

Supporting Information

Highly Efficient and Durable P, Ru-CeO₂ Self-supporting Electrodes Toward Industrial-level Hydrogen Production

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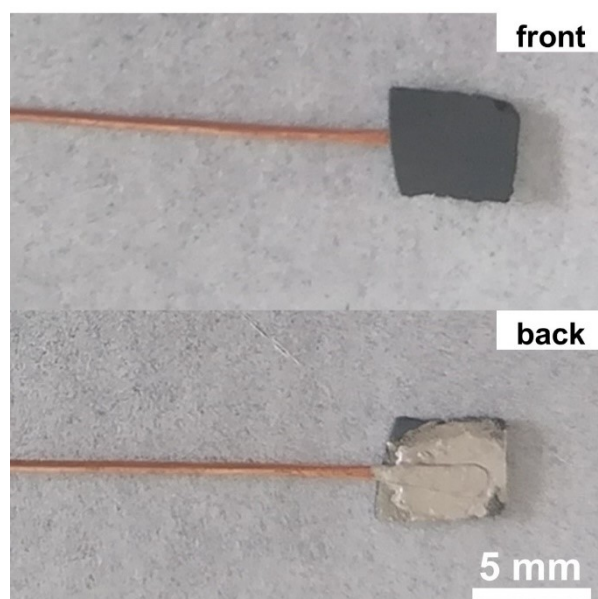


Figure S1. The optical photo of the P, Ru-CeO₂ self-supporting electrode.

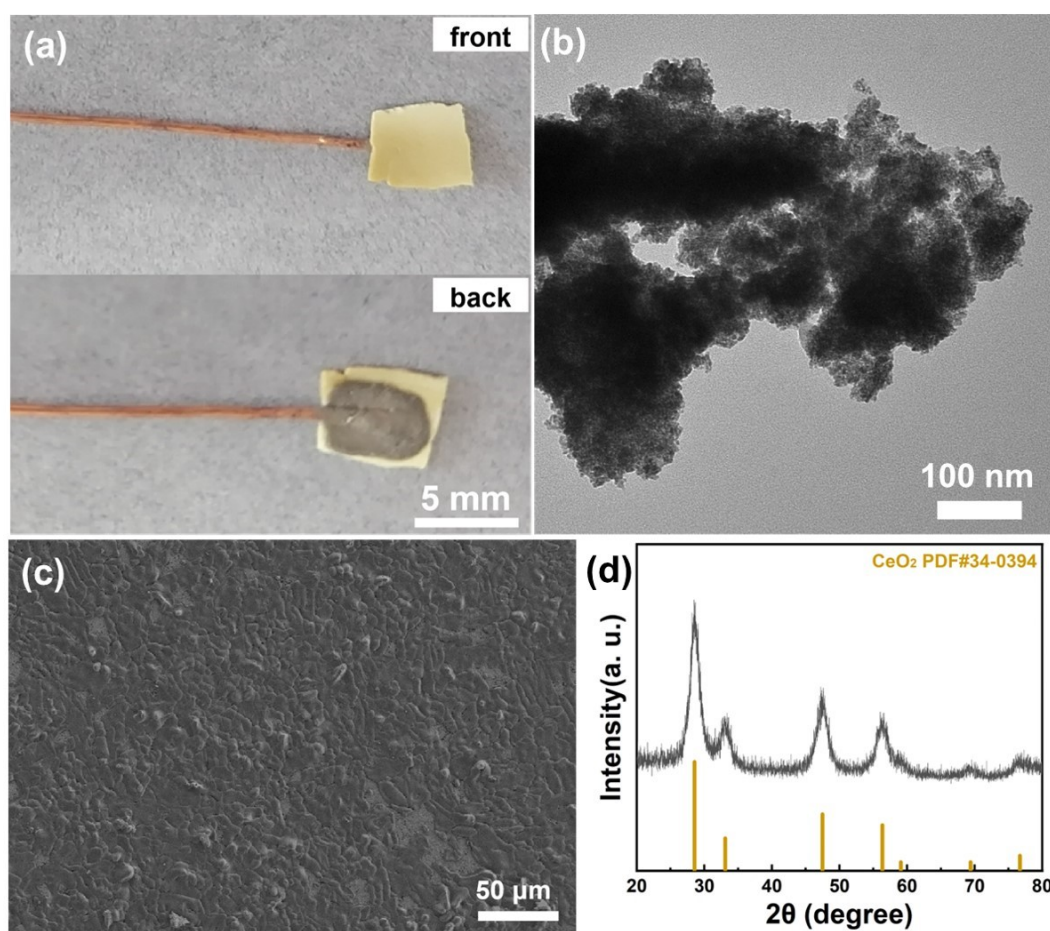


Figure S2. (a) Optical photo, (b) TEM image, (c) TEM image and (d) XRD pattern of the pristine CeO₂ self-supporting electrode.

