Electronic Supplementary Information

N-doped graphene wrapped hexagonal metal cobalt hierarchical nanosheet as a highly efficient water oxidation electrocatalyst

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1. Material synthesis

1.1. Chemicals. All chemicals are analytical grade and used as received without further purification.

1.2. Synthesis of the Co-CN SS. Typically, 99.5 mg phenanthroline monohydrate was dissolved in 2.5 mL methanol and 952 mg $CoCl_2 \cdot H_2O$ was dispersed in the same volume of methanol, respectively. After the two methanol solution (molar ratio of phenanthroline monohydrate to cobalt is 1:8) was mixed together, the dark blue mixture was dropped to 80 g NaCl in a 300 mL beaker with continuously mechanical stirring for over 20 minutes to get a homogenous violet mixture. Then the product is dried in a vacuum oven for 6 h. In the calcination step, the precursor was placed in the center of a tube furnace. Prior to raising the temperature, the furnace was degassed

and refilled with high purity Ar for more than 3 times to obtain an oxygen-free atmosphere. Then the furnace is sealed and heated to 600 °C for 2 h in static Ar atmosphere with a heating rate of 2 °C/min. The black product was taken out after the furnace cooled down naturally, and washed with water for 6 times. At last, the product was re-dispersed in 5 mL water, frozen and lyophilized.

1.3. Synthesis of Ni₃Fe-CN SS. In a typical procedure, 99.5 mg phenanthroline monohydrate was first dissolved in 2 mL methanol to get solution A. Solution B was to dissolved 199 mg of $FeCl_2 \cdot 4H_2O$, 713 mg $NiCl_2 \cdot 6H_2O$ and 200 mg hydroxylamine hydrochloride in 6 mL methanol to get a emerald solution. The molar ratio of Ni:Fe was 3:1. Then solution A was added to solution B with the emerald green changing to bloody red immediately. The molar ratio of phenanthroline monohydrate to the total metal ions was kept 1:8. Then the mixed solution was added to 80 g NaCl, stirred and dried in a vacuum oven for 6 h. The following calcination and wash steps were analogous to the synthesis of Co-CN SS.

1.4. Synthesis of NiCo-CN SS. The procedure was analogous to the synthesis of Co-CN SS except for replacing the 952 mg $CoCl_2 \cdot H_2O$ by a mixture of 476 mg $CoCl_2 \cdot H_2O$ and 476 mg $NiCl_2 \cdot H_2O$.

1.5. Synthesis of Co-C SS. The preparation is analogous to the synthesis of Co-CN SS except for replacing phenanthroline monohydrate by 110 mg catechol to keep the similar amount of carbon.

2. Characterization. The scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 scanning electron microscope equipped with the Thermo Scientific energy-dispersion X-ray fluorescence analyzer. Transmission electron microscopy (TEM) images, high resolution transmission electron microscopy (HRTEM) images, energy-dispersive X-ray spectroscopic (EDS) analysis and scanning transmission electron microscopy EDS (STEM-EDS) elemental distribution mapping were carried out with a JEM-2100F microscope. The X-ray diffraction

(XRD) patterns were recorded with D8-Focus diffraction system with a Cu $K\alpha$ source (λ = 1.54056 Å). X-ray photoelectron spectroscopy (XPS) was performed using Perkin Elmer PHI 1600 Versa Probe (Al $K\alpha$). Raman spectroscopy was recorded on RENISHAW inVia reflex Raman microscope under an excitation of 532 nm laser light with power of 20 mW.

