Supplementary Information

The in-situ Formation of Defective CoOOH Catalysts from Semi Oxidized Co for Alkaline Oxygen Evolution Reaction

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Experimental details

Synthesis of Co-GO. Graphene oxide (GO) was purchased from XFNANO. cnpowder (Article number. 100602). First, GO (40 mg) in distilled water (10 mL), 440 mg $Co(NO_3)_2 \cdot 6H_2O$ in distilled water (14 mL), 146 mg trimesic acid in methanol (24 mL) and 1500 mg of polyvinylpyrrolidone in N,N-Dimethlformamide (24 mL) were respectively sonicated for 30 min to make a good dispersion. Then, the above four solutions were mixed and continuously sonicated for 30 min. Next, the mixed solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 150 °C for 10 h. Finally, the precipitate was washed with ethanol three times and dried under vacuum at 60 °C.

Annealing of Co-GO. The as-prepared Co/GO was placed in a tube furnace and heated to 450 °C with a heating procedure of 1 °C/min and preserved for 0.5 h. The H₂ and Ar were respectively used as carrier gas at a same flow rate of 20 mL/min to get Co/GO and Co-CoO/GO. The as-prepared Co-GO was put in muffle furnace with the same heating rate, temperature and time to realize the annealing under air atmosphere to get Co_3O_4 /GO.

Characterization Methods

X-ray diffraction (XRD) patterns were recorded by using a Philips X'Pert Pro Super diffractometer with Cu K α radiation (λ = 1.54178 Å). Transmission electron microscopy (TEM) and energy dispersive X-ray spectra (EDS) were performed using a JEM-ARM 200F FETEM with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB MK II X-ray photoelectron spectrometer with an excitation source of Mg K α = 1253.6 eV.

Electrochemical measurements

All electrochemical measurements were carried out in a typical three-electrode system with an electrochemical workstation at room temperature, and using carbon rod as the counter electrode and saturated Hg/HgO as the reference electrode. To prepare the working electrode, 5 mg electrocatalyst and 20 μ l Nafion solution (5 wt%) were ultrasonically dispersed in 1 ml water/ethanol (vol : vol = 3 : 1) solution to form a homogeneous ink. The electrocatalyst suspension (6 μ L) was loaded onto the glass carbon electrode with a diameter of 3 mm to form the working electrode. Commercial

RuO₂ catalyst was from Sigma Aldrich Company. The reference sample loading was determined to be ~0.3 mg cm⁻². For OER, linear sweep voltammetry with a 30 mV s⁻¹ scan rate was performed in 1 M KOH (pH = 14.0). Electrochemical impedance spectroscopy measurements were carried out by applying an a.c. voltage with 5 mV amplitude in a frequency range from 1 Hz to 1 MHz at an overpotential of 420 mV. The stability of Co-CoO/GO was assessed by current-time (i-t) measurements on carbon paper. All potentials were calibrated versus RHE using

 $E(RHE) = E(Hg/HgO) + 0.098 V + 0.059 \times pH$ (1)

XAFS measurements and EXAFS fitting details

The Co L-edge (7709 eV) XAFS spectra were measured at the BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF), China. The storage ring of SSRF was operated at 3.5 GeV with a maximum electron current of 250 mA. The hard X-ray was monochromatized with Si (111) double-crystal monochromator and the detuning was done by 30% to remove harmonics. In-situ XAFS measurements were performed with catalyst-coated carbon cloth. The catalyst powders were dispersed in ethanol with 20 µL Nafion solution (5%, Sigma-Aldrich), and then sonicated for 30 min. The catalyst ink was dropcast onto the center of carbon paper ($\sim 3 \text{ cm} \times 3 \text{ cm}$) taped with Kapton film on the back as the working electrode ($\sim 1 \text{ cm} \times 1 \text{ cm}$) to ensure all of the electrocatalyst reacted with KOH electrolyte at a geometric metal loading of ~ 0.4 mg cm⁻². The XAFS spectra were collected through the transmission mode. To monitor the changes during OER process, the two potentials are carried out: Co-CoO/GO catalyst was put in the 1.0 M KOH (pH = 13.5) with applied anodic voltage at 0.1 V and 0.6V (1.1 V and 1.6 V vs. RHE), where the OER process does not happen and has already occurred in alkaline media. All the XAS spectra were collected until the catalytic reaction is stable. During the XAFS measurements, we seriously calibrate the position of absorption edge (E_0) using Co foil, and all the XAFS data were collected during one period of beam time.

The acquired EXAFS data were processed according to the standard procedures using the ATHENA module implemented in the IFEFFIT software packages.¹ The k^3 -weighted $\chi(k)$ data in the *k*-space ranging from 2.0-10 Å⁻¹ were Fourier transformed to real (*R*) space using a hanning windows (dk = 1.0 Å⁻¹) to separate the EXAFS contributions from different coordination shells. To obtain the detailed structural parameters around Co atom in the as-prepared samples, quantitative

curve-fittings were carried out for the Fourier transformed $k^3\chi(k)$ in the *R*-space using the ARTEMIS module of IFEFFIT.² Effective backscattering amplitudes F(k) and phase shifts $\Phi(k)$ of all fitting paths were calculated by the ab initio code FEFF8.0.³ For these Fe₁/NC samples, a *k*-range of 2.0-10 Å⁻¹ was used and curve-fittings were done in the *R*-space within the *R*-range of [1.0, 3.5] Å for k^3 -weighted $\chi(k)$ functions. The number of independent points are:

$$N_{\text{int}} = 2 \Delta k \cdot \Delta R / \pi = 2 \times (10.5 - 2) \times (2.1 - 1.0) / \pi = 6$$

