Electronic Supplementary Information

Electrochemically accessing ultrathin Co (oxy)-hydroxide

nanosheet and operando identifying its active phase for

oxygen evolution reaction

Jing Zhou^{b,†}, Yu Wang^{a,b,†}, Xiaozhi Su^a, Songqi Gu^a, Renduo Liu^b, Yibo Huang^{a,b}, Shuai Yan^a, Jiong Li^{a,b,*} and Shuo Zhang^{a,b,c,*}

 ^aShanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China
 ^bShanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China
 ^cUniversity of Chinese Academy of Sciences, Beijing 100049, China

E-mail: lijiong@sinap.ac.cn; zhangshuo@sinap.ac.cn

Contents:

Supplementary Figures 1 to 29

Supplementary Tables 1 to 5

Supplementary Figures

Fig. S1 SEM image of $Na_xCoFe(CN)_6$. The well-defined cubic morphology with typical size of ~500 nm was shown.



Fig. S2 EDS of $Na_xCoFe(CN)_6$. The ratio of Na, Co and Fe gives a formula of $Na_2CoFe(CN)_6$.



Fig. S3 TEM image and EDX elemental mapping images of $Na_xCoFe(CN)_6$. The elemental mapping results exhibited that all elements of $Na_xCoFe(CN)_6$ distributed uniformly.



Fig. S4 Co $L_{2,3}$ -edge X-ray absorption spectroscopy (XAS) of Na_xCoFe(CN)₆ and CoO. It is clearly shown that cobalt in Na_xCoFe(CN)₆ is divalent.



Fig. S5 Fe $L_{2,3}$ -edge XAS of Na_xCoFe(CN)₆ as well as K₄Fe(CN)₆•3H₂O for comparison. The similar line shape indicates iron is divalent in Na_xCoFe(CN)₆.



Fig. S6 Co *K*-edge (a) X-ray absorption near-edge structure (XANES) and (b) Fourier transformed extended X-ray absorption fine structure (FT-EXAFS) of $Na_xCoFe(CN)_6$ along with reference samples. The fitting results are listed in Supplementary Table 1.



Fig. S7 Fe *K*-edge (a) XANES and (b) FT-EXAFS of $Na_xCoFe(CN)_6$ along with reference samples. The fitting results are listed in Supplementary Table 1.



Fig. S8 Pictures of the reactor with different voltages. (a) The reactor was under the condition of open circuit. (b) When the voltage was increased to 1.5 V, the bubbles kept emerging. (c) When the applied voltage reached 1.6 V, the solution looks muddy due to the large amount of bubbles.



Fig. S9 Optical image of colloidal solution of CoOOH-NS. Tyndall effect was observed as irradiated with the laser beam.



Fig. S10 EDS of CoOOH-NS. The results indicated there are only Co and O in the electrochemically treated catalysts, while no obvious Na, Fe and N peaks are detected.



Fig. S11 TEM image and EDX elemental mapping images of CoOOH-NS. The elemental mapping results exhibited that Co and O distributed uniformly in the electrochemically treated catalyst.



Fig. S12 XRD pattern of CoOOH-bulk. The XRD pattern can be indexed to the structure of β -CoOOH with *R-3m* space group (JCPDS: 07-0169).



Fig. S13 SEM images of CoOOH-bulk.





Fig. S14 O K-edge XAS of CoOOH nanosheet and its bulk counterpart.

Fig. S15 Co *K*-edge (a) XANES and (b) FT-EXAFS of CoOOH-NS along with reference samples. The fitting results are listed in Supplementary Table 1.



Fig. S16 (a) In-situ Fe *K*-edge XANES; (b) Raw data of in-situ Fe *K*-edge XANES; (c) Fe *K*-edge XANES of electrolyte after 10 h; (d) XPS spectra of the product after electrochemical treatment for 10 h at different potentials.



