Supplementary Information

Cobalt Layered Double Hydroxides Nanosheets Synthesized in Water-Methanol Solution as Oxygen Evolution Electrocatalysts

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Supplementary Electrochemical measurements

A rotating ring-disk electrode (RRDE, PINE Research Instrumentation, 6.5~8.5 mm, 5.5 mm) was used as the working electrode to test the H_2O_2 yield. The catalyst loading is 0.084 mg cm^{-2}. The ring potential was set at 0.6 V vs Ag/AgCl. The electron transfer number (n) is calculated from the disk current (J_d), ring current (J_r) and current collection efficiency (N=0.38) of the RRDE based on the following Equation.

$$n = \frac{4 \times J_d}{J_d + \dfrac{J_r}{N}}$$

CV curves were carried out from 0.22 to 0.3 V vs Ag/AgCl to obtain electrochemical double-layer capacitance (C_{dl}) by plotting charging current density differences (J_a-J_c) at 0.25 V vs Ag/AgCl against scan rates.
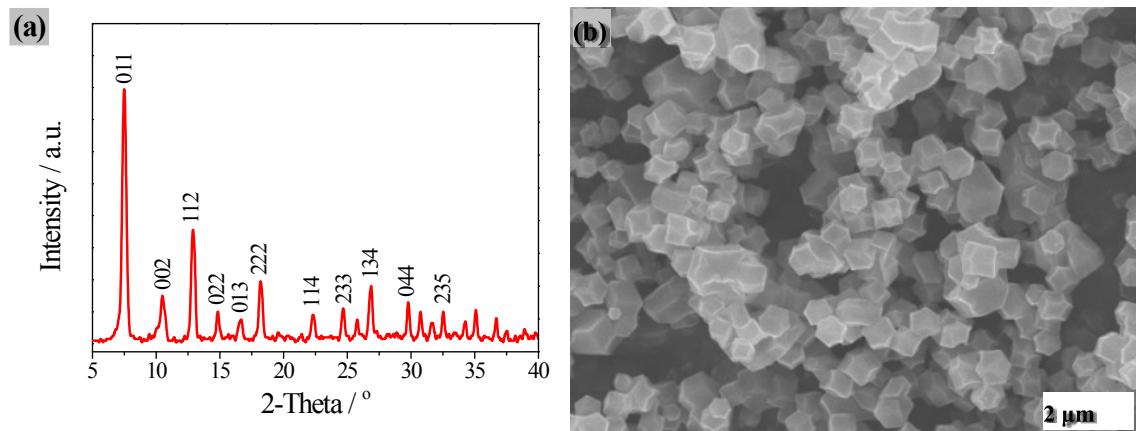
Fig. S1. (a) XRD pattern and (b) SEM image of ZIF-67 particles synthesized at 90 °C for 4 h in pure methanol.
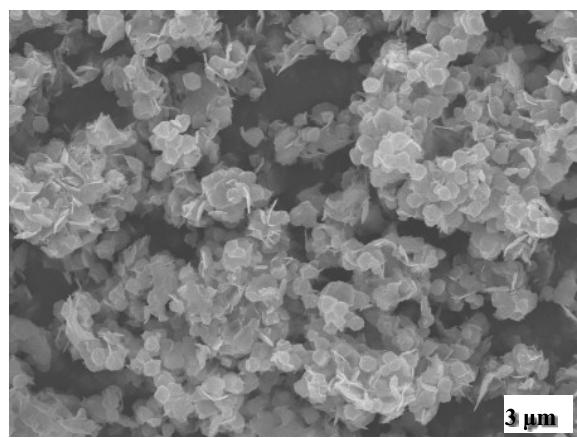

