

***Supplementary Materials:***

**Ru nanoclusters confined on  $\alpha/\beta$  cobalt hydroxide nanosheets as efficient bifunctional oxygen electrocatalysts for Zn-air battery**

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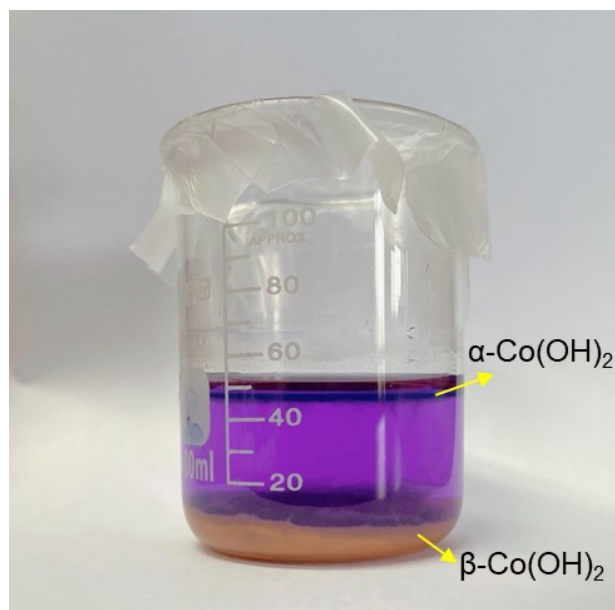
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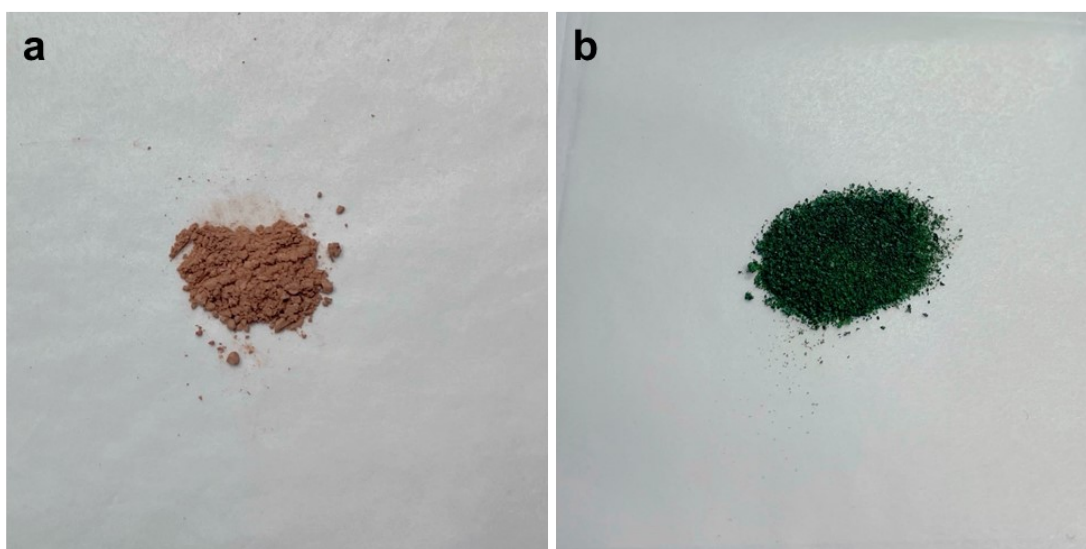
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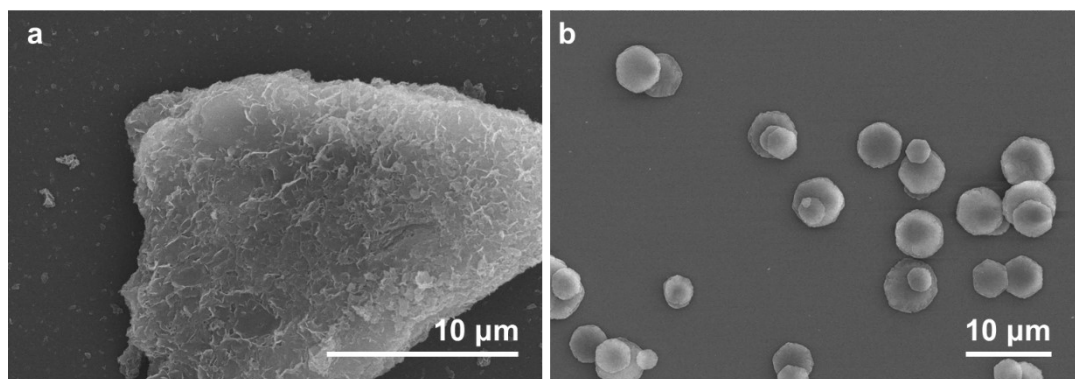
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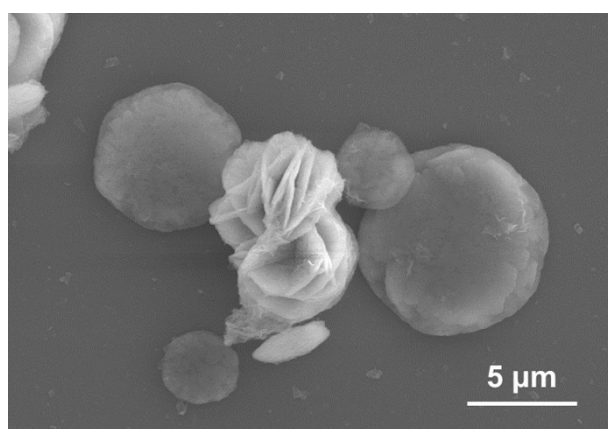
**Figure S1** Digital photograph of the mixed  $\text{Co(OH)}_2$  after 24 h-standing.



