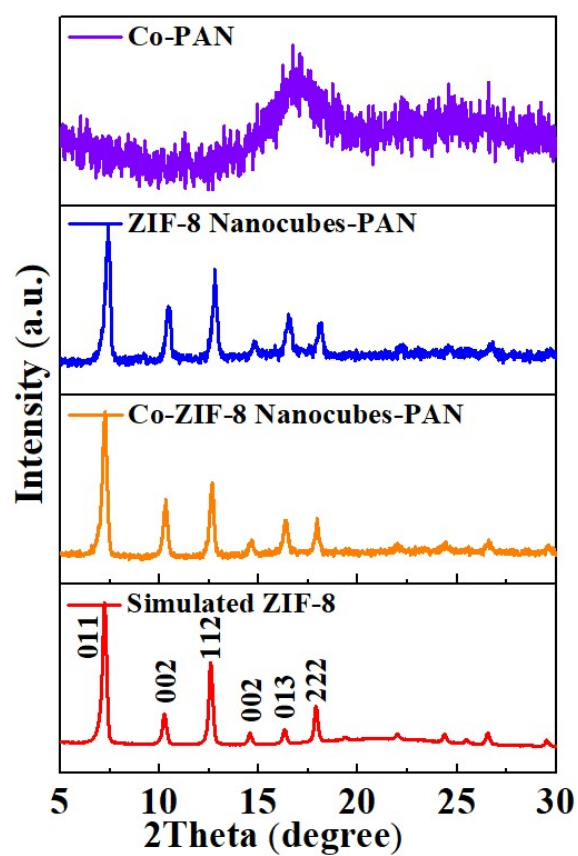
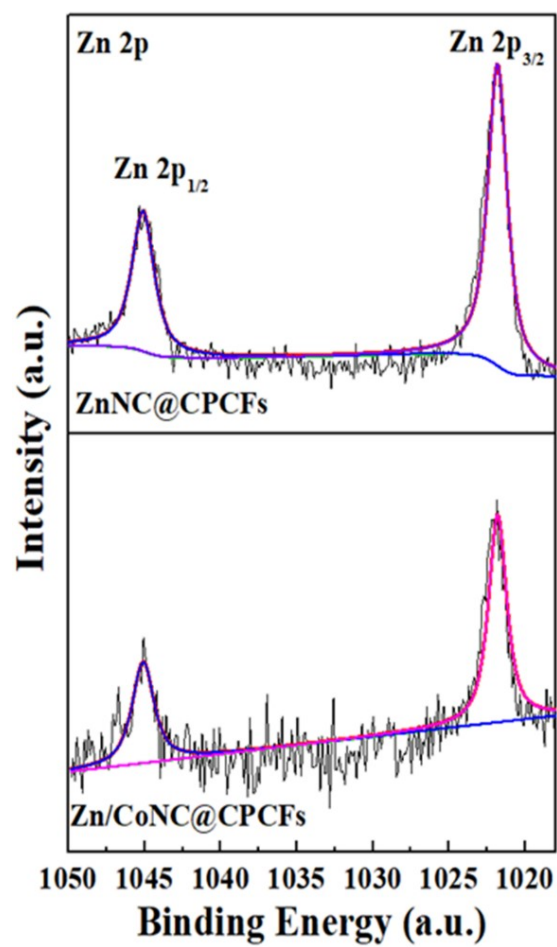
