Supporting Information

Co_3O_4 Hollow Nanospheres Doped with $ZnCo_2O_4$ via Thermal Vapor Mechanism for Fast Lithium Storage

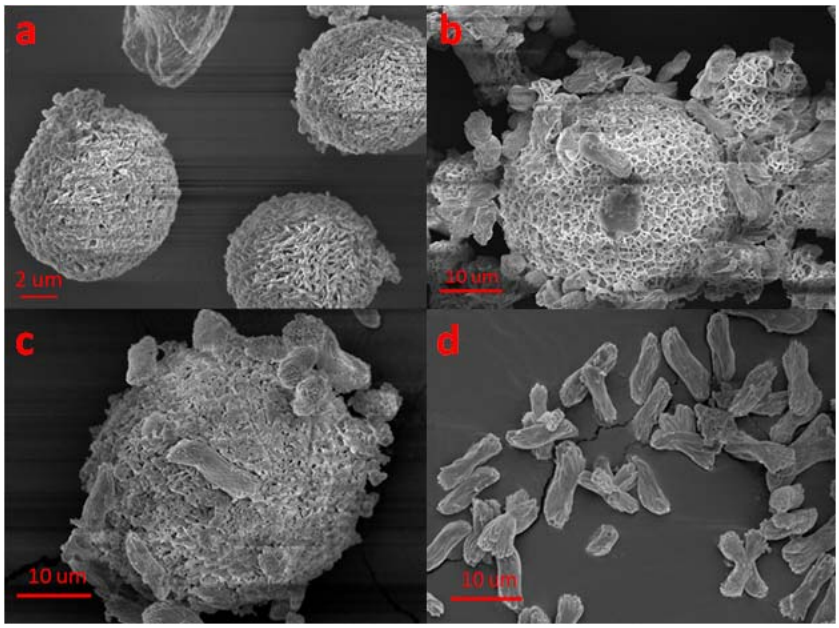

Fig. S1 SEM images of as-prepared ZnCoMOF. (a) Use of 1.3mmol H_2BDC for 12h. Use of 3.5mmol H_2BDC for (b) 3h, (c) 8h and (d) 12h.

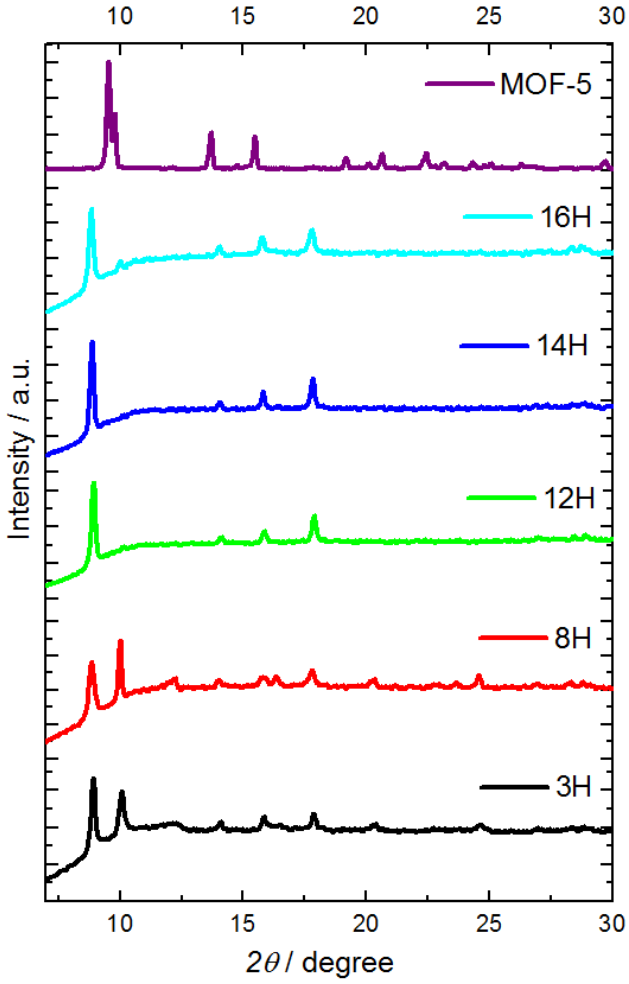

Fig. S2 XRD patterns of as-prepared MOF using 3.5mmol H_2BDC by solventhermal (ST) reaction for 3, 8, 12, 14 and 16 hrs in comparison with the XRD pattern of MOF-5.

