

Supporting Information

Morphology control of metal-modified zirconium phosphate support structures for the oxygen evolution reaction

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Surface-area-to-volume ratio (SA:V) calculations:

All SA:V calculations are based off the average dimensions of the ZrP structures obtained through TEM/STEM.

 α -ZrP:

Average diameter = 120 nm; side length = 60 nm; average height = 14 nm

$$\text{Surface Area (assuming a regular hexagon structure)} = 3 \frac{\sqrt{3}s^2}{2} = 9353 \text{ nm}^2$$

$$\text{Volume} = 3 \frac{\sqrt{3}s^2}{2} * h = 1.31 * 10^5 \text{ nm}^3$$

$$\text{SA:V} = 0.071$$

ZrP_{rods}:

Average length = 760 nm

Average diameter = 25 nm

$$\text{Surface area (assuming a cylinder structure)} = 2\pi rh + 2\pi r^2 = 6062 \text{ nm}^2$$

$$\text{Volume} = \pi r^2 h = 3.73 * 10^5 \text{ nm}^3$$

$$\text{SA:V} = 0.16$$

ZrP_{cubes}:

Average side length = 175 nm

$$\text{Surface area (assuming a perfect cube)} = 6s^2 = 1.84 * 10^5 \text{ nm}^2$$

$$\text{Volume} = 5.36 * 10^6 \text{ nm}^3$$

$$\text{SA:V} = 0.034$$

ZrP_{spheres}:

Average radius = 765 nm

$$\text{Surface area (assuming a perfect sphere)} = 7.35 * 10^6 \text{ nm}^2$$

$$\text{Volume} = 1.88 * 10^9 \text{ nm}^3$$

$$\text{SA:V} = 0.0039$$

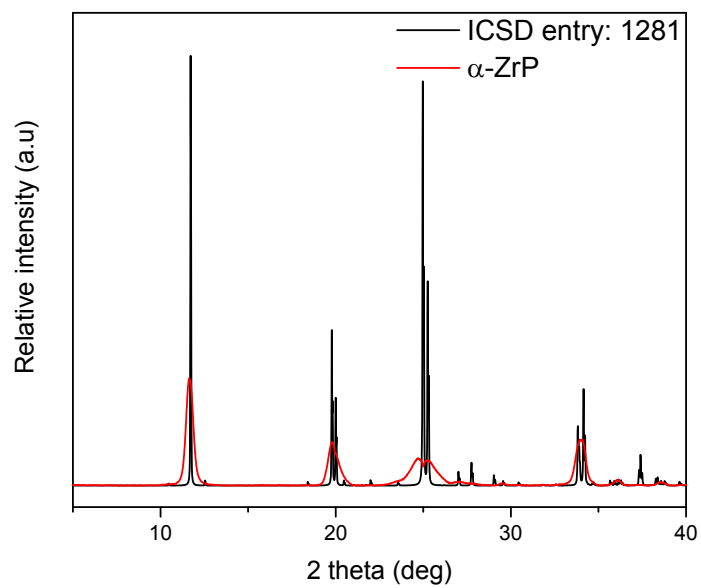


Figure S1. Experimentally determined XRPD pattern of α -ZrP and ICSD entry 1281.

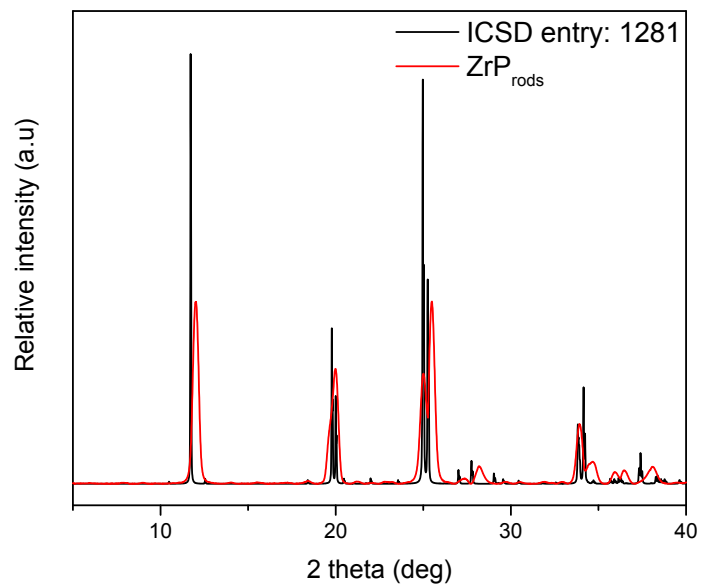


Figure S2. Experimentally determined XRPD pattern of ZrP_{rods} and ICSD entry 1281.

