Experimental Section

Synthetic procedures

The synthesis of $ZnCo_2O_4$@ZnCo-LDHs. The synthesis of Zn-Co LDHs involve a simple two-step process. 1 mmol of $Zn(CH_3COO)_2$ and 2 mmol of $Co(CH_3COO)_2$ is dissolved into 50 mL of ethylene glycol to form a transparent solution after mixing for 30 min. Then the mixture is heated to 170 °C. After reaction for 2 h, the solution is cooled down naturally, and then the product of ZnCo-glycolate is collected by centrifugation and washed with alcohol for three times. After drying, 25 mg ZnCo-glycolate powder is dispersed into 10 mL ethanol by ultrasonication for 15 min to form a solution, which is injected 1 mL deionized (DI) water and then transferred into a 15 mL Teflon-lined autoclave. The $ZnCo_2O_4$@ZnCo-LDH-1000 is obtained after reaction at 105 °C for 4 h. The obtained $ZnCo_2O_4$@ZnCo-LDH-1000 is collected by centrifugation, washed with methanol three times and dried under vacuum at 60 °C for 12h. As for the other two samples, the amount of DI water is 0.5 mL ($ZnCo_2O_4$@ZnCo-LDH-500) and 2 mL (ZnCo-LDH-2000) with other conditions unchanged.

Characterization

The morphology and microstructure of the products are characterized using a transmission electron microscope (TEM, TECNAI G2), a high resolution transmission electron microscope (HR-TEM, TECNAI G2) with an accelerating voltage of 200 kV. Field-emission scanning electron microscope (FE-SEM) images are obtained on a HITACHI S-4800 SEM. X-ray photoelectron spectra (XPS) measurements are taken on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.). X-ray diffraction patterns of the products are collected on a Bruker D8 ADVANCE with Ni filtered Cu Kα radiation (λ=1.54 Å). Micromeritics ASAP2020 surface area analyzer is utilized to measure gas adsorption. The thermogravimetric analysis (TGA) of samples are performed by SDT 2960 thermal analyzer at a heating rate of 5 °C·min^{-1} under air within the temperature range 50-800 °C.

Electrode Fabrication and Measurements

Evaluation of the electrocatalytic activity toward OER. 5 mg of catalysts ($ZnCo_2O_4$@ZnCo-LDHs) and 1 mg of carbon black (Super P) are mixed in 1mL solution containing 750 μL of water, 200 μL of isopropanol and 50 μL of 5 wt% Nafion solution by ultrasonication for 30 min to form a homogeneous ink. 10 μL catalyst inks are droped onto a glassy carbon electrode of 3 mm in diameter and dried at room temperature. The loading amount of all catalysts is 0.19 mg cm^{-2}. The standard three-electrode system is performed to evaluate electrochemical properties in with a CHI760e electrochemical workstation in 1.0 M KOH solution using Pt wire and an Ag/AgCl (3 M KCl) electrode as counter-electrode and reference electrode, respectively. All the measured potentials are referred to RHE with the following equation:

$$E(RHE)=E(Ag/AgCl)+1.035 \quad (1)$$

Linear sweep voltammetry (LSV) is carried out at a scan rate of 5 mV s^{-1} for the polarization with iR corrected.

Electrochemical impedance spectroscopy is recorded at overpotential of 500 mV in the frequency range from 50 kHz to 1Hz with oscillation potential amplitudes of 5 mV in 1 M KOH.

The stability tests of $ZnCo_2O_4$@ZnCo-LDHs are carried in a 1 M KOH aqueous solution at room temperature. Around 2000 CVs are carried out between 0 and 0.7 V (vs. Ag/AgCl) at a scan rate of 100 mV s^{-1}**.** After the CVs test, the LSV is carried out at a scan rate of 5 mV s^{-1} for the polarization with iR corrected again. The electrochemically active surface areas of the samples are investigated from double-layer charging curves using CVs (0.2 V to 0.3 V vs.) at various scan rate from 5 mV s^{-1} to 50 mV s^{-1}.

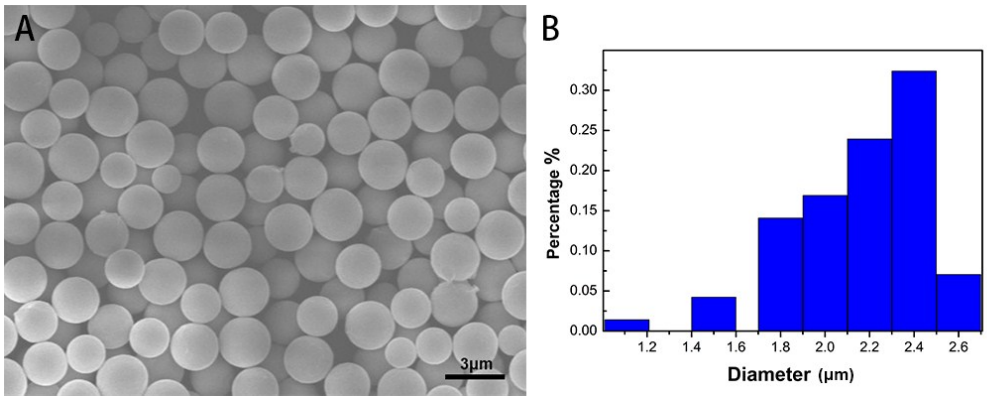

Fig. S1. (A) SEM image and (B) particle size distributions of ZnCo-EG.

