Supplementary materials

Co_3O_4@$NiCo_2O_4$ Double-Shelled Nanocages with Hierarchical Hollow Structure and Oxygen Vacancies as Efficient Bifunctional Electrocatalysts for Rechargeable Zn-Air Batteries

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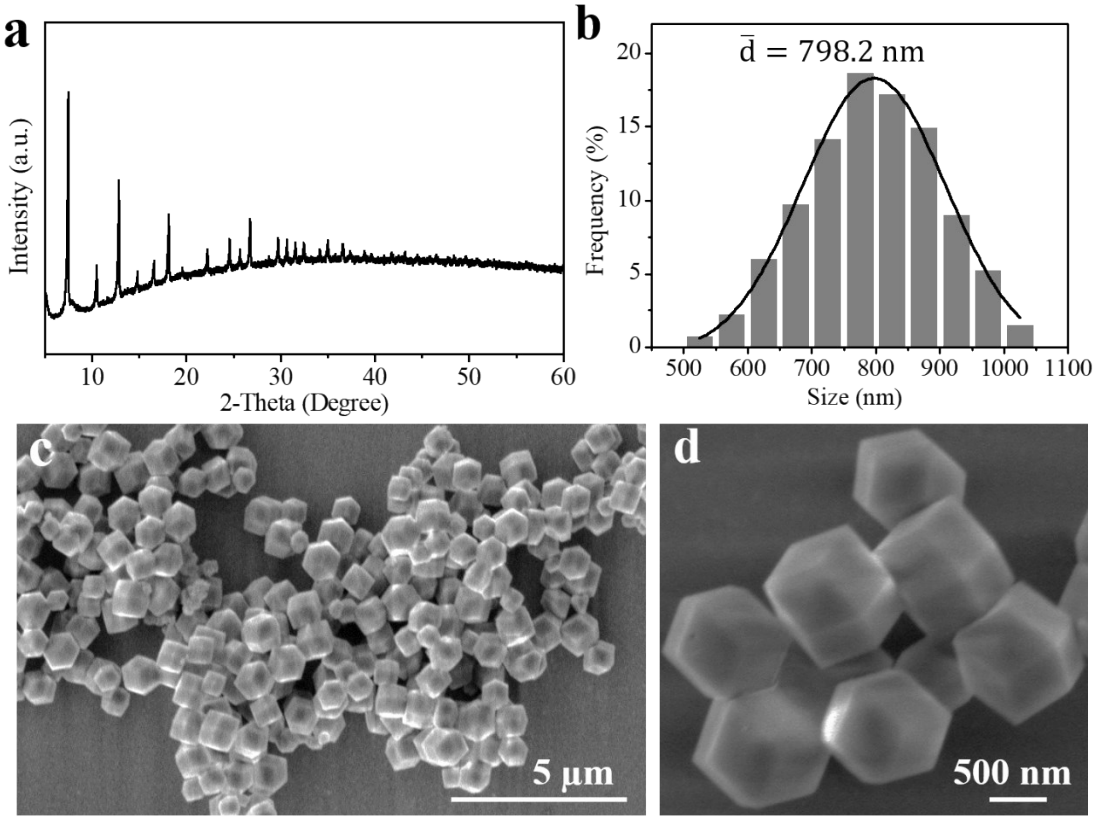

Fig. S1 (a) XRD patterns of as-obtained ZIF-67 nanocrystals. (b) Particle size distribution of as-obtained ZIF-67 nanocrystals. (c) Low-magnification and (d) high-magnification SEM images of as-obtained ZIF-67 nanocrystals.

