High-performance Co-doped RuO_2 nanoparticles for alkaline hydrogen evolution reaction

Zhe Liu [a ‡], Tao Zhou [a ‡], Jeonghoon Kim [a], Taekyung Yu [a *]

[a] Department of Chemical Engineering, College of Engineering, Integrated Engineering Major, Kyung Hee University, Yongin 17140, Korea

‡These authors contributed equally to this work.

* Correspondence: tkyu@khu.ac.kr (T.Y.)

1. DFT calculations

We performed density functional theory (DFT) computations using CP2K. The exchange–correlation interaction was evaluated using the Perdew–Burke–Ernzerhof (PBE) functional within the framework of the generalized gradient approximation (GGA). In this computational model, the plane wave basis set was specified with a kinetic energy cutoff of 400 eV. Geometry optimization was performed iteratively until energy change dropped below 10^{-5} eV and the forces on all atoms were less than 0.03 eV/Å.

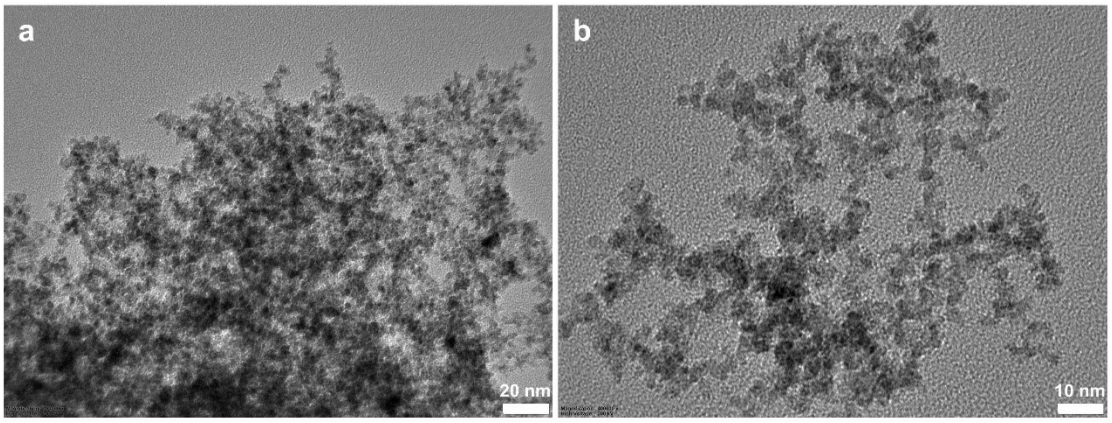

Figure S1. TEM images of the RuCo-2.

