

Supplementary Materials

Joule heating to grain-boundary-rich RuP₂ for efficient electrocatalytic hydrogen evolution in a wide pH range

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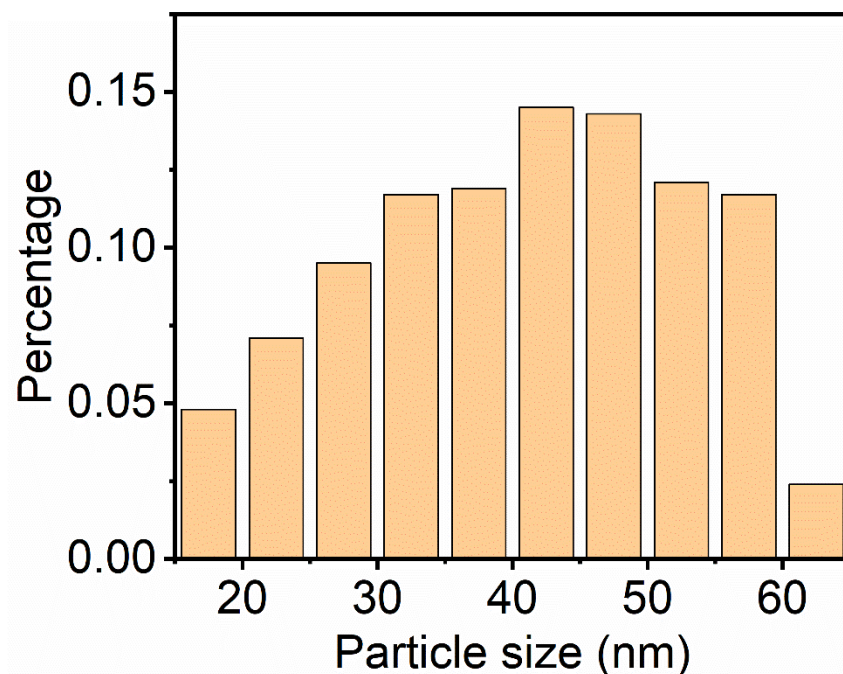
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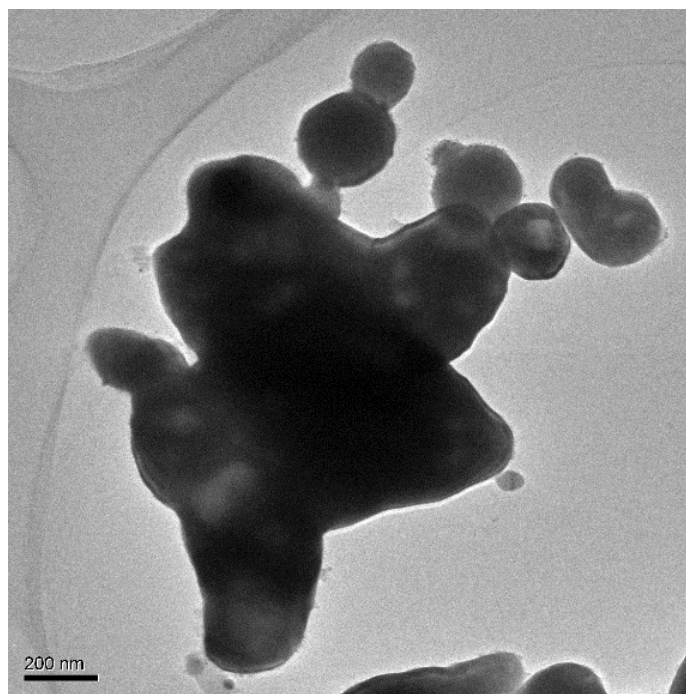
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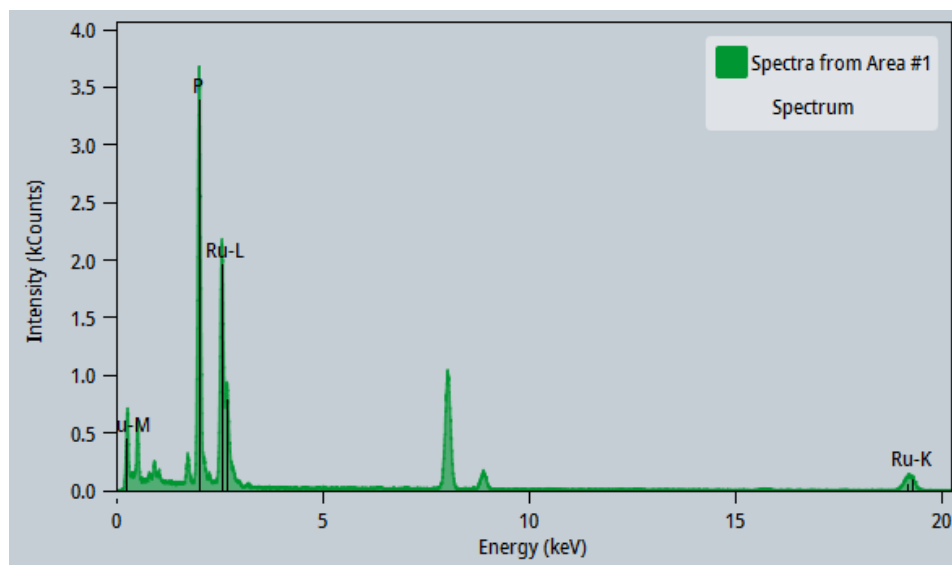
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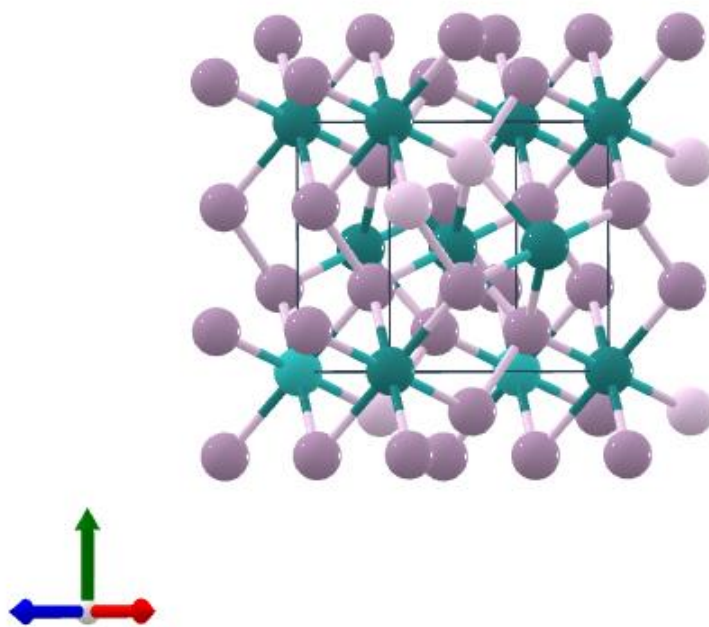
Supplementary Figure 1. The size distribution of RuP₂ JH.



