Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Integrating $ZnCo_2O_4$ Submicro-/Nanospheres with Co_xSe_y Nanosheets for Oxygen Evolution Reaction and Zinc Air Batteries

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Calculation of electrochemically active surface area (EASA), turnover frequency (TOF), and mass activity (MA):

The EASA value can be calculated by the following equation and the results of the calculation are summarized in **Table 1**:

$$EASA = \frac{C_{dl}}{C_s}$$

where C_s is the specific capacitance of the catalyst. Here, we use general specific capacitances of C_s= 0.040 mF·cm^{-2} based on typical reported values.[1, 2]

The TOF and MA values of the catalyst were calculated by following the equations in previous report.[3]

$$MA = \frac{j}{m}$$

where j (mA·cm$_{geo}^{-2}$) is the measured current density at an overpotential of 350 mV and m (1.02 mg·cm$_{geo}^{-2}$) is the catalyst loading.

$$TOF = \frac{j \times A}{4 \times F \times n}$$

where j (mA·cm$_{geo}^{-2}$) is the measured current density at an overpotential of 350 mV, A (0.196 cm^2) is the area of the glass carbon electrode, F is Faraday's constant (96485.3 C·mol^{-1}) and n is the moles of the metal atom on the electrode. In this work, we assumed that all metal atoms were catalytically active no matter whether they are accessible to the electrolyte or not according to the reported literature.[4] The metal content is calculated by ICP-AES as shown in **Table S2**.

Calculation of power density, specific capacity, and round-trip efficiency in zinc-air batteries:

Power density and the specific capacity of zinc-air battery can be calculated by the following equations:

$$Power\ density\ \left(mW\ cm^{-2}\right) = voltage \times current\ density$$

$$Specific\ capacity\ (mAh\ g^{-1}) = \frac{current \times service\ hours}{weight\ of\ consumed\ zinc}$$

The round-trip efficiency is determined by the following equation:

$$Round - trip\ efficiency\ (\%) = \frac{E_{dis}}{E_{cha}} \times 100\%$$

where E_{dis} and E_{cha} represent the voltages at the end of charge and discharge profiles of each cycle.

Before and after the specific capacity tests of $ZnCo_2O_4/Co_xSe_y$, the weights of consumed zinc (Δm) were 415.64 mg and 71.8 mg, respectively, while for IrO_2/C, the weights were 462.79 mg and 47.0 mg, respectively. The specific calculations are shown as follows:

$ZnCo_2O_4/Co_xSe_y$: $\Delta m = 415.64 - 71.8 = 343.84\ mg$

IrO_2/C: $\Delta m = 462.79 - 47.0 = 415.79\ mg$

Table S1 Summary of the fitting parameters obtained from the equivalent circuit model shown in the inset of **Figure 4d**.

Sample	R_s (Ω)	R_1 (Ω)	C_1 (F)	R_2 (Ω)	C_2 (F)
$ZnCo_2O_4/Co_xSe_y$	7.9	0.19	4.95E-04	7.60	7.42 E-02
Co_xSe_y	8.2	3.69	3.88 E-02	9.99	6.78 E-02
$ZnCo_2O_4$	10.1	3.76	1.17 E-03	78.43	4.10 E-03
IrO_2	8.1	2.91	7.59 E-04	9.09	1.74 E-03

Table S2. The ICP-AES results of metal contents for the catalysts.

Samples	Element	Content (%)
CS/ZCO	Co	34.16
	Zn	2.09
CS	Co	40.53
ZCO	Co	61.32
	Zn	15.66

Table S3. Comparison of OER performance for $Co_xSe_y/ZnCo_2O_4$ with recently reported Co-based electrocatalysts in alkaline solution.