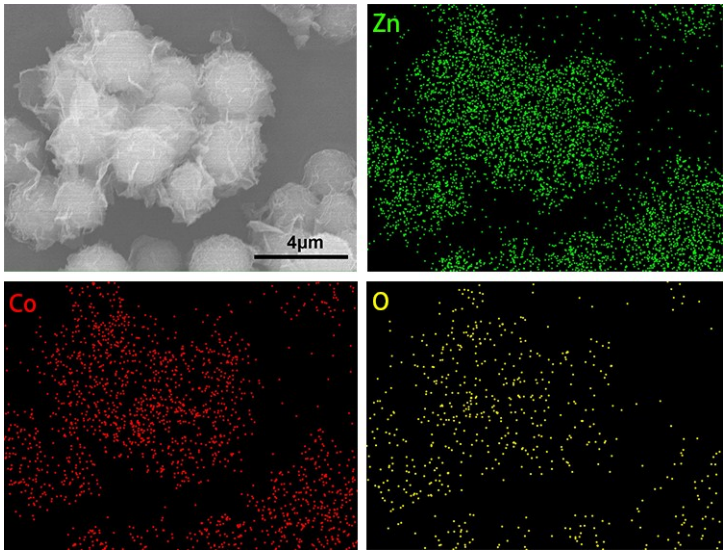

Fig. S2. SEM image of $ZnCo_2O_4$@ZnCo-LDH-1000 and the elemental maps of Zn, Co and O.

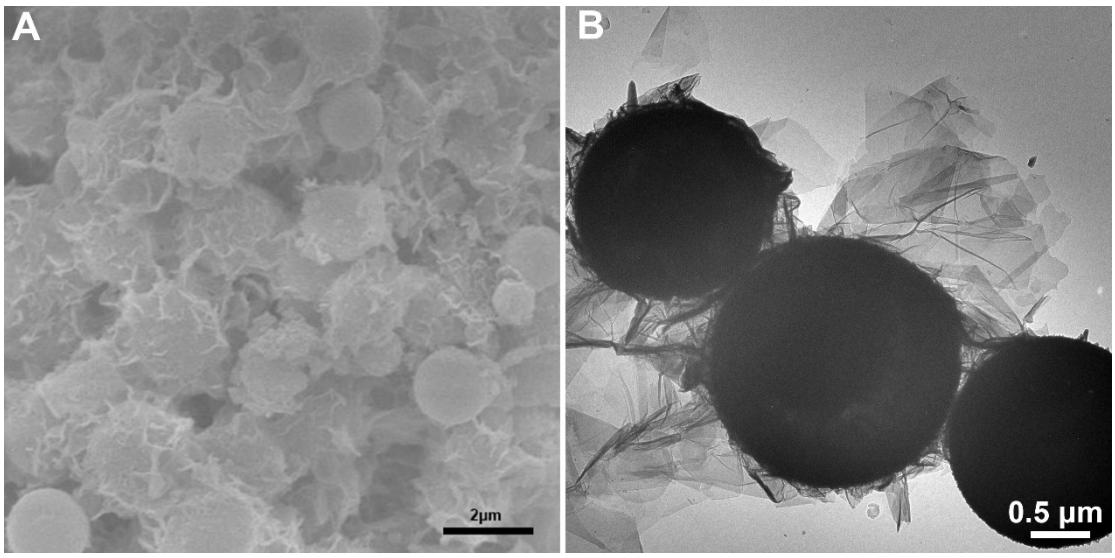

Fig. S3. (A) SEM and (B) TEM image of $ZnCo_2O_4$@ZnCo-LDH-500.

