Electronic Supplementary Material (ESI) for Materials Horizons.

Developing energy-efficient N-doping technology to controllably construct N-Ru_2P@Ru nanospheres for high-efficient hydrogen evolution at an ampere-level current density

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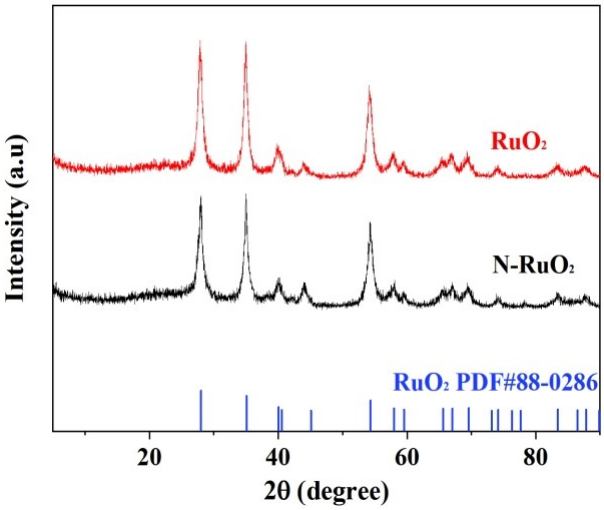

Figure S1 XRD pattern of RuO_2 and N-RuO_2.

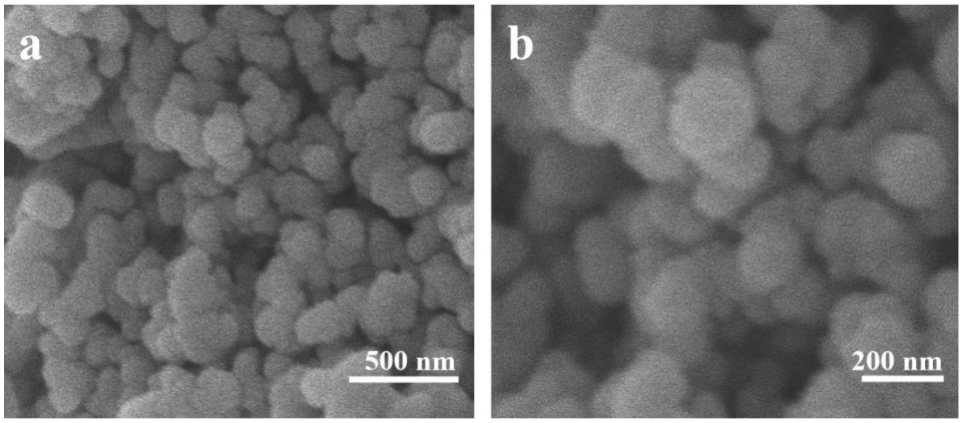

Figure S2 SEM images of Ru_2P@Ru.

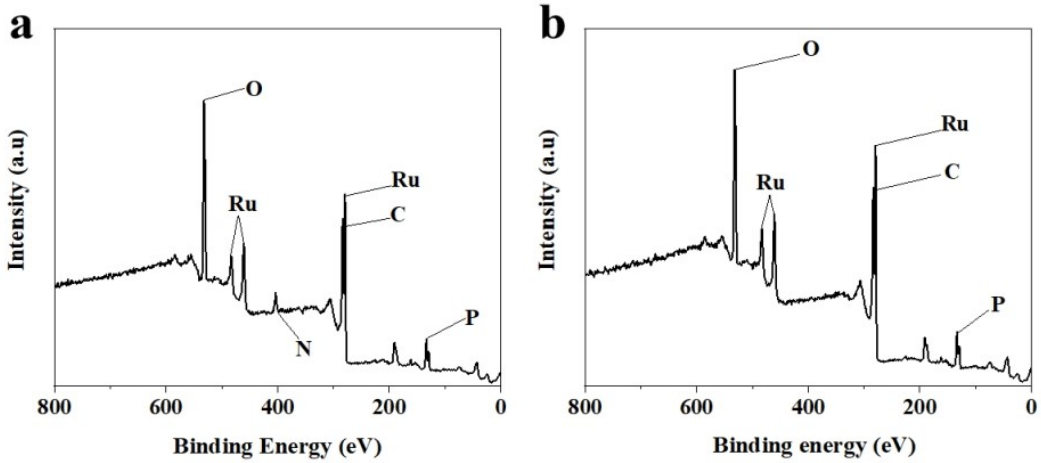

Figure S3 XPS survey of N-Ru_2P@Ru and Ru_2P@Ru.

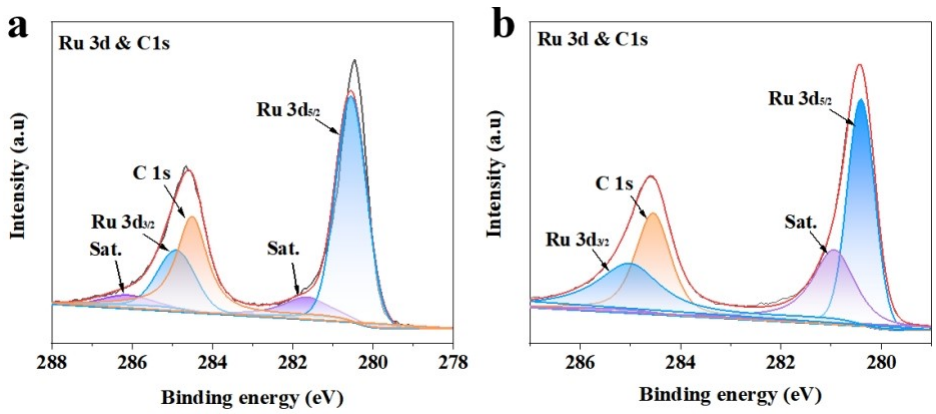

Figure S4 High-resolution spectra of Ru 3d and C1s for N-Ru_2P@Ru and Ru_2P@Ru.

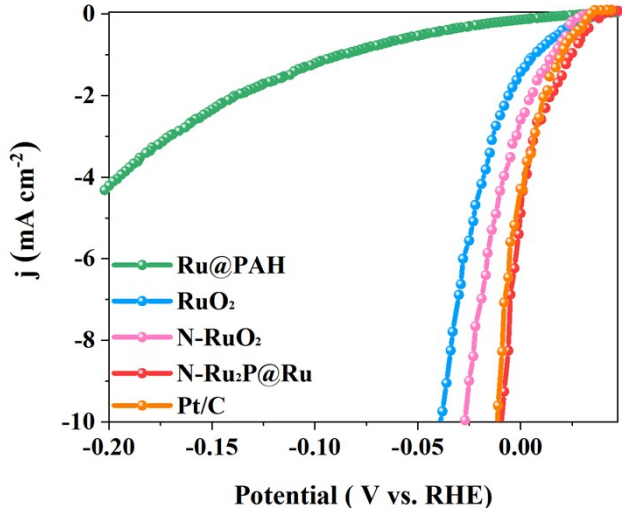

Figure S5 LSV curves of Ru@PAH, RuO_2, N-RuO_2, N-Ru_2P@Ru, and Pt/C in 1.0 M KOH.