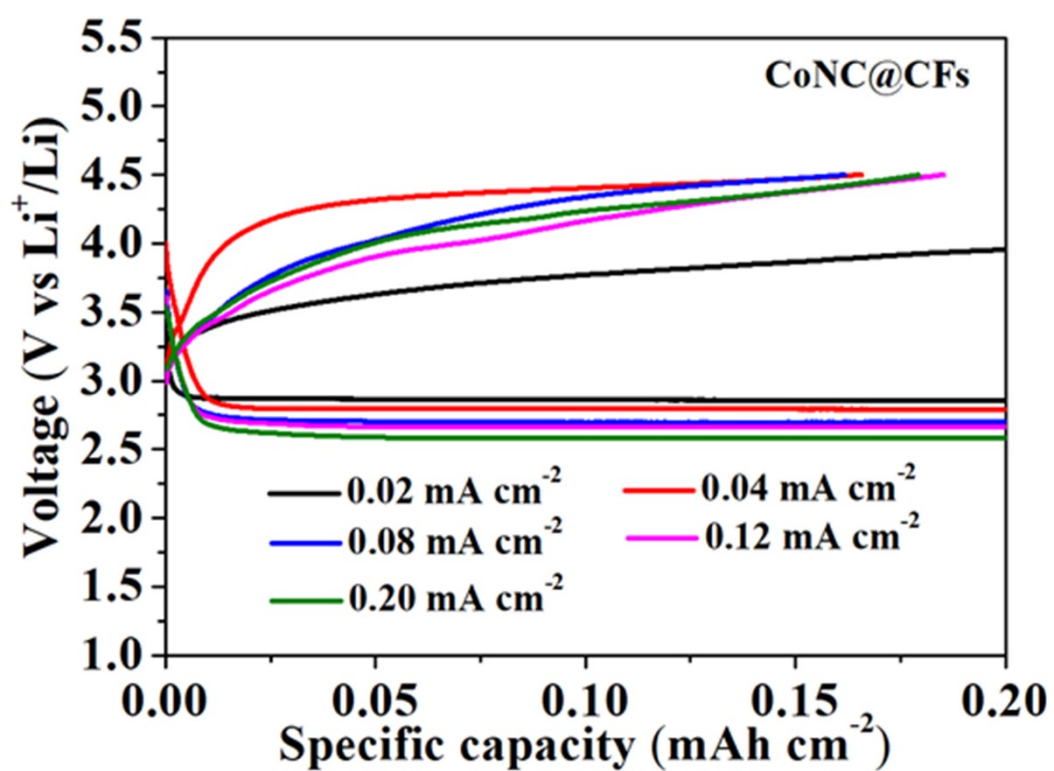


