

Supplementary Information

Heteroatom dopants overcome the activity-stability trade-off in RuO₂ for acidic oxygen evolution

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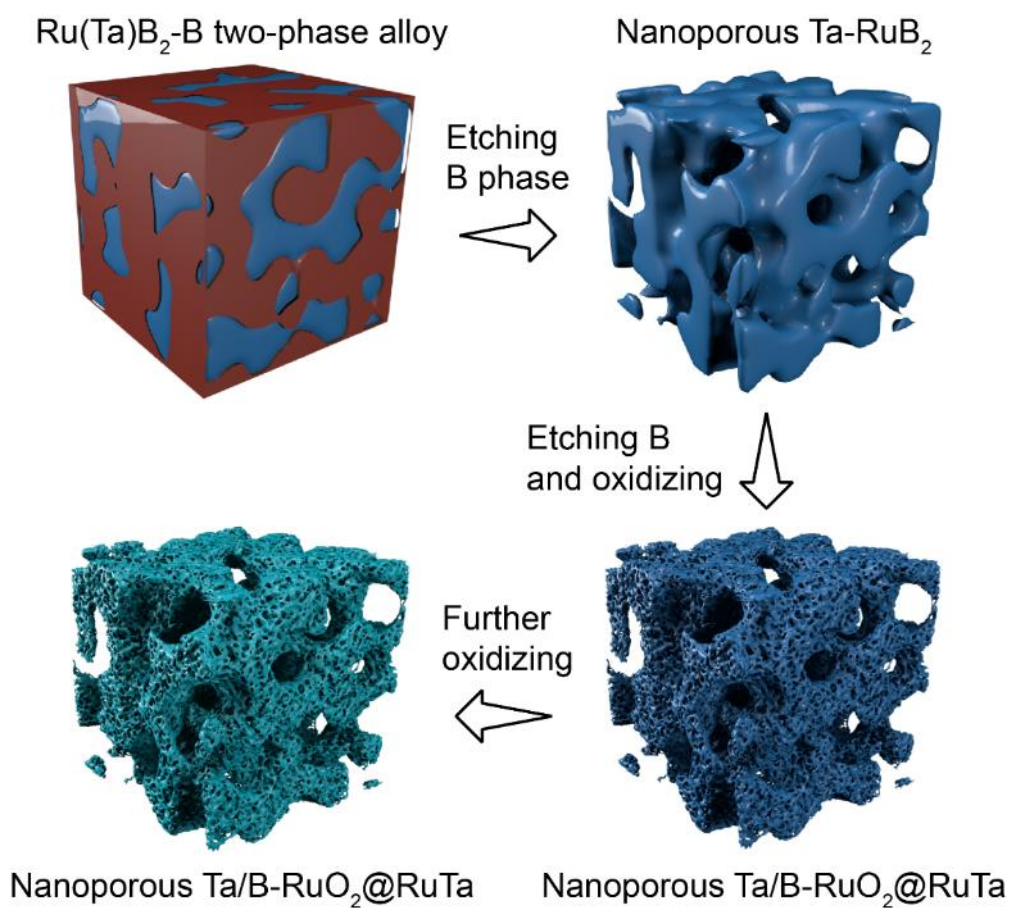
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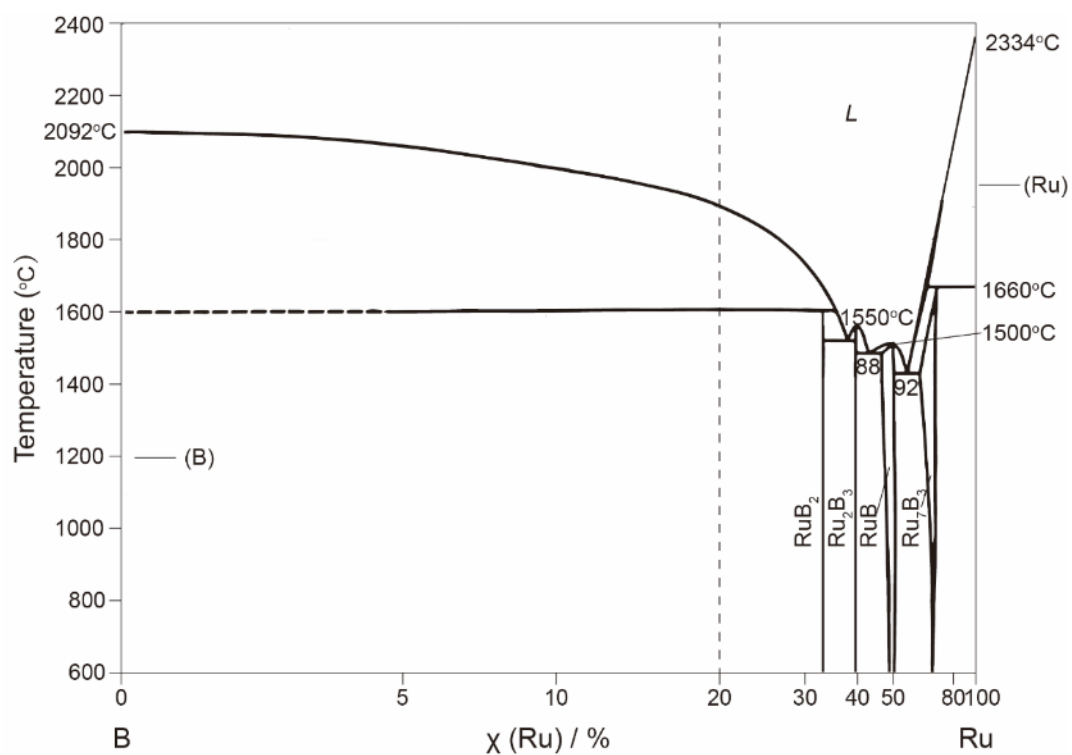
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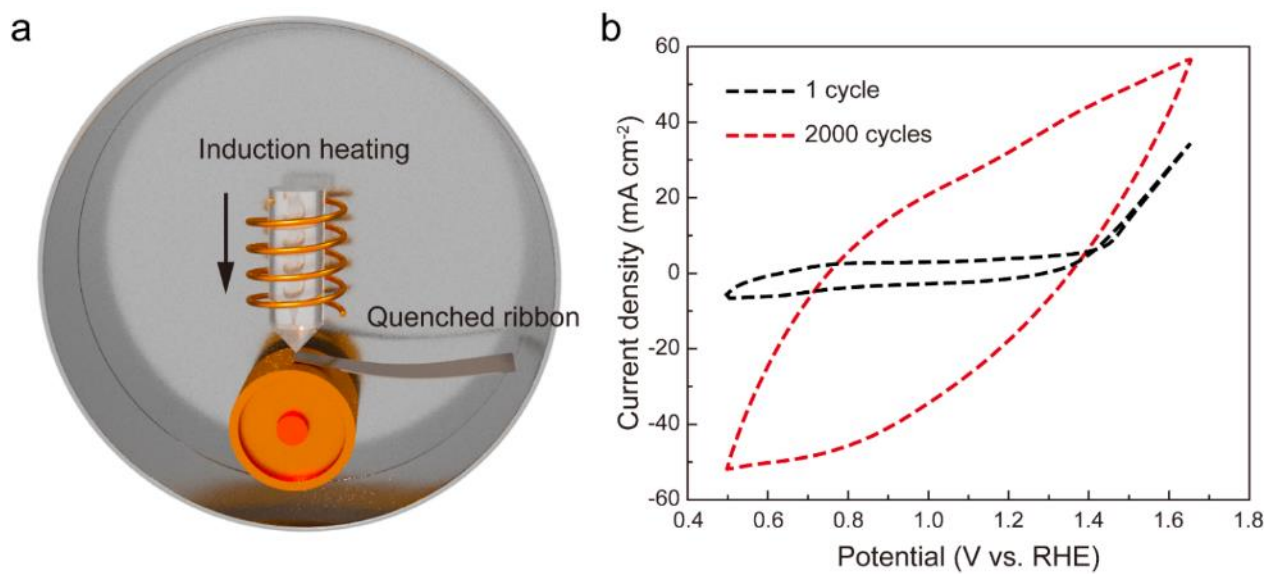
Supplementary Figures