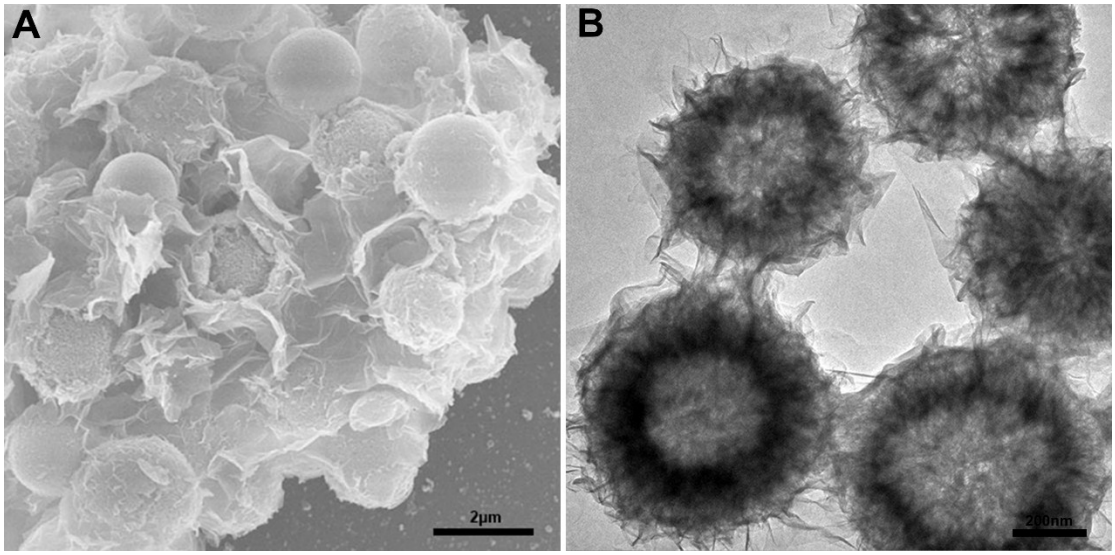

Fig. S4. (A) SEM and (B) TEM image of ZnCo-LDH-2000.

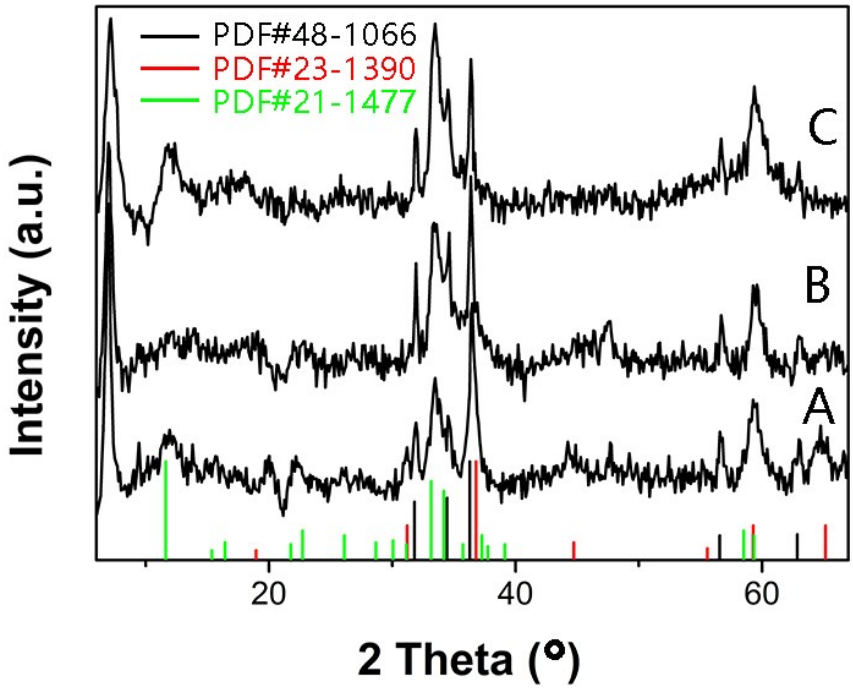

Fig. S5. XRD patterns of (A) $ZnCo_2O_4$@ZnCo-LDH-500, (B) $ZnCo_2O_4$@ZnCo-LDH-1000 and (C) ZnCo-LDH-2000.