3. Electrochemical measurements. All the electrochemical measurements were recorded on a CHI 660D (CH Instruments, Austin, TX) electrochemical workstation. 1.0 M KOH, which was used as electrolyte, was bubbled with oxygen for 30 minutes before every measurement. A standard three-electrode system was carried out with a glassy carbon rod as counter electrode and a Hg/HgO electrode as reference electrode. The standard electrode potential of Hg/HgO electrode with the inner reference electrolyte of 1.0 M KOH was considered as 0.098 V. All the potential mentioned in this manuscript were against reversible hydrogen electrode (RHE). For a typical preparation of working electrode, 4 mg electrocatalyst was first dispersed in a mixture of 0.8 mL deionized water, 0.2 mL isopropyl alcohol and 20 μL 5 wt % Nafion 117 solution. Then the mixture was under ultrasonic for 30 min to acquire a homogeneous ink. 5 μL ink was then carefully dropped on the glassy carbon (GC) electrode with a diameter of 3 mm (mass loading ~ 0.285 mg cm^{-2}). All the data presented in this manuscript were *iR* corrected without additional description. The LSV (linear sweep voltammetry) curves of different samples were collected in the scan range of 0-1.0 V vs. Hg/HgO with a scan rate of 10 mV/s. And Tafel slopes were obtained by linear fitting the Tafel plots, which were got from re-plotted overpotential vs. log current density. The EIS spectra were carried out at the potential of 0.7 V vs. Hg/HgO with an amplitude of 5 mV in the frequency of 100,000 to 1 Hz.
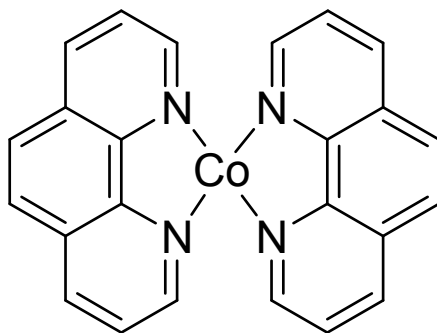
Fig. S1. Structure of cobalt (II)-phenanthroline complex with molar ligand-to-cobalt ratio of 2:1.
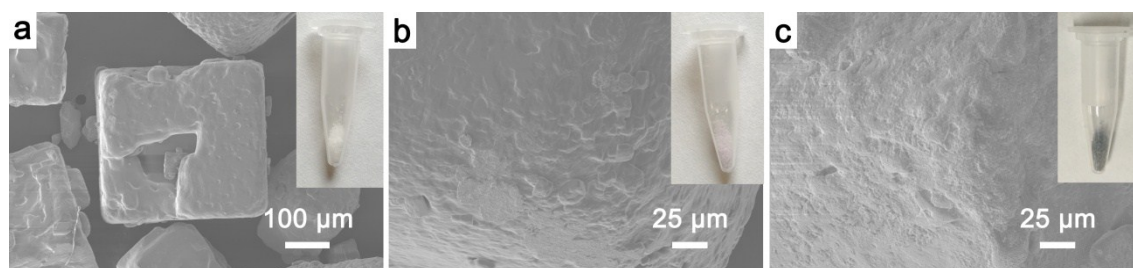

Fig. S2. SEM images of (a) NaCl, (b) NaCl@precursor and (c) NaCl@Co. The inset in each panel is the corresponding optical photo.
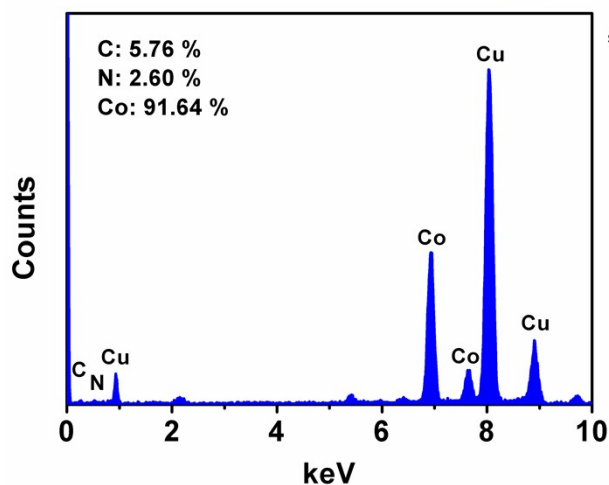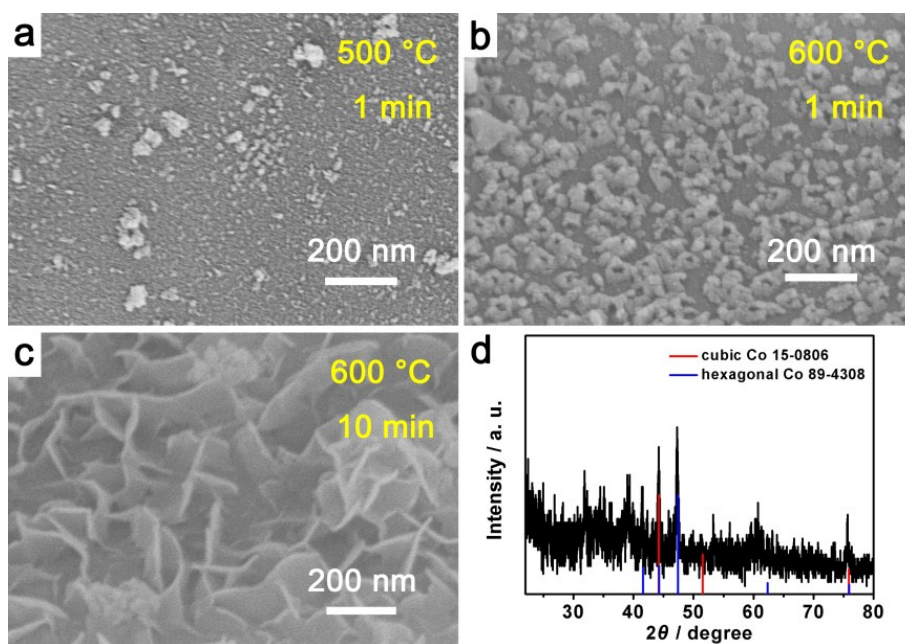