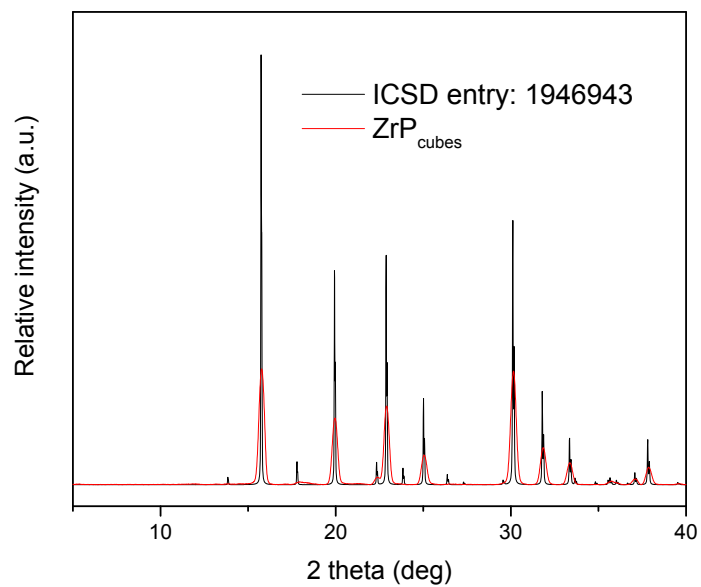


Figure S3. Experimentally determined XRPD pattern of ZrP_{cubes} and ICSD entry 1946943.

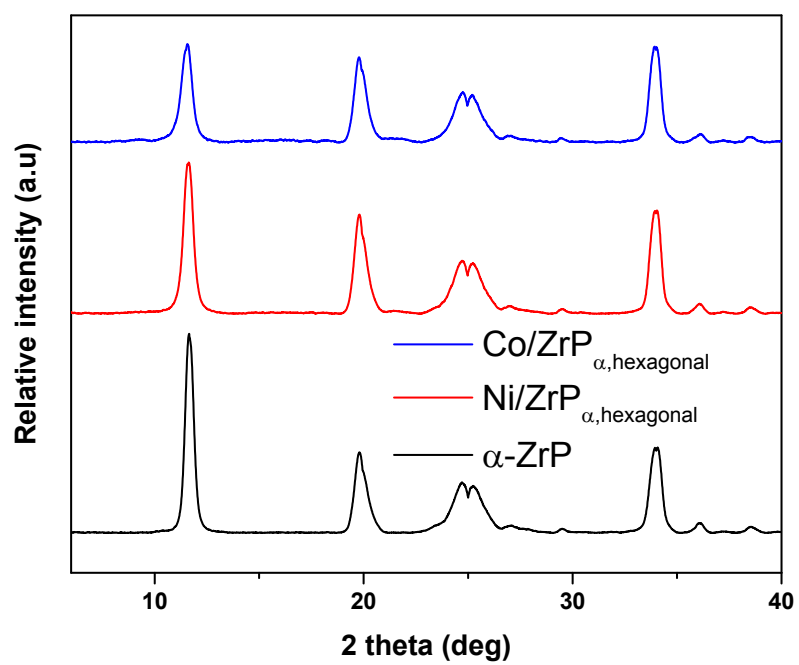


Figure S4. XRPD patterns of α -ZrP, Ni/ZrP $_{\alpha,\text{hexagonal}}$, and Co/ ZrP $_{\alpha,\text{hexagonal}}$.