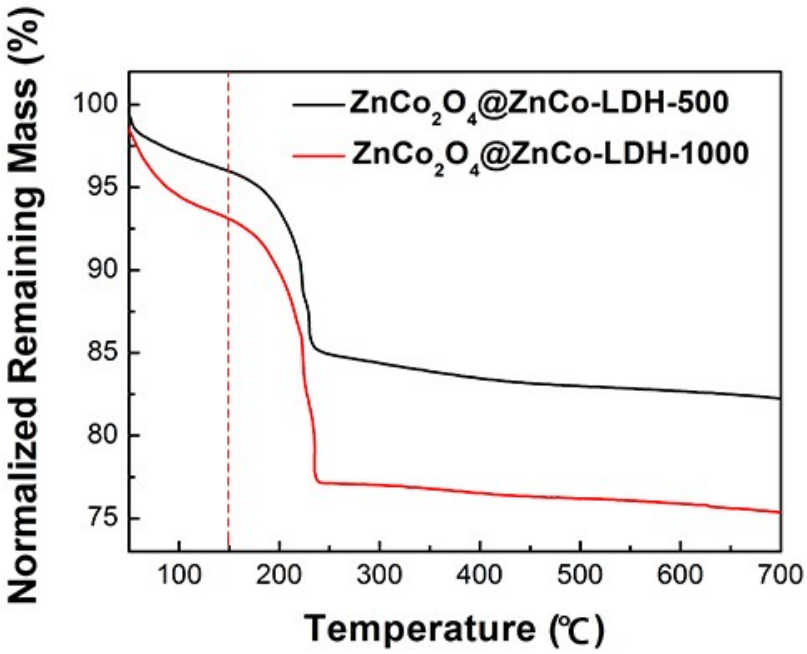

Fig. S6. TG curves of $ZnCo_2O_4$@ZnCo-LDHs under air atmosphere.

Table S1. The weight percentage content of dehydroxylation in $ZnCo_2O_4$@ZnCo-LDHs from TGA and the atom percentage of ZnCo-LDHs from calculation.

	Weight loss of dehydroxylation	Percentage of ZnCo-LDHs
$ZnCo_2O_4$@ZnCo-LDH-500	10.61%	56.00%
$ZnCo_2O_4$@ZnCo-LDH-1000	15.92%	84.00%

Table S2. The yield of $ZnCo_2O_4$@ZnCo-LDHs yolk-shell nanospheres

	Theoretical value of production (mg)	Quality of the products(mg)	Yields (%)
$ZnCo_2O_4$@ZnCo-LDH-500	14.21	12.9	90.78%
$ZnCo_2O_4$@ZnCo-LDH-1000	14.78	13.2	89.3%
ZnCo-LDH-2000	15.11	13.8	91.33%

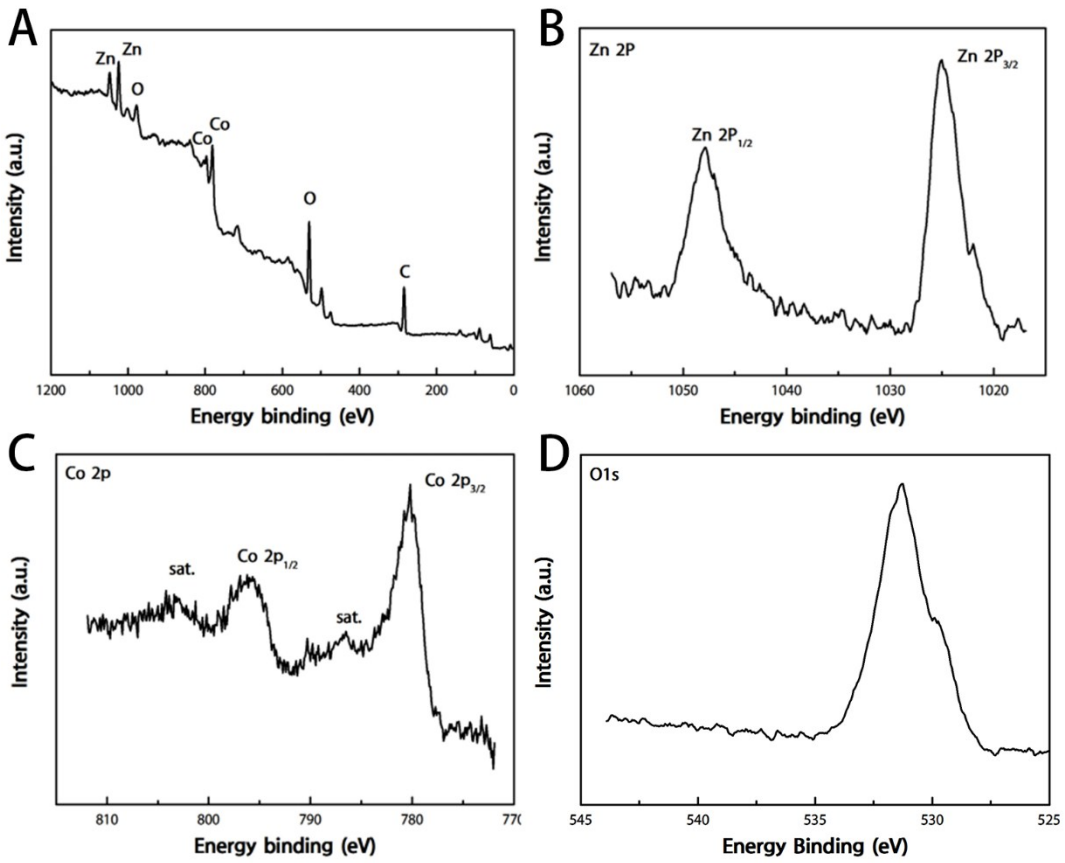

Fig. S7. (A) XPS spectra of $ZnCo_2O_4$@ZnCo-LDH-1000 spectrum; XPS spectra of (B) Zn 2p spectrum, (C) Co 2p spectrum and (D) O 1s spectrum.