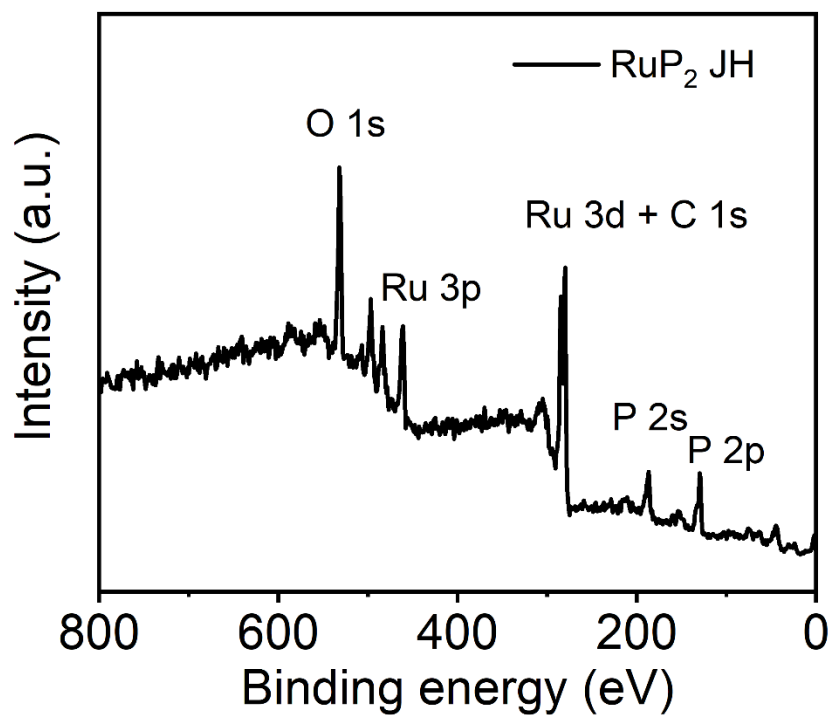
Supplementary Figure 2. TEM image of bulk RuP₂.