Catalyst	Electrolyte	Mass loading ($mg\cdot cm^{-2}$)	Current density ($mA\cdot cm^{-2}$)	η (mV)	Reference
$ZnCo_2O_4/Co_xSe_y$	1.0 M KOH	1.02	@10	324	This work
			@20	360	
			@50	422	
$Co_3O_4/NiCo_2O_4$ DSNCs	1.0 M KOH	1.0	@10	340	*J. Am. Chem. Soc.* **2015**, *137*, 5590-5595
$ZnCo_2O_4/Co_3O_4$/NC-CNT-700	1.0 M KOH	0.131	@50	420	*Chem. Eur. J.* **2018**, *24*, 18689-18695
$ZnCo_2O_4$/N-CNT	1.0 M KOH	1.42	@20	470	*Adv. Mater.* **2016**, *28*, 3777-3784
$ZnCo_2O_4$@C-MWCNTs	1.0 M KOH	0.351	@10	327	*Electrochim. Acta* **2017**, *257*, 233-242
$Zn_xCo_{3-x}O_4$ film	1.0 M NaOH	-	@10	~330	*ACS Appl. Mater. Interfaces* **2017**, *9*, 17186-17194
P-$Mn_xCo_{3-x}O_{4-d}$	0.1M KOH	0.204	@10	350	*Chem. Eur.* J. **2014**, *20*, 12669-12676
2.0 wt. % Au/$NiCo_2O_4$	1.0 M KOH	-	@10	~360	*ChemCatChem* **2014**, *6*, 2501
$Mn_3O_4/CoSe_2$	0.1 M KOH	~0.2	@10	450	*J. Am. Chem. Soc.* **2012**, *13*, 2930-2933
$ZnCo_2O_4$/Au/CNTs	1.0 M KOH	0.2	@10	441	*J Power Sources*, **2017**, *357*, 1-10
NiCo@$NiCoO_2$/CPMRAs	1.0 M KOH	3.2	@20	366	*Adv. Mater.* **2018**, *30*, 1705442
$ZnCo_2O_4$ spindle	1.0 M KOH	0.24	@10	389	*RSC Adv.* **2016**, *6*, 92699-92704
Co_xS_y@C-1000	0.1 M KOH	0.141	@10	470	*Nanoscale* **2015**, *7*, 20674 -20684
$ZnCo_2O_4$	0.1 M KOH	0.051	@20	420	*J. Mater. Chem. A* **2016**, *4*, 10014-10022
ZNCO-0.15 NFs	0.1 M KOH	0.283	@10	560	*Chem. Eur. J.* **2018**,

					24, 13002-13008

Table S4. The zinc-air battery performance of various bifunctional Co-based electrocatalysts.

Catalyst	Power density ($mW\cdot cm^{-2}$)	Specific capacity ($mA\cdot h\cdot g^{-1}$)	Reference
$ZnCo_2O_4/Co_xSe_y$	212.9	570.1	This work
Co@NCNTAs	38.6 (j=2 $mA\cdot cm^{-2}$)	368	*Small Methods*, **2019**, 1900571
$ZnCo_2O_4$/N-CNT	82.3	428.47	*Adv. Mater.* **2016**, *28*, 3777-3784
Zn-Co-S NN/CFP	-	484.7	*ACS Appl. Mater. Inter face* **2017**, *9*, 12574-12583
(Mg, Co)$_3O_4$@NGC	125	-	*ACS Energy Lett.* **2017**, *2,* 2706-2712
MnO_2/Co_3O_4 hybrid nanomaterials	33	-	*Nanoscale,* **2013**, *5*, 4657-4661
FeCo/NB-Cs	218.07	-	*Chem. Eng. J.*, **2019**, *371*, 433-442
Co_3O_4 NS/CC	107	535	*ACS Appl. Mater. Interfaces* **2017**, *9*, 22694-22703
$NiFe_2O_4/FeNi_2S_4$ HNSs	187	-	*J. Am. Chem. Soc.* **2018**, *140*, 17624-17631
Co_3O_4-NCNT/SS	160.7	652.6	*Adv. Mater.* **2016**, *28*, 6421-6428
Co_4N/CNW/CC	174	-	*J. Am. Chem. Soc.* **2016**, *138*, 10226-10231

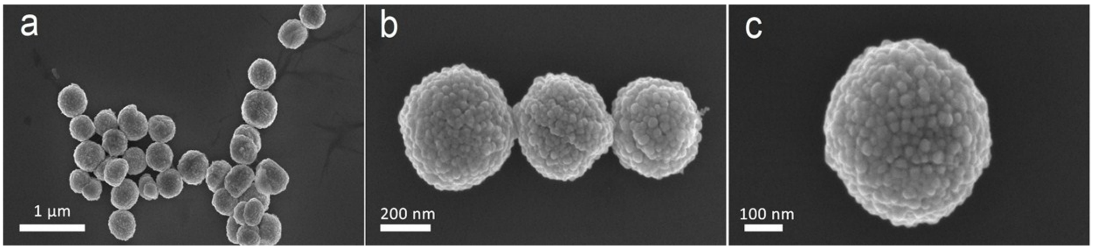

Figure S1. The typical SEM images of $ZnCo_2O_4$.