As for the sample under various conditions, the Fourier-transformed curves of Co-CoO/GO showed a peak at ~1.36 Å assigned to the Co-O coordination, and two dominant peak at ~2.11 and 2.66 Å that assigned to the Co-Co coordination of Co metal and CoO. That of Co/GO shows only peak at 2.08 Å assigned to the Co-Co coordination of Co metal. That of Co₃O₄/GO shows peak at 1.56, 2.54 and 3.09 Å assigned to the Co-O, Co-Co and Co-Co coordination. For all the Co-based sample before OER, the paths were used for fitting. At 1.6 V, the Co-O and Co-Co coordination from CoOOH were used to fit for Co/GO and Co-CoO/GO, and the paths of Co₃O₄/GO were the same. During curve fittings, the Debye-Waller factors (σ^2) and bond length (*R*) were treated adjustably for all samples in all paths. For the ex situ sample, *N* and *R* were treated as adjustable parameters for Fe-N shell, whereas the σ^2 and ΔE_0 were set equal in order to reduce the number of fitting parameters. Thus, the number of the adjustable parameters for the ex situ sample is N_{para} = $6 \le N_{ipt}$. Following the above fitting strategies, the obtained structural parameters are summarized in Table S1. Using these strategies, all generated R factors are smaller than 0.01, indicating excellent quality.



Fig. S1 Co L-edge XANES spectra of Co/GO, Co-CoO/GO, Co₃O₄/GO with the reference standards of Co foil, CoO and Co₃O₄ (a). The corresponding Re($k^3\chi(k)$) oscillations (b).



Fig. S2 Least-squares curve-fitting analysis of Co/GO, Co-CoO/GO, Co₃O₄/GO at Co K-edge.



Fig. S3 Co K-edge XANES for LCF Co-CoO/GO and Co-CoO/GO.



Fig. S4 TEM image of (a) Co/GO, (c) Co-CoO/GO, and (e) Co₃O₄/GO, and corresponding size distribution of (b) Co/GO, (d) Co-CoO/GO, and (f) Co₃O₄/GO.



Fig. S5 The CV curves at different scan rate of (a) Co/GO, (b) Co-CoO/GO, and (c) Co_3O_4/GO . (d)

Estimation of C_{dl} of Co/GO, Co-CoO/GO, Co₃O₄/GO.



Fig. S6 TEM and HRTEM of Co/GO after OER.



Fig. S7 TEM and HRTEM of Co-CoO/GO after OER.



Fig. S8 TEM and HRTEM of Co_3O_4/GO after OER.



Fig. S9 (a) In-situ Co K-edge XANES spectra of CO/GO, Co-CoO/GO and Co $_3O_4$ /GO at 1.1 V. (b)

Corresponding $\operatorname{Re}(k^3\chi(k))$ oscillations.



Fig. S10 The corresponding $\operatorname{Re}(k^3\chi(k))$ oscillations from Fig. 4c.



Fig. S11 Least-squares curve-fitting analysis of in-situ Co K-edge XANES spectra of Co-/GO,

Co-CoO/GO and Co₃O₄/GO at 1.6 V.

Supplementary Tables

Table S1 Structural parameters extracted from quantitative EXAFS curve-fitting using theARTEMIS module of IFEFFIT (The fixed parameters are underlined).

Sample	Path	Ν	R (Å)	$\sigma^{2}(10^{-3}\text{\AA}^{2})$	$\Delta E_0 (\mathrm{eV})$	R-factor
Co foil	Co-Co	12	2.49			
СоО	Со-О	6	2.12			
	Co-Co	12	3.00	-		
Co ₃ O ₄	Со-О	5.3	1.91			
	Co-Co _i	4.0	2.85	-		
	Co-Co _{ii}	9.3	3.37			
СоООН	Со-О	6	1.91			
	Co-Co	6	2.83	-		
Co(OH) ₂	Co-O	6	2.10			
	Co-Co	6	3.18	-		
Co/GO	Co-Co	11.8	2.49	7.9	-4.39	0.003
Co-CoO/GO	Со-О	3.61	2.07	8.1	-1.33	
	Co-Co _i	5.44	2.51	8.1	-2.51	0.005
	Co-Co _{ii}	5.04	3.03	8.1	-2.51	-
Co ₃ O ₄ /GO	Со-О	5.38	1.92	2.6	-5.21	
	Co-Co _i	4.66	2.86	3.5	-6.52	0.002
	Co-Co _{ii}	9.39	3.35	6.6	-9.57	-
Co/GO at 1.6 V	Со-О	5.81	1.91	3.1	-0.82	• 0.002
	Co-Co	5.95	2.83	7.1	-4.95	
Co-CoO/GO	Со-О	5.24	1.89	4.1	-2.89	0.006

	Со-Со	5.94	2.84	7.0	-4.91	
Co ₃ O ₄ /GO at 1.6 V	Со-О	5.34	1.91	2.6	-5.48	
	Co-Co _i	4.63	2.86	3.56	-5.93	0.003
	Co-Co _{ii}	9.36	3.42	7.5	-12.61	

N, coordination number; *R*, bond length; σ^2 Debye-Waller factor; ΔE_0 inner potential shift.

Supplementary reference

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- 3. J. J. Rehr, A. L. Ankudinov, S. D. Conradson, Phys. Rev. B, 1998, 58, 7565.