Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information

for

Robust hydrogen evolution reaction activity catalyzed by ultrasmall Rh-Rh_2P nanoparticles

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Table S1 The ΔE_{H^*}, ΔZPE, $T\Delta S$, ΔG_{H^*} values of the H* adsorbed on the surface of different models.

Models	ΔE_{H^*}/eV	ΔZPE/eV	$T\Delta S$/eV	ΔG_{H^*}/eV
Rh(111)	-0.530	0.042	-0.196	-0.292
Rh_2P(220)	-0.383	0.001	-0.186	-0.196
Rh/Rh_2P	-0.187	0.015	-0.131	-0.041
Pt(111)	-0.353	0.028	-0.221	-0.104

Table S2 Quantitative analysis of Rh3d XPS spectra of Rh@C, Rh_2P@C and Rh-Rh_2P@C electrocatalysts.

Electrocatalyst	**Rh@C**	**Rh_2P@C**	**Rh-Rh_2P@C**
Metallic Rh: oxidized Rh	2.5:1	1.7:1	2:1

Table S3 R_s and R_{ct} obtained from HER of various electrocatalysts.

Catalyst	**R_s / Ω (0.5 M H_2SO_4)**	**R_{ct} / Ω (0.5 M H_2SO_4)**	**R_s / Ω (1 M KOH)**	**R_{ct} / Ω (1 M KOH)**
Rh@C	7.3	42	8.4	194
Rh_2P@C	7.6	37	8.1	144
Rh-Rh_2P@C	7.1	8	8.6	53

Table S4 Comparison of HER activities of noble-metal phosphide based electrocatalysts.

Electrocatalyst	**metal loading** ($\mu g\ cm^{-2}$)	η_{10} (0.5 M H_2SO_4)	η_{10} (1 M KOH)	**Ref.**
Rh-Rh_2P@C	14.2	24	37	this work
Rh_2P/C	30.6	10	30	[1]
Rh_2P/C	70	9	10	[2]
IrP_2@NC	77	8	28	[3]
PdP_2@CB	14.2	27.5	35.4	[4]
Ru-Ru_2P/NPC	42.5	NA	43.4	[5]
RuP_2@NPC	233	38	52	[6]
Ru_2P/graphene	50	18	NA	[7]
Ru_2P/NPG	7.3	NA	57	[8]
RuP_x/C	14.3	NA	31	[9]
Ru_2P	340	55	50	[10]

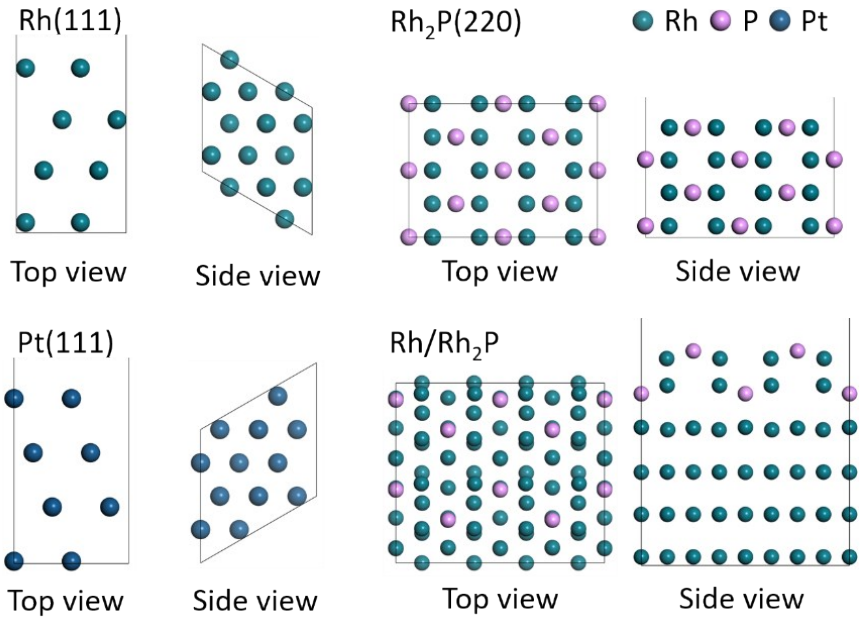

Figure S1 DFT calculated models of Rh(111), Rh_2P(220), Pt(111), and Rh-Rh_2P.