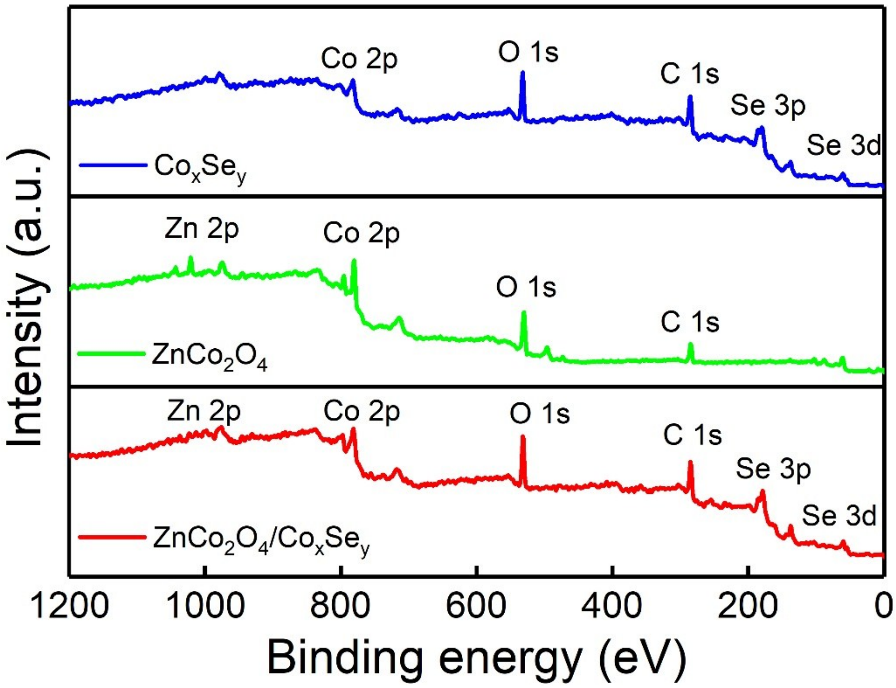

Figure S2. The XPS survey-scan spectra of Co_xSe_y, $ZnCo_2O_4$, and $ZnCo_2O_4/Co_xSe_y$.

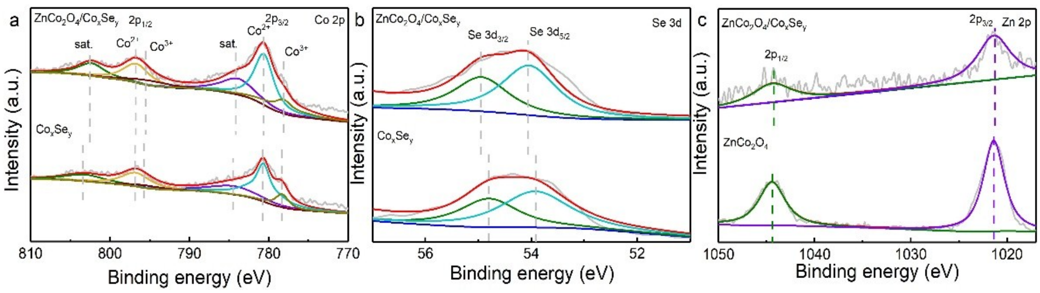

Figure S3. The core-level XPS spectra of the (a) Co2p, (b) Zn2p, (3) Se3d electrons of $ZnCo_2O_4/Co_xSe_y$, $ZnCo_2O_4$, and Co_xSe_y.

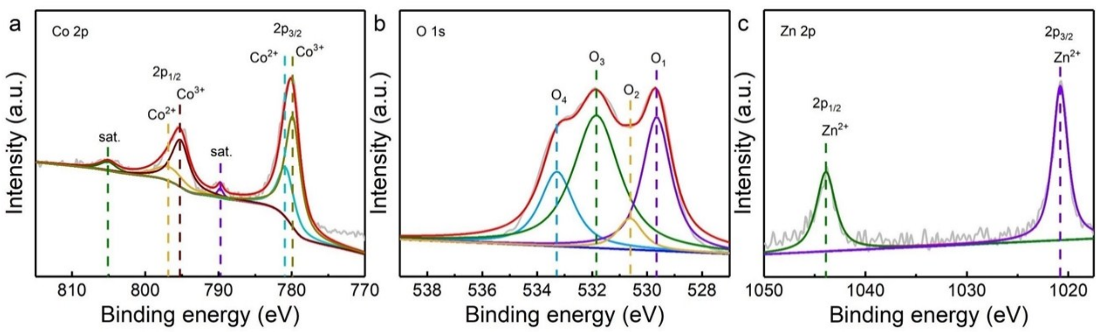

Figure S4. High-resolution XPS spectra of $ZnCo_2O_4$ for the (a) Co 2p, (b) O 1s, (c) Zn 2p electrons.