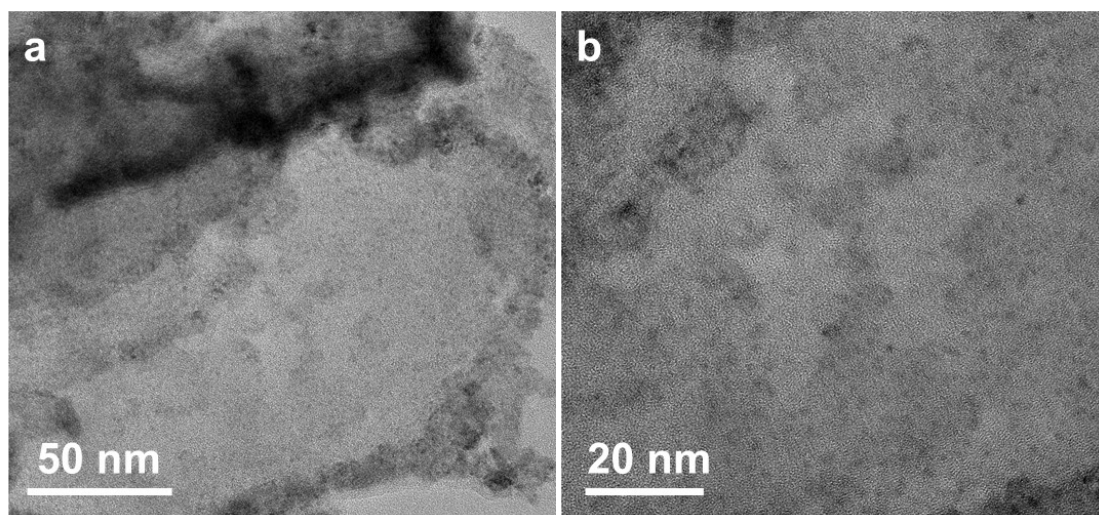
**Figure S2** Digital photograph of  $\beta\text{-Co(OH)}_2$  (a) and  $\alpha\text{-Co(OH)}_2$  (b) powders.