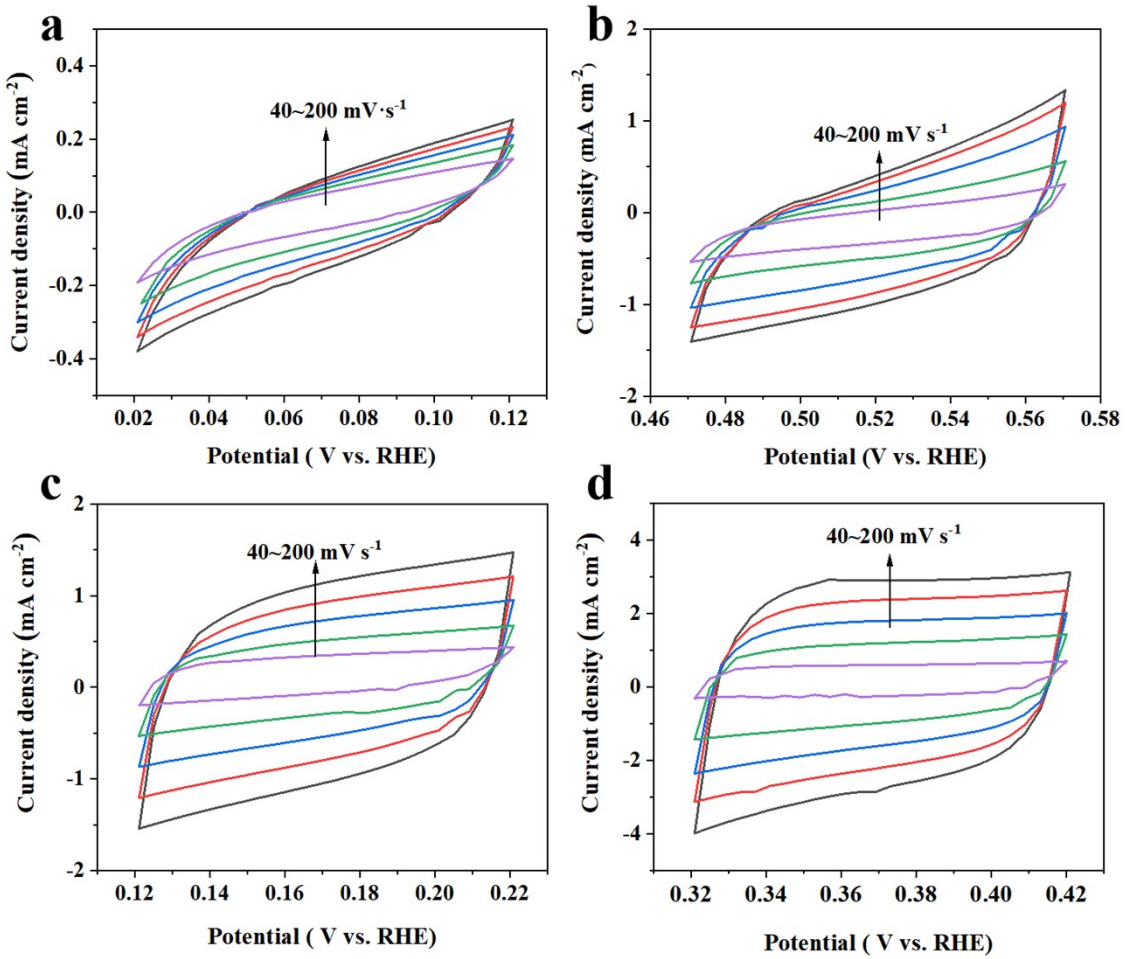

Figure S6 CVs curves at different scan rates of HER in 1.0 M KOH. (a) Ru@PAH. (b) RuO_2. (c) N-RuO_2. (d) N-Ru_2P@Ru.

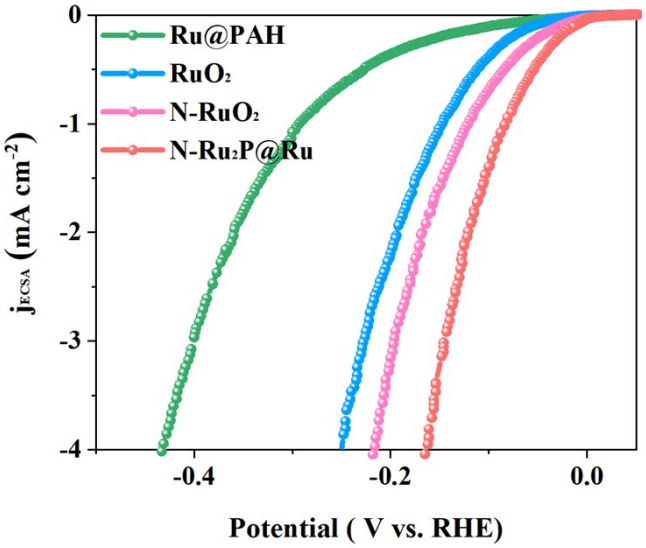

Figure S7 The ECSA normalized polarization curve of HER.

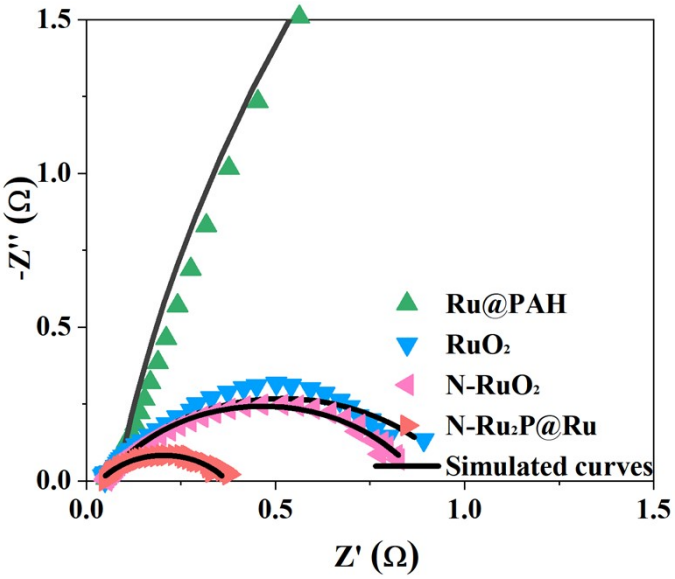

Figure S8 EIS Nyquist plots of HER in 1.0 M KOH.

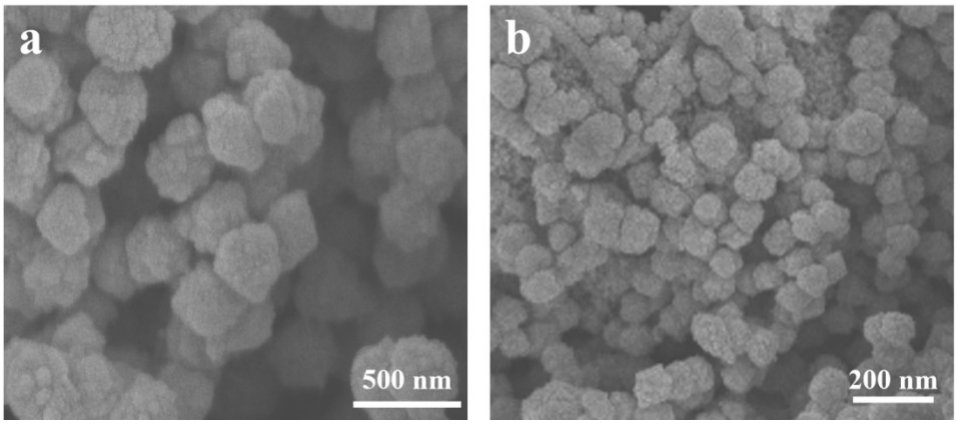

Figure S9 SEM images of N-Ru_2P@Ru after HER.