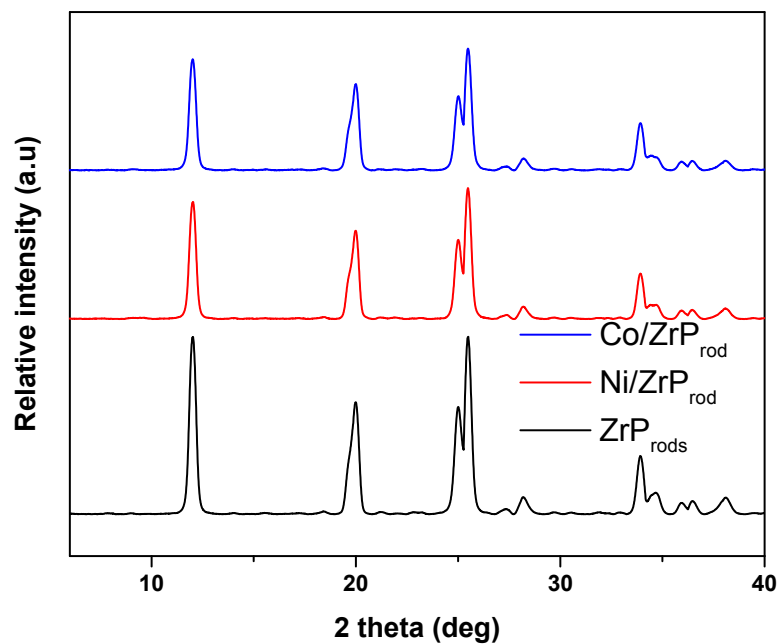


Figure S5. XRPD patterns of ZrP_{rods}, Ni/ZrP_{rod}, and Co/ZrP_{rod}.

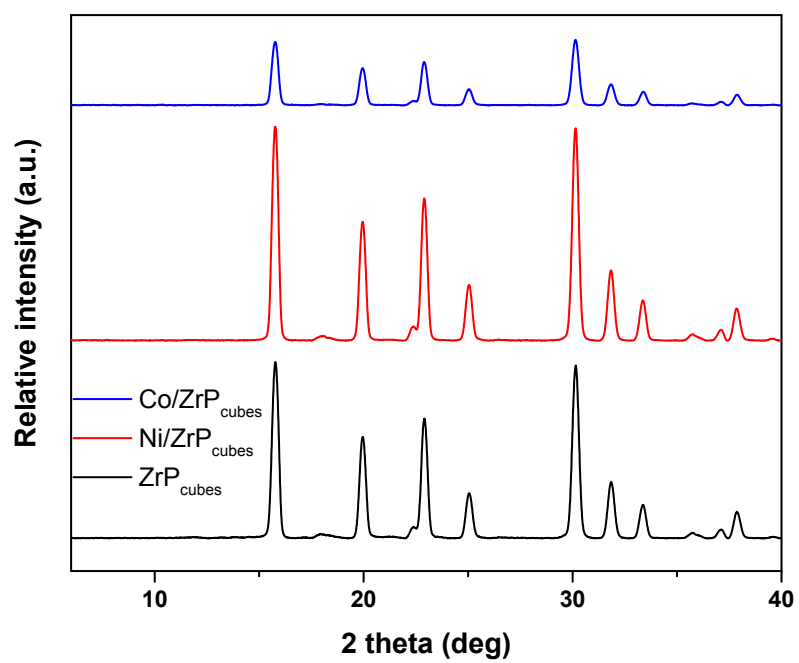


Figure S6. XRPD patterns of $\text{ZrP}_{\text{cubes}}$ (τ' - ZrP), $\text{Ni/ZrP}_{\text{cube}}$, and $\text{Co/ZrP}_{\text{cube}}$.

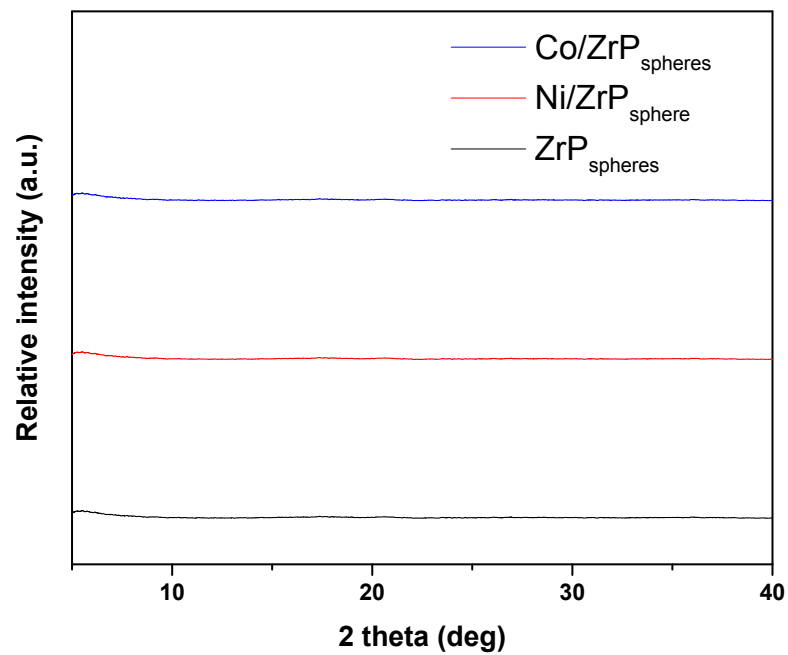


Figure S7. XRPD patterns of $\text{ZrP}_{\text{spheres}}$, $\text{Ni/ZrP}_{\text{spheres}}$, and $\text{Co/ZrP}_{\text{sphere}}$.



