Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

In Situ Coupling of $Co_{0.85}Se$ and N–Doped Carbon via One–Step Selenizing of Metal–Organic Frameworks as Trifunctional Catalysts for Overall Water Splitting and Zn–air Batteries

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1. Supplementary figures

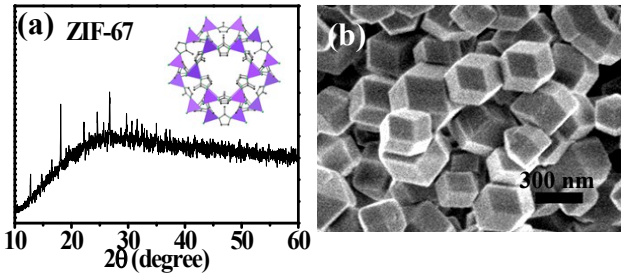

Fig. S1 (a) XRD pattern and (b) FE-SEM image of ZIF–67.

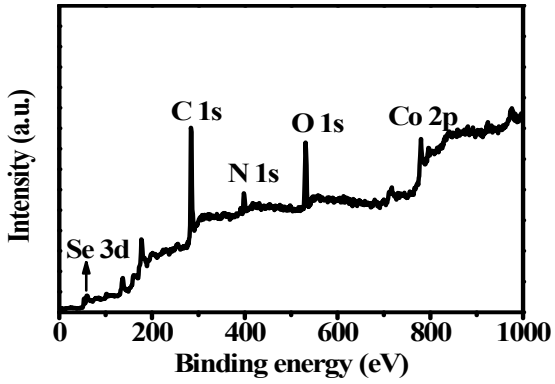

Fig. S2 The survey XPS spectrum of $Co_{0.85}Se$@NC.

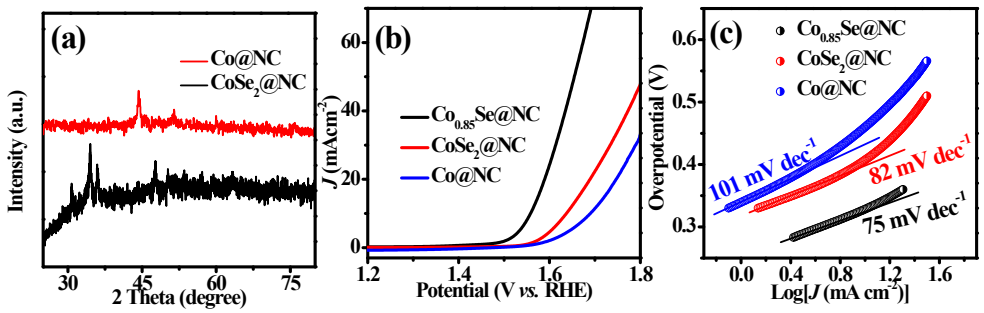

Fig. S3 (a) XRD patterns for $CoSe_2$@NC and Co@NC; (b) Polarization curves and (c) Tafel plots of $Co_{0.85}Se$@NC, $CoSe_2$@NC and Co@NC.

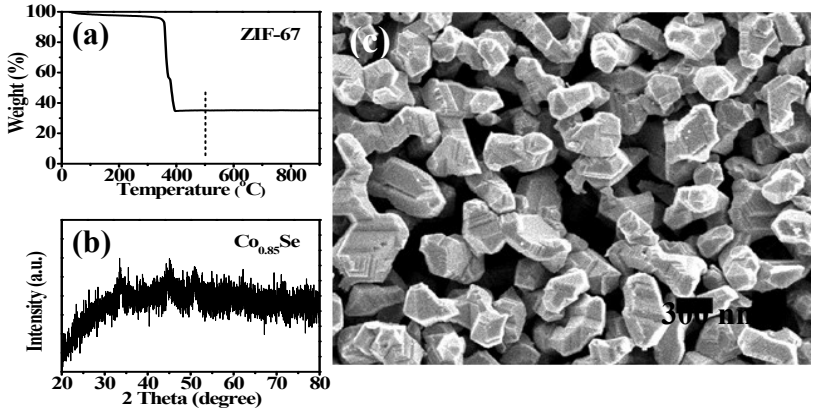

Fig. S4 (a) The TGA curve of ZIF–67. (b) The XRD pattern and (c) FE-SEM image of $Co_{0.85}Se$.