Fig. S6. XRD patterns of as-prepared three samples.

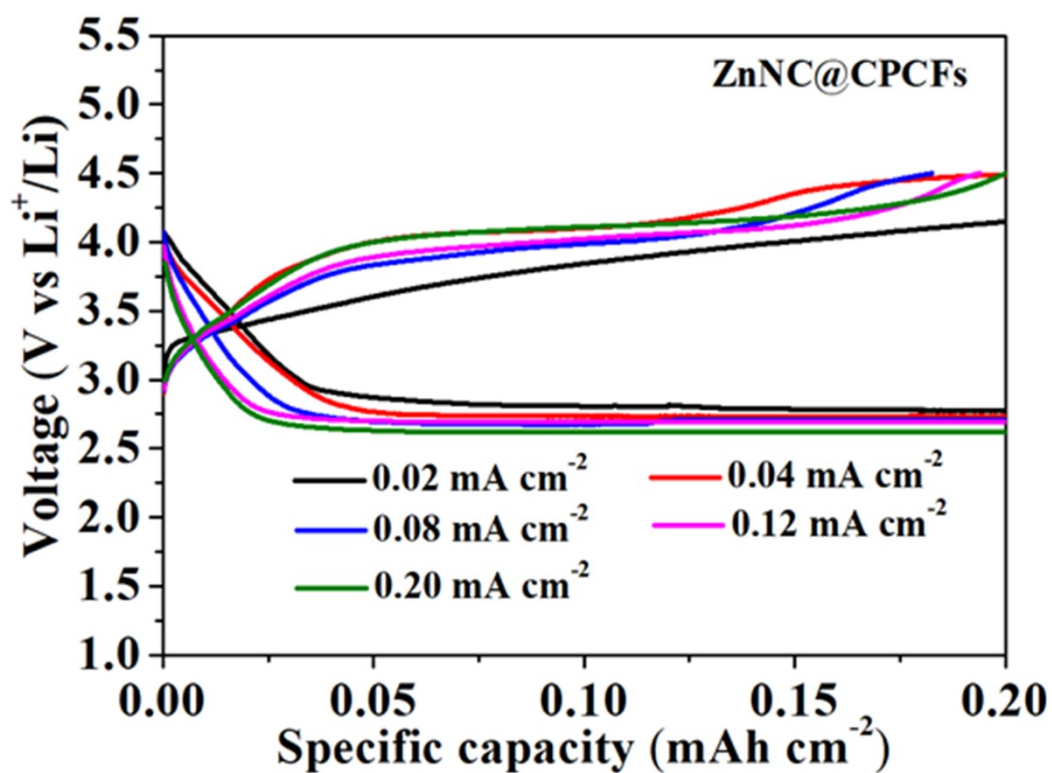


**Fig. S7.** The X-ray photoelectron spectroscopy (XPS) measurement.

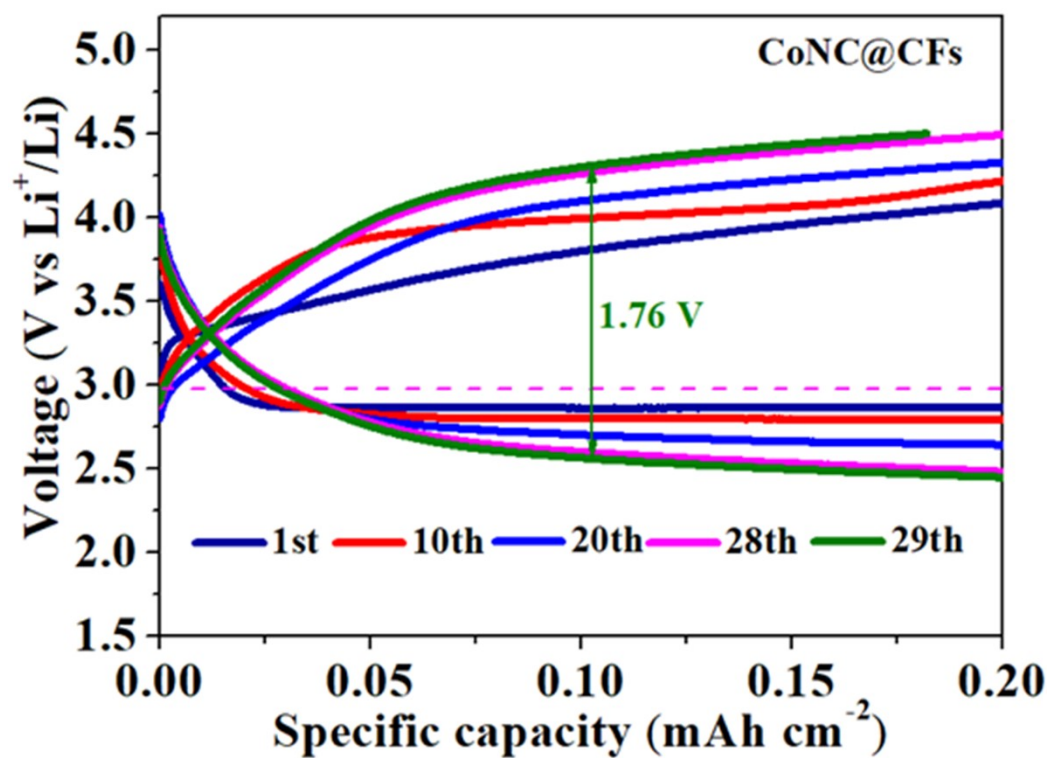


**Fig. S8.** Discharge–charge voltage curves of CoNC@CFs electrodes at different current densities with a cut-off capacity of 0.20 mAh cm<sup>-2</sup>.