Figure S8. EDS spectrum of ZrP_{rods} .

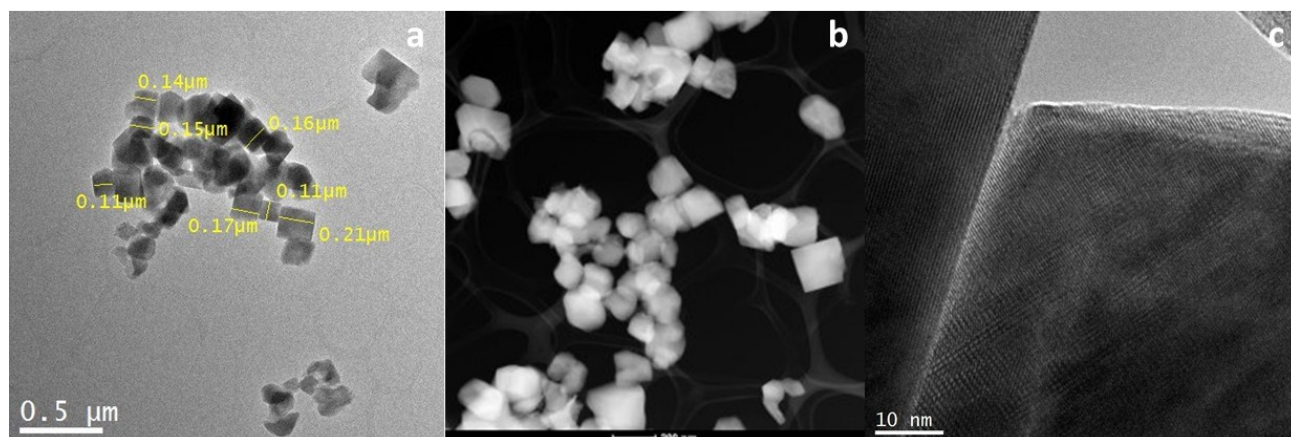


Figure S9. TEM/STEM micrographs of cobalt-modified ZrP_{cubes}. Scale bar: 0.5 μ m, 200 nm, and 10 nm; respectively.

