

### Supplementary Information

## **Chemical and Electrochemical Synthesis of Cobalt Hydroxides: Selective Phase Transformation and Application to Distinct Electrocatalytic Reaction**

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## Methods

**Materials.** Glassy carbon (GC, 0.5 mm thick, Type G, HTW, GmbH), dimensionally stable anodes (DSA(Ir+Ru); Ir@Ru and DSA(Ir+Ta); Ir@Ta alloys, TI-Mesh, Techwin), platinum foil (Pt, 99.9%, TI-453212, Nilaco), silver foil (Ag, 99.9%, FI-011440, Alfa Aesar), gold foil (Au, 99.95%, FF-014721, Alfa Aesar), zinc foil (Zn, 99.994%, FI-011912, Alfa Aesar), copper foil (Cu, 99.8%, FI-035818, Alfa Aesar), and stainless steel foil (SUS, 788210, Nilaco) was used as the substrate for the electrode. Cobalt(II) chloride hexahydrate (97%, Sigma-Aldrich), sodium chloride (99.5%, Oriental Chemical Industry), hexamethylenetetramine (HMT, 99.0%, Sigma-Aldrich), ruthenium (IV) oxide (99%, Sigma-Aldrich), sodium hydroxide (97.0%, Daejung), sodium hypochlorite (9.0–11.0%, Daejung), potassium hydroxide (99.5%, Sigma-Aldrich), lithium hydroxide (95%, Kokusan) were used as received. Ethanol (99.5%) and acetone (99.5%) were purchased from Daejung Chemicals. Active chlorine reagents, R1 solution (potassium iodide, KI, < 20%) and R2 solution (acetic acid glacial, < 30%), were purchased from Shenzhen Sinsche Technology Co., Ltd.

**Synthesis of  $\alpha$ -Co(OH)<sub>2</sub>.** A mixture of CoCl<sub>2</sub>·6H<sub>2</sub>O (10 mM), NaCl (50 mM), and HMT (60 mM) was dissolved in 150 ml of a mixture of ethanol and deionized water (1:9).<sup>1</sup> The mixture was allowed to react at 90 °C for 1 h with magnetic stirring. The resulting green product was washed several times and air-dried at room temperature with anhydrous ethanol and deionized water.

**Synthesis of  $\beta$ -Co(OH)<sub>2</sub>.** The obtained  $\alpha$ -Co(OH)<sub>2</sub> powder (30 mg) was dispersed in 0.5 M NaOH (5 ml) and heated to 50 °C for 3 h under Ar. The product was collected via centrifugation and washed several times with anhydrous ethanol and water.

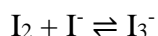
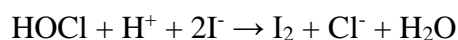
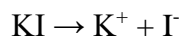
**Synthesis of  $\beta$ -CoOOH.** The  $\alpha$ -Co(OH)<sub>2</sub> or  $\beta$ -Co(OH)<sub>2</sub> powders were dispersed in a mixture of 0.5 M NaOH (1.7 ml) and NaOCl (5.2%, 500  $\mu$ l), and heated at 50 °C for 18 h under atmospheric conditions. The product was collected via centrifugation, washed several times with ethanol and water, and air-dried at room temperature. Similar results were obtained when H<sub>2</sub>O<sub>2</sub> oxidizing agents were used instead of NaOCl.

**Synthesis of  $\gamma$ -CoOOH.** The  $\alpha$ -Co(OH)<sub>2</sub> powder was dispersed in a mixture of 0.5 M NaOH (1.7 ml) and NaOCl (5.2%, 20 ml) and heated at 50 °C for 30 min under atmospheric conditions. The product was collected via centrifugation and washed several times with ethanol and water.

**Material Characterization.** XRD patterns for cobalt hydroxides were recorded over a  $2\theta$  range of 5–80° at a step size of 0.01° using Cu K $\alpha$ 1 radiation with a primary monochromator Ge(111) in the reflection geometry (SmartLAB, Rigaku). The electrodes were characterized using Scanning electron microscopy (SEM, Magellan 400, operated at 10 kV). Transmission electron microscopy (TEM) was performed using a Talos F200X microscope at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed using a K-alpha spectrometer with an Al K $\alpha$  X-ray source and a pass energy level of 40 eV. The UV-Vis diffuse reflectance spectra were acquired with a UV-3600 UV-Vis-NIR spectrophotometer using solid sample holder and UV quartz cell for wavelengths ranging from 250 to 1500 nm with the references.

**Quantitative Titration of HOCl.** Quantitative detection of HOCl was performed by indirect method with the presence of triiodide.<sup>2,3</sup> The detection of HOCl was conducted with reagent

solutions, R1, containing potassium iodide (KI), and R2, involving acetic acid glacial as an iodine scavenger. The production of HOCl in the electrochemical progress was detected as following chemical reaction.



The strong absorbance was observed at  $\lambda_{352 \text{ nm}}$ , where detect triiodide.

**Electrochemical Measurements.** The catalysts were loaded on a glassy carbon (GC) plate (10 mm  $\times$  20 mm  $\times$  0.5 mm (Th)), which served as the working electrode and Hg/HgO and Pt electrodes served as the reference and counter electrode, respectively. The electrochemical measurements were performed in an alkaline 0.1 M NaOH solution for water oxidation. Four microliters of the catalyst ink (0.11 mg/cm<sup>2</sup>) was drop-casted onto the GC surface and then dried for at least 30 min. The obtained cobalt oxyhydroxides were initially cycled thrice using cyclic voltammetry (CV) until a stable peak was obtained. The electrochemical properties were studied using CV, linear sweep voltammetry (LSV), and chronoamperometry. The potentials reported in this study were converted to a reversible hydrogen electrode (RHE) scale using the following equation.

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.059 \times \text{pH}$$

## Supplementary Tables

**Table S1.** Refined structural parameters of ( $\alpha$ -cobalt hydroxide using XRD data at 297 K. The symbols,  $g$  and  $B_{\text{eq}}$ , represent the occupation factor and the isotropic thermal parameter, respectively. The numbers in parentheses are the estimated standard deviations of the last significant figure. The result is corresponded to the formula,  $[\text{Co}^{\text{Oh}}_{0.77} \text{Co}^{\text{Td}}_{0.23}(\text{OH})_{1.77}]^{0.23+}[\text{Cl}_{0.23} \cdot 0.64\text{H}_2\text{O}]$ .