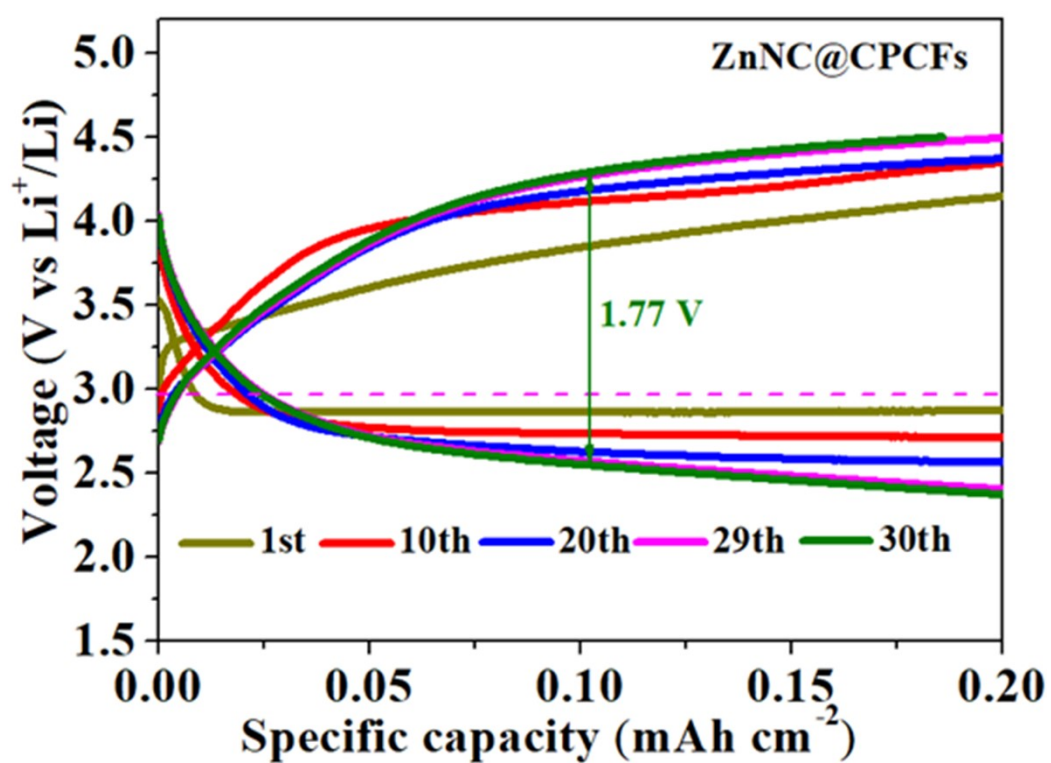




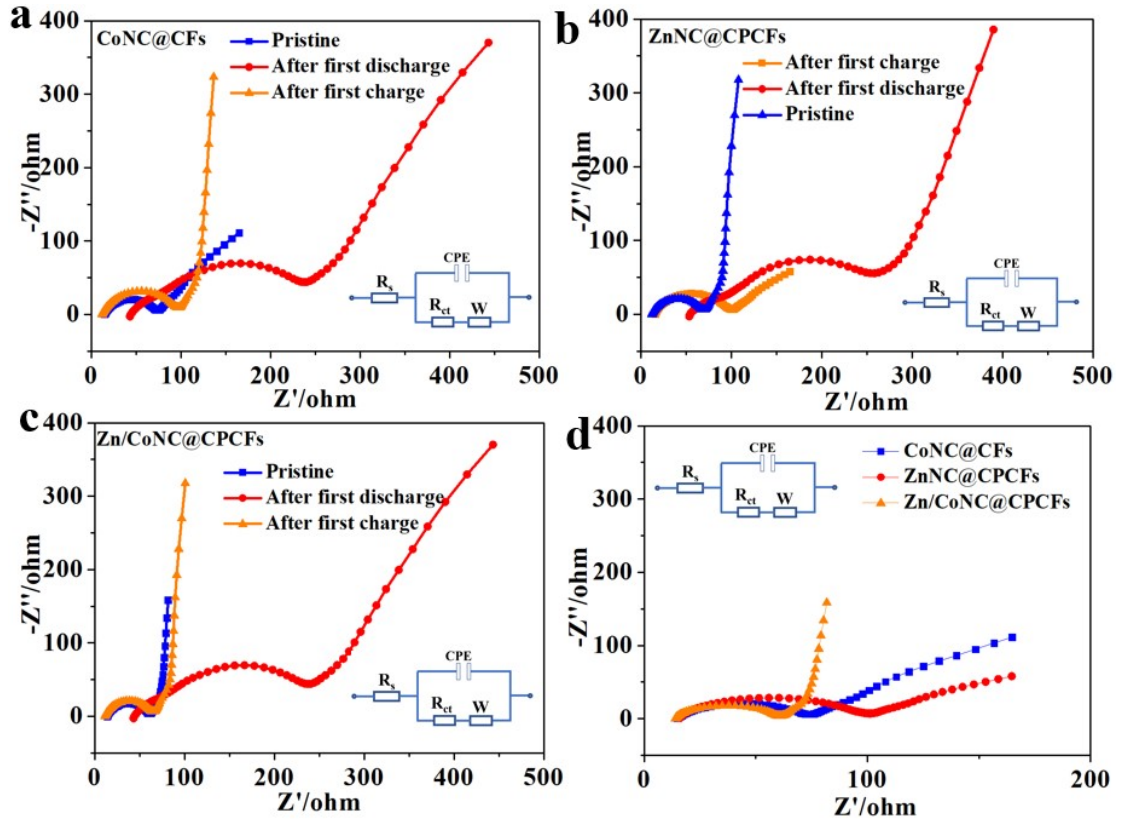
**Fig. S9.** Discharge-charge voltage curves of ZnNC@CPCNFs electrodes at different current densities with a cut-off capacity of 0.20 mAh cm<sup>-2</sup>.



