Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Galvanic Replacement-Induced the preparation of bloom-like $Pt_{23}Ni_{77}$ for methanol coupled efficient hydrogen production

Jin Zhao, Jinjin Wang, Ying Wang, Junming Zhang, Ergui Luo, Baoliang Lv, Tianjun Hu*, Jianfeng Jia*

Key Laboratory of Magnetic Molecules and Magnetic Information Materials of Ministry of Education & School of Chemistry and Materials Science of Shanxi Normal University, Taiyuan 030032, China

*Corresponding authors.

E-mail: hutj@ sxnu.edu.cn (T.-J Hu), jiajf@dns.sxnu.edu.cn (J.-F Jia)

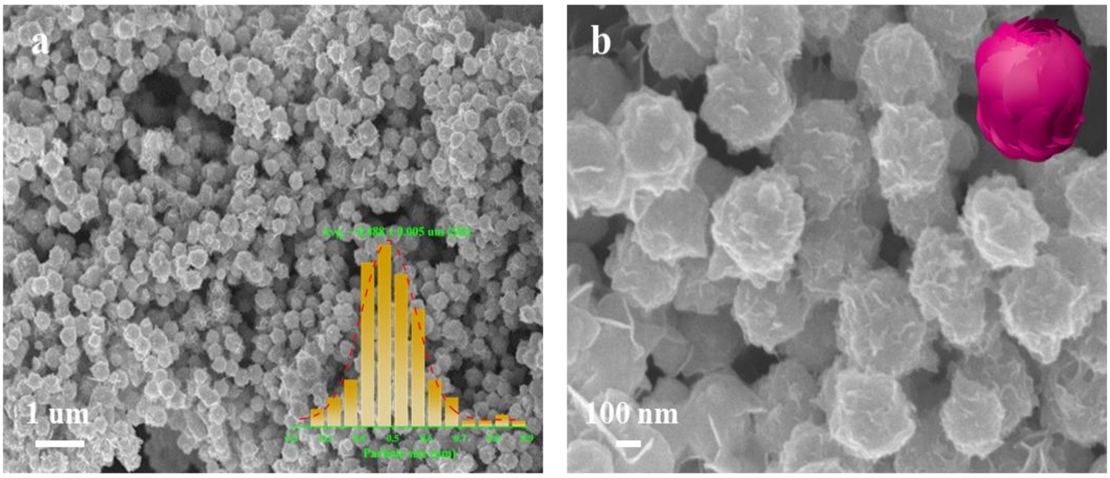

Fig. S1 The SEM images. a, b) Ni NPs.

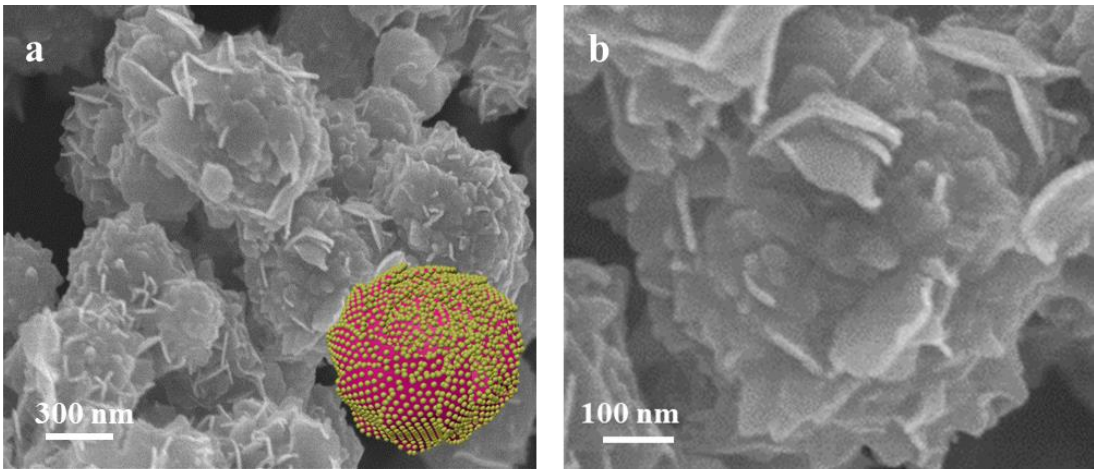

Fig. S2 The SEM images. a, b) $Pt_{12}Ni_{88}$.