- $R$ -factors:  $R_{\text{wp}} = 2.40 \%$ ,  $R_{\text{p}} = 1.86 \%$ ,  $R_{\text{e}} = 2.14 \%$ , GOF (goodness of fit) = 1.12
- Lattice parameter:  $a (= b) = 0.314613(2) \text{ nm}$ ,  $c = 2.4074(3) \text{ nm}$ ,  $\alpha (= \beta) = 90^\circ$ ,  $\gamma = 120^\circ$

**Space group:  $R\bar{3}m$  (No. 166),  $Z = 3$**

Atom	Site	$x$	$y$	$z$	$g$	$B_{\text{eq}}/\text{\AA}^2$
Co <sub>Oh</sub>	3a	0.0	0.0	0.0	0.766(1) <sup>[a]</sup>	2.78(1) <sup>[b]</sup>
Co <sub>Td</sub>	6c	0.0	0.0	0.0542(1)	0.117(1)	2.78(1)
O <sub>1</sub>	6c	0.0	0.0	0.0617(1)	1.0	3.11(1)
Cl	6c	0.0	0.0	0.1634(1)	0.1172(1) <sup>[c]</sup>	3.53(1)
O <sub>2</sub>	18h	0.0081(1)	$= -x(\text{O}_2)$	0.4835(1)	0.1073(1)	3.86(1)

[a] Constraint on occupancy:  $g(\text{Co}_{\text{Oh}}) - 2g(\text{Co}_{\text{Td}}) = 1.0$

[b] Constraint on isotropic thermal factor:  $B_{\text{eq}}(\text{Co}_{\text{Oh}}) = B_{\text{eq}}(\text{Co}_{\text{Td}})$

[c] Constraint on occupancy:  $g(\text{Co}_{\text{Td}}) = g(\text{Cl})$

**Table S2.** Refined structural parameters of  $\gamma$ -CoOOH using XRD data at 297 K. The result is corresponded to the formula,  $[\text{H}_{0.50}\text{Na}_{0.16}\text{CoO}_2 \cdot 0.34(\text{H}_2\text{O})]$ .

- $R$ -factors:  $R_{\text{wp}} = 4.15 \%$ ,  $R_{\text{p}} = 2.71 \%$ ,  $R_{\text{e}} = 3.79 \%$ , GOF (goodness of fit) = 1.10
- Lattice parameter:  $a (= b) = 0.28592(2) \text{ nm}$ ,  $c = 2.0209(3) \text{ nm}$ ,  $\alpha (= \beta) = 90^\circ$ ,  $\gamma = 120^\circ$

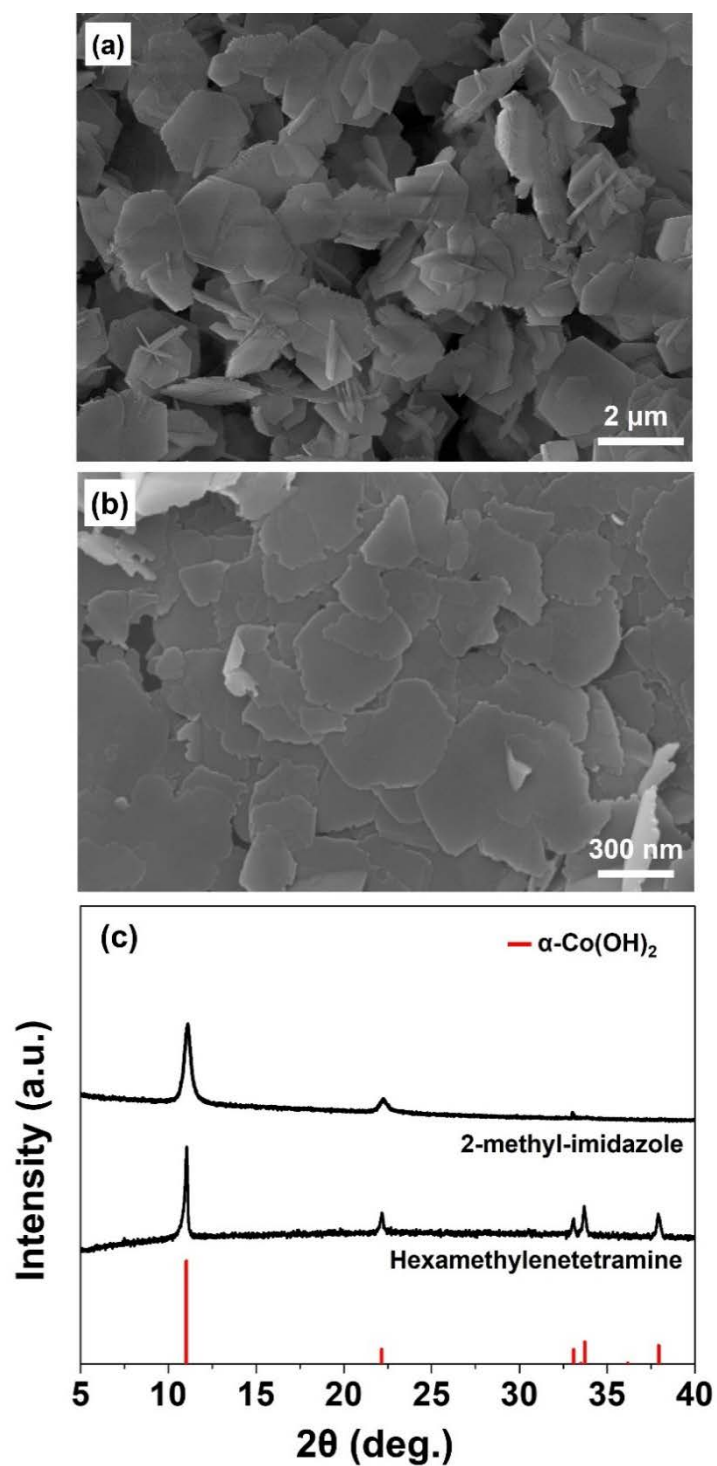
**Space group:  $R \bar{3} m$  (No. 160),  $Z = 3$**

Atom	Site	$x$	$y$	$z$	$g$	$B_{\text{eq}}/\text{\AA}^2$
Co <sub>slab</sub>	$3a$	0.0	0.0	0.0	1.0	1.87(1)
O <sub>1_slab</sub>	$3a$	0.0	0.0	0.3657(1)	1.0	2.19(1)
O <sub>2_slab</sub>	$3a$	0.0	0.0	0.6108(1)	1.0	2.21(1)
Na <sub>intersla</sub>	$3a$	0.0	0.0	0.1721(1)	0.471(1)	3.19(1)
O <sub>1_interslab</sub>	$3a$	0.0	0.0	0.1406(1)	0.338(1)	3.02(1)