**Fig. S2.** SEM image of composites derived at 90 °C for 4 h in water-methanol solution containing 2 vol% of water.
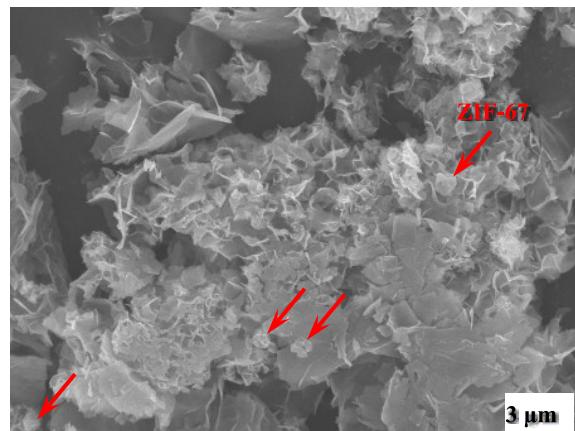
**Fig. S3.** SEM image of composites derived at 90 °C for 4 h in water-methanol solution containing 5 vol% of water.
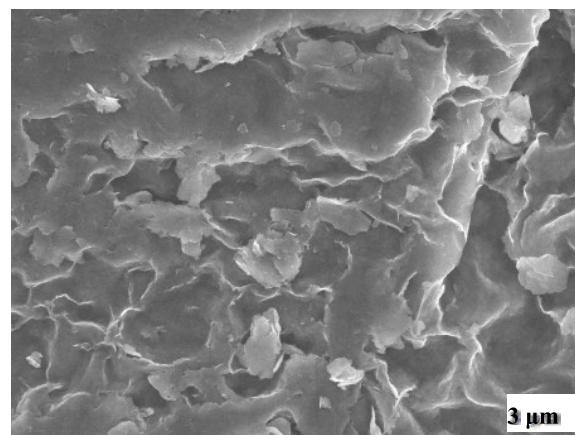
Fig. S4. SEM image of composites derived at 90 °C for 4 h in water-methanol solution containing 50 vol% of water.
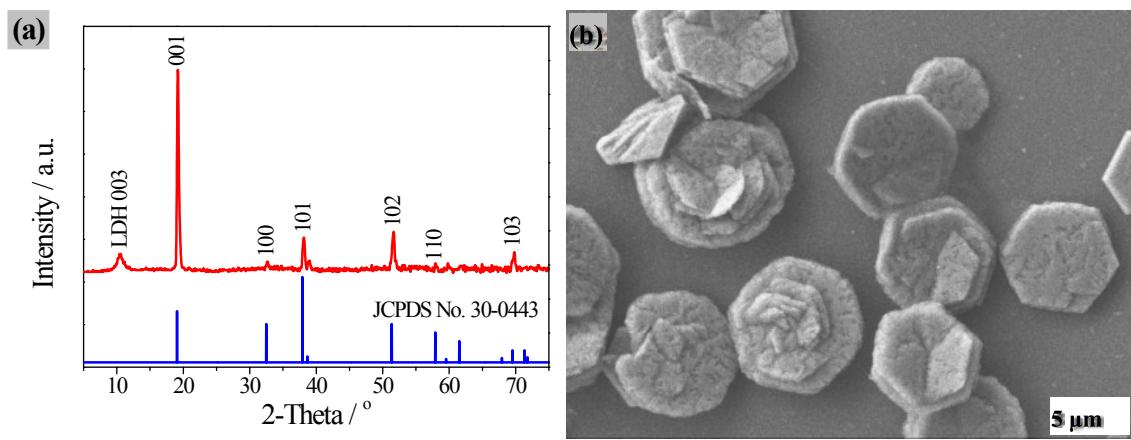
Fig. S5. (a) XRD pattern and (b) SEM image of Co(OH)$_2$ plates synthesized at 90 °C for 4 h in DI water.
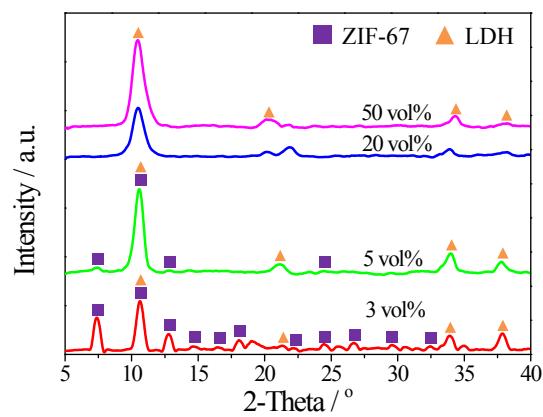

Fig. S6. XRD patterns of composites derived at 90 °C for 4 h in water-methanol solution containing different amounts of water.
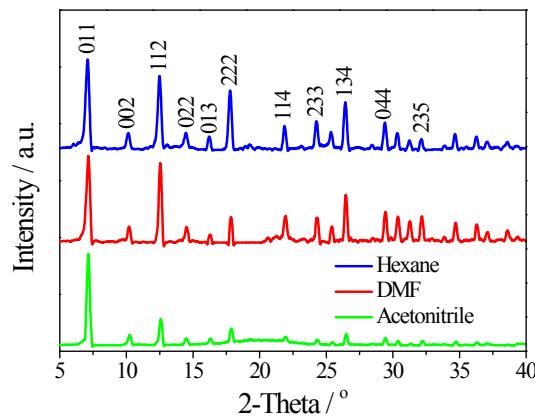
Fig. S7. XRD patterns of ZIF-67 particles synthesized at 90 °C for 4 h in methanol solution

containing 10 vol% of different solvent: (a) hexane; (b) DMF and (c) acetonitrile.
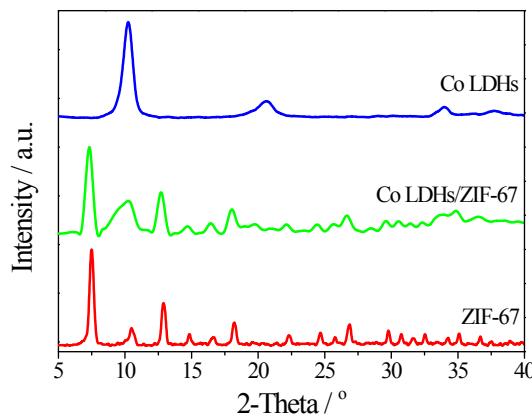

Fig. S8. XRD pattern of Co LDHs/ZIF-67 prepared by the hydrolysis reaction of pre-synthesized