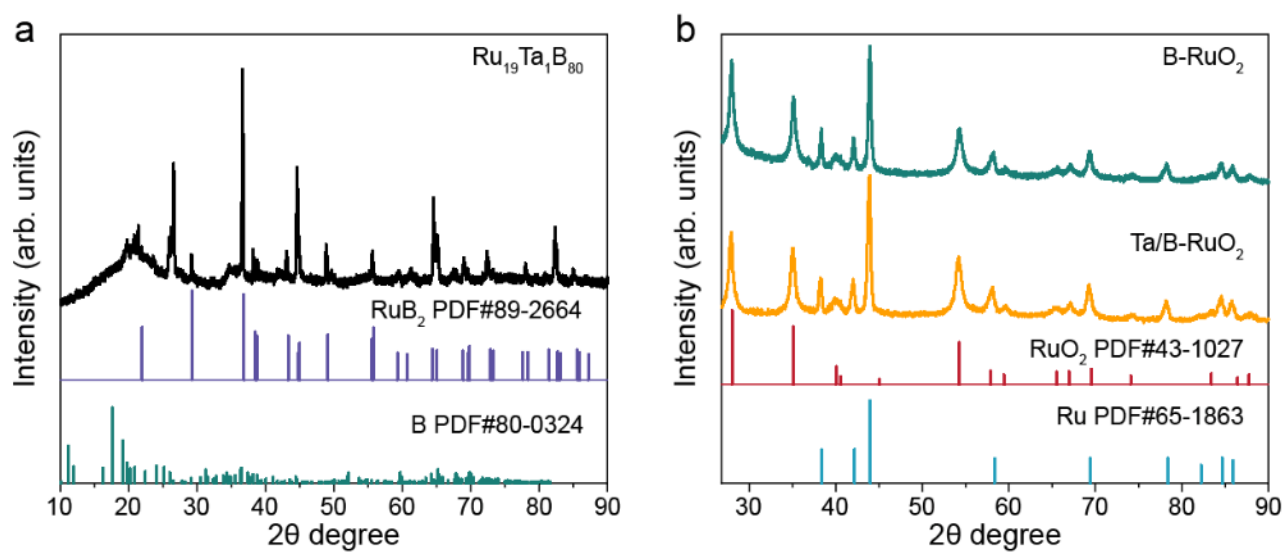
Supplementary Figure 1. Schematic illustration of synthesizing Ta/B-RuO₂ catalysts through melt spinning and selective electrochemical corrosion strategy.



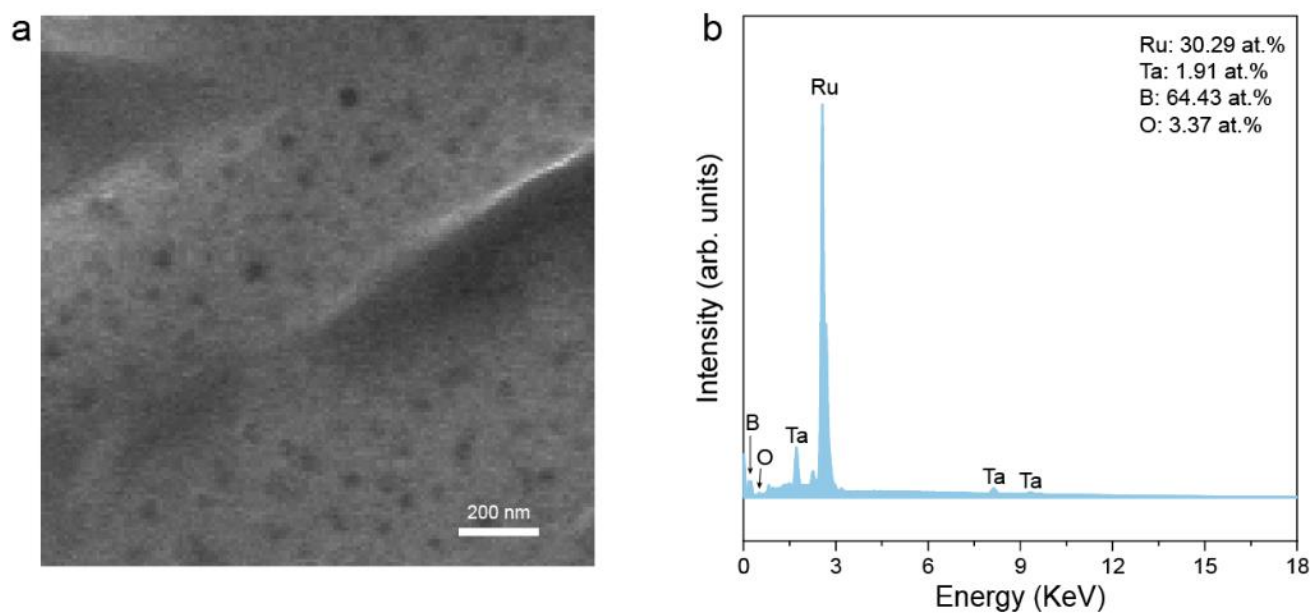
Supplementary Figure 2. The Ru-B phase diagram (**Ref. 1**).



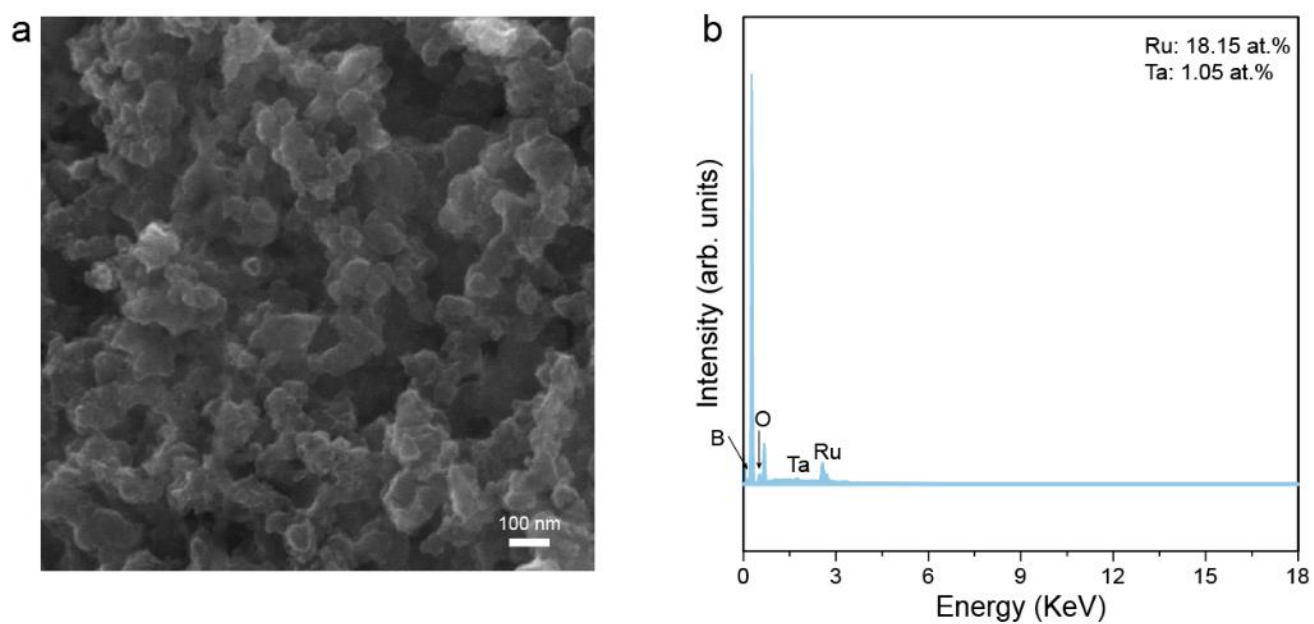
Supplementary Figure 3. (a) The melt-spinning system. (b) The CVs of dealloying by potential cycling between 0.5 V and 1.65 V vs. RHE in Ar purged 0.1 M HClO₄.



