

Electronic Supplementary Information

Bridged Ov-Ru-O-Co coordination induced by Co^{2+δ} substitution in Co/RuO₂ Catalysts for Enhanced Alkaline Hydrogen and Oxygen Evolution

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†Electronic supplementary information (ESI) available.

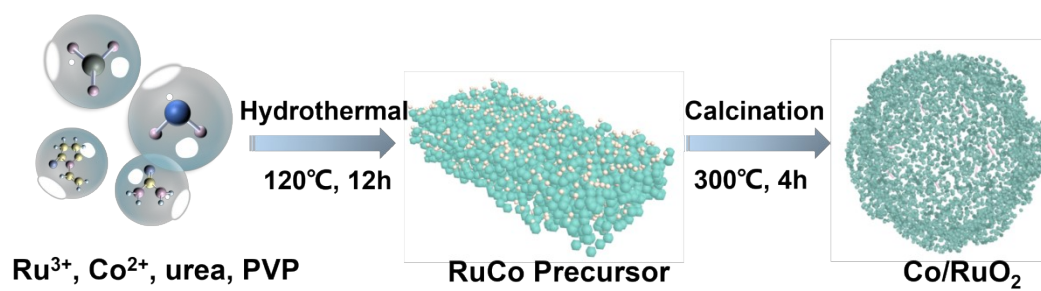


Figure S1. The synthesis process and the microstructure model of products.

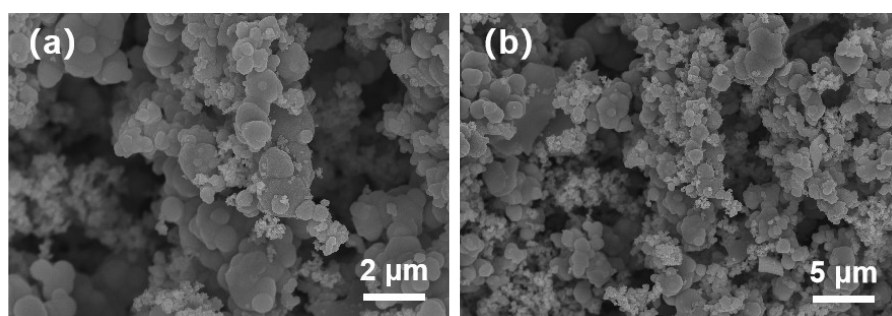


Figure S2. FESEM images of RuCo-based precursors.

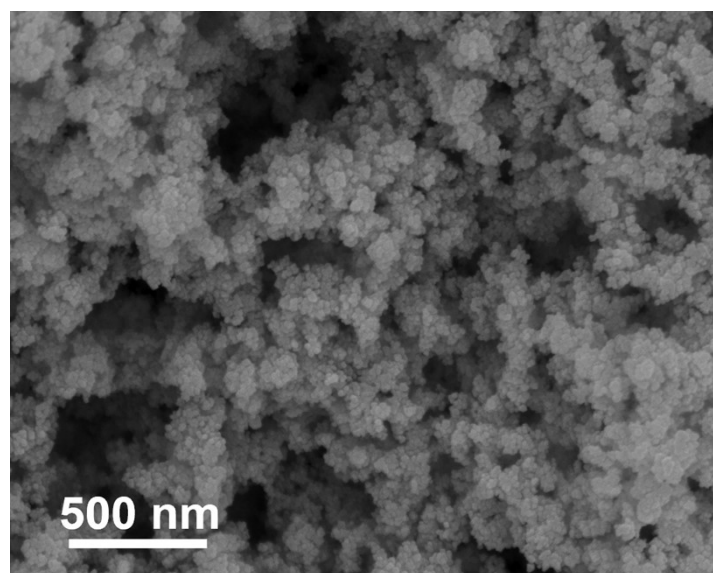


Figure S3. FESEM image of Co/RuO₂-50/1.