Table S1 Ratios of Co to Zn in the prepared MOFs.

ZnCoMOF	H_2BDC	Reaction time	Co:Zn ratio
ZnCoMOF(3.5mmol, 3h)	3.5mmol	3h	5.3
ZnCoMOF(3.5mmol, 8h)	3.5mmol	8h	5.0
ZnCoMOF(3.5mmol, 12h)	3.5mmol	12h	4.4
ZnCoMOF(3.5mmol, 14h)	3.5mmol	14h	4.1
ZnCoMOF(3.5mmol, 16h)	3.5mmol	16h	3.8
ZnCoMOF(1.3mmol, 12h)	1.3mmol	12h	13.4

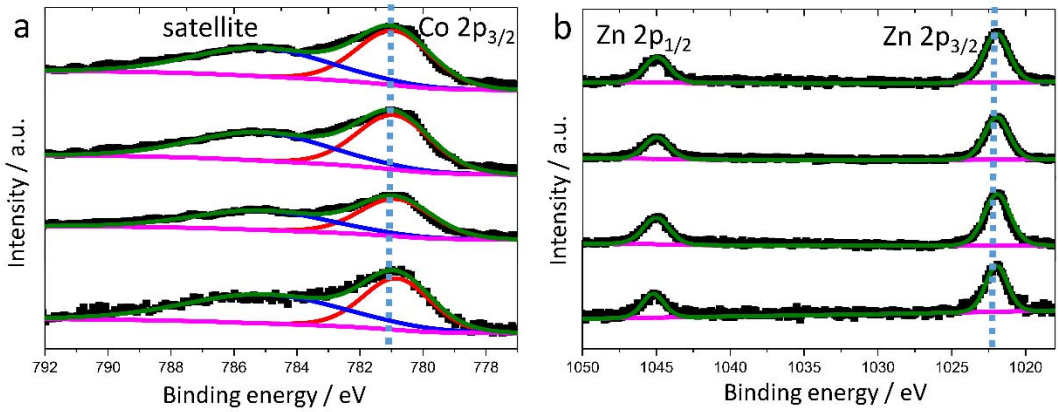

Fig. S3 High resolution XPS of core-level (a) Co $2p_{3/2}$ and (b) Zn 2p of ZnCoMOF using 3.5mmol H_2BDC by solvothermal reaction for 3, 8, 12 and 16h, respectively.

