Supporting Information

Nitrogen-Doped $NiCo_2S_4$/CoO hollow multi-layered heterostructure microsphere for efficient oxygen evolution in the Zn-air battery

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Table S1. OER performances of **N-$NiCo_2S_4$/CoO** microsphere in comparison of recently representative electrocatalysts in alkaline medium (1.0 M KOH, at 10 mA cm^{-2}).

catalyst	Overpotential (mV)	Reference
N-$NiCo_2S_4$/CoO	**238**	**This work**
NiFe/$NiCo_2O_4$/NF	340	1
amorphous CoP/NF	284	2
Ni-Co-P HNBs	270	3
NiCoP@NF	280	4
$NiCo_2S_4$ nanoflake/NF	319	5
Ni_3S_2@MoS_2/FeOOH	260	6
Mo-$Co(OH)_2$ HNTs	218	7
$Ni_3(BO_3)_2$-Ni_3S_2/NF	217	8
Ni/$Ni(OH)_2$ nanosheets	270	9
FeNiB/FeNi foam-700	272	10
Pt@Co_3O_4/NF	260	11
Co_4N-CeO_2	239	12

Table S2. The main differences of **N-$NiCo_2S_4$/CoO** microsphere in comparison of **Ni-Co-S** multi-shell hollow microspheres.

	NiCoS	N-$NiCo_2S_4$/CoO
catalyst composition	NiS_2 /NiO	N-$NiCo_2S_4$/CoO
synthesis method	sulfur powder vulcanization	sulfur powder vulcanization in the presence of NH_4HCO_3
working electrode	glassy carbon electrode	nickel foam electrode
electrocatalytic property	HER	OER

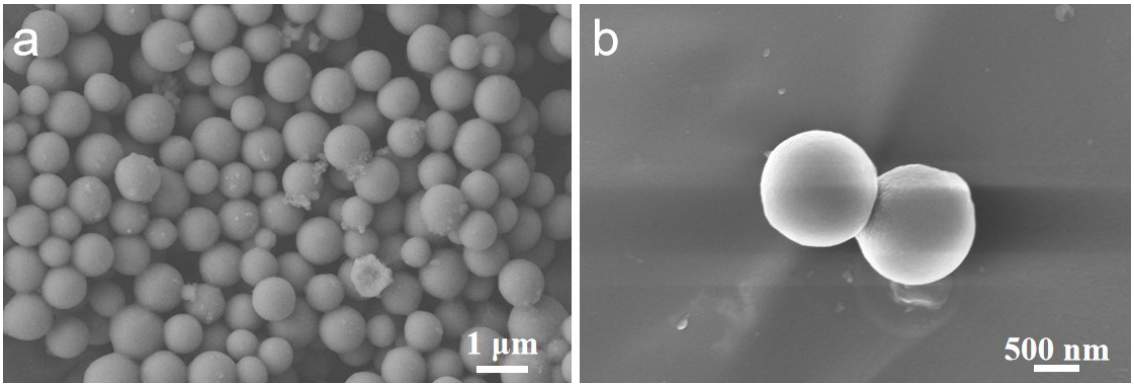

Fig. S1. SEM images of **NiCo-BTC MOF** microsphere.

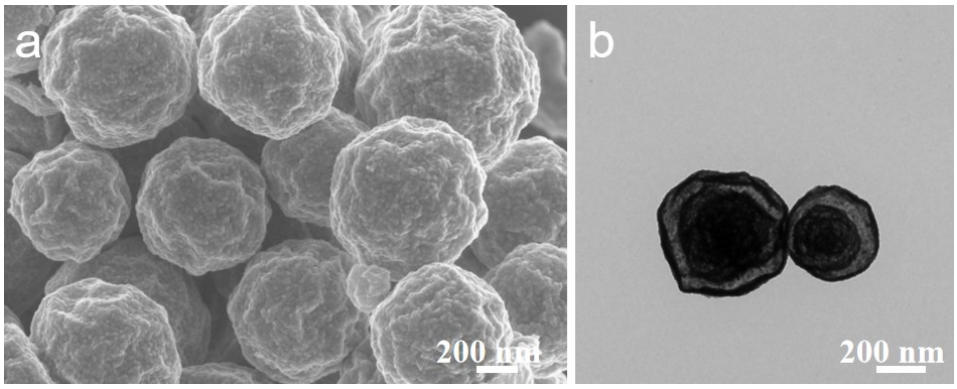

Fig. S2. (a) SEM and (b) TEM images of the **$NiCo_2O_4$** microsphere.