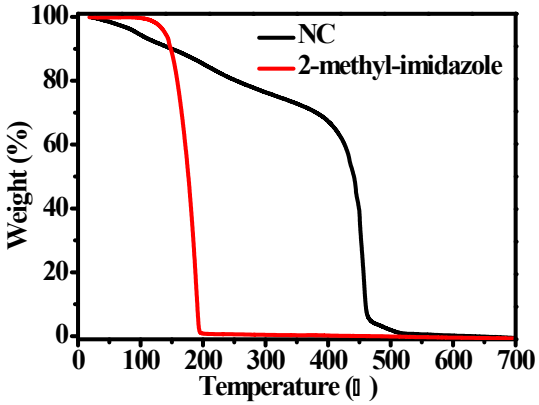

Fig. S5 The TGA curves of NC and 2–methyl–imidazole.

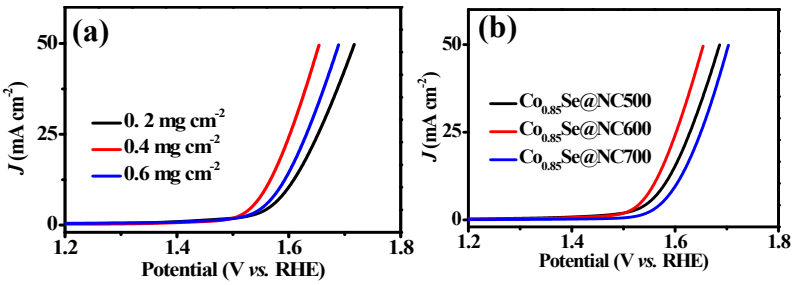

Fig. S6 (a) Polarization curves of $Co_{0.85}Se$@NC coated on glass carbon (GC) electrode with different mass rates at 2 mV s^{-1}. (b) Polarization curves of $Co_{0.85}Se$@NC prepared with different temperatures.

Fig. S6 (b): The $Co_{0.85}Se$@NC500 and $Co_{0.85}Se$@NC700 both exhibit slightly inferior oxygen evolution activity, which is probably due to either the poor crystallinity at the low temperature or the aggregation of $Co_{0.85}Se$@NC nanocrystallites at the high temperature.

Table S1 Comparison of the OER activity for several recently reported highly active transition-/noble-metal and non-metal catalysts supported on different substrates.

Catalyst	Mass loading (mg cm^{-2})	Potential @ 10.0 mA cm^{-2} (V *vs.* RHE)	Tafel slope (mV dec^{-1})	Electrolyte	Substrate	Ref.
$Co_{0.85}Se$@NC	**0.4**	**1.55**	**75**	**1 M KOH**	**Glassy carbon**	**This work**
IrO_2/C	0.2	1.60	N.A.	0.1 M KOH	Glassy carbon	1
Pt/C	~0.25	1.83	169	0.1 M KOH	Glassy carbon	2
$CoSe_2$ ultrathin nanosheets	0.142	1.55	44	0.1 M KOH	Glassy carbon	3
$CoSe_2$/N–graphene	~0.2	1.596	~40	0.1 M KOH	Glassy carbon	4
Mn_3O_4/$CoSe_2$ hybrids	~0.2	1.68	49	0.1 M KOH	Glassy carbon	5
CoS_2/N,S–GO	0.25	1.61	75	0.1 M KOH	Glassy carbon	6
Co_3O_4/N–graphene	1	1.54	67	1 M KOH	Ni foam	7
Co_3O_4C–NA	~0.2	1.52	70	0.1 M KOH	Cu foil	8
TCCN	~1.4	1.65	74.6	0.1 M KOH	self-supported membrane	9
CoP	6.2	1.52	65	1 M KOH	Ni foam	10
$Zn_xCo_{3-x}O_4$ nanoarrays	~1	1.55	51	1 M KOH	Ti foil	11
$Ni_xCo_{3-x}O_4$ nanoarrays	N.A.	~1.6	59-64	1 M NaOH	Ti foil	12

