Supporting Information (SI) for:

Growing Nanocrystalline Ru on Amorphous/Crystalline Heterostructure for Efficient and Durable Hydrogen Evolution Reaction

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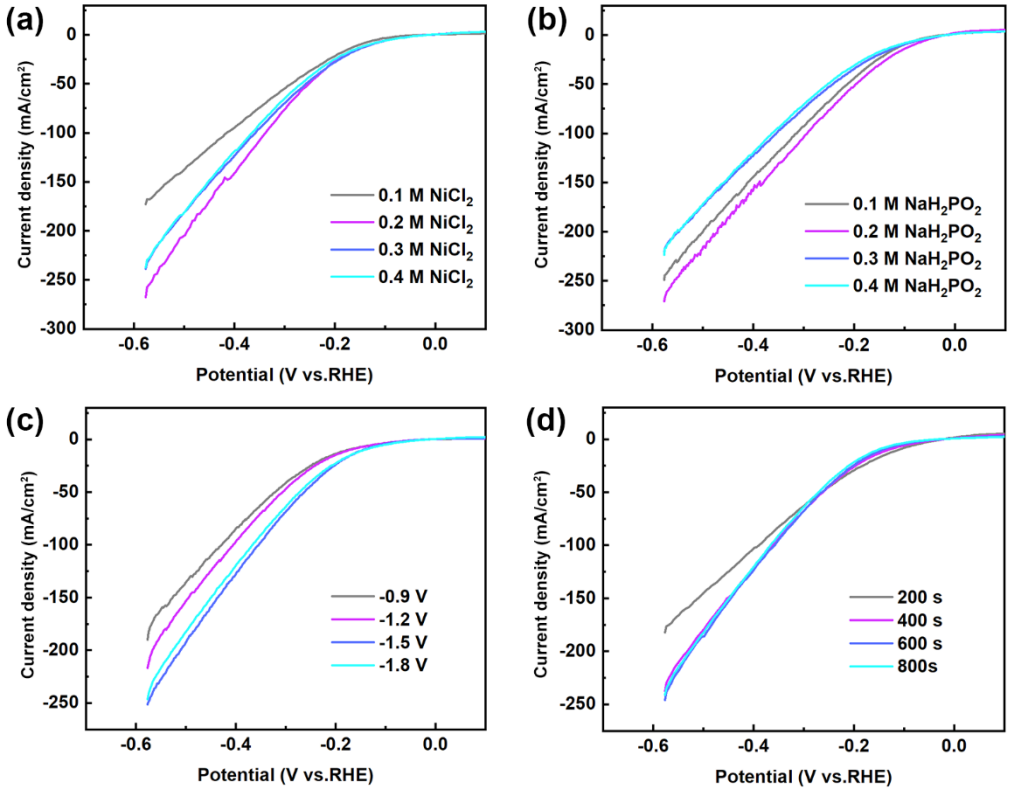


Figure S1. Optimization of NiP_x-Ni electrodeposition parameters: (a) $NiCl_2$ concentration, (b) NaH_2PO_2 concentration, (c) deposition voltage, (d) deposition time.

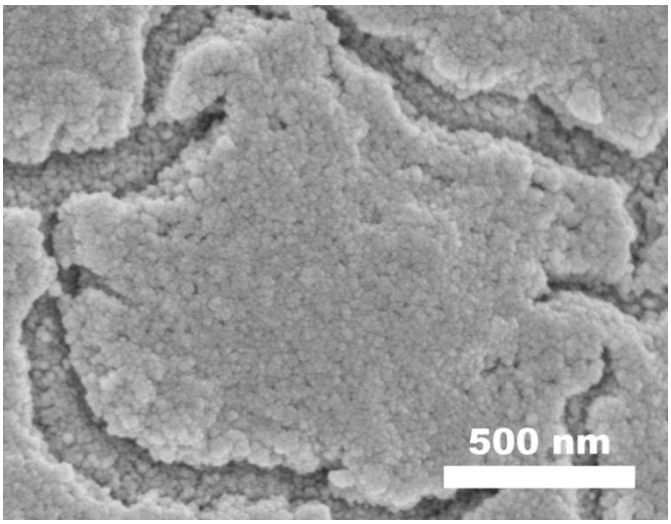


Figure S2. SEM image of NiP_x-Ni.