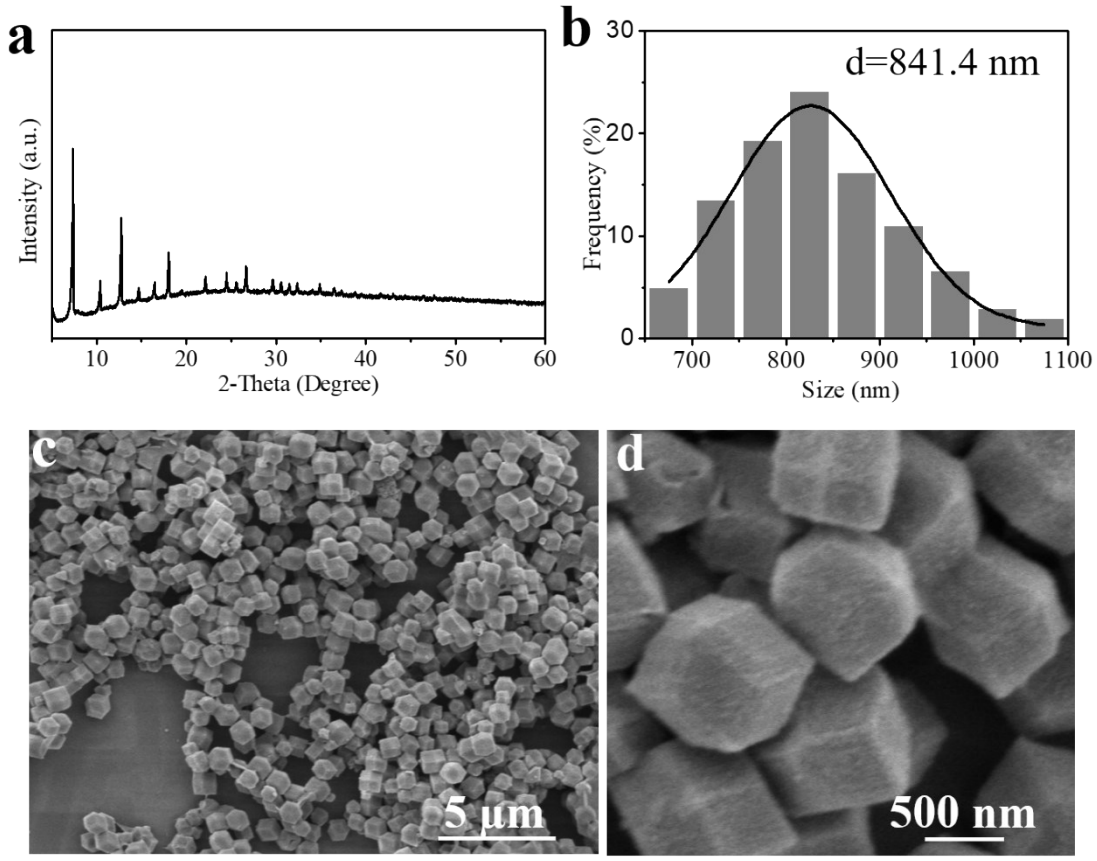

Fig. S2 (a) XRD patterns of as-obtained ZIF-67@Ni-Co LDH nanocrystals. (b) Particle size distribution of as-obtained ZIF-67@Ni-Co LDH nanocrystals. (c) Low-magnification and (d) high-magnification SEM images of as-obtained ZIF-67@Ni-Co LDH nanocrystals.