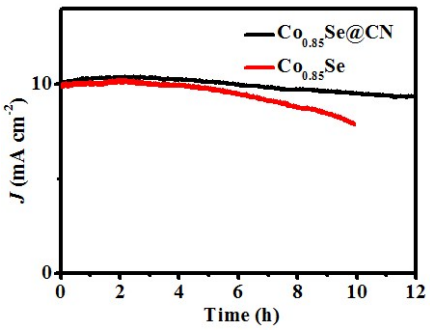

Fig. S7 Chronoamperometric responses at a constant potential (the potential at 10 mA cm^{-2}) of $Co_{0.85}Se$@NC and $Co_{0.85}Se$.

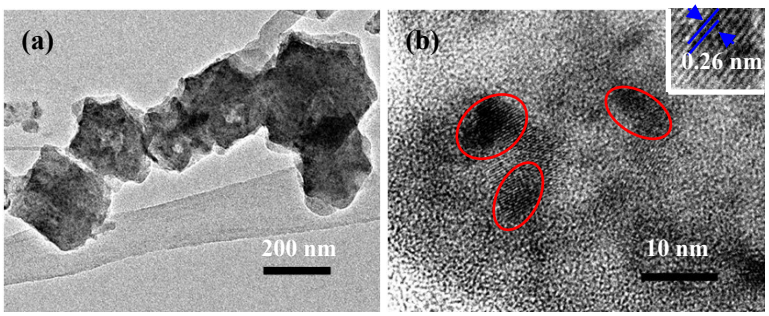

Fig. S8 (a) TEM image and (b) HRTEM image of $Co_{0.85}Se$@NC after 12 h reaction.

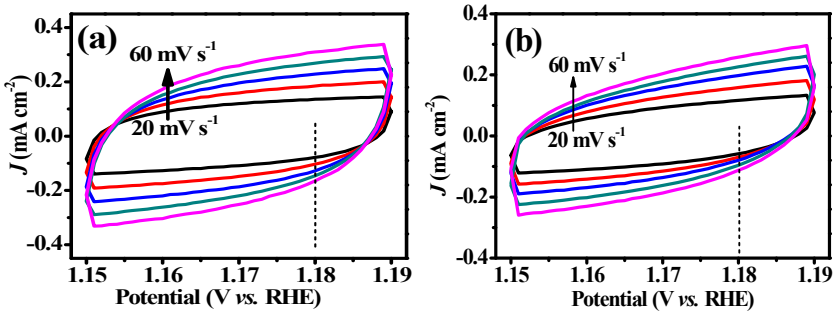

Fig. S9 CVs tested at the potential range of 1.15 –1.19 V *vs.* RHE with the scan rates increasing from 20 to 60 mV s^{-1} for $Co_{0.85}Se$@NC (a) and $Co_{0.85}Se$ (b).

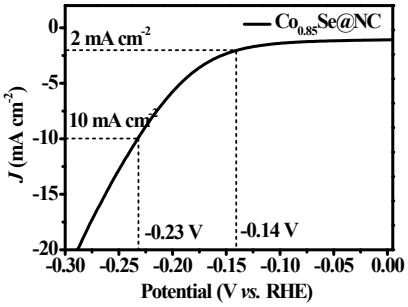

Fig. S10 Polarization curve of $Co_{0.85}Se$@NC for HER (N_2-saturated 1.0 M KOH solution with a scan rate of 2 mV s^{-1}).