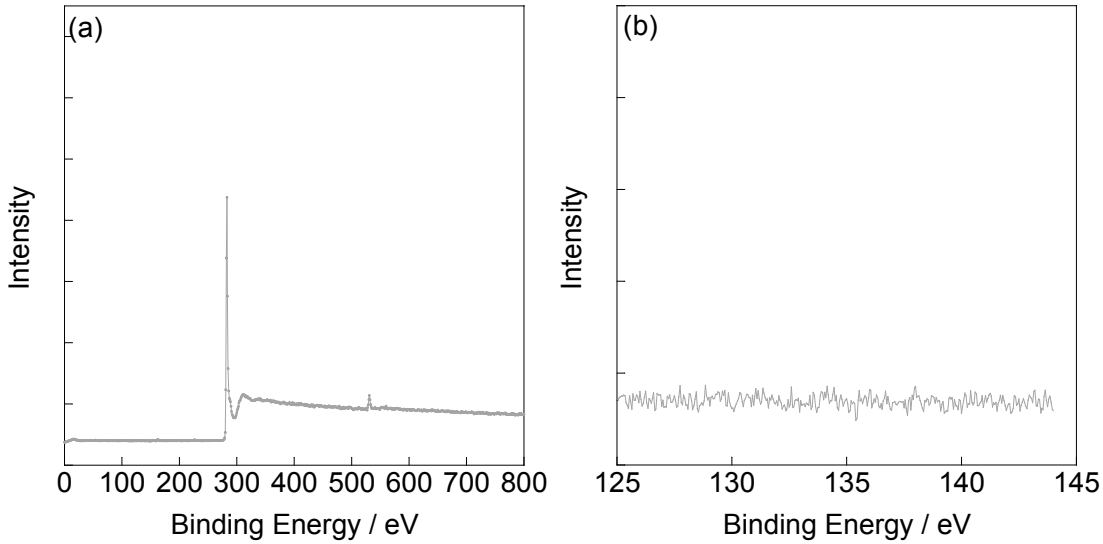

Figure S2 P2p XPS spectra of the sample prepared by heating carbon black and NaH_2PO_2.

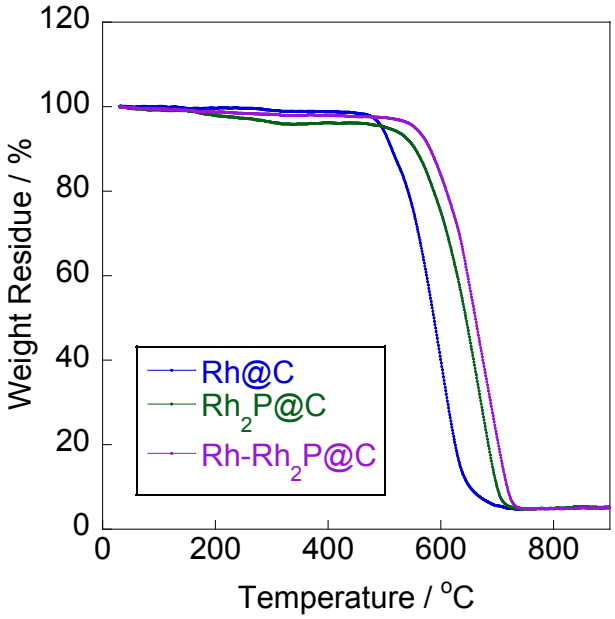

Figure S3 TGA curves of Rh@C, Rh_2P@C and Rh-Rh_2P@C electrocatalysts tested from room temperature to 900 °C under air flow.

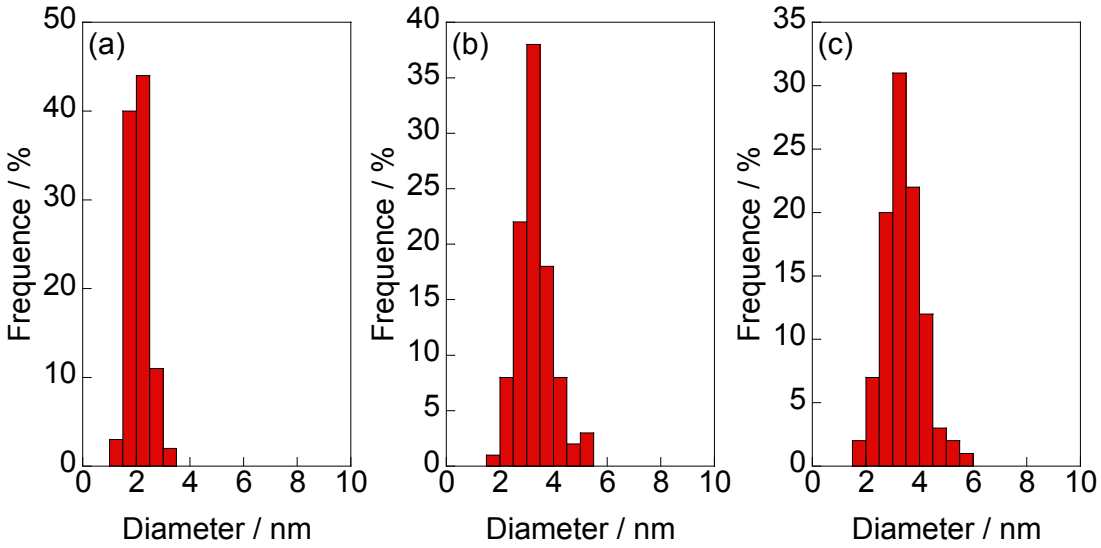

Figure S4 Histograms of particle size of Rh@C, Rh_2P@C and Rh-Rh_2P@C electrocatalysts.