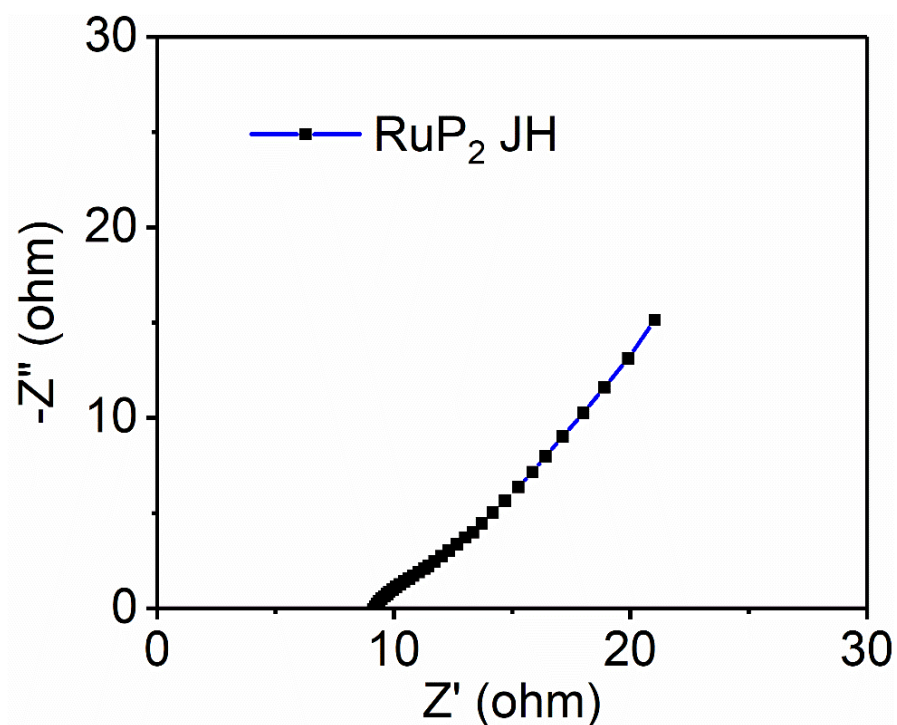
Supplementary Figure 3. EDS pattern for RuP₂ JH.



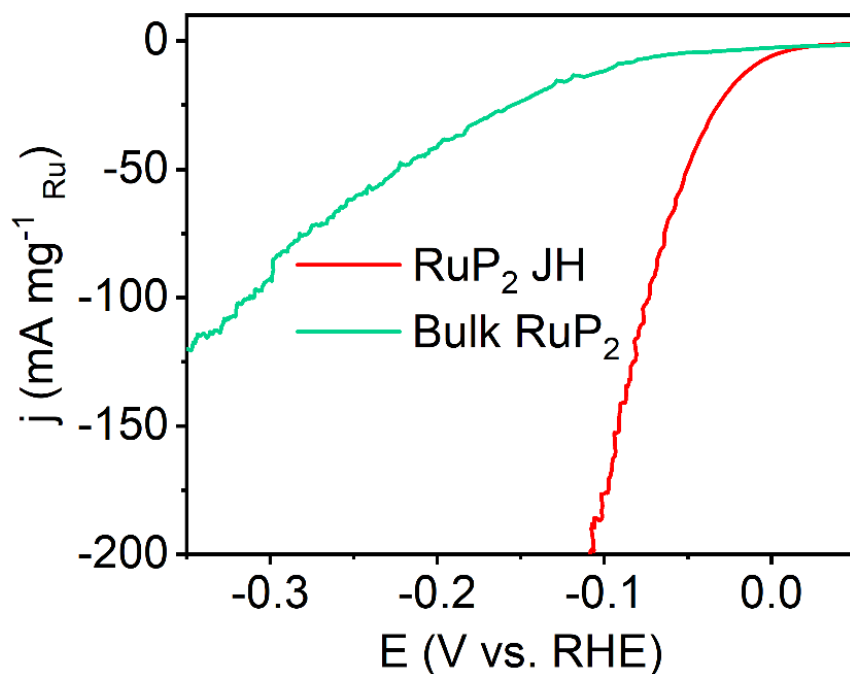
Supplementary Figure 4. Structure models of RuP₂.