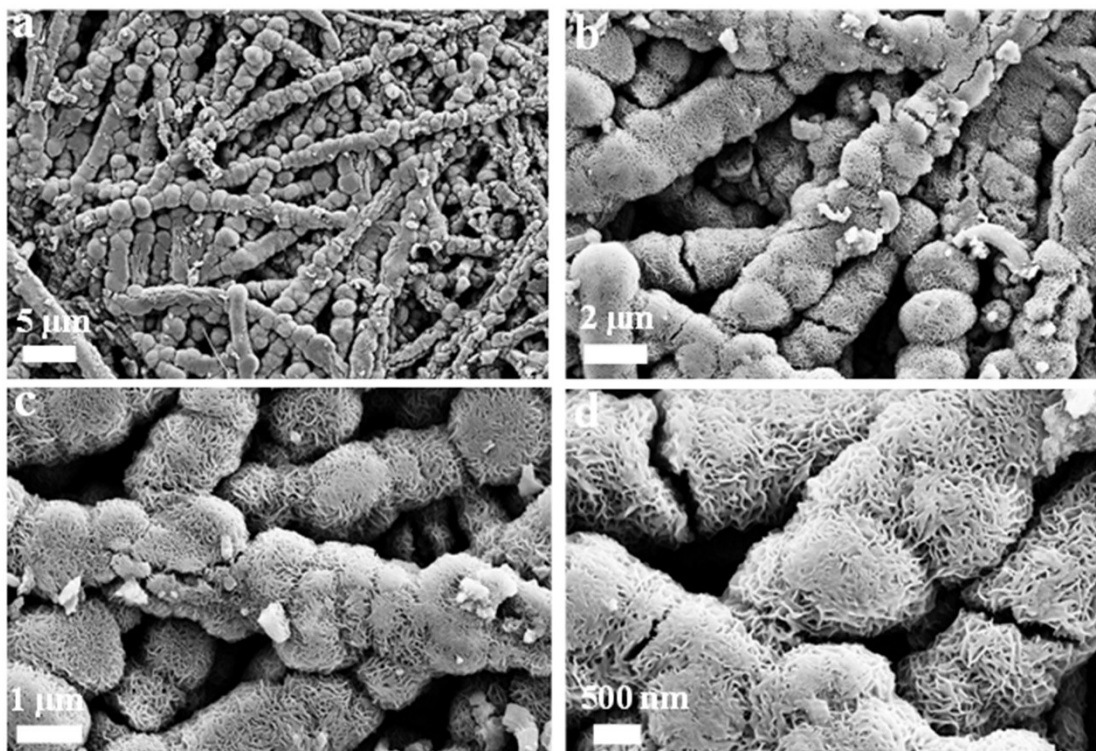
**Fig. S10.** Cycle performance of CoNC@CNFs electrodes at a current density of  $0.02 \text{ mA cm}^{-2}$ .