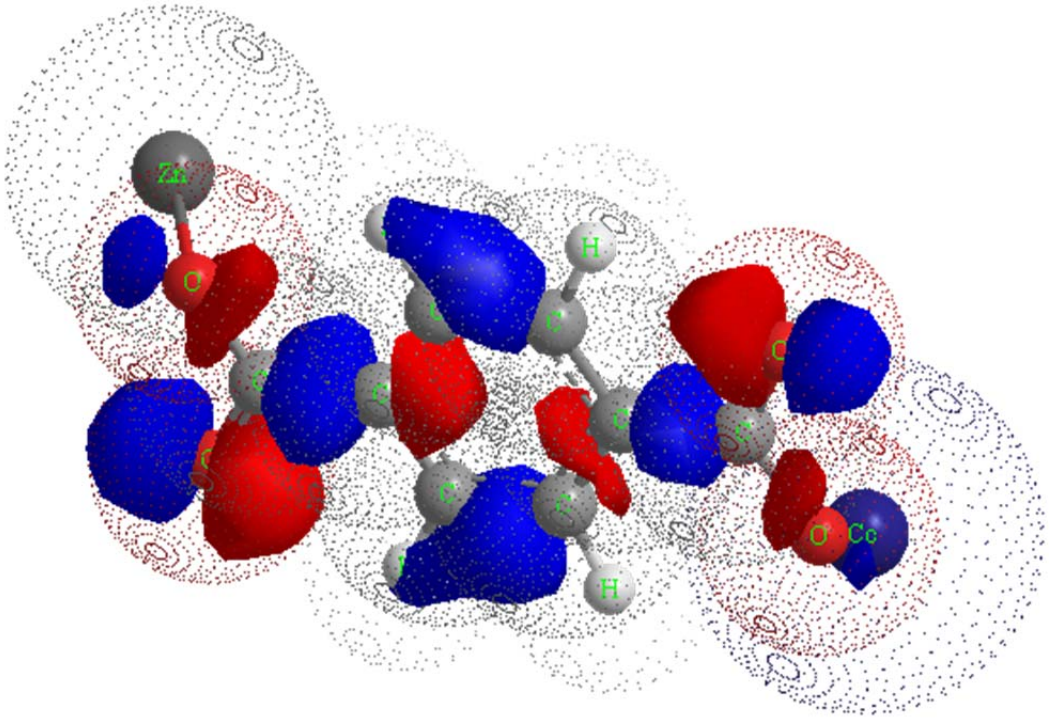

Figure S4 Molecular orbital in the H_2BDC molecule bonded with Co^{2+} and Zn^{2+} ion.

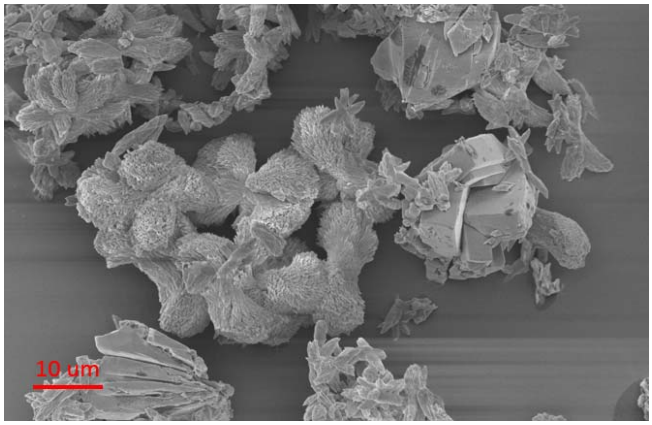

Fig. S5 SEM image of CoMOF using 3.5mmol H_2BDC by solventhermal (ST) reaction for 12 hrs.

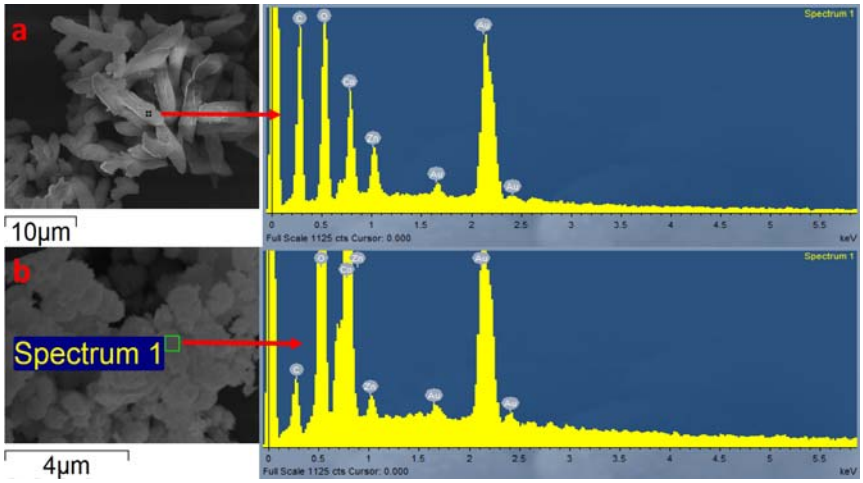

Fig. S6 EDX of (a) ZnCoMOF (3.5mmol, 12h) and (b) Co_3O_4/ZCO decomposed from MOF.