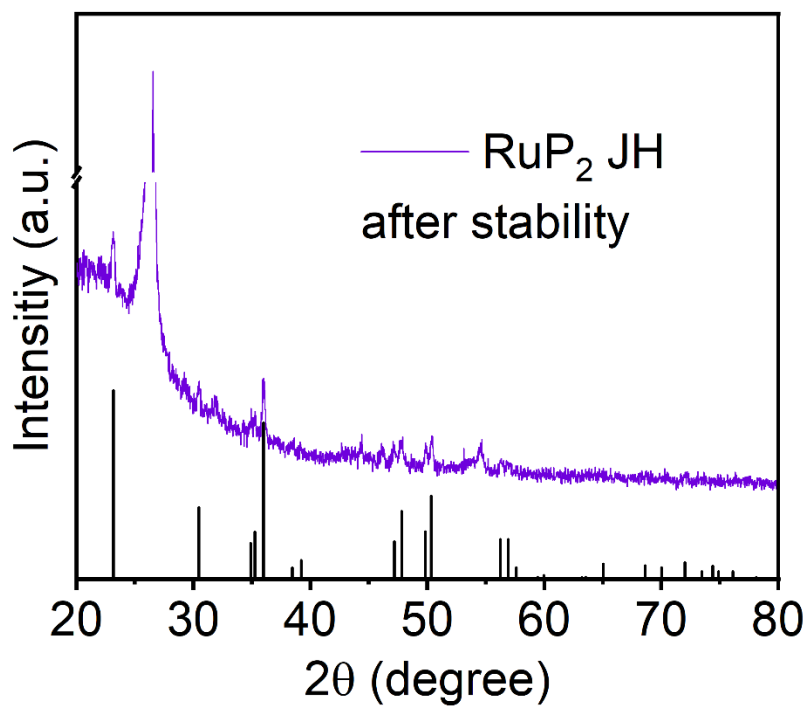
Supplementary Figure 5. XPS survey spectrum for RuP₂ JH.



Supplementary Figure 6. Nyquist plots of RuP₂ JH recorded at 0 V vs. RHE in 0.5 M H₂SO₄.



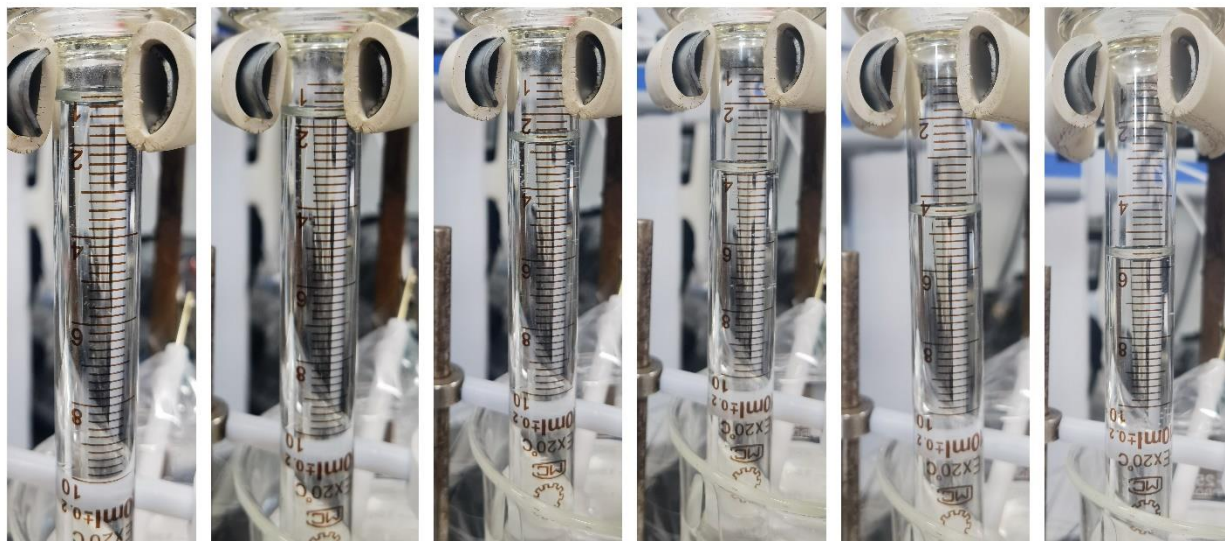
Supplementary Figure 7. HER polarization curves for RuP₂ JH and bulk RuP₂ normalized by the mass of Ru.