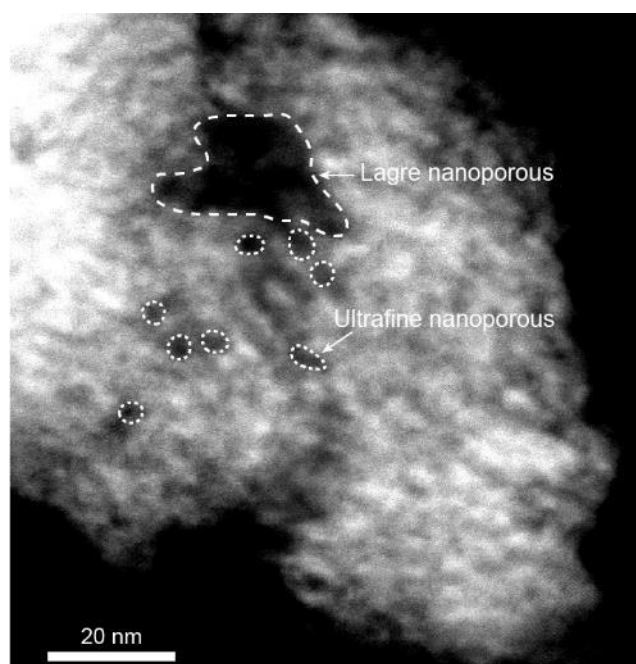
Supplementary Figure 4. (a) XRD patterns of $\text{Ru}_{19}\text{Ta}_1\text{B}_{80}$ ribbons. (b) XRD patterns of Ta/B-RuO_2 and B-RuO_2 .



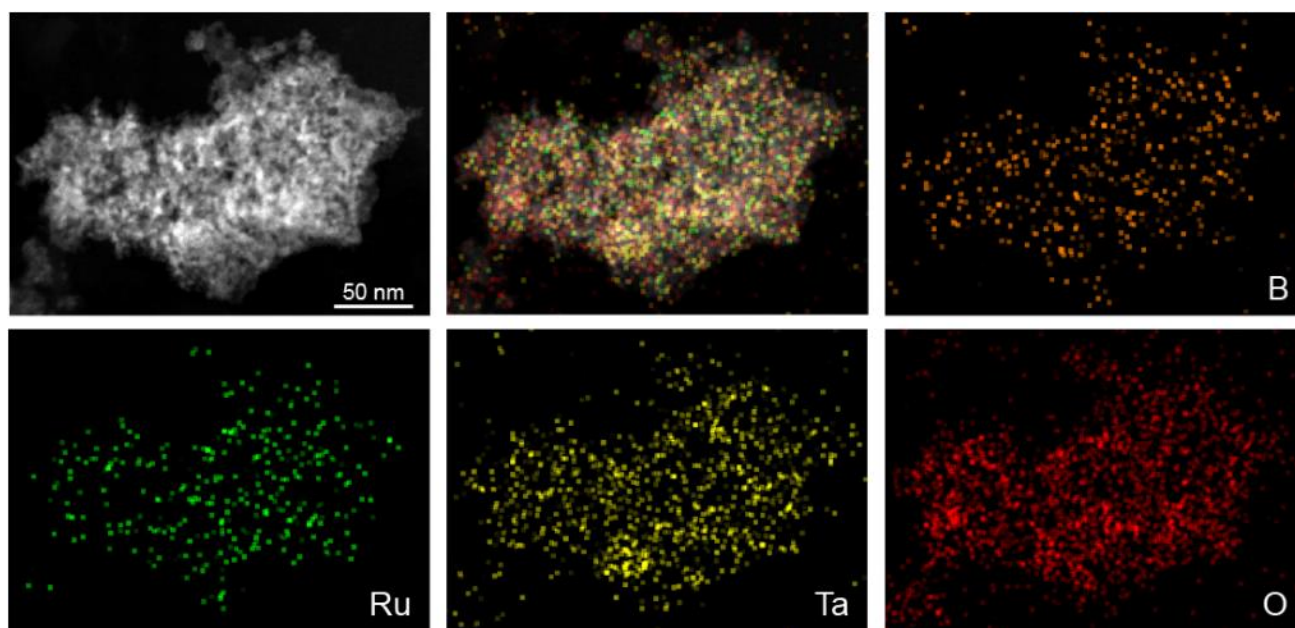
Supplementary Figure 5. (a) SEM image of Ta-RuB₂. (b) SEM-EDS spectrum of Ta-RuB₂.



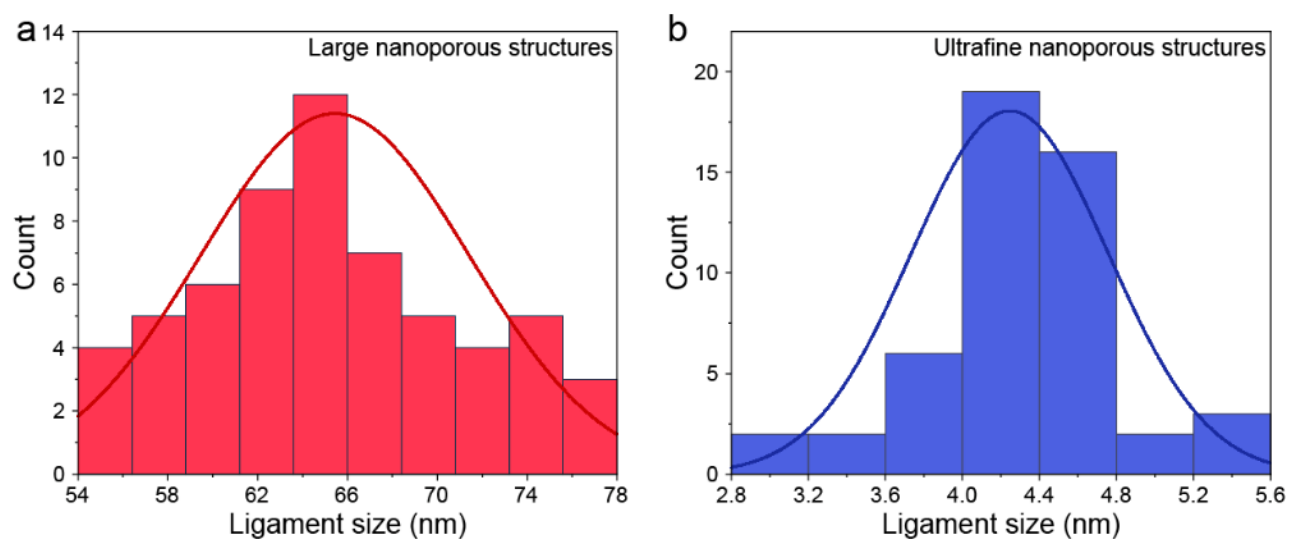
Supplementary Figure 6. (a) SEM image of Ta/B-RuO₂. (b) SEM-EDS spectrum of Ta/B-RuO₂.



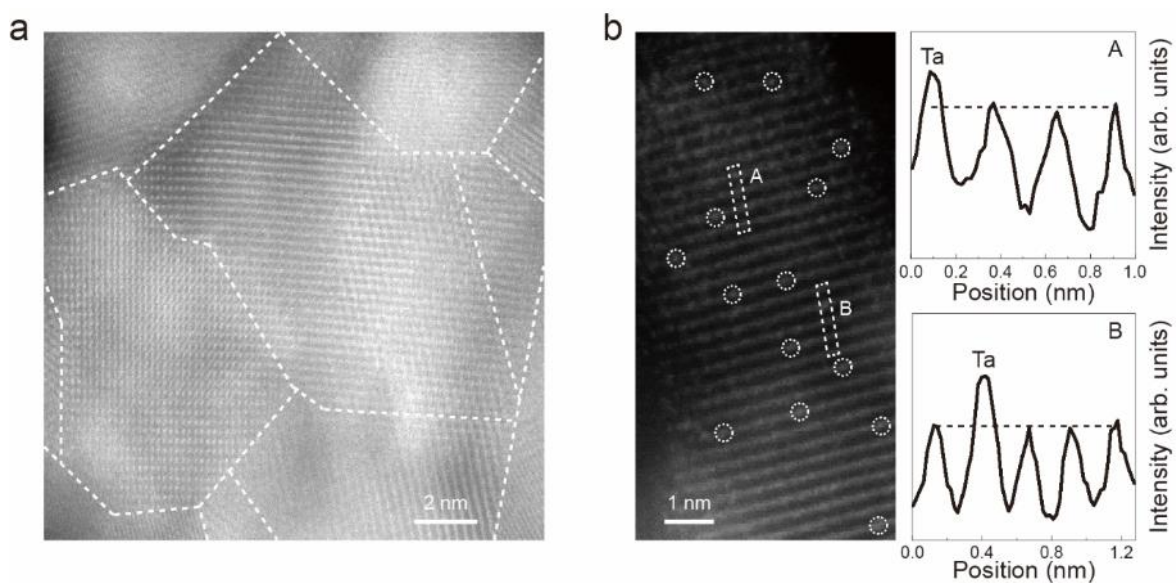
Supplementary Figure 7. HAADF-STEM image of Ta/B-RuO₂.