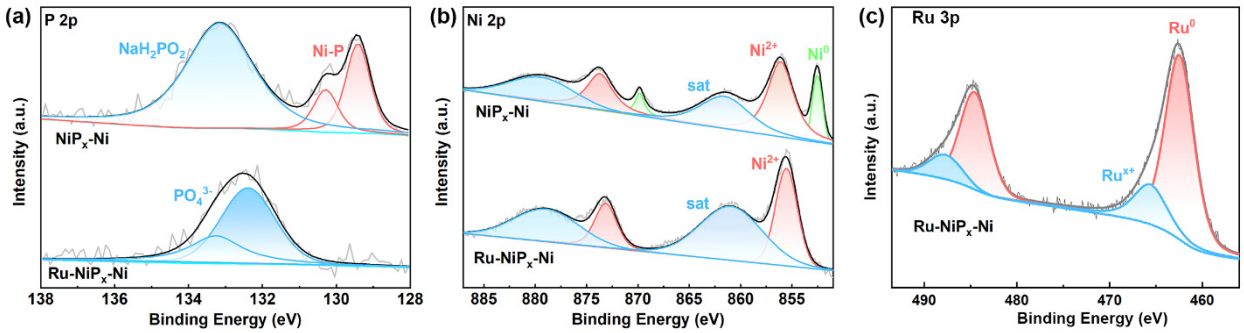


Figure S3. (a) P 2p and (b) Ni 2p spectra of NiP_x-Ni and Ru-NiP_x-Ni. (c) Ru 3p spectra of Ru-NiP_x-Ni.

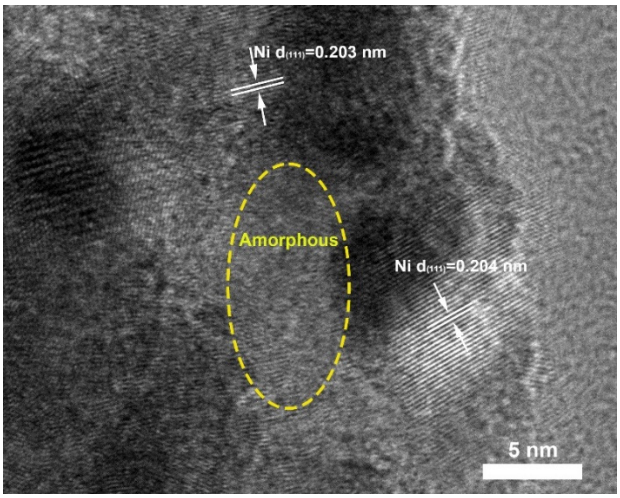


Figure S4. TEM image of NiP_x-Ni.

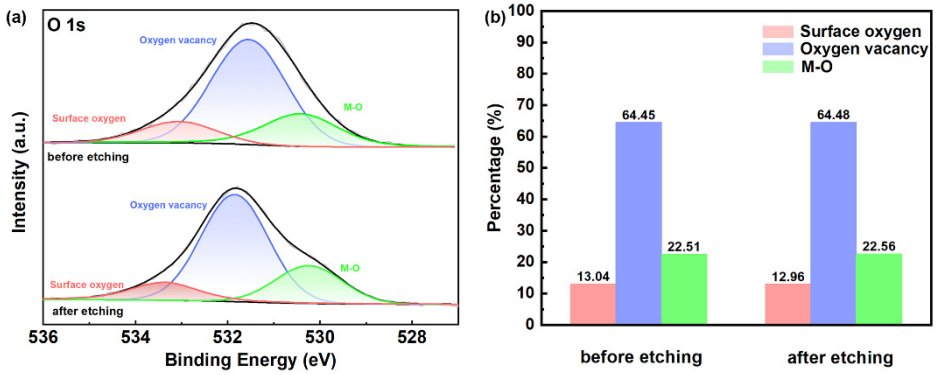


Figure S5. (a) O 1s XPS spectra and (b) corresponding surface oxygen species distribution in Ru–NiP_x–Ni before and after etching.

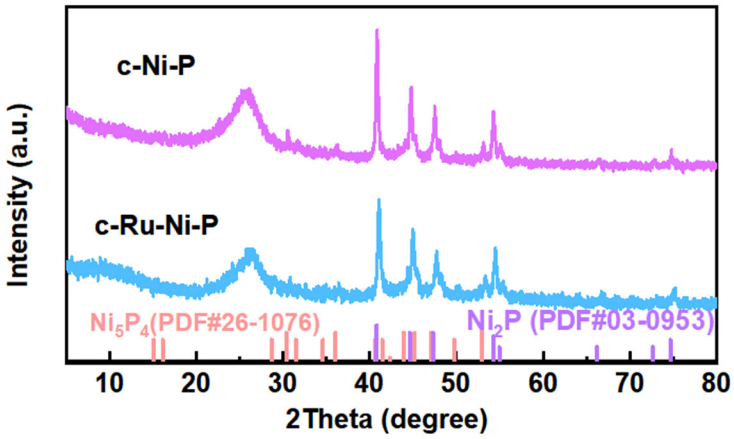


Figure S6. XRD patterns of c-Ni-P and c-Ru-Ni-P.