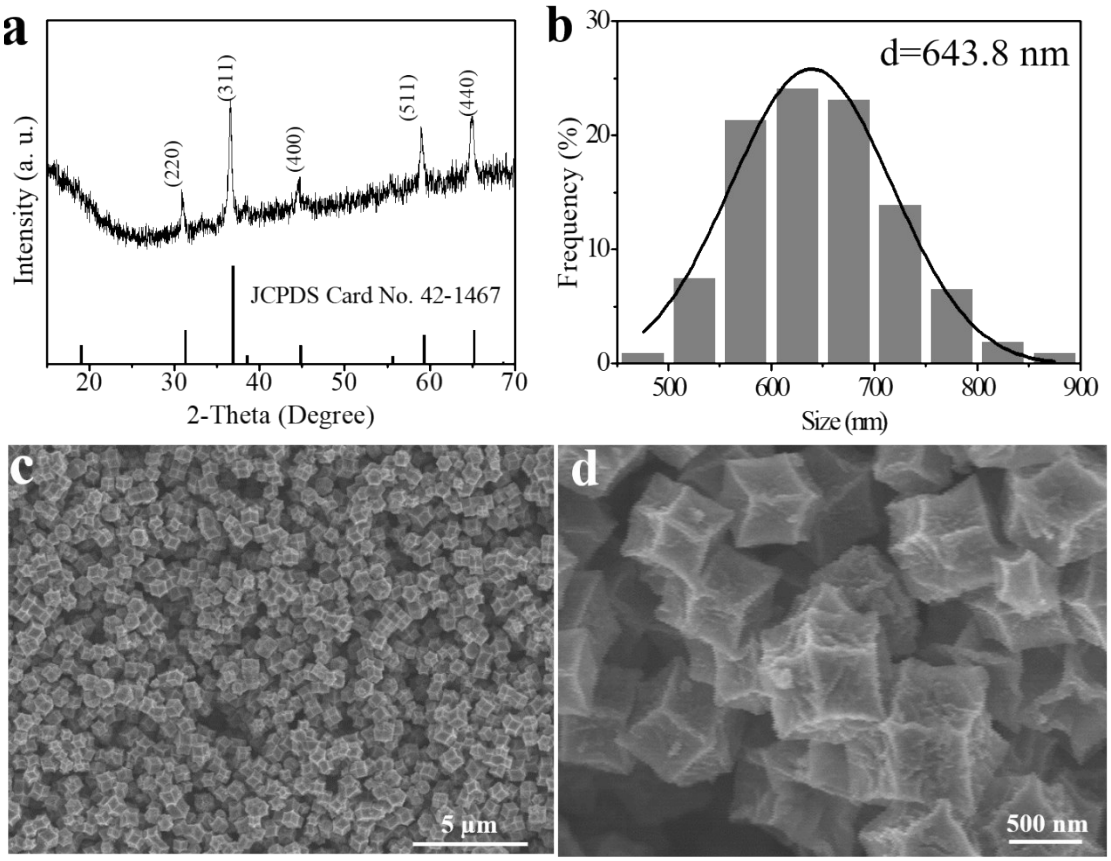

Fig. S3 (a) XRD patterns of as-obtained Co_3O_4 NCs. (b) Particle size distribution of as-obtained Co_3O_4 NCs. (c) Low-magnification and (d) high-magnification SEM images of as-obtained Co_3O_4 NCs.

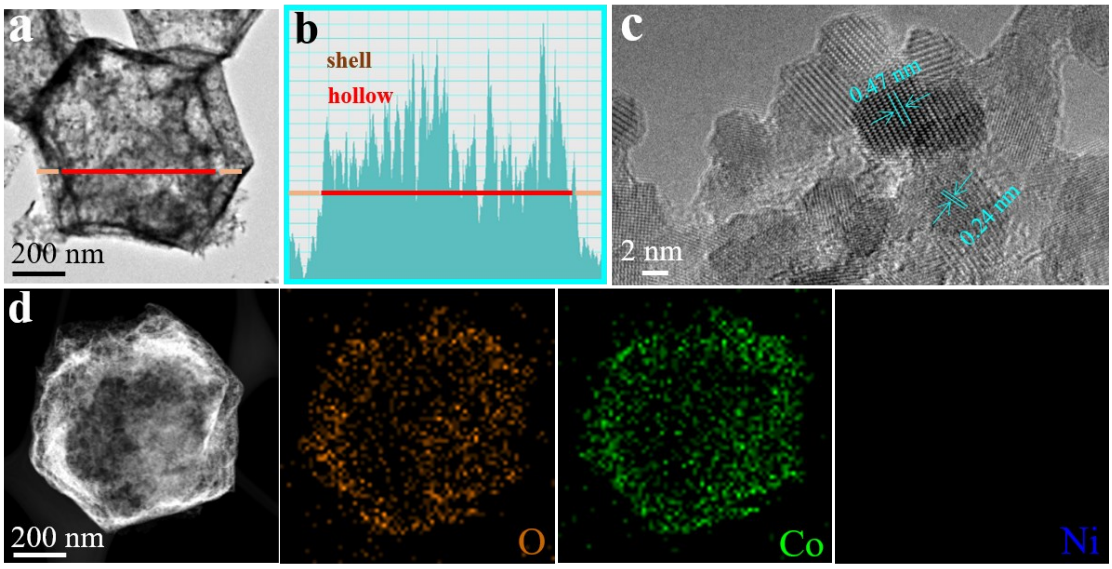

Fig. S4 (a) TEM image of as-obtained Co_3O_4 NCs. (b) Intensity profiles of TEM image of one Co_3O_4 NC nanoparticle. (c) HRTEM image of a fragment of Co_3O_4 shell. (d) EDS elemental mapping images of as-obtained Co_3O_4 NC, showing as-obtained Co_3O_4 NCs feature hollow nanocage structure.