ZIF-67 (100 mg) at 90 °C for 4 h in water-methanol solution (70 mL) containing 10 vol% of

water in the absence of cobalt (II) nitrate.
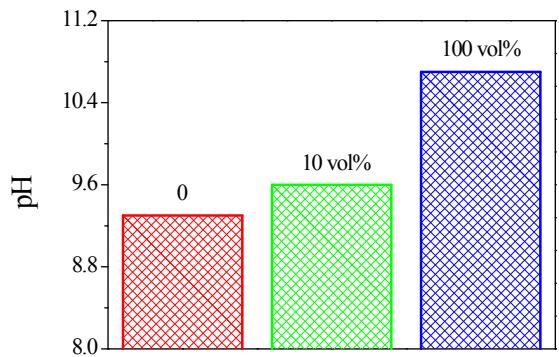
Fig. S9. pH value of 2MI (840 mg) in water-methanol solution (70 mL) containing different amounts of water.
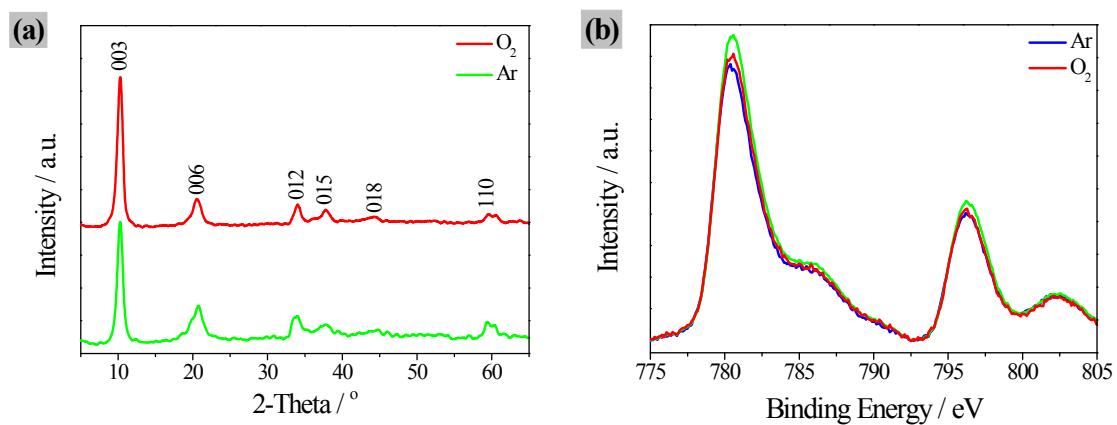

Fig. S10. (a) XRD patterns and (b) Co 2p high-resolution XPS spectra for Co LDHs synthesized at 90 °C for 4 h in Ar and O_2-saturated water-methanol solution containing 10 vol% of water.