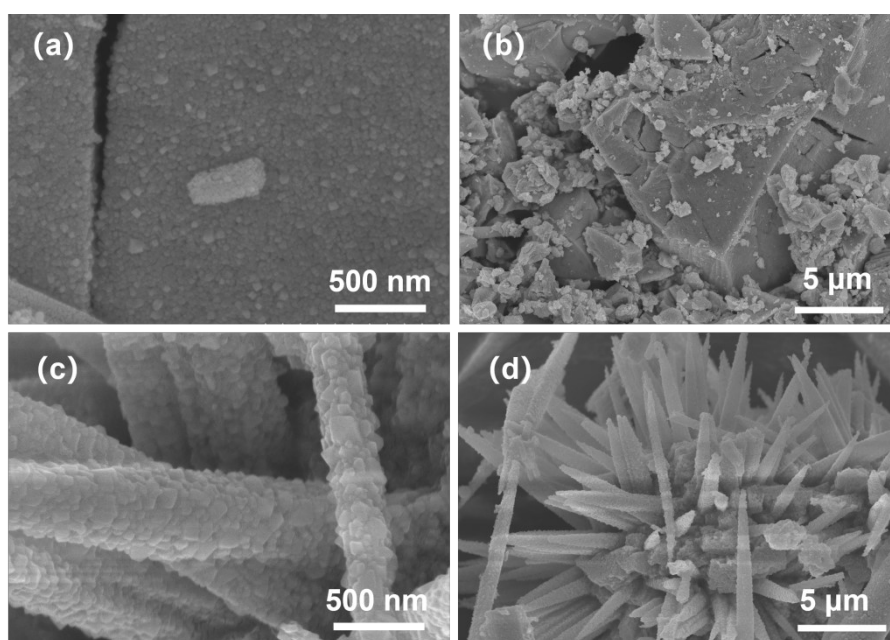


Figure S4. FESEM images of (a,b) RuO_2 and (c,d) Co_3O_4 .

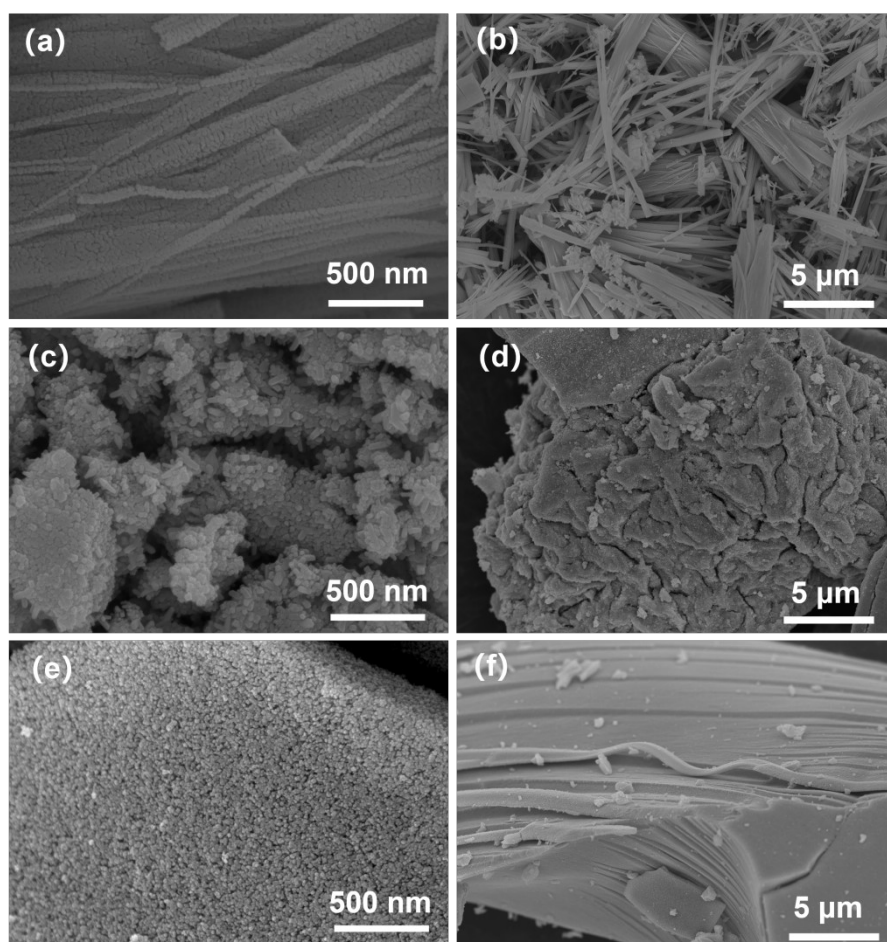


Figure S5. FESEM images of (a,b) Co/RuO₂-50/1, (c,d) Co/RuO₂-1/10 and (e,f) Co/RuO₂-1/20.