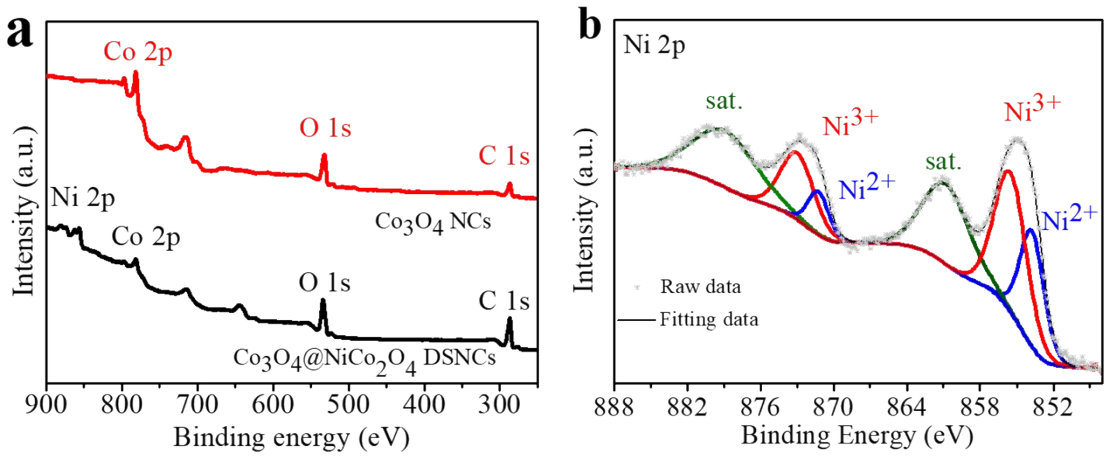

Fig. S5 (a) XPS survey spectrum for Co_3O_4@$NiCo_2O_4$ DSNCs and Co_3O_4 NCs. (b) The experimental and fitted high-resolution XPS spectra for Ni 2p of Co_3O_4@$NiCo_2O_4$ DSNCs.

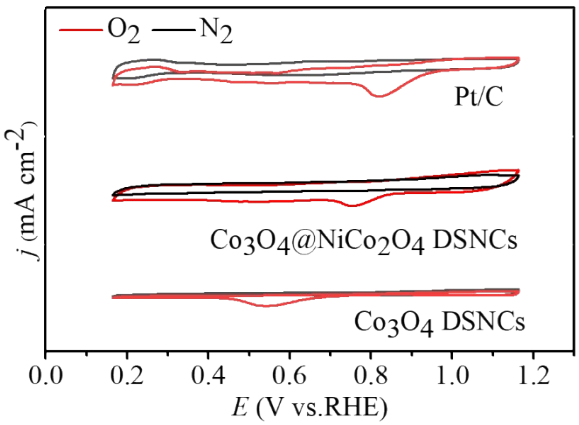

Fig. S6 CV curves of Co_3O_4@$NiCo_2O_4$ DSNCs, Co_3O_4 NCs and Pt/C catalysts were recorded in O_2-and N_2 saturated 0.1 M KOH with at a scan rate of 50 mV s^{-1}.