Fig. S11. Optical images of Co-LDHNS-II: (a) Tyndall effect of colloidal solutions and (b) about 100 mg of dried powders in 5 mL centrifuge tube.
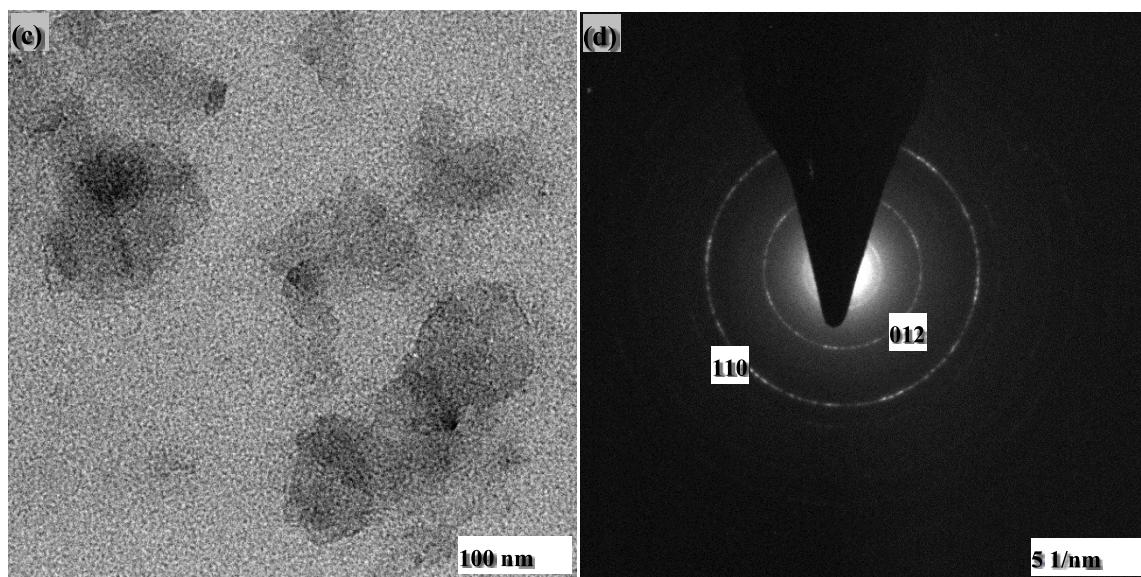
**Fig. S12.** (a) TEM image and (b) selected area diffraction pattern of Co-LDHNS-III.
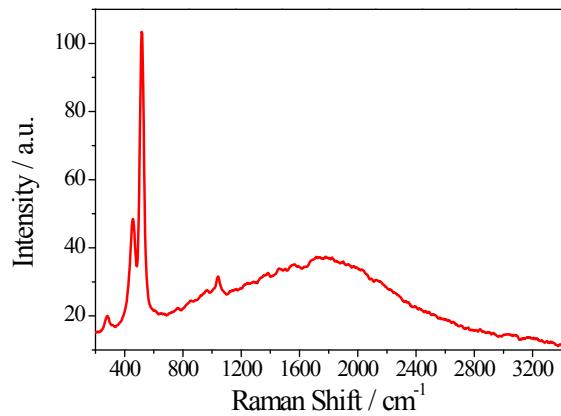
Fig. S13. Raman spectrum of Co-LDHNS-II.
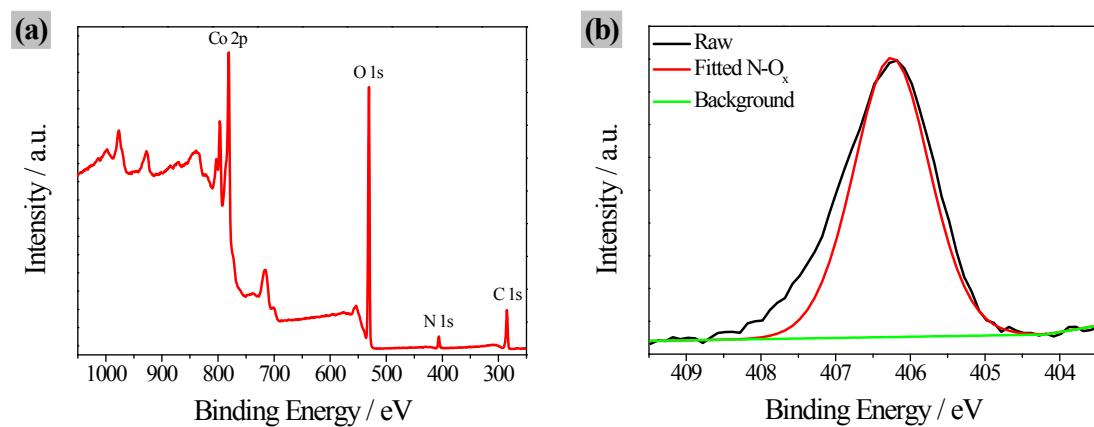
Fig. S14. (a) XPS survey spectrum and (b) N 1s high-resolution spectrum of Co-LDHNS-II.
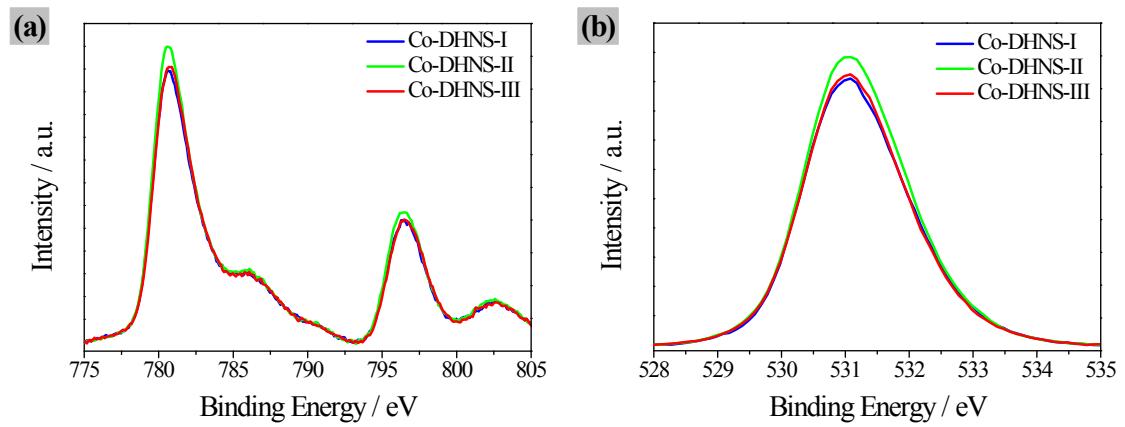
Fig. S15. (a) Co 2p and (b) O 1s high-resolution XPS spectra.
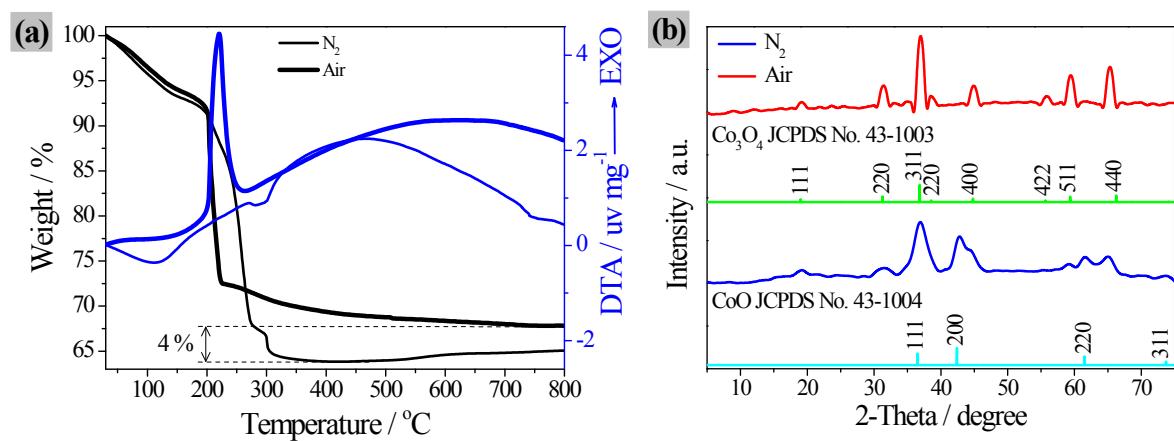
Fig. S16. (a) TG-DTA and DSC curves conducted in N_2 and air atmosphere for Co-LDHNS-II and (b) the corresponding XRD patterns after TG measurements.