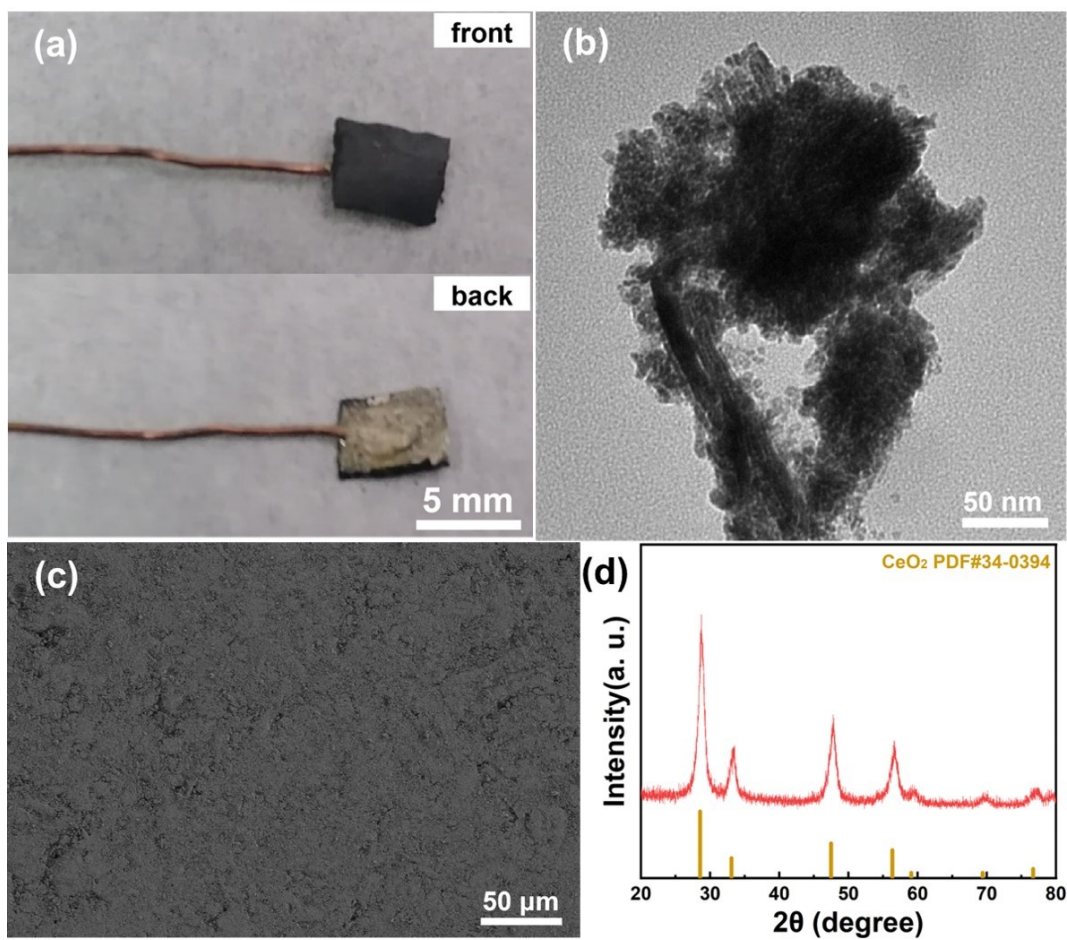


Figure S3. (a) Optical photo, (b) TEM image, (c) TEM image and (d) XRD pattern of the Ru-CeO₂ self-supporting electrode.

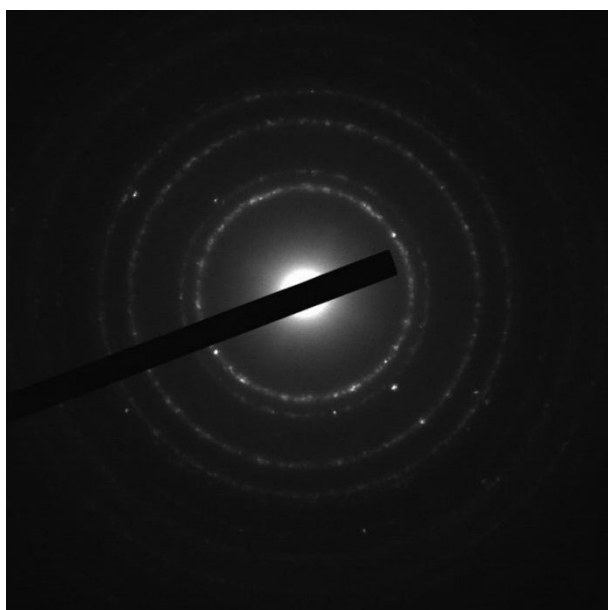


Figure S4. SAED pattern of the P, Ru-CeO₂ catalyst.

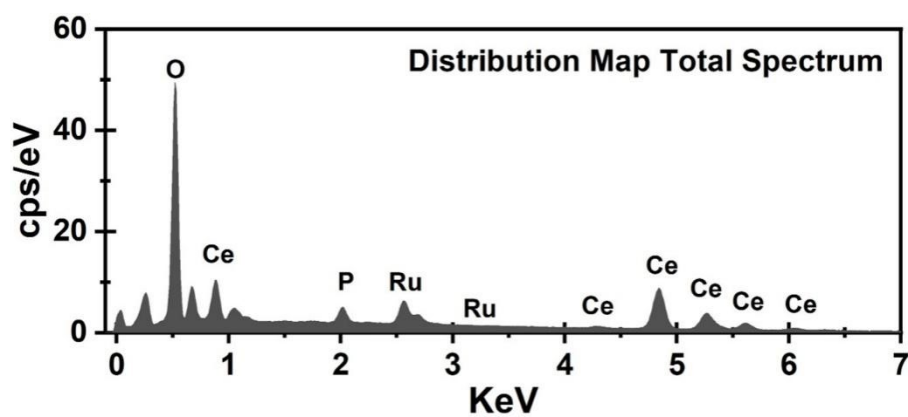


Figure S5. EDX spectrum of the P, Ru-CeO₂ self-supporting electrode.

Distribution Map Total Spectrum				
element	Line Type	Weight%	wt% Sigma	Atomic%
O	K	17.03	0.10	54.05
P	K	1.48	0.03	2.49
Ru	L	6.66	0.10	3.43
Ce	M	71.57	0.18	26.62
Other	-	3.26	-	13.41
total	—	100	—	100

Table S1. Relative proportions of main elements, corresponding to Figure S5.

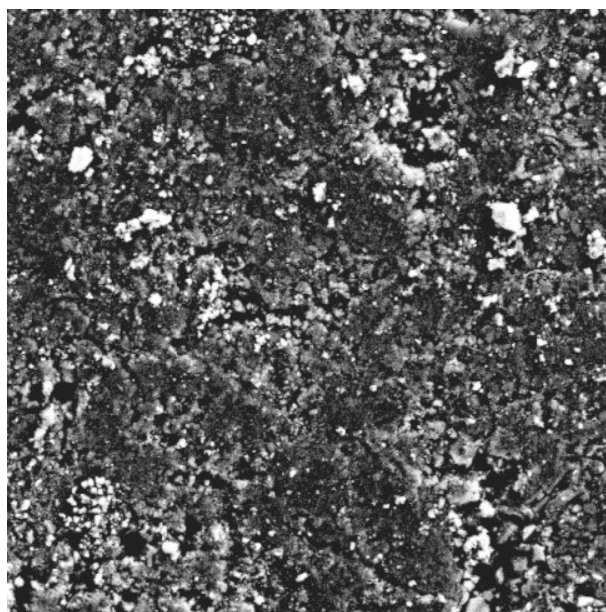


Figure S6. The SEM image for elemental mapping of the P, Ru-CeO₂ self-supporting electrode.