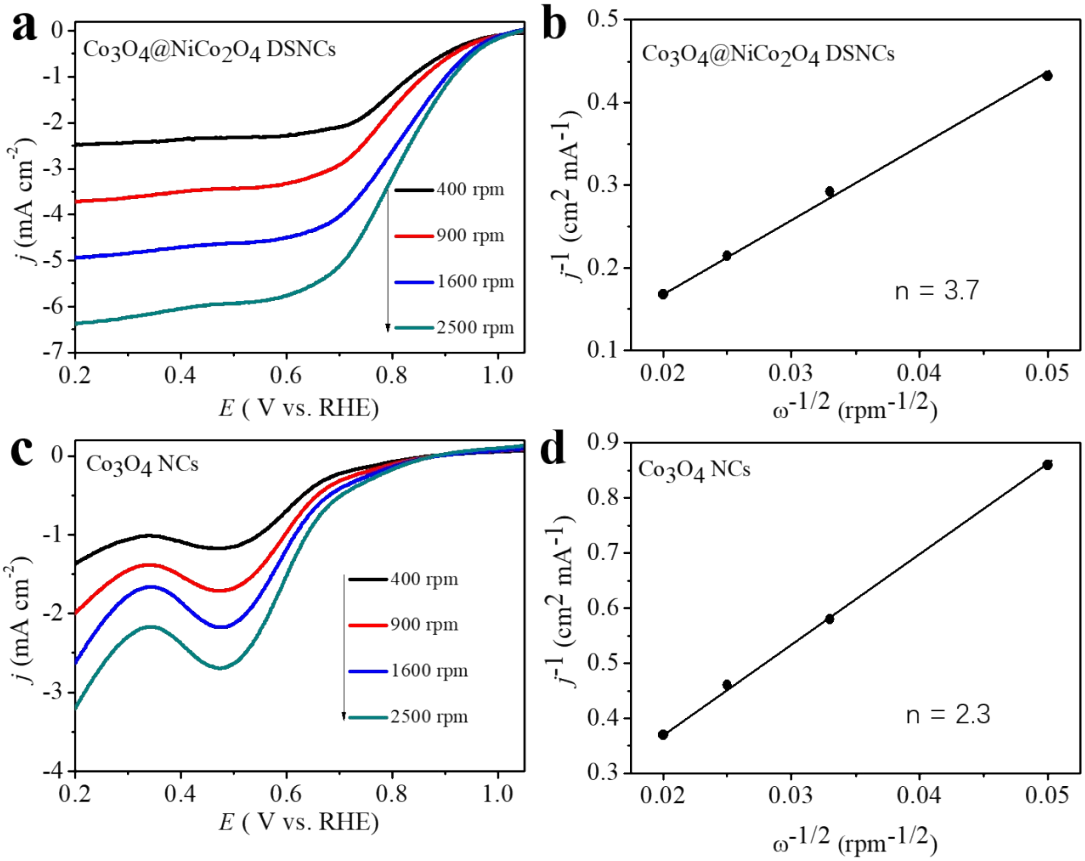

Fig. S7 ORR polarization curves (left) at various rotation rates and the corresponding Koutecky-Levich plots (right) obtained at different potentials from (a), (b) Co_3O_4@$NiCo_2O_4$ DSNCs and (c), (d) Co_3O_4 NCs.