Table S3 Electrochemical performance of $ZnCo_2O_4$@ZnCo-LDHs and the control samples

Samples	η_{onset}[a] (V)	$\eta_{10\ mA\ cm^{-2}}$ (V)	Tafel slope (mV dec^{-1})	Cdl (mF cm^{-2})	Electrolyte	Ref.
$ZnCo_2O_4$@ZnCo-LDH-1000	0.365	0.375	73	0.112	1 M KOH	Present work
$ZnCo_2O_4$@ZnCo-LDH-500	0.390	0.392	88	0.0062	1 M KOH	Present work
ZnCo-LDH-2000	0.384	0.399	75	0.141	1 M KOH	Present work
$Zn(OH)_2$	0.436	0.471	59	0.0001	1 M KOH	Present work
$Co(OH)_2$	0.372	0.413	106	0.0098	1 M KOH	Present work
ZnCo-LDH-100[b]	0.33	0.427[c]	83	0.05036	0.1 M KOH	[S1]
Co-OH[b]	0.33	0.453[c]	119	0.03185	0.1 M KOH	[S1]
Zn-OH[b]	0.42	0.619[c]	128	-	0.1 M KOH	[S1]
Zn-Co-LDH nanosheets[b]	0.23	0.375[c]	101	-	0.1 M KOH	[S2]
Zn-Co-LDH-nanoparticles[b]	0.35	0.461[c]	145	-	0.1 M KOH	[S2]
RGO/ZnCo-LDH[b]	0.409	0.599	73	-	0.1 M KOH	[S3]
ZnCo-200[b]	-	0.370	54.7	23.19	1.0 M KOH	[S4]
$ZnCo_2O_4$[b]	-	0.39	46	-	1 M KOH	[S5]
Co_3O_4[b]	-	0.41	54	-	1 M KOH	[S5]

Co_3O_4[b]	0.27	0.49	61	-	0.1 M KOH	[S6]
NiCo LDH nanosheets[b]	0.29	0.42	113		0.1 M KOH	[S7]
NiCo LDH[b]	-	0.367	40	0.0041	1 M KOH	[S8]
CoMn LDH[b]	-	0.324	43	-	1 M KOH	[S9]

a. The potential is vs. RHE here. b. Powder sample coated on a glassy carbon electrode reported in the literature. c. The overpotential at the current density of 2 mA cm^{-2}.