Fig. S3. EDS analysis of the Co-CN SS.

Fig. S4. SEM images of Co-CN SS intermediates collected at different reaction stages, (a) 500 °C, 1 min, (b) 600 °C, 1 min and (c) 600 °C, 10 min. (d) XRD pattern of Co-CN SS collected at 600 °C for 10 min.
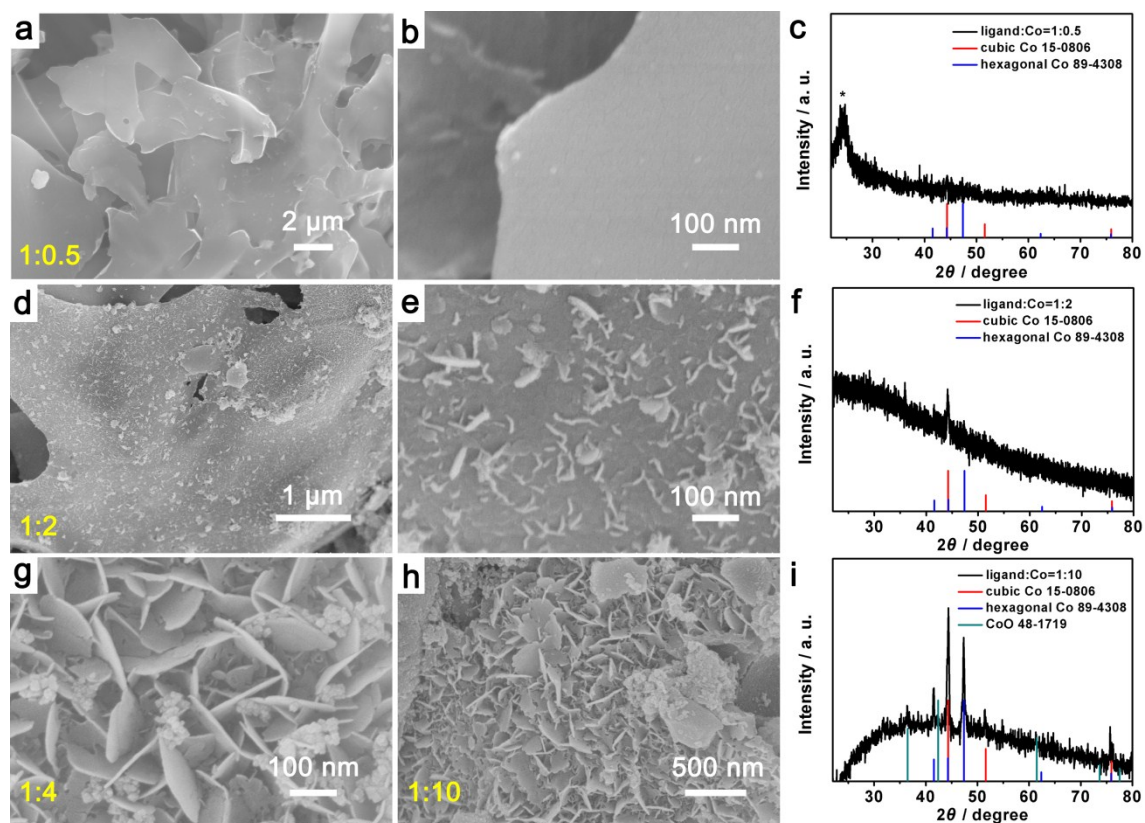
Fig. S5. SEM images and corresponding XRD patterns of sample prepared by different ligand-to-cobalt ratio. The ligand-to-cobalt ratios are: (a-c) 1:0.5, (d-f) 1:2, (g) 1:4 and (h-i) 1:10. The peak labeled by "*" in (c) represents the (002) facet of graphite, which clearly indicates the formation of graphitic carbon when the content of cobalt is relatively low.
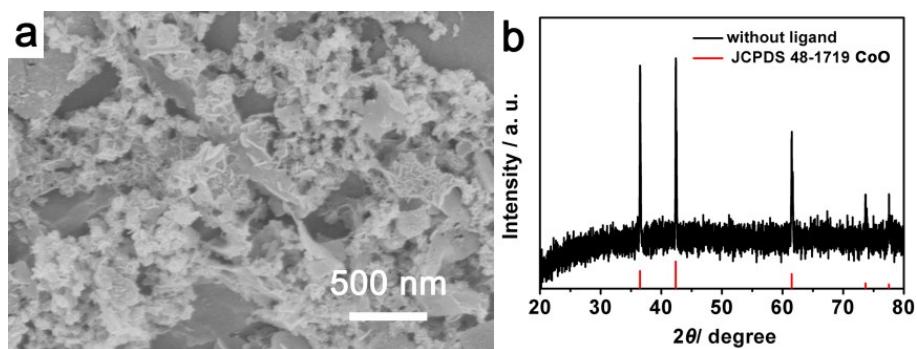
Fig. S6. (a) SEM image and (b) XRD pattern of the sample synthesized under the same condition without the addition of phenanthroline.
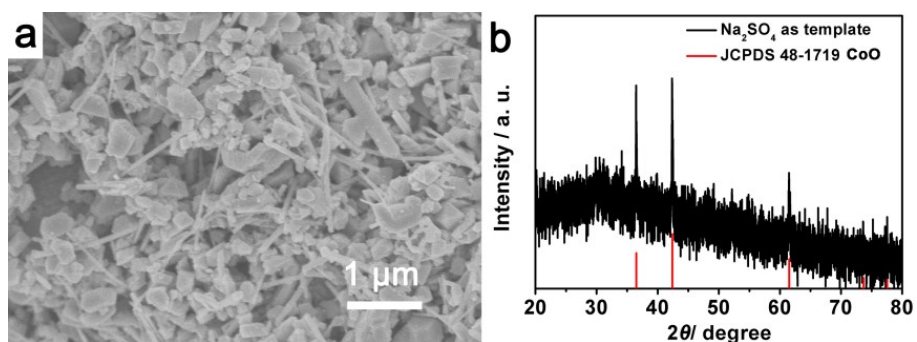

