Supporting Information

Rapid synthesis of active Pt single atoms and Ru clusters on carbon black via high-efficiency microwave strategy for hydrogen evolution reaction in acidic and alkaline media

Xinyu Zhu[a], Minghao Fang[a, *], Bozhi Yang[a], Meiling Zhan[a], Shaorou Ke[a], Fan Yang[a], Xiaowen Wu[a], Yangai Liu[a], Zhaohui Huang[a], Xin Min[a, *]

[a] *Engineering Research Center of Ministry of Education for Geological Carbon Storage and Low Carbon Utilization of Resources, Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences (Beijing), Beijing 100083, PR China*

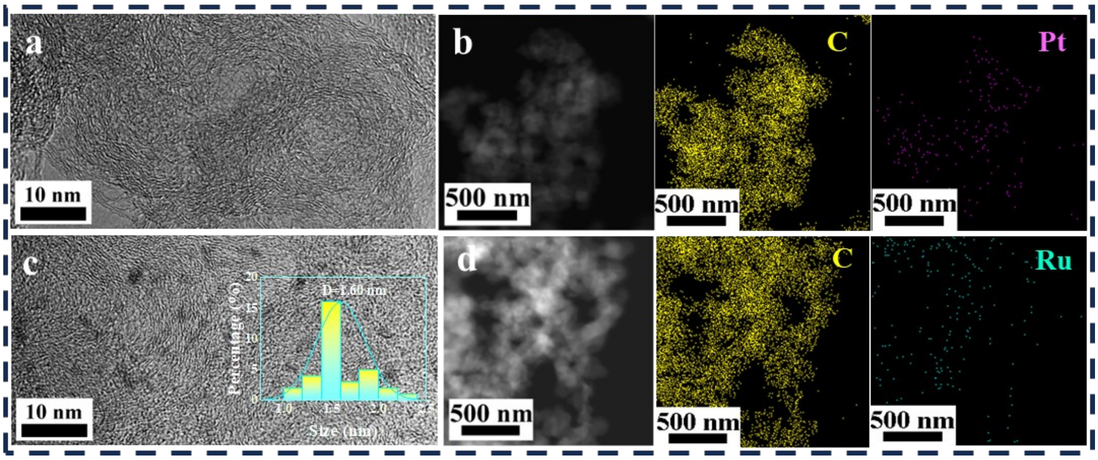

Fig. S1. TEM images at a range of magnifications of (a) Pt_1@C and (c) Ru_x@C, respectively. EDS selected area and corresponding mappings of (c) Pt_1@C (d) and Ru_x@C, respectively.

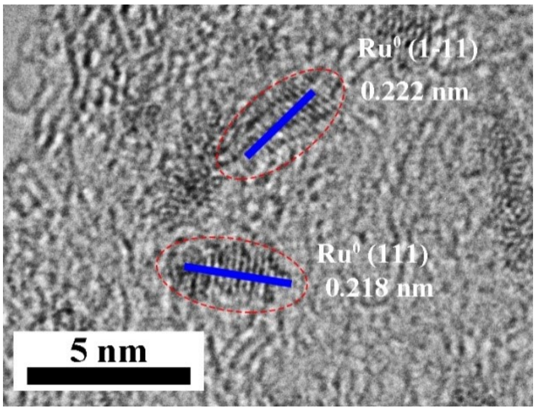

Fig. S2. TEM images at a range of magnifications of Ru_x@C.

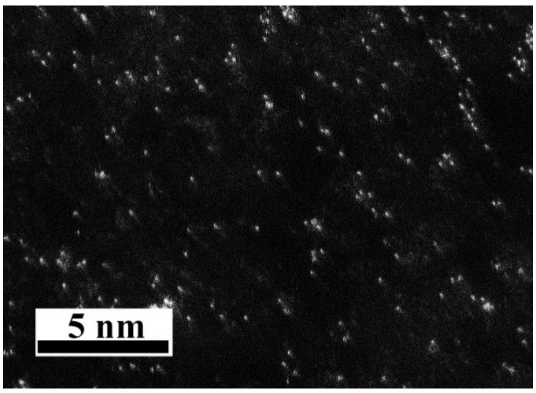

Fig. S3. HAADF-STEM image of Pt_1@C.