Table S2 Ratios of Co to Zn in the prepared metal oxides.

ZnCoMOF	Metal oxide	Pyrolysis process	Co/Zn ratio
ZnCoMOF(1.3mmol,12h)	CO/ZCO(1.3mmol,12h,2)	550°C-2hAr-350°C-2hAir	34.9
ZnCoMOF(1.3mmol,12h)	CO/ZCO(1.3mmol,12h,10)	550°C-2hAr-350°C-2hAir	29.1
ZnCoMOF(3.5mmol,3h)	CO/ZCO(3.5mmol,3h,2)	550°C-2hAr-350°C-2hAir	6.4
ZnCoMOF(3.5mmol,12h)	CO/ZCO(3.5mmol,12h,2)	550°C-2hAr-350°C-2hAir	17
ZnCoMOF(3.5mmol,16h)	CO/ZCO(3.5mmol,16h,2)	550°C-2hAr-350°C-2hAir	14.2
ZnCoMOF(3.5mmol,12h)	CO/ZCO(3.5mmol,12h,2, 550C-0hAr)	550°C-0hAr	3.3
ZnCoMOF(3.5mmol,12h)	CO/ZCO(3.5mmol,12h,2, 550C-2hAr)	550°C-2hAr	18.4
ZnCoMOF(3.5mmol,12h)	CO/ZCO(3.5mmol,12h,2, 550C-0hAr-350C-2hAir)	550°C-0hAr-350°C-2hAir	3.1
ZnCoMOF(3.5mmol,12h)	CO/ZCO(3.5mmol,12h,2, 350C-2hAir)	350°C-2hAir	3.2

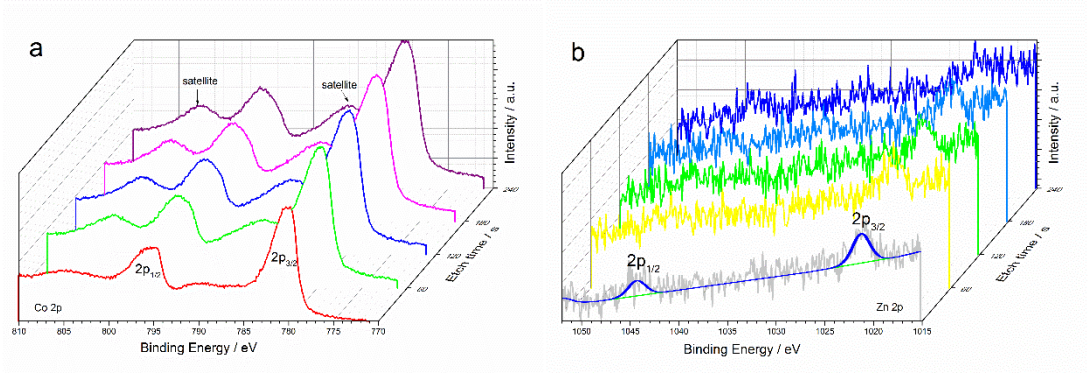

Fig. S7 High resolution XPS of (a) Co and (b) Zn in CO/ZCO (3.5mmol, 12h, 2) by etching from 0-240 s, the etching rate is around 0.2 nm/s.