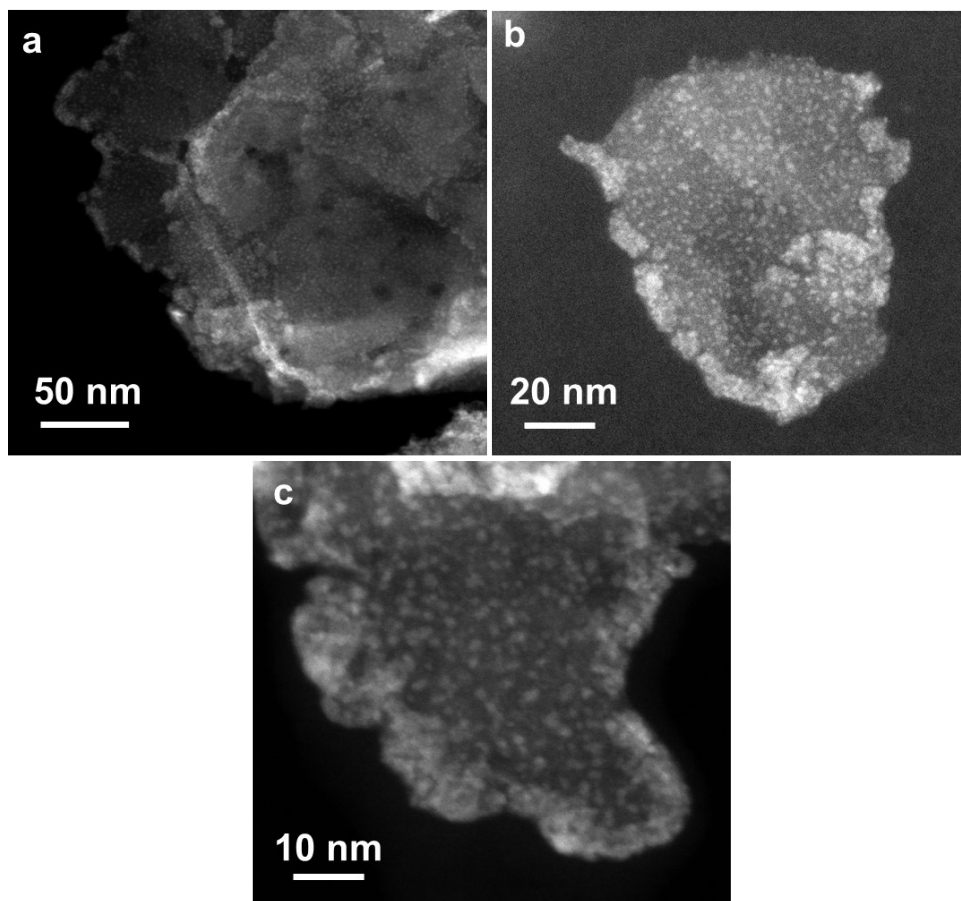
**Figure S3** SEM images of (a)  $\alpha$ -Co(OH)<sub>2</sub>, (b)  $\beta$ -Co(OH)<sub>2</sub>.



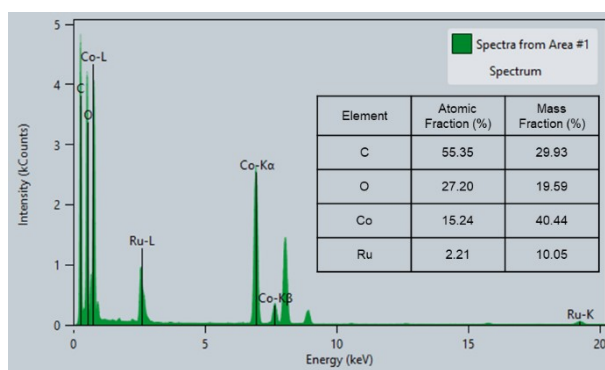
**Figure S4** SEM image of mixed phase of Co(OH)<sub>2</sub>.



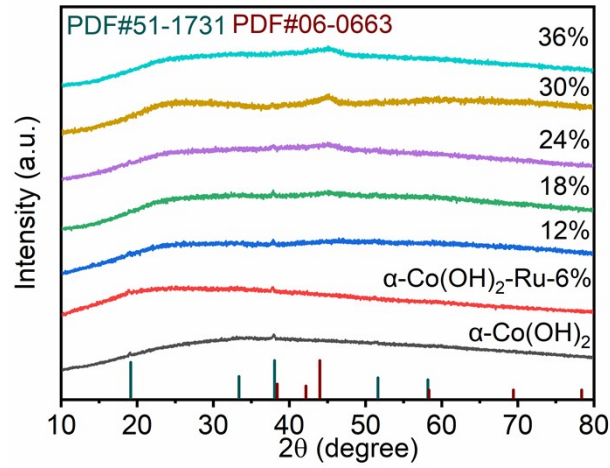
**Figure S5** HRTEM images of  $\alpha$ -Co(OH)<sub>2</sub>-Ru.



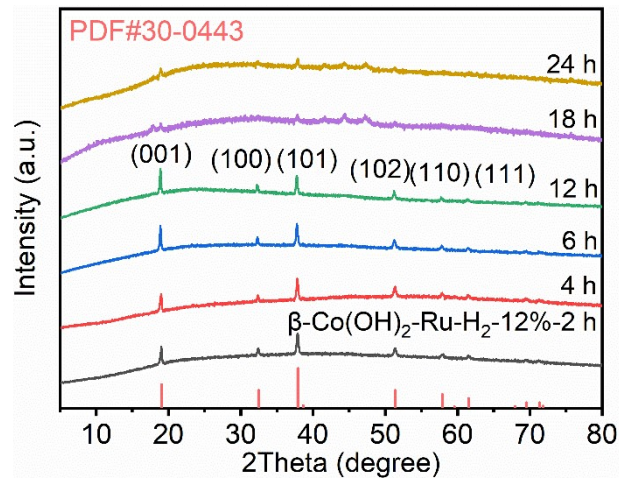
**Figure S6** STEM images of  $\alpha$ -Co(OH)<sub>2</sub>-Ru.