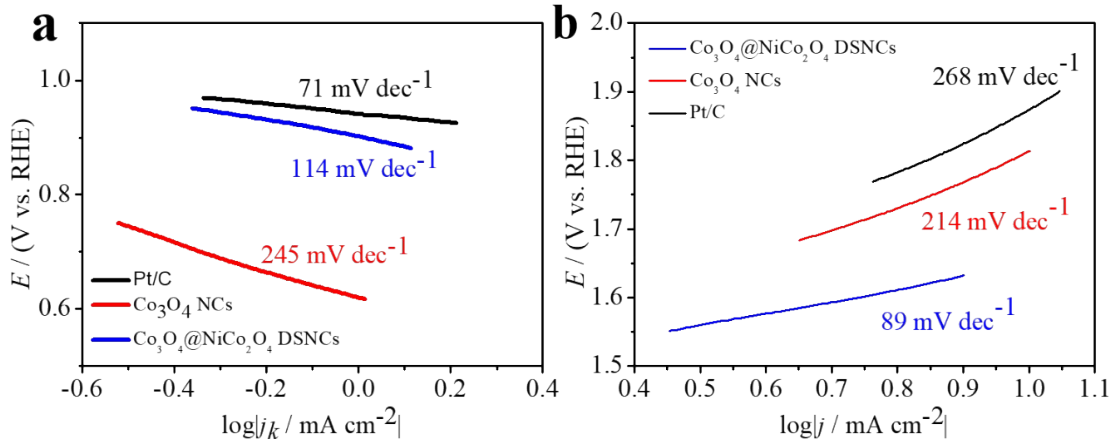

Fig. S8 (a) ORR Tafel plots of Co_3O_4@$NiCo_2O_4$ DSNCs compared with Co_3O_4 NCs, and Pt/C. (b) OER Tafel plots of Co_3O_4@$NiCo_2O_4$ DSNCs compared with Co_3O_4 NCs, and Pt/C.

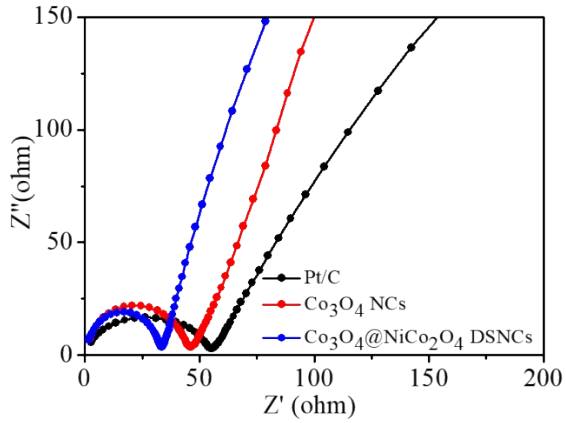

Fig. S9 Nyquist plots for Co_3O_4@$NiCo_2O_4$ DSNCs, Co_3O_4 NCs, and Pt/C at anodic potential value of 1.6 V, in O_2 free 0.1 M KOH solution.

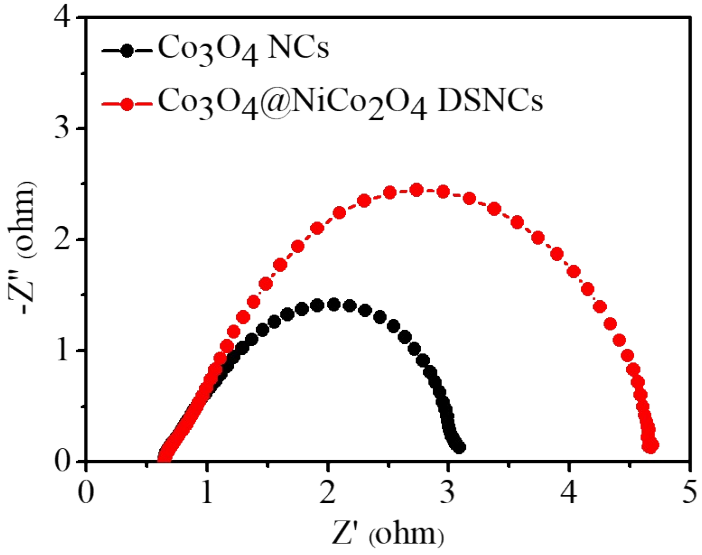

Fig. S10 Nyquist spectra for RZRBs with Co_3O_4@$NiCo_2O_4$ DSNCs and Pt/C as air electrode.

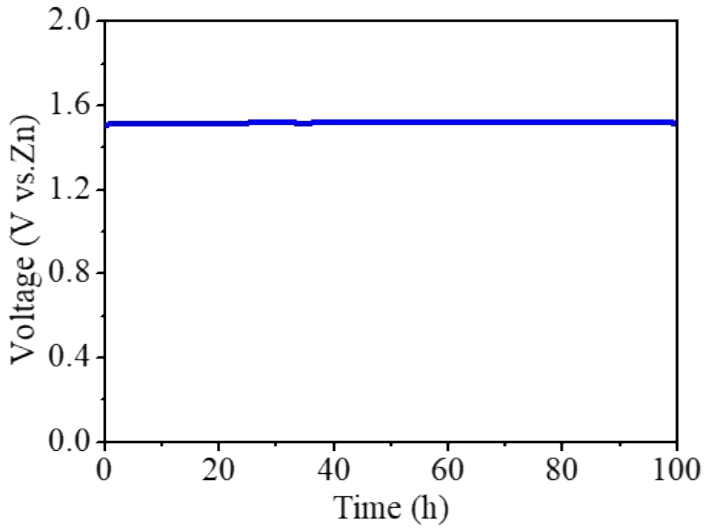

Fig. S11 The open-circuit voltage curve for RZAB based on Co_3O_4@$NiCo_2O_4$.