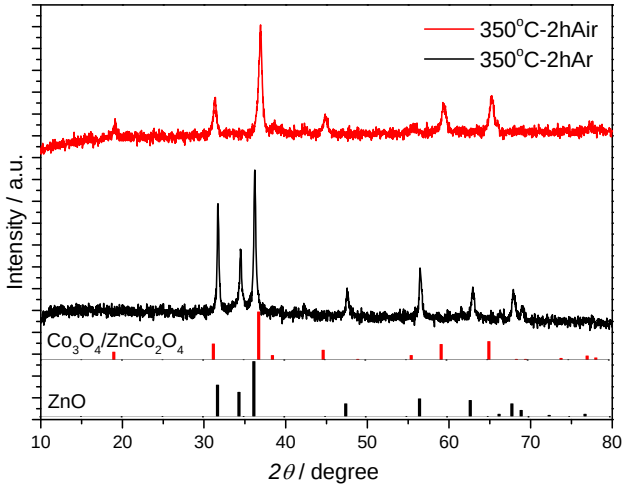

Fig. S8 XRD pattern of the pyrolyzed composite from ZnCoMOF (3.5mmol, 12h) in the air for 2h at slow rate of 2°C min^{-1}.

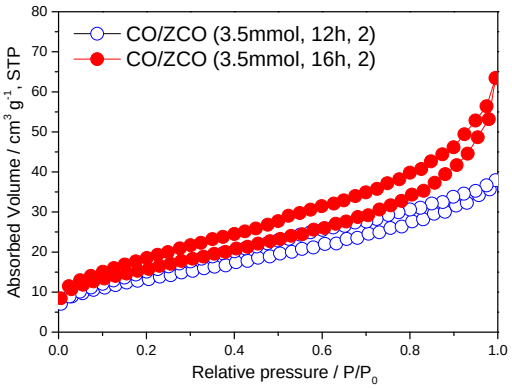

Fig. S9 N_2 isotherms of CO/ZCO (3.5mmol, 12h, 2) and CO/ZCO (3.5mmol, 16h, 2).

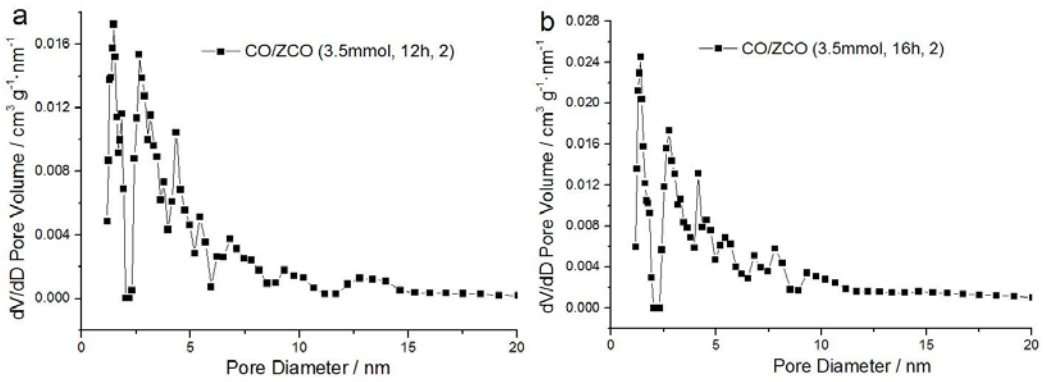

Fig. S10 Pore size distribution of CO/ZCO from DFT model. (a) CO/ZCO (3.5mmol, 12h, 2), (b) CO/ZCO (3.5mmol, 16h, 2)