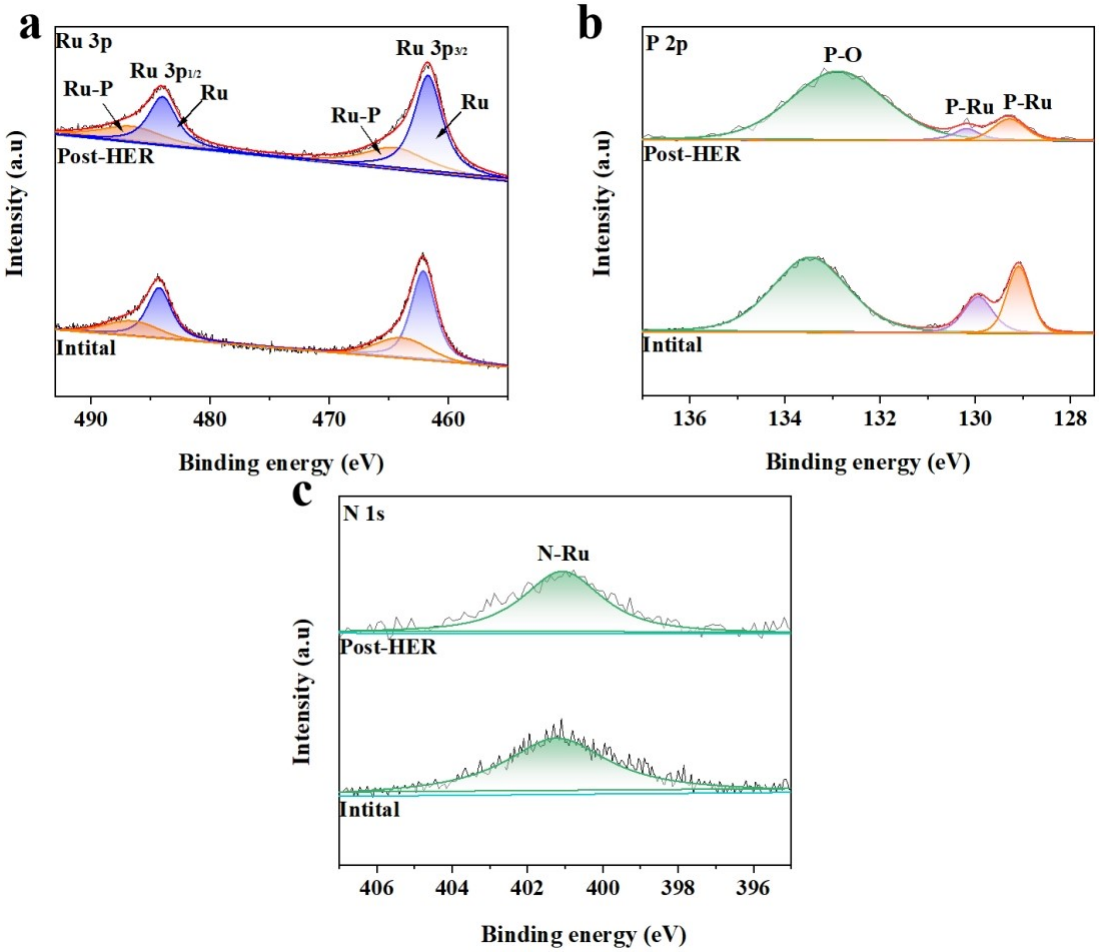

Figure S10 XPS spectra of N-Ru_2P@Ru after HER.

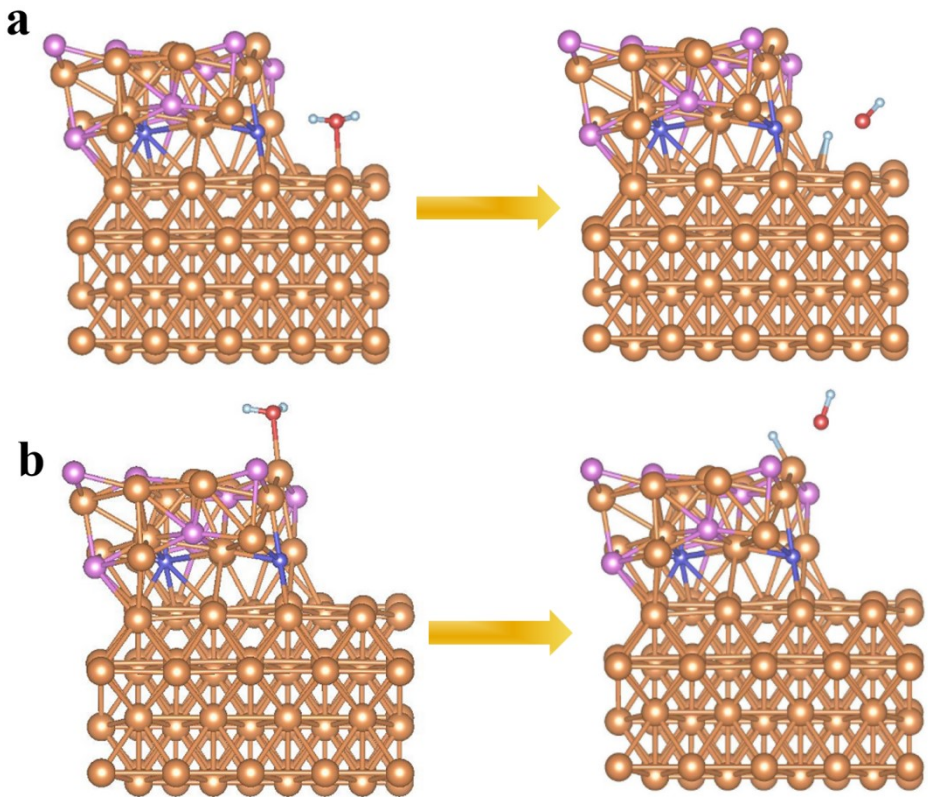

Figure S11 The structures of *H and *OH on freestanding N-Ru_2P@Ru heterointerface.

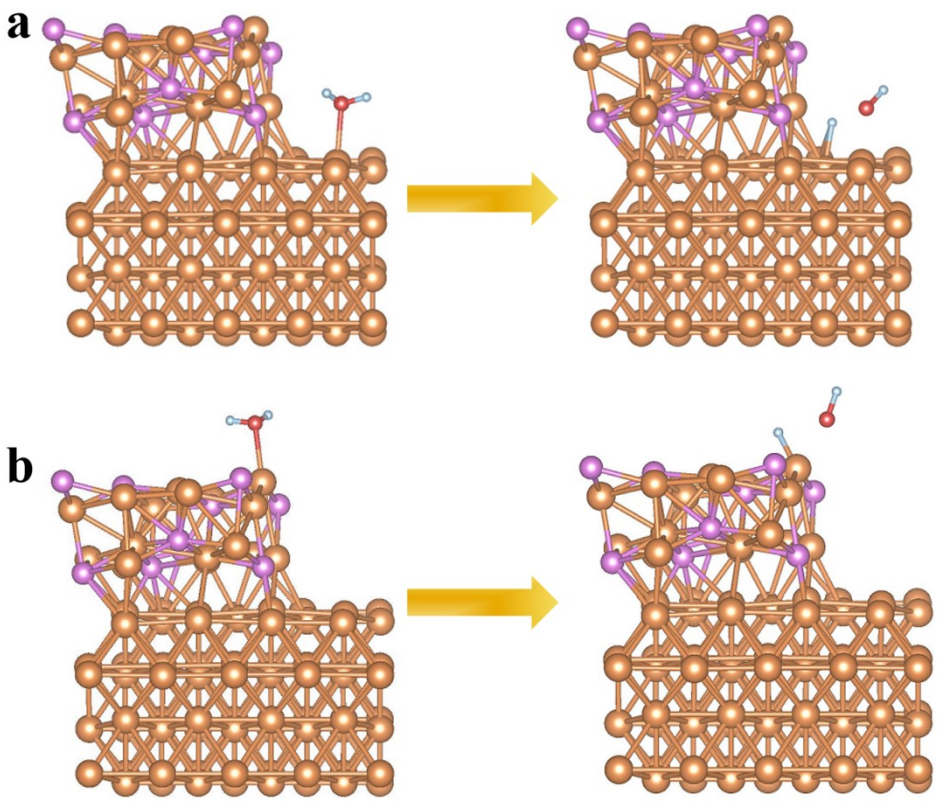

Figure S12 The structures of *H and *OH on freestanding Ru_2P@Ru heterointerface.