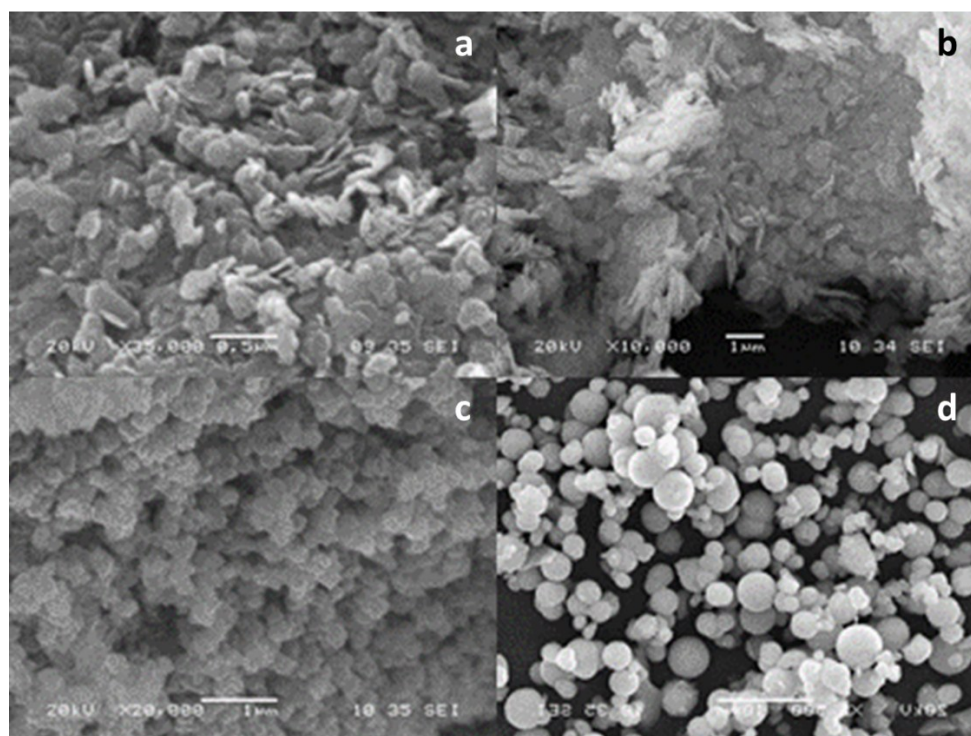


Figure S10. SEM micrographs of (a) α -ZrP, (b) ZrP_{rods}, (c) ZrP_{cubes}, and (d) ZrP_{spheres}. Scale bar: 0.5 μ m, 1 μ m, 1 μ m, and 10 μ m; respectively.

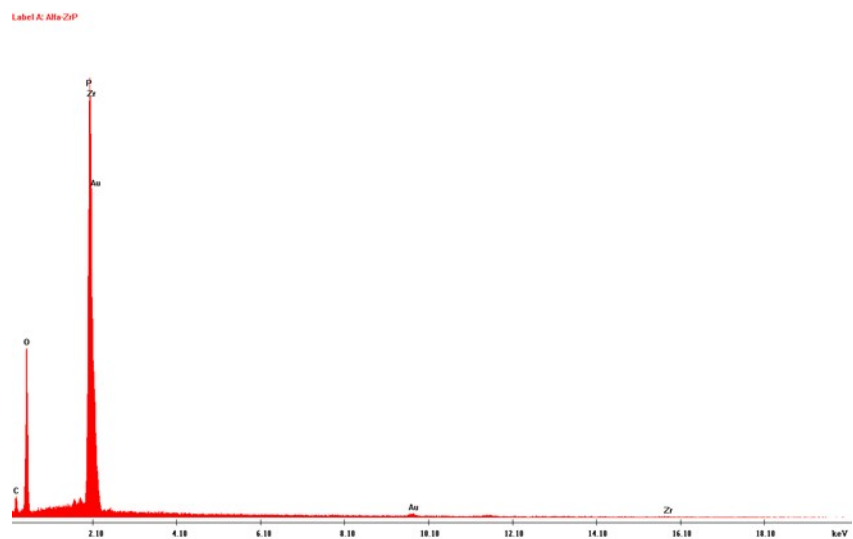


Figure S11. EDS spectrum of α -ZrP.

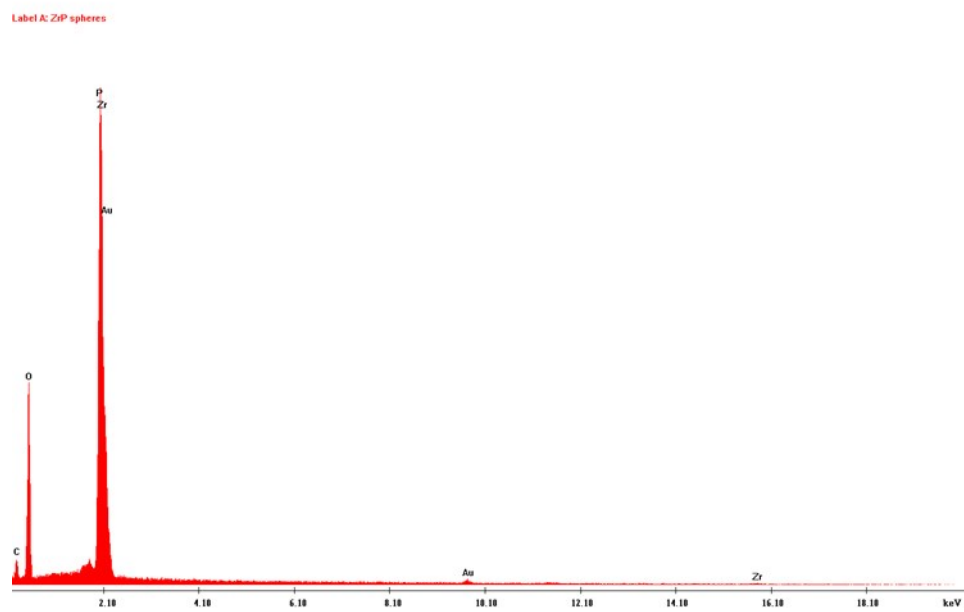


Figure S12. EDS spectrum of ZrP_{spheres}.