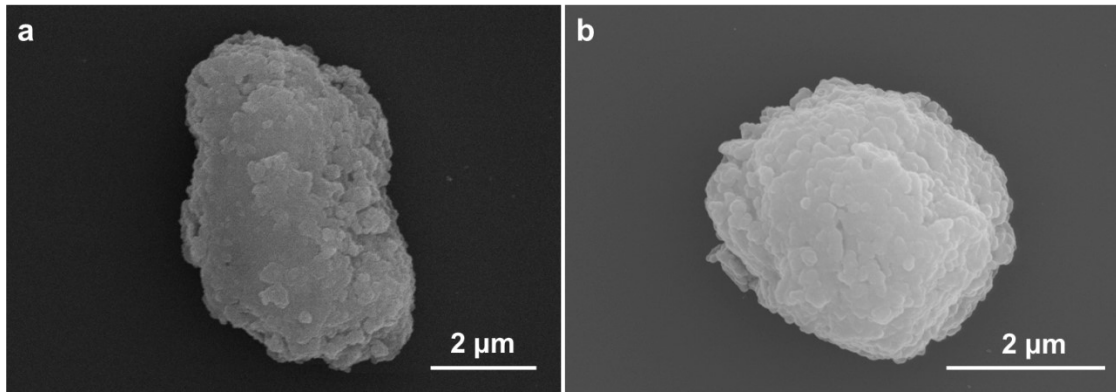
**Figure S7** EDX image and corresponding analysis of spectrum of  $\alpha$ -Co(OH)<sub>2</sub>-Ru.



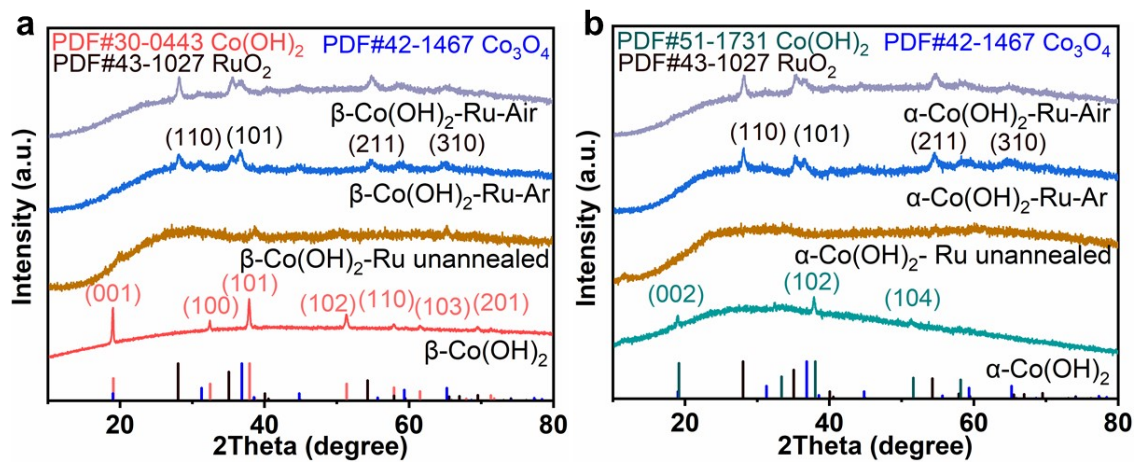
**Figure S8** XRD pattern of  $\alpha$ -Co(OH)<sub>2</sub>-Ru with different loadings of Ru.



**Figure S9** XRD pattern of  $\beta$ -Co(OH)<sub>2</sub>-Ru with different stirring time.

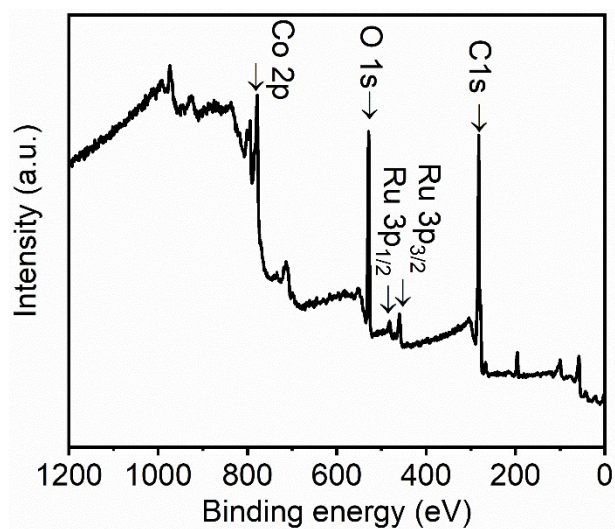


**Figure S10** SEM images of  $\alpha$ -Co(OH)<sub>2</sub>-Ru and  $\beta$ -Co(OH)<sub>2</sub>-Ru after stirring for 18 h.