In-situ Fe K-edge XANES for 10 h shows that Fe ions always exist with the form of $Na_xCoFe(CN)_6$. However, it was found that the signal of iron ions gradually decreases with increasing reaction time, suggesting that iron ions dissociated from the $Na_xCoFe(CN)_6$ molecular framework under the applied potential and alkali condition. Hence, we checked the electrolyte after 10 h fabrication process. The result shows that Fe ions in the electrolyte are in the form of hydrated ions. XPS and XAFS was performed on the product and results showed that a few of residual iron ions in the CoOOH and exist with the form of $Na_xCoFe(CN)_6$. We concluded that Fe ions didn't incorporate into the CoOOH lattice. Finally, we re-prepared fresh 1 M KOH solution to check the OER activity of CoOOH nanosheets. The result shows that the reactivity remains. This illustrated that the Fe³⁺ hydrated ions have no obvious effect on OER activity.

Fig. S17 Measurement of double layer capacitance (Cdl) for determining active electrochemical surface area (ECSA) of CoOOH-NS and CoOOH-bulk. Plots of capacitive currents at 1.125 V as a function of the scan rates are also shown. The ECSA of CoOOH-NS was nearly an order of magnitude larger than that of CoOOH-bulk, consistent with the characteristic of the nanosheet.



Fig. S18 Cyclic voltammetry curves (CVs) of CoOOH-NS and CoOOH-bulk recorded at a scan rate of 1 mV s⁻¹.



Fig. S19 Tafel plots for CoOOH-NS, CoOOH-bulk and IrO₂.



Fig. S20 Turnover frequency (TOF) plots of CoOOH-NS and CoOOH-bulk.



Assuming that all the metal sites are electrochemically active, The TOF was calculated from the equation below:

$$\Gamma OF = \frac{j \times A}{4 \times F \times n}$$

Where *j* is the current density, *A* is the area of the electrode (4 cm²), *F* is the Faraday constant (96485.3 C mol⁻¹), and *n* is the mole number of active metals on the electrode.

The TOF of CoOOH-NS is much higher than that of CoOOH-bulk, indicating that there are actually more Co sites which are electrochemically active in CoOOH-NS.

Fig. S21 Electrochemical impedance spectroscopy (EIS) of CoOOH-NS recorded at 1.48 V (vs. RHE) under the influence of an AC voltage of 10 mV. The equivalent circuit is shown in the inset. The semicircles in the high- and low-frequency range of the Nyquist plot attributed to the charge-transfer resistance R_{CT} and solution resistance R_{S} , respectively, are related to the electrocatalytic kinetics and a lower value corresponds to a faster reaction rate.



Fig. S22 EIS of CoOOH-bulk recorded at 1.48 V (vs. RHE) under the influence of an AC voltage of 10 mV. The equivalent circuit is shown in the inset.



Fig. S23 EIS of IrO_2 recorded at 1.48 V (vs. RHE) under the influence of an AC voltage of 10 mV. The equivalent circuit is shown in the inset.



Fig. S24 The in-house designed electrochemical cell and the integral setup for the *operando* experiment.



(1) *In-situ* cell; (2) working electrode on the window; (3) reference electrode; (4) counter electrode; (5) pipes of the peristaltic pump to cycle the electrolyte; (6) Lytle type detector with silver slit (focal length of 100 mm) to eliminate the scattering noise.

Fig. S25 EXAFS fitting of *operando* Co *K*-edge for CoOOH-NS. The FT range is 2.9 -10.6 Å⁻¹ and the fitting range is 1.3 -2.4 Å. The black lines are the Co *K*-edge FT-EXAFS data, and the red dots are the best fitting results. The plots are not corrected for phase shift.



Fig. S26 *Operando* Co *K*-edge XANES spectra recorded at potentials from 1.40 to 1.53 V vs. RHE in 1 M KOH.



Fig. S27 Operando Co K-edge XANES spectra of CoOOH-NS and CoOOH-bulk at open circuit and 1.53 V vs. RHE in 1 M KOH.