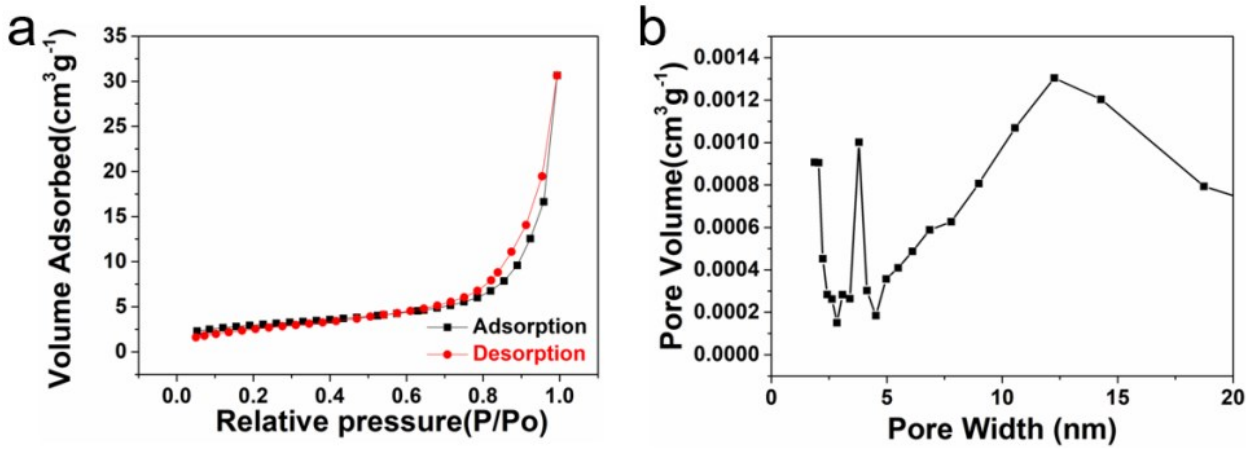

Fig. S3. Nitrogen adsorption-desorption isotherms and Pore size distributions of N-$NiCo_2S_4$/CoO.

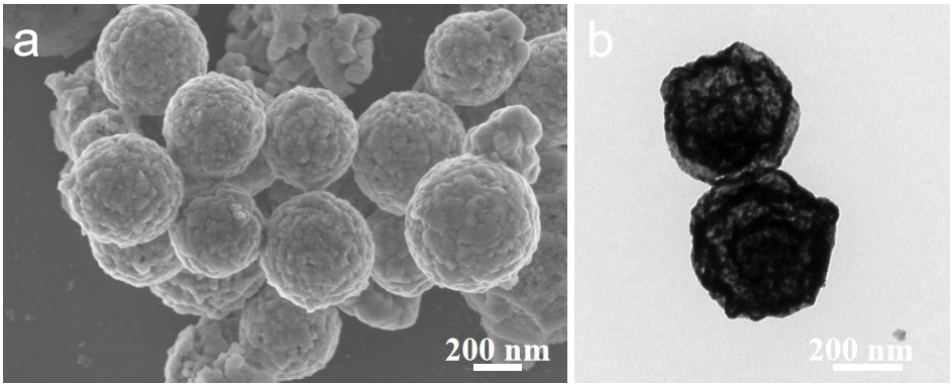

Fig. S4. SEM (a) and TEM image (b) of the **$NiCo_2S_4$/CoO** microsphere.

