

## Supplementary Information For

### **Boosting the hydrogen evolution performance of ultrafine ruthenium electrocatalysts by a hierarchical phosphide array promoter**

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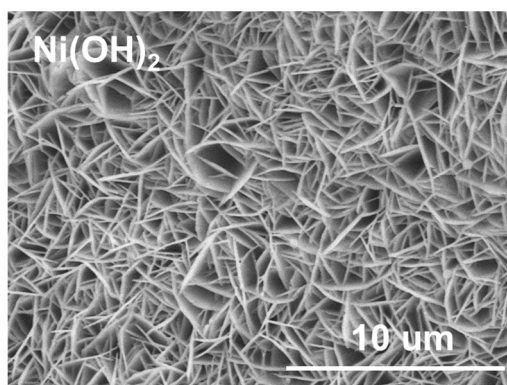
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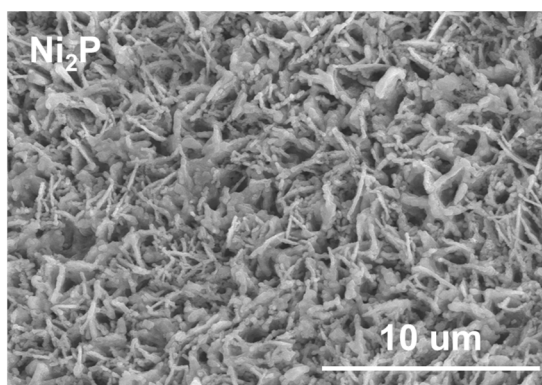
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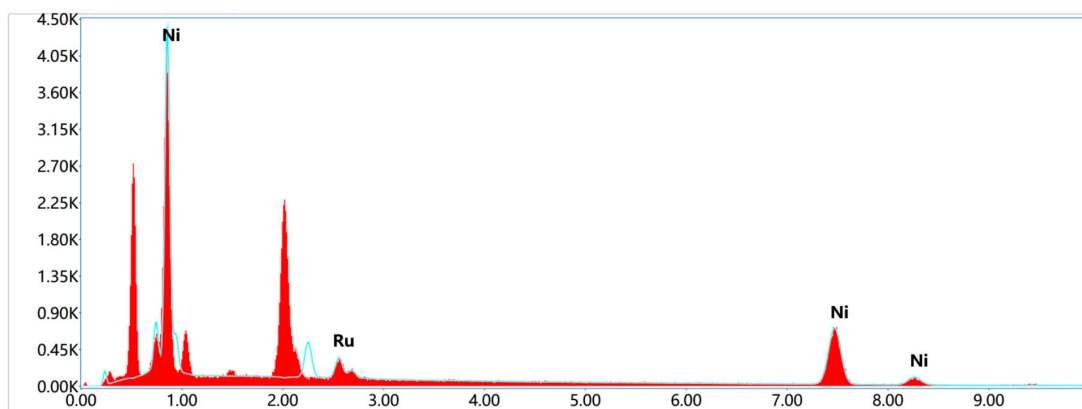
## Supplementary Figures



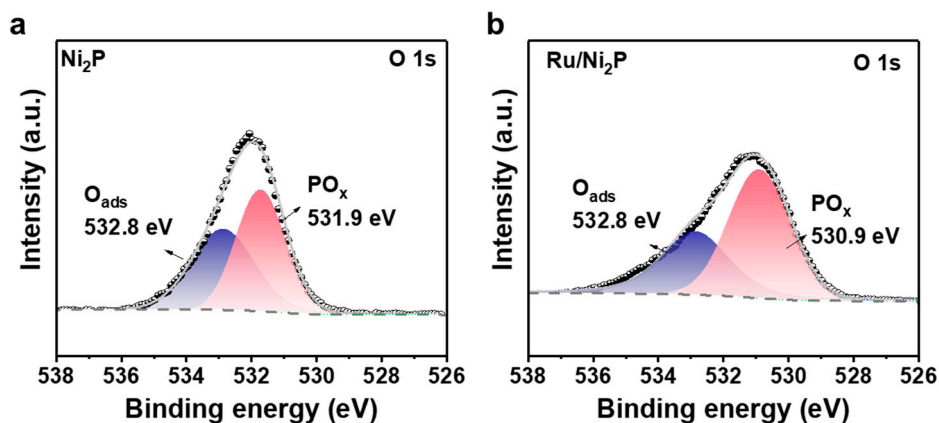
**Figure S1** SEM image of the as-prepared  $\text{Ni}(\text{OH})_2$  nanosheets.