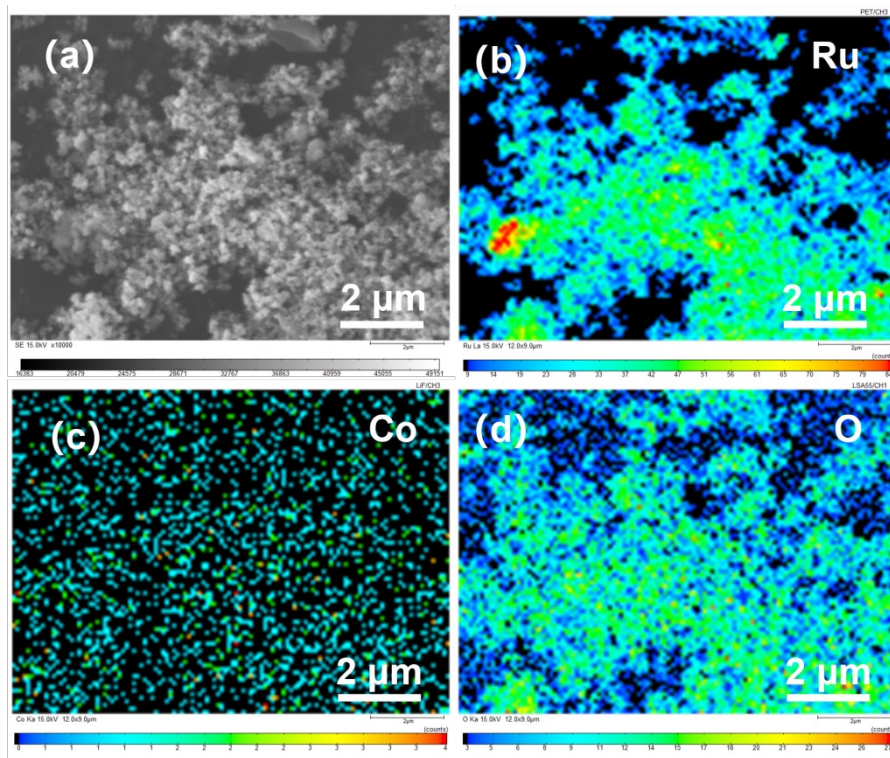


Figure S6. EPMA analysis of Co/RuO₂-1/50.

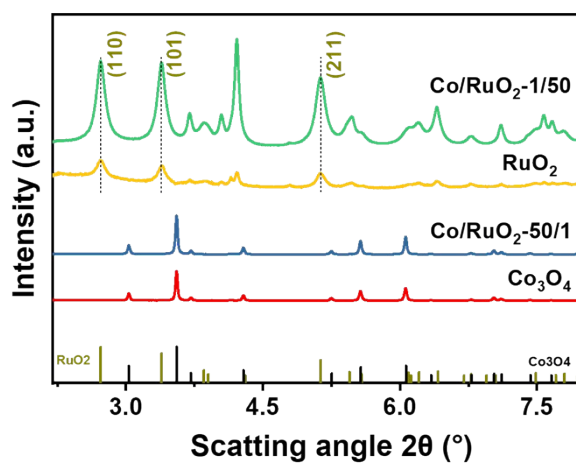


Figure S7. The 1D WAXS profiles of samples corresponding to the 2D WAXS patterns of Fig.

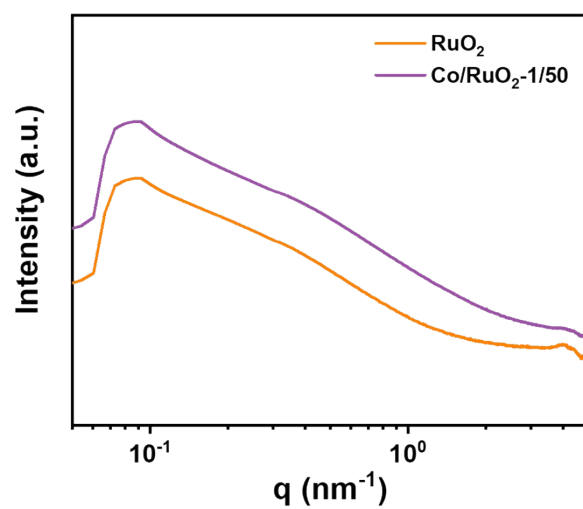


Figure S8. X-Ray scattering curves of RuO₂ and Co/RuO₂-1/50 in the SAXS region.

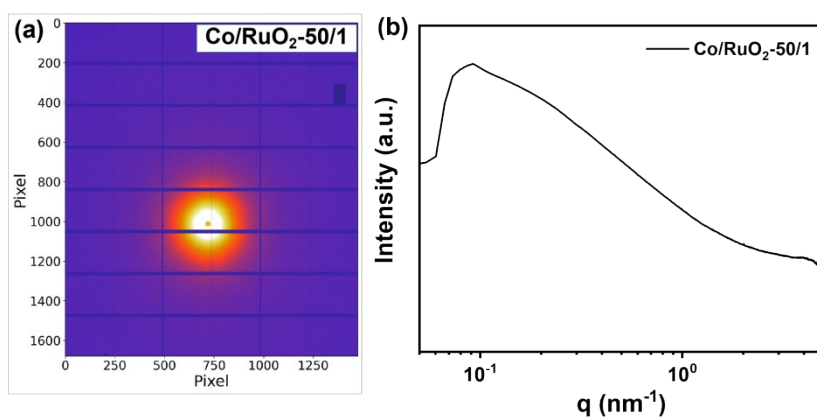


Figure S9. X-Ray scattering curves in the SAXS region of Co/RuO₂-50/1 (a) 2D profile, (b) 1D curve.