**Table S3.** Specific surface areas of the samples based on the BET method.

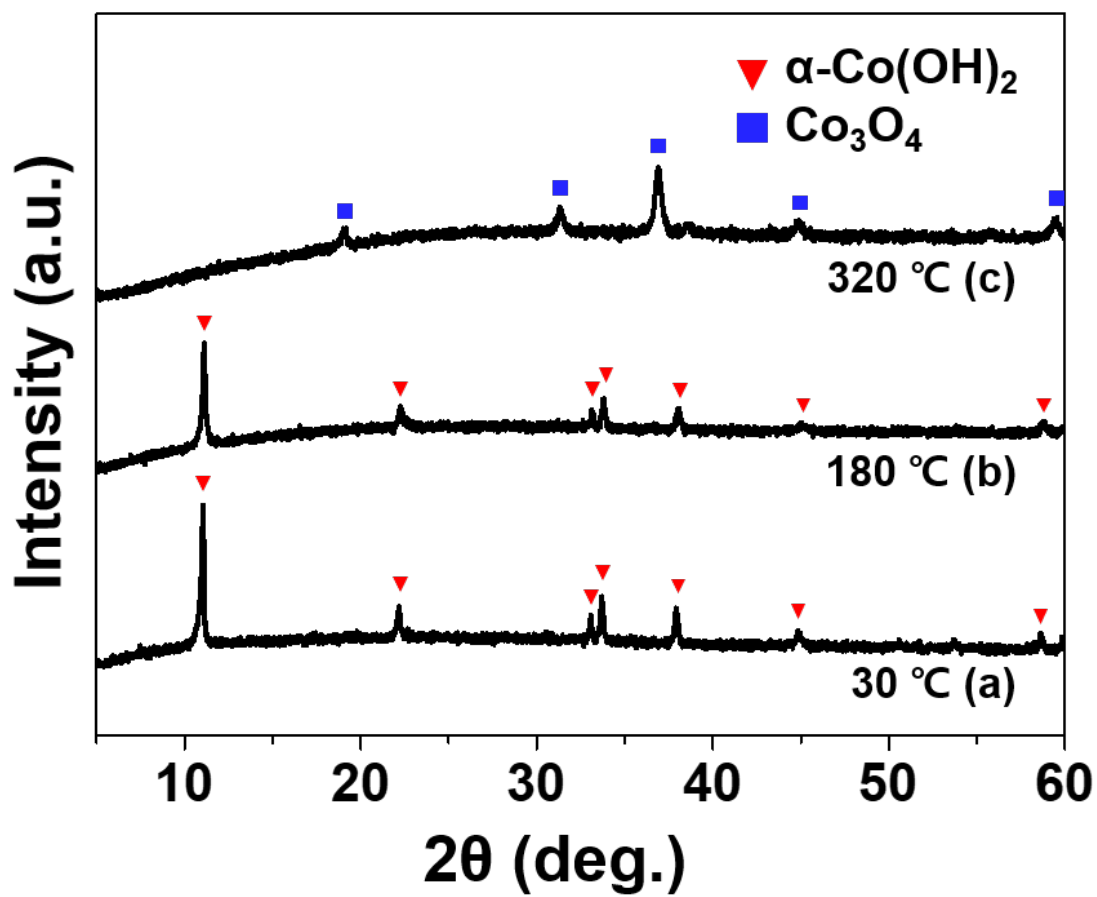
<b>sample</b>	<b>V<sub>m</sub></b> <b>[cm<sup>3</sup>(STP) g<sup>-1</sup>]</b>	<b>a<sub>s,BET</sub></b> <b>[m<sup>2</sup> g<sup>-1</sup>]</b>	<b>C</b>	<b>Total pore</b> <b>volume(p/p<sub>0</sub>)</b> <b>[cm<sup>3</sup> g<sup>-1</sup>]</b>	<b>Mean pore</b> <b>diameter</b> <b>[nm]</b>
<b>α-Co(OH)<sub>2</sub></b>	5.5294	24.067	31.267	0.011966	1.9888
<b>β-Co(OH)<sub>2</sub></b>	4.5219	19.682	24.001	0.0092476	1.8794
<b>β-CoOOH</b>	15.411	67.076	57.96	0.033466	1.9957
<b>γ-CoOOH</b>	5.4599	23.764	45.303	0.012109	2.0382

## Supplementary Figures

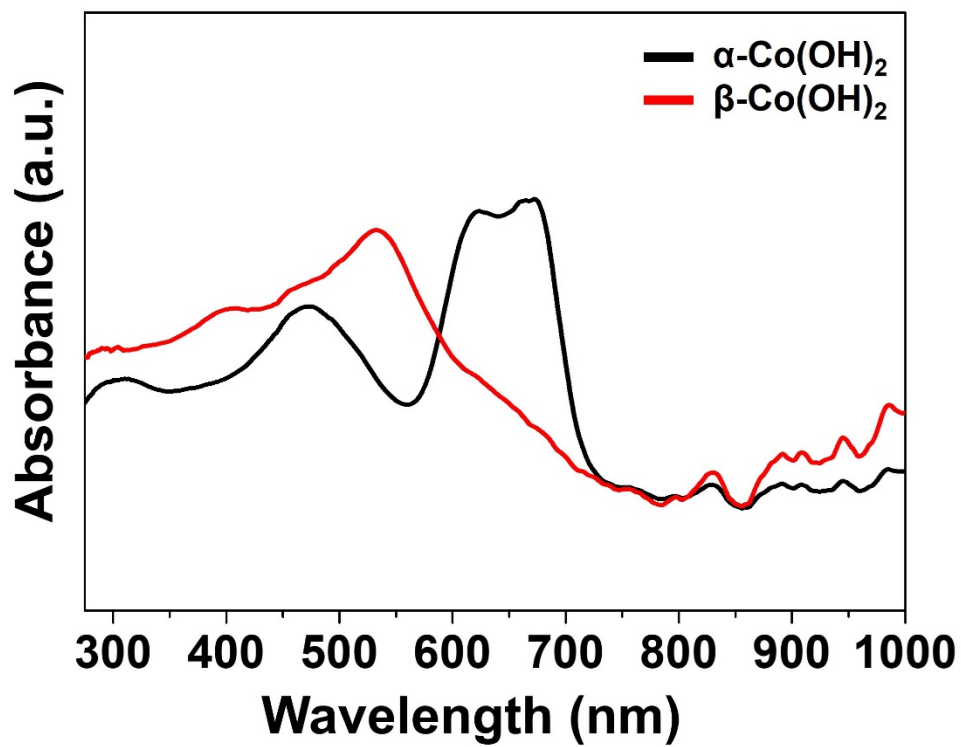


**Fig. S1** SEM images of  $\alpha$ -Co(OH)<sub>2</sub> prepared in the presence of (a) hexamethylenetetramine (HMT) and (b) 2-methyl-imidazole. (c) XRD patterns of each  $\alpha$ -Co(OH)<sub>2</sub> samples.