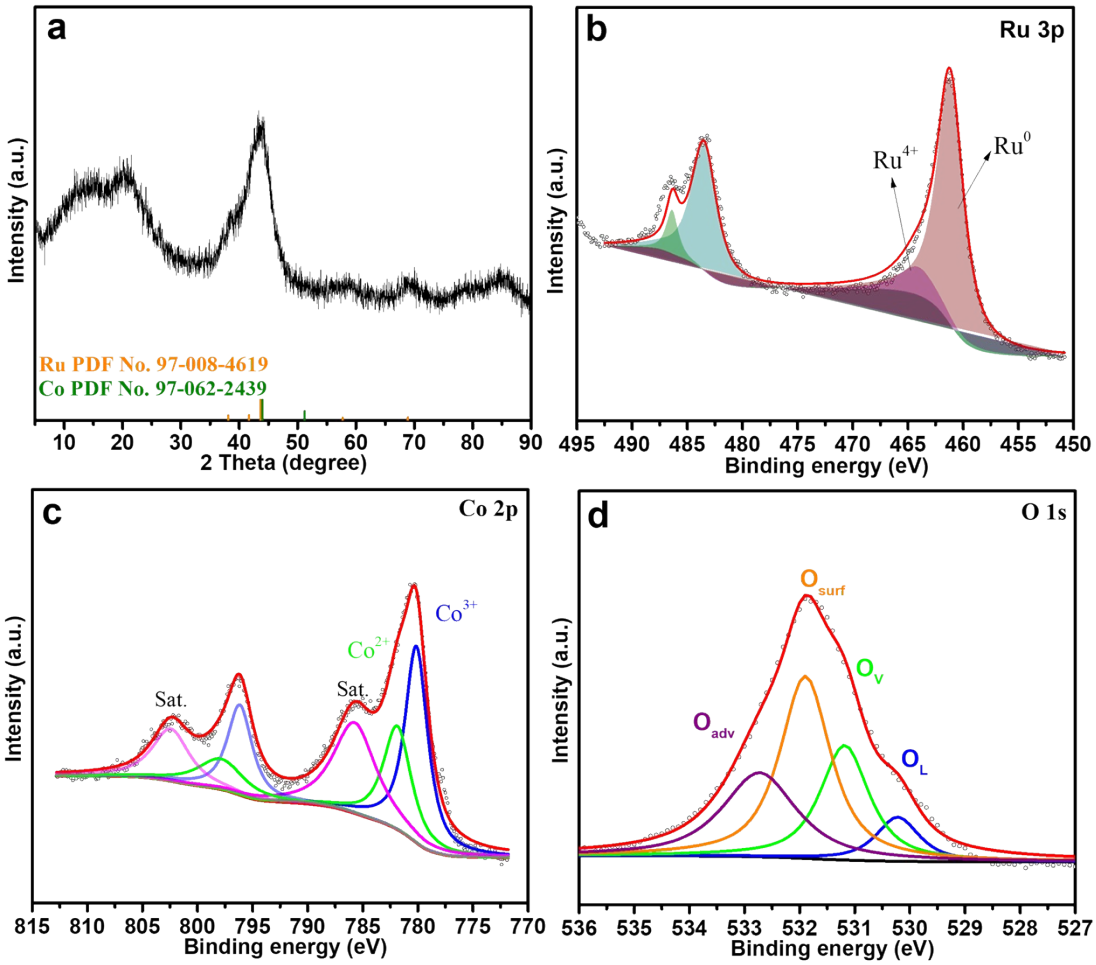

Figure S2. (a) XRD patterns of the RuCo-2. High-resolution XPS spectra of (b) Ru 3p, (c) Co 2p, (d) and O 1s of the RuCo-2.

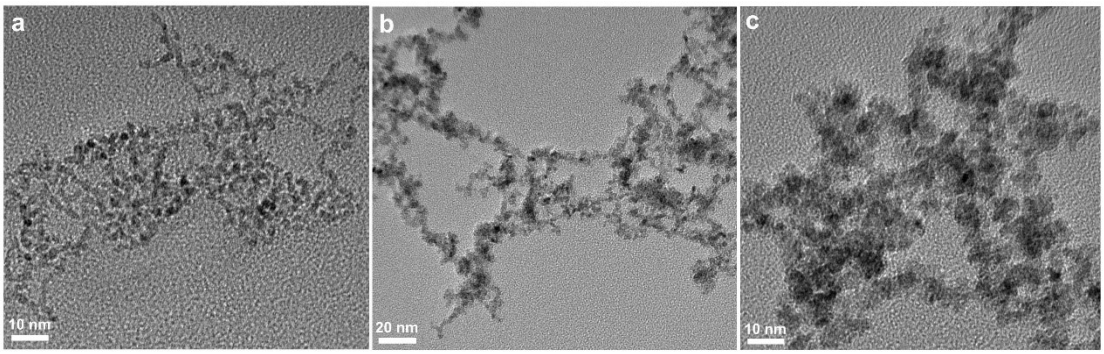

Figure S3. TEM images of (a) RuC precursor, (b) RuCo-1, and (c) RuCo-3.