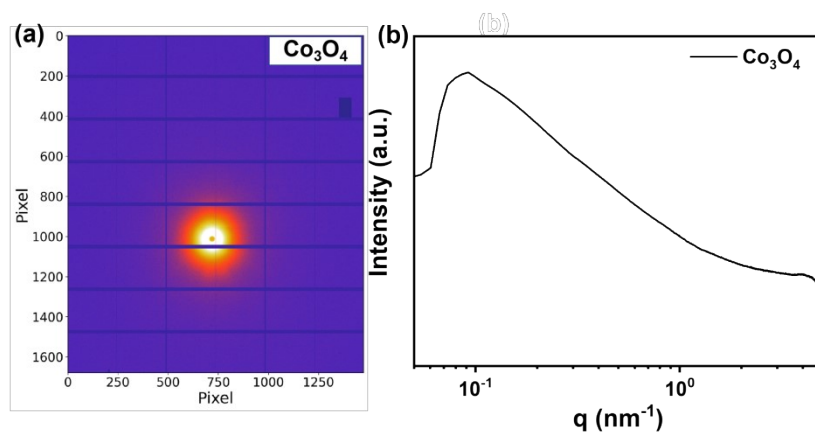


Figure S10. X-Ray scattering curves in the SAXS region of Co_3O_4 (a) 2D profile, (b) 1D curve.

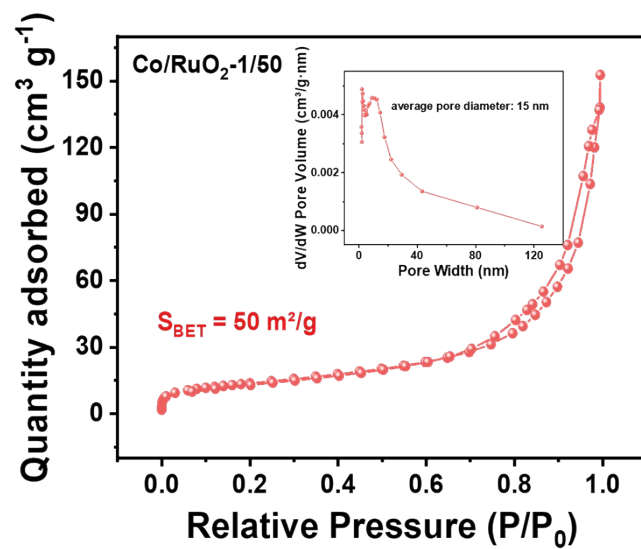


Figure S11. Nitrogen adsorption-desorption isotherms (inset: the pore diameter distribution curve) of $\text{Co/RuO}_2\text{-1/50}$.

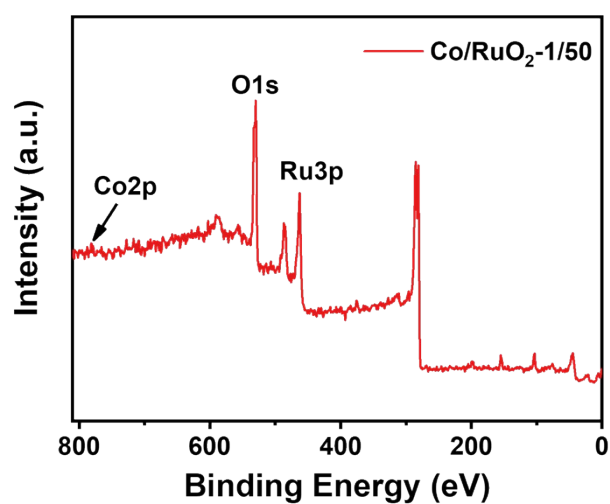


Figure S12. The XPS survey spectrum of Co/RuO₂-1/50.