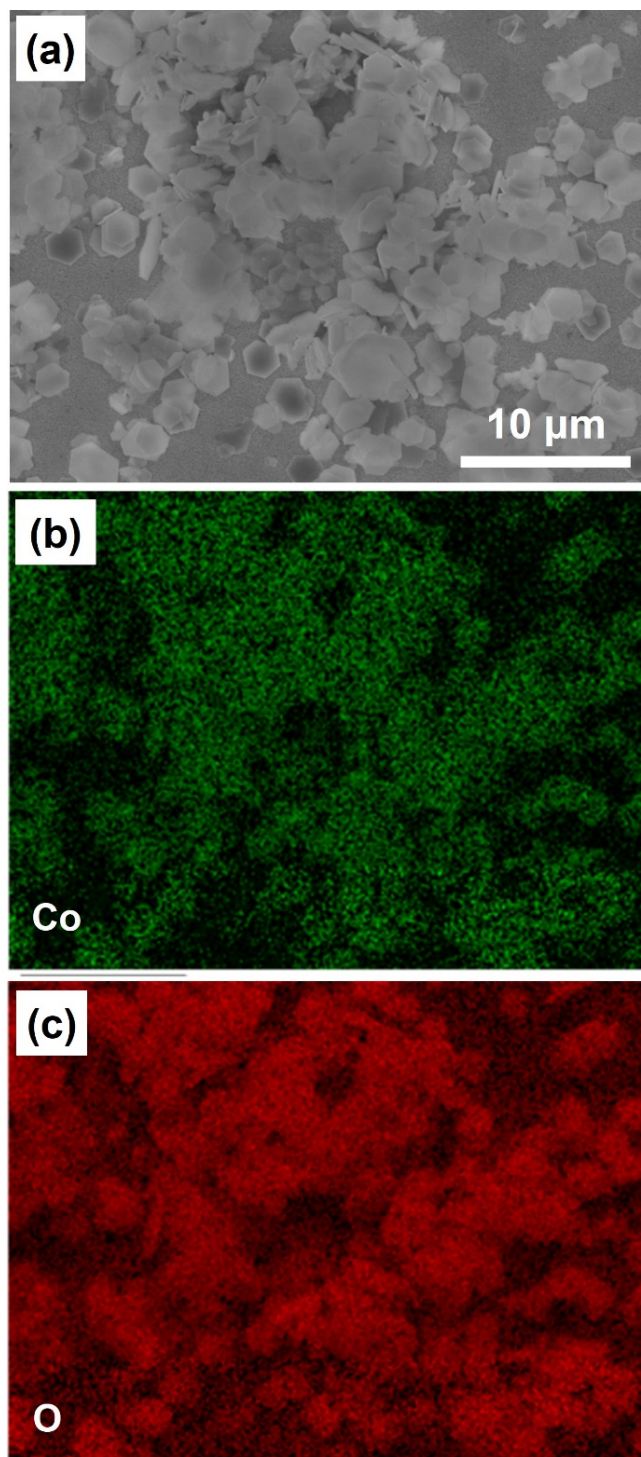




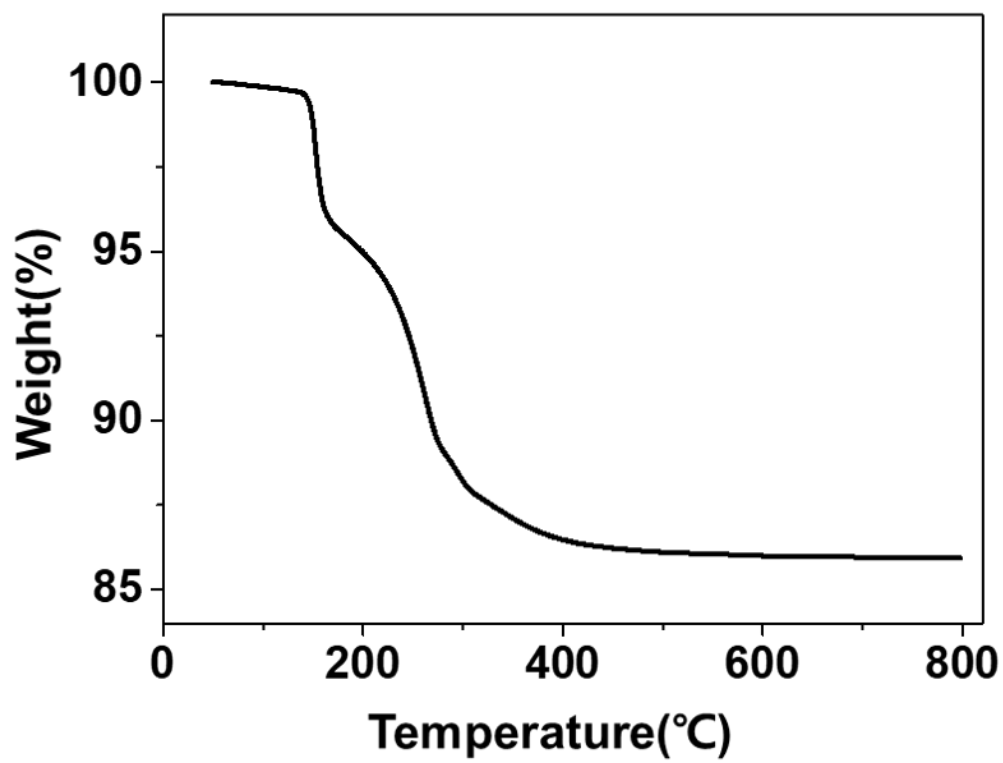
**Fig. S2** XRD patterns of  $\alpha\text{-Co(OH)}_2$  (a) before and after annealing at (b) 180 °C, and (c) 320 °C for 3 h under inert conditions.