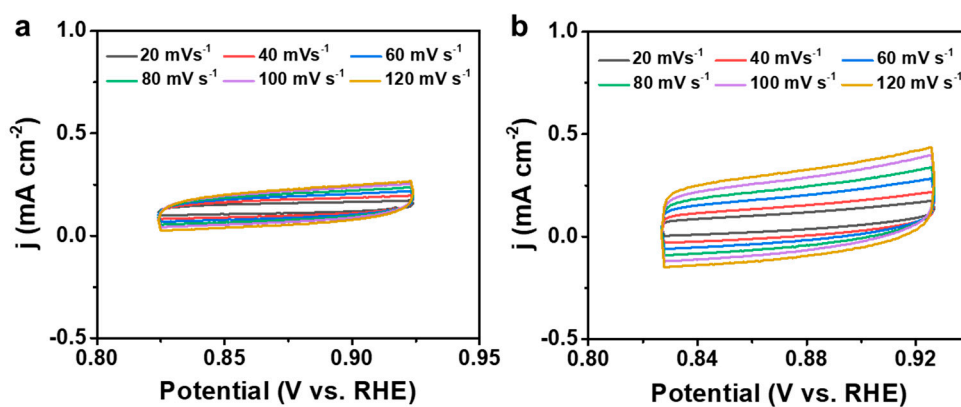
**Figure S2** SEM image of the as-prepared hierarchical  $\text{Ni}_2\text{P}$  promoter.



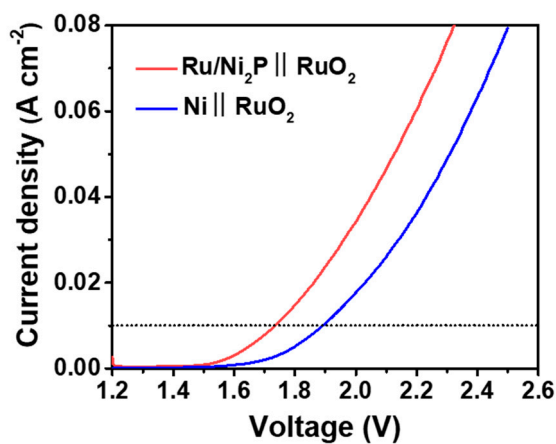
**Figure S3** EDS spectrum of the  $\text{Ru}/\text{Ni}_2\text{P}$  electrode, demonstrating a Ru content of 5.9 at%.



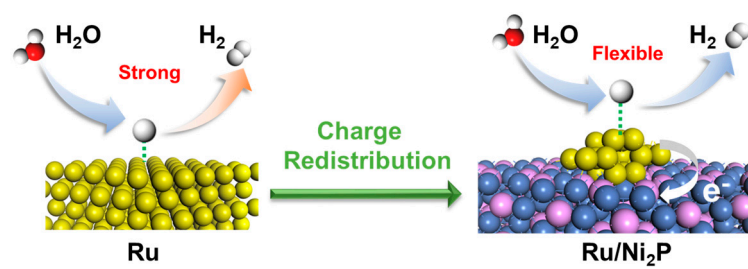
**Figure S4** O 1s XPS spectra of (a)  $\text{Ni}_2\text{P}$  (b)  $\text{Ru}/\text{Ni}_2\text{P}$ .



**Figure S5** CV profiles of the (a) Ni foam and (b)  $\text{Ni}_2\text{P}$  promoter.



**Figure S6** The overall water splitting performance of the Ni foam and  $\text{Ru}/\text{Ni}_2\text{P}$  HER catalyst after pairing with a commercial  $\text{RuO}_2$  OER catalyst.



**Figure S7** Schematic illustration of the enhanced HER activity at the Ru sites on as-designed Ru/Ni<sub>2</sub>P electrode.

## Supplementary Tables

**Table S1** Performance comparison of the Ru/Ni<sub>2</sub>P electrode with recently reported high-performance HER electrodes.

Electrodes	Overpotentials@10 mA cm <sup>-2</sup> (mV)	Tafel slopes (mV dec <sup>-1</sup> )	References
Ru/Ni <sub>2</sub> P	57	95.4	This work
Ni <sub>2</sub> P-Fe <sub>2</sub> P-Ru <sub>2</sub> P/NF	78.6	85.1	1
Pt/Rh <sub>2</sub> O <sub>3</sub> -CN <sub>x</sub>	26.7	35	2
2.20 wt% Ru SAs-Ni <sub>2</sub> P	57	75	3
Ru@N-P-C-800	43	115	4
RhSe <sub>2</sub>	81.6	96	5
S-RuP@NPS-900	92	90.2	6
CoMoRu/CC	210	149.1	7
Ru-Ru <sub>2</sub> P/PC	57	35.1	8
CoRu-O/A@HNC-2	85	72.5	9
RuNi alloy@SC	93	96	10

**Table S2** Equivalent circuit parameters of the Ni, Ni<sub>2</sub>P and Ru/Ni<sub>2</sub>P electrodes at a HER overpotential of 100 mV.

Electrodes	R <sub>s</sub> (Ω)	R <sub>ct</sub> (Ω)	Q (×10 <sup>-3</sup> Ω <sup>-1</sup> cm <sup>-2</sup> S <sup>n</sup> )	χ <sup>2</sup> ×10 <sup>-4</sup>
Ni	1.64	7.5	3.54	2.87
Ni <sub>2</sub> P	1.62	3.3	4.56	2.65
Ru/Ni <sub>2</sub> P	1.66	2.5	4.44	1.29

## Supplementary References

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