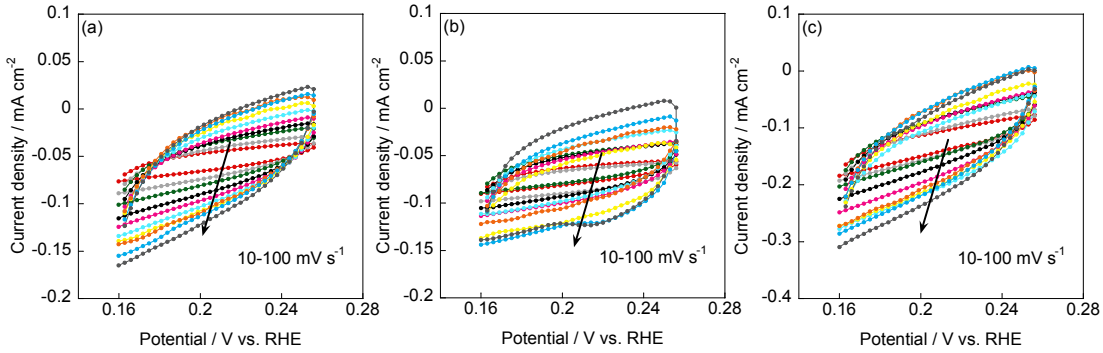

Figure S5 Cyclic voltammetry curves of Rh@C (a), Rh_2P@C (b) and Rh-Rh_2P@C (c) electrocatalysts in 0.5 M H_2SO_4 electrolyte.

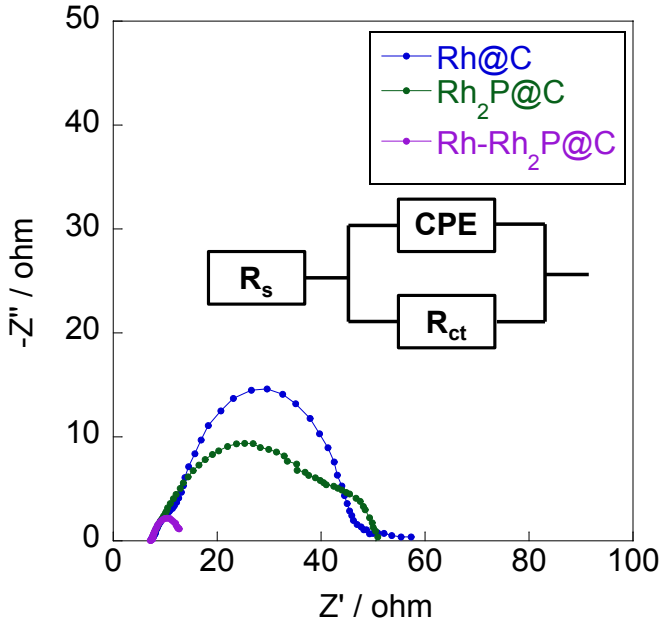

Figure S6 Electrochemical impedance spectroscopies (EIS) of Rh@C, Rh_2P@C and Rh-Rh_2P@C electrocatalysts in 0.5 M H_2SO_4 electrolyte.