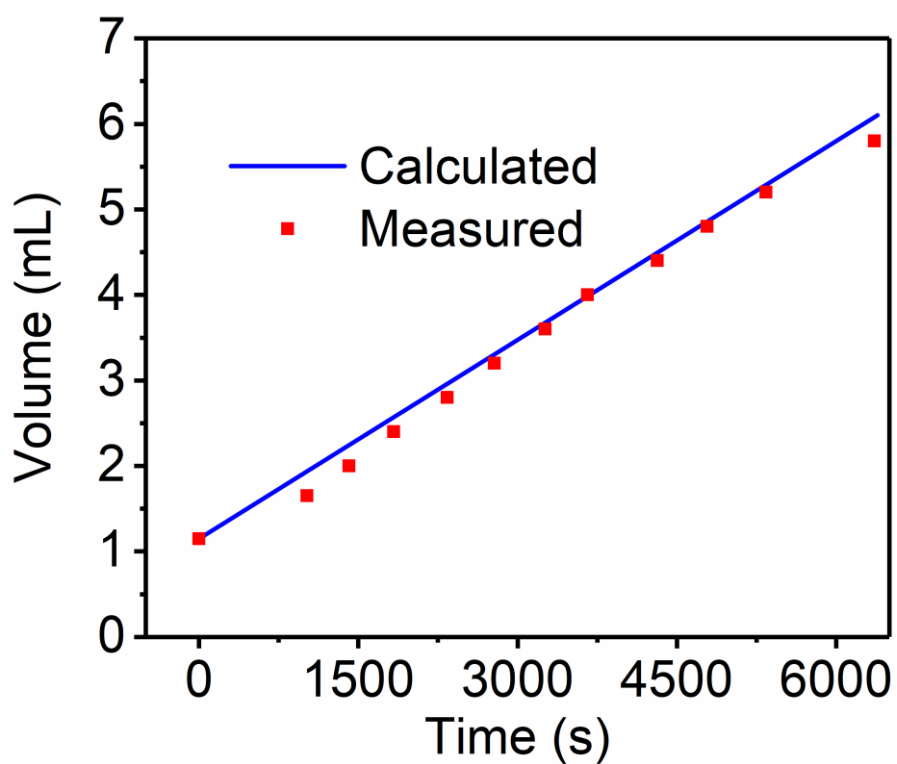
Supplementary Figure 8. XRD pattern of RuP₂ JH after the stability test.



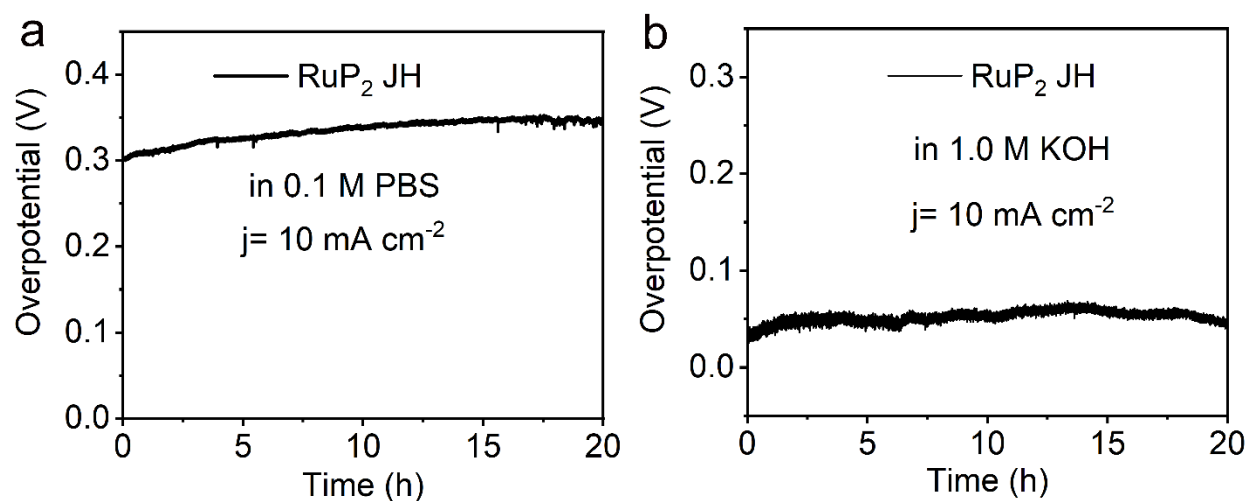
Supplementary Figure 9. The digital photograph captures the hydrogen generated by water drainage strategy.