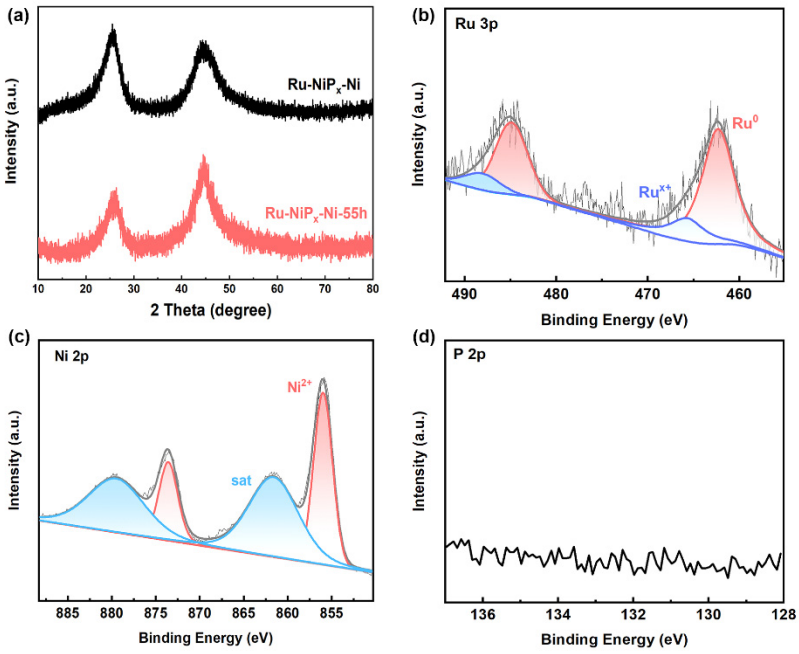


Figure S7. (a) XRD patterns of Ru-NiP$_x$-Ni before and after 55 h stability test. (b) Ni 2p, (c) Ru 3p, and (d) P 2p spectra of Ru-NiP$_x$-Ni after 55 h HER stability test (100 mA cm^{-2}) in 1 M KOH solution.