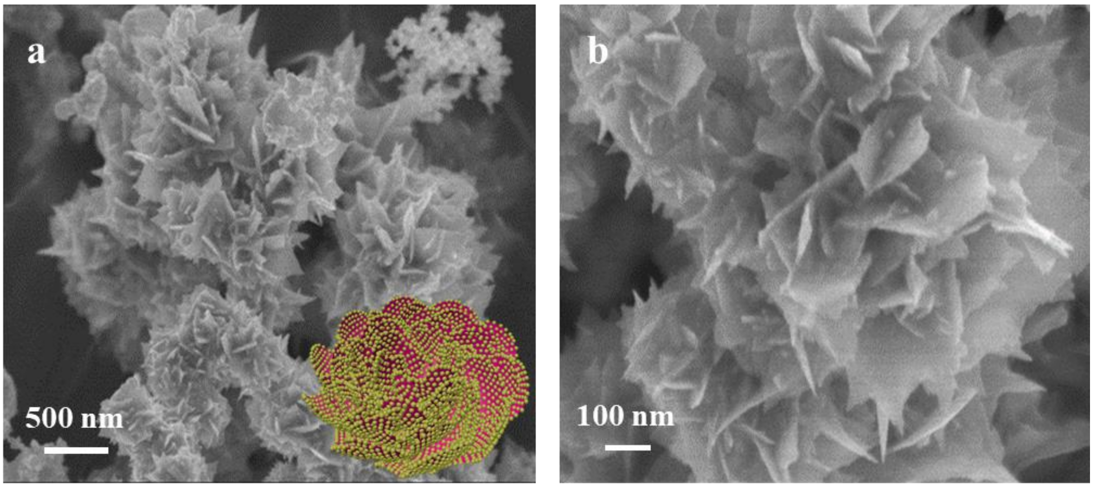

Fig. S3 The SEM images. a, b) $Pt_{23}Ni_{77}$.

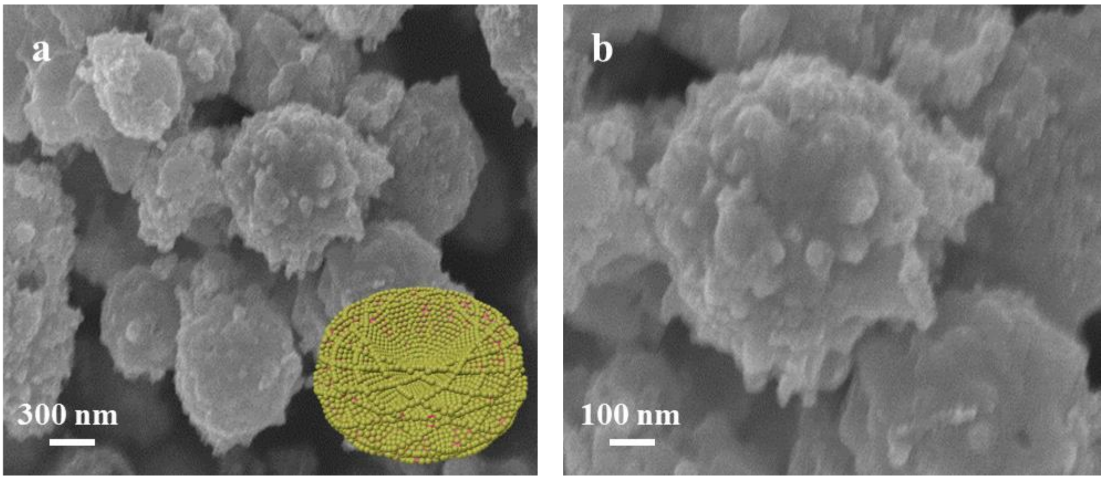

Fig. S4 The SEM images. a, b) $Pt_{42}Ni_{58}$.