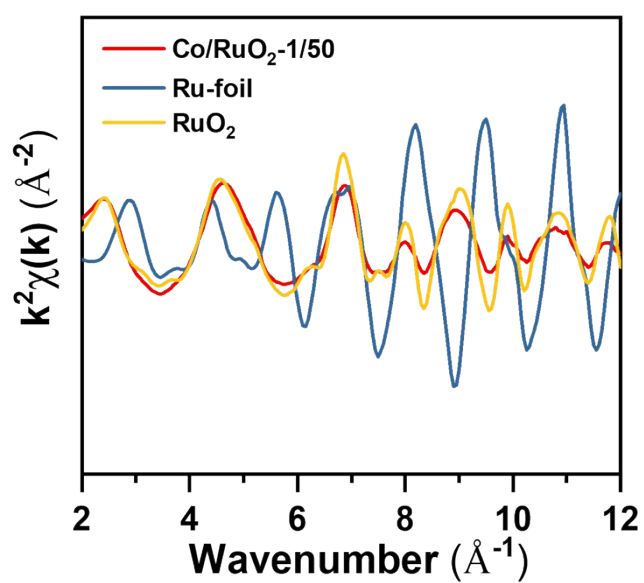


Figure S13. Ru K-edge EXAFS oscillations for Co/RuO₂-1/50, RuO₂ and Ru foil.

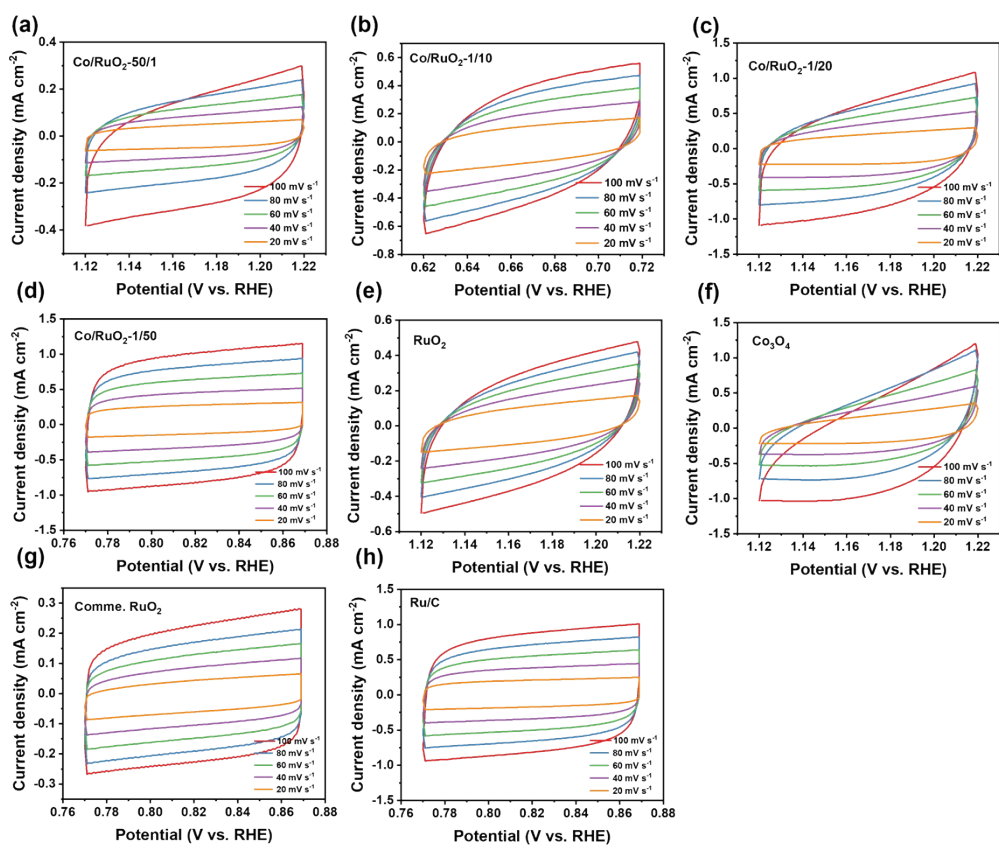


Figure S14. CVs of (a) Co/RuO₂-50/1, (a) Co/RuO₂-1/10, (b) Co/RuO₂-1/20, (c) Co/RuO₂-1/50, (d) RuO₂, (e) Co₃O₄, (f) commercial RuO₂, and (a) Ru/C at varied scan rates (20, 40, 60, 80, 100 mV s⁻¹).