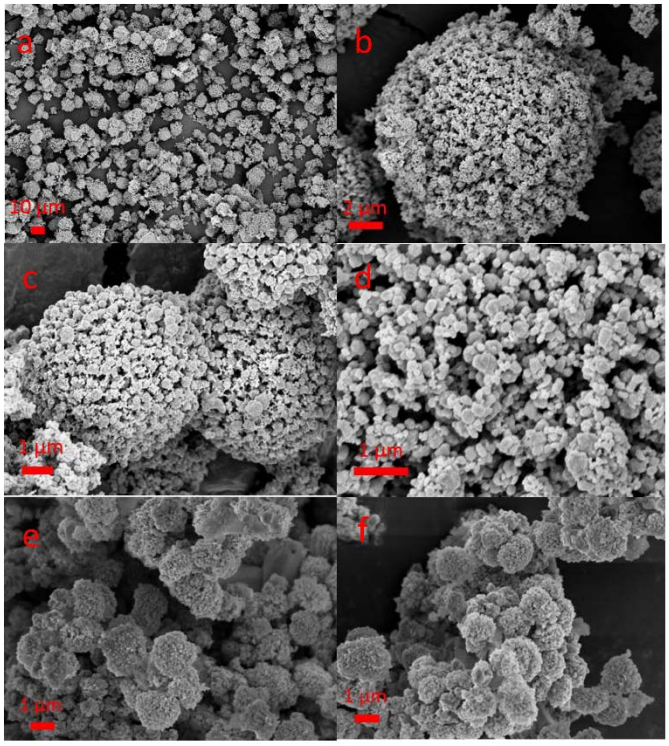

Fig. S11 SEM images of (a, b) CO/ZCO (3.5mmol,3h,2), (c,d) CO/ZCO (3.5mmol,8h,2), (e) CO/ZCO(3.5mmol,3h,10) and (f) CO/ZCO (3.5mmol,8h,2). Samples are the products from the pyrolysis of the as-prepared ZnCoMOF at a same procedure.

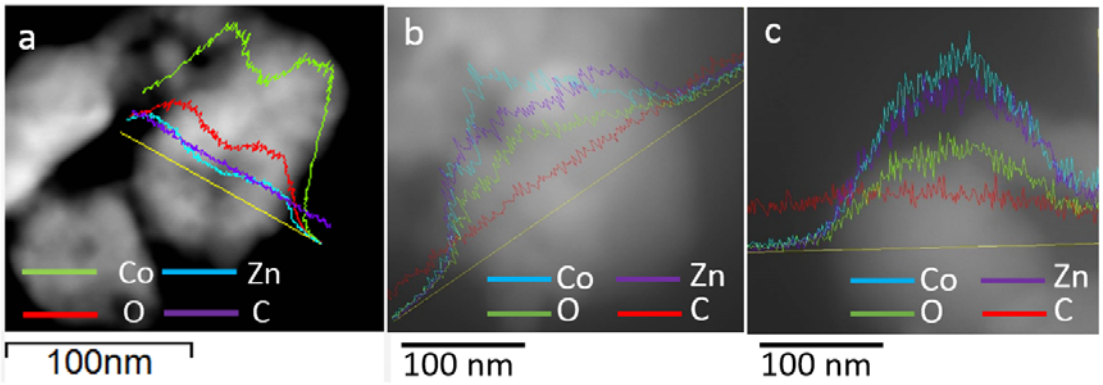

Fig. S12 Line scan mapping of (a) CO/ZCO (3.5mmol, 12h, 2) with small diameter, (b) CO/ZCO (3.5mmol, 12h, 2, 350C-2hAir) with a low temperature of 350 ^{o}C for pyrolysis and (c) CO/ZCO (3.5mmol, 12h, 2, 550C-0hAr-350C-2hAir) with 550 ^{o}C for pyrolysis.