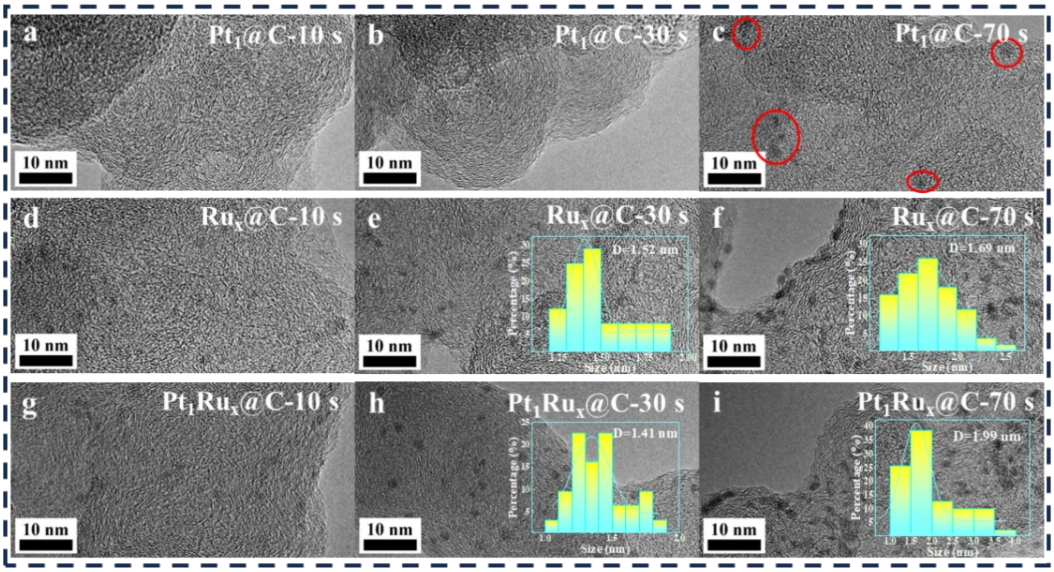

Fig. S4. TEM images of samples under different microwave durations.

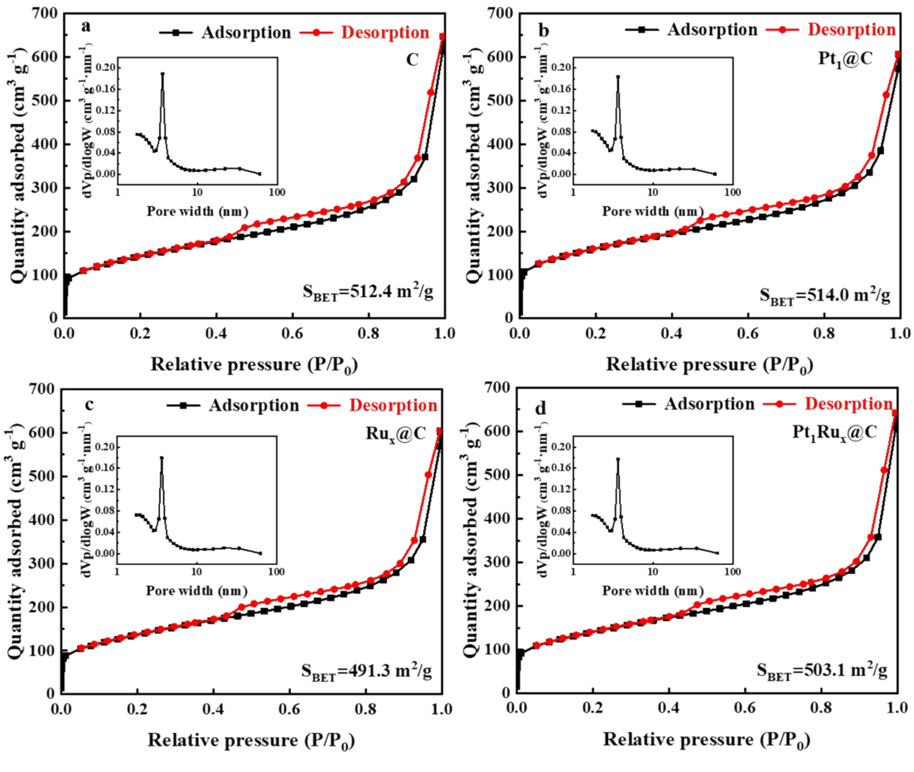

Fig. S5. N_2 adsorption-desorption isotherm curves of samples.

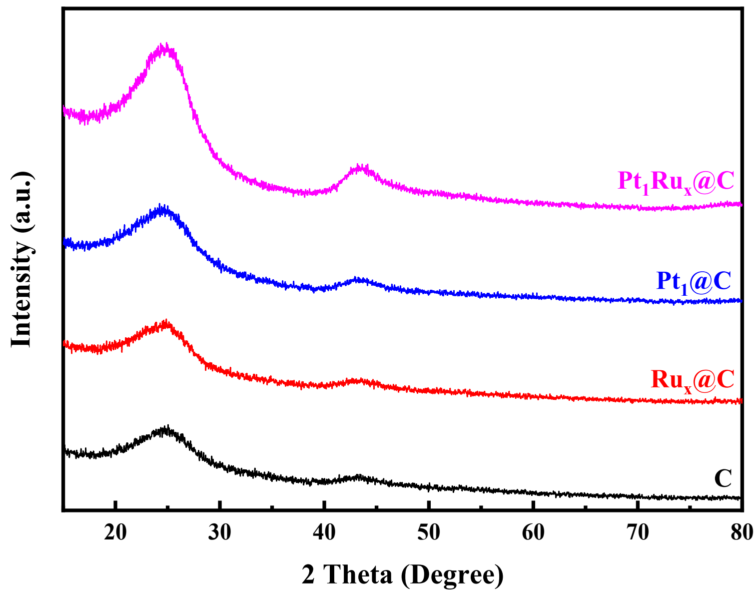

Fig. S6. XRD spectra of Pt_1Ru_x@C, Pt_1@C, Ru_x@C and C.