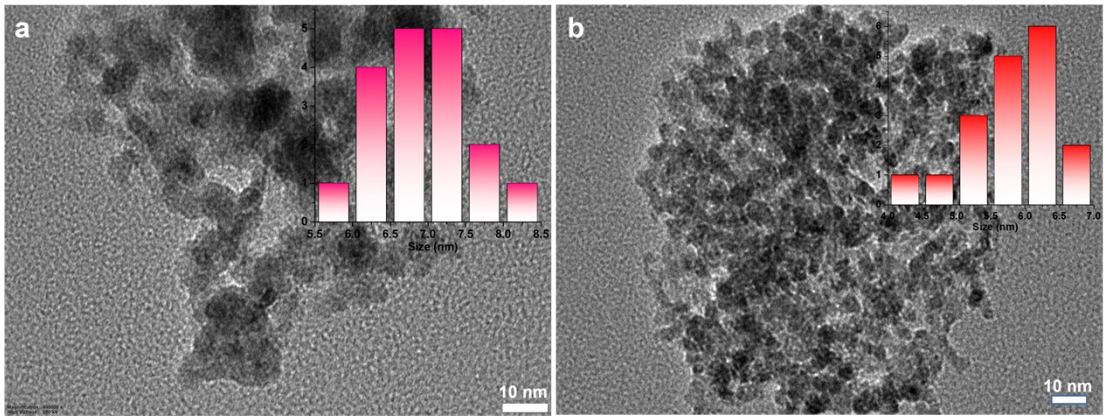

Figure S4. TEM images of (a) RuCoC-1 and (b) RuCoC-3. Size distributions of (c) RuCoC-1 and (d) RuCoC-3.

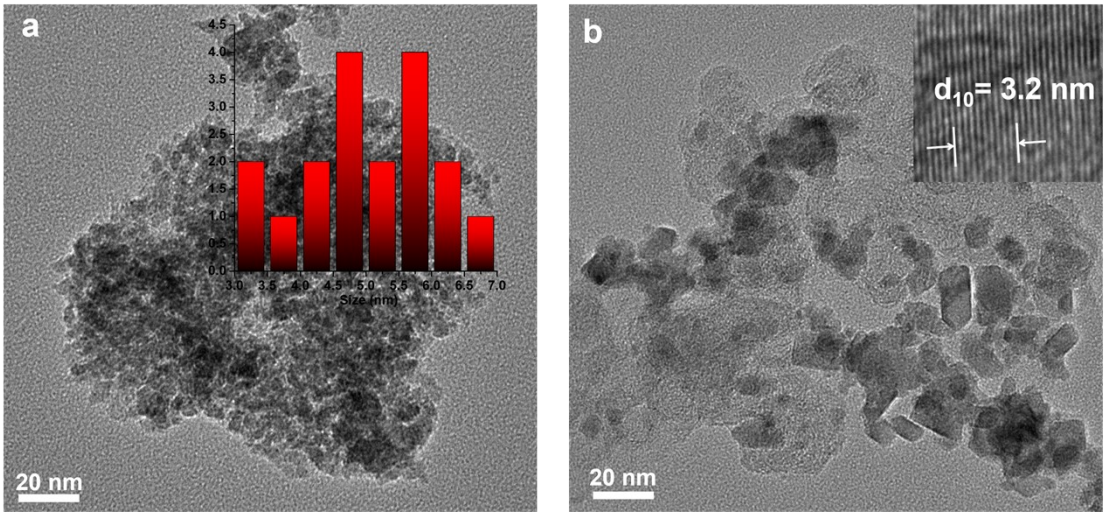

Figure S5. (a) TEM image and (b) size distribution of RuC.

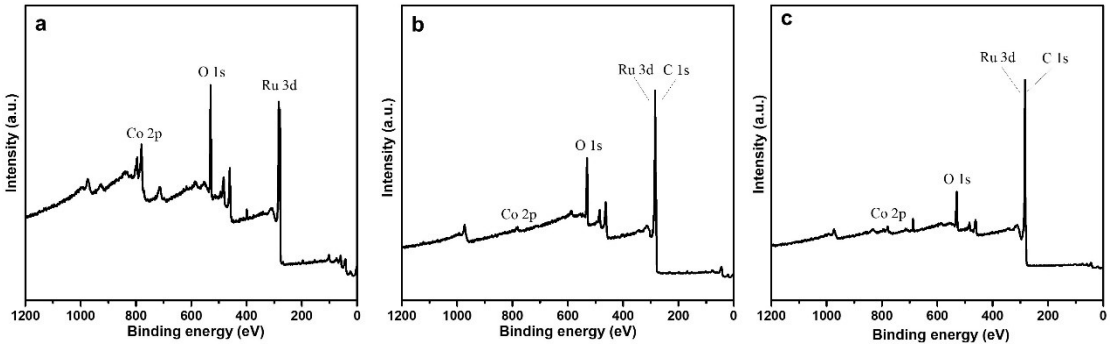

Figure S6. XPS full survey spectra of the (a) RuCo-2, (b) RuCoC-2, and (c) RuCoC-2 after HER stability test.