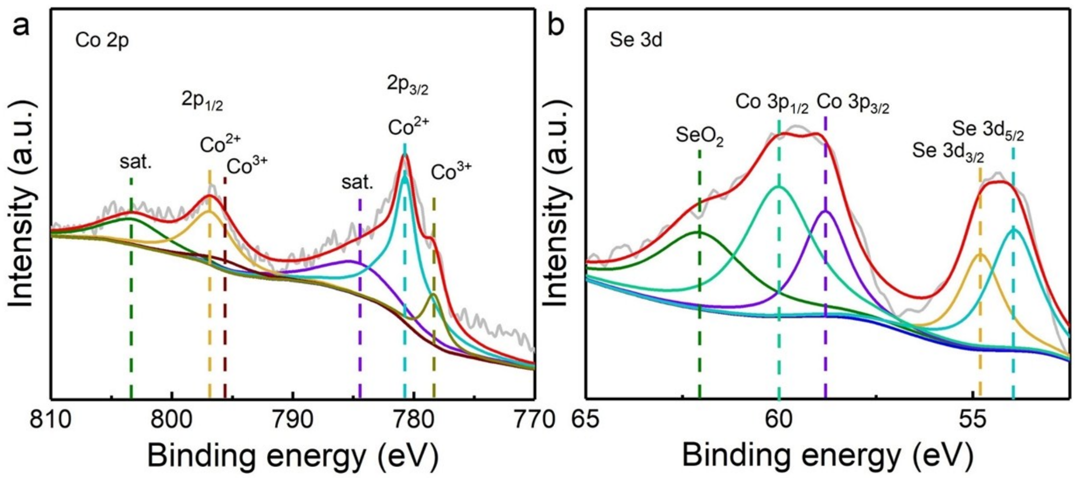

Figure S5. High-resolution XPS spectra of Co_xSe_y for the (a) Co 2p and (b) Se 3d electrons.