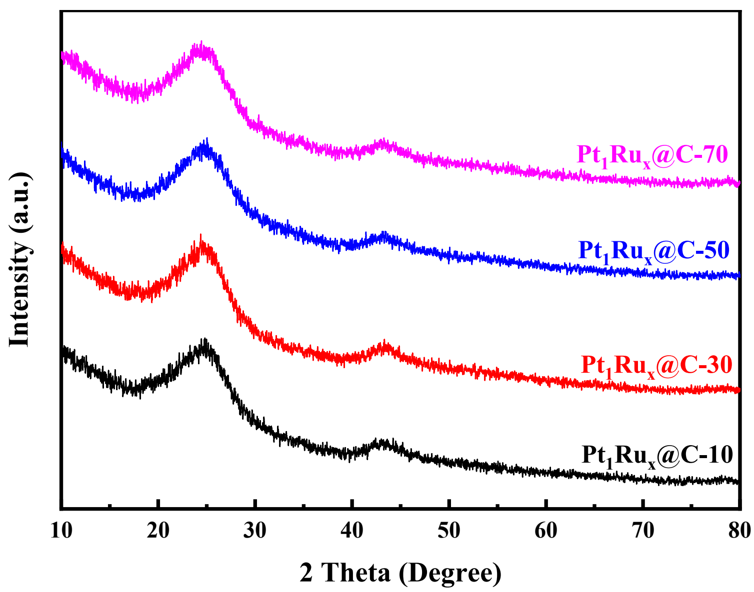

Fig. S7. XRD spectra of Pt_1Ru_x@C at different microwave time.

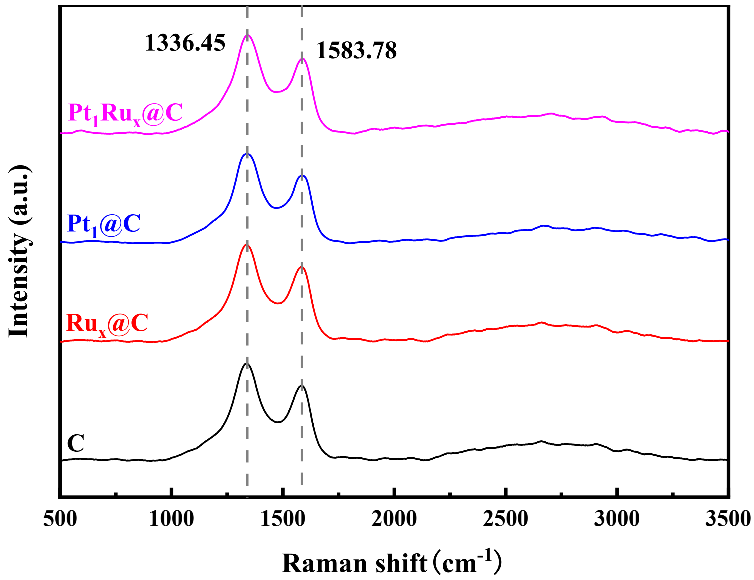

Fig. S8. Raman spectra of Pt_1Ru_x@C, Pt_1@C, Ru_x@C and C.

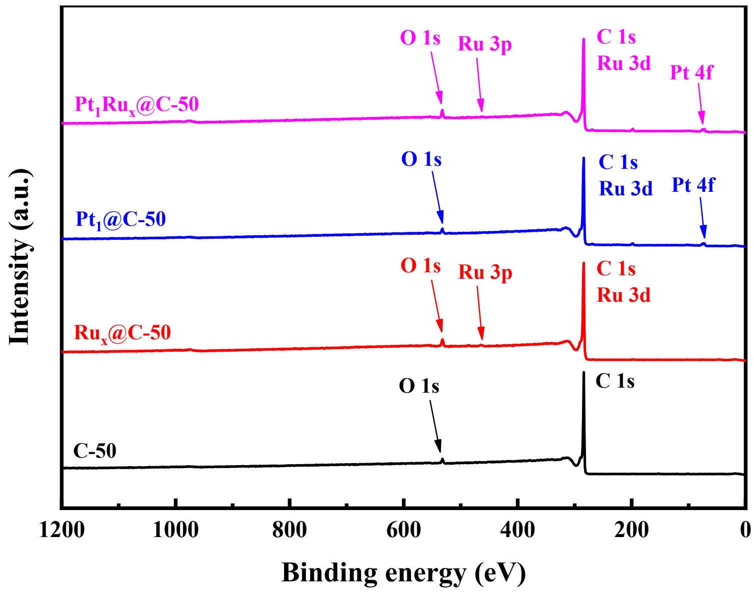

Fig. S9. XPS survey spectra of samples of Pt_1Ru_x@C, Pt_1@C, Ru_x@C and C.

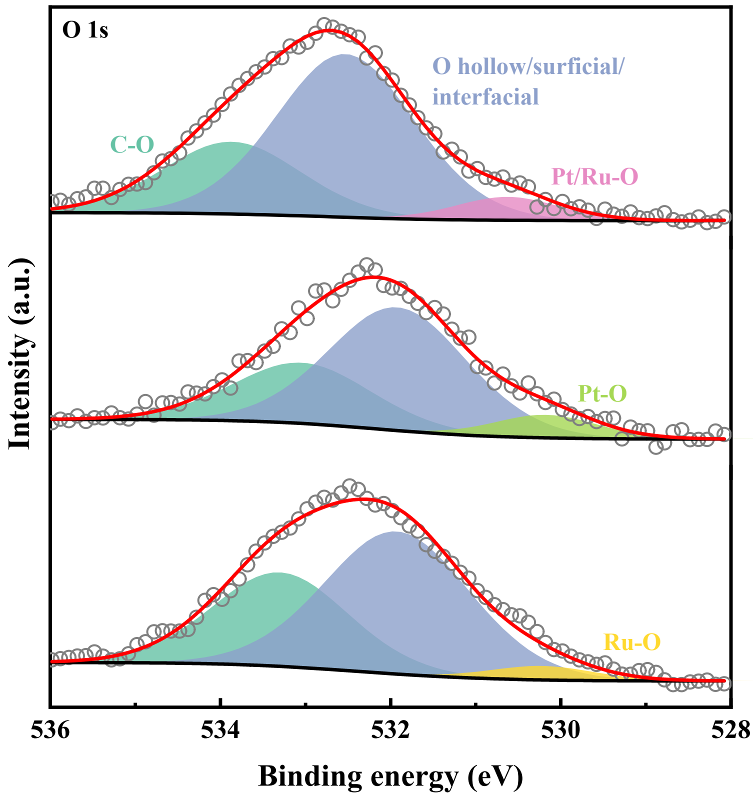

Fig. S10. XPS O 1s spectra of samples.