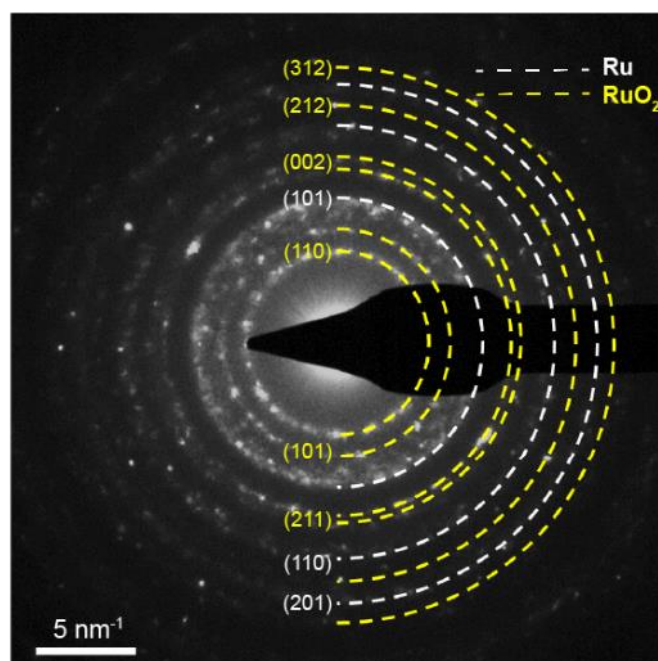
Supplementary Figure 8. STEM-EDX mappings of Ta/B-RuO₂.



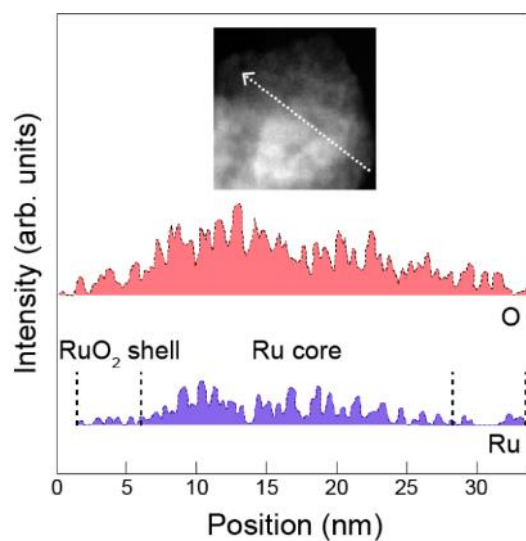
Supplementary Figure 9. (a) Ligament size distribution of large nanoporous structures derived from SEM images. (b) Ligament size distribution of ultrafine nanoporous structures derived from HAADF-STEM images.



Supplementary Figure 10. HAADF-STEM image (a) and corresponding line intensity profiles (b) of Ta/B-RuO₂.

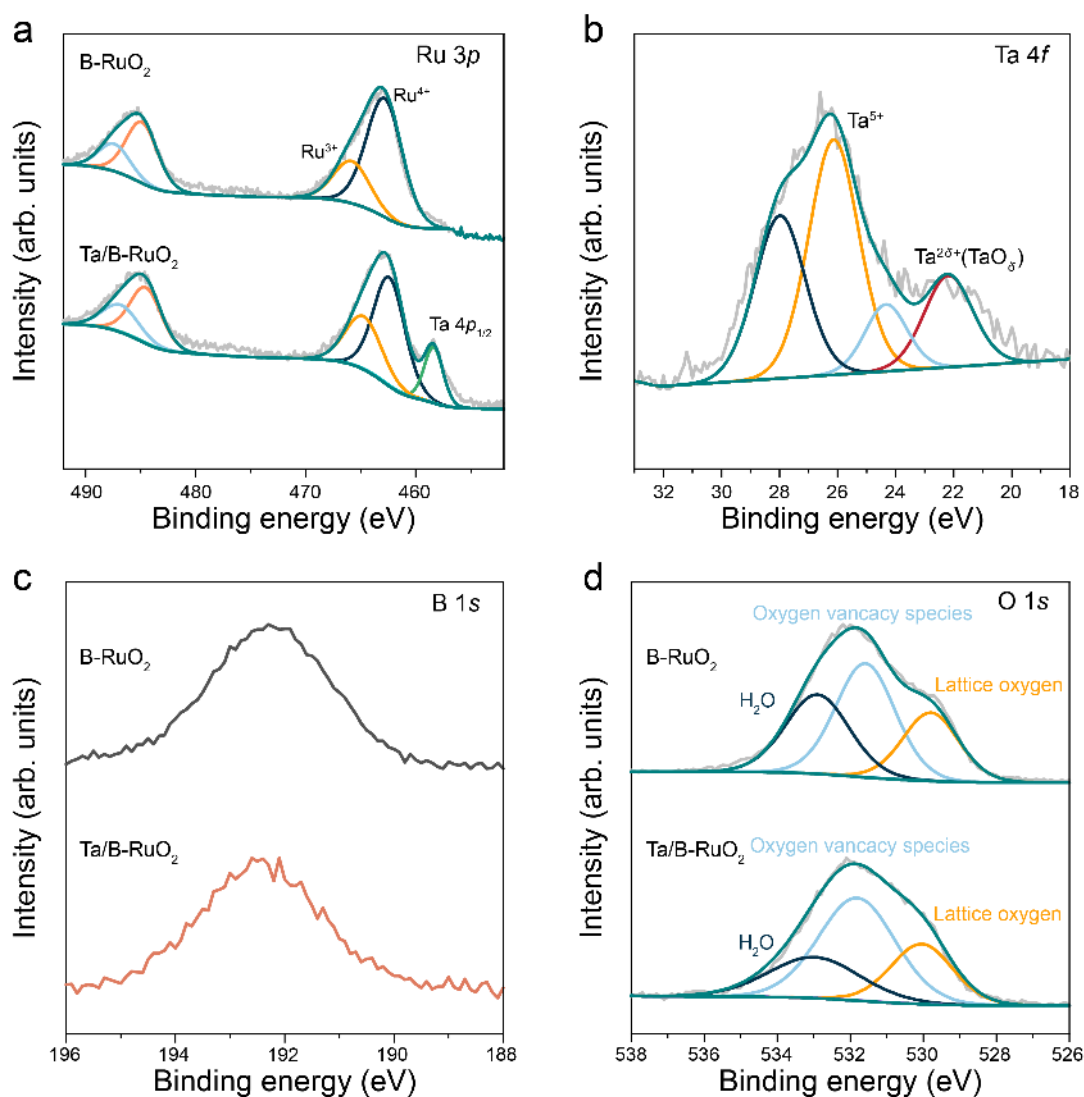


Supplementary Figure 11. SAED patterns for Ta/B-RuO₂.

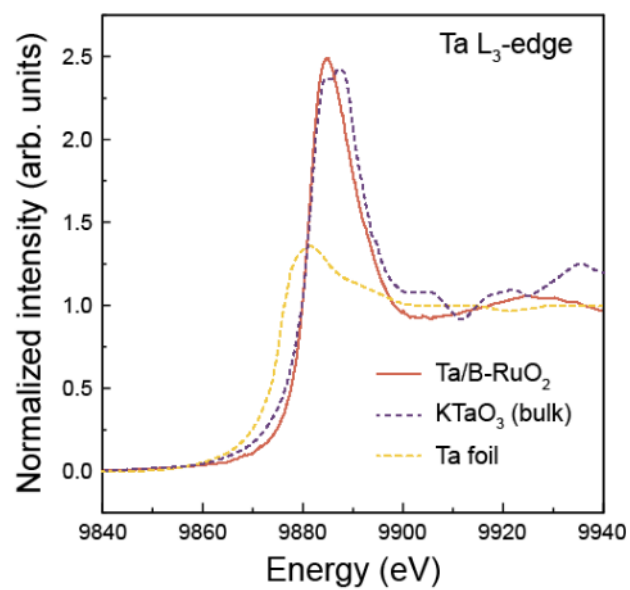


Supplementary Figure 12. STEM-EDX line profile across a ligament.