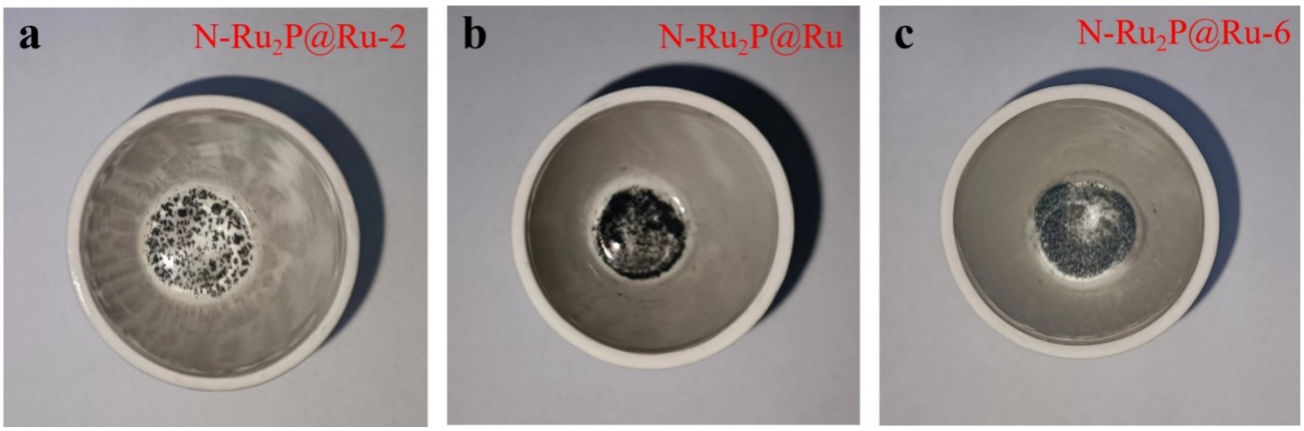

Figure S13 Crucible state at ammoniation time of 2, 4, and 6, respectively.

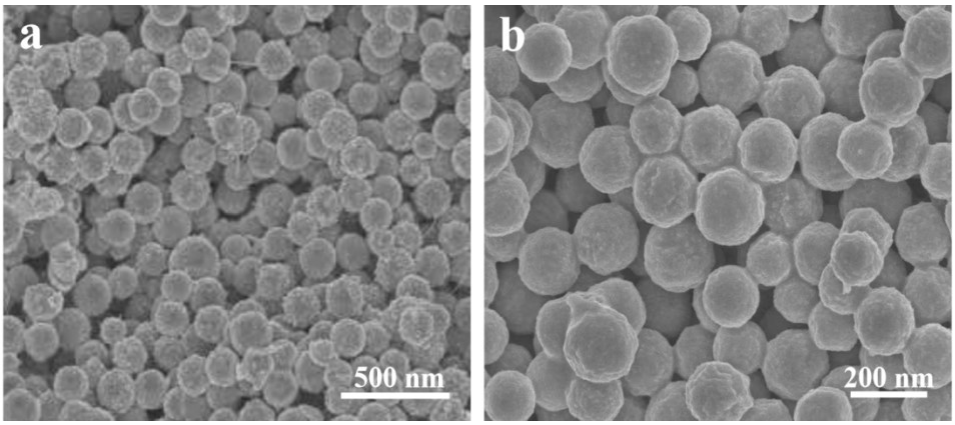

Figure S14 SEM images of N-Ru_2P@Ru-2.

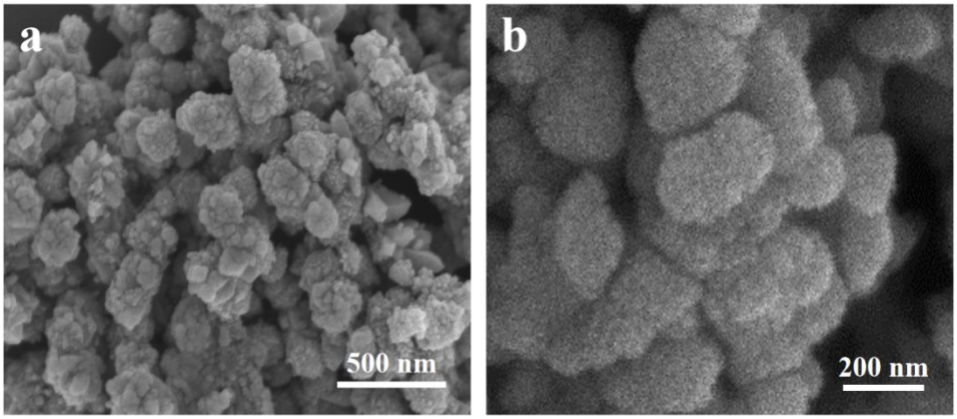

Figure S15 SEM images of N-Ru_2P@Ru-6.

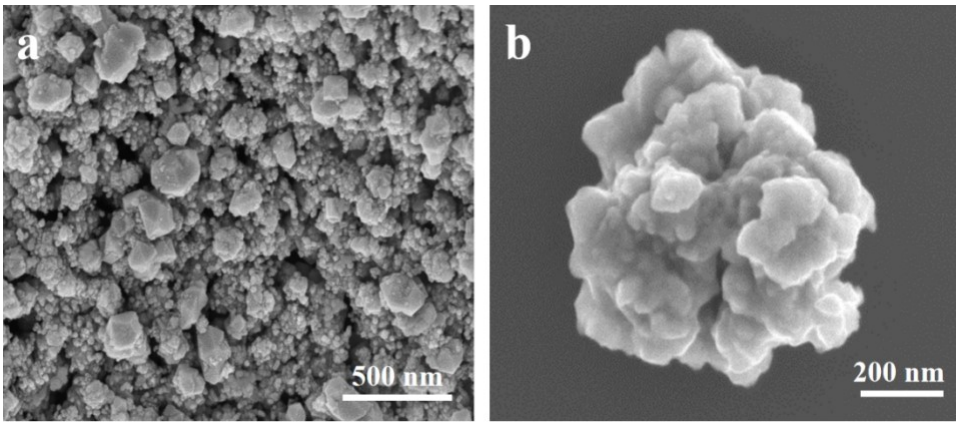

Figure S16 SEM images of N-Ru_2P@Ru-8.