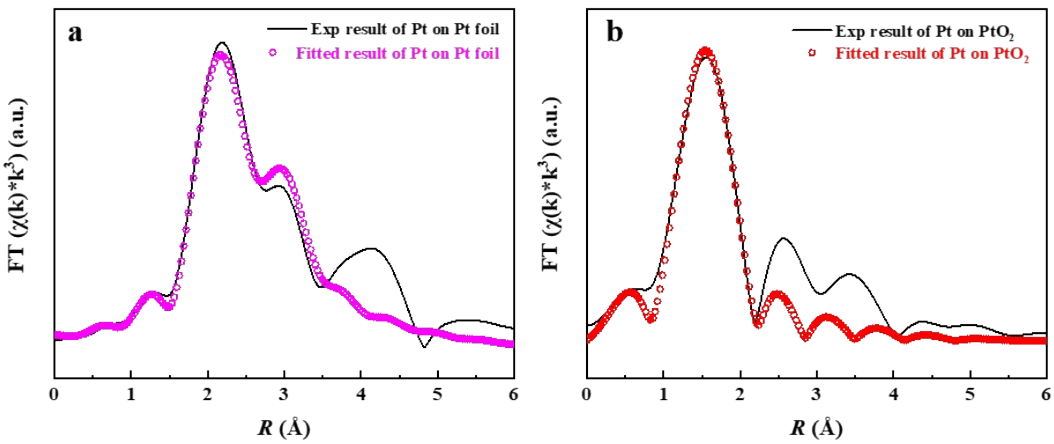

Fig. S11. Fitted spectra of Pt sites in (a) Pt foil and (b) PtO_2.

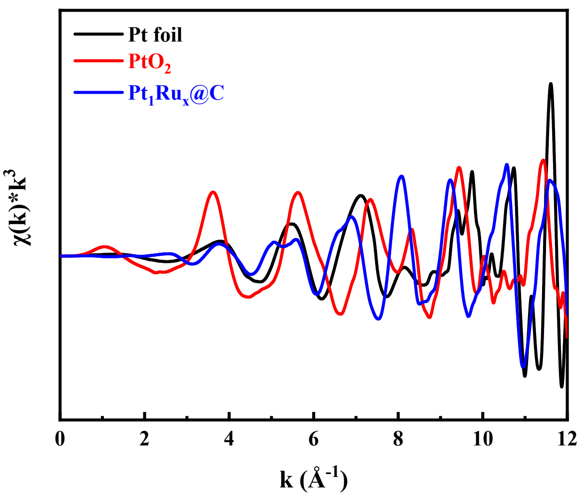

Fig. S12. The k^3-weighted EXAFS in Pt K-space for Pt foil, PtO_2, and Pt_1Ru_x@C.

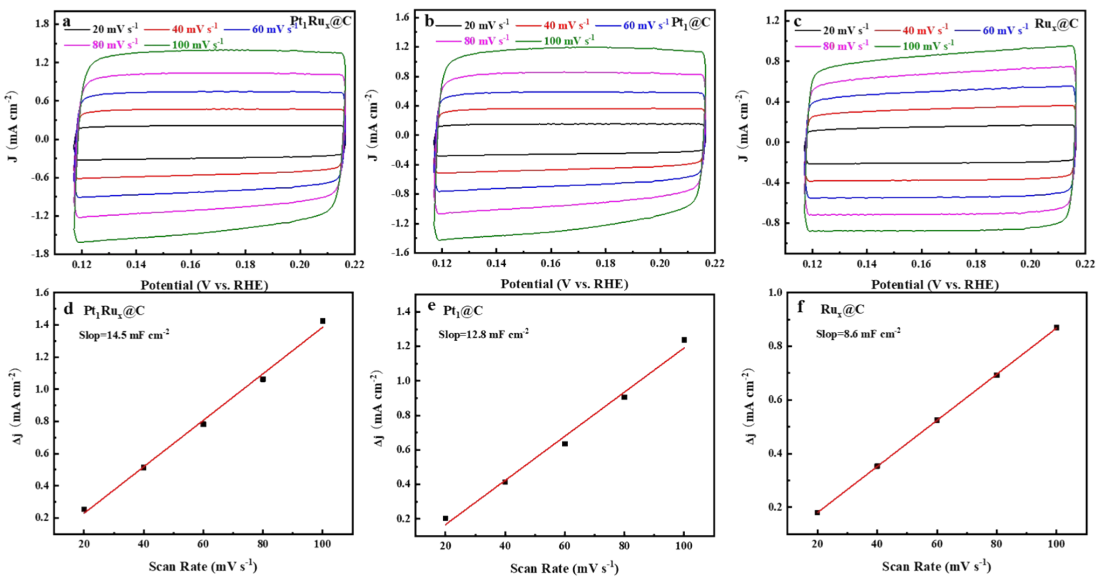

Fig. S13. CV curves at different scan rates from 20 to 100 mV s^{-1} in 0.5 ᴍ H_2SO_4 and capacitive current at 0.167 V as function of scan rates for (a, d) Pt_1Ru_x@C, (b, e) Pt_1@C, and (c, f) Ru_x@C.