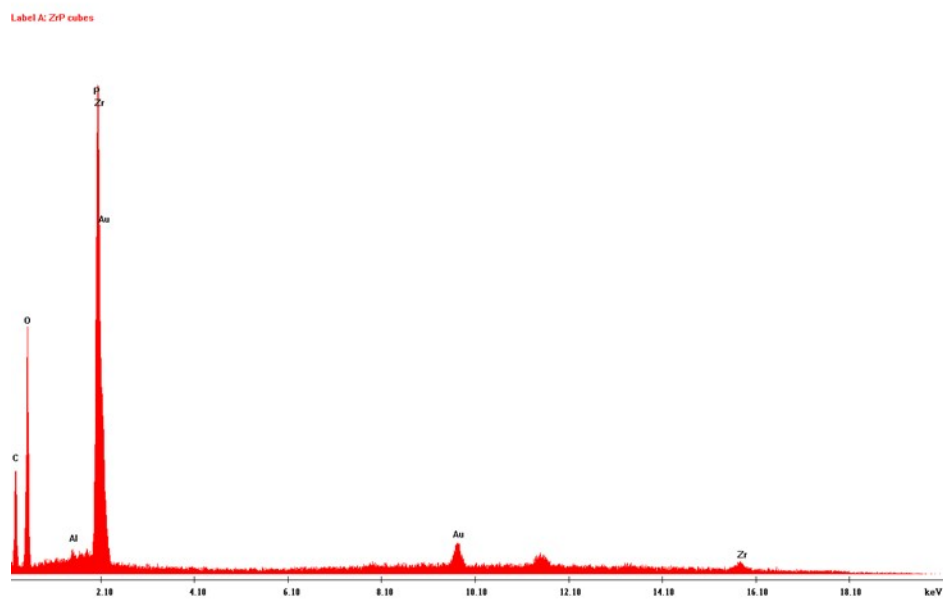


Figure S13. EDS spectrum of $\text{ZrP}_{\text{cubes}}$.

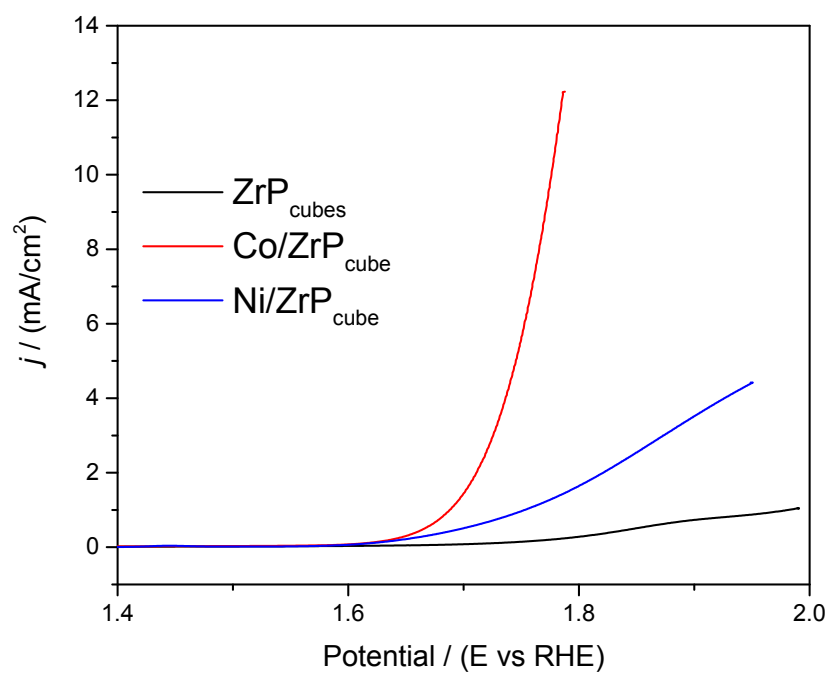


Figure S14. Linear sweep voltammograms of $\text{ZrP}_{\text{cubes}}$, and both metal-modified ZrP_{cube} catalysts.