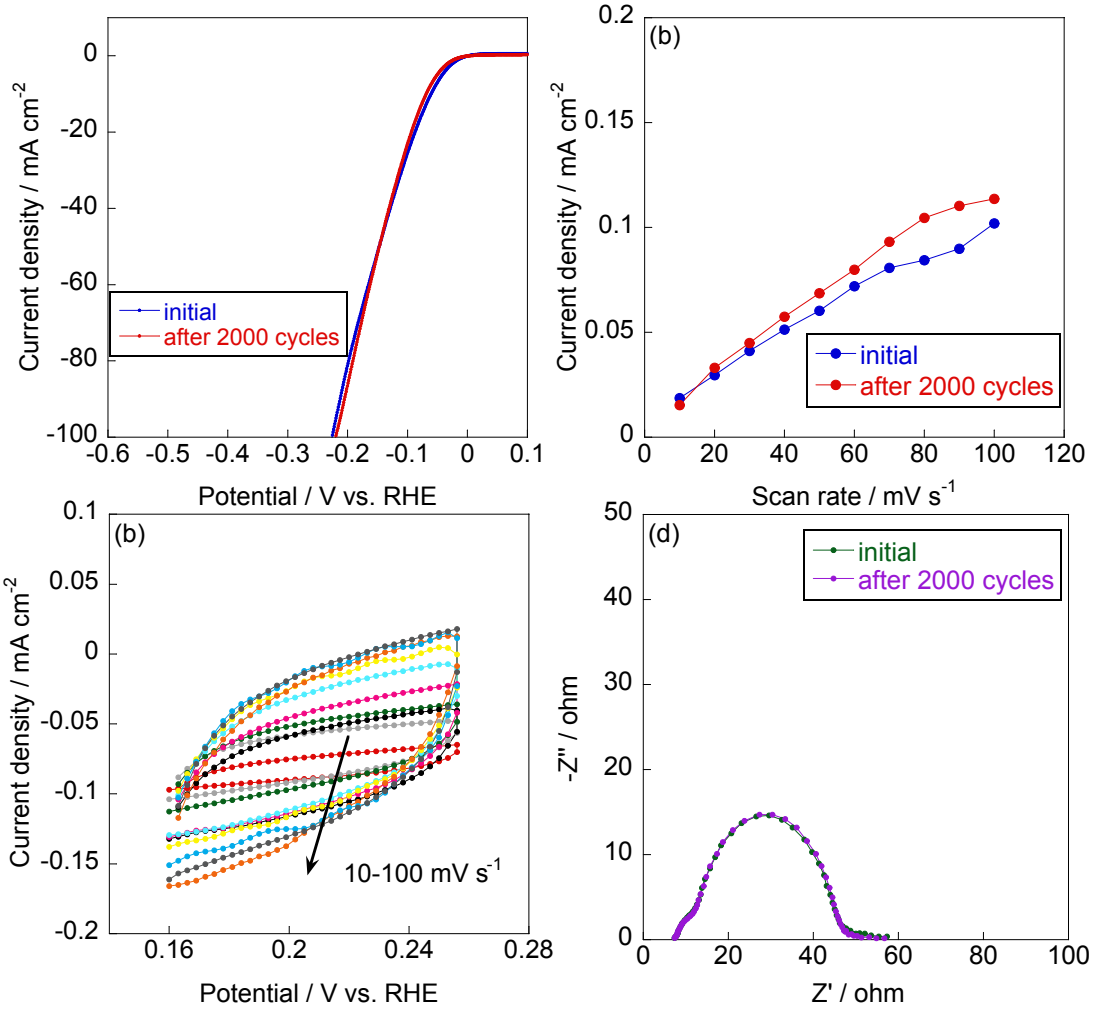

Figure S7 LSV (a), ECSA (b), cyclic voltammetry (c) and EIS (d) curves of Rh@C before and after durability test.

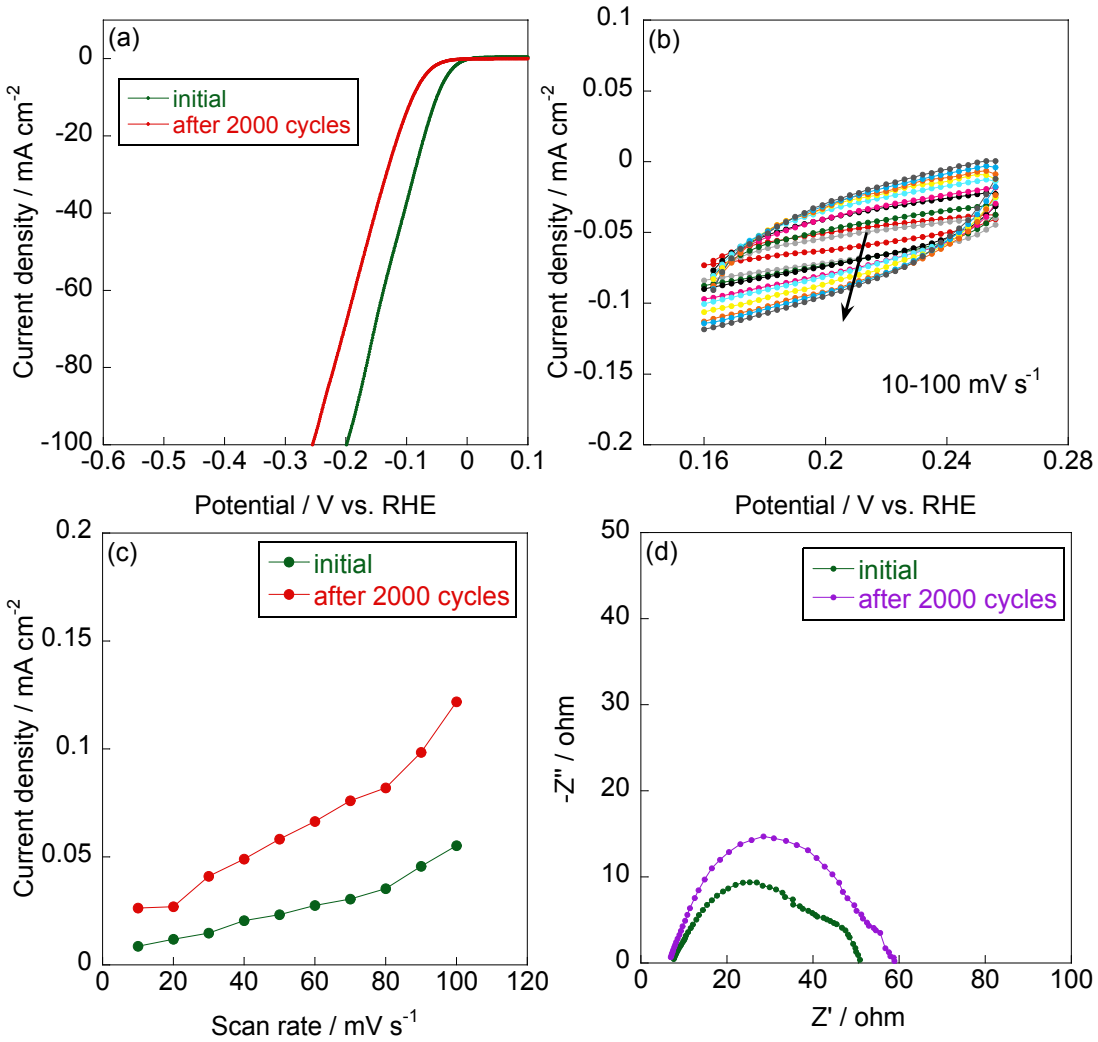

Figure S8 LSV (a), ECSA (b), cyclic voltammetry (c) and EIS (d) curves of Rh_2P@C before and after durability test.