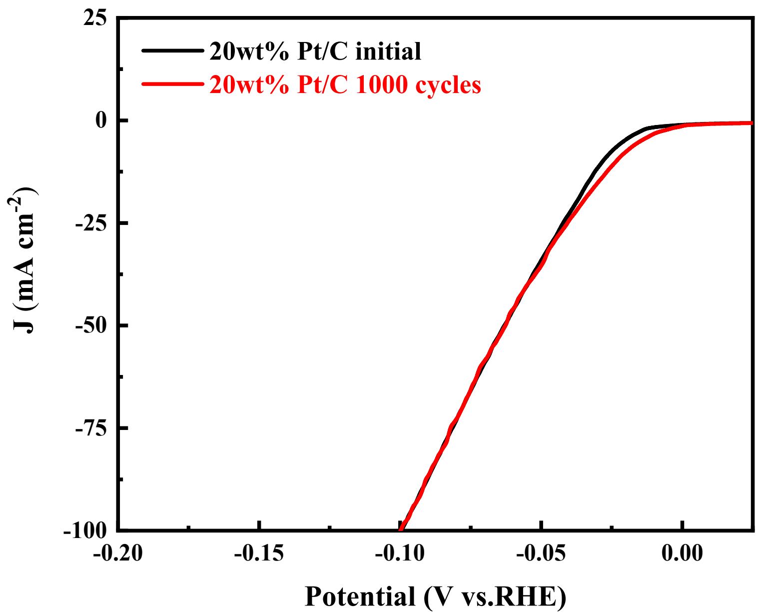

Fig. S14. Linear sweep voltammetry curves of 20wt% Pt/C before and after 1,000 CV cycles in 0.5 м H_2SO_4.

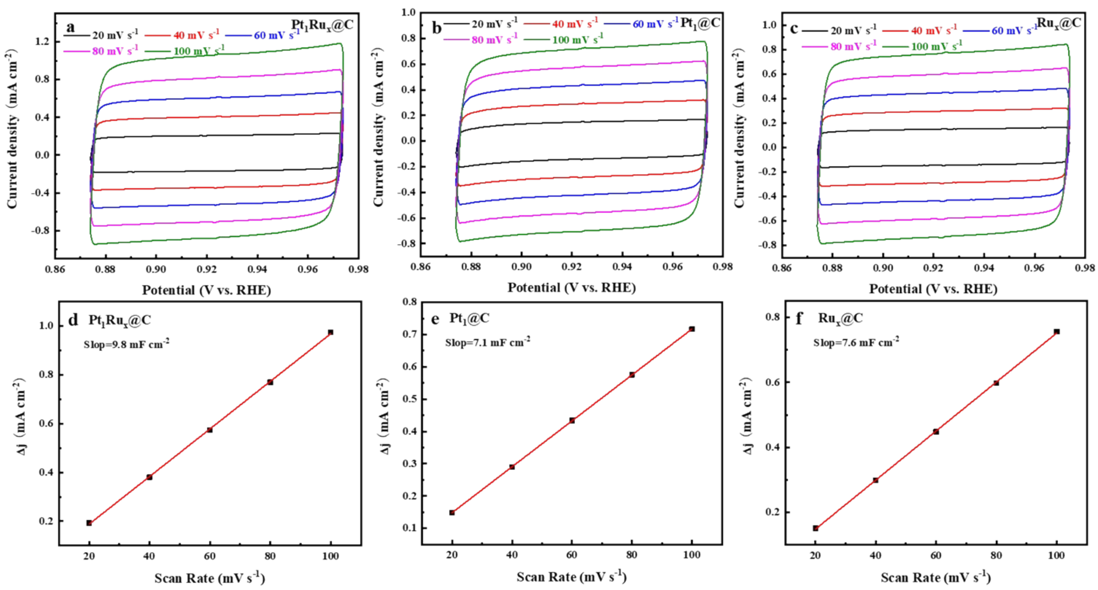

Fig. S15. CV curves at different scan rates from 20 to 100 mV s^{-1} in 1.0 м KOH and capacitive current at 0.167 V as function of scan rates for (a, d) Pt_1Ru_x@C, (b, e) Pt_1@C, (c, f) and Ru_x@C.

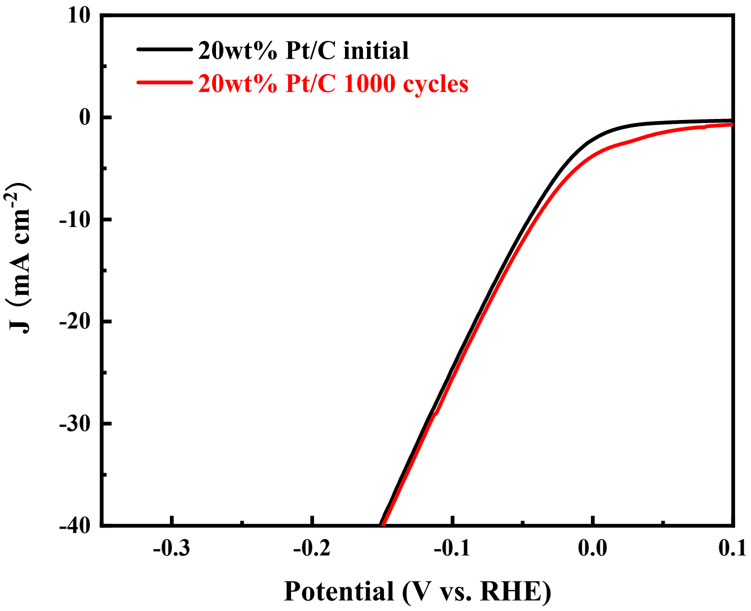

Fig. S16. Linear sweep voltammetry curves of 20wt% Pt/C before and after 1,000 CV cycles in 1.0 м KOH.