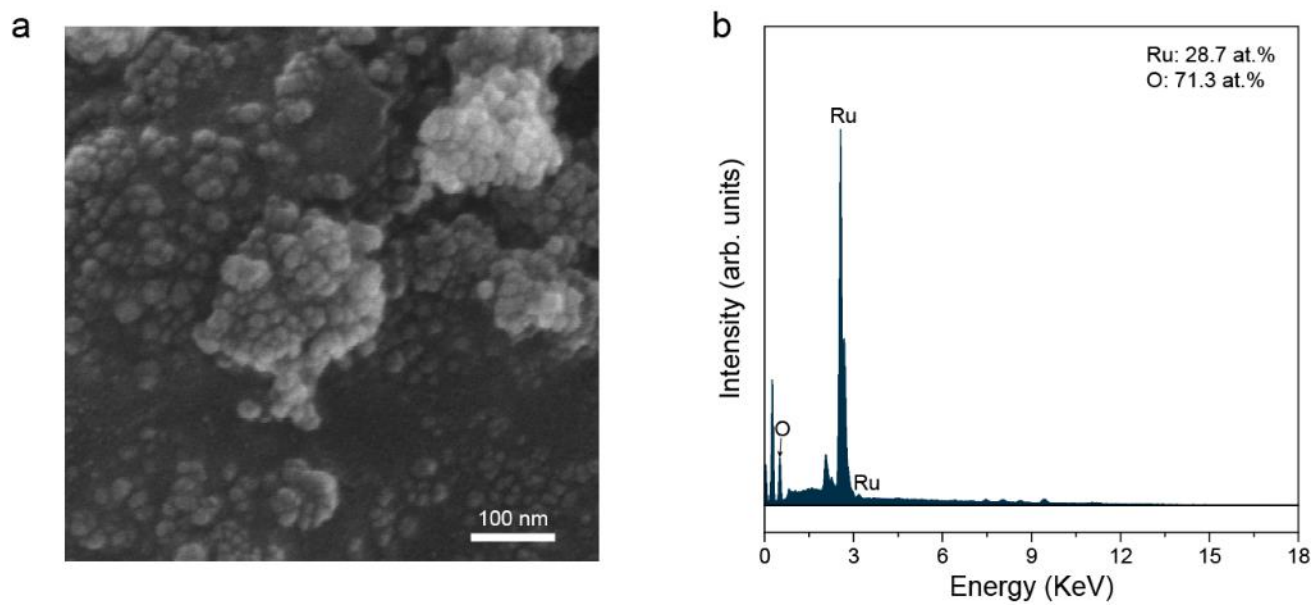
The surface oxide layer, with a thickness of approximately 5 nm, effectively suppresses the electronic coupling interactions between the internal alloy matrix and the surface-active sites. As a result, the internal alloy structure has a negligible impact on the catalytic activity of the surface oxide layer, thereby ensuring the catalytic properties of the surface layer are predominantly determined by its own characteristics (**Ref. 2**).



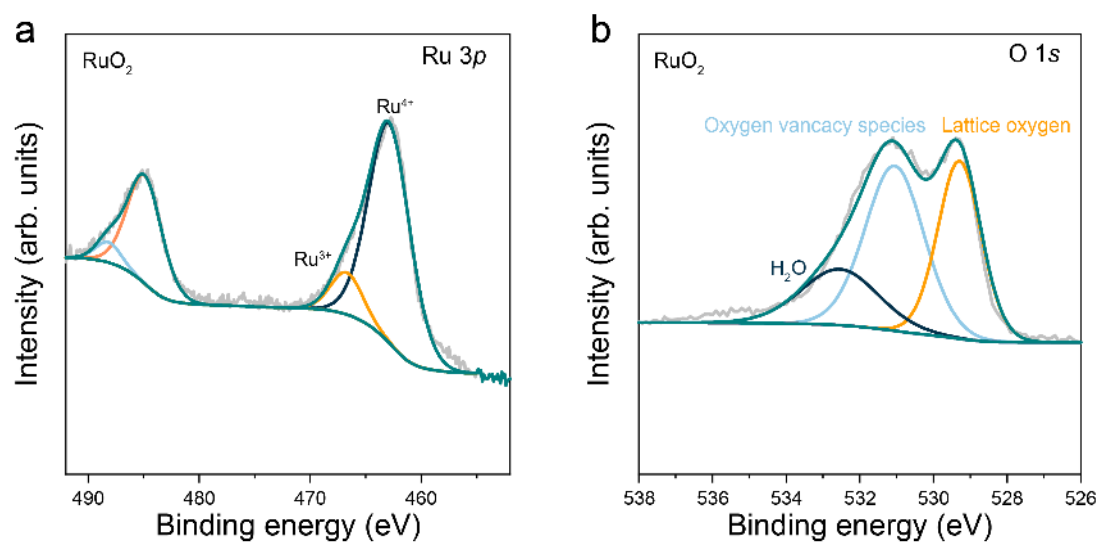
Supplementary Figure 13. High-resolution XPS spectra of Ta/B-RuO₂ and B-RuO₂ at (a) Ru 3p, (b) Ta 4f, (c) B 1s, and (d) O 1s.



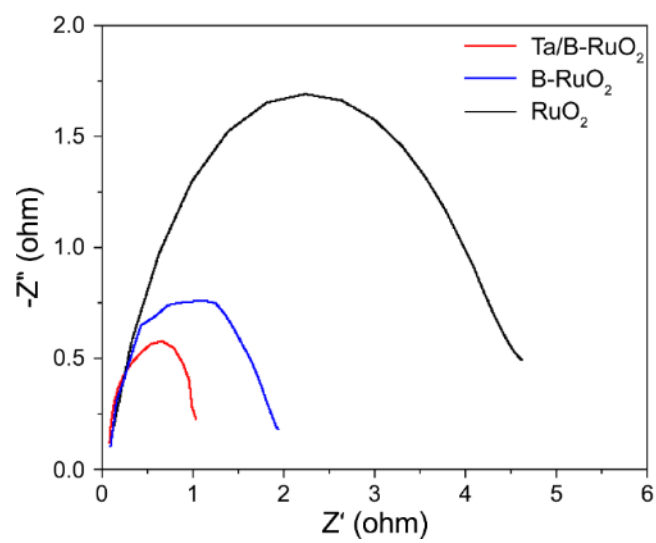
Supplementary Figure 14. Ta L₃-edge XANES spectra of Ta/B-RuO₂ and references (**Ref. 3**).



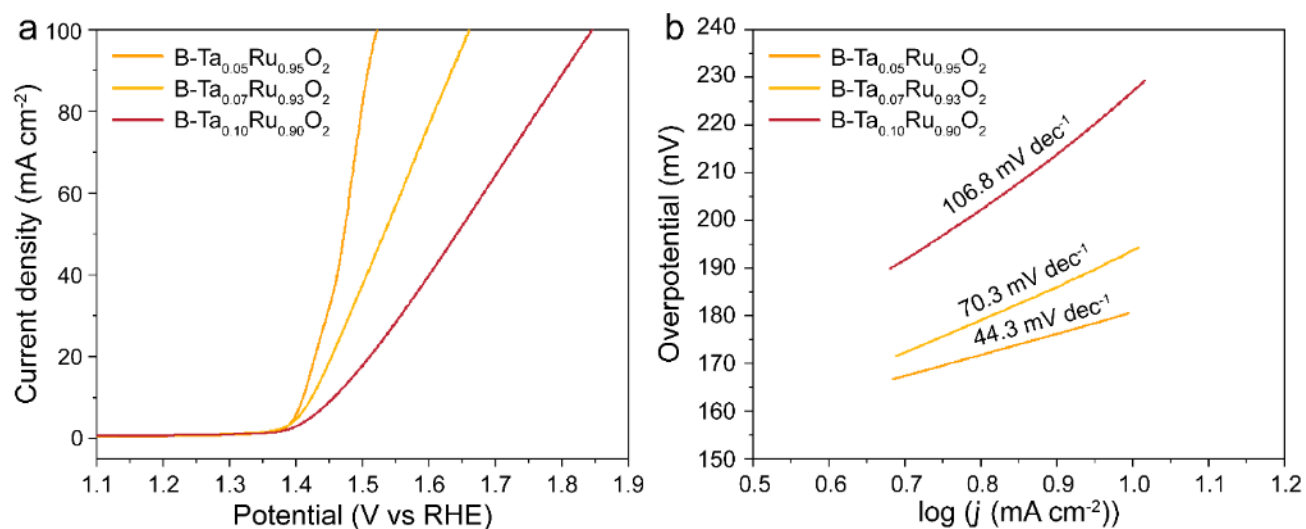
Supplementary Figure 15. (a) SEM image of RuO₂. (b) SEM-EDS spectrum of RuO₂.