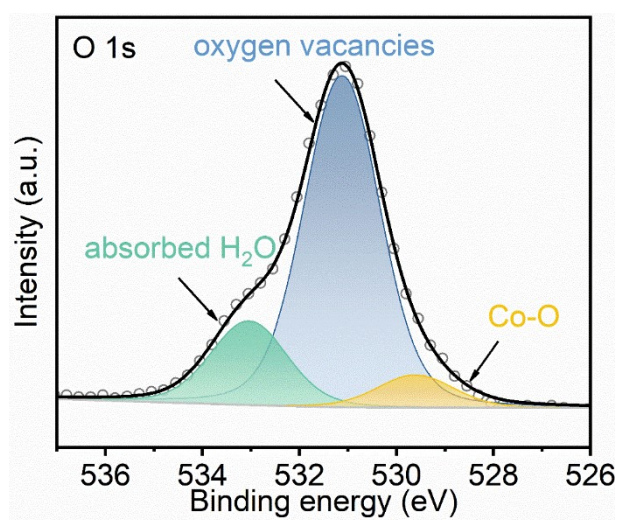


**Figure S11** XRD pattern of  $\beta$ -Co(OH)<sub>2</sub>-Ru  $\alpha$ -Co(OH)<sub>2</sub>-Ru annealed under different atmosphere.

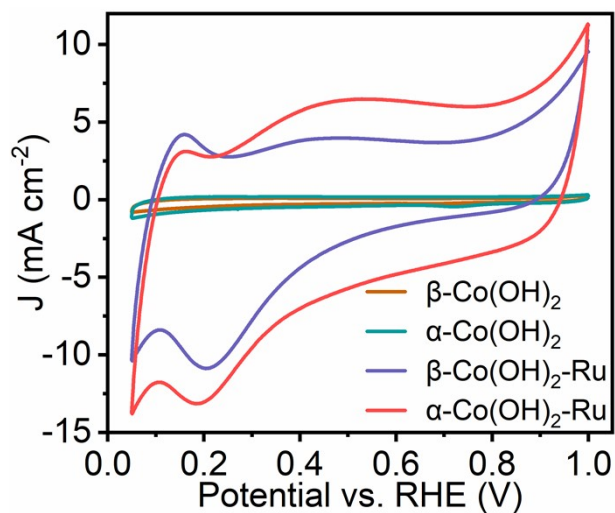




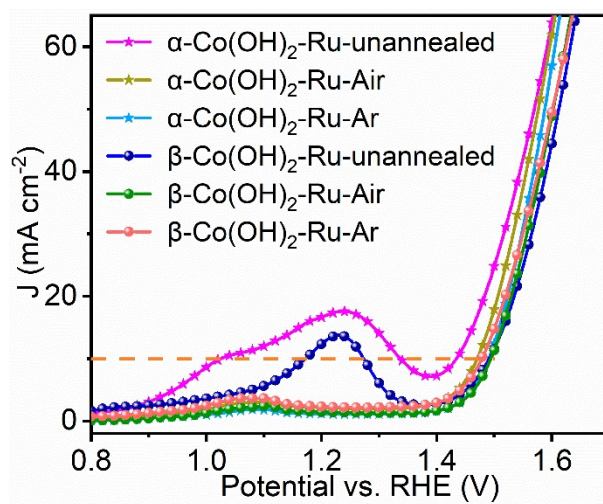
**Figure S12** The XPS survey spectra of  $\alpha\text{-Co(OH)}_2\text{-Ru}$ .