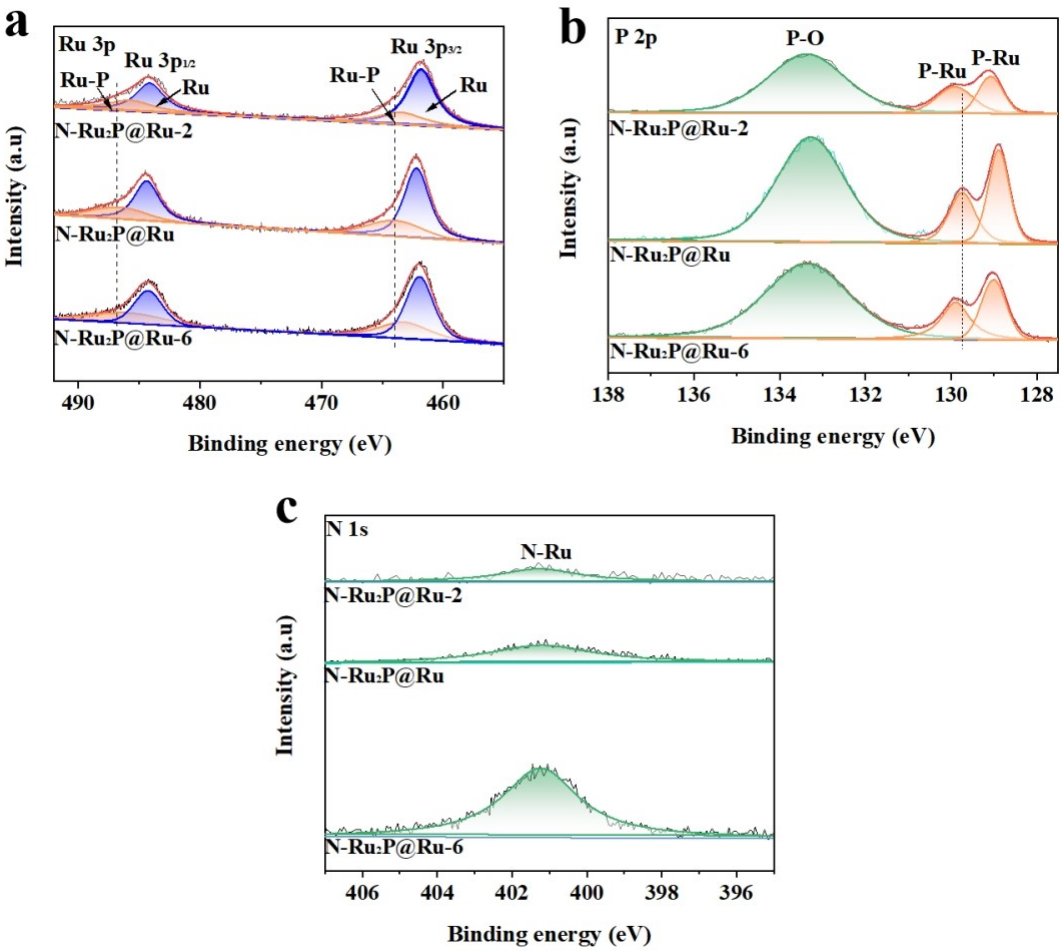

Figure S17 XPS spectraof N-Ru_2P@Ru-2, N-Ru_2P@Ru, and N-Ru_2P@Ru-6.

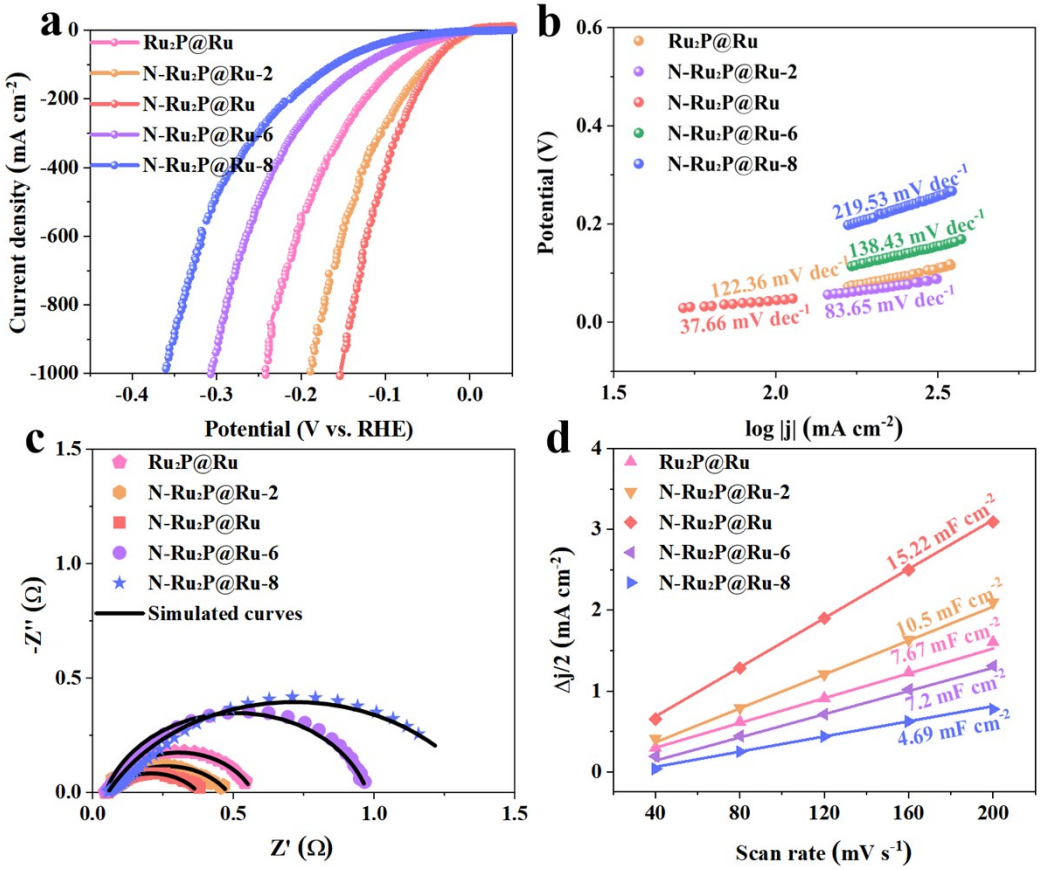

Figure S18 HER properties of catalyst samples in 1.0 M KOH. (a) LSV curves. (b) Tafel slopes. (c) EIS charts. (d) ECSA plots of Ru_2P@Ru, N-Ru_2P@Ru-2, N-Ru_2P@Ru, N-Ru_2P@Ru-6, and N-Ru_2P@Ru-8.

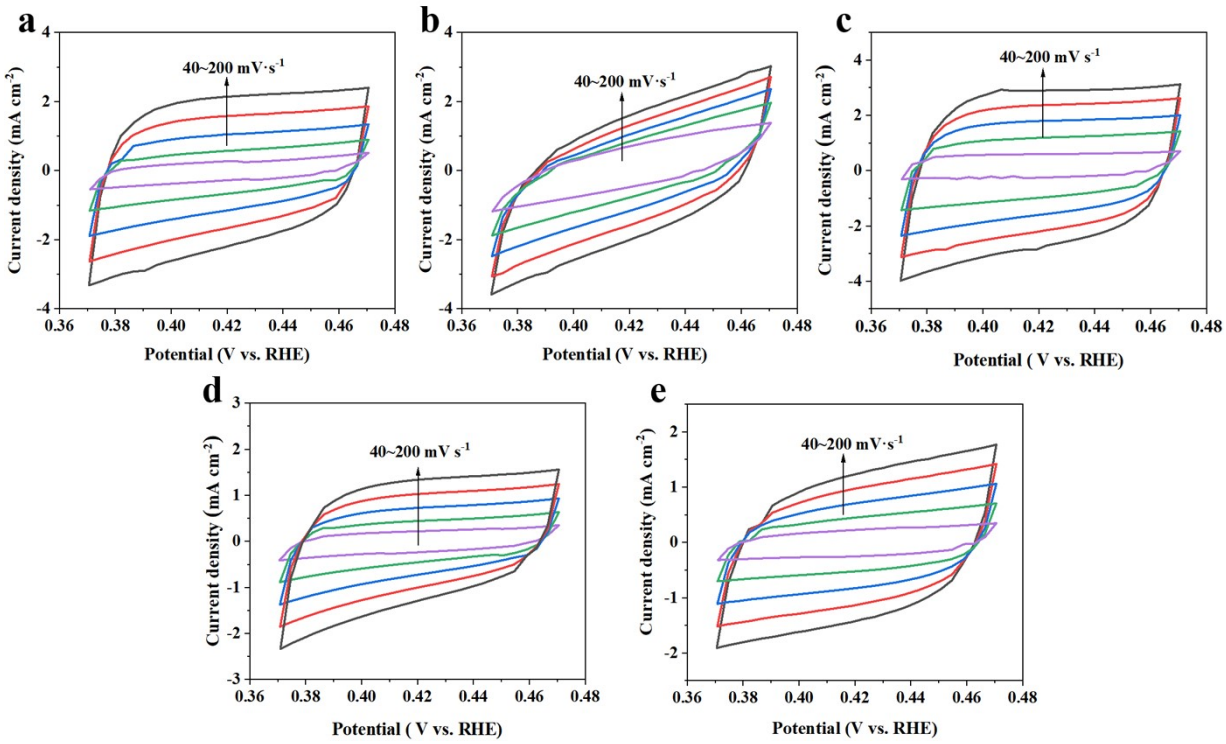

Figure S19 CVs curves at different scan rates of HER in 1.0 M KOH. (a) Ru_2P@Ru. (b) N-Ru_2P@Ru-2. (c) N-Ru_2P@Ru. (d) N-Ru_2P@Ru-6. (e) N-Ru_2P@Ru-8.