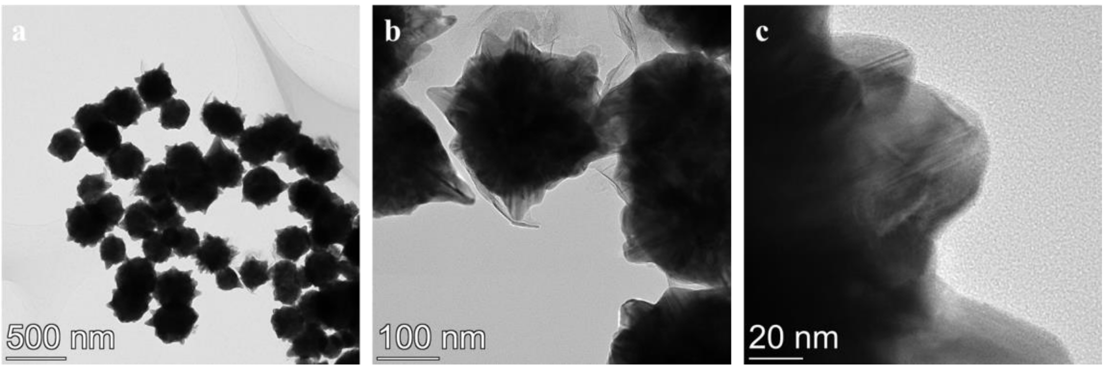

Fig. S5 (a-c) Low-magnification TEM images for Ni.

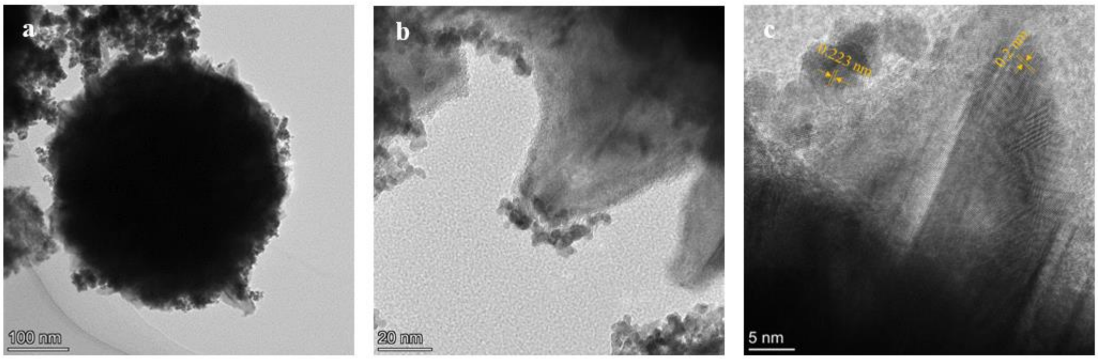

Fig. S6 (a-c) Low-magnification TEM images for $Pt_{12}Ni_{88}$.

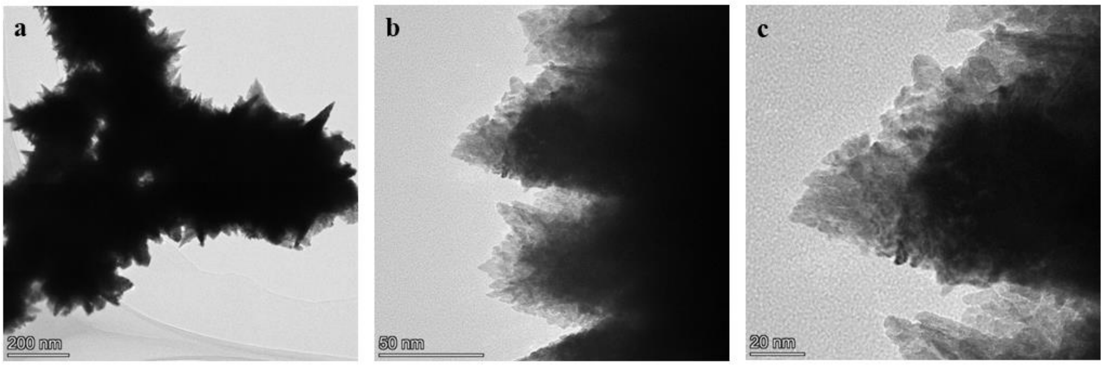

Fig. S7 (a-c) Low