Fig. S28 The calculated reaction path and relative energies for the hydroxyl filling and deprotonation process of CoOOH-NS. Co, O and H atoms are shown in cyan, red and white, respectively. There are two obvious local minimum during the reaction. One is that about half of the surface hydroxyl are filled, suggesting this may be the initial structure of the CoOOH-NS with unsaturated coordination and oxidation state of Co lower than 3+. Upon increasing the potential, the surface of CoOOH-NS are fully filled with hydroxyl, and another local minimum is present with fractional hydrogen atoms removed. This result is consistent with the *operando* XAS that at the critical potential point, the oxidation environment. After this point, the deprotonation energy increases with the dehydrogen number, supporting that the oxidation state is dependent on the applied potential.



The whole reaction process can be divided into two parts according to the following equations:

$$Co^{(3-y)+}O(OH)_{1-y} + yOH^{-} \rightarrow Co^{3+}OOH + ye^{-}$$
 (1)
 $Co^{3+}OOH + xOH^{-} \rightarrow Co^{(3+x)+}OOH_{1-x} + xH_2O + xe^{-}$ (2)

The Gibbs reaction free energies of these electrochemical reaction steps were obtained by using the standard hydrogen electrode model (ref. S1, ESI[†]), where the chemical potential (μ) of the proton–electron pair is equal to that of half a hydrogen molecule at a potential of U = 0 V versus RHE. The reaction free energies ΔG of the above steps (1) and (2) can be calculated as follows:

$$\Delta G_{1} = G(\text{CoO}(\text{OH})_{1-y} + y\text{OH}^{-} \rightarrow \text{CoOOH} + y\text{e}^{-})$$

= G(CoOOH) + yG(e^{-}) - G(CoO(OH)_{1-y}) - yG(OH^{-})
= G(CoOOH) - G(CoO(OH)_{1-y}) + y(G(e^{-}) + G(H^{+}) - G(H_{2}O))
= G(CoOOH) - G(CoO(OH)_{1-y}) + y(0.5 \times G(H_{2}) - G(H_{2}O))

$$\Delta G_2 = G(\text{CoOOH} + x\text{OH}^- \rightarrow \text{CoOOH}_{1-x} + x\text{H}_2\text{O} + x\text{e}^-)$$

= $G(\text{CoOOH}_{1-x}) - G(\text{CoOOH}) + x(G(\text{H}_2\text{O}) + G(\text{e}^-) - G(\text{OH}^-))$
= $G(\text{CoOOH}_{1-x}) - G(\text{CoOOH}) + 0.5 \times x\text{G}(\text{H}_2)$

The free energy G can be expressed by G = E + ZPE - TS, where *E* is the total energy obtained from DFT calculations, ZPE is the correction of zero point energy which can be obtained by calculating the vibrational frequency, and *S* is the entropy at 298.15 K.

Fig. S29 Co K-edge FT-EXAFS of CoOOH-NS at 1.53 V vs. RHE and in air after operando experiment.



Fig. S30 Schematic band diagrams for Co compounds upon deprotonation. As the oxidation state of Co^{3+} is increased to Co^{4+} by deprotonation, the Co^{4+} 3d band deeply inserts into the O 2p band and consequently pushes up the latter to higher energy. The concentration of O 2p holes increase due to the rising of O 2p band via the strong interaction between Co^{4+} and O. As a result, these O ions with 2p holes can play the role of electrophilic centers during OER.



Fig. S31 Diagram of energy levels for Co-O hybridization with different oxidation states of cobalt ions. In Co3+-O system, the Co-3d orbital lies above the O-2p orbital. In this condition, the valence orbital is dominantly comprised of Co-3d states. In Co4+-O system, the Co-3d orbital lies below the O-2p orbital and the O-2p states become closer to the Fermi level. Therefore, significant ligand to metal charge transfer (LMCT) occurs that partial electrons of O transfer to Co, leaving 2p hole on O ions which can act as electrophilic centers.



Fig. S32 TEM images of Ni-based 2D (oxy)-hydroxide nanosheets synthesized by electrochemical treatment of $Na_xNiFe(CN)_6$.