Fig. S7. (a) SEM image and (b) XRD pattern of the sample synthesized with Na_2SO_4 crystal as template. When NaCl is replaced by Na_2SO_4, SEM image shows that the sample appears with irregular particles and wires rather than hierarchical nanosheet-on-nanosheet structure. And the corresponding XRD pattern indicates that this sample composes of CoO instead of metal Co. The mismatched lattice and oxygen-enriched Na_2SO_4 crystals may be responsible for this result.
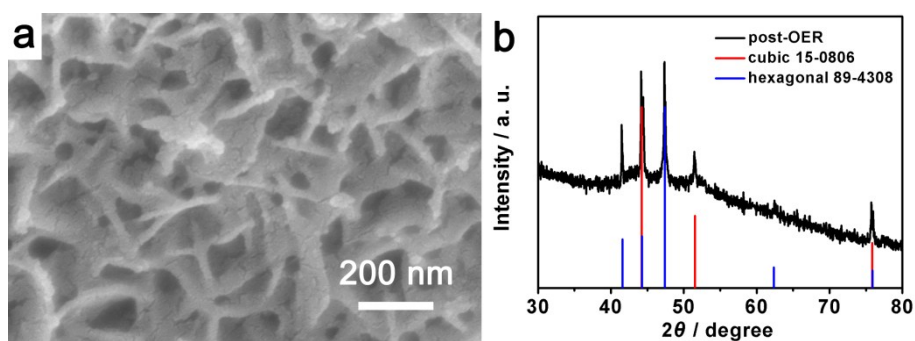
Fig. S8. (a) SEM image and (b) XRD pattern of the Co-CN SS after long-term OER measurement. The slight sintering of the nanosheets in (a) may result from the addition of Nafion.
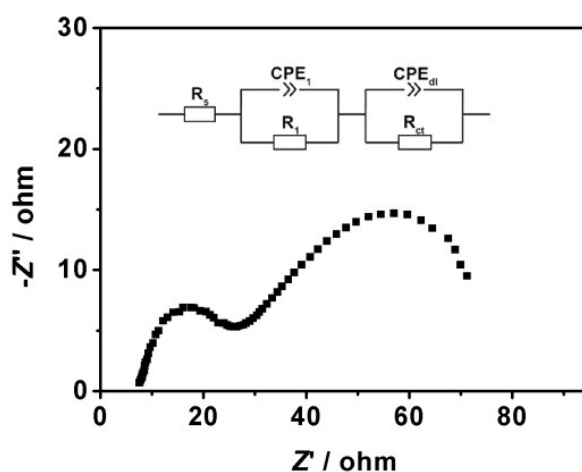

Fig. S9. EIS spectrum of Co-CN SS at 0.7 V vs. Hg/HgO. The inset is the corresponding covalent circuit. The first semicircle near the origin may represent the electron transport between the GC electrode and catalyst, and the primary nanosheets and the secondary nanosheets. And the other semicircle reflects the charge transfer process of the electrode reaction at current applied potential.
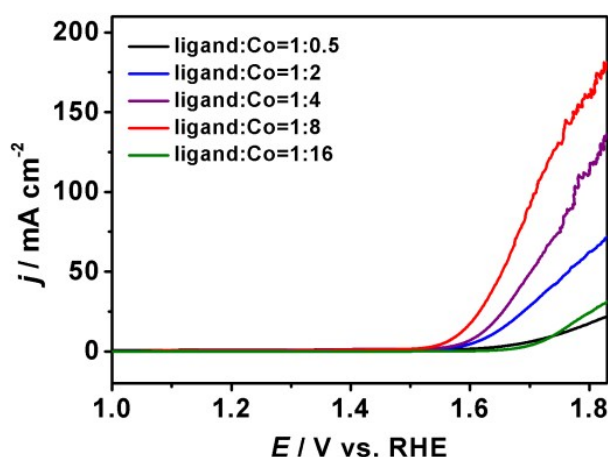
Fig. S10. LSV curves of samples synthesized with different ligand-to-cobalt ratios. It can be found that the optimal ratio is 1:8.
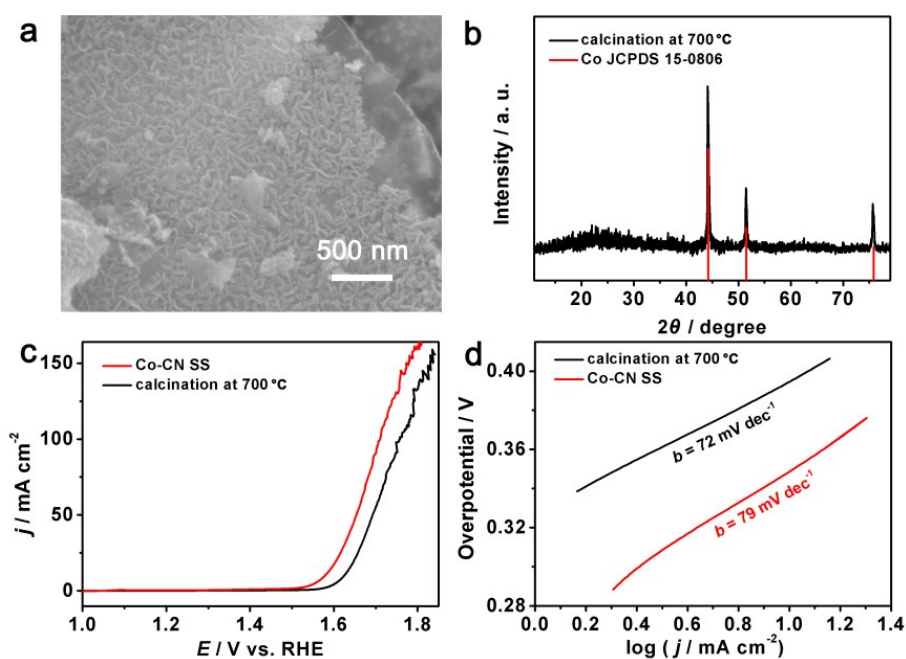