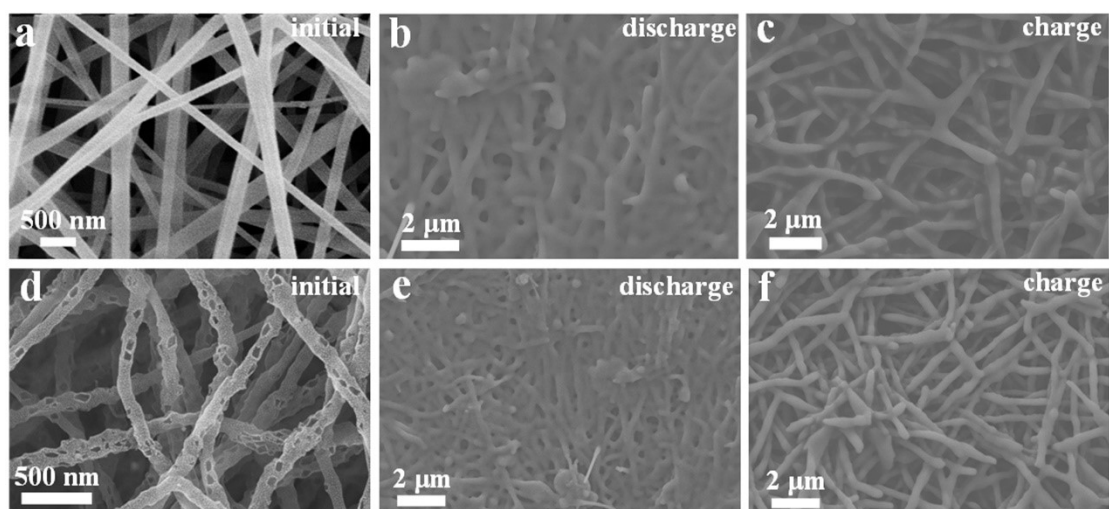
**Fig. S11.** Cycle performance of ZnNC@CPCNFs electrodes at a current density of 0.02 mA cm<sup>-2</sup>.



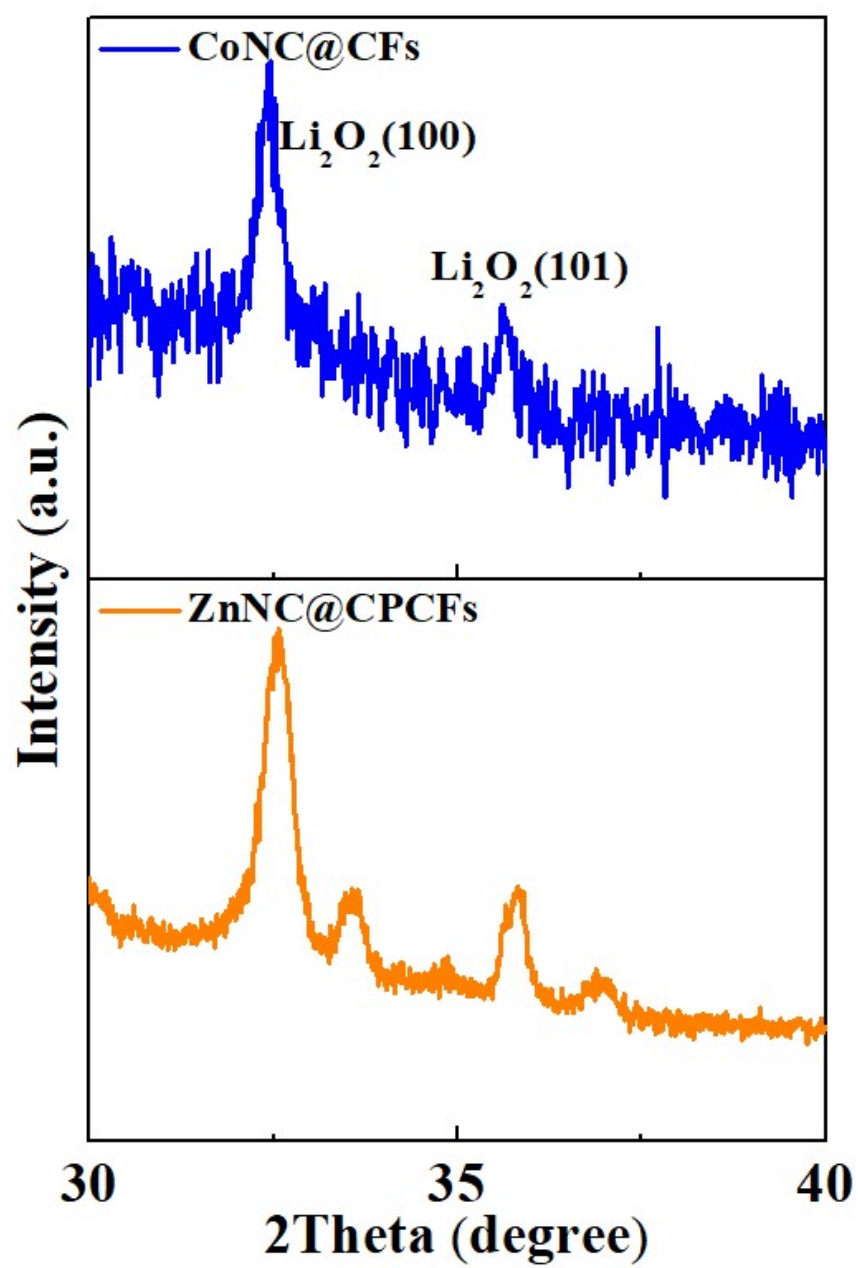
**Fig. S12.** Nyquist plots of Li-O<sub>2</sub> cells with different fabricated air-cathodes under different cycling conditions of original state, discharge to 6 mAh cm<sup>-2</sup>, and charge to 6 mAh cm<sup>-2</sup> (a-c); comparison of the Nyquist plots of three kinds air-cathodes of Li-O<sub>2</sub> cells in the original state (d).