Samples	Atomic scatter	N of atoms (CN)	Interatomic distance (Å)	Debye-Waller factor (10 ⁻³ ×Å ²)	ΔE ₀ (eV)
Co-foil	Co-Co	12	2.49±0.03	6.2±0.3	6.8
	Co-N	6	2.11±0.02	7.8±1.6	-3.4
Na _x CoFe(CN) ₆	Co-C	6	3.07±0.03	3.8±1.9	5.5
	Co-Fe	6	5.03±0.05	3.4±1.5	-3.2
	Co-O	6	1.90±0.02	2.4±0.9	-3.8
	Co-Co	6	2.83±0.03	2.9±0.6	-9.7
CoOOH-NS	Co-O	5.0±0.5	1.91±0.02	3.1±0.9	-4.9
	Co-Co	4.9±0.5	2.84±0.03	5.8±3.3	-9.3

Table S1 Structural parameters of Co with reference samples extracted from the Co *K*-edge EXAFS fitting. ($S_0^2 = 0.70$)

Samples	Atomic scatter	N of atoms (CN)	Interatomic distance (Å)	Debye-Waller factor (10 ⁻³ ×Å ²)	ΔE ₀ (eV)
	Fe-C	6	1.92±0.02	5.2±1.9	-4.1
Na _x CoFe(CN) ₆	Fe-N	6	2.89±0.03	1.5±0.6	4.0
	Fe-Ni	6	4.98±0.05	6.5±2.3	-12.7
Na₄Fe(CN) ₆	Fe-C	6	1.90±0.02	2.6±0.7	-6.1
	Fe-N	6	2.91±0.03	2.2±0.4	7.0

Table S2 Structural parameters of Fe with reference samples extracted from the Fe *K*-edge EXAFS fitting. ($S_0^2 = 0.95$)

Catalysts	Electrolyte	Potential at 10 mA cm ⁻² (V)	Substrate	Reference
CoOOH NS	1 M KOH	1.483	Carbon paper	This work
FeCo-PBA	1 M KOH	1.47	Carbon cloth	S2
Fe/CoOOH	1 M KOH	1.496	Carbon fiber cloth	S3
G-FeCoW	1 M KOH	1.421	Au foam	S4
LCF-700	0.1 M KOH	1.52	Glass carbon	S5
Amorphous Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ} nano film	1 М КОН	1.52	Ni foam	S6
Co ₃ O ₄ /N-rmGO	1 M KOH	1.54	Ni foam	S7
γ-CoOOH NS	1 M KOH	1.53	Glass carbon	S8
CoFeOx	1 M KOH	1.50	Ni foam	S9
CoNi(OH)x	1 M KOH	1.51	Cu-foil	S10
NiCo-LDH-NA	1 M KOH	1.537	Carbon fiber paper	S11
CoFe-LDH	1 M KOH	1.63	ITO	S12
CoSn-T1	1 M KOH	1.543	Glass carbon	S13
Fe-CoOOH/G	1 M KOH	1.56	Glass carbon	S14
W _{0.5} Co _{0.4} Fe _{0.1}	1 M KOH	1.48	Ni foam	S15
CoFe LDHs NS	1 M KOH	1.551	Glass carbon	S16
NaCo _{0.8} Fe _{0.2} O ₂	1 M KOH	1.56	Glass carbon	S17

Table S3 Comparison of OER activities of different cobalt based systems.

NS = Nanosheet, rmGO = reduced Mildly Oxidized Graphene Oxide, NA = Nanoarray, G = Graphene