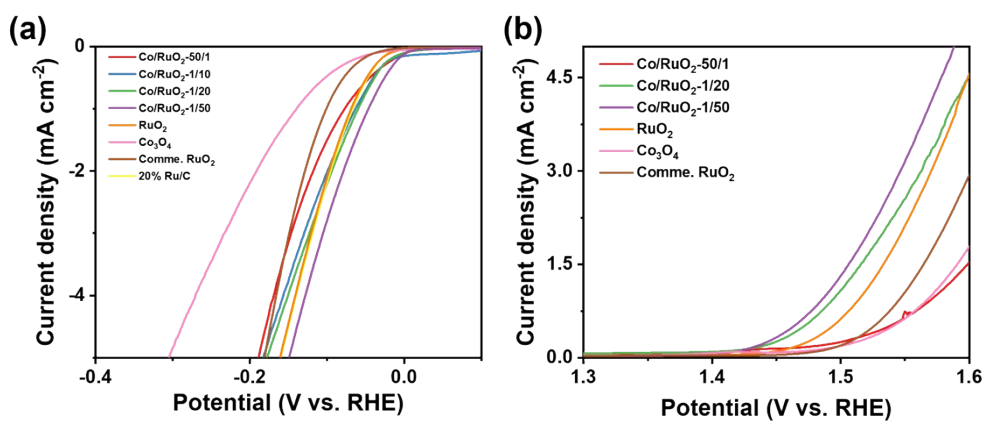


Figure S15. ECSA-normalized LSV curves of samples in 1 M KOH. (a)HER, (b) OER.

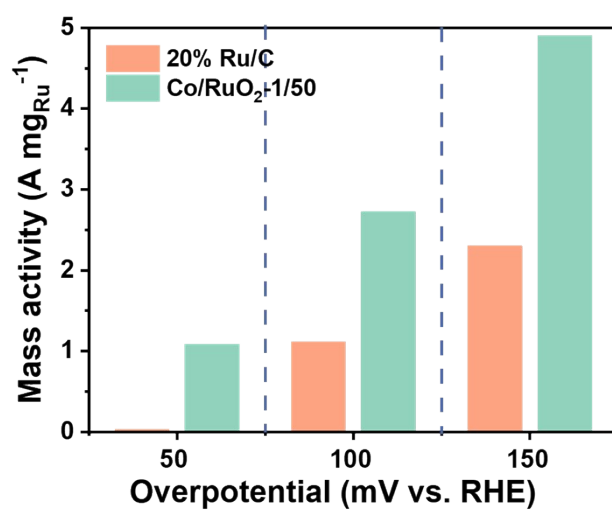


Figure S16. The mass activities of Ru element for Co/RuO₂-1/50 and 20% Ru/C toward HER process.

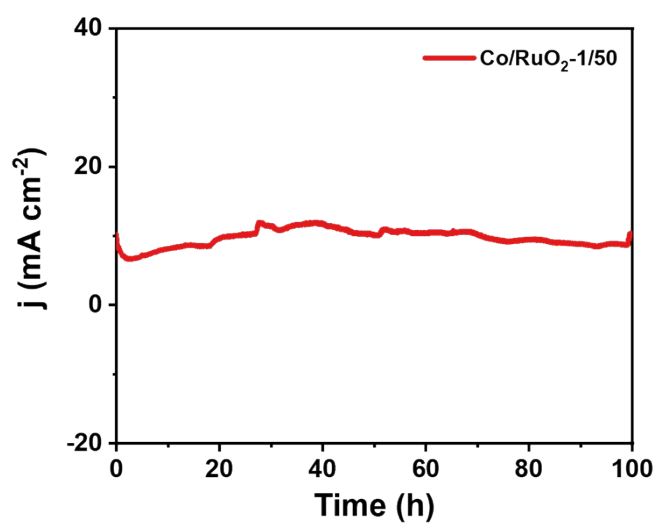


Figure S17. I-t curve for Co/RuO₂-1/50 at 10 mA cm⁻¹ in 1 M KOH.

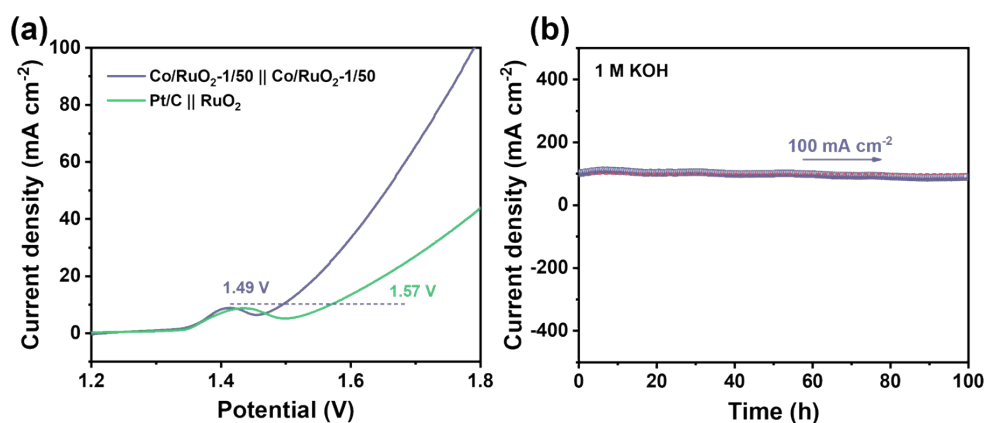


Figure S18. (a) LSV curves of water electrolysis in alkaline environment. (b) i-t stability test curve of water electrolysis in alkaline environment.