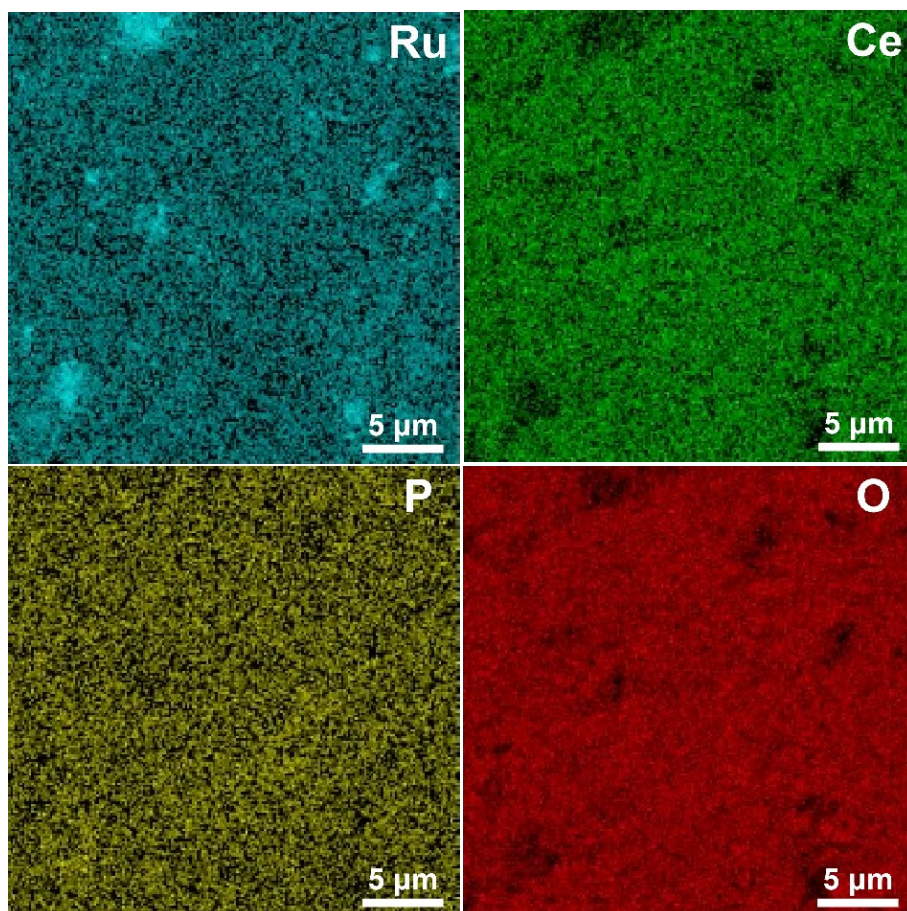


Figure S7. The corresponding elemental mapping image in Figure S5 of the P, Ru-CeO₂ self-supporting electrode.

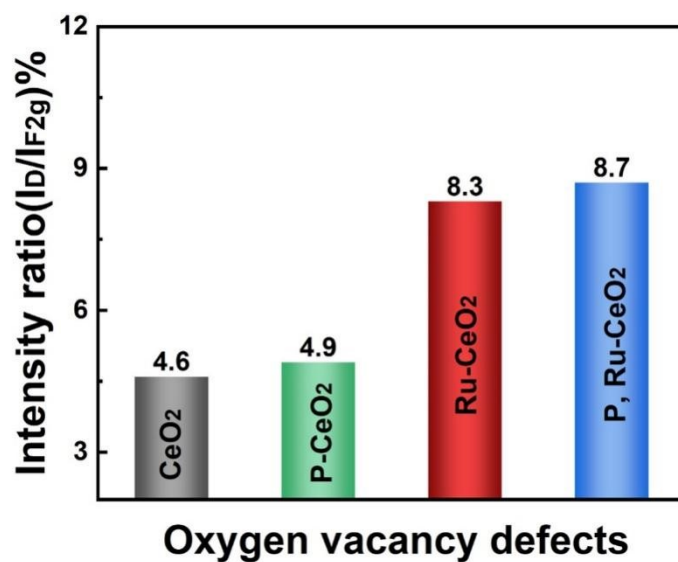


Figure S8. Peak intensity ratio of I_D/I_{F2g} over CeO₂, P-CeO₂, Ru-CeO₂ and P, Ru-CeO₂ catalysts.

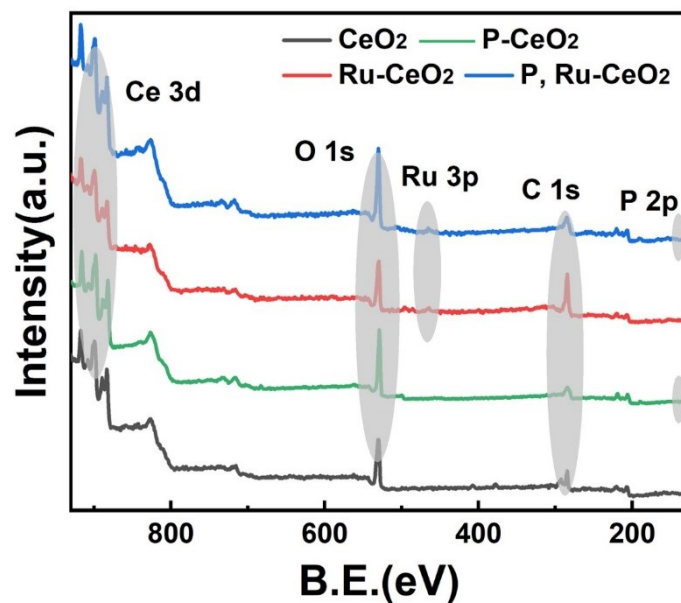


Figure S9. XPS survey scan spectrum of the pristine CeO₂, P-CeO₂, Ru-CeO₂ and P, Ru-CeO₂ catalysts.

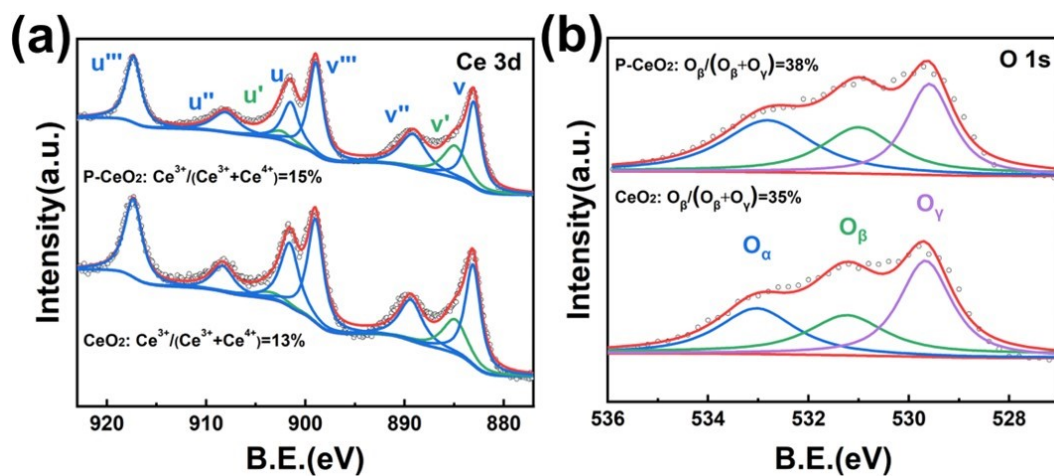


Figure S10. XPS of the pristine CeO₂, P-CeO₂ catalysts: (a) Ce 3d orbitals, (b) O 1s orbitals.