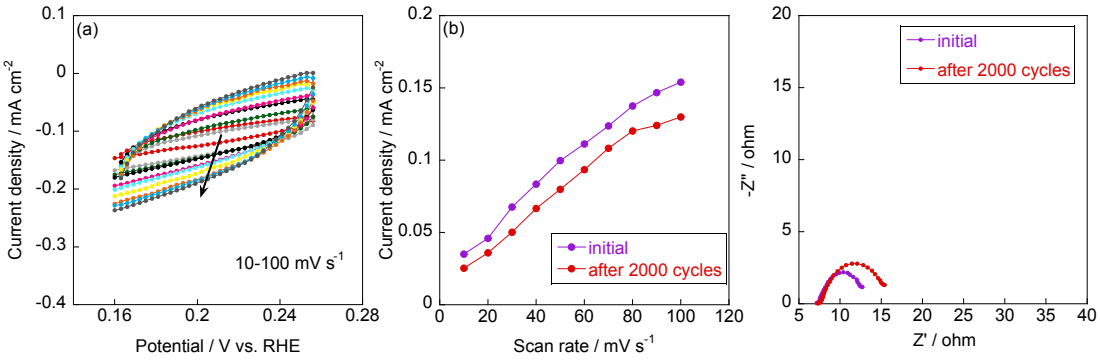

Figure S9 Cyclic voltammetry (a), ECSA (b) and EIS (c) curves of Rh-Rh_2P@C before and after durability test in 0.5 M H_2SO_4 electrolyte.

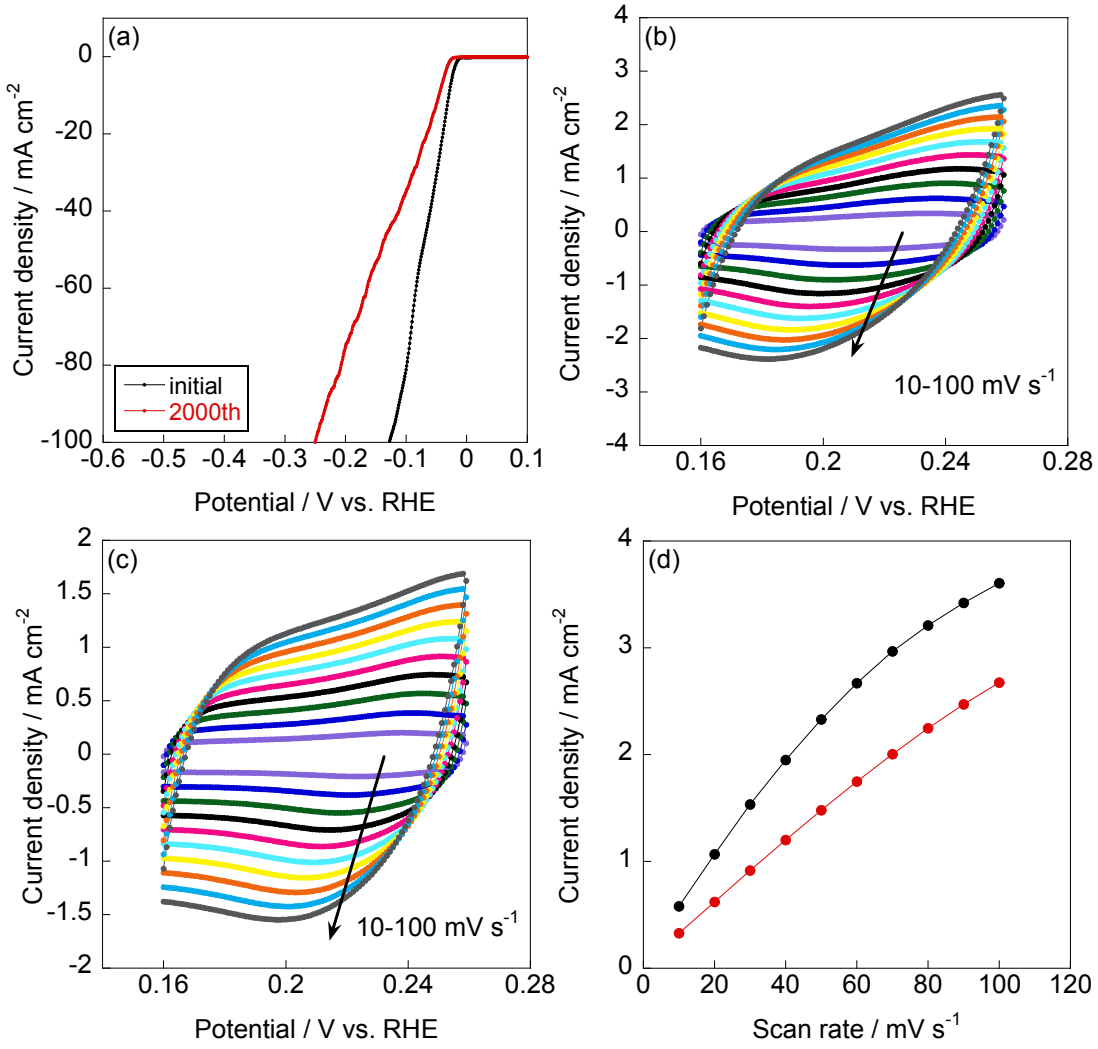

Figure S10 LSV (a), cyclic voltammetry (b, c) and ECSA (d) curves of Pt/C before and after durability test.