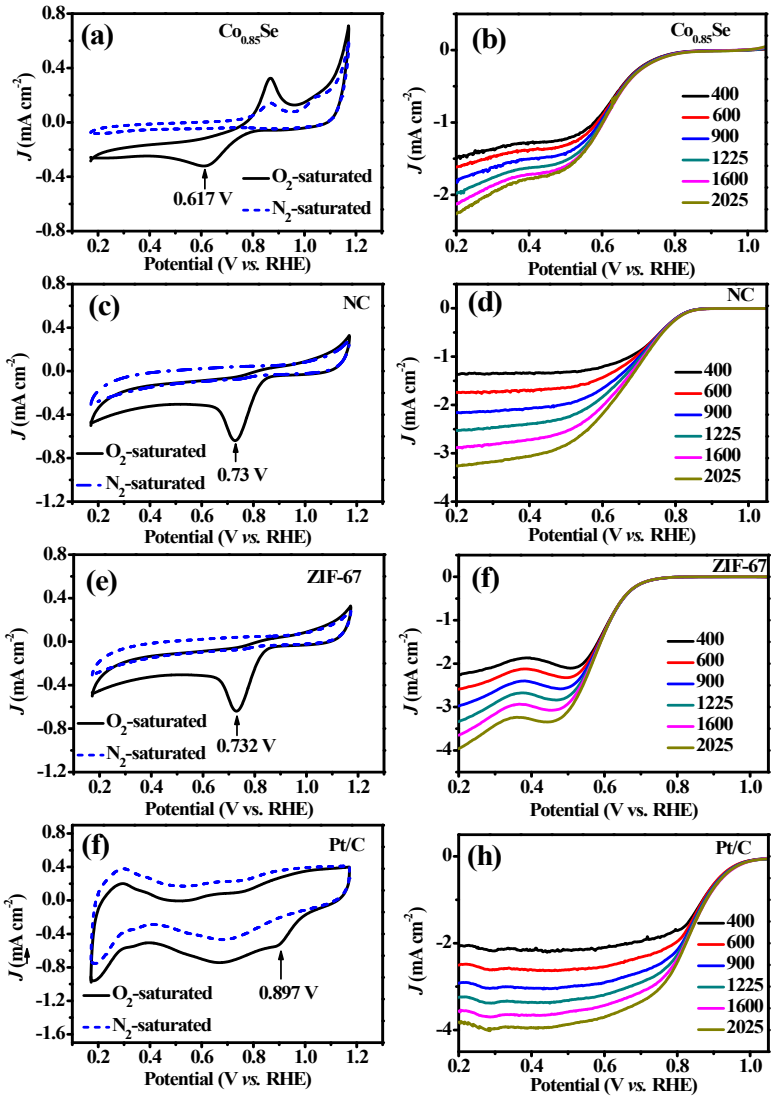

Fig. S11 The CVs in 0.1 M KOH solution and polarization curves in O_2–saturated 0.1 M KOH solution with rotating speeds from 400 to 2025 rpm for $Co_{0.85}Se$ (a,b), NC (c,d), ZIF–67(e,f) and Pt/C (g,h).

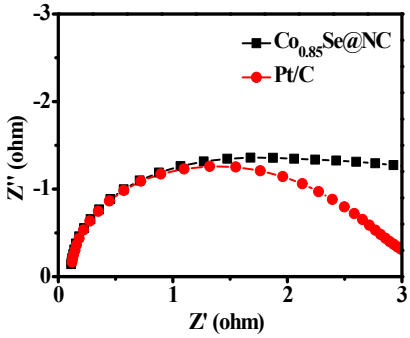

Fig. S12 The EIS of $Co_{0.85}Se$@NC and commercial Pt/C at open–circuit voltage for Zn–air battery.

Table S2 Comparison of the primary Zn–air batteries with several key parameters for several recently reported highly active transition–/noble–metal and non–metal catalysts.