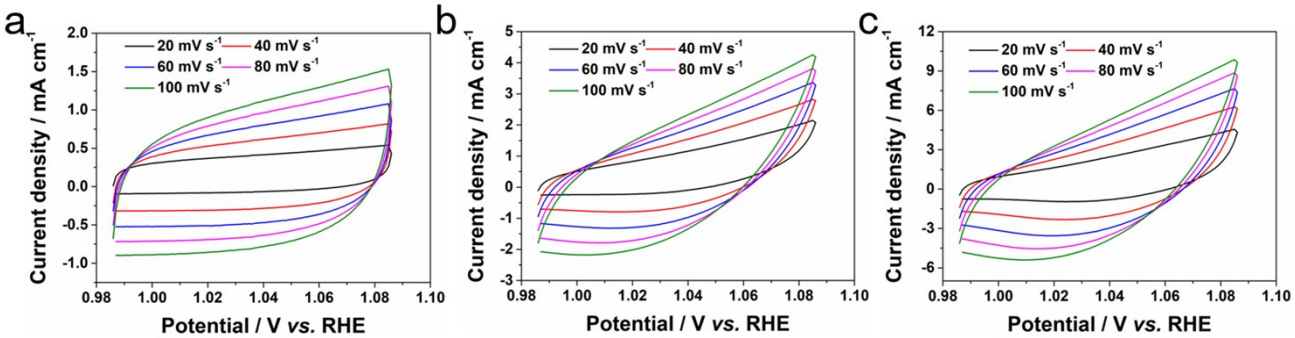

Fig. S5. Cyclic voltammogram (CV) curves of (a) **$NiCo_2O_4$**, (b) **$NiCo_2S_4$/CoO** and (c) **N-$NiCo_2S_4$/CoO** samples.

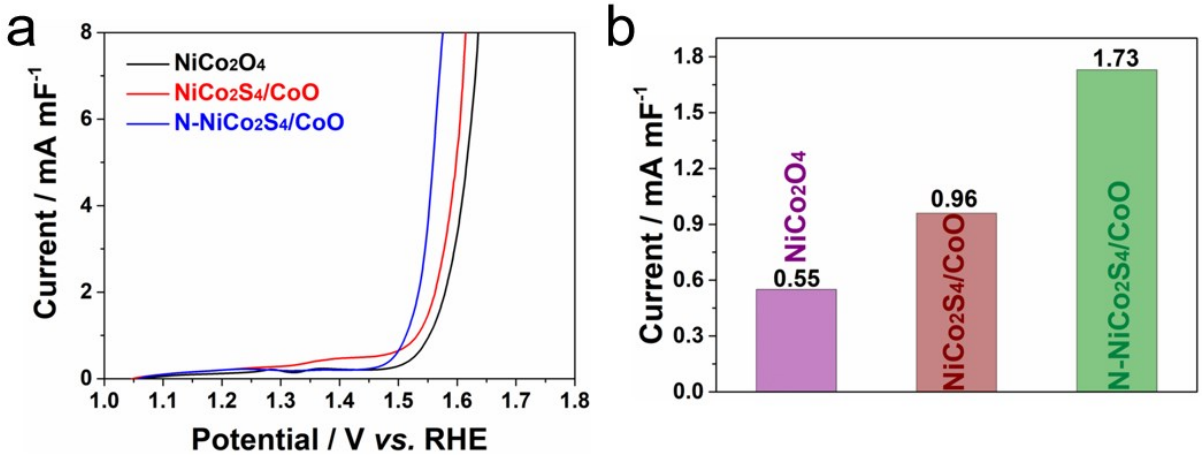

Fig. S6. (a) LSV curves normalized by ECSA and (b) The normalized current density by ECSA at 300 mV overpotential of **$NiCo_2O_4$**, **$NiCo_2S_4$/CoO** and **N-$NiCo_2S_4$/CoO**.