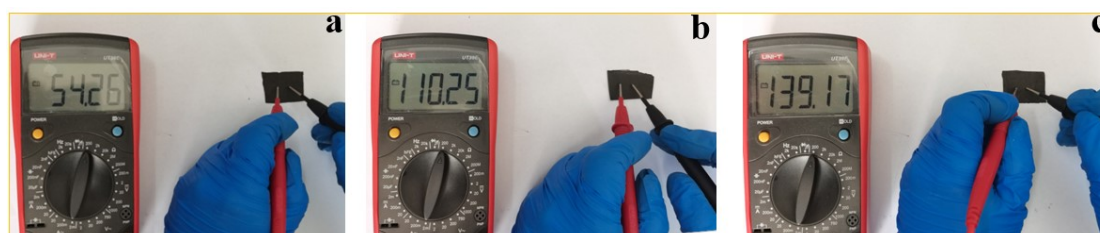
**Fig. S13.** (a–d) the corresponding SEM images of Zn/CoNC@CPCNFs electrode at a discharge capacity of 6 mAh cm<sup>-2</sup>.



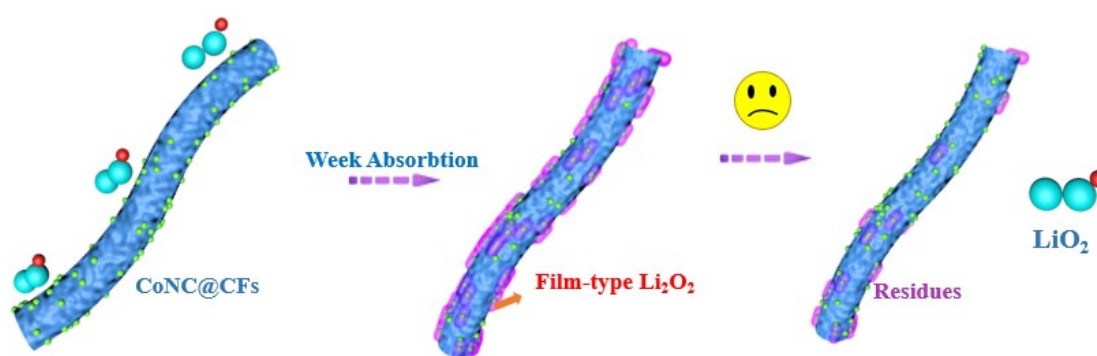
**Fig. S14.** (a–c) the corresponding SEM images of CoNC@CNFs electrode at different discharge and charge states; (d–f) the corresponding SEM images of ZnNC@CPCNFs electrode at different discharge and charge states.