**Figure S13** O1s XPS spectrum of  $\alpha\text{-Co(OH)}_2\text{-Ru}$ .

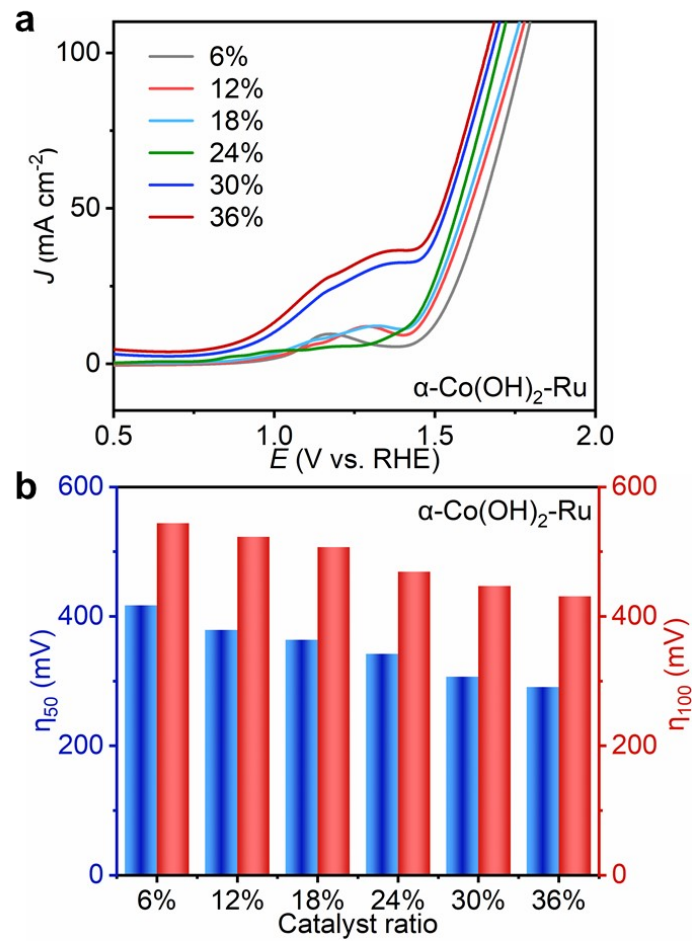


**Figure S14** CV curves of different samples at the scan rate of 50 mV s<sup>-1</sup>.

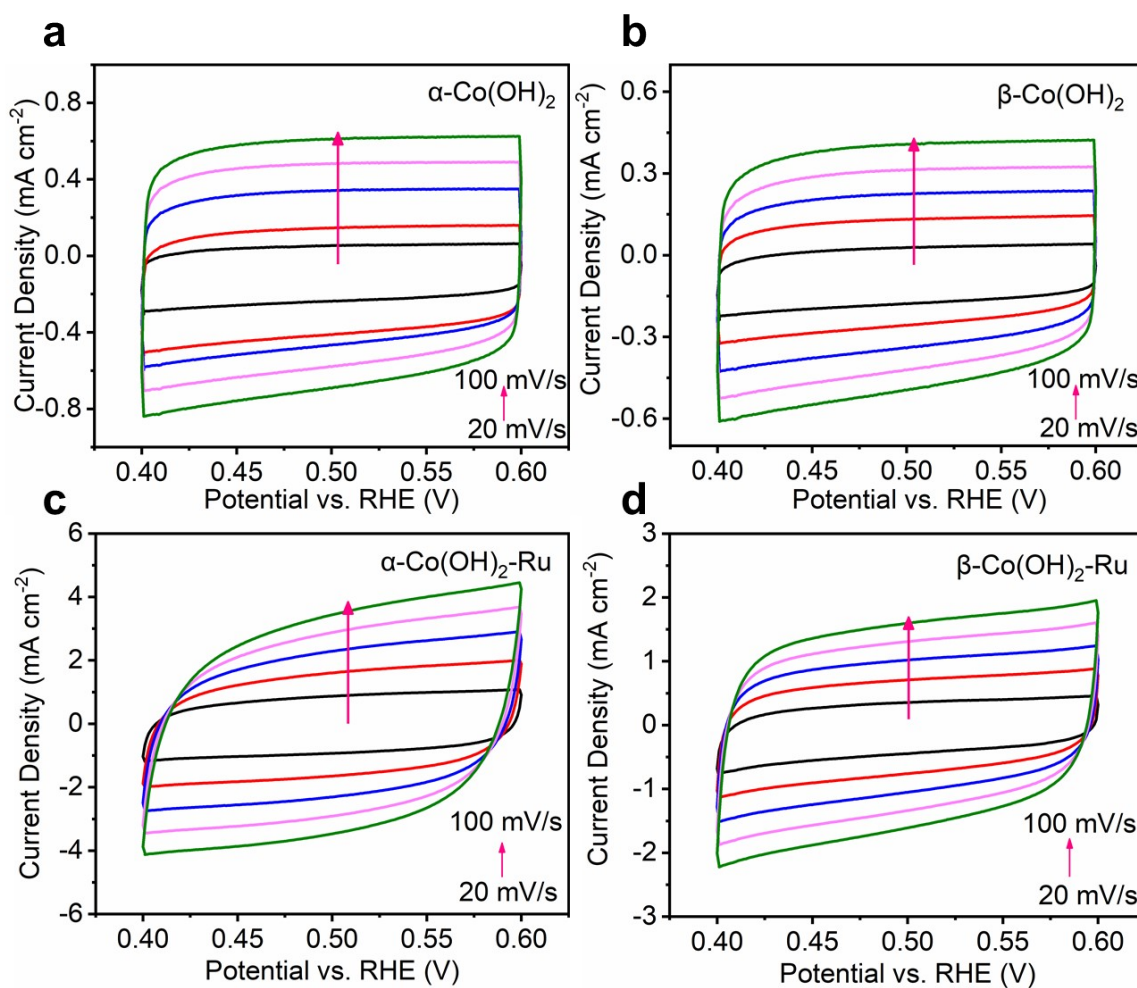


**Figure S15** LSV curves of  $\beta$ -Co(OH)<sub>2</sub>-Ru  $\alpha$ -Co(OH)<sub>2</sub>-Ru annealed under different atmosphere.