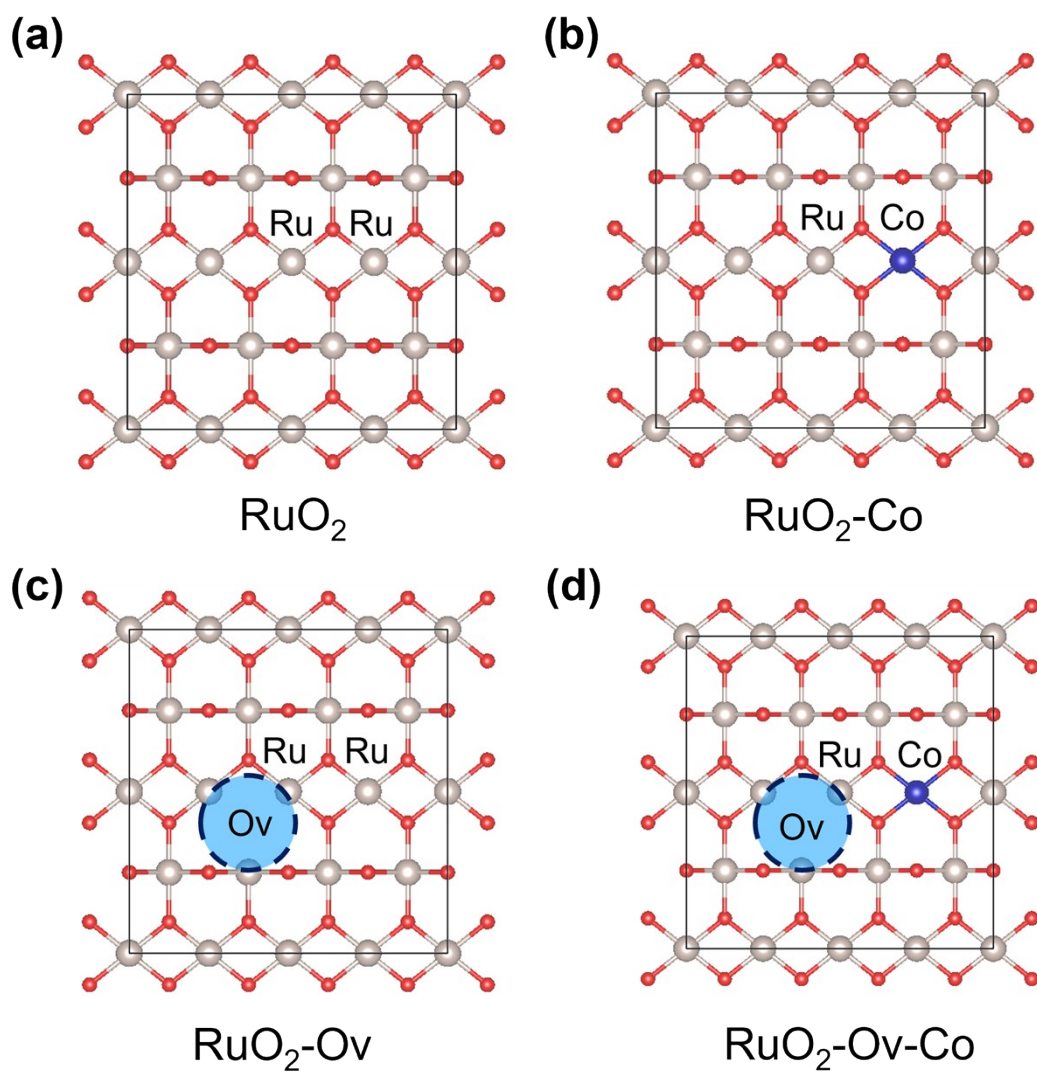


Figure S19. Schematic diagram of the model structure.

Table S1. EXAFS fitting parameters at the Ru K-edge for various samples.