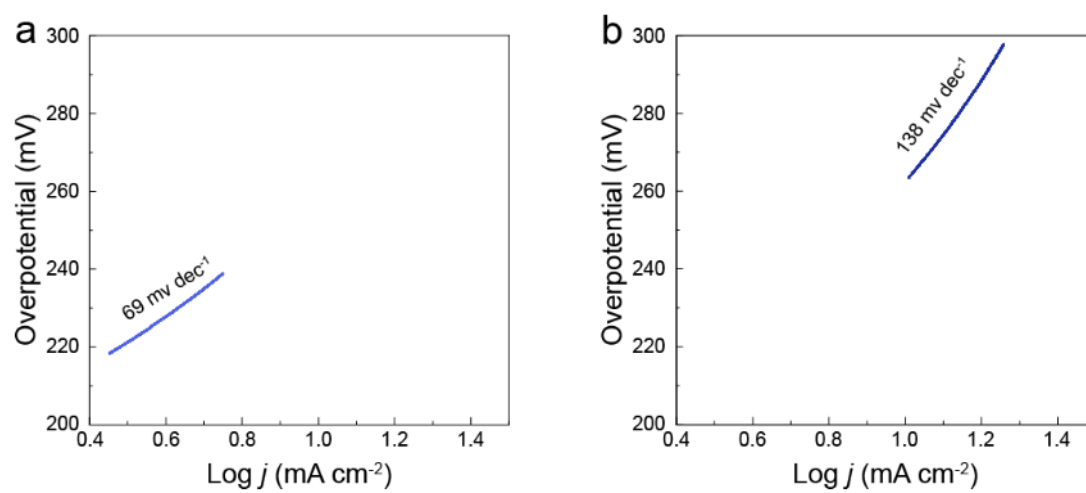
Supplementary Figure 16. High-resolution XPS spectra of RuO₂ at (a) Ru 3p and (b) O 1s.



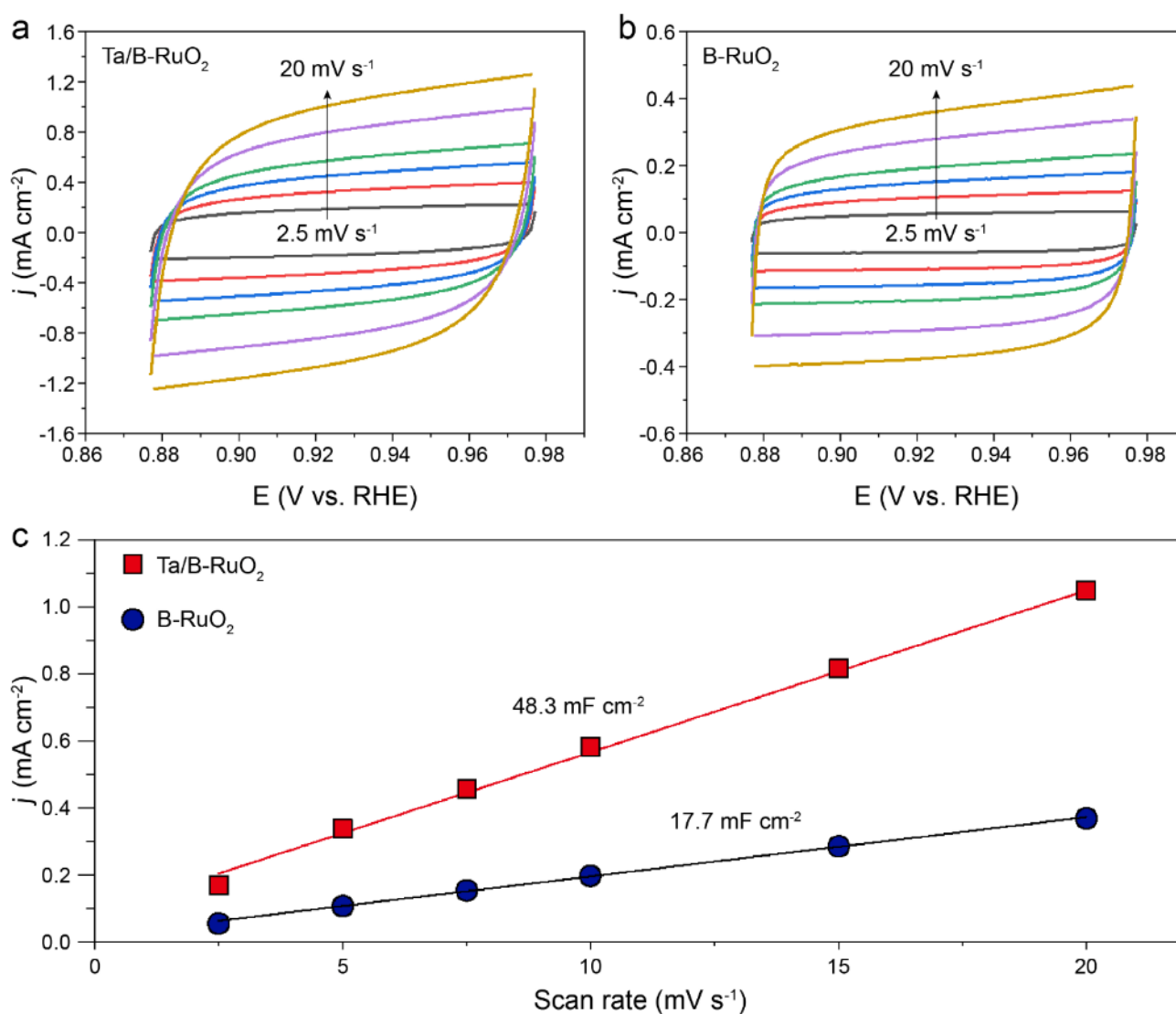
Supplementary Figure 17. Nyquist plots of Ta/B-RuO₂, B-RuO₂, and RuO₂ for the acid OER under 1.6 V vs. RHE.



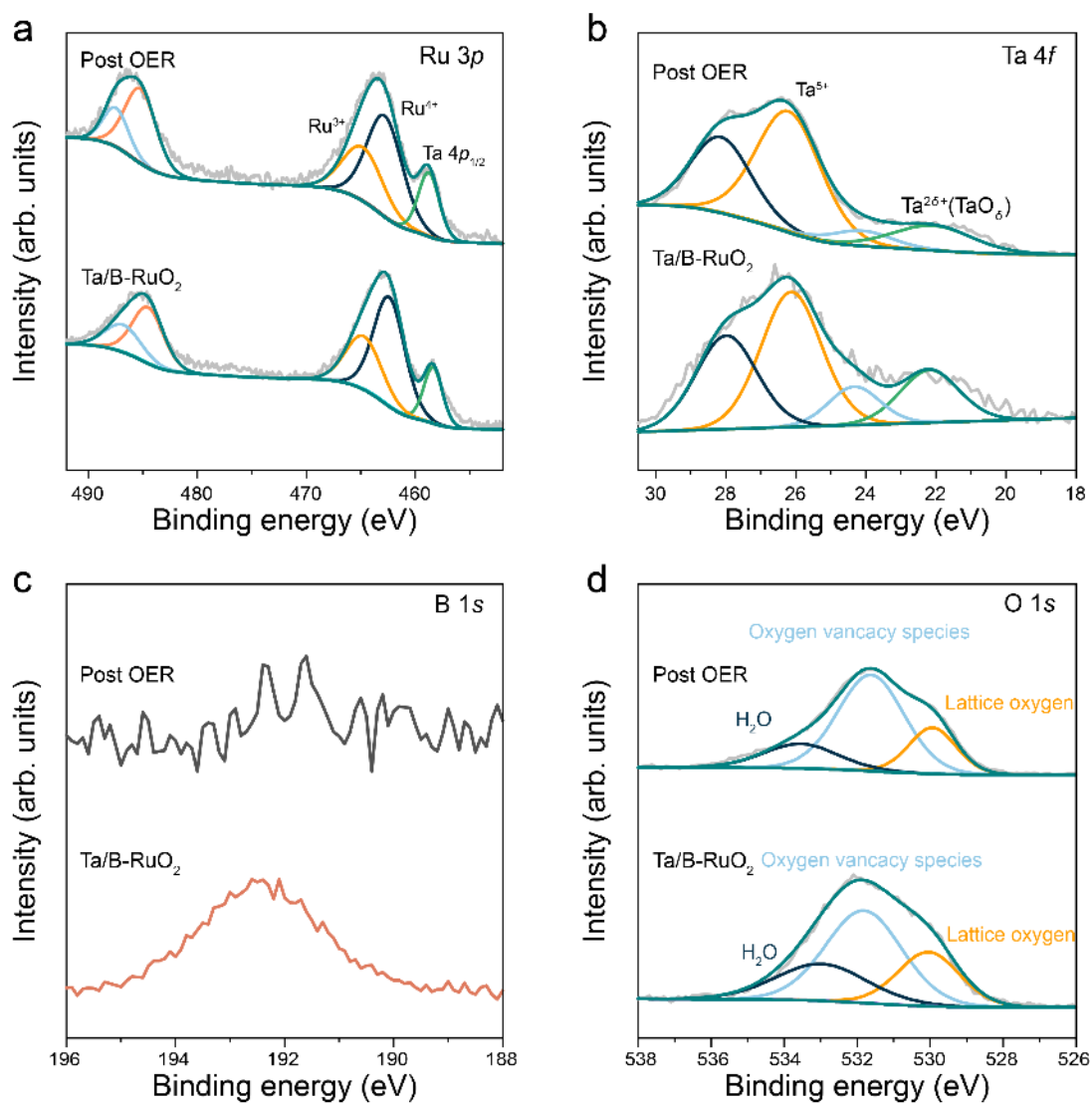
Supplementary Figure 18. (a) The OER polarization curves of B-Ta_{0.05}Ru_{0.95}O₂, B-Ta_{0.07}Ru_{0.93}O₂, and B-Ta_{0.10}Ru_{0.90}O₂. (b) Tafel plots of B-Ta_{0.05}Ru_{0.95}O₂, B-Ta_{0.07}Ru_{0.93}O₂, and B-Ta_{0.10}Ru_{0.90}O₂.