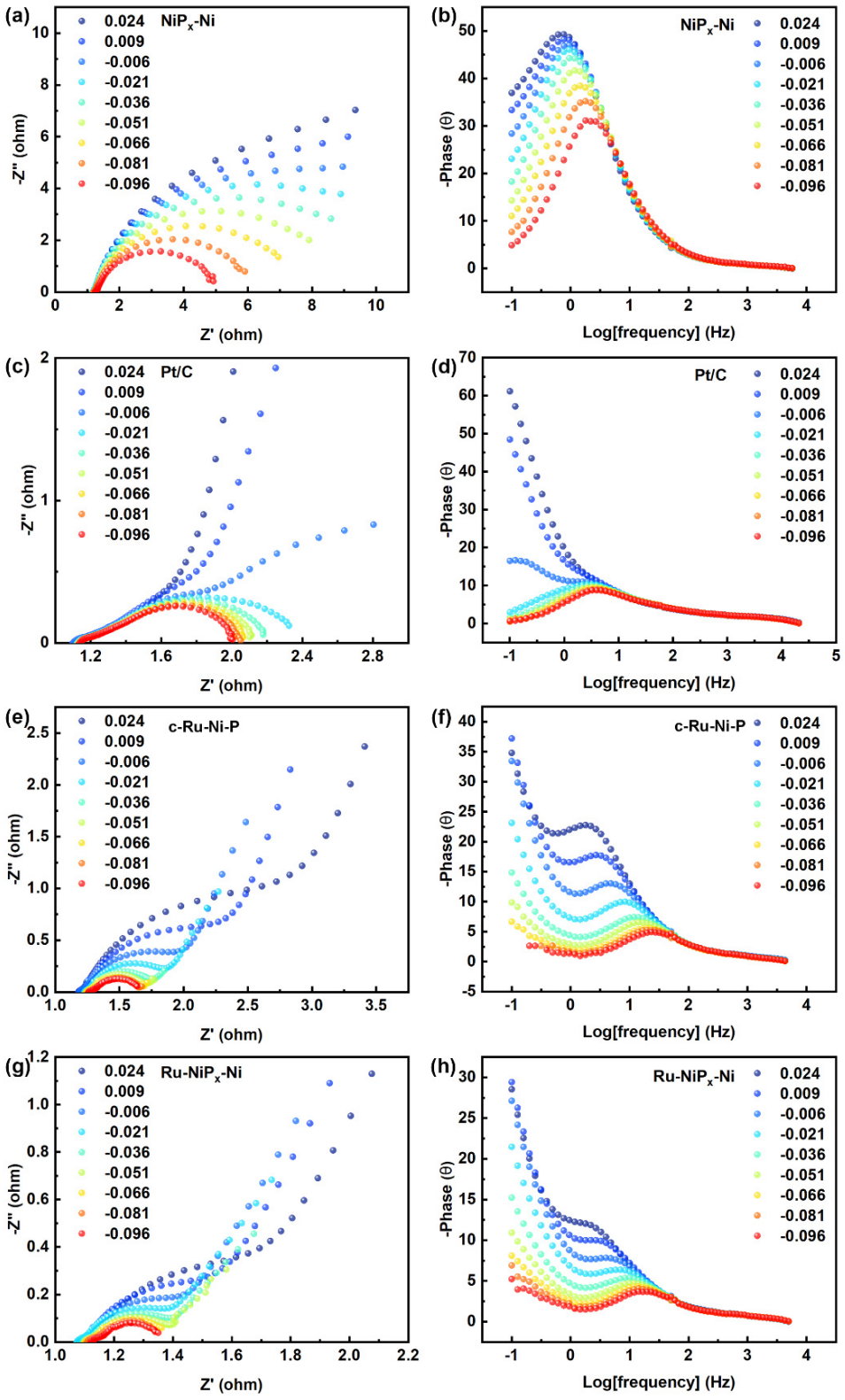


Figure S8. Nyquist plots and corresponding Bode plots for (a, b) NiP_x-Ni, (c, d) Pt/C, (e, f) c-Ru-Ni-P and (g, h) $RuNiP_x$-Ni measured at applied potentials ranging from 0.024 to -0.096 V (V vs. RHE).

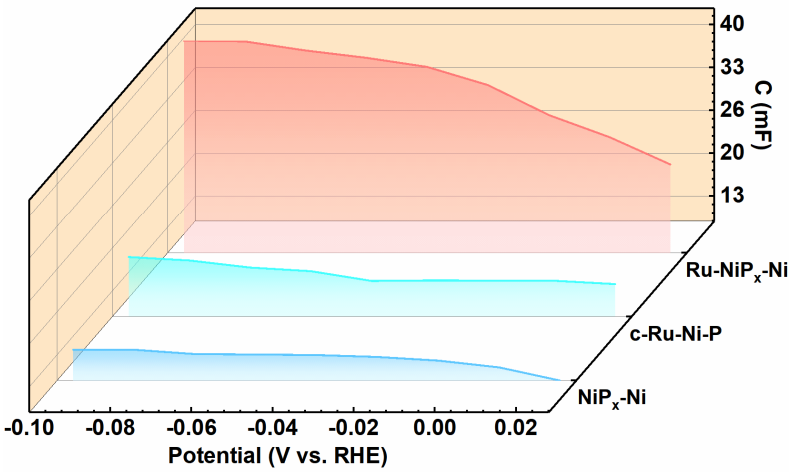


Figure S9. The simulated C_3 values for NiP_x-Ni, c-Ru-Ni-P and Ru-NiP_x-Ni.

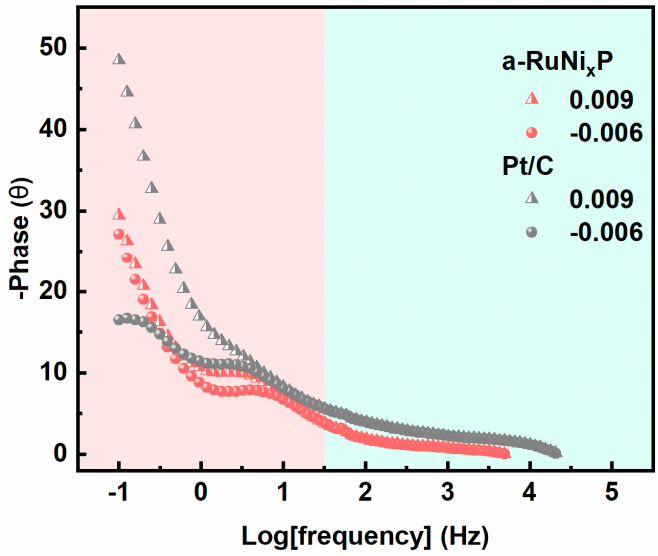


Figure S10. Bode Plots of Pt/C and Ru-NiP_x-Ni at 0.009 V and -0.006 V (V vs. RHE).