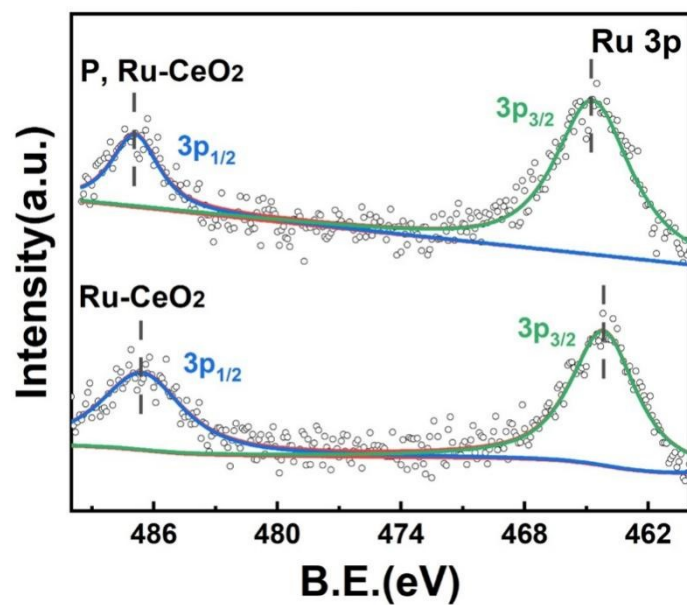


Figure S11. XPS of Ru-CeO₂ and P, Ru-CeO₂ catalysts: Ru 3p orbitals.

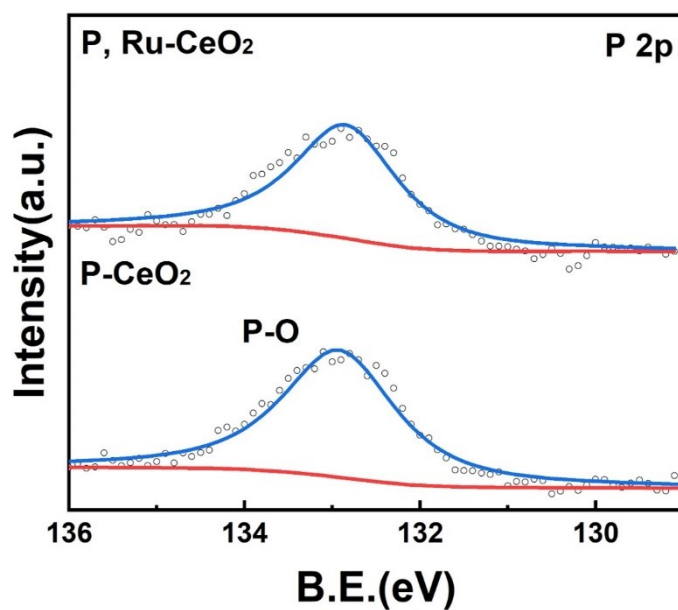


Figure S12. XPS of P-CeO₂ and P, Ru-CeO₂ catalysts: P 2p orbitals.

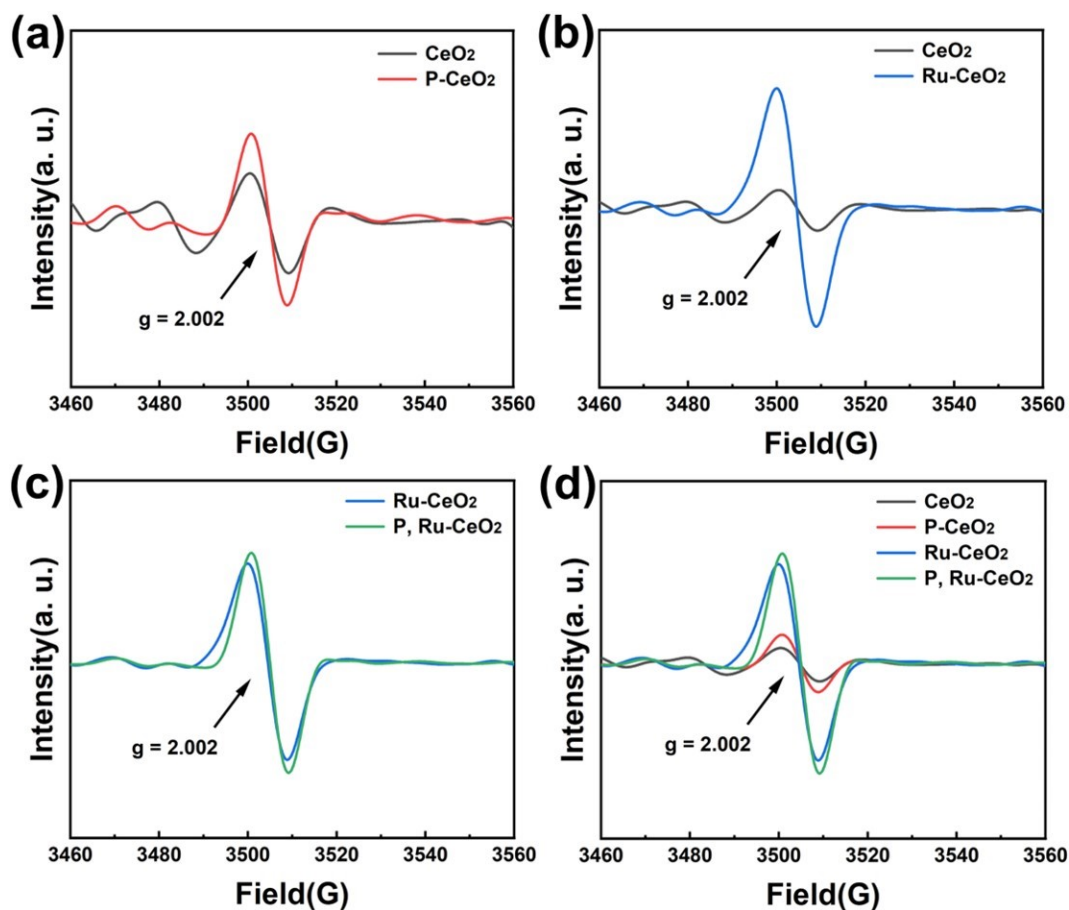


Figure S13. EPR spectrum of the catalysts: (a) CeO_2 and P- CeO_2 , (b) CeO_2 and Ru- CeO_2 , (c) Ru- CeO_2 and P, Ru- CeO_2 , (d) CeO_2 , P- CeO_2 , Ru- CeO_2 and P, Ru- CeO_2 .