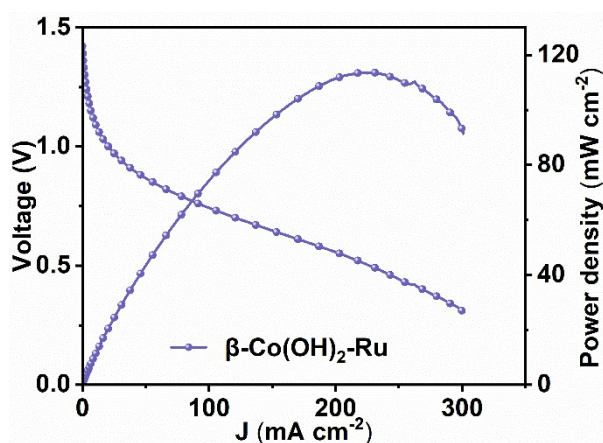




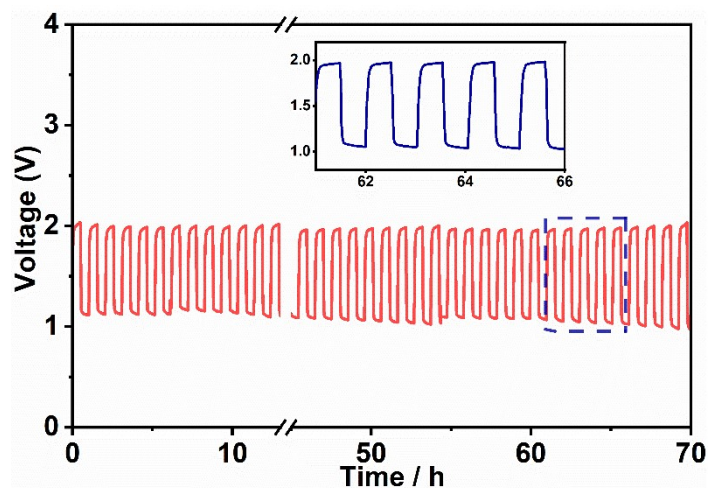
**Figure S16** OER performance of  $\alpha$ -Co(OH)<sub>2</sub>-Ru with different Ru loading and its corresponding overpotential @50 mA cm<sup>-2</sup> ( $\eta_{50}$ ), @100 mA cm<sup>-2</sup> ( $\eta_{100}$ ).