Sample	Shell	CN ^a	R(Å) ^b	$\sigma^2(\text{\AA}^2)^c$	ΔE_0 (eV) ^d	K-range /Å ⁻¹	R-range /Å	R factor
Ru foil	Ru-Ru	12*	2.68	0.0039	-4.7	4.0-13.0	1.0-3.0	0.0048
	Ru-O	6.0	1.97	0.0013	-0.4			
RuO ₂	Ru-Ru	9.1	3.14	0.0089	-3.7	2.2-12.0	1.0-3.8	0.0105
	Ru-Ru	5.1	3.59	0.0006	5.3			
	Ru-O	5.6	1.98	0.0035	-0.3			
Co/RuO ₂ -1/50	Ru-O-Co	0.7	3.00					
				0.0129	-3.8	2.2-12.0	1.0-3.8	0.0062
	Ru-Ru	8.3	3.13					
	Ru-Ru	2.4	3.58	0.0018	3.3			

^aCN, coordination number; ^bR, the distance to the neighboring atom; ^c σ^2 , Debye-Waller factor, the Mean Square Relative Displacement (MSRD); ^d ΔE_0 , inner potential correction; R factor indicates the goodness of the fit. S02 was fixed to 0.853, according to the experimental EXAFS fit of Ru foil by fixing CN as the known crystallographic value. * This value was fixed during EXAFS fitting, based on the known structure of Ru. Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as $CN \pm 20\%$; $R \pm 1\%$; $\sigma^2 \pm 20\%$; $\Delta E_0 \pm 20\%$. A reasonable range of EXAFS fitting parameters: $0.700 < S02 < 1.000$; $CN > 0$; $\sigma^2 > 0 \text{ \AA}^2$; $|\Delta E_0| < 15 \text{ eV}$; $R \text{ factor} < 0.02$.

Table S2. Comparison of HER performance in 1M KOH of Co/RuO₂-1/50 with previously reported RuCo-based catalysts. (η_{10} : Overpotential at 10 mA cm⁻², mV. b: Tafel slope, mV dec⁻¹)

Catalysts	η	b	Reference
Co/RuO ₂ -1/50	26	54	This work
Co-SAC/RuO ₂	45	58	1
RuO ₂ @Co ₃ O ₄	90	103	2
Ru/Co ₃ O ₄ NWs	31	70	3
Ru/Co(OH) ₂ NWAs	96	68	4
Ru@RuO ₂	137	113	5

Table S3. The actual Ru amount of Co/RuO₂-1/50 by ICP-MS.

Metal	Wt%
Ru	60.7
Co	1.3

Table S4. Comparison of OER performance in 1M KOH of Co/RuO₂-1/50 with previously reported Ru-based catalysts. (E: Potential at 10 mA cm⁻², V. b: Tafel slope, mV dec⁻¹)

Catalysts	E	b	Reference
Co/RuO ₂ -1/50	1.47	88.0	This work
IW-Co ₃ O ₄ -RuO ₂ -HS	1.48	55.4	6
1-RuO ₂ /CeO ₂	1.58	74.0	7
Ru@RuO ₂	1.55	86.0	8
Ru-RuP _x -Co _x P	1.52	85.4	9

CoCrRu LDHs	1.51	56.1	10
Ru@g-CN _x	1.51	49.5	11
Ru/FeCo	1.51	82.8	12
NiCo _{1.7} Ru _{0.3} O ₄	1.51	78.0	13

Table S5. Calculated Gibbs free energies (G) of adsorption species for HER on different catalysts' surfaces (in eV).

	RuO ₂	RuO ₂ -Co	RuO ₂ -Ov	RuO ₂ - Ov-Co
*H ₂ O	-0.61	-0.637	-0.527	-0.503
*H+*OH	0.361	0.114	-0.014	-0.357
*H	0.438	0.184	0.42	0.165

Table S6. The correction of zero-point energy (ZPE) of adsorption species on different catalysts' surfaces (in eV). All the slab atoms were fixed during the vibrational analyses. (T = 298.15 K)

	RuO ₂	RuO ₂ -Co	RuO ₂ -Ov	RuO ₂ - Ov-Co
*H ₂ O	0.65	0.63	0.66	0.64
*H+*OH	0.54	0.51	0.53	0.53
*H	0.17	0.18	0.17	0.16

Table S7. The correction of entropy (TS) of adsorption species on different catalysts' surfaces (in eV). All the slab atoms were fixed during the vibrational analyses. (T = 298.15 K)

	RuO ₂	RuO ₂ -Co	RuO ₂ -Ov	RuO ₂ - Ov-Co
*H ₂ O	0.16	0.15	0.15	0.16

*H+*OH	0.09	0.09	0.08	0.07
*H	0	0	0	0

Supplemental References

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