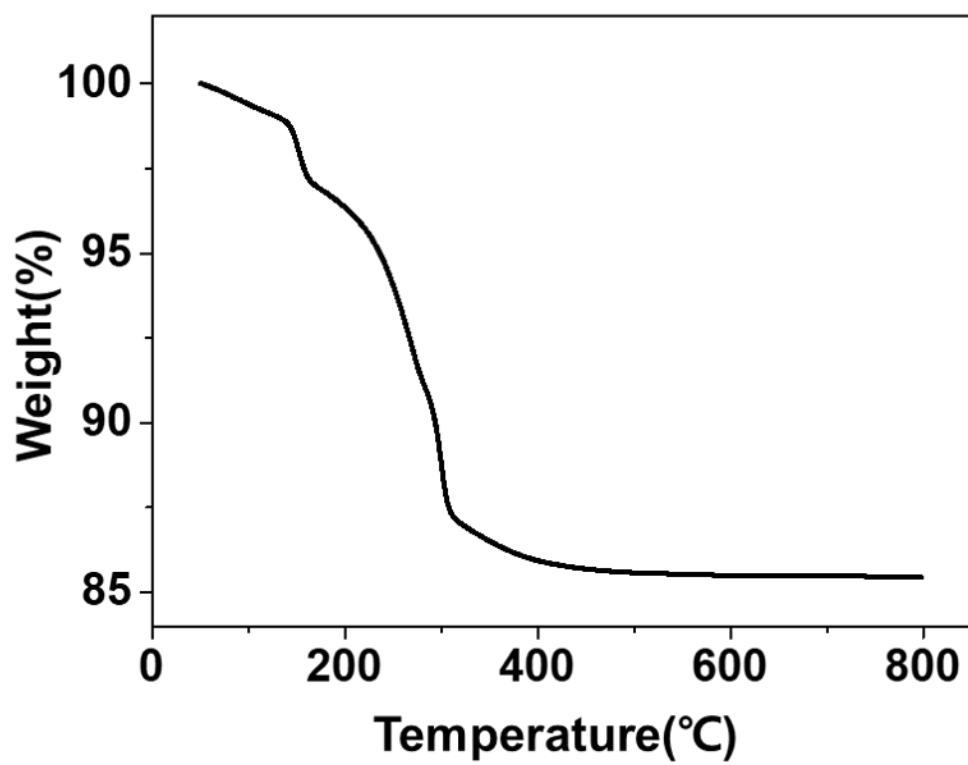
**Fig. S3** UV-visible diffuse reflectance spectra of  $\alpha$ -Co(OH)<sub>2</sub> (black), and  $\beta$ -Co(OH)<sub>2</sub> (red).



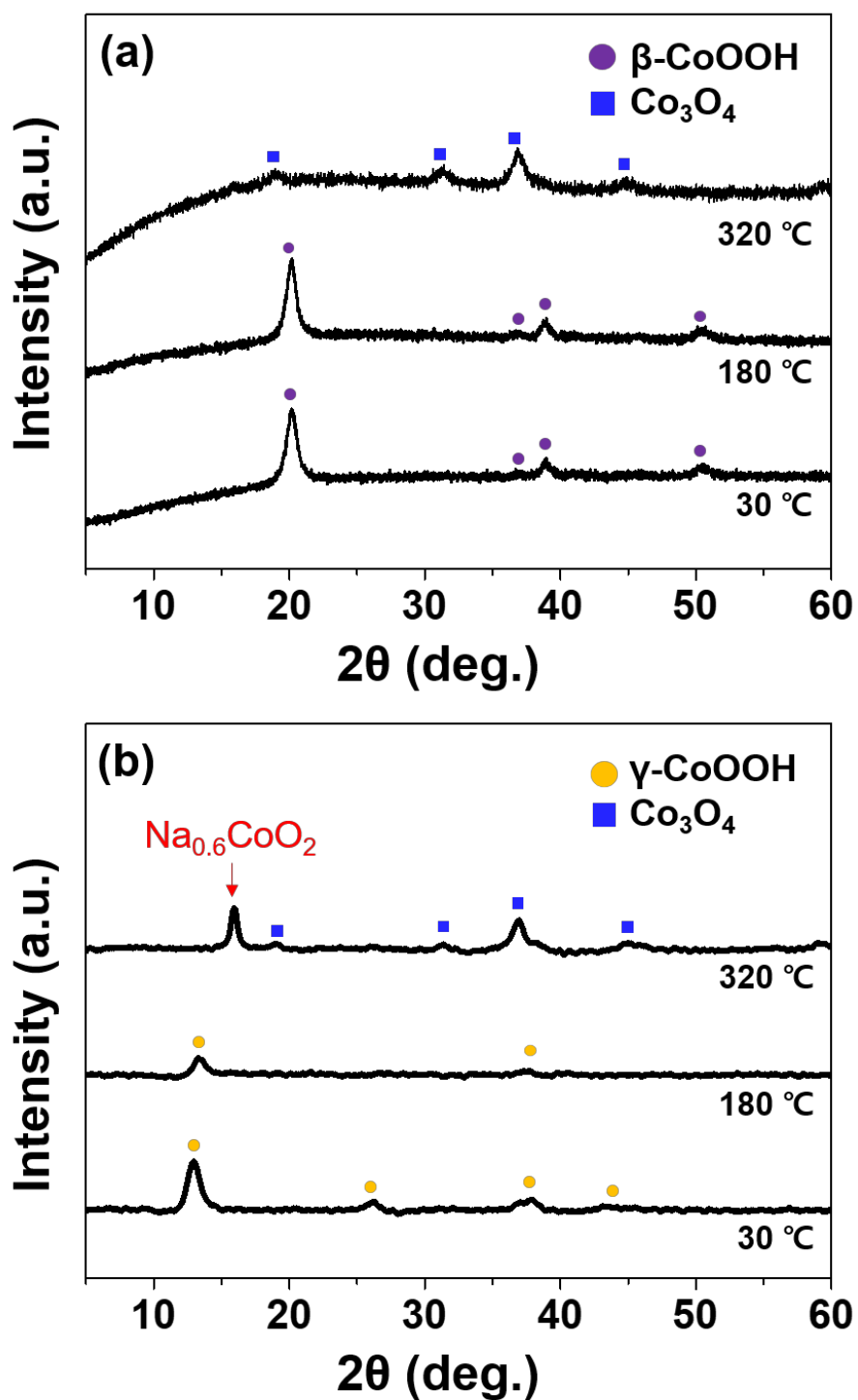
**Fig. S4** (a) SEM image of  $\beta$ -Co(OH)<sub>2</sub>. Elemental map of  $\beta$ -Co(OH)<sub>2</sub> and corresponding distributions of (b) Co and (c) O.