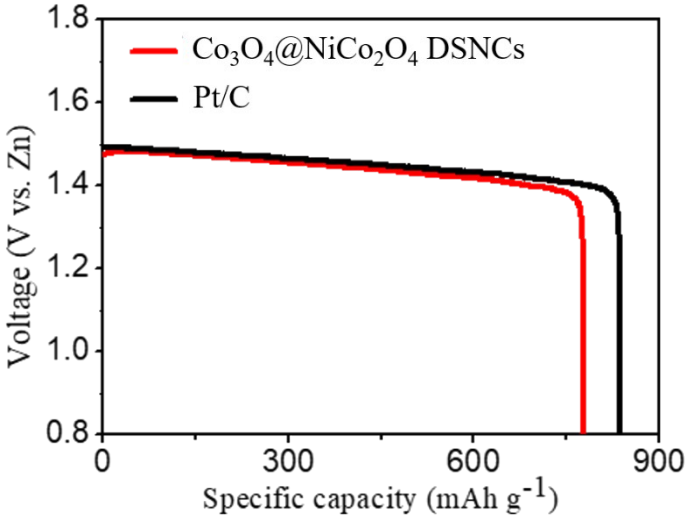

Fig. S12 Specific capacities of the RZABs using Co_3O_4@$NiCo_2O_4$ DSNCs and Pt/C as air electrode, which is normalized to the mass of the consumed Zn.

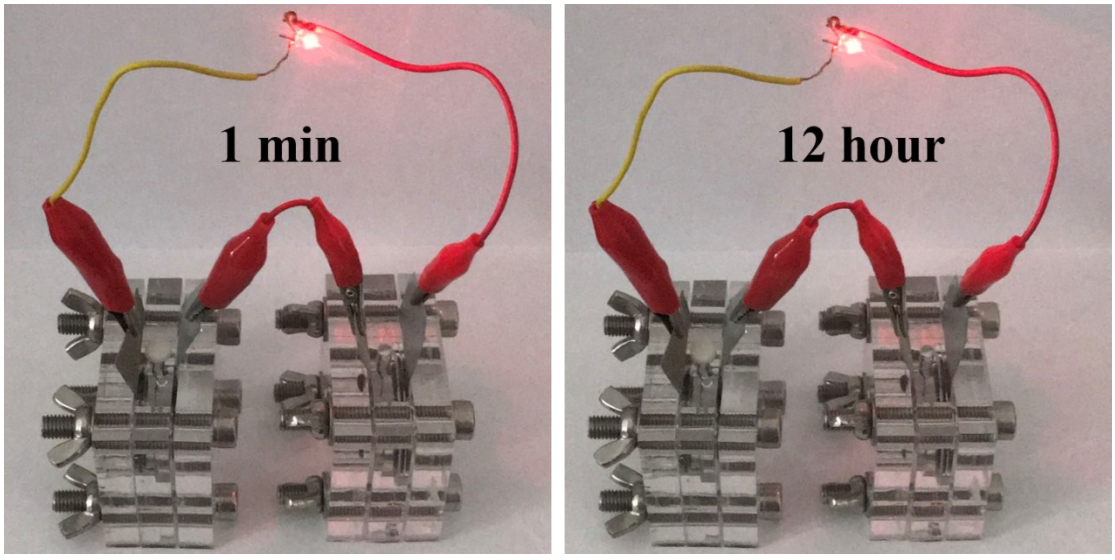

Fig. S13 Photograph of a red LED (1.8 V) powered by two RZABs connected in series with Co_3O_4@$NiCo_2O_4$ DSNCs as the air cathode.