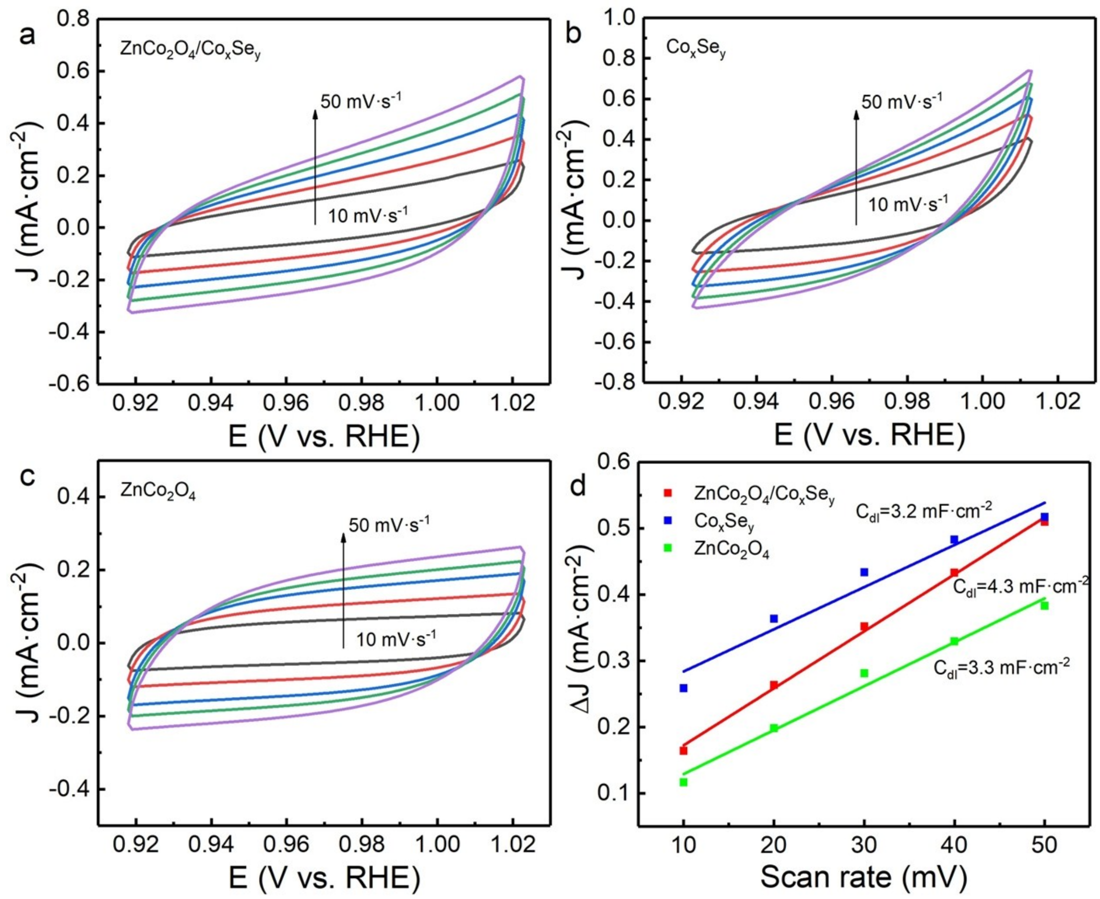

Figure S6. Cyclic voltammetric curves of (a) $ZnCo_2O_4/Co_xSe_y$, (b) Co_xSe_y and (c) $ZnCo_2O_4$ at varying scan rates ranging from 10 to 50 mV s^{-1} in 1 M KOH, (d) Electrochemical double-layer capacitance measurements. Linear fitting of the capacitive currents (data obtained from the CVs (a), (b) and (c)) of the catalysts against the scan rate to fit a linear regression. The value of the double-layer capacitance C_{dl} is equivalent to one-half of the linear slope calculated from the fitted line of the current density against the scan rate, which was used to determine the EASA value.

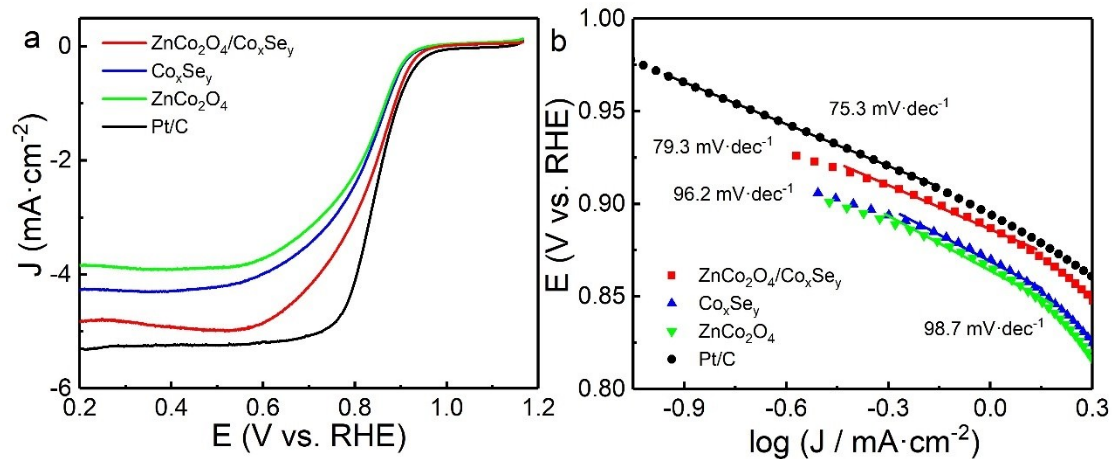

Figure S7. The ORR performance of the as-prepared catalysts and Pt/C in O_2-saturated 0.1 M KOH solution, (a) LSV polarization curves under the rotating speed of 1600 rpm at a scan rate of 10 mV s^{-1}, (b) Corresponding Tafel plots.

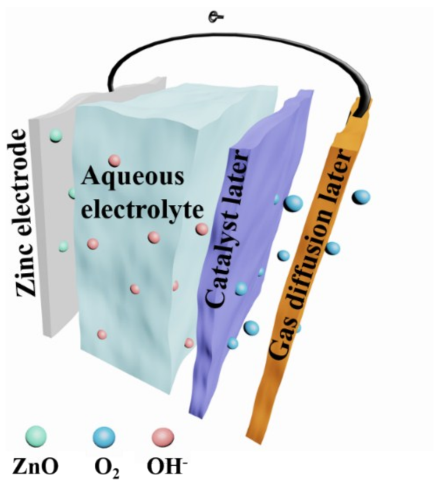

Figure S8. The schematic sketch of zinc-air batteries.