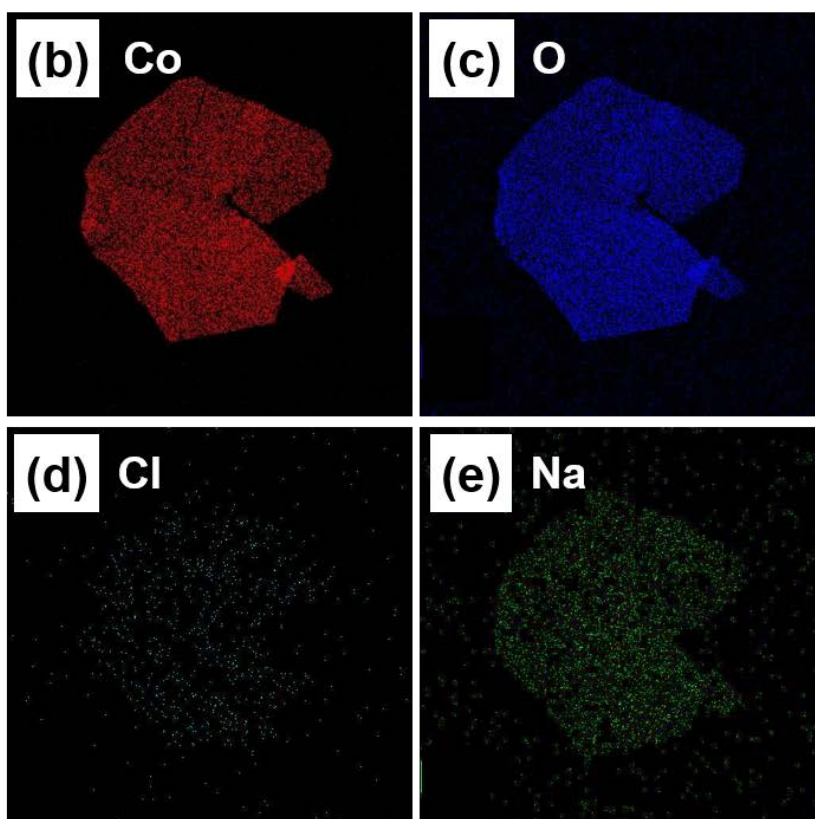
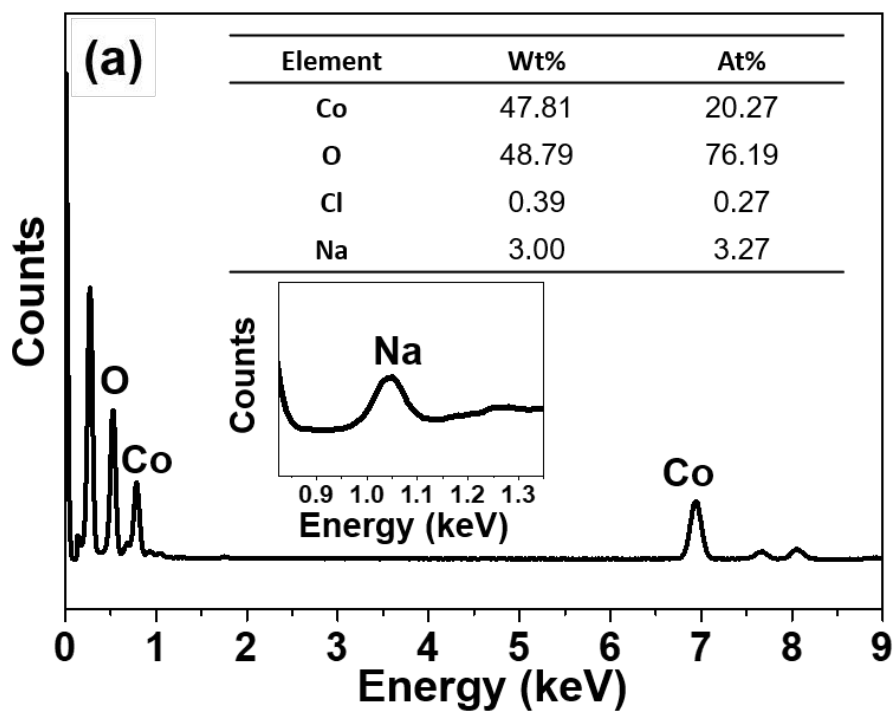
**Fig. S5** TGA data of  $\beta$ -Co(OH)<sub>2</sub> sample in the range of 50–800 °C in air.



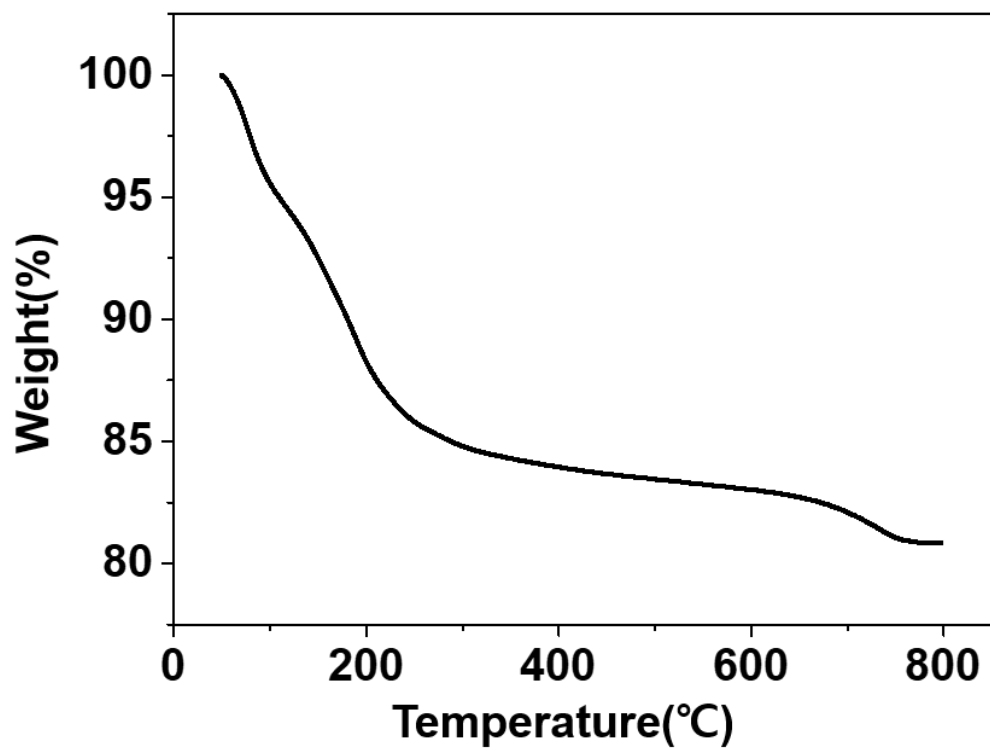
**Fig. S6** TGA data of  $\beta$ -CoOOH sample in the range of 50–800 °C in air.



**Fig. S7** XRD patterns of (a)  $\beta$ -CoOOH and (b)  $\gamma$ -CoOOH before and after annealing at 180 °C, and 320 °C for 3 h under inert conditions.