Table S1. Summary of HER performance of reported Ru-based electrocatalysts.

Catalyst	η_{100}	Tafel slope	DOI
	mV	mV cm^{-2}	
Ru-NiP_x-Ni	70	41	This work
Ru/Ni_2P/NF	131	42.6	10.1021/acsami.1c10971 [58]
Ru_cNiFe-LDH	87	64	10.1002/adma.202401694 [20]
Ru-Fe-O_x/CC	83	40	10.1016/j.jcis.2024.05.049 [10]
Ru/d-NiFe LDH	93	50.4	10.1002/aenm.202400059 [21]
Ru-Ni_2P/Fe_3P	129.5	50.4	10.1002/smll.202311335 [59]
Co@Ni_mP_n–Ru	130	79.3	10.1002/smll.202309122 [55]
Ru-a-CoNi	83	34	10.1002/anie.202114160 [25]
Ru-$NiPS_3$ NSs	131	64	10.1038/s41467-023-42221-6 [35]
D/NFF-Ru-Zn	90	41	10.1039/d2ta04789f [27]
Ru/WO_3-V_O	139	35.8	10.1016/j.apcatb.2023.123502 [60]
FF-Na-Ru	140	33	10.1002/adfm.202010437 [61]
Ru SAs-MoO_{3-x}/NF	86	41.3	10.1002/advs.202300342 [16]

Table S2. Fitted parameters of the EIS data of NiP_x-Ni catalyst for HER.

E	R_1	Q_2	n_2	R_2	C_3	R_3
V vs.RHE	Ω	μS s^n cm^{-2}		Ω	μF cm^{-2}	Ω
0.024	1.193	66.13	0.7786	0.5528	9.23	16.16
0.009	1.170	58.66	0.8016	0.5167	11.26	12.80
-0.006	1.166	58.75	0.7906	0.4265	12.30	11.59
-0.021	1.176	54.22	0.8355	0.4102	12.86	9.94
-0.036	1.185	49.14	0.8490	0.4030	13.16	8.49
-0.051	1.217	45.47	0.8550	0.3934	13.24	7.20
-0.066	1.221	43.38	0.8559	0.3926	13.30	5.80
-0.081	1.200	39.45	0.8667	0.3627	13.98	4.49
-0.096	1.253	37.07	0.8599	0.3374	13.98	3.43

Table S3. Fitted parameters of the EIS data of c-Ru-Ni-P catalyst for HER.

E	R_1	Q_2	n_2	R_2	C_3	R_3
V vs.RHE	Ω	μS s^n cm^{-2}		Ω	μF cm^{-2}	Ω
0.024	1.183	115.0	0.6662	0.2219	14.26	2.97
0.009	1.183	113.7	0.6498	0.1857	14.77	1.91
-0.006	1.186	110.2	0.6426	0.1552	14.79	1.10
-0.021	1.223	89.56	0.6527	0.1307	14.81	0.70
-0.036	1.248	60.15	0.7265	0.1443	14.74	0.41
-0.051	1.247	44.19	0.7610	0.1317	16.23	0.34
-0.066	1.247	39.22	0.7774	0.1477	16.80	0.26

-0.081	1.271	23.22	0.8225	0.1203	17.89	0.26
-0.096	1.272	16.86	0.8410	0.1123	18.43	0.25

Table S4. Fitted parameters of the EIS data of Ru-NiP_x-Ni catalyst for HER.

E	**R_1**	**Q_2**	**n_2**	**R_2**	**C_3**	**R_3**
V vs.RHE	**Ω**	**μS s^n cm^{-2}**		**Ω**	**μF cm^{-2}**	**Ω**
0.024	1.086	370.4	0.5526	0.2133	23.00	1.35
0.009	1.077	271.2	0.6121	0.1778	27.19	0.74
-0.006	1.074	240.6	0.6114	0.1178	30.61	0.51
-0.021	1.073	153.5	0.6664	0.1110	35.23	0.32
-0.036	1.093	123.7	0.6749	0.1063	38.02	0.25
-0.051	1.101	100.5	0.6832	0.1016	39.42	0.21
-0.066	1.103	52.19	0.7611	0.0735	40.55	0.19
-0.081	1.112	39.56	0.7911	0.0732	41.96	0.16
-0.096	1.125	37.55	0.8022	0.0718	42.08	0.14