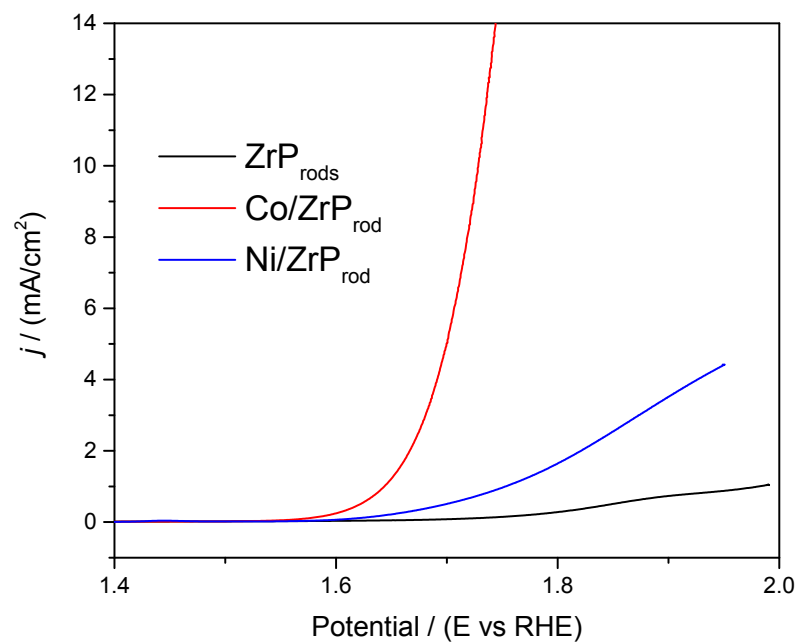


Figure S15. Linear sweeps voltammograms of ZrP_{rod} , and both metal-modified ZrP_{rod} catalysts.

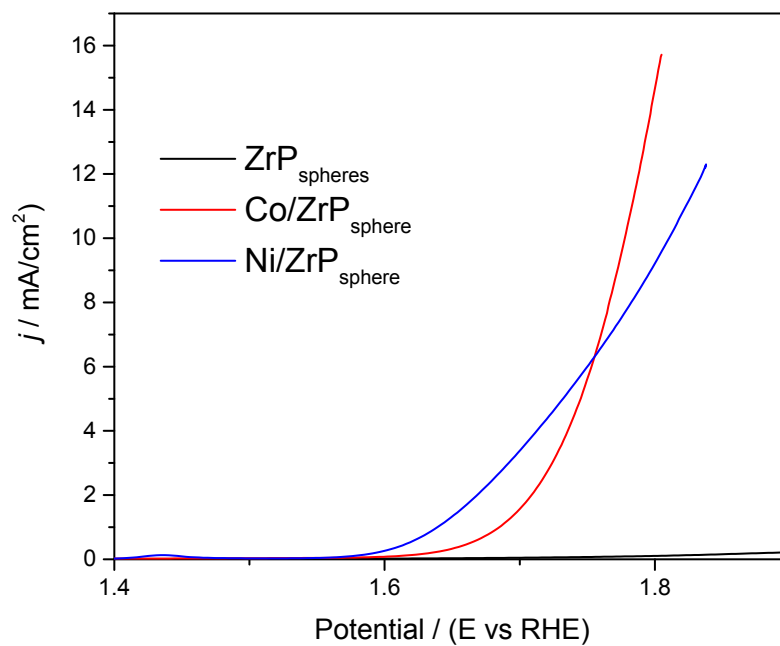


Figure S16. Linear sweeps voltammograms of $\text{ZrP}_{\text{spheres}}$, and both metal-modified $\text{ZrP}_{\text{sphere}}$ catalysts.

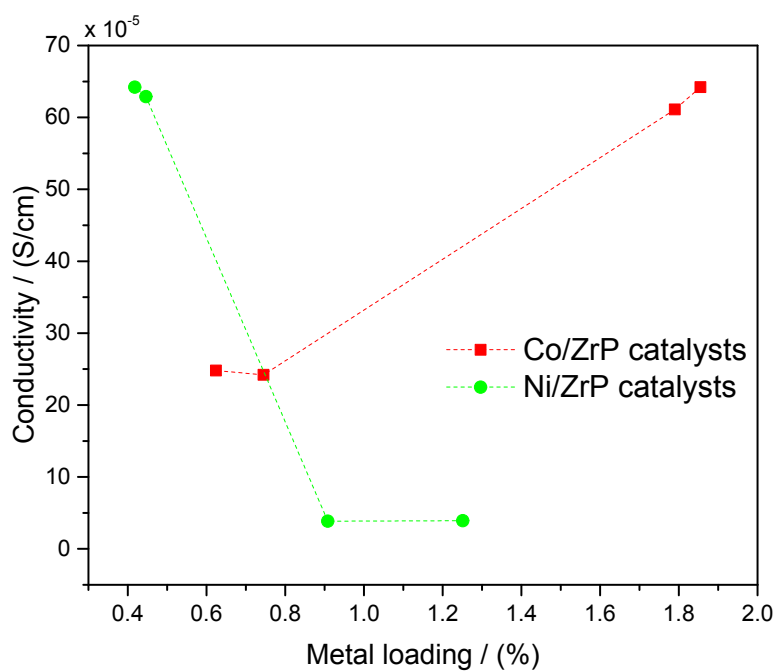


Figure S17. Conductivity vs metal loading for Co and Ni/ZrP catalysts.