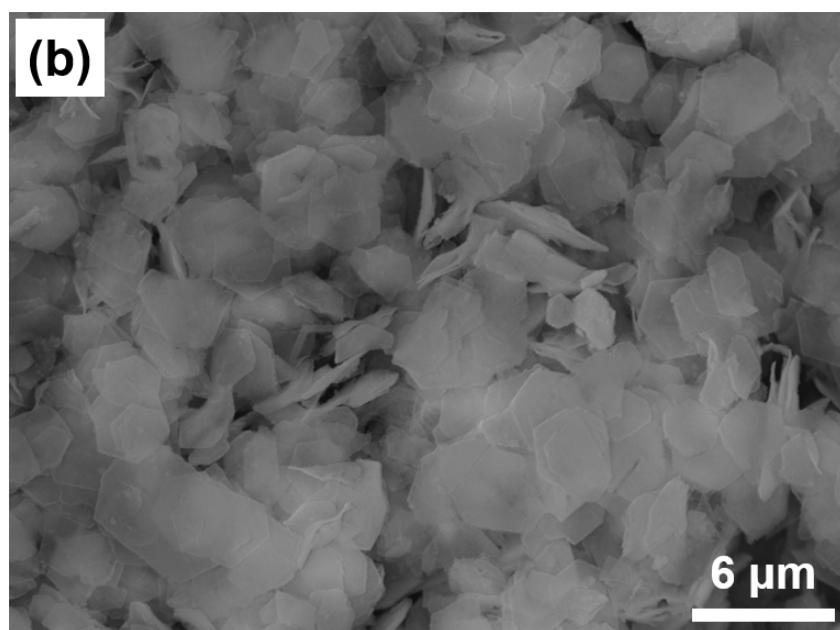
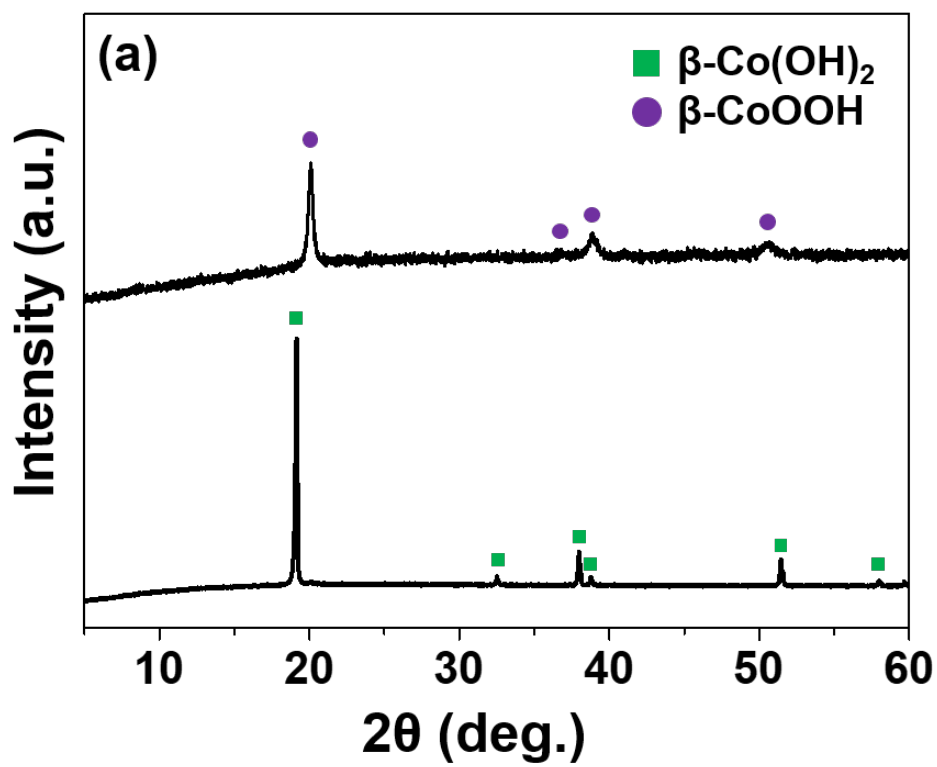


**Fig. S8** (a) TEM-EDS results of  $\gamma$ -CoOOH. Elemental map of  $\gamma$ -CoOOH and corresponding distributions of (b) Co, (c) O, (d) Cl, and (e) Na.