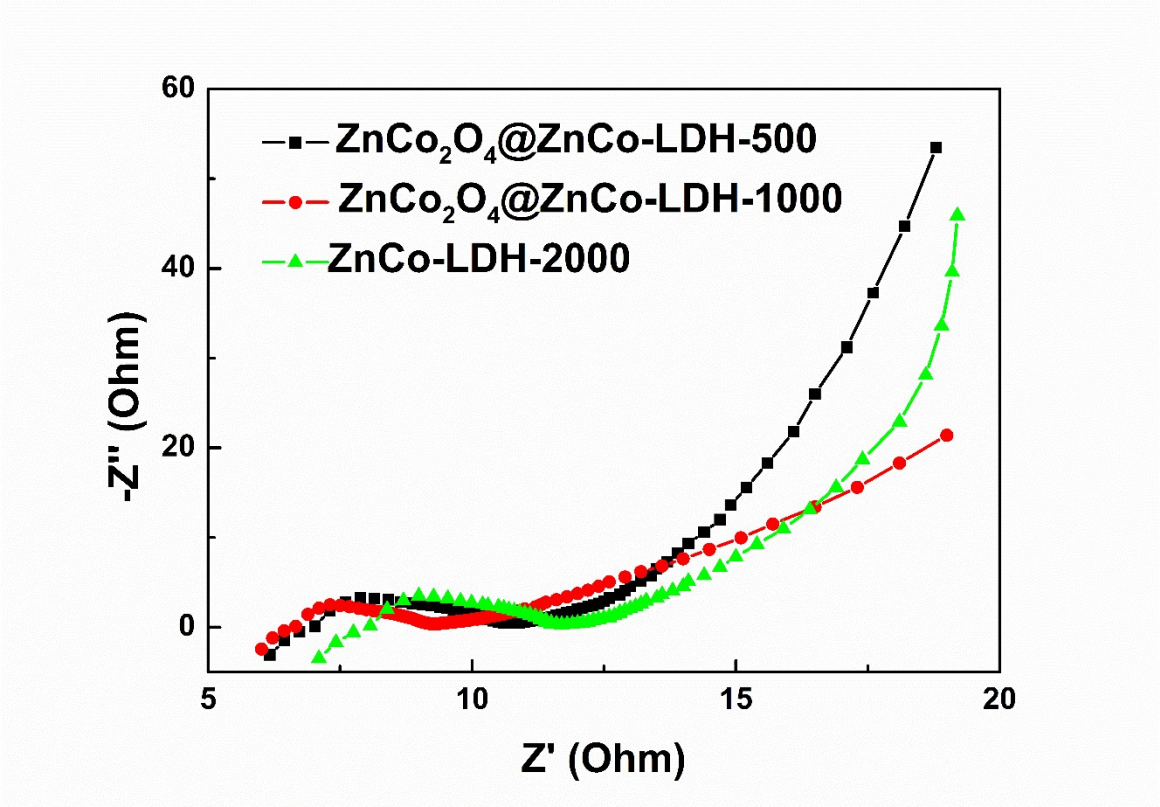

Fig. S8. Nyquist plots (Z' vs. –Z'') of $ZnCo_2O_4$@ZnCo-LDH-500, $ZnCo_2O_4$@ZnCo-LDH-1000 and ZnCo-LDH-2000.

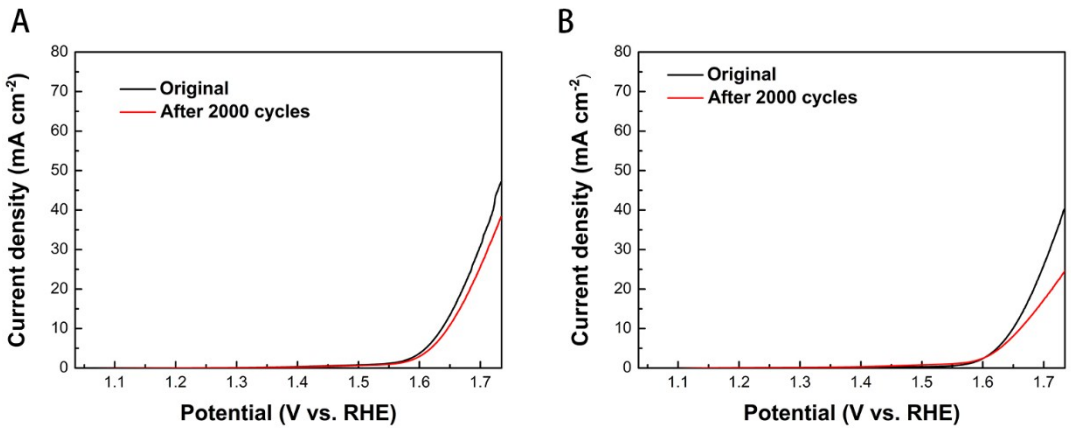

Fig. S9. OER polarization curves of (A) $ZnCo_2O_4$@ZnCo-LDH-500 and (B) ZnCo-LDH-2000 measured before and after 2000 potential cycles at a scan rate of 5 mV s^{-1} at room temperature with *iR*

compensation in 1 M KOH.

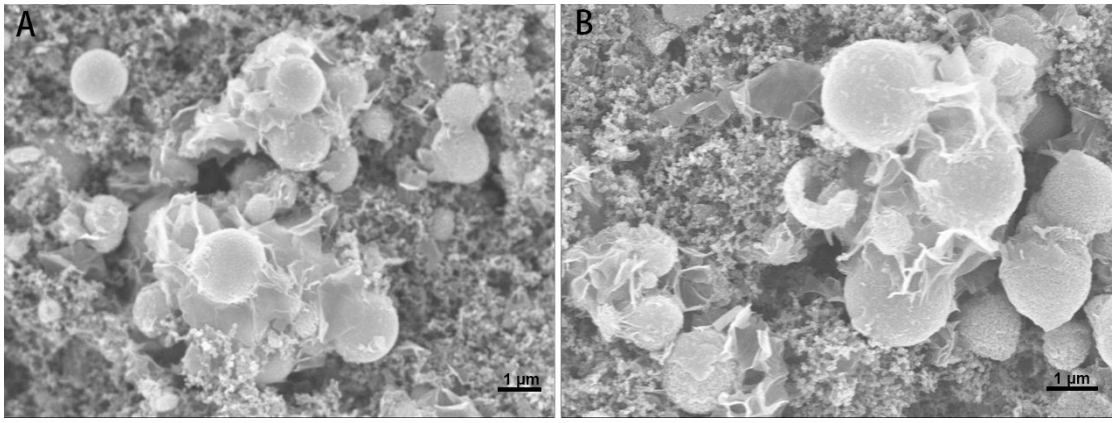

Fig. S10. SEM image of $ZnCo_2O_4$@ZnCo-LDH-1000 (A) before and (B) after 2000 potential cycles.