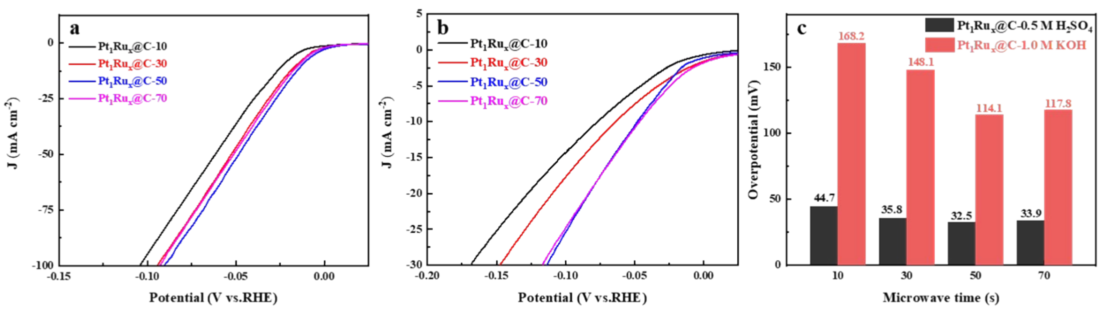

Fig. S17. HER performance in 0.5 м H_2SO_4/1.0 м KOH solution under different microwave time (a-b) Linear sweep voltammetry curves, (c) overpotentials.

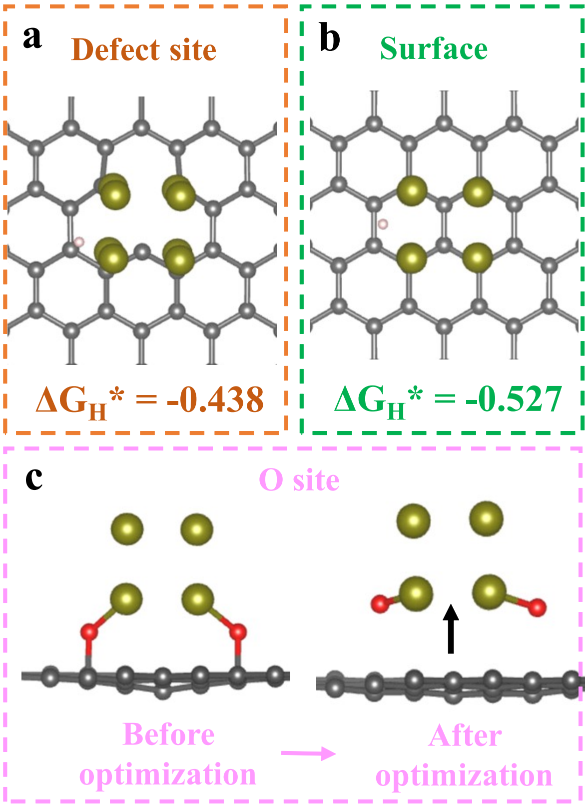

Fig. S18. (a-b) Chemisorption atomic models with of H on the surfaces of Ru_x@C at different sites; (c) Optimization process of Ru_x@C with O at site.

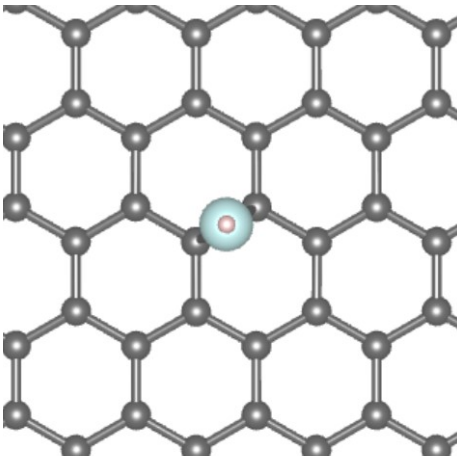

Fig. S19. Chemisorption atomic models with of H on the surfaces of Pt_1@C at site3.

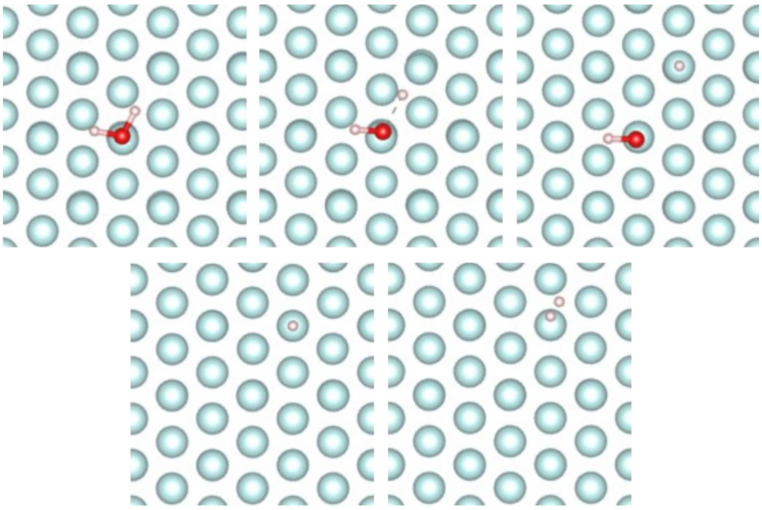

Fig. S20. Chemisorption atomic models with of H and OH intermediates on the surfaces of Pt(111).