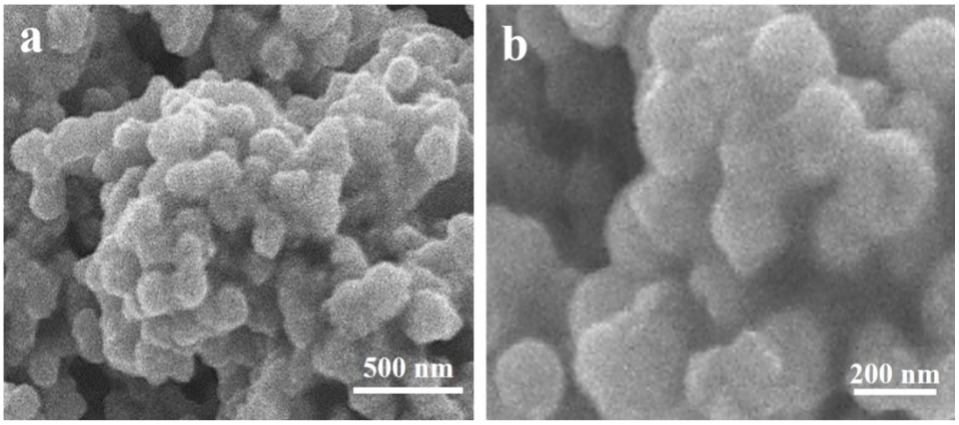

Figure S20 SEM images of N-Ru_2P@Ru-350.

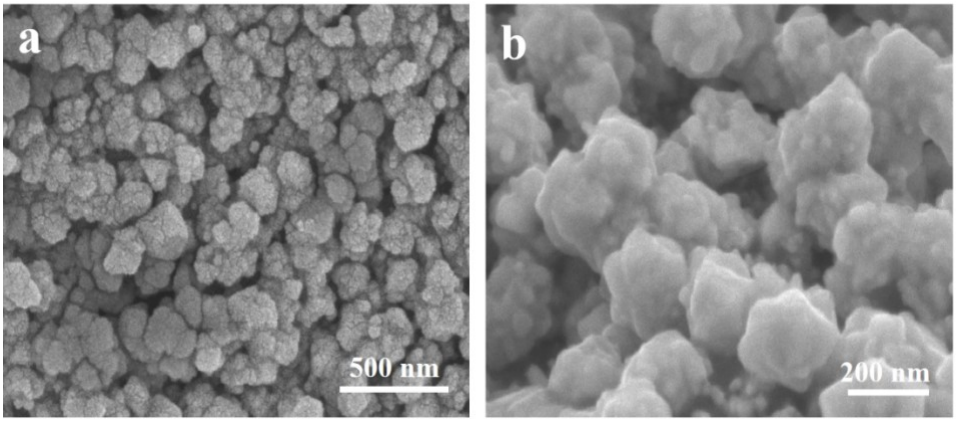

Figure S21 SEM images of N-Ru_2P@Ru-550.

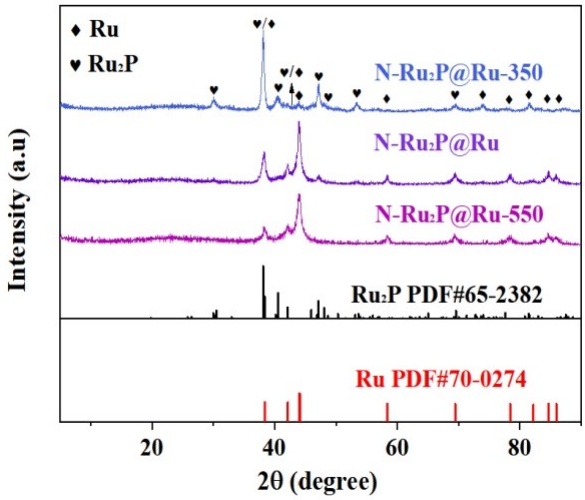

Figure S22 XRD pattern of N-Ru_2P@Ru-350, N-Ru_2P@Ru, and N-Ru_2P@Ru-550.

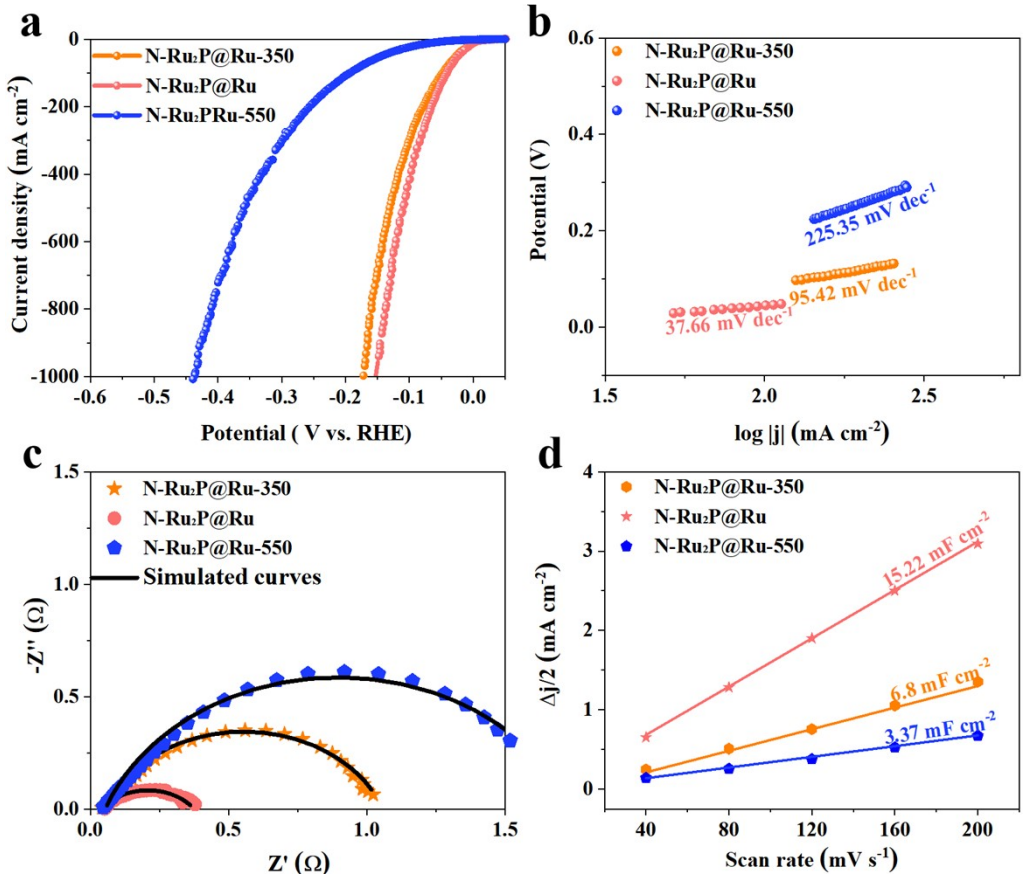

Figure S23 HER properties of catalyst samples in 1.0 M KOH. (a) LSV curves. (b) Tafel slopes. (c) EIS charts. (d) ECSA plots of N-Ru_2P@Ru-350, N-Ru_2P@Ru, and N-Ru_2P@Ru-550.