Fig. S11. (a) SEM image and (b) XRD pattern of the Co-CN SS after calcination at 700 °C for 5 h. (c) LSV curves and (d) Tafel slopes of the Co-CN SS before and after calcination at 700 °C for 5 h. After calcination, the hierarchical nanosheet-on-nanosheet structure is retained. However, the corresponding XRD pattern shows that all the hexagonal Co is transformed into cubic Co.
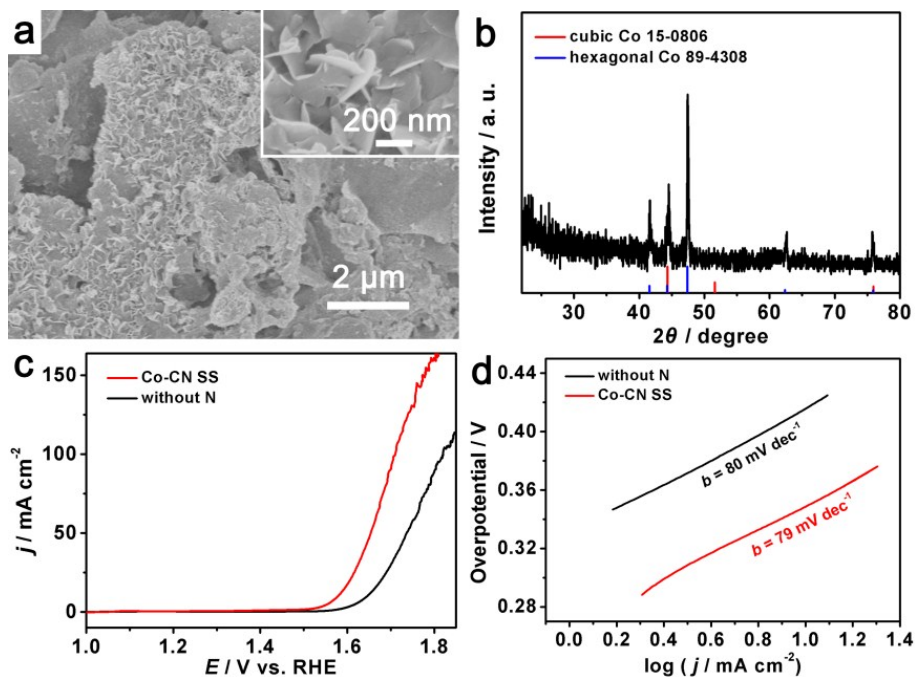
Fig. S12. (a) SEM image and (b) XRD pattern of Co-C SS without N. (c) LSV curves and (d) Tafel slopes of Co-CN SS and Co-C SS. The inset of (a) is the high magnification SEM image of (a).
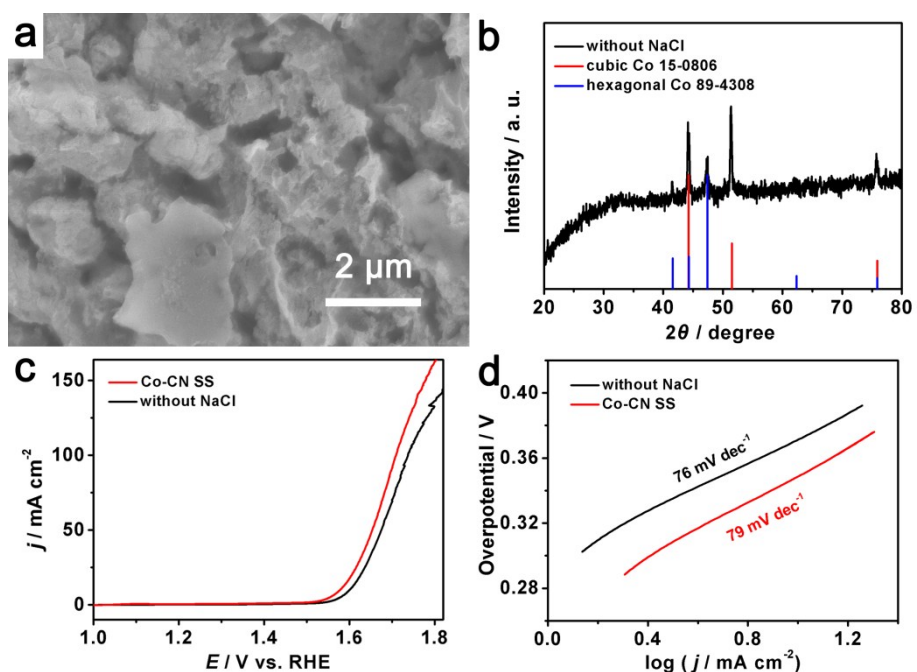