ORR catalyst used	Zn electrode/electrolyte	Current density @ V = 1.0 V (mA cm^{-2})	Peak power density (mW cm^{-2})	Ref.
$Co_{0.85}Se$@NC	**Zn foil/6M KOH**	**186**	**268**	**This work**
CoO/N–CNT	Zn foil/6 M KOH	197	265	13
Co@NG–acid	Zn foil/6 M KOH	255	350	14
Co_3O_4 nanoparticles decorated carbon nanofiber	Zn plate/6 M KOH	81	125	15
Fe, Co and N precursors pyrolyzed with carbon	Zn plate/6 M KOH	150	232	16
Graphene supported Mn_3O_4 nanoparticles	Zn power/(N.A.M) KOH	70	120	17
Ketjenblack carbon supported amorphous MnO_x	Zn power/(6 M) KOH	120	190	18
Fe@N–C–700	Zn plate/6 M KOH	157	220	19
FeCu@GC	Zn plate/6 M KOH	100	212	20
Nanoporous carbon fiber films–1000	Zn plate/6 M KOH	~150	185	21
N–doped carbon nanotubes	Zn plate/6 M KOH	50	75	22
N,P–doped carbon foam	Zn plate/6 M KOH	<70	55	23

Table S3 Comparison of the rechargeable Zn–air batteries with several key parameters for several recently reported highly active transition–/noble–metal and non–metal catalysts.

Air catalyst used	Cycling conditions and stability	Voltage polarization V (@ j, mA cm^{-2})	Ref.
$Co_{0.85}Se$@NC	**10 mA cm^{-2}, 600 s per cycle periods for 180 cycles: polarization increased ~0.16 V at the end**	**0.8 (10)**	**This work**
MnO_2 nanotube and carbon nanotube composite	~8 mA cm^{-2}, 600 s per cycle periods for 50 cycles: polarization increased ~0.4 V at the end	1.5 (20)	24
Co_3O_4 nanoparticles decorated carbon nanofibers	2 and 20 mA cm^{-2}, 1 h per cycle periods for 160 and 55 cycles: polarization increased 0.09 V at the end for 20 mA cm^{-2}	0.7 (2) 0.85 (20)	15
Tri-electrode: CoO/N–CNT + NiFe LDH	20-50 mA cm^{-2}, 4-20 h per cycle period for >200 h: negligible voltage change at the end	0.7 (20)	13
Co_3O_4 NP modified MnO_2 nanotubes	15 mA cm^{-2}; 14 min per cycle period for 60 cycles; voltage gap increased ~0.3-0.4 V at the end	~0.85 (15)	25
$ZnCo_2O_4$/N–CNT	10-100 mA cm^{-2}, 20 min per cycle for 17 cycles (340 min); negligible voltage change at the end	0.84(10-100)	26
TCCN	20 mA cm^{-2}, 10 min per cycle for 15 cycles; negligible voltage change at the end	1.68 (20)	9

2. Supplementary video

Video S. $Co_{0.85}Se$@NC coated on nikel foam was used as the working electrode for overall water splitting at the current density of 10 mA cm^{-2}. This video instinctively reflects the generation rate of O_2 or H_2 gas with the $Co_{0.85}Se$@NC catalyst during the overall water splitting, indicating its excellent overall water splitting performance.

3. References

1 Y. Zhao, R. Nakamura, K. Kamiya, S. Nakanishi and K. Hashimoto, *Nat. Commun.*, 2013, **4**, 2390—2396.

2 X. Lv, Y. Zhu, H. Jiang, X. Yang, Y. Liu, Y. Su, J. Huang, Y. Yao and C. Li, *Dalton Transactions*, 2015, **44**, 4148—4154.

3 Y. Liu, H. Cheng, M. Lyu, S. Fan, Q. Liu, W. Zhang, Y. Zhi, C. Wang, C. Xiao and S. Wei, *J. Am. Chem. Soc.,* 2014, **136**, 15670—15675.