Tab. S1. The content of different kind of Pt and Ru in the catalysts.

Sample	Elements	
	Pt [wt%]	Ru [wt%]
$Pt_1@C$	5.45	/
$Ru_x@C$	/	1.49
$Pt_1Ru_x@C$	4.78	1.32

Tab. S2. The content of different kind of Pt and Ru of $Pt_1Ru_x@C$ at different microwave time.

Sample	Elements	
	Pt [wt%]	Ru [wt%]
$Pt_1Ru_x@C$-10	2.15	0.72
$Pt_1Ru_x@C$-30	4.22	1.03
$Pt_1Ru_x@C$-70	4.80	1.26

Tab. S3. Information on the bands that make up the first-order Raman spectrum of samples.

Peak	Raman shift [cm^{-1}]			
	C	Ru_x@C	Pt_1@C	Pt_1Ru_x@C
G	1219.8	1224.1	1236.3	1225.8
D2	1336.9	1337.6	1343.8	1340.8
D1	1504.3	1506.9	1509.4	1509.3
D3	1586.9	1589.1	1594.1	1592.9

Tab. S4. The binding energy of Pt 4f, Ru $3p_{3/2}$ and O 1s from XPS.

Catalysts	Binding energy [eV]		Component	Binding energy [eV]	Component	Binding energy [eV]	Component
	Pt $4f_{7/2}$	Pt $4f_{5/2}$		Ru $3p_{3/2}$		O 1s	
Pt_1Ru_x@C	72.62	76.00	Pt^{2+}	463.59	Ru^0	530.60	Pt/Ru-O
	74.51	78.01	Pt^{4+}	/	/	/	/
Pt_1@C	72.13	75.46	Pt^{2+}	/	/	530.17	Pt-O
	74.16	77.63	Pt^{4+}	/	/	/	/
Ru_x@C	/	/	/	463.79	Ru^0	530.22	Ru-O

Tab. S5. XAFS parameters of Pt_1Ru_x@C, Pt foil and PtO_2.

Sample	Shell	N[a)]	R [Å][b)]	σ^2 [10^{-3} Å^2][c)]	R-factor[d)]
Pt_1Ru_x@C	Pt-C/O	1.5	2.51	8.42	0.02
Pt foil	Pt-Pt	12	2.76	1.90	0.02
PtO_2	Pt-O	6	1.99	2.35	0.02

[a)]N, coordination number; [b)]R, distance between absorber and backscattered atoms; [c)]σ^2, Debye-Waller factor; [d)]R-factor, closeness of the fit, if < 0.05, consistent with broadly correct models. Estimated error: N: ±20%, R: ±0.03.

Tab. S6. Summarized acidic/alkaline HER performance of some reported atomic level catalysis with present work.

Catalyst	Electrolyte	η@10 mA cm^{-2} [mV]	Tafel slope [mV dec^{-1}]	Ref.
Pt_1Ru_x@C	**0.5 M H_2SO_4**	**13.15**	**20.7**	**This work**
Pt_1Ru_x@C	**1.0 M KOH**	**48.7**	**55.6**	**This work**
Fe/GD	0.5 M H_2SO_4	66	37.8	[1]
Co_1/PCN	0.5 M H_2SO_4	151	52	[2]
NiO/Ni@NCNTs	0.5 M H_2SO_4	87.5	80	[3]
Mo@NMCNFs	0.5 M H_2SO_4	66	84.9	[4]
PtW_6/C	0.5 M H_2SO_4	22	/	[5]
Pt-Ru dimer	0.5 M H_2SO_4	50	28.9	[6]
Pt_1@Fe-C	0.5 M H_2SO_4	60	42	[7]
$Pt_1/Ti_{1-x}O_2$	0.5 M H_2SO_4	22.2	31	[8]
PtNi-NC	0.5 M H_2SO_4	30	27	[9]
NeC@CoP/Ni_2P	0.5 M H_2SO_4	153	53.01	[10]
Cu/Ru@G_N	0.5 M H_2SO_4	10	25	[11]
W_1Mo_1-NG	1.0 M KOH	67	45	[12]
Ir_1@Co/NC	1.0 M KOH	55	119	[13]
Ru-SA/$Ti_3C_2T_x$	1.0 M KOH	70	27.7	[14]
Ru/Ni-MoS_2	1.0 M KOH	32	41	[15]
Ru/Co-CAT/CC	1.0 M KOH	38	/	[16]
Ru-MoS_2/CC	1.0 M KOH	41	114	[17]
Ru-W/WO_2-800	1.0 M KOH	11	31.3	[18]
12%Rh-Co_2Fe-P	1.0 M KOH	48	53	[19]
Fe-N_4 SAs/NPC	1.0 M KOH	202	123	[20]
Co_1/PCN	1.0 M KOH	89	/	[2]

References

1. Y. Xue, B. Huang, Y. Yi, Y. Guo, Z. Zuo, Y. Li, Z. Jia, H. Liu and Y. Li, *Nat. Commun.*, 2018,

9, 1460.