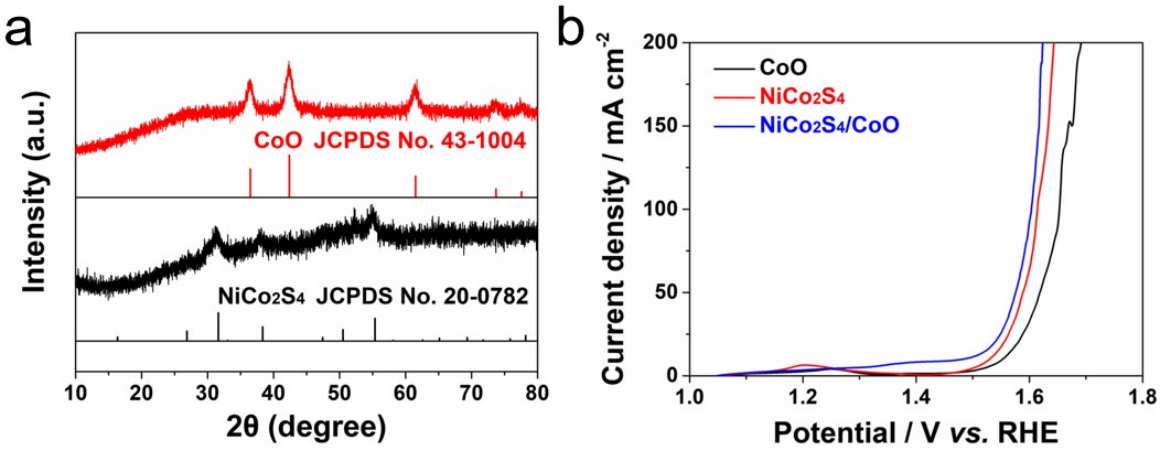

Fig. S7. (a) XRD patterns of **$NiCo_2S_4$** and **CoO**, (b) LSV polarization curves of **$NiCo_2S_4$**, **CoO** and **$NiCo_2S_4$/CoO**.

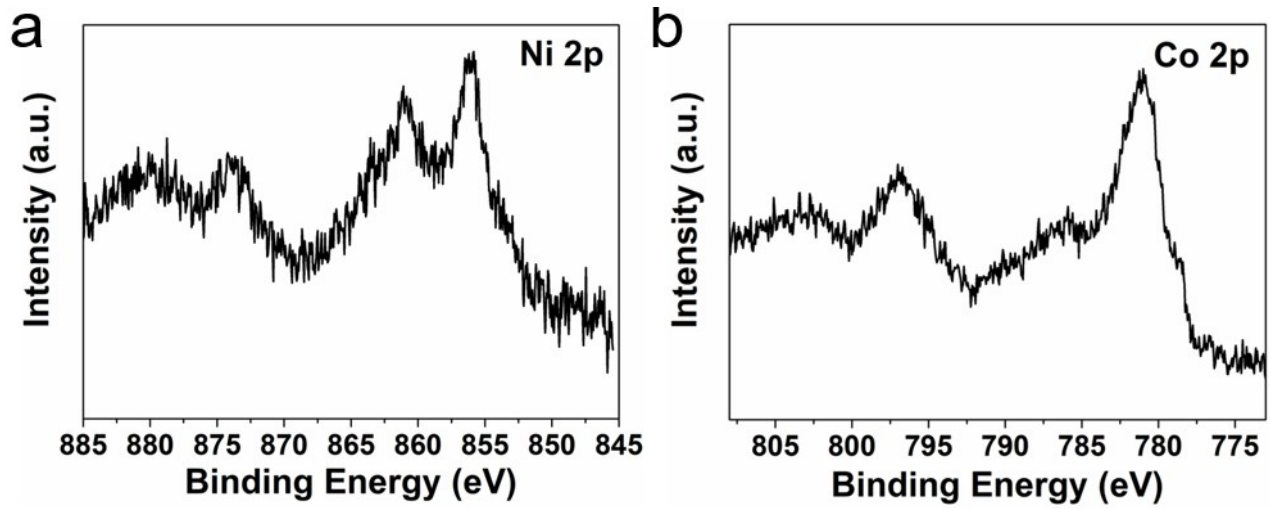

Fig. S8. High-resolution XPS spectra at Ni 2p (a) and Co 2p (b) for **N-$NiCo_2S_4$/CoO** microshphere after OER test.