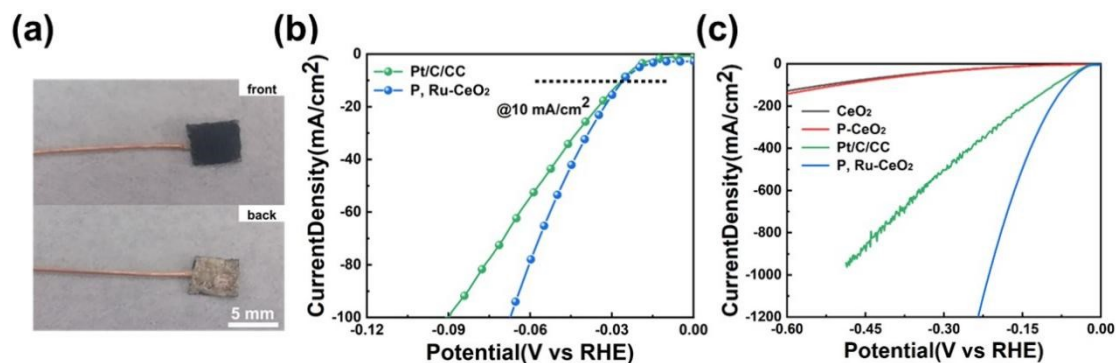


Figure S14. (a) Commercial Pt/C working electrode loaded on CC. iR-corrected polarization curves of the pure CeO_2 , P- CeO_2 , P, Ru- CeO_2 self-supporting working electrodes and commercial Pt/C/CC: (b) @low-current density; (c) @high-current density.

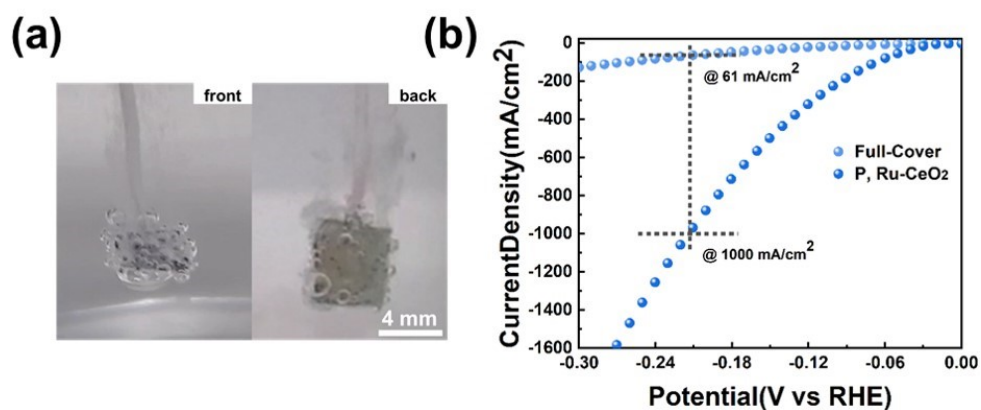


Figure S15. (a) the comparison between the front and back of the P, Ru-CeO₂ self-supporting working electrode. (b) iR-corrected polarization curves of the Full-Cover-P, Ru-CeO₂, P, Ru-CeO₂ self-supporting working electrodes.

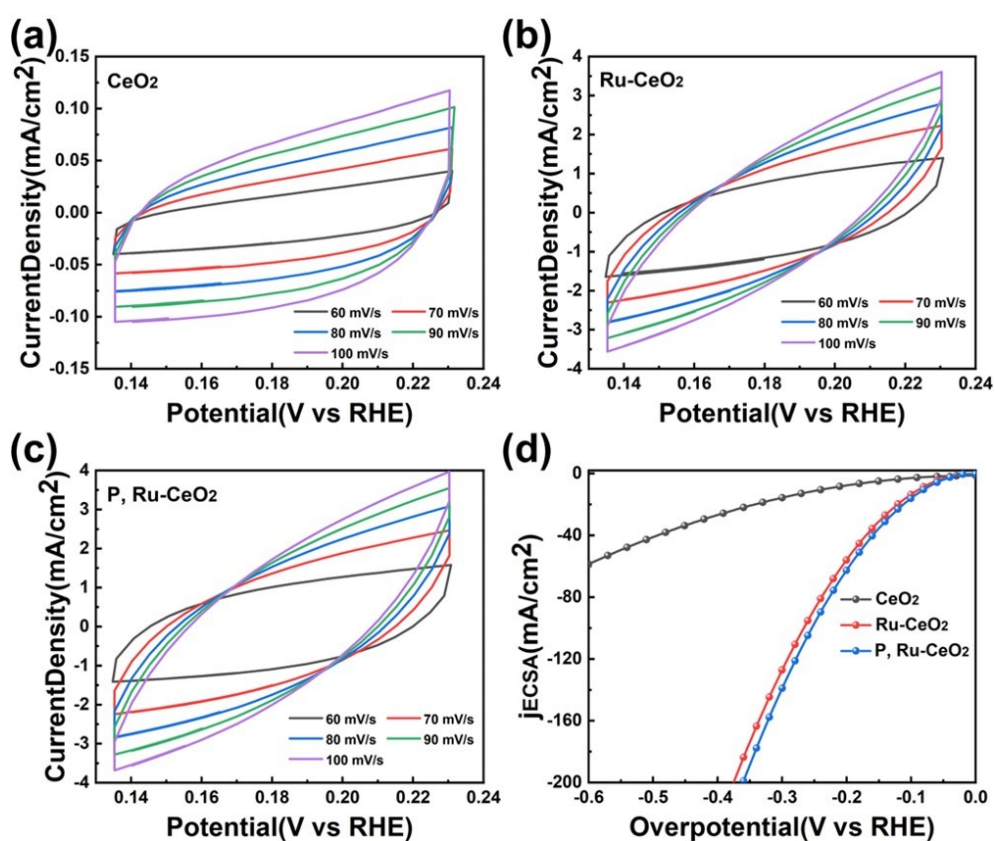


Figure S16. Electrochemical double-layer capacitance measurements at different scan rates for HER. Cyclic voltammograms of (a) pure CeO₂, (b) Ru-CeO₂ and (c) P, Ru-CeO₂ self-supporting working electrodes. (d) HER polarization curves normalized by the electrochemical double-layer capacitance.