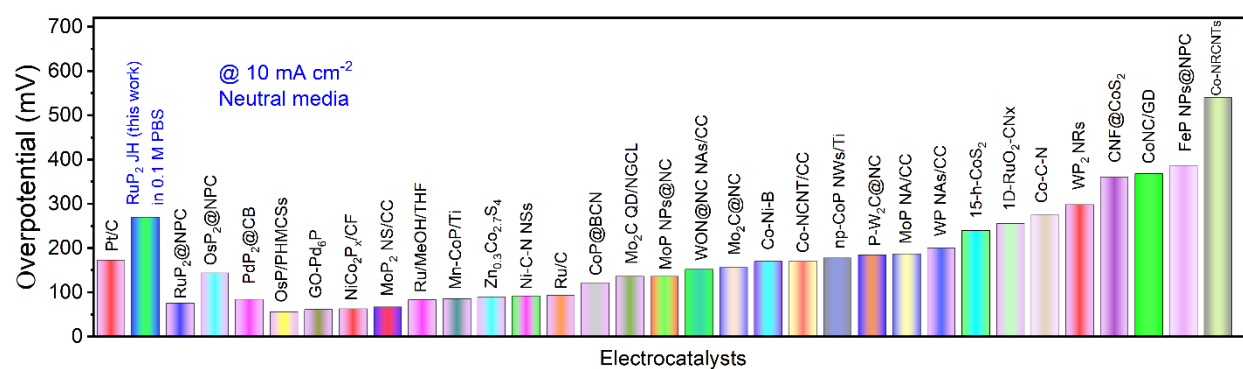
Supplementary Figure 10. Enlarged digital images of the measuring cylinders, and levels of hydrogen gas generated at different times.



Supplementary Figure 11. Amount of hydrogen theoretically calculated and experimentally measured versus time for RuP_2 JH in 0.5 M H_2SO_4 .



Supplementary Figure 12. Galvanostatic tests for the RuP₂ JH in (a) 0.1 M PBS and (b) 1.0 M KOH solutions held at a constant current density of 10 mA cm^{-2} for the HER (without iR-correction).



Supplementary Figure 13. Comparison of the overpotentials at 10 mA cm^{-2} with recently reported HER electrocatalysts in neutral media.

Supplementary Table 1. Comparison of HER performance for RuP₂ JH with other HER electrocatalysts in acidic solution