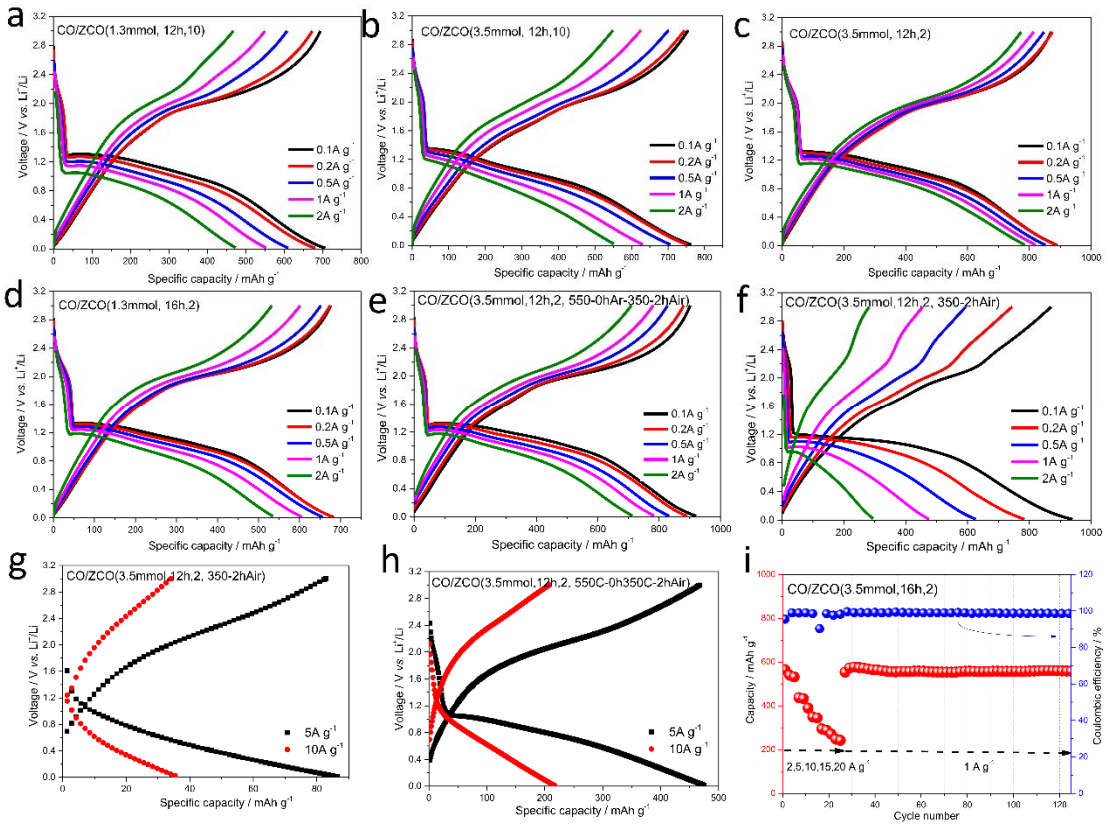

Fig. S13 Charge/discharge curves of (a) CO/ZCO (1.3mmol, 12h, 10), (b) CO/ZCO (3.5mmol, 12h, 10), (c) CO/ZCO (3.5mmol, 12h, 2), (d) CO/ZCO (3.5mmol, 16h, 2), (e) CO/ZCO (3.5mmol, 12h, 2, 550-0hAr-350-2hAir) and (f) CO/ZCO (3.5mmol, 12h, 2, 350-2hAir). High-rate charge-discharge curve at 5 and 10 A g^{-1} of (g) CO/ZCO (3.5mmol, 12h, 2, 350-2hAir) and (h) CO/ZCO (3.5mmol, 12h, 2, 550-0hAr-350-2hAir). (i) The cycling performance at different current rates of 2, 5, 10, 15, 20 and then 1 A g^{-1} of CO/ZCO (3.5mmol, 16h, 2).