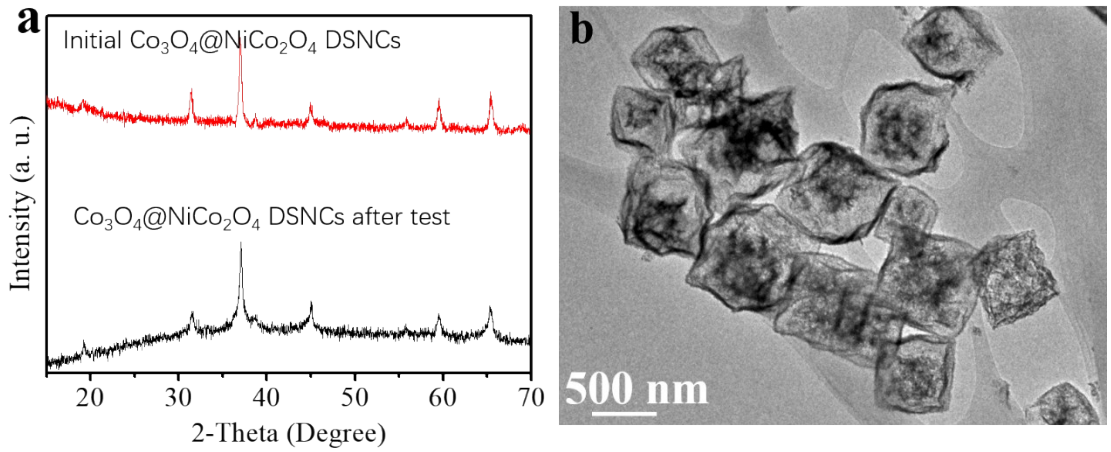

Fig. S14 (a) XRD patterns and (d) TEM image of Co_3O_4@$NiCo_2O_4$ DSNCs catalysts as air electrode in RZAB after a 140 h long-term battery test, respectively.

Table S1. Thorough comparison of performances of recently reported bifunctional oxygen electrocatalysts.

Catalysts	ORR ($E_{1/2}$,V)	OER ($E_{j=10}$,V)	Activity ($\Delta E=E_{j=10}-E_{1/2}$, V)	Stability	Reference
CoNi@NCNTs	0.8	1.6	0.8	/	1
Co_2P/CoN-in-NCNTs	0.85	1.65	0.8	96h (5mA cm^{-2})	2
Co-Co_XO/NC	0.8	1.63	0.83	420h (5mA cm^{-2})	3
Co_3O_4-CoFe	0.81	1.59	0.78	65h (5mA cm^{-2})	4
CoNCF	0.92	1.76	0.84	166h (10mA cm^{-2})	5
Co_4N/Co-N-C	0.8	1.54	0.74	136h (10mA cm^{-2})	6
NiSx/NMC	0.89	1.57	0.68	100h (10mA cm^{-2})	7
MnO/Co/PGC	0.78	1.537	0.82	350cycles (5mA cm^{-2})	8
FeCo/FeN_2/NHOPC	0.86	1.57	0.71	100h (10mA cm^{-2})	9
FeCo/FeCoNi@NCNTs-HF	0.85	1.61	0.76	240h (5mA cm^{-2})	10
MnO@Co-N/C	0.83	1.76	0.93	178h (10mA cm^{-2})	11
$Co_{0.5}Ni_{0.5}Mn_2O_4$	0.71	1.72	1.01	10h (2mA cm^{-2})	12
$MnCo_2O_4$@C	0.8	1.69	0.89	70h (10mA cm^{-2})	13
$CaMnO_3$/S	0.76	1.7	0.94	120cycles (5mA cm^{-2})	14
Mn/Co-N-C	0.8	1.66	0.86	250h (5mA cm^{-2})	15
CMN-231	0.75	1.63	0.88	100h (10mA cm^{-2})	16

$NiCo_2O_4$ Nanosheet	0.74	1.68	0.94	29h (10mA cm^{-2})	17
Co_3O_4@$NiCo_2O_4$ DSNCs	**0.81**	**1.65**	**0.84**	**140h (10mA cm^{-2})**	**This work**

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