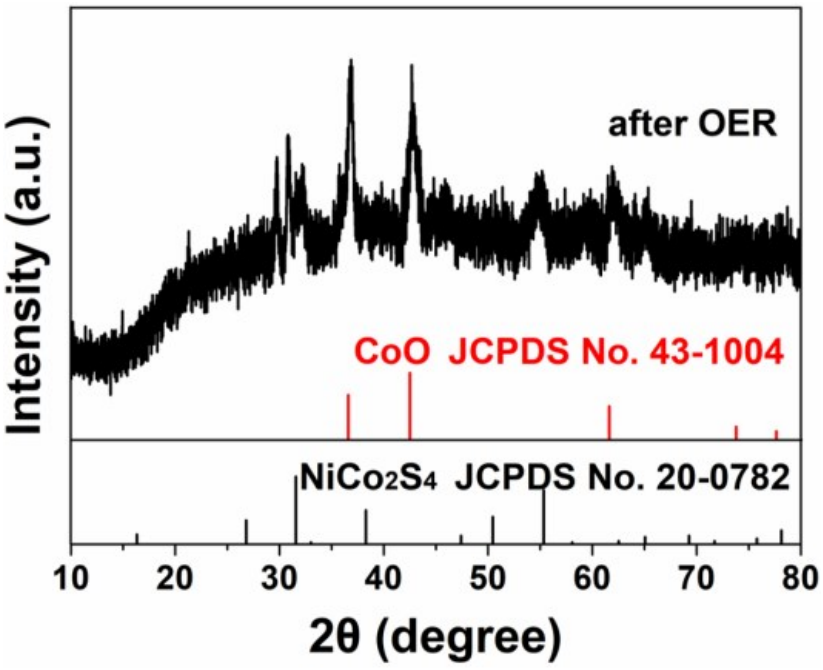

Fig. S9. XRD pattern of **N-NiCo$_2$S$_4$/CoO** microshphere after OER test.

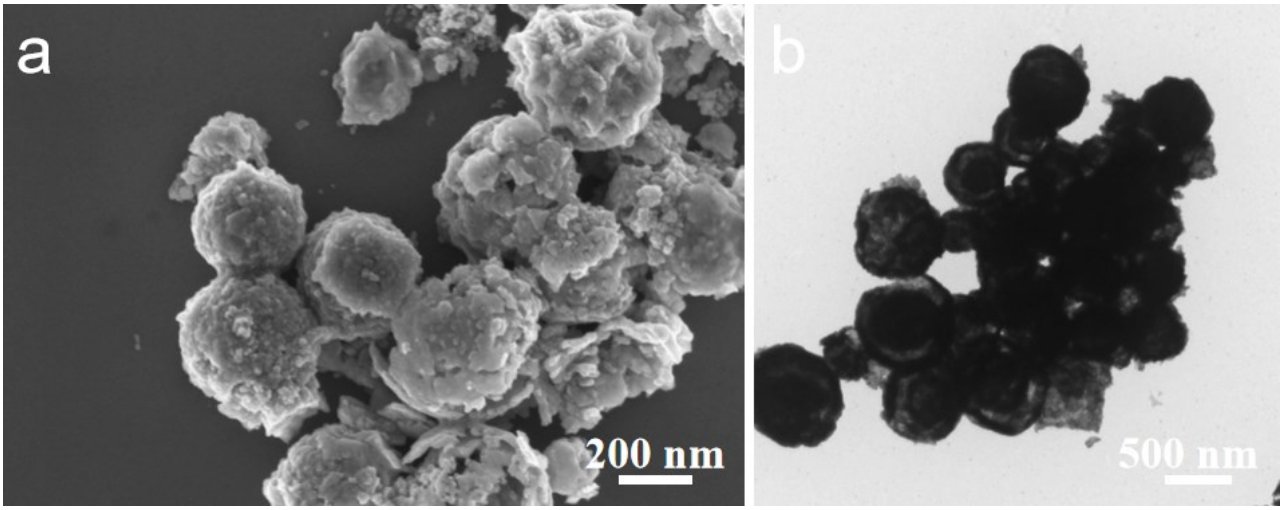

Fig. S10. SEM (a) and TEM images (b) for **N-NiCo$_2$S$_4$/CoO** microsphere after OER test.

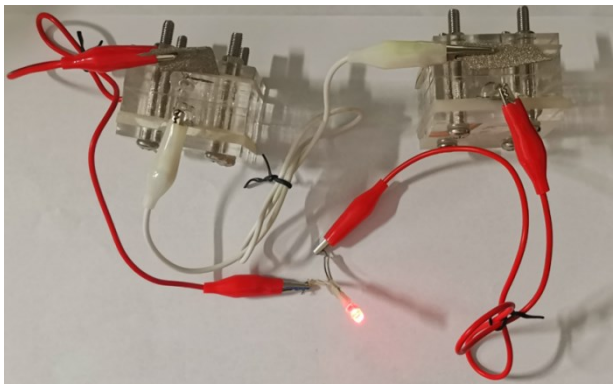

Fig. S11. A LED lamp (~ 3.0 V) could be powered up by two Zn-air batteries in serious with the **N-$NiCo_2S_4$/CoO** + Pt/C catalyst as air-cathode.

References

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