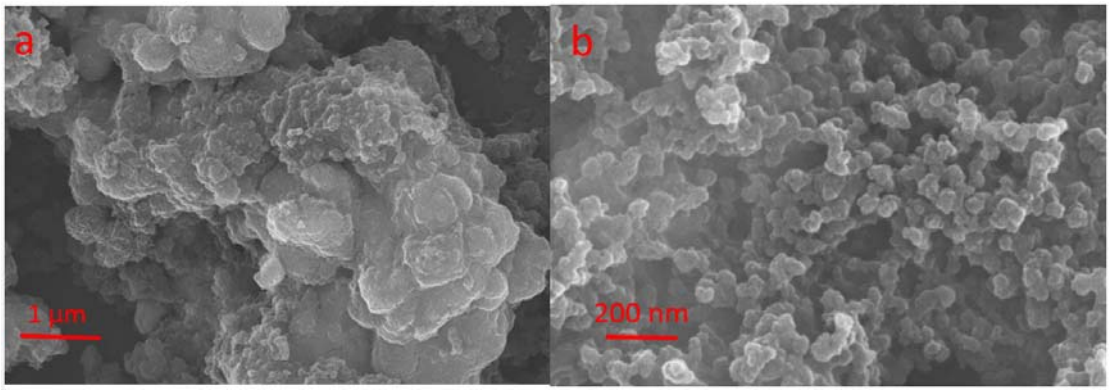

Fig. S14 SEM images of (a) CO/ZCO (1.3mmol, 12h, 10) and (b) CO/ZCO (3.5mmol, 12h, 2) after the long-term cycling at a current rate of 2 A g^{-1}. The electrode material was sonicated in ethanol and drop cast on the flat Si wafer for SEM imaging.

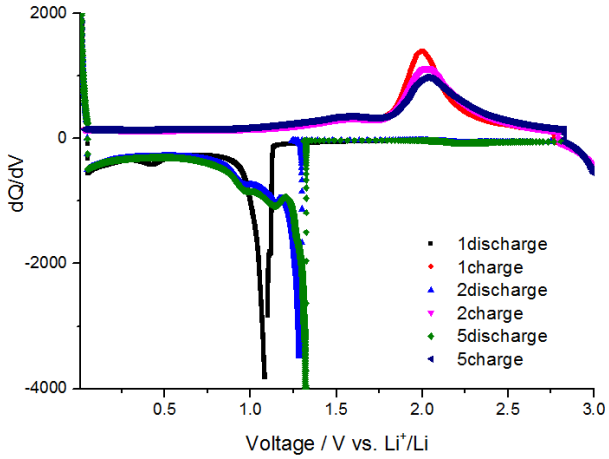

Fig. S15 dq/dV *vs*. Voltage of CO/ZCO (3.5mmol, 12h, 2) for the first 5 cycles at 100 mA g^{-1}.

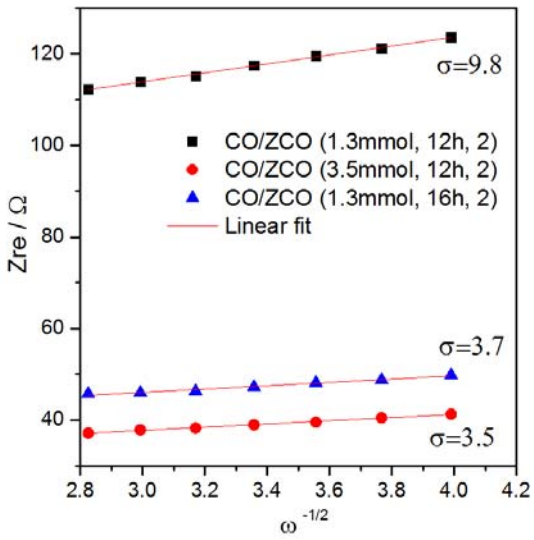

Figure S16 The linear relationship between Zre and $\omega^{-1/2}$.

Table S3 Parameters from equivalent circuit model. The unit for R is ohm, CPE-T is S s^n, C is Faraday, W-R is ohm, W-T is Faraday.

Sample	R	R1	CPE1-T	CPE1-P	R2	C1	W1-R	W1-T	W1-P
CO/ZCO (1.3mmol,12h,2)	31.13	28.72	2E-3	0.32	25.17	4.2E-5	1.06	0.01	0.29
Error/%	1.3	4.36	8.99	3.41	4.06	3.6	479.2	817.6	0.89
CO/ZCO (3.5mmol,12h,2)	7.82	7.56	6.2E-4	0.68	7.18	0.019	35.51	13.52	0.42
Error/%	0.36	0.8	5.58	1.05	3.11	1.88	3.37	4.57	1.1
CO/ZCO (3.5mmol,12h,10)	8.9	13.52	2.8E-4	0.73	9.45	0.017	30.01	9.31	0.42
Error/%	0.39	0.67	4.9	0.85	3.99	2.69	6.27	8.28	1.27