Samples	Atomic scatter	No. of atoms (CN)	Interatomic distance (Å)	Debye-Waller factor (10 ⁻³ ×Å ²)	∆ <i>E</i> ₀(eV)
Co-foil	Co-Co	12	2.49±0.03	6.2±0.3	6.8
	Co-O	6	1.90±0.02	2.4±0.9	-3.8
COOOH-DUIK	Co-Co	6	2.83±0.03	2.9±0.6	-9.7
	Co-O	5.0±0.5	1.91±0.02	3.1±0.9	-4.9
C000H-NS-0CV	Co-Co	4.9±0.5	2.84±0.03	5.8±3.3	-9.3
	Co-O	5.0±0.5	1.91±0.02	3.3±1.2	-4.4
C000H-NS-1.30V	Co-Co	5.0±0.5	2.84±0.03	5.3±2.4	-10.0
	Co-O	5.2±0.5	1.91±0.02	3.4±1.5	-4.6
C000H-N3-1.35V	Co-Co	5.1±0.5	2.84±0.03	5.5±2.6	-9.9
	Co-O	6.0±0.6	1.90±0.02	3.5±1.6	-3.7
C000H-NS-1.40V	Co-Co	6.0±0.6	2.84±0.03	4.9±2.2	-9.2
CoOOH-NS-1.46V	Co-O	6.0±0.6	1.90±0.02	3.6±1.7	-3.6
	Co-Co	6.1±0.6	2.83±0.03	5.1±2.8	-9.8
	Co-O	6.1±0.6	1.89±0.02	3.4±1.6	-4.5
COUCH-NS-1.53V	Co-Co	5.7±0.6	2.83±0.03	4.9±2.3	-8.5

Table S4 Structural parameters of Co foil, CoOOH-bulk and CoOOH-NS under different potentials extracted from the Co *K*-edge EXAFS fitting. ($S_0^2 = 0.70$)

Table S5 Values used for the zero point energy corrections and entropies in determining the free energies of the reactants and products. The zero point energies are obtained by calculation of the vibration frequencies, and the entropy values are acquired from the NIST Standard Reference Database (<u>https://janaf.nist.gov/</u>).

Chasica		T×S (eV)	
Species	ZPE (ev)	(298.15 K)	
H ₂ (g)	0.287	0.404	
H ₂ O (g)	0.576	0.583	

Table S6 Calculated p-band center of oxygen atoms and the number of holes per oxygen atom in CoOOH-NS-nH, where n denote the dehydrogen number. CoOOH-NS-4H means a bare surface with all the hydrogen atoms extracted. The p-band center is defined as the average energy of occupied 2p electronic states of oxygen relative to the Fermi level. The number of holes is obtained by integrate the unoccupied states within the range of 0~5 eV above the Fermi level.

	p-band center (eV)	hole (e ⁻ /O)
CoOOH-NS	-7.171	0.419
CoOOH-NS-1H	-6.552	0.462
CoOOH-NS-2H	-4.366	0.503
CoOOH-NS-3H	-3.803	0.605
CoOOH-NS-4H	-3.242	0.758

We further calculated the partial atomic charges from a Bader analysis, as listed in the table below. The average Bader charge of Co is calculated from all the Co ions, and the average Bader charge of O is calculated from the surface O ions.

	Bader charge of	Bader charge of
	Co (e ⁻ /Co)	O (e ⁻ /O)
CoOOH-NS	7.7132	7.0796
CoOOH-NS-1H	7.7012	7.0250
CoOOH-NS-2H	7.6827	6.9535
CoOOH-NS-3H	7.6789	6.8359
CoOOH-NS-4H	7.6764	6.6911

We can see that the Bader charge of Co gradually decreases upon deprotonation, but only a small difference is found between different oxidation states. This phenomenon has a fundamental reason, which is the so-called charge self-regulation mechanism proposed by Zunger (ref. S18, ESI[†]). The intrinsic picture is that the depletion of electrons is not localized at metal centers, resulting in small difference between different oxidation states. Therefore, the Bader charge on metal ions can only provide a relative, and not an absolute measure of the oxidation state of metal ions. For example, Goodenough et.al found that the partial charge on V is similar from V^{3+} to V^{4+} (ref. S19, ESI[†]). By contrast, the Bader analysis of O is more sensitive to the metal oxidation state. For example, the difference between O ions is more obvious that the average Bader charges decrease from 7.0796 in CoOOH-NS to 6.6911 in CoOOH-NS-4H, indicating that the more deprotonated system has stronger covalence. Therefore, the Bader analysis of metal ions can give a qualitative rather than a quantitative result of the metal oxidation state. Instead, the energy position of the metal ions XANES can directly reflect their oxidation states, as implemented in the manuscript.