S10
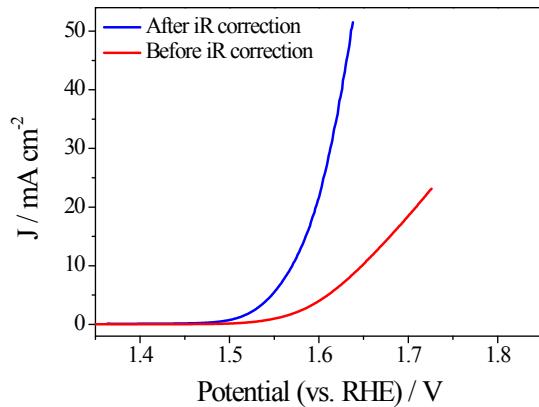
Fig. S17. LSV curves of Co-LDHNS-II before and after iR correction at 1600 rpm and 2 mV s^{-1} in 1 M KOH.
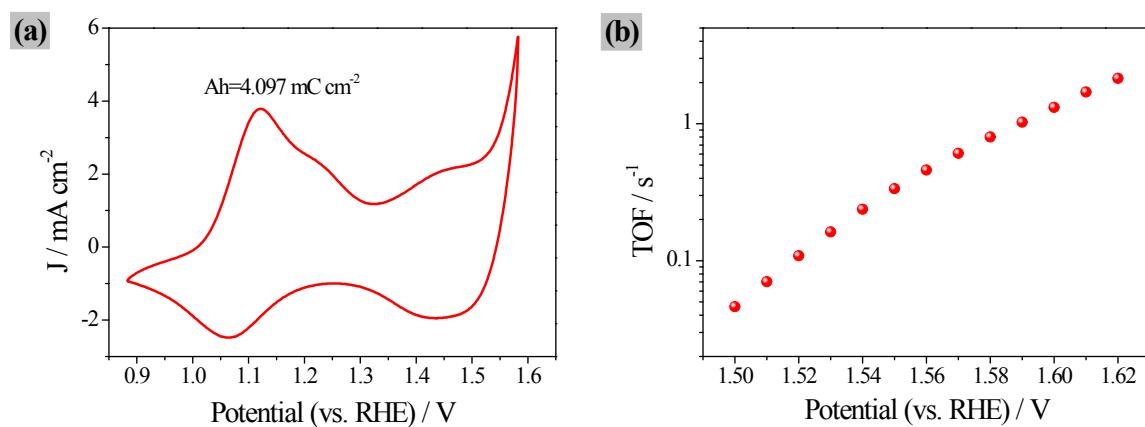
Fig. S18. (a) CV curve at 50 mV s^{-1} in 1 M KOH and (b) TOF for Co-LDHNS-II.
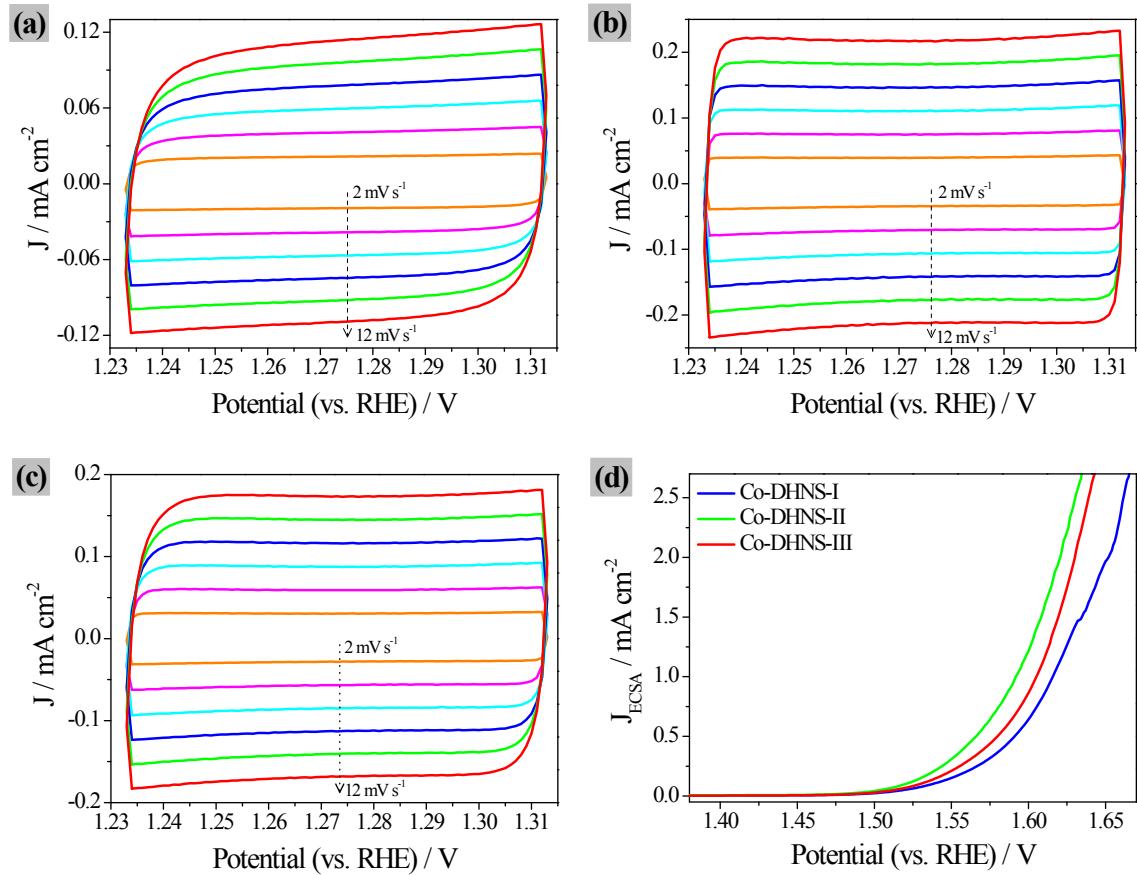
Fig. S19. CV curves in the double layer region at 2, 4, 6, 8, 10 and 12 mV s^{-1} in 1 M KOH for (a) Co-LDHNS-I, (b) Co-LDHNS-II and (c) Co-LDHNS-III. (d) LSV curves normalized by electrochemical surface area (ECSA).
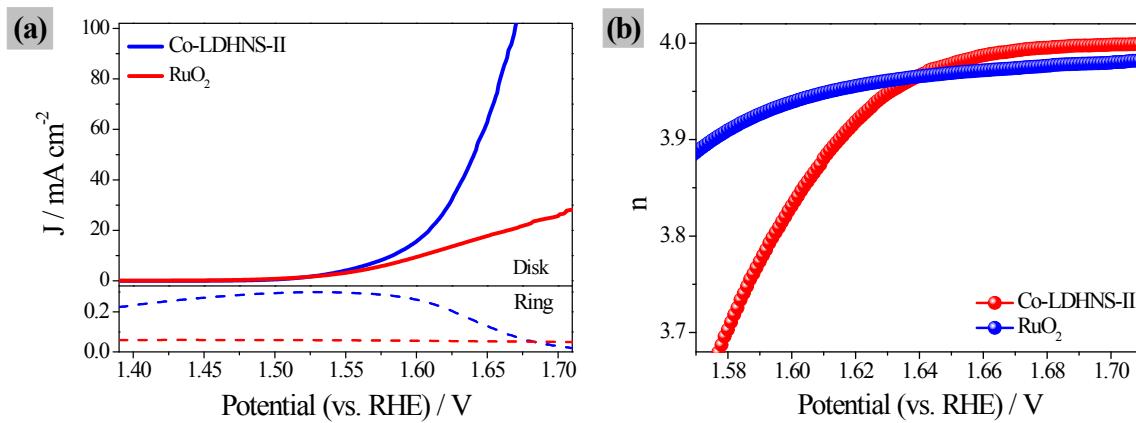