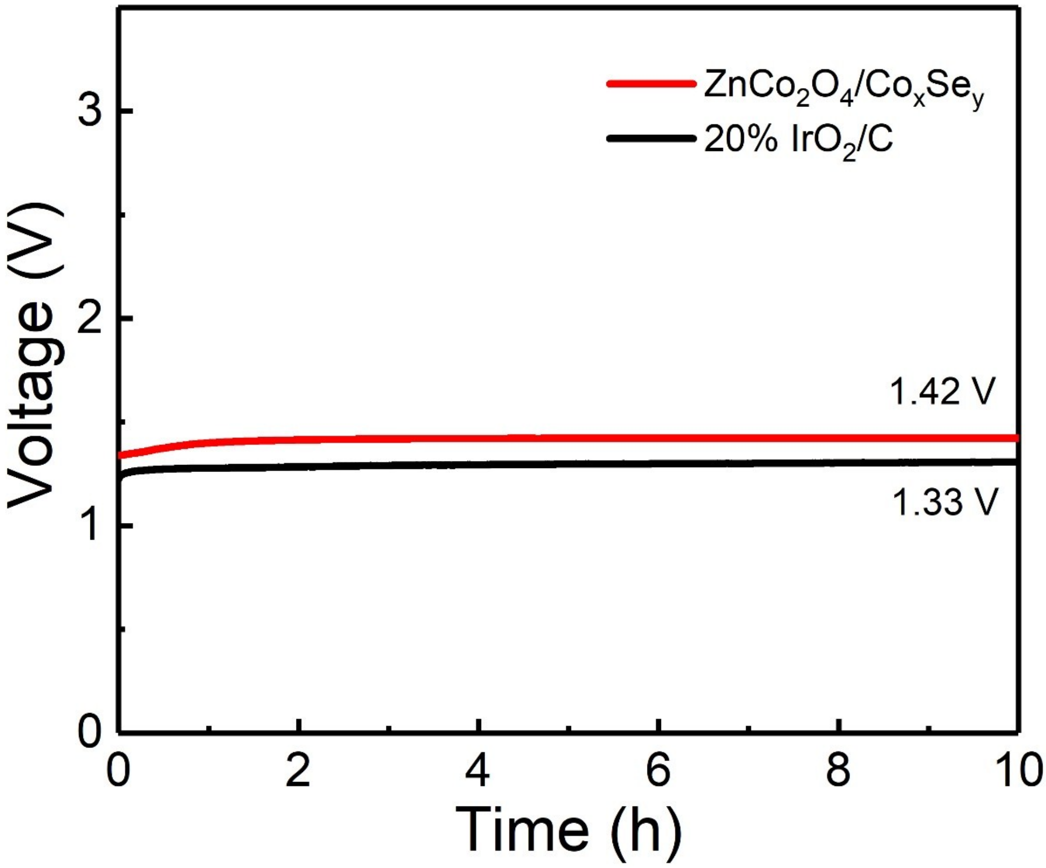

Figure S9. The open-circuit voltage plots of zinc-air batteries with $ZnCo_2O_4/Co_xSe_y$ and IrO_2/C as the air cathode catalyst.

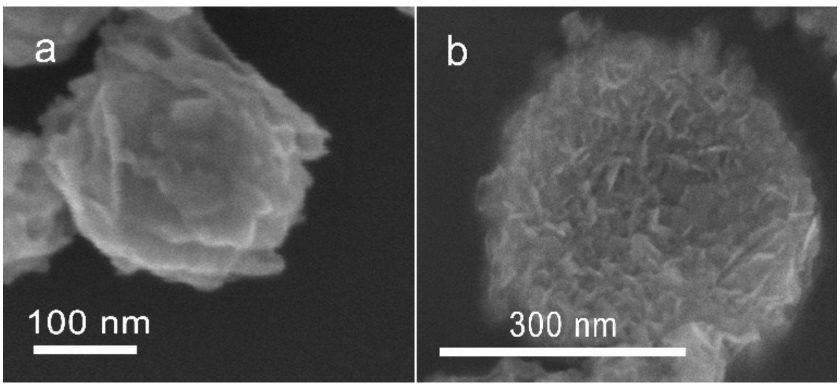

Figure S10. The SEM images (a) before and (b) after the galvanostatic charge-discharge test of $ZnCo_2O_4/Co_xSe_y$.

References

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