| Catalysts | Electrolytes | $\eta@j$ (mV@mA cm ⁻²) | Tafel slope (mV dec ⁻¹) | Stability | Catalyst loading (mg cm ⁻²) | Ref. |
|---|--------------------------------------|---|-------------------------------------|-----------------------------|---|-----------|
| RuP ₂ JH | 0.5 M H ₂ SO ₄ | 22@10 | 49 | 45h@10mA cm ⁻² | 0.97 | This work |
| RuP ₂ @NPC | 0.5 M H ₂ SO ₄ | 38@10 | 38 | 11h@10mA cm ⁻² | 1.0 | 1 |
| RuP ₂ -C@RuP ₂ -C | 0.5 M H ₂ SO ₄ | 17@10 | 19 | 20h@10mA cm ⁻² | 0.85 | 2 |
| RuP-475 | 0.5 M H ₂ SO ₄ | 46@10 | | 20h@20mA cm ⁻² | - | 3 |
| Ru ₂ P/RGO-20 | 0.5 M H ₂ SO ₄ | 22@10 | 29 | 10h@20mA cm ⁻² | 1.0 | 4 |
| Ru ₂ P nanoparticles | 0.5 M H ₂ SO ₄ | 55@10 | 30 | 10h@10mA cm ⁻² | - | 5 |
| IrP ₂ @NC | 0.5 M H ₂ SO ₄ | 8@10 | 50 | 20h@10mA cm ⁻² | 0.7 | 6 |
| IrP ₂ /NPC | 0.5 M H ₂ SO ₄ | 221@10 | 89 | 12h@10mA cm ⁻² | 1.6 μg _{Ir} | 7 |
| OsP ₂ @NPC | 0.5 M H ₂ SO ₄ | 38@10 | 40 | 80h@10mA cm ⁻² | | 8 |
| RhP ₂ @NPGC | 0.5 M H ₂ SO ₄ | 0.21 mA cm _{ECSA} ⁻² @-0.1V | - | 8h@10mA cm ⁻² | - | 9 |
| RhP ₂ /Rh@NPG | 0.5 M H ₂ SO ₄ | 20.1@10 | 21.6 | 40h@50mA cm ⁻² | 0.3 | 10 |
| RhPx@NPC | 0.5 M H ₂ SO ₄ | 20@10 | 32 | 10h@10mA cm ⁻² | - | 11 |
| Rh ₂ P/C | 0.5 M H ₂ SO ₄ | 5.5@5 | - | - | 0.0037 | 12 |
| PdP ₂ @CB | 0.5 M H ₂ SO ₄ | 27.5@10 | 29.5 | 10h@10mA cm ⁻² | - | 13 |
| Rh ₂ S ₃ | 0.5 M H ₂ SO ₄ | 122@10 | 44 | 10000 CV | 0.92 | 14 |
| IrNi NCs | 0.5 M H ₂ SO ₄ | 32@20 | - | 1h@5mA cm ⁻² | - | 15 |
| IrCo-PHNC | 0.1 HClO ₄ | 21@10 | | 1h@5mA cm ⁻² | - | 16 |
| Ir/Si | 0.5 M H ₂ SO ₄ | 22@10 | 20 | ~13.9h@5mA cm ⁻² | - | 17 |
| RuB ₂ | 0.5 M H ₂ SO ₄ | 18@10 | 38.9 | 50h@10mA cm ⁻² | 0.281 | 18 |
| Ru/NG-750 | 0.5 M H ₂ SO ₄ | 53@10 | 44 | 5000 CV | 0.082 | 19 |

| | | | | | | |
|---|--------------------------------------|--------|------|-----------------------------|-------|----|
| Ru@C ₂ N | 0.5 M H ₂ SO ₄ | 22@10 | 30 | 10000 CV | 0.285 | 20 |
| 1D-RuO ₂ -CN _x | 0.5 M H ₂ SO ₄ | 93@10 | 40 | 5000 CV | 0.17 | 21 |
| Ru/C ₃ N ₄ /C | 0.5 M H ₂ SO ₄ | ~75@10 | - | - | 0.204 | 22 |
| Ru/MeOH/THF | 0.5 M H ₂ SO ₄ | 83@10 | 46 | 12h@10mA cm ⁻² | 0.352 | 23 |
| Ru/NC | 0.5 M H ₂ SO ₄ | 75@10 | - | - | 0.013 | 24 |
| Ru-MoO ₂ | 0.5 M H ₂ SO ₄ | 55@10 | 44 | 12h@10mA cm ⁻² | 0.57 | 25 |
| C ₃ N ₄ -Ru-F | 0.5 M H ₂ SO ₄ | 140@10 | 57 | 1000 CV | 0.153 | 26 |
| Ru particles | 0.5 M H ₂ SO ₄ | 185@10 | 100 | 1000 CV | 0.257 | 27 |
| Ru/GLC | 0.5 M H ₂ SO ₄ | 35@10 | 30 | 1000 CV | 0.4 | 28 |
| CoP/CC | 0.5 M H ₂ SO ₄ | 67@10 | 51 | 22h@~100mA cm ⁻² | 0.92 | 29 |
| np-CoP NWs/Ti | 0.5 M H ₂ SO ₄ | 95@10 | 65 | 50h@50mA cm ⁻² | 0.8 | 30 |
| CoP@BCN | 0.5 M H ₂ SO ₄ | 87@10 | 46 | 3.6h@10mA cm ⁻² | 0.4 | 31 |
| Mn-CoP/Ti | 0.5 M H ₂ SO ₄ | 49@10 | 55 | 10h@~20mA cm ⁻² | 5.61 | 32 |
| NiCo ₂ P _x /CF | 0.5 M H ₂ SO ₄ | 104@10 | 59.6 | 30h@20mA cm ⁻² | 5.9 | 33 |
| NiP ₂ NS/CC | 0.5 M H ₂ SO ₄ | 75@10 | 51 | 60h@40mA cm ⁻² | 4.3 | 34 |
| Co _{0.59} Fe _{0.41} P | 0.5 M H ₂ SO ₄ | 72@10 | 52 | 20h@10mA cm ⁻² | 0.35 | 35 |