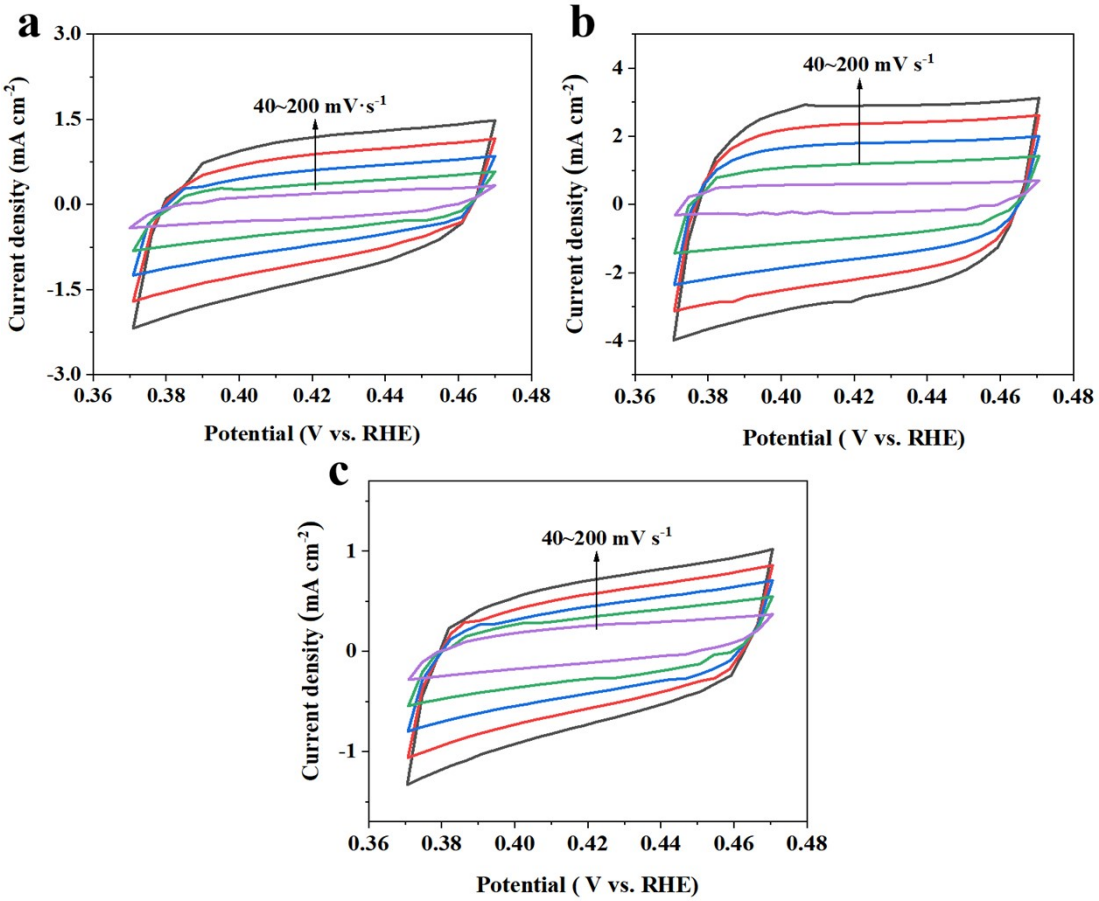

Figure S24 CVs curves at different scan rates of HER in 1.0 M KOH. (a) N-Ru_2P@Ru-350. (b) N-Ru_2P@Ru. (c) N-Ru_2P@Ru-550.

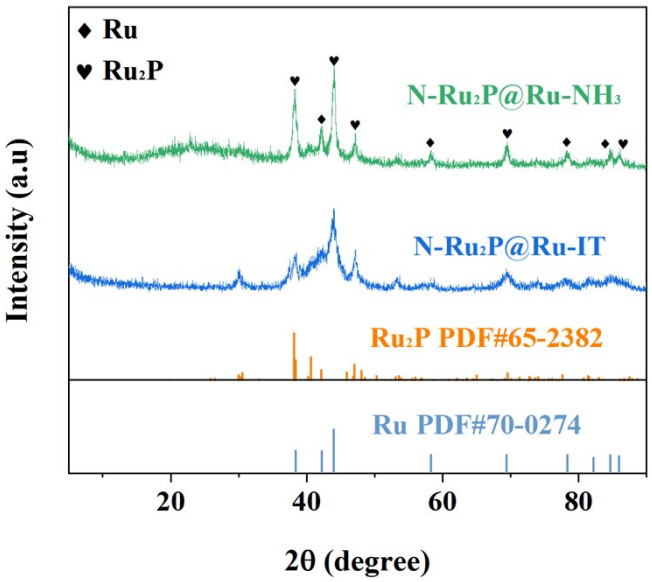

Figure S25 XRD pattern of N-Ru_2P@Ru-NH_3 and N-Ru_2P@Ru-IT.

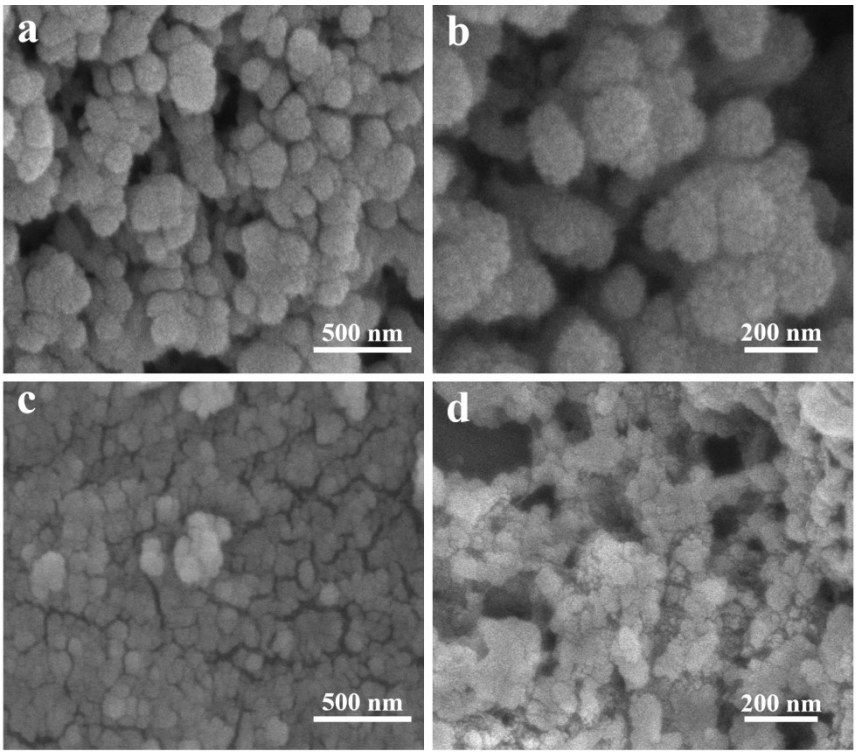

Figure S26 SEM images of (a-b) N-Ru_2P@Ru-IT and (c-d) N-Ru_2P@Ru-NH_3.