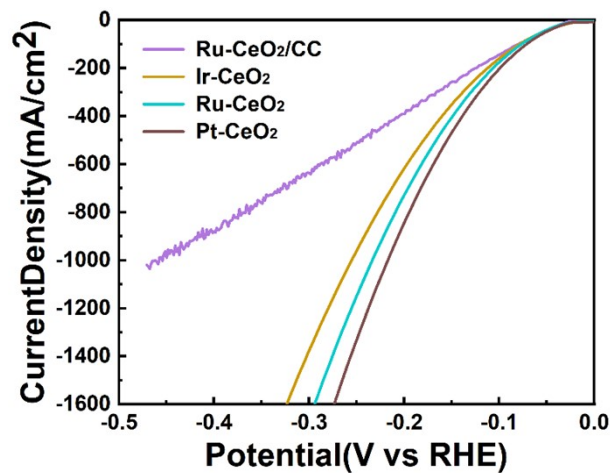


Figure S17. iR-corrected polarization curves of the Ir-CeO₂, Ru-CeO₂, Pt-CeO₂ self-supporting working electrodes, and the Ru-CeO₂/CC.

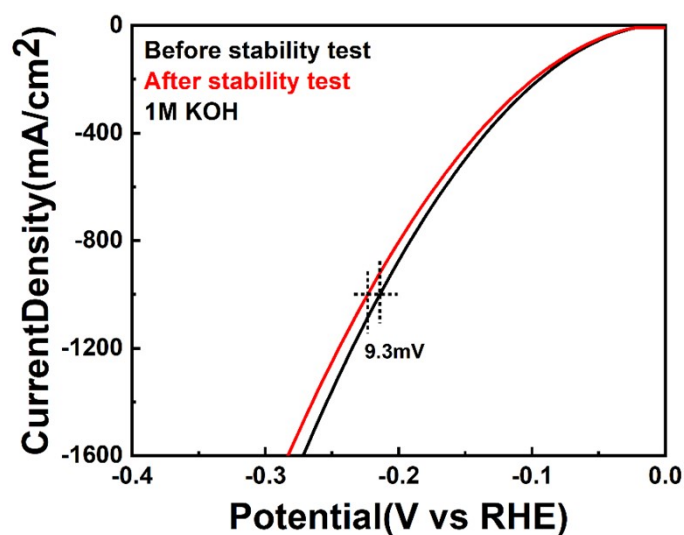


Figure S18. iR-corrected polarization curves of the Pt, Ru-CeO₂ self-supporting electrode before and after 5000 CV cycles in 1 M KOH.

materials	$\eta_{\text{HER}}(\text{mV})$	Tafel(mV/dec)	Reference
This work	215	25	—
Pt/TiO ₂ /Ni(OH) ₂ /NF	227	39	Ref.1 ¹
NiCo@RuO ₂ HNAs/NF	236	69	Ref.2 ²
FeNiZn/FeNi ₃ @NiFe	245	45	Ref.3 ³
Ru-CoO _x /NF	252	28	Ref.4 ⁴
Ni-W ₂ N@NF	276	46	Ref.5 ⁵
Sr ₂ RuO ₄ bulk SC	278	26	Ref.6 ⁶
Co-SA/CC	294	97	Ref.7 ⁷
Ni-Co-P/CFP	295	31	Ref.8 ⁸
Self-Standing Pt NC/CF	331	61	Ref.9 ⁹
Cu ₃ P-FeP@CC	338	84	Ref.10 ¹⁰

Table S2. Comparison of the HER performance of the P, Ru-CeO₂ self-supporting working electrode with the similar catalysts at 1000 mA·cm⁻² in 1.0 M KOH.

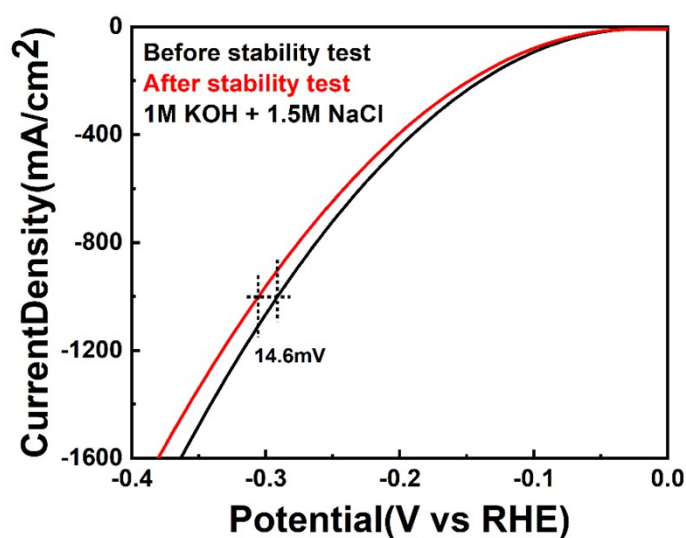


Figure S19. iR-corrected polarization curves of the P, Ru-CeO₂ self-supporting electrode before and after 5000 CV cycles in 1 M KOH+1.5 M NaCl.