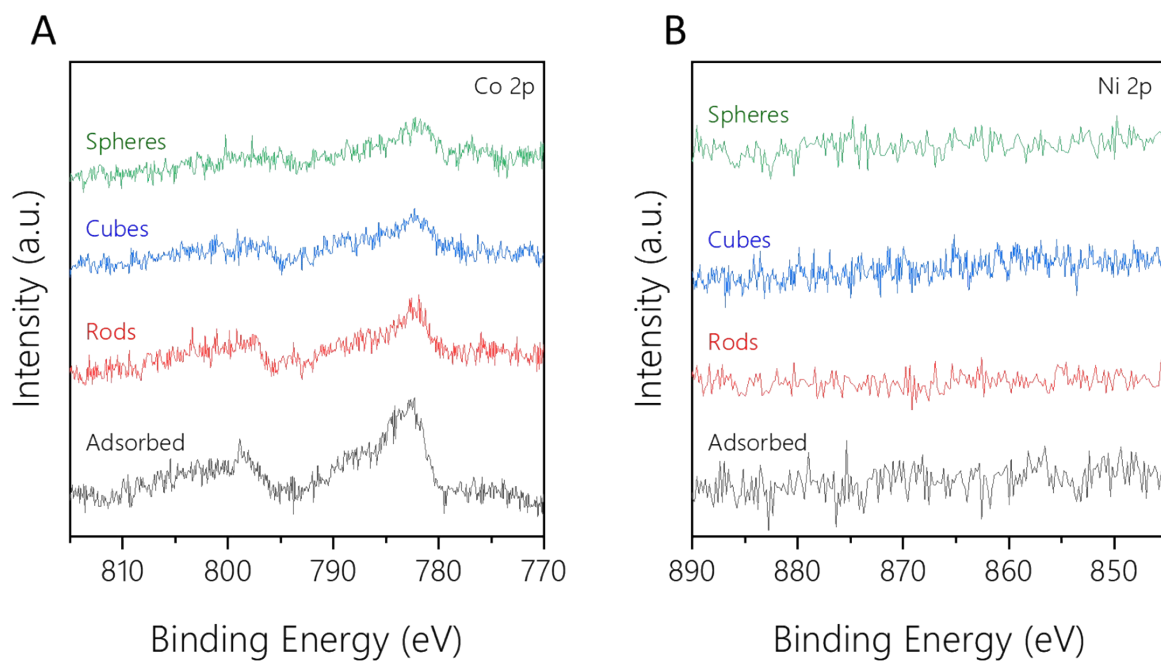


Figure S18. XPS spectra for A) Co-modified ZrP catalysts and B) Ni-modified ZrP catalysts.

Table S1. Mass activity (at $\eta = 350$ mV) and Tafel slope comparison for metal-modified ZrP catalysts and selected state-of-the-art OER catalysts in alkaline electrolyte.¹

Catalyst	Mass activity @ $\eta = 350$ mV (A/g)	Tafel Slopes (mV/dec)
Co/ZrP _{α,hexagonal}	115	79
Co/ZrP _{rod}	4	79
Co/ZrP _{cube}	72	82
Co/ZrP _{sphere}	56	86
Ni/ZrP _{α,hexagonal}	50	132
Ni/ZrP _{rod}	85	127
Ni/ZrP _{cube}	91	134
Ni/ ZrP _{sphere}	272	67
IrO _x	257	47
Co ₃ O ₄	30	49
NiFeO _x H _y	633	42

References:

- 1) D. Xu, M. Stevens, M. Cosby, S. Z. Oener, A. Smith, L. J. Enman, K. E. Ayers, C. B. Capuano, J. Renner, N. Danilovic, Y. Li, H. Wang, Q. Zhang and S. W. Boettcher, *ACS Catal.* 2019, **9**, 7-15.