Fig. S13. (a) SEM image and (b) XRD pattern of sample prepared without NaCl as template. (c) LSV curves and (d) Tafel slopes of sample prepared with and without NaCl.

Table S1. Comparison of OER performances for some cobalt-contained electrocatalysts.

Catalyst	Substrate	Electrolyte	Mass loading (mg cm^{-2})	Overpotential (mV)		Tafel slope (mV dec^{-1})	Ref.
				η_{onset}	η_{10}		
Co-CN SS	GC	1.0 M KOH	0.285	290	340	79	This work
Co@NC	GC	1.0 M NaOH	0.32		390		[1]
N/Co-doped PCP//NRGO	GC	0.1 M KOH	0.714		430	292	[2]
Co$_3$O$_4$ nanowires	GC	1.0 M KOH	0.136		403	72	[3]
Co$_3$O$_4$ mesoporous nanotubes	GC	0.1 M KOH	0.208	310	390	76	[4]
Co$_3$O$_4$ ultrathin nanosheets	GC	1.0 M KOH	0.34	366		25	[5]
CoP nanoparticles	GC	1.0 M KOH	0.71		340	99	[6]
NiCoP nanoboxes	GC	1.0 M KOH	0.255		370	115	[7]
CoMn LDH	GC	1.0 M KOH	0.142		324	43	[8]
CoS$_2$/N,S-GO	GC	0.1 M KOH	0.25		380	75	[9]
Amorphous Co$_2$B	GC	0.1 M KOH	0.21		380	45	[10]

References

1. X. Cui, P. Ren, D. Deng, J. Deng and X. Bao, *Energy Environ. Sci.*, 2015, **9**, 123-129.
2. Y. Hou, Z. Wen, S. Cui, S. Ci, S. Mao and J. Chen, *Adv. Funct. Mater.*, 2015, **25**, 872-882.
3. Y. Wang, T. Zhou, K. Jiang, P. Da, Z. Peng, J. Tang, B. Kong, W.-B. Cai, Z. Yang and G. Zheng, *Adv. Energy Mater.*, 2014, **4**, 1400696.
4. H. Wang, S. Zhuo, Y. Liang, X. Han and B. Zhang, *Angew. Chem. Int. Ed.*, 2016, **55**, 9055-9059.
5. Y. Sun, S. Gao, F. Lei, J. Liu, L. Liang and Y. Xie, *Chem. Sci.*, 2014, **5**, 3976-3982.
6. J. Chang, Y. Xiao, M. Xiao, J. Ge, C. Liu and W. Xing, *ACS Catal.*, 2015, **5**, 6874-6878.
7. P. He, X.-Y. Yu and X. D. Lou, *Angew. Chem. Int. Ed.*, 2017, **129**, 3955-3958.
8. F. Song and X. Hu, *J. Am. Chem. Soc.*, 2014, **136**, 16481-16484.
9. P. Ganesan, M. Prabu, J. Sanetuntikul and S. Shanmugam, *ACS Catal.*, 2015, **5**, 3625-3637.
10. J. Masa, P. Weide, D. Peeters, I. Sinev, W. Xia, Z. Sun, C. Somsen, M. Muhler and W. Schuhmann, *Adv. Energy Mater.*, 2016, **6**, 1502313.