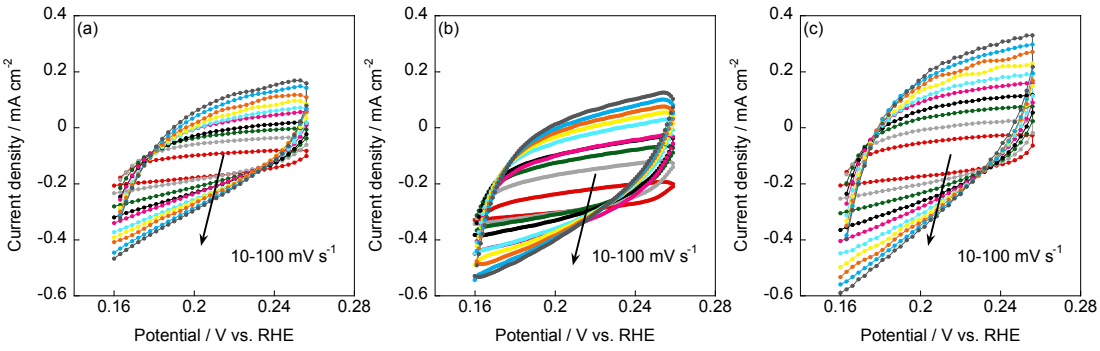

Figure S11 Cyclic voltammetry curves of Rh@C (a), Rh_2P@C (b) and Rh-Rh_2P@C (c) electrocatalysts in 1 M KOH electrolyte.

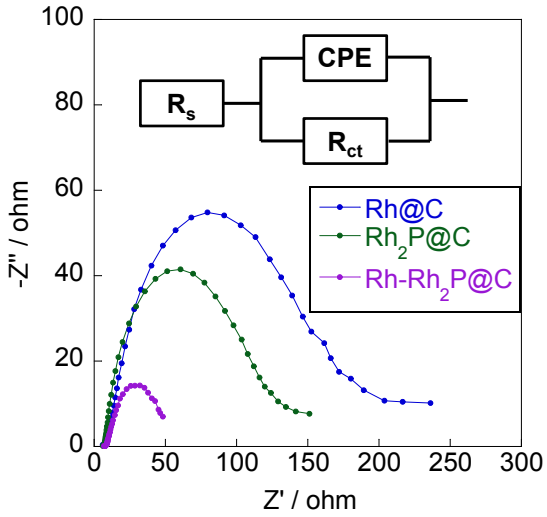

Figure S12 Electrochemical impedance spectroscopies (EIS) of Rh@C, Rh_2P@C and Rh-Rh_2P@C electrocatalysts in 1 M KOH electrolyte.

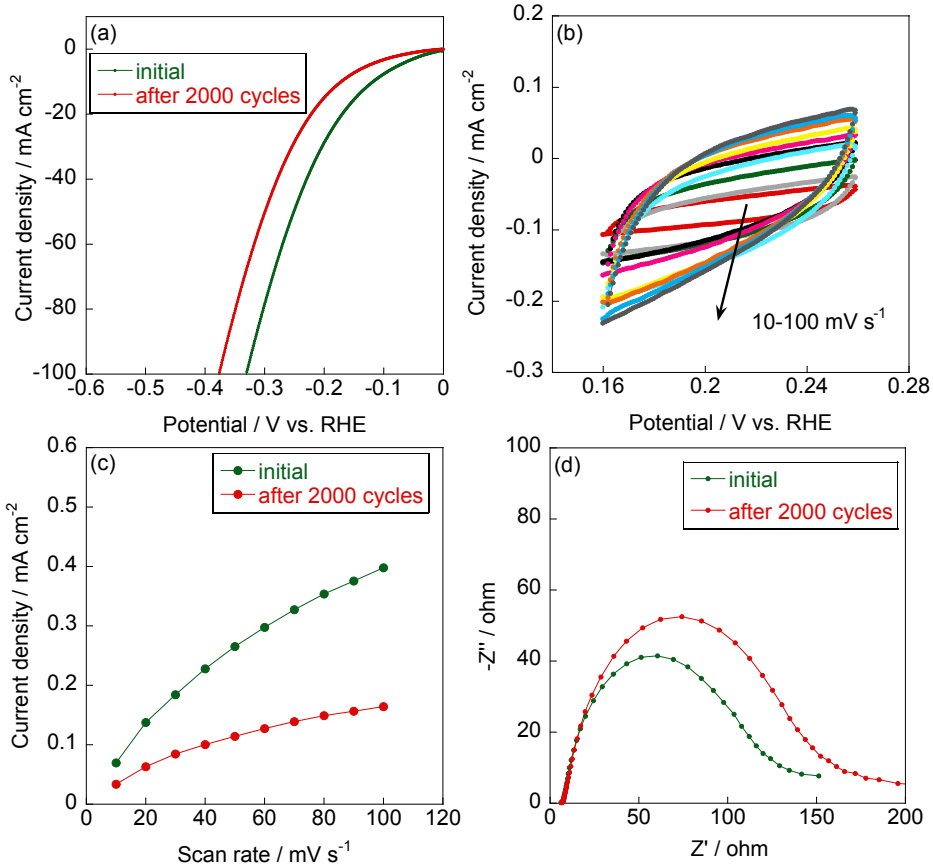

Figure S13 LSV (a), cyclic voltammetry (b, c) and ECSA (d) curves of Rh_2P@C before and after durability test in 1 M KOH electrolyte.