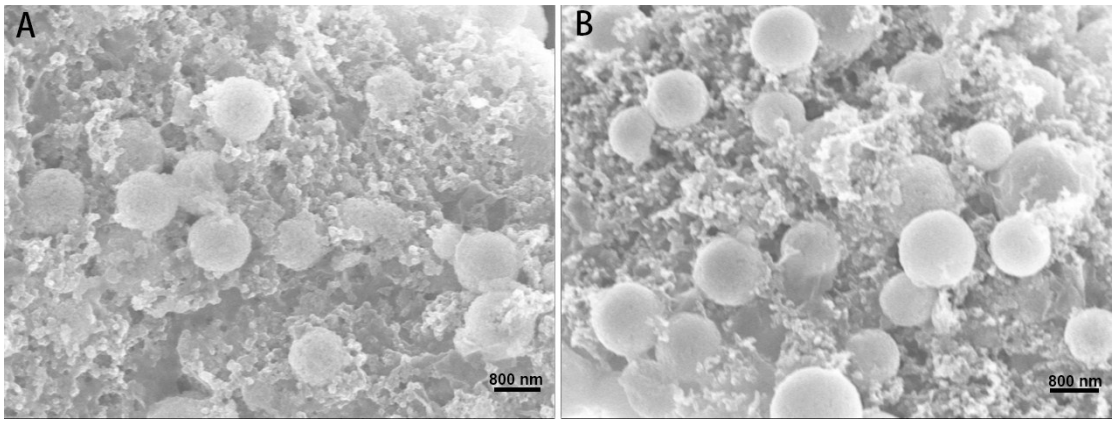

Fig. S11. SEM image of $ZnCo_2O_4$@ZnCo-LDH-500 (A) before and (B) after 2000 potential cycles.

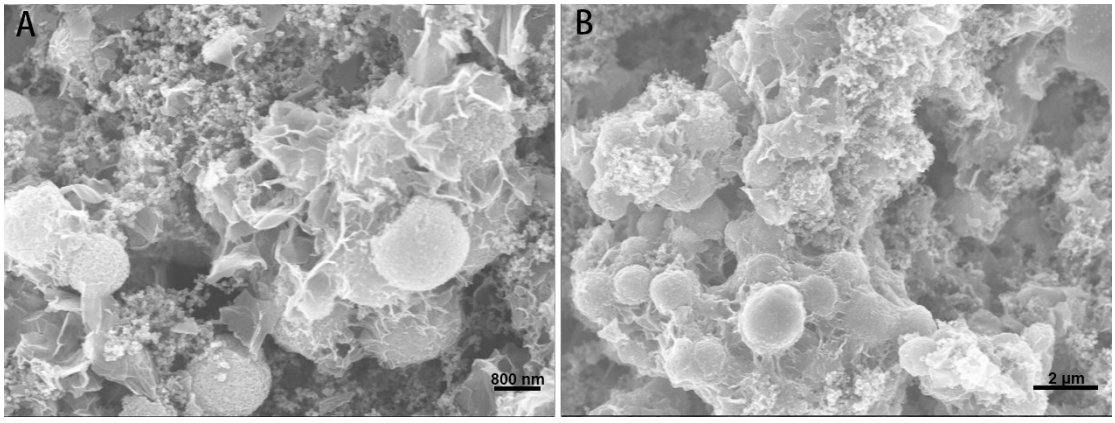

Fig. S12. SEM image of $ZnCo_2O_4$@ZnCo-LDH-1000 (A) before and (B) after 2000 potential cycles.