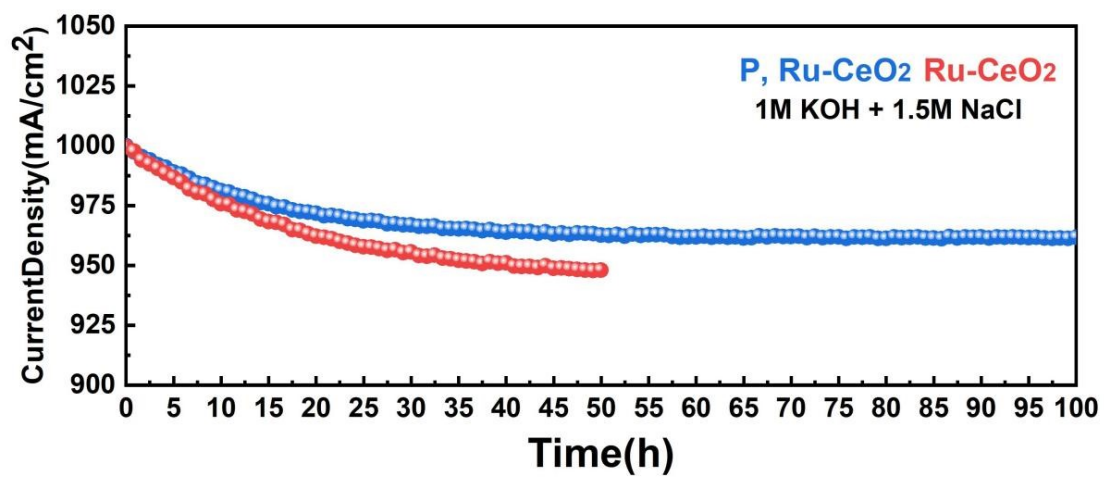


Figure S20. Chronoamperometric curves of the Ru-CeO₂ self-supporting electrodes and the P, Ru-CeO₂ self-supporting electrodes.

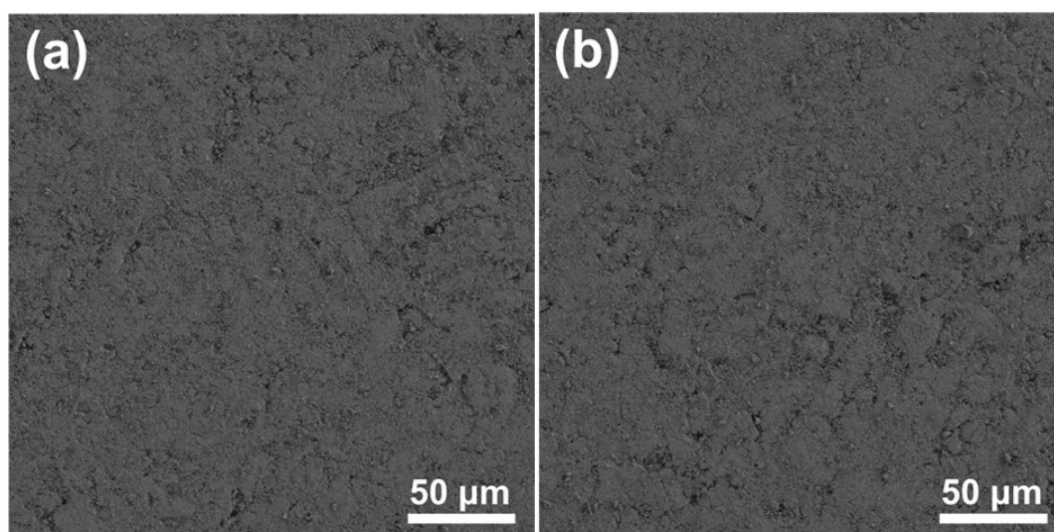


Figure S21. SEM images of the P, Ru-CeO₂ self-supporting electrode (a) before and (b) after durability test in 1 M KOH+1.5 M NaCl.

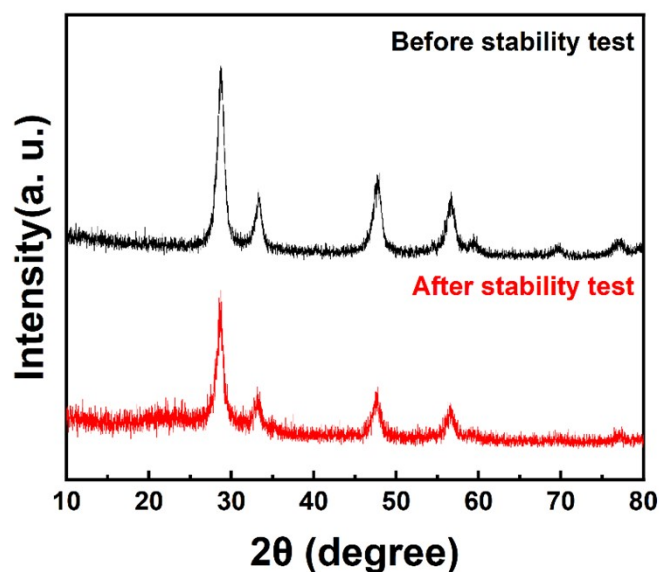


Figure S22. XRD pattern of the P, Ru-CeO₂ catalyst after durability test in 1 M KOH+1.5 M NaCl.