References:

- M. Bajdich, M. García-Mota, A. Vojvodic, J. K. Nørskov and A. T. Bell, J. Am. Chem. Soc., 2013, 135, 13521-13530.
- (S2) A. Indra, U. Paik and T. Song, Angew. Chem. Int. Ed., 2018, 57, 1241-1245.
- (S3) S.-H. Ye, Z.-X. Shi, J.-X. Feng, Y.-X. Tong and G.-R. Li, *Angew. Chem. Int. Ed.*, 2018, **57**, 2672-2676.
- (S4) B. Zhang, X. Zheng, O. Voznyy, R. Comin, M. Bajdich, M. García-Melchor, L. Han, J. Xu, M. Liu, L. Zheng, F. P. García de Arquer, C. T. Dinh, F. Fan, M. Yuan, E. Yassitepe, N. Chen, T. Regier, P. Liu, Y. Li, P. De Luna, A. Janmohamed, H. L. Xin, H. Yang, A. Vojvodic and E. H. Sargent, *Science*, 2016, **352**, 333-337.
- (S5) S. Song, J. Zhou, X. Su, Y. Wang, J. Li, L. Zhang, G. Xiao, C. Guan, R. Liu, S. Chen, H.-J. Lin, S. Zhang and J.-Q. Wang, *Energy Environ. Sci.*, 2018, **11**, 2945-2953.
- (S6) G. Chen, W. Zhou, D. Guan, J. Sunarso, Y. Zhu, X. Hu, W. Zhang and Z. Shao, *Science Advances*, 2017, **3**, e1603206.
- (S7) Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat. Mater.*, 2011, 10, 780-786.
- (S8) J. Huang, J. Chen, T. Yao, J. He, S. Jiang, Z. Sun, Q. Liu, W. Cheng, F. Hu, Y. Jiang, Z. Pan and S. Wei, *Angew. Chem. Int. Ed.*, 2015, 54, 8722-8727.
- (S9) C. G. Morales-Guio, L. Liardet and X. Hu, J. Am. Chem. Soc., 2016, 138, 8946-8957.
- (S10) S. Li, Y. Wang, S. Peng, L. Zhang, A. M. Al-Enizi, H. Zhang, X. Sun and G. Zheng, Adv. Energy Mater., 2016, 6, 1501661.
- (S11) C. Yu, Z. Liu, X. Han, H. Huang, C. Zhao, J. Yang and J. Qiu, *Carbon*, 2016, **110**, 1-7.
- (S12) L. Feng, A. Li, Y. Li, J. Liu, L. Wang, L. Huang, Y. Wang and X. Ge, *ChemPlusChem*, 2017, 82, 483-488.
- (S13) F. Song, K. Schenk and X. Hu, *Energy Environ. Sci.*, 2016, **9**, 473-477.
- (S14) X. Han, C. Yu, S. Zhou, C. Zhao, H. Huang, J. Yang, Z. Liu, J. Zhao and J. Qiu, *Adv. Energy Mater.*, 2017, **7**, 1602148.
- (S15) Y. Pi, Q. Shao, P. Wang, F. Lv, S. Guo, J. Guo and X. Huang, *Angew. Chem. Int. Ed.*, 2017, 129, 4573.
- (S16) Y. Wang, Y. Zhang, Z. Liu, C. Xie, S. Feng, D. Liu, M. Shao and S. Wang, Angew. Chem. Int. Ed., 2017, 56, 5867-5871.
- (S17) B. Weng, F. Xu, C. Wang, W. Meng, C. R. Grice and Y. Yan, *Energy Environ. Sci.*, 2017, **10**, 121-128.
- (S18) H. Raebiger, S. Lany and A. Zunger, *Nature*, 2008, **453**, 763-766.
- (S19) M. Xu, P. Xiao, S. Stauffer, J. Song, G. Henkelman and J. B. Goodenough, *Chem. Mater.*, 2014, 26, 3089-3097.