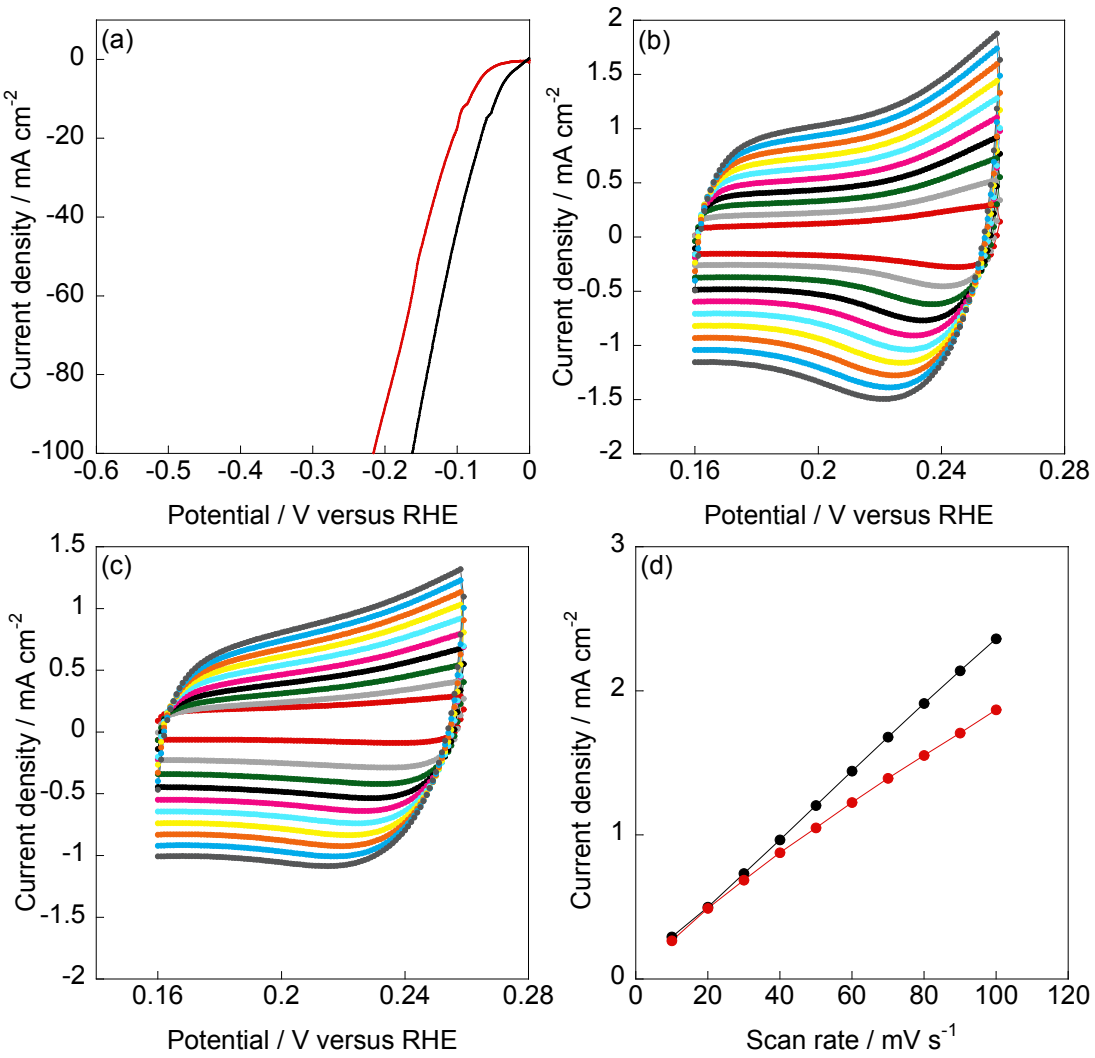

Figure S14 LSV (a), cyclic voltammetry (b, c) and ECSA (d) curves of Pt/C before and after durability test.