Supplementary Table 2. Comparison of HER performance for RuP₂ JH with other HER electrocatalysts in alkaline electrolyte

| Catalysts | Electrolytes | $\eta@j$ (mV@mA cm ⁻²) | Ref. |
|---|--------------|------------------------------------|-----------|
| RuP ₂ JH | 1.0 M KOH | 22 | This work |
| RuP ₂ -C@RuP ₂ -C | 1.0 M KOH | 9 | 2 |
| RuP ₂ NPs CPM | 1.0 M KOH | 24 | 36 |
| Br-Ru/RuP ₂ | 1.0 M KOH | 34 | 37 |

| | | | |
|---|-----------|------|----|
| RuP ₂ /CNT | 1.0 M KOH | 40 | 38 |
| Ru ₂ P | 1.0 M KOH | 54 | 39 |
| Rh ₂ P | 1.0 M KOH | 30 | 40 |
| Rh _x P/NPC | 1.0 M KOH | 24 | 41 |
| GO-Pd ₆ P | 1.0 M KOH | 40.7 | 42 |
| PdP ₂ @CB | 1.0 M KOH | 35.4 | 43 |
| OsP ₂ @NPC | 1.0 M KOH | 70 | 44 |
| IrP ₂ @NC | 1.0 M KOH | 28 | 6 |
| IrP ₂ @PC | 1.0 M KOH | 25 | 45 |
| IrP ₂ -rGO | 1.0 M KOH | 28 | 46 |
| Ordered PtP ₂ | 1.0 M KOH | 33.6 | 47 |
| Pt ₅ P ₂ NCs/a-NiPi | 1.0 M KOH | 9 | 48 |
| hydrous RuO ₂ | 1.0 M KOH | 60 | 49 |
| RuCo alloy | 1.0 M KOH | 28 | 50 |

Supplementary Table 3. Comparison of HER performance for RuP₂ JH with other HER electrocatalysts in neutral electrolyte

| Catalysts | Electrolytes | Overpotential@j (mV@mA cm ⁻²) | Ref. |
|--------------------------------------|--------------|--|-----------|
| RuP ₂ JH | 0.1 M PBS | 270@10 | This work |
| RuP ₂ @NPC | 1.0 M PBS | 57@10 | 1 |
| RuP (L-RP/C) | 1.0 M PBS | 80@10 | 51 |
| GO-Pd ₆ P | 1.0 M PBS | 113@10 | 42 |
| Ru/C | 3.5 wt% NaCl | 93@10 | 52 |
| 1D-RuO ₂ -CN _x | 0.1 M PBS | 256@10 | 53 |
| Ru/MeOH/THF | 0.1 M PBS | 83@10 | 54 |
| Ru@Co-SAs/N-C | 1.0 M PBS | 55@10 | 55 |
| OsP ₂ @NPC | 1.0 M PBS | 54@10 | 44 |
| Rh ₂ S ₃ /NC | 1.0 M PBS | 46@10 | 56 |
| RhCu NTs | 0.1 M PBS | 57@10 | 57 |
| np-CoP NWs/Ti | 1.0 M PBS | 178@10 | 58 |
| CoP@BCN | 1.0 M PBS | 122@10 | 59 |
| WP NAs/CC | 1.0 M PBS | 200@10 | 60 |

| | | | |
|---------------------|-----------|--------|----|
| WP ₂ NRs | 1.0 M PBS | 298@10 | 61 |
| MoP NA/CC | 1.0 M PBS | 187@10 | 62 |
| MoP NPs@NC | 1.0 M PBS | 136@10 | 63 |
| FeP NPs@NPC | 1.0 M PBS | 386@10 | 64 |

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