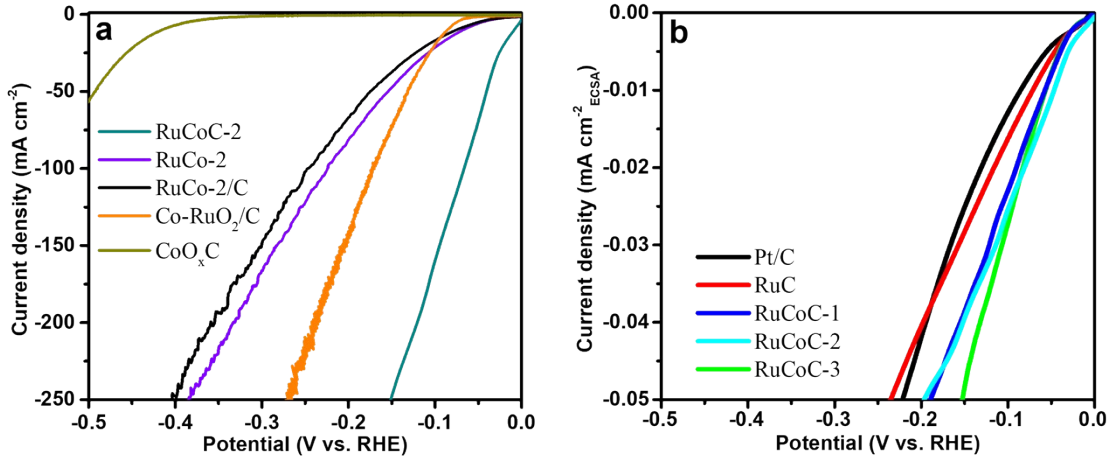

Figure S7. (a) LSV curves of the RuCoC-2 and control samples in 1 M KOH. (b) LSV curves of all samples normalized by ECSA.