2. L. Cao, Q. Luo, W. Liu, Y. Lin, X. Liu, Y. Cao, W. Zhang, Y. Wu, J. Yang and T. Yao, *Nat. Catal.*, 2019, **2**, 134-141.
3. J. Wang, X. Ge, L. Shao, J. Zhang, D. Peng, G. Zou, H. Hou, W. Deng, S. Xu, X. Ji and W. Zhang, *Mater. Today Energy*, 2020, **17**.
4. T. F. Li, T. Y. Lu, X. Li, L. Xu, Y. W. Zhang, Z. Q. Tian, J. Yang, H. Pang, Y. W. Tang and J. M. Xue, *ACS Nano*, 2021, **15**, 20032-20041.
5. F.-Y. Yu, Z.-L. Lang, Y.-J. Zhou, K. Feng, H.-Q. Tan, J. Zhong, S.-T. Lee, Z.-H. Kang and Y.-G. Li, *ACS Energy Lett.*, 2021, **6**, 4055-4062.
6. L. Zhang, R. T. Si, H. S. Liu, N. Chen, Q. Wang, K. Adair, Z. Q. Wang, J. T. Chen, Z. X. Song, J. J. Li, M. N. Banis, R. Y. Li, T. K. Sham, M. Gu, L. M. Liu, G. A. Botton and X. L. Sun, *Nat. Commun.*, 2019, **10**.
7. X. Zeng, J. Shui, X. Liu, Q. Liu, Y. Li, J. Shang, L. Zheng and R. Yu, *Adv. Energy Mater.*, 2018, **8**, 1701345.
8. F. Lu, D. Yi, S. J. Liu, F. Zhan, B. Zhou, L. Gu, D. Golberg, X. Wang and J. N. Yao, *Angew. Chem., Int. Ed.*, 2020, **59**, 17712-17718.
9. Y. M. Da, Z. L. Tian, R. Jiang, Y. Liu, X. Lian, S. B. Xi, Y. Shi, Y. P. Wang, H. T. Lu, B. H. Cui, J. F. Zhang, X. P. Han, W. Chen and W. B. Hu, *Sci. China Mater.*, 2023, **66**, 1389-1397.
10. T. Feng, F. Wang, Y. Xu, M. Chang, X. Jin, z. Yulin, J. Piao and J. Lei, *Int. J. Hydrogen Energy*, 2021, **46**, 8431-8443.
11. A. M. Harzandi, S. Shadman, M. Ha, C. W. Myung, D. Y. Kim, H. J. Park, S. Sultan, W.-S. Noh, W. Lee, P. Thangavel, W. J. Byun, S.-h. Lee, J. N. Tiwari, T. J. Shin, J.-H. Park, Z. Lee, J. S. Lee and K. S. Kim, *Appl. Catal., B*, 2020, **270**, 118896.
12. Y. Yang, Y. Qian, H. Li, Z. Zhang, Y. Mu, D. Do, B. Zhou, J. Dong, W. Yan, Y. Qin, L. Fang, R. Feng, J. Zhou, P. Zhang, J. Dong, G. Yu, Y. Liu, X. Zhang and X. Fan, *Sci. Adv.*, 2020, **6**, eaba6586.
13. W.-H. Lai, L.-F. Zhang, W.-B. Hua, S. Indris, Z.-C. Yan, Z. Hu, B. Zhang, Y. Liu, L. Wang, M. Liu, R. Liu, Y.-X. Wang, J.-Z. Wang, Z. Hu, H.-K. Liu, S.-L. Chou and S.-X. Dou, *Angew. Chem., Int. Ed.*, 2019, **58**, 11868-11873.
14. X. Peng, S. Zhao, Y. Mi, L. Han, X. Liu, D. Qi, J. Sun, Y. Liu, H. Bao, L. Zhuo, H. L. Xin, J.

Luo and X. Sun, *Small*, 2020, **16**, 2002888.

15. B. Guo, R. Ma, Z. Li, J. Luo, M. Yang and J. Wang, *Mater. Chem. Front.*, 2020, **4**, 1390-1396.
16. Y. He, F. Yan, X. Zhang, C. Zhu, Y. Zhao, B. Geng, S. Chou, Y. Xie and Y. Chen, *Adv. Energy Mater.*, 2023, **13**, 2204177.
17. D. W. Wang, Q. Li, C. Han, Z. C. Xing and X. R. Yang, *Appl. Catal., B*, 2019, **249**, 91-97.
18. W. L. Ma, X. Y. Yang, D. D. Li, R. X. Xu, L. P. Nie, B. P. Zhang, Y. Wang, S. Wang, G. Wang, J. X. Diao, L. R. Zheng, J. B. Bai, K. Y. Leng, X. L. Li and Y. T. Qu, *Adv. Sci.*, 2023.
19. L. Li, Y. Lu, X. Liu, X. Wang and S. Zhou, *J. Alloys Compd.*, 2022, **895**, 162549.
20. Y. Pan, S. Liu, K. Sun, X. Chen, B. Wang, K. Wu, X. Cao, W. C. Cheong, R. Shen and A. Han, *Angew. Chem., Int. Ed.*, 2018, **57**, 8614-8618.