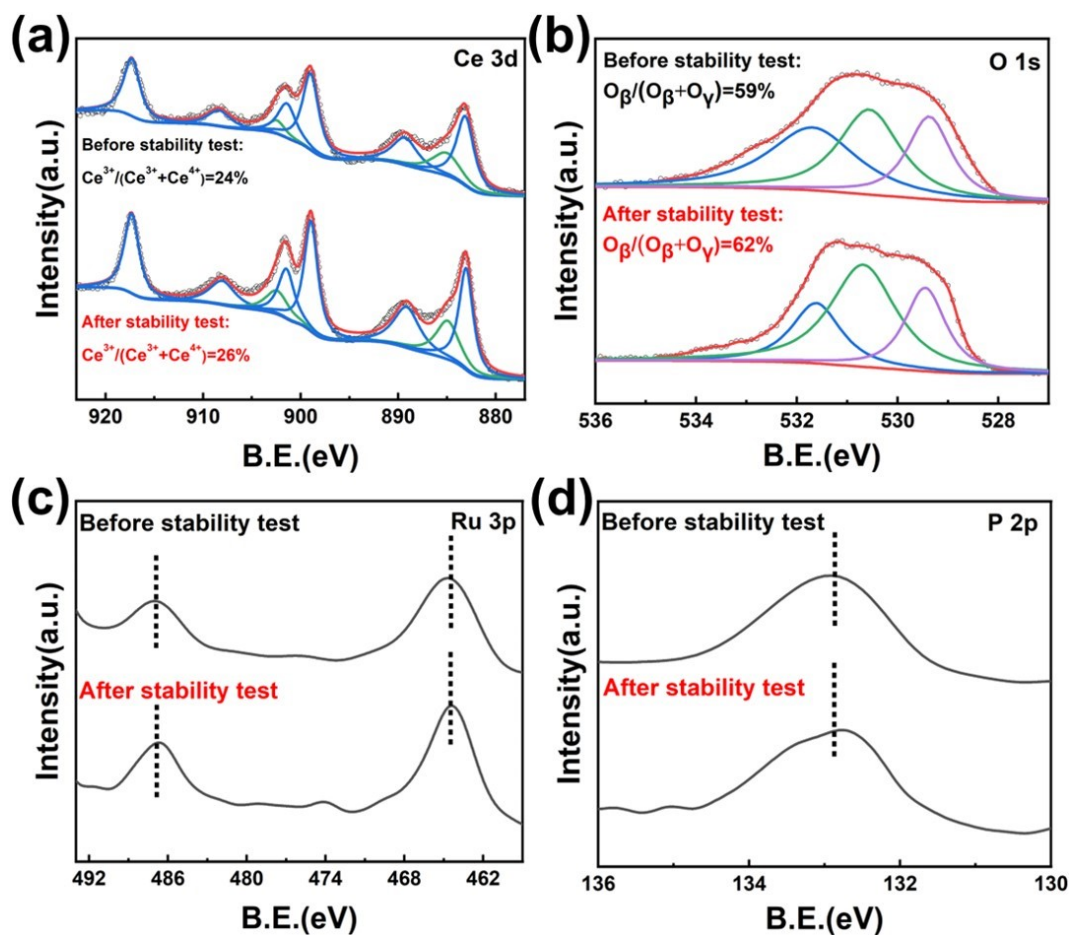


Figure S23. XPS of the P, Ru-CeO₂ catalyst after durability test in 1 M KOH+1.5 M NaCl. (a) Ce 3d. (b) O 1s. (c) Ru 3p. (d) P 2p.

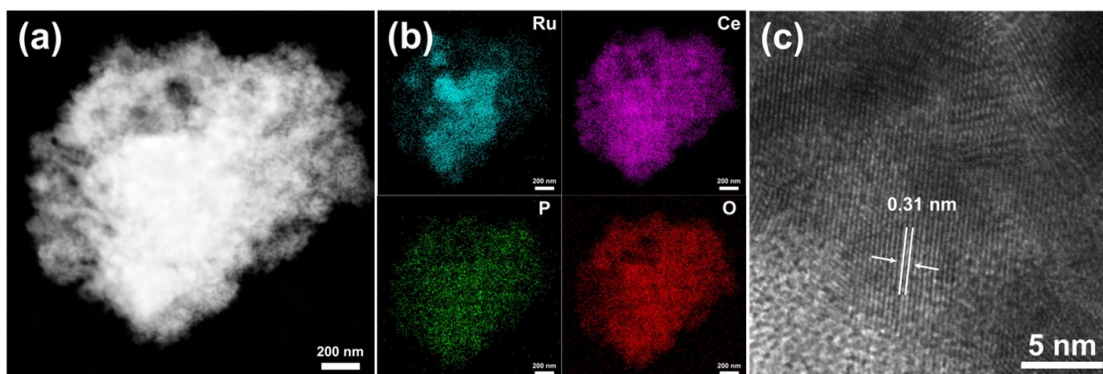


Figure S24. TEM images of the P, Ru-CeO₂ catalyst after durability test in 1 M KOH+1.5 M NaCl. (a) HADDF-STEM. (b) EDS. (c) HRTEM.

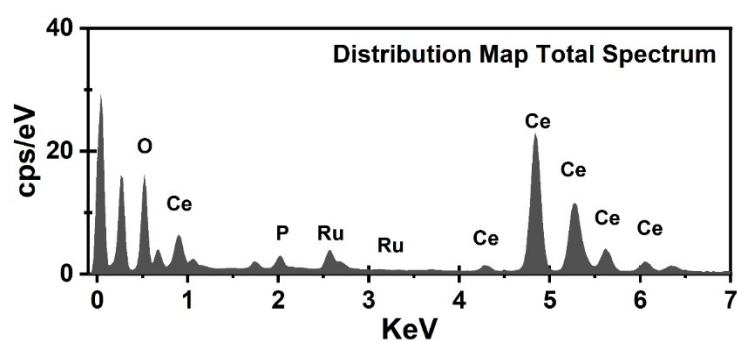


Figure S25. EDX spectrum of the P, Ru-CeO₂ catalyst, corresponding to **Figure S24**.

Distribution Map Total Spectrum			
element	Line Type	Weight%	σ
Ce	M	72.48	0.2
O	K	17.57	0.1
Ru	L	6.12	0.2
P	K	1.61	0.1
Other	-	2.22	-
total	—	100	—

Table S3. Relative proportions of main elements, corresponding to **Figure S25**.

References

- 1 A. Kong, M. Peng, M. Liu, Y. Lv, H. Zhang, Y. Gao, J. Liu, Y. Fu, W. Li and J. Zhang, *Applied Catalysis B-Environmental*, 2022, **316**, 121654.
- 2 H. Yi, X. Zhang, Z. Ai, S. Song and Q. An, *ChemSuSchem*, 2022, **15**, 2201532.

- 3 Q. Zhou, C. Xu, J. Hou, W. Ma, T. Jian, S. Yan and H. Liu, *Nano-Micro Letters*, 2023, **15**, 95.
- 4 D. Wu, D. Chen, J. Zhu and S. Mu, *Small*, 2021, **17**, 2102777.
- 5 Z. Dan, W. Liang, X. Gong, X. Lin, W. Zhang, Z. Le, F. Xie, J. Chen, M. Yang, N. Wang, Y. Jin and H. Meng, *ACS Materials Letters*, 2022, **4**, 1374-1380.
- 6 Y. Zhang, K. E. Arpino, Q. Yang, N. Kikugawa, D. A. Sokolov, C. W. Hicks, J. Liu, C. Felser and G. Li, *Nature Communications*, 2022, **13**, 7784.
- 7 P. Zhao, C. Peng, Q. Zhang, X. Fan, H. Chen, Y. Zhu and Y. Min, *Chemical Engineering Journal*, 2023, **461**, 142037.
- 8 X. Chen, X. Zhao, Y. Wang, S. Wang, Y. Shang, J. Xu, F. Guo and Y. Zhang, *ChemCatChem*, 2021, **13**, 3619-3627.
- 9 Y. Tan, R. Xie, S. Zhao, X. Lu, L. Liu, F. Zhao, C. Li, H. Jiang, G. Chai, D. J. L. Brett, P. R. Shearing, G. He and I. P. Parkin, *Advanced Functional Materials*, 2021, **31**, 2105579.
- 10 C. Chai, J. Yang, C. Jiang, L. Liu and J. Xi, *Acs Applied Energy Materials*, 2022, **5**, 2909-2917.