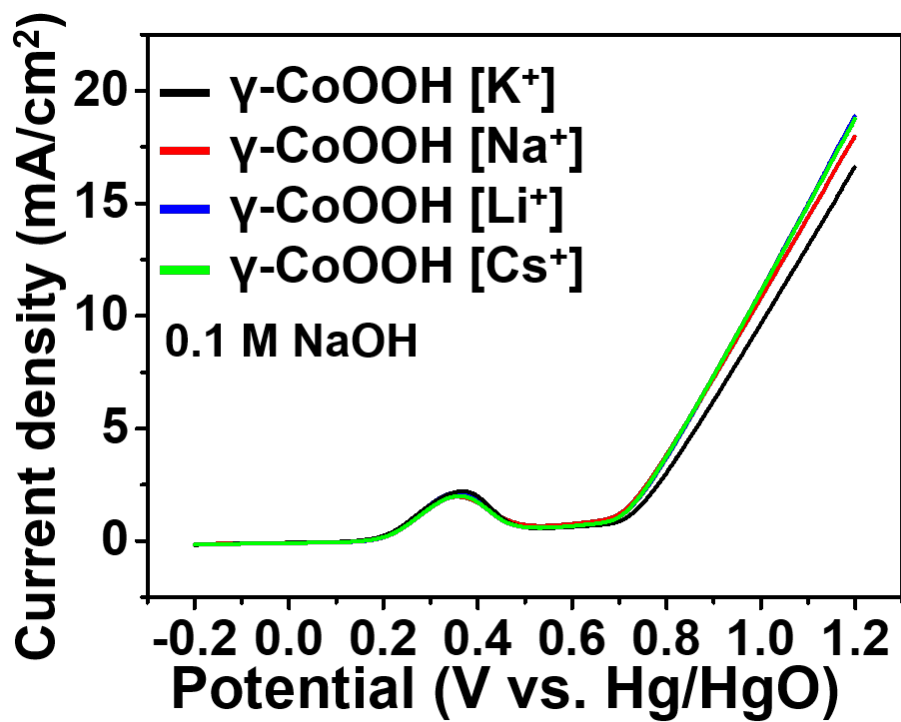


**Fig. S9** TGA data of  $\gamma$ -CoOOH sample in the range of 50–800 °C in air.

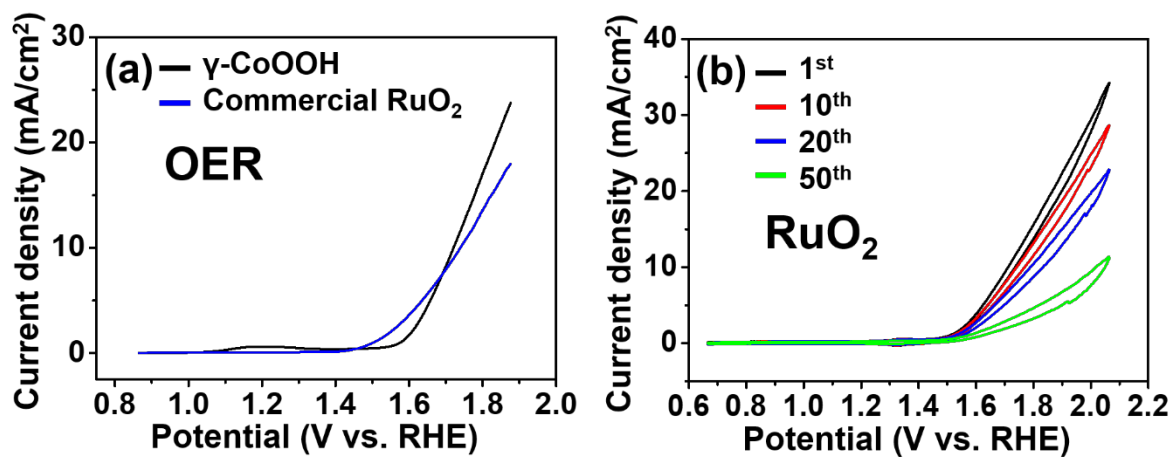




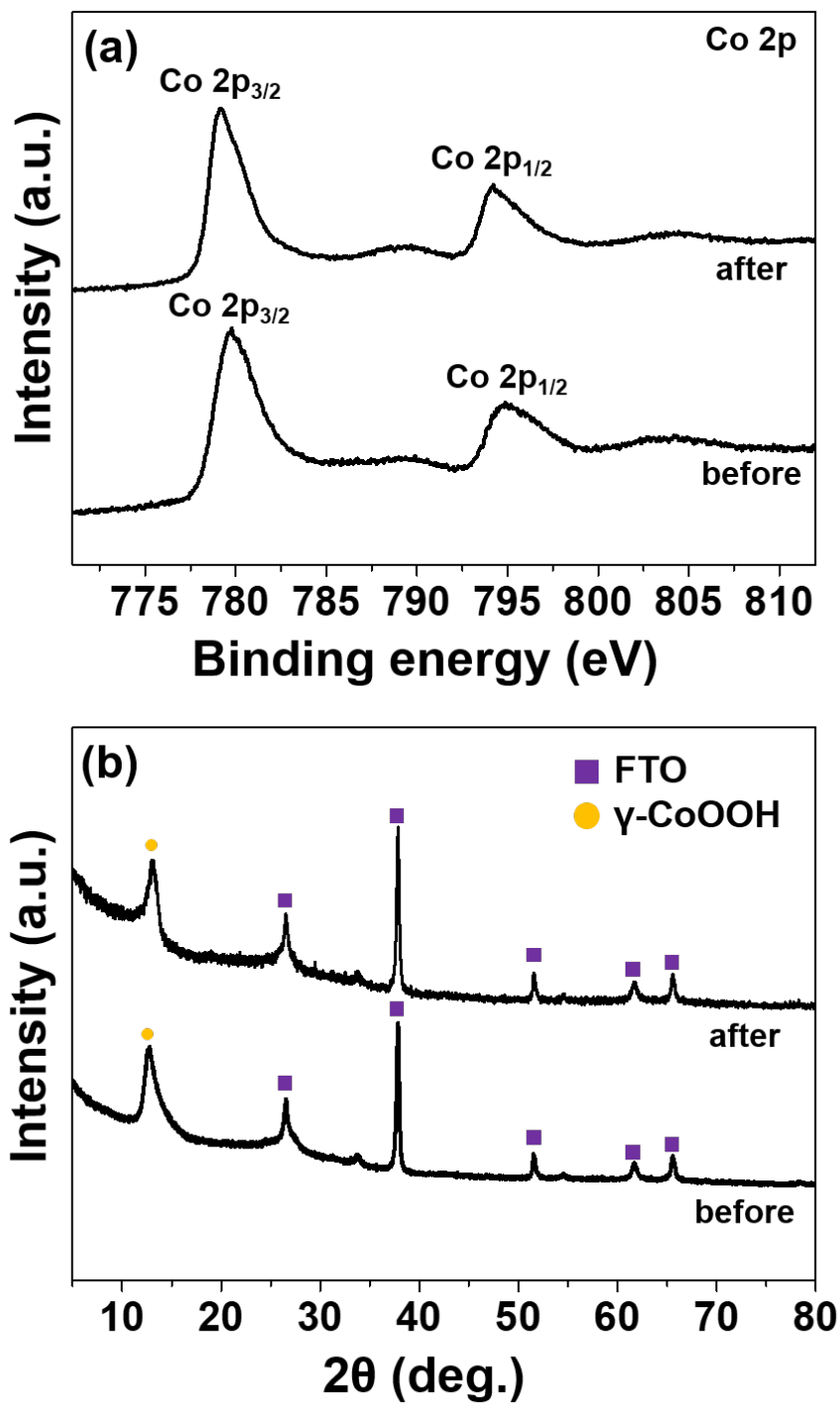
**Fig. S10** (a) XRD patterns and (b) SEM images of  $\beta\text{-CoOOH}$  from  $\beta\text{-Co(OH)}_2$ .



**Fig. S11** LSVs of  $\gamma$ -CoOOH containing Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup> under 0.1 M NaOH (Scan rate: 10 mV/s).



**Fig. S12** (a) LSVs of  $\gamma$ -CoOOH (black line) and commercial RuO<sub>2</sub> (blue line) in 0.1 M NaOH (Scan rate: 10 mV/s). (b) CVs of commercial RuO<sub>2</sub> in 0.1 M NaOH (Scan rate: 50 mV/s).



**Fig. S13** XPS of (a) Co 2p region and (b) XRD patterns before and after the stability test of the  $\gamma$ -CoOOH.

## References

1. Z. Liu, R. Ma, M. Osada, K. Takada and T. Sasaki, *J. Am. Chem. Soc.*, 2015, **127**, 40, 13869–13874.
2. A. E. Burgess and J. C. Davidson, *J. Chem. Educ.*, 2012, **89**, 6, 814–816.
3. I. Z. Shirgaonkar, and A. B. Pandit, *Ultrason. Sonochem.*, 1997, **4**, 245-253.