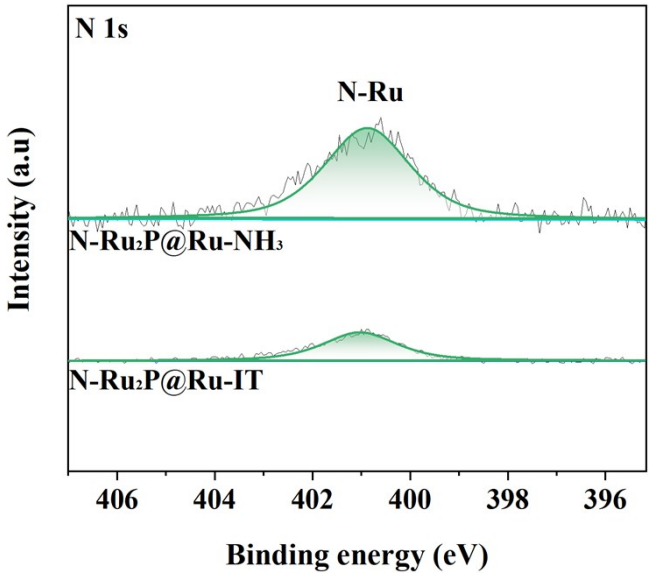

Figure S27 XPS spectra of N 1s for N-Ru_2P@Ru-NH_3 and N-Ru_2P@Ru-IT.

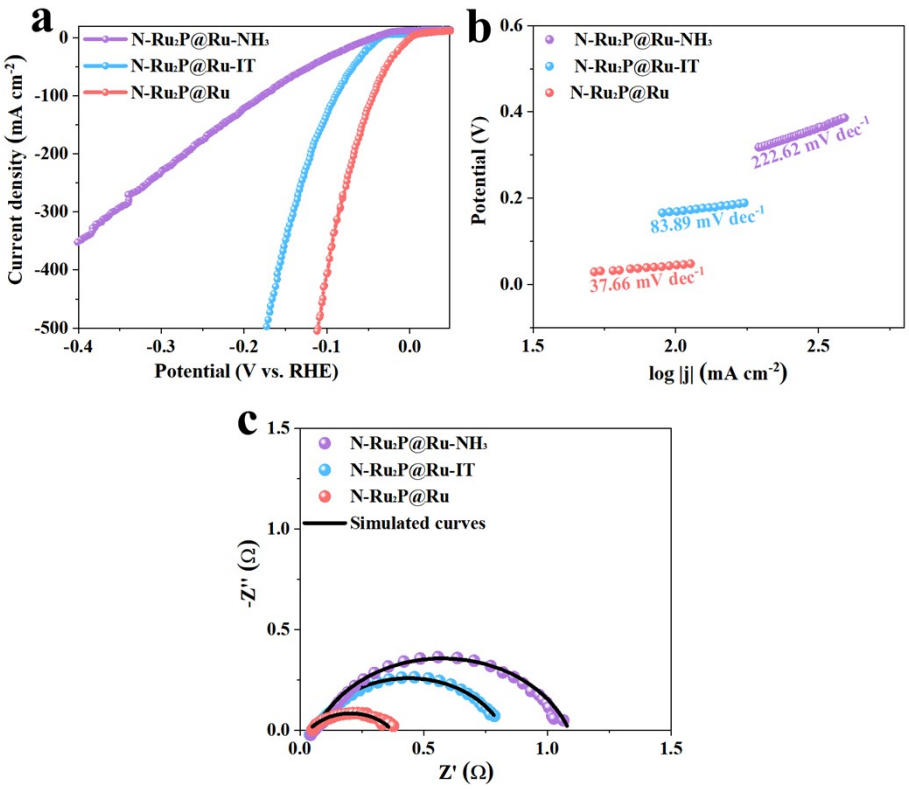

Figure S28 HER properties of catalyst samples in 1.0 M KOH. (a) LSV curves. (b) Tafel slopes. (c) EIS charts of N-Ru_2P@Ru-NH_3, N-Ru_2P@Ru-IT, and N-Ru_2P@Ru.

Table S1 Comparison of electrochemical surface area (ECSA) of N-Ru_2P@Ru catalyst and other comparative samples for HER.

Electrocatalysts	C_{dl} (mF cm^{-2})	C_{DI} (mF)	ECSA (cm^{-2})
Ru@PAH	0.47	0.47	11.75
RuO_2	7.18	7.18	179.5
N-RuO_2	7.22	7.22	180.5
N-Ru_2P@Ru	11.98	11.98	299.5

$C_{DL}=C_{dl}*S$; $S=1*1$ cm^2; $ECSA=C_{DL}/C_s$; $C_s=0.04$ mF cm^{-2}.

Table S2 Internal resistance (R_Ω) and charge transfer resistance (R_{ct}) of N-Ru_2P@Ru catalyst and other comparative samples for HER

Electrocatalysts	**R_Ω(Ω)**	**R_{ct}(Ω)**
Ru@PAH	0.0629	51.4
RuO_2	0.0567	0.822
N-RuO_2	0.0561	0.779
N-Ru_2P@Ru	0.0523	0.328

Table S3 The overpotential required for a noble metal-based electrocatalyst in an alkaline environment at 10 mA cm^{-2} has recently been reported.

Electrocatalysts	**j (mA cm^{-2})**	**η (mV)**	**References**
N-Ru_2P@Ru	10	9	This work
RuCo	10	10	[S1]
Ru/Mo_2C@NC	10	13	[S2]
$Ru_{1,n}$-NC	10	14.8	[S3]
Ru@$MoO(S)_3$	10	15.26	[S4]
Ru/RuO_2	10	20	[S5]
Ru@CDs	10	22	[S6]
Ru-Cu-MoO2	10	23	[S7]
Ru_2P@Ru/CNT	10	23	[S8]
Ru NRs/TiN	10	25	[S9]
Ru@β-HATB/CC	10	25	[S10]
Ru_2P	10	26	[S11]
Ru/RuO_2	10	27	[S12]
Co_1Ru@Ru/CN	10	30	[S13]
RuO_2-RuP_2/Ru	10	33	[S14]
M-Co NPs@Ru SAs/NC	10	34	[S15]
$NiRu_{0.13}$-BDC	10	34	[S16]
a-Ru@Co-DHC	10	40	[S17]

Table S4 Comparison of P, Ru and N contents in different electrocatalysts obtained from XPS tests.

Electrocatalysts	P content (at%)	Ru content (at%)	N content (at%)
Ru_2P@Ru	13.57	12.77	0
N-Ru_2P@Ru-2	10.11	9.12	0.54
N-Ru_2P@Ru	20.16	18.31	2.42
N-Ru_2P@Ru-6	17.86	17.59	9.28

Table S5 Internal resistance (R_Ω) and charge transfer resistance (R_{ct}) of N-Ru_2P@Ru catalyst and other comparative samples for HER

Electrocatalysts	**R_Ω(Ω)**	**R_{ct}(Ω)**
Ru_2P@Ru	0.0593	0.524
N-Ru_2P@Ru-2	0.0566	0.428
N-Ru_2P@Ru	0.0523	0.328
N-Ru_2P@Ru-6	0.054	0.924
N-Ru_2P@Ru-8	0.0595	1.276

Table S6 Internal resistance (R_Ω) and charge transfer resistance (R_{ct}) of N-Ru_2P@Ru catalyst and other comparative samples for HER

Electrocatalysts	**R_Ω(Ω)**	**R_{ct}(Ω)**
N-Ru_2P@Ru-350	0.0592	0.987
N-Ru_2P@Ru	0.0523	0.328
N-Ru_2P@Ru-550	0.064	1.645

Table S7 Nitrogen content in different electrocatalysts obtained from XPS tests.

Electrocatalysts	N content (at%)
N-Ru_2P@Ru-NH_3	6.18
N-Ru_2P@Ru	2.42
N-Ru_2P@Ru-IT	1.02

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