**Fig. S15.** XRD patterns of ZnNC@CPCFs and CoNC@CFs electrodes upon recharge.



**Fig. S16.** the value of conductivity of fabricated three electrode. (a) Zn/CoNC@CPCFs; (b) ZnNC@CPCFs; (c) CoNC@CFs.



**Fig. S17.** Schematic diagram of the working mechanism of CoNC@CFs electrodes.

**Table S1.** The information of BET surface area, total pore volume, pore width of as-prepared three samples.

Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{total}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{micro}}$ ( $\text{cm}^3/\text{g}$ )	Pore width (nm)	Pore size (nm)
Zn/CoNC@CPCFs	321.78	0.307	0.100	3.825	~2.0, 100
CoNC@CFs	20.90	0.037	0.003	7.088	~2.0, 100
ZnNC@CPCFs	276.85	0.278	0.084	4.022	~2.0, 100

**Table S2.** The surface atom percentage of Zn/CoNC@CPCFs, ZnNC@CPCFs and CoNC@CFs.

Samples	Percentage of different elements (%)				
	C	Zn	Co	N	O
Zn/CoNC@CPCFs	69.67	3.55	1.65	8.00	17.43
CoNC@CFs	69.93		10.68	6.81	12.58
ZnNC@CPCFs	77.58	8.99		7.09	6.35

**Table S3.** ICP-OES results of Zn/CoNC@CPCFs catalysts.

Catalyst	Co (wt%)
Zn/CoNC@CPCFs	1.80



**Table S4.** The terminal value discharge/charge voltage difference.

Catalyst	terminal value discharge/charge voltage difference (V)			
	0.02 mA cm <sup>-2</sup>	0.04 mA cm <sup>-2</sup>	0.08 mA cm <sup>-2</sup>	0.12 mA cm <sup>-2</sup>
Zn/CoNC@CPCFs	0.36	0.78	0.99	1.16
ZnNC@CPCFs	1.49	1.73	1.80	1.88
CoNC@CFs	1.40	1.73	1.84	1.92

**Table S5.** The detailed values of  $R_{ct}$  and  $R_s$  of the EIS equivalent circuit.

Catalyst	Pristine		After first discharge		After first charge	
	$R_{ct}$ ( $\Omega$ )	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$R_s$ ( $\Omega$ )
Zn/CoNC@CPCFs	49.4	12.8	195.7	43.6	51.8	13.4
ZnNC@CPCFs	86.2	15.8	210.2	53.2	85.0	16.5
CoNC@CFs	60.3	14.6	195.7	43.6	83.8	14.0

**Table S6.** Comparison of various catalysts in their half-recharge overpotential and discharge capacity.

Catalyst	Half-recharge Overpotential	Specific capacity	Current density (mA cm <sup>-2</sup> )	Ref
Zn/CoNC@CPCFs	0.59 V	12451 mAh g <sup>-1</sup> (12.12 mAh cm <sup>-2</sup> )	0.02	This work
Ru <sub>0.3</sub> SAs-NC	1.21 V	13424 mAh g <sup>-1</sup>	0.02	[1]
CMPACs-Fe		7800 mAh g <sup>-1</sup>	0.02	[2]
C <sub>p</sub>	1.44 V	20300 mAh g <sup>-1</sup>	0.02	[3]
Ru/ITO	0.67 V	2.5 mAh cm <sup>-2</sup>	0.025	[4]
Ag/ $\beta$ -MnO <sub>2</sub>	0.96 V	811 mAh g <sup>-1</sup>	0.02	[5]
CA	0.78 V	500 mAh g <sup>-1</sup>	0.02	[6]

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