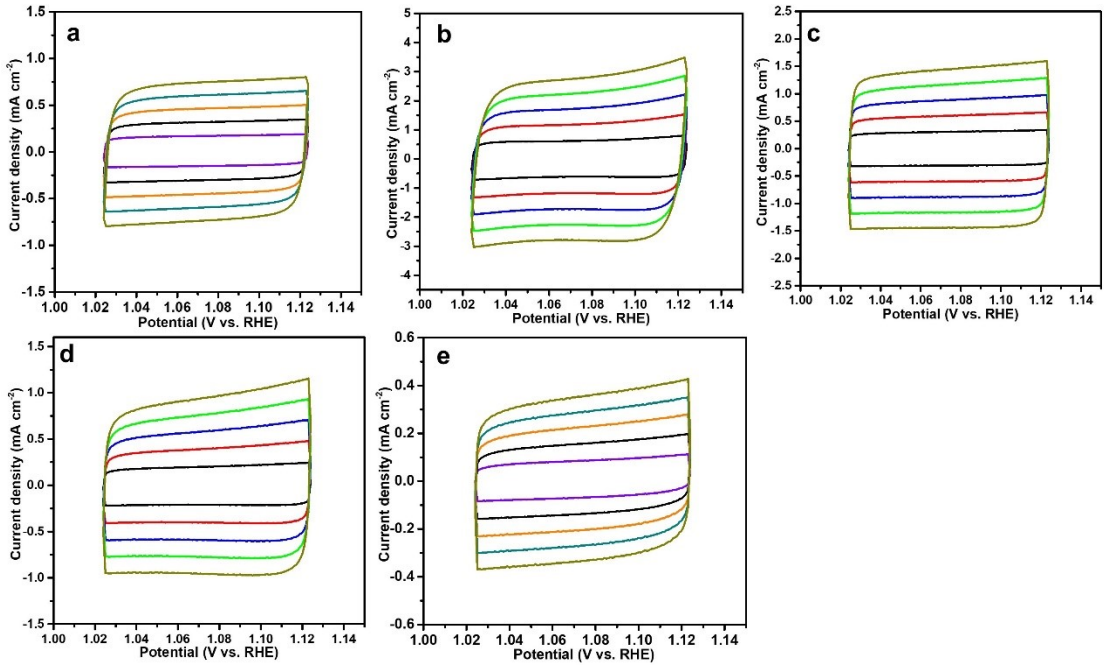

Figure S8. Typical CV curves obtained at scan rates of 20, 40, 60, 80, and 100 mVs^{-1} of (a) RuC, (b) RuCoC-2, (c) RuCoC-1, (d) RuCoC-3, and (e) Pt/C.

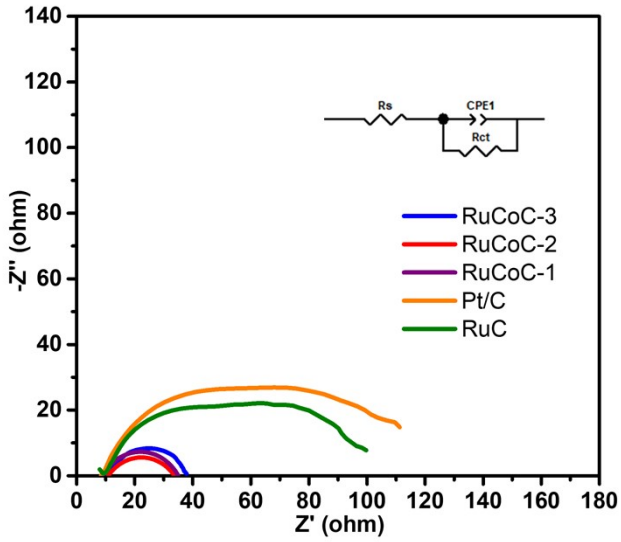

Figure S9. EIS of all samples at an applied potential of –0.025 V (vs. RHE) in 1 M KOH.