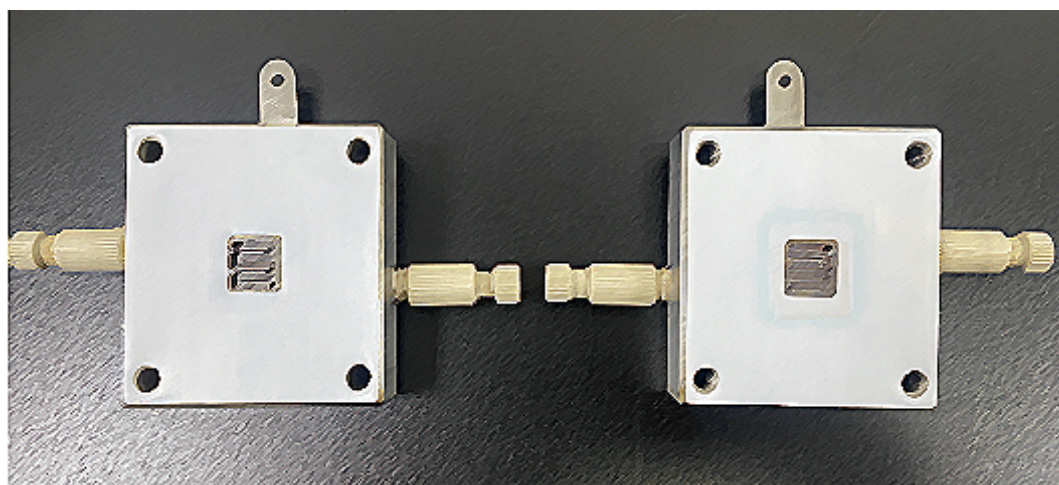
Supplementary Figure 19. Tafel plots of RuO₂ at (a) low potential and (b) high potential.



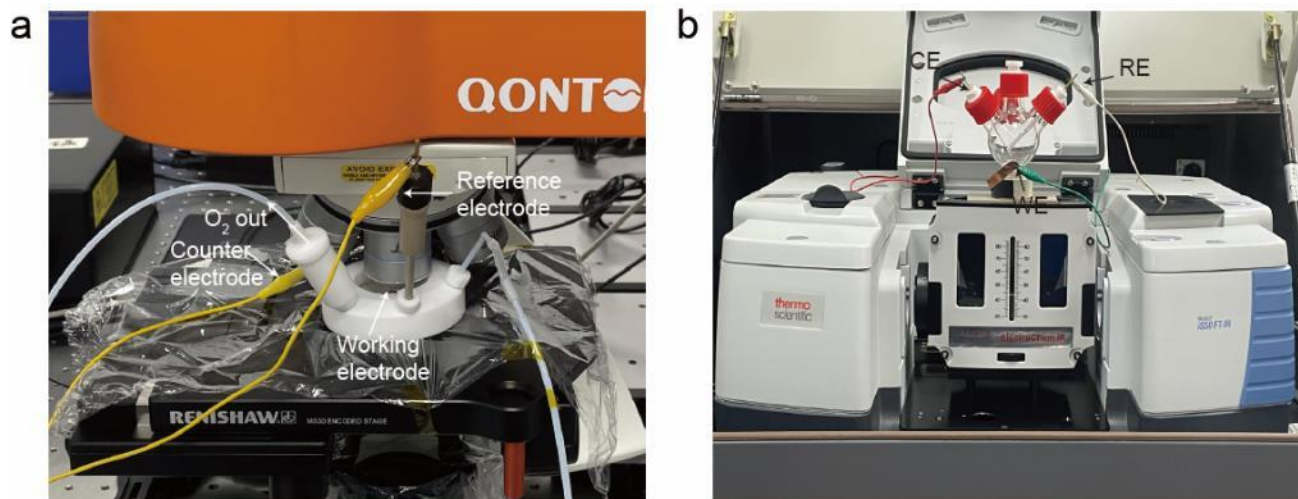
Supplementary Figure 20. Typical cyclic voltammograms at the scan rates ranging from 2.5 to 20 mV s⁻¹ of (a) Ta/B-RuO₂ and (b) RuO₂. (c) The linear fitting of the capacitive current densities versus the scan rates.



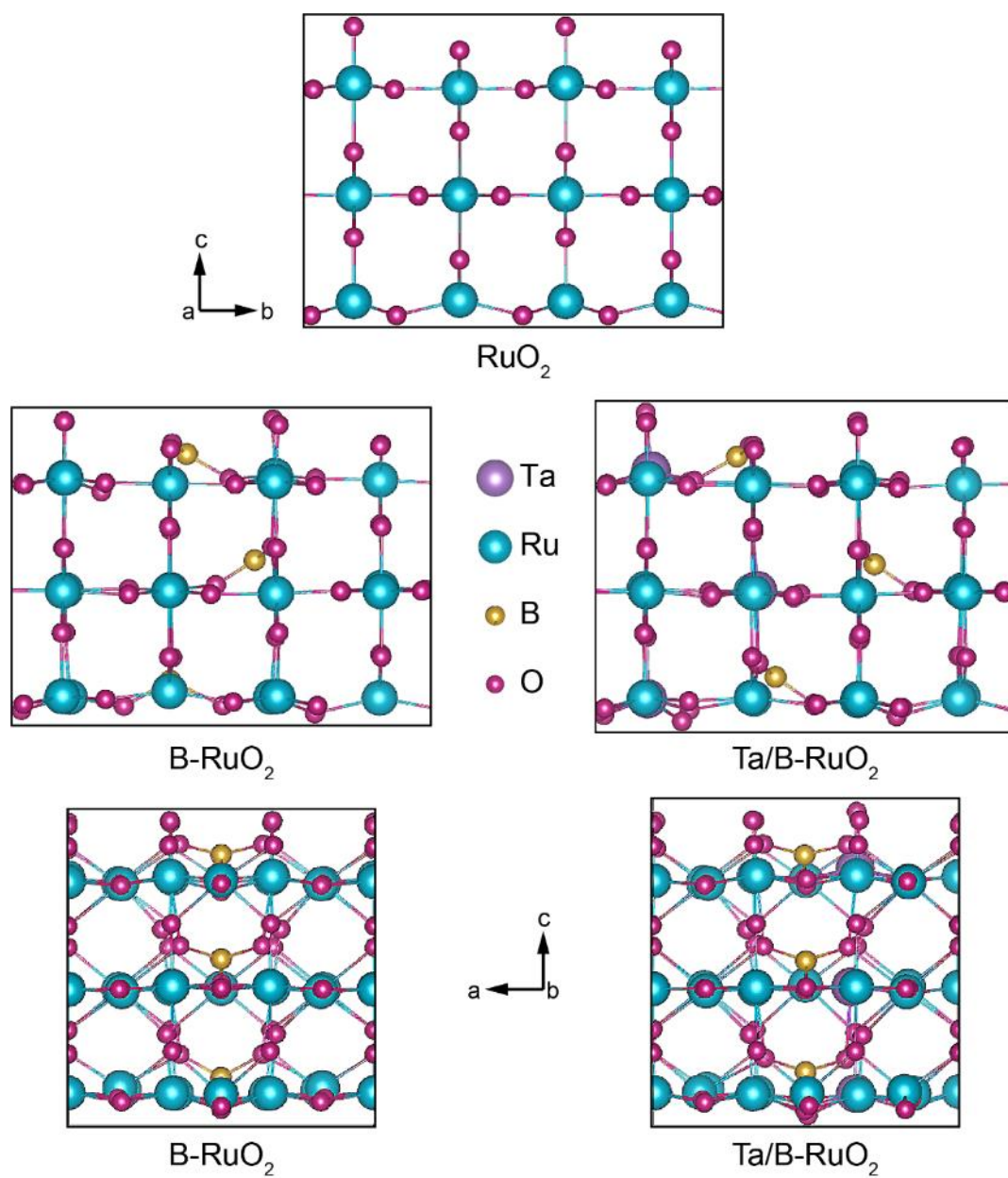
Supplementary Figure 21. High-resolution XPS spectra of Ta/B-RuO₂ before and after OER stability test. (a) Ru 3p, (b) Ta 4f, (c) B 1s, and (d) O 1s.