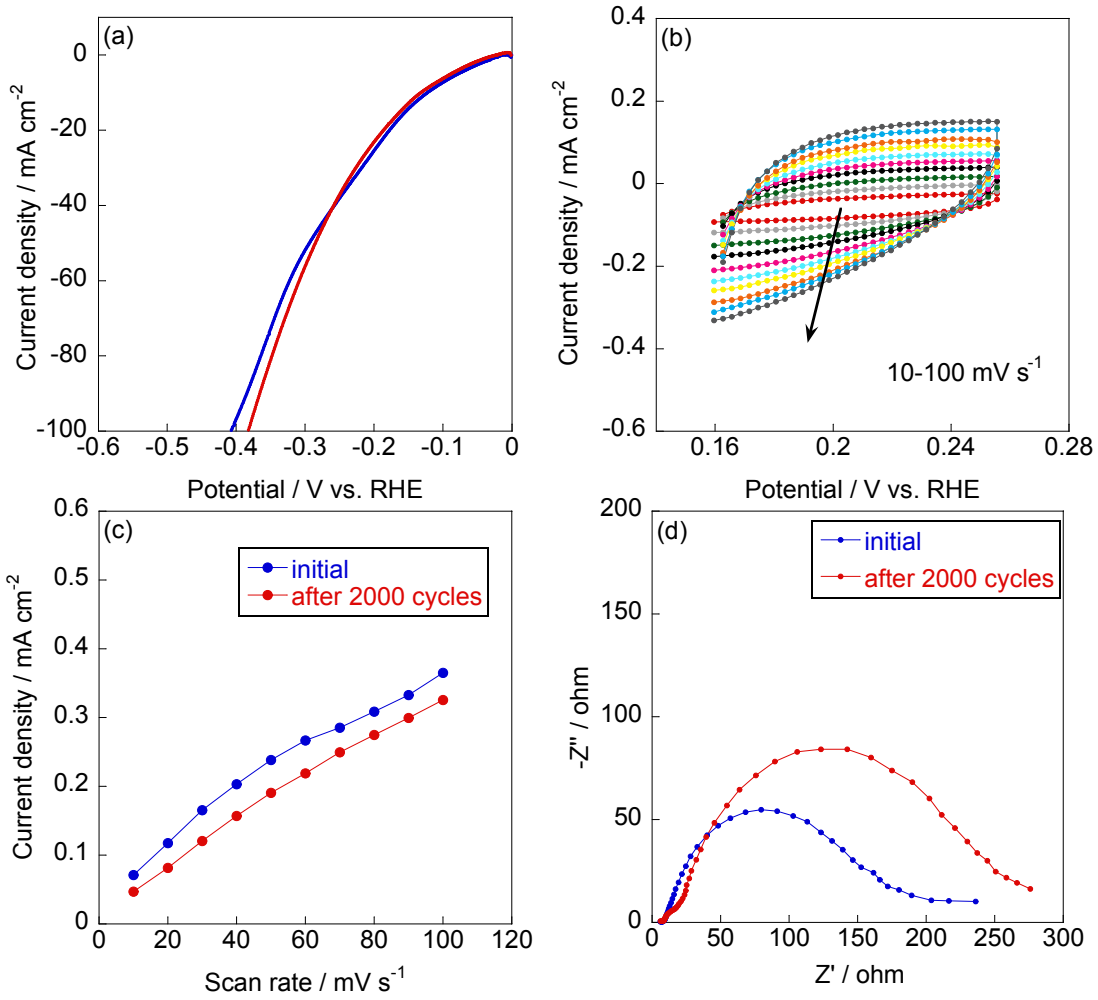

Figure S15 LSV (a), ECSA (b), cyclic voltammetry (c) and EIS (d) curves of Rh@C before and after durability test.

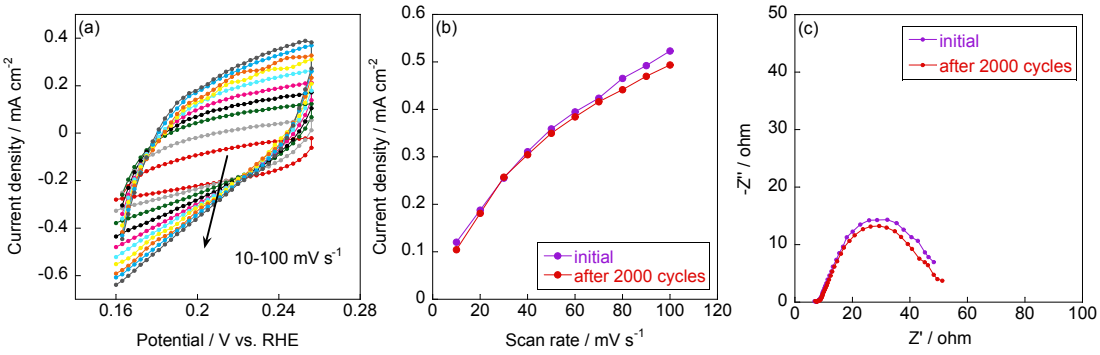

Figure S16 Cyclic voltammetry (a), ECSA (b) and EIS (c) curves of Rh-Rh_2P@C before and after durability test in 1 M KOH electrolyte.

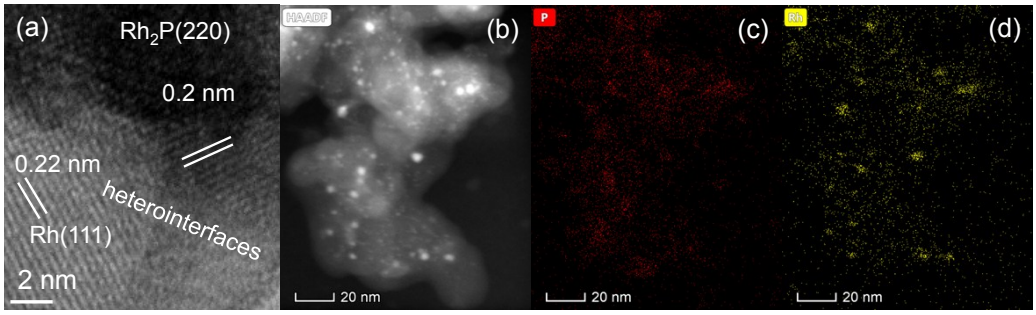

Figure S17 TEM image of Rh-Rh2P@C after stability test in 1 M KOH electrolyte.

References

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