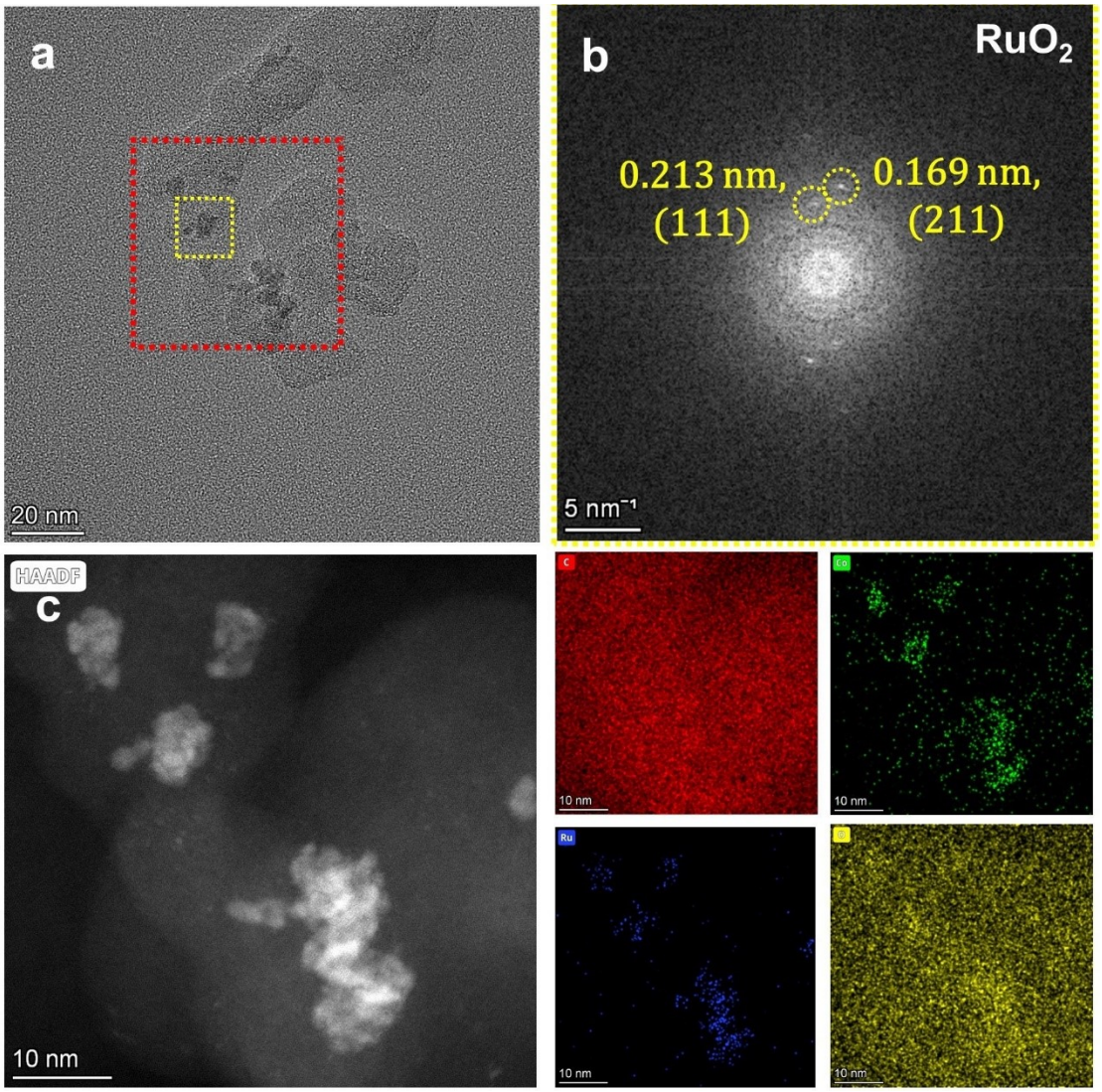

Figure S10. (a) TEM image of the RuCoC-2 after HER, (b) FFT pattern from the selected area (yellow square in Fig. S7a) and (c) HAADF-STEM images and elements mapping of the RuCoC-2 after HER (red square in Fig. S7a).

Table S1. Area ratio between deconvoluted Co^{3+} and Co^{2+} peaks in the Ru $3p_{3/2}$ XPS spectra of different catalysts.

Sample name	RuCoC-3	RuCoC-2	RuCoC-1
Co^{3+}: Co^{2+}	1:1.36	1:1.44	1:2.08

Table S2. Area percentages of the deconvoluted O 1s peaks in the XPS spectra from different catalysts.

Sample name	O_L (%)	O_V (%)	O_{surf} (%)	O_{adv} (%)
RuCoC-1	17.2	25.5	36.5	20.8
RuCoC-2	19.9	22.3	34.5	23.3
RuCoC-3	22.7	28.1	32.3	16.9
RuC	17.3	20.3	34.9	27.5

Table S3. ECSA values of all the samples calculated from C_{dl}.

	RuCoC-1	RuCoC-2	RuCoC-3	RuC	Pt/C
ECSA /cm^2	237.3	682.5	358.3	180.1	128.3

Table S4. Molar ratio of Ru and Co determined by ICP-OES in the RuCo-1, RuCo-2, and RuCo-3.

Sample name	ICP Ru: Co (molar ratio)
RuCo-1	3.4: 1
RuCo-2	6.5: 1
RuCo-3	12.6: 1

Table S5. Molar ratio of Ru and Co in the RuCoC-1, RuCoC-2, and RuCoC-3 measured by ICP-OES, TEM-EDX, and XPS.

Sample name	ICP Ru: Co (molar ratio)	EDX Ru: Co (Atomic %)	XPS Ru: Co (Atomic %)
RuCoC-1	3.2: 1	75.9: 24.1	75.4: 24.6
RuCoC-2	6.7: 1	88.7: 11.3	86.4: 13.6
RuCoC-3	12.2: 1	92.2: 7.8	90.4: 9.6