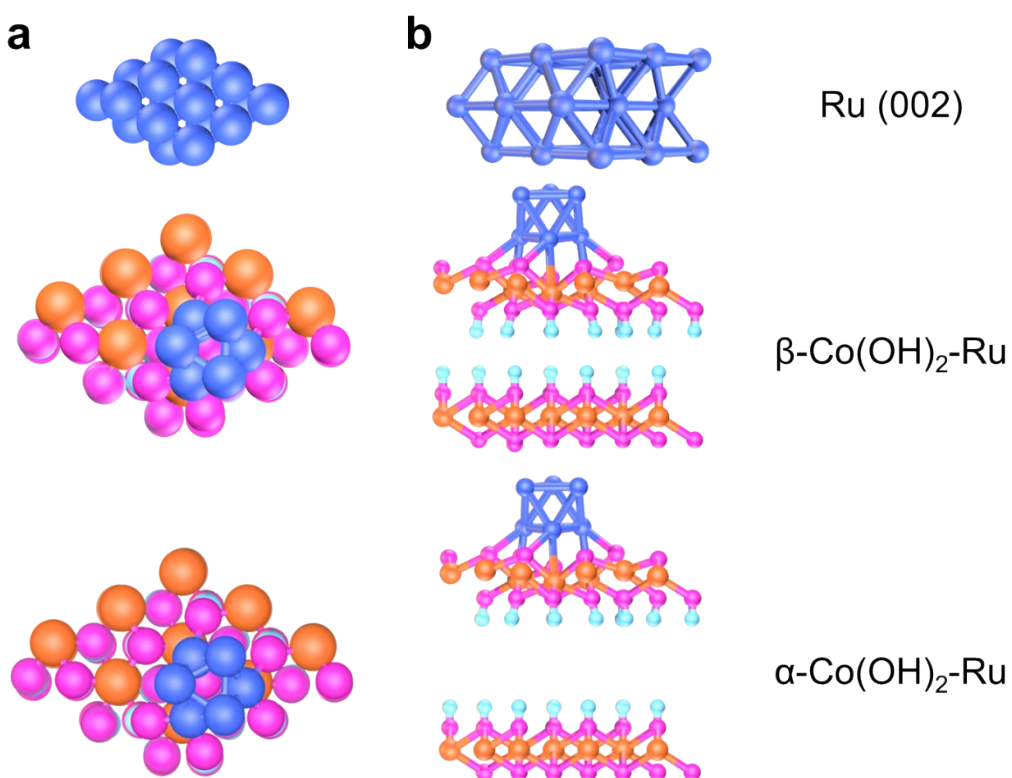
**Figure S17** The CV curves of (a)  $\alpha$ -Co(OH)<sub>2</sub>, (b)  $\beta$ -Co(OH)<sub>2</sub>, (c)  $\alpha$ -Co(OH)<sub>2</sub>-Ru and (d)  $\beta$ -Co(OH)<sub>2</sub>-Ru in the potential region of 0.4-0.6 V (vs. RHE) in 1 M KOH.



**Figure S18** The discharge voltage curve and the corresponding power density plot of  $\beta$ -Co(OH)<sub>2</sub>-Ru.



**Figure S19** The in-depth discharge/charge plot at  $5 \text{ mA cm}^{-2}$  followed by 30 min charging and 30 min discharging.



**Figure S20** Schematic structure model of Ru (002),  $\beta\text{-Co(OH)}_2\text{-Ru}$  and  $\alpha\text{-Co(OH)}_2\text{-Ru}$  from top(a) and side(b) views.

**Table S1.** Ru content was determined by the ICP-OES analysis for the  $\alpha$ -Co(OH)<sub>2</sub>-Ru and  $\beta$ -Co(OH)<sub>2</sub>-Ru catalysts.

Samples	Ru(wt%) (ICP-OES)
$\alpha$ -Co(OH) <sub>2</sub> -Ru	0.117
$\beta$ -Co(OH) <sub>2</sub> -Ru	0.104

**Table S2.** The advanced bifunctional ORR/OER catalysts

Samples	E <sub>j=10</sub> (V)	E <sub>1/2</sub> (V)	$\Delta E$ (V)	Reference
$\alpha$ -Co(OH) <sub>2</sub> -Ru	1.429	0.872	0.557	This work
$\beta$ -Co(OH) <sub>2</sub> -Ru	1.465	0.851	0.614	This work
Mn-RuO <sub>2</sub>	1.498	0.862	0.636	1
Bi <sub>2</sub> Ru <sub>2</sub> O <sub>7</sub>	1.68	0.83	0.85	2
La <sub>1.5</sub> Sr <sub>0.5</sub> NiMn <sub>0.5</sub> Ru <sub>0.5</sub> O <sub>6</sub>	1.66	0.73	0.93	3
Ru-FeRu@C/NC	1.575	0.900	0.675	4
Ru-RuO <sub>2</sub> @NPC	1.52	0.86	0.56	5
Ru@Co <sub>3</sub> O <sub>4</sub> -1.0	1.61	0.77	0.84	6
Ru-Cl-N SAC	1.463	0.9	0.563	7
Ca <sub>2</sub> FeRuO <sub>6</sub>	1.63	0.78	0.85	8
CoRu-O/A@HNC-2	1.483	0.821	0.662	9
RuO <sub>x</sub> -nc@Co <sub>3</sub> O <sub>4</sub> -250	1.51	0.8	0.71	10
Co-Fe-Ru/PNCS	1.54	0.843	0.697	11
RuCo/NPC	1.58	0.8	0.78	12

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