4 M. R. Gao, X. Cao, Q. Gao, Y. F. Xu, Y. R. Zheng, J. Jiang and S. H. Yu, *ACS nano*, 2014, **8**, 3970—3978.

5 M. R. Gao, Y. F. Xu, J. Jiang, Y. R. Zheng and S. H. Yu, *J. Am. Chem. Soc.,* 2012, **134**, 2930—2933.

6 P. Ganesan, M. Prabu, J. Sanetuntikul and S. Shanmugam, *ACS Catalysis,* 2015, **5**, 3625—3637.

7 Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nat. Mater.,* 2011, 10, 780—786.

8 T. Y. Ma, S. Dai, M. Jaroniec and S. Z. Qiao, *J. Am. Chem. Soc.,* 2014, **136**, 13925—13931.

9 T. Y. Ma, J. L. Cao, M. Jaroniec and S. Z. Qiao, *Angew. Chem. Int. Ed.,* 2016, **55**, 1138—1142.

10 Y. P. Zhu, Y. P. Liu, T. Z. Ren and Z. Y. Yuan, *Adv. Funct. Mater*., 2015, **25**, 7337—7347.

11 X. Liu, Z. Chang, L. Luo, T. Xu, X. Lei, J. Liu, X Sun, *Chem. Mater.*, 2014, **26**, 1889—1895.

12 Y. Li, P. Hasin, Y. Wu, *Adv. Mater.*, 2010, **22**, 1926—1929.

13. Y. G. Li, M. Gong, Y. Y. Liang, J. Feng, J. E. Kim, H. L. Wang, G. S. Hong, B. Zhang and H. J. Dai, *Nat. Commun.,* 2013, **4**, 1805—1811.

14. M. Zeng, Y. Liu, F. Zhao, K. Nie, N. Han, X. Wang, W. Huang, X. Song, J. Zhong and Y. Li, *Adv. Funct. Mater.,* 2016, **26**, 4397—4404.

15. B. Li, X. Ge, F. T. Goh, T. A. Hor, D. Geng, G. Du, Z. Liu, J. Zhang, X. Liu and Y. Zong, *Nanoscale,* 2015, **7**, 1830—1838.

16. Z. Chen, J. Y. Choi, H. Wang, H. Li and Z. Chen, *J. Power Sources,* 2011, **196**, 3673—3677.

17. J. S. Lee, T. Lee, H. K. Song, J. Cho, B. S. Kim, *Energy Environ. Sci.*, 2011, **4**, 4148—4154.

18. J. S. Lee, G. S. Park, H. I. Lee, S. T. Kim, R. Cao, M. Liu and J. Cho, *Nano Lett.,* 2011, **11**, 5362—5366.

19. J. Wang, H. Wu, D. Gao, S. Miao, G. Wang and X. Bao, *Nano Energy*, 2015, **13**, 387—396.

20. G. Nam, J. Park, M. Choi, P. Oh, S. Park, M. G. Kim, N. Park, J. Cho and J. S. Lee, *ACS nano,* 2015, **9**, 6493—6501.

21. Q. Liu, Y. B. Wang, L. M. Dai and J. N. Yao, *Adv. Mater.*, 2016, **28**, 3000—3006.

22. S. Zhu, Z. Chen, B. Li, D. Higgins, H. Wang, H. Li and Z. Chen, *Electrochim. Acta,* 2011, **56**, 5080—5084.

23. J. Zhang, Z. Zhao, Z. Xia and L. Dai, *Nat. Nanotech.,* 2015, **10**, 444—452.

24. Z. Chen, A. Yu, R. Ahmed, H. Wang, H. Li and Z. Chen, *Electrochim. Acta,* 2012, **69**, 295—300.

25. G. Du, X. Liu, Y. Zong, T. A. Hor, A. Yu, Z Liu, *Nanoscale,* 2013, **5**, 4657—4661.

26. Z. Q. Liu, H. Cheng, N. Li, T. Y. Ma and Y. Z. Su, *Adv. Mater.,* 2016, **28**, 3777—3784.