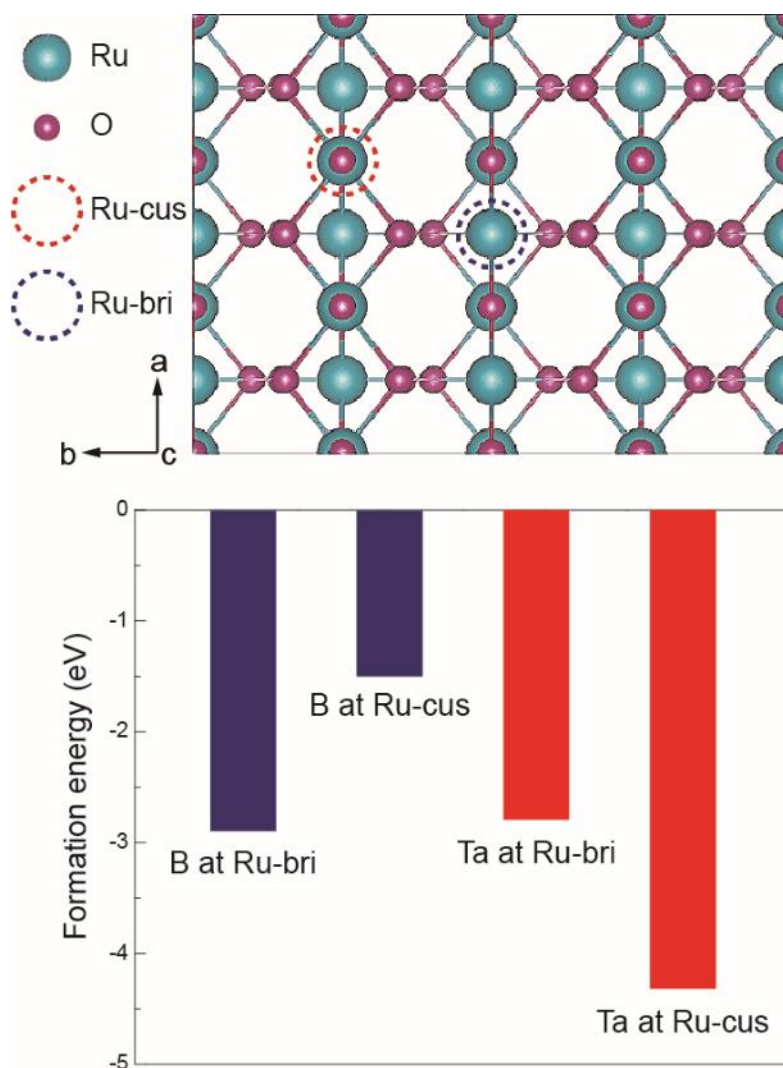
Supplementary Figure 22. Photographs of the PEMWE device.



Supplementary Figure 23. Photographs of the in situ Raman and ATR-SEIRAS apparatuses.



Supplementary Figure 24. Models of RuO_2 , B-RuO_2 , and Ta/B-RuO_2 for DFT calculations.



Supplementary Figure 25. Formation energies of B and Ta doped at different sites.

Considering that B atoms are oxidized during the preparation and OER processes, they are expected to coordinate with O atoms to form a BO_2 structure. DFT calculations were employed to investigate the possible doping models of B and Ta atoms in RuO_2 , specifically focusing on the Ru-cus and Ru-bri sites. The calculated energies were utilized as a criterion for assessing the thermodynamic stability of B and Ta doping. Among these models, the Ru-bri site exhibited the lowest energy for B doping, while the Ru-cus site demonstrated the lowest energy for Ta doping.

Supplementary Tables

Supplementary Table 1. Catalyst composition obtained from XPS analysis.

Catalysts	Element	At %	Wt %
Ta/B-RuO ₂	Ru	81.5	89.0
	Ta	4.8	9.4
	B	13.7	1.6
B-RuO ₂	Ru	85.6	98.2
	B	14.4	1.8
Ta/B-RuO ₂ Post OER	Ru	86.3	88.3
	Ta	5.9	10.8
	B	7.8	0.9

Supplementary Table 2. The comparison of overpotential and Tafel slope for Ta/B-RuO₂ with recently reported catalysts.

Catalysts	Electrolyte	Overpotential@10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	Ref.
Ta/B-RuO ₂	0.5 M H ₂ SO ₄	165	44	This work
B-RuO ₂	0.5 M H ₂ SO ₄	211	61	
RuO ₂	0.5 M H ₂ SO ₄	264	69	
Cr _{0.6} Ru _{0.4} O ₂	0.5 M H ₂ SO ₄	178	56	4
RuO ₂ -CeO ₂	0.5 M H ₂ SO ₄	180	59	5
IrRuMn/C	0.1 M HClO ₄	260	46	6
Cu-RuO ₂ -300	0.5 M H ₂ SO ₄	201	55	7
Ru/S NSs-400	0.5 M H ₂ SO ₄	219	46	8
IrO ₂ -RuO ₂ @Ru	0.5 M H ₂ SO ₄	281	55	9
PdO@RuO ₂	0.1 M HClO ₄	257	63	10
Ru@IrO _x	0.05 M H ₂ SO ₄	282	69.1	11
RuO ₂ nanowires	0.5 M H ₂ SO ₄	250	52	12
a-RuTe ₂ PNRs	0.5 M H ₂ SO ₄	245	47	13
fcc-Ru ₃ Ir	0.5 M H ₂ SO ₄	190	52	14
Ru/RuS ₂	0.5 M H ₂ SO ₄	292	47	15
Ru@Ir-O	0.5 M H ₂ SO ₄	238	91.3	16

Supplementary Table 3. The comparison of the PEMWE cell voltage at 1.0 A cm⁻² for Ta/B-RuO₂ with those of recently reported catalysts.

Catalysts	Electrolyte	Cell voltage (V)	Ref.
Ta/B-RuO ₂	0.5 M H ₂ SO ₄	1.60	This work
B-RuO ₂	0.5 M H ₂ SO ₄	1.86	
RuO ₂	0.5 M H ₂ SO ₄	2.14	
LD-B-RuO ₂	0.5 M H ₂ SO ₄	1.63	17
Ni-RuO ₂	0.1 M HClO ₄	1.95	18
Ba _{0.3} (SO ₄) _δ W _{0.2} Ru _{0.5} O _{2-δ}	0.5 M H ₂ SO ₄	1.68	19
RuCo/RuCoO _x	/	1.78	20
Ru _{0.5} Ir _{0.5} O ₂	0.5 M H ₂ SO ₄	1.63	21
RuO ₂ @IrO _x	0.5 M H ₂ SO ₄	1.68	22
40-Ir ₂ Ni/TiN	0.5 M H ₂ SO ₄	1.71	23
ZnRuO _x	/	1.68	24
Pb-RuO ₂	/	1.69	25
RuCoO _x	0.5 M H ₂ SO ₄	1.60@ 0.4 A cm ⁻²	26
Nb _{0.1} Ru _{0.9} O ₂	/	1.69	27
(Ru-W)O _x	/	1.62	28
RuO ₂ /MoO ₃ -SO ₄	/	1.75	29
RuO ₂ NSs	/	1.65@ 0.93 A cm ⁻²	30

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