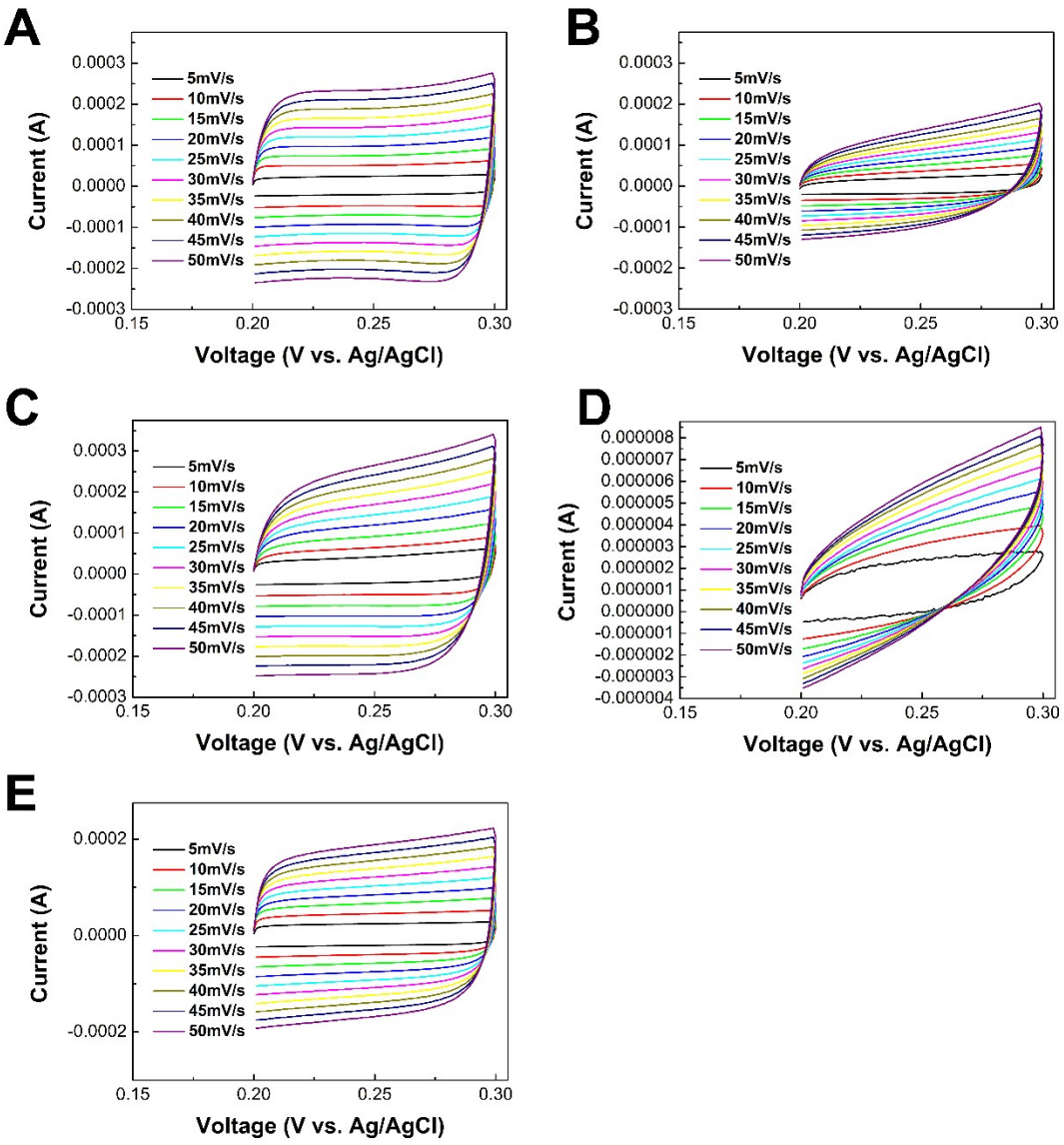

Fig. S13. Voltammograms of the (A) $ZnCo_2O_4$@ZnCo-LDH-1000, (B) $ZnCo_2O_4$@ZnCo-LDH-500, (C) ZnCo-LDH-2000, (D) $Zn(OH)_2$ and (E) $Co(OH)_2$ at various scan rate (5-50 mV s^{-1}) in 1 M KOH solution.

References

[S1] Y. Li, L. Zhang, X. Xiang, D. Yan, F. Li, *J. Mater. Chem. A,* 2014, **2**, 13250-13258.

[S2] C. Qiao, Y. Zhang, Y. Zhu, C. Cao, X. Bao, J. Xu, *J. Mater. Chem. A,* 2015, **3**, 6878-6883.

[S3] D. Tang, Y. Han, W. Ji, S. Qiao, X. Zhou, R. Liu, X. Han, H. Huang, Y. Liu, Z. Kang, *Dalt. Trans.,* 2014, **43**, 15119-15125.

[S4] Y. Xu, Z. Wang, L. Tan, Y. Zhao, H. Duan and Y.-F. Song, *Ind. Eng. Chem. Res.*, 2018, **57**, 10411-10420.

[S5] T. W. Kim, M. A. Woo, M. Regis, K.-S. Choi, *J. Phy. Chem. Lett.*, 2014, **5**, 2370-2374.

[S6] X. Leng, Q. Zeng, K.-H. Wu, I. R. Gentle and D.-W. Wang, *Rsc Adv.*, 2015, **5**, 27823-27828.

[S7] J. Jiang, A. Zhang, L. Li, L. Ai, *J. Power Sources*, 2015, **278**, 445

[S8] H. F. Liang, F. Meng, M. Caban-Acevedo, L. S. Li, A. Forticaux, L. C. Xiu, Z. C. Wang and S. Jin, *Nano Lett.*, 2015, **15**, 1421-1427.

[S9] F. Song, X. Hu, *J. Am. Chem. Soc.*, 2014, **136**, 16481.