Fig. S20. (a) RRDE LSV curves of Co-LDHNS-II and RuO$_2$ in 1 M KOH. (b) Electron transfer number (n) as a function of applied potentials obtained from (a).
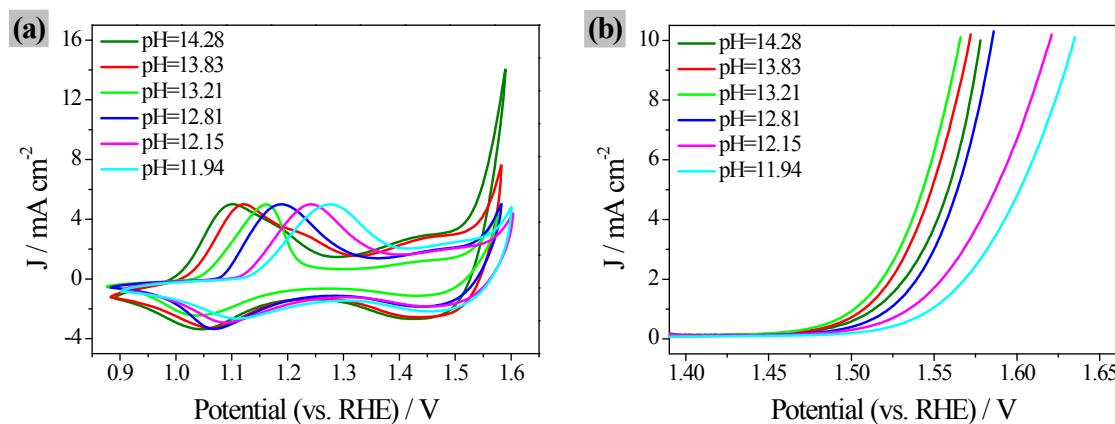
Fig. S21. (a) CV curves and (b) LSV curves of Co-LDHNS-II recorded in KOH aqueous solution with varied pH value.
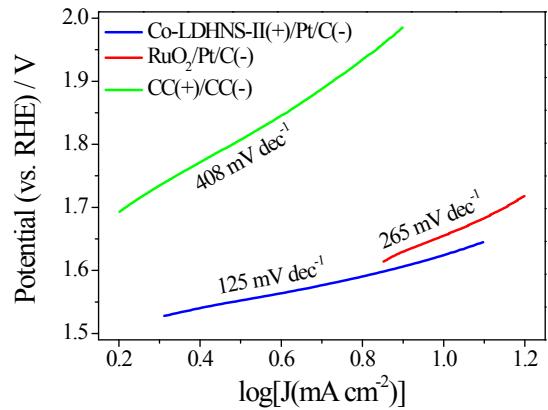
Fig. S22. Tafel plots obtained from LSV curves for overall water splitting.
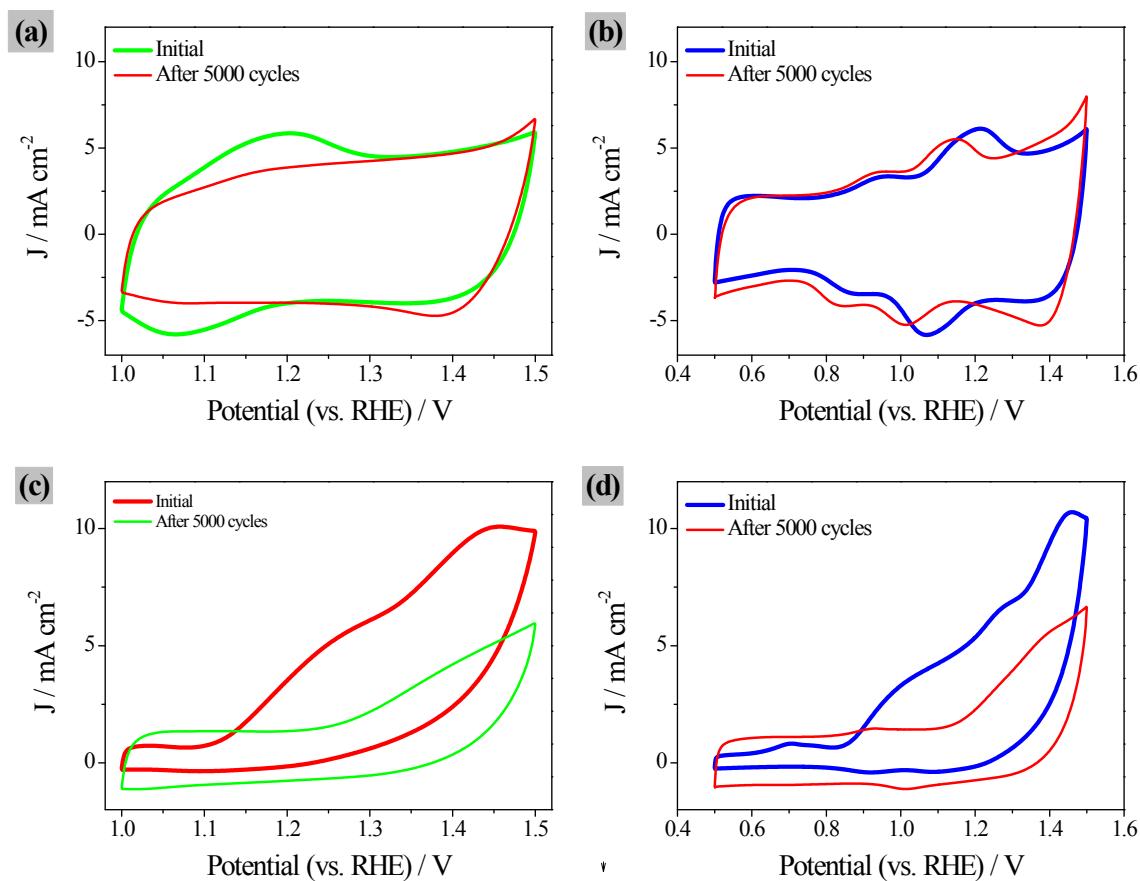
Fig. S23. CV curves before and after 5000 cycles: (a, b) Co-LDHNS-II(+)||Pt/C(-) and (c, d)

$RuO_2(+)\|Pt/C(-)$.
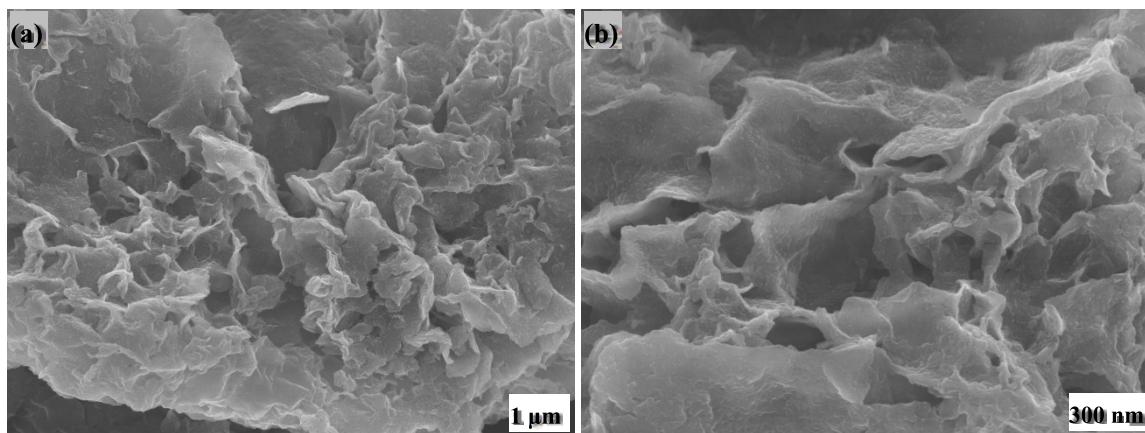
Fig. S24. SEM images for Co-LDHNS-II after 5000 cycles of Co-LDHNS-II$(+)\|Pt/C(-)$.

Table S1. Summary of recently reported electrocatalysts for OER.

| Electrocatalysts	Substrate	Mass loading [mg cm^{-2}]	Electrolyte	η@10 mA cm^{-2} [mV]	Tafel slope [mV dec^{-1}]	TOF [s^{-1}]	Ref.
Co-LDHNS-II	GCE	0.1	1 M KOH	340	56	0.801@η=350 mV	This
	GCE	0.1	0.1 M KOH	356	58	0.262@η=350 mV	work
RuO$_2$	GCE	0.1	1 M KOH	364	78	/	
Co^{2+}@SNG	GCE	/	1 M KOH	370	62	0.266@η=350 mV	S1
CTs/Co-S	CP[c]	0.32	1 M KOH	306	72	0.016@η=300 mV	S2
CoCo LDH NS[a]	NF	1	1 M KOH	353	45	0.0035@η=300 mV	S3
NiCo LDH NS	NF	1	1 M KOH	332	40	0.01@η=300 mV	
NCNTFs	GCE	0.2	1 M KOH	370	93	/	S4
20 wt. % Pt/C	GCE	0.2	1 M KOH	550	118	/	
Co-Bi NS/G	GCE	0.285	1 M KOH	290	53	/	S5
RuO$_2$	GCE	0.285	1 M KOH	305	60	/	
NiCo LDH NB[b]	GCE	0.25	1 M KOH	420	135	/	S6
CoFe LDH-Ar	GCE	0.204	1 M KOH	266	38	4.78@η=300 mV	S7
CoFe LDH-F	GCE	0.2	1 M KOH	300	40	/	S8
	NF	1	1 M KOH	260	47	/	
CoAl-NS	3DGN[d]	0.05±0.01	1 M KOH	252	36	1.14@η=350 mV	S9
IrO$_2$	3DGN	0.05±0.01	1 M KOH	277	45	0.73@η=350 mV	
CoMn LDH	GCE	0.142	1 M KOH	324	43	0.13@η=350 mV	S10
IrO$_2$	GCE	0.142	1 M KOH	337	49	0.007@η=300 mV	
CoFe LDH NS	CP	0.17	1 M KOH	367	40	/	S11
γ-CoOOH NS	GCE	0.15	1 M KOH	300	38	/	S12
CoAl-LDH array	NF	/	1 M KOH	335	128	/	S13
C-Co/Co$_3$O$_4$ HS[e]	GCE	0.408	1 M KOH	352	80	/	S14
RuO$_2$	GCE	0.408	1 M KOH	364	120	/	

[a]Nanosheets; [b]Nanoboxes; [c]Carbon paper; [d]3D graphene network; [e]hollow spheres

Table S2. Comparison of the water splitting activity of the Co-LDHNS-II with recently reported

electrocatalysts in basic solutions.

Electrocatalysts	Substrate	Mass loading [mg cm^{-2}]	Electrolyte	E@10 mA cm^{-2} [mV]	Tafel slope [mV dec^{-1}]	Ref.
Co-LDHNS-II(+)‖Pt/C(-)	CC	1	1 M KOH	1.625	125	This
RuO$_2$(+)‖Pt/C(-)	CC	1	1 M KOH	1.656	265	work
CTs/Co-S(+)‖CTs/Co-S(-)	CP	0.32	1 M KOH	1.743	/	S2
RuO$_2$(+)‖Pt/C(-)	CP	0.32	1 M KOH	1.679	/	
CoFe LDH-F(+)‖CoFe LDH-F(-)	NF	1	1 M KOH	1.63	126	S8
IrO$_2$(+)‖Pt/C(-)	NF	1	1 M KOH	1.63	241	
Pt/C(+)‖Pt/C(-)	NF	1	1 M KOH	1.7	206	
VOOH(+)‖VOOH(-)	NF	0.8	1 M KOH	1.62	/	S15
RuO$_2$(+)‖Pt/C(-)	NF	0.8	1 M KOH	1.55	/	
NiFe-MOF(+)‖NiFe-MOF(-)	NF	0.3	0.1 M KOH	1.55	256	S16
IrO$_2$(+)‖Pt/C(-)	NF	/	0.1 M KOH	1.62	267	
CuCoO-NWs(+)‖CuCoO-NWs(-)	NF	1.2	1 M KOH	1.61	/	S17
Na$_{0.08}$Ni$_{0.9}$Fe$_{0.1}$O$_2$(+)‖NiP(-)	NF	0.13	1 M KOH	1.54	/	S18
RuO$_2$(+)‖Pt/C(-)	NF	0.13	1 M KOH	1.62	/	

References

S1   *J. Am. Chem. Soc.*, 2017, **139**, 1878-1884.

S2   *ACS Nano*, 2016, **10**, 2342-2348.

S3   *Nat. Commun.*, 2014, **5**, 4477.

S4   *Nat. Energy*, 2016, **1**, 15006.

S5   *Angew. Chem. Int. Ed.*, 2016, **55**, 2488-2492.

S6   *Angew. Chem.*, 2017, **129**, 3955-3958.

S7   *Angew. Chem.*, 2017, **129**, 5961-5965.

S8   *ACS Appl. Mater. Interfaces*, 2016, **8**, 34474-34481.

S9   *Adv. Mater.,* 2016, **28**, 7640-7645.

S10   *J. Am. Chem. Soc.*, 2014, **136**, 16481-16484.

S11   *Nano Lett.*, 2015, **15**, 1421-1427.

S12   *Angew. Chem. Int. Ed.*, 2015, **54**, 8722-8727.

S13   *Nano Energy*, 2017, **37**, 98-107.

S14   *J. Mater. Chem. A*, 2017, **5**, 11163-11170.

S15   *Angew. Chem.*, 2017, **129**, 588-592.

S16   *Nat. Commun.*, 2017, **8**, 15341.

S17   *Adv. Funct. Mater.*, 2016, **26**, 8555-8561.

S18   *Energy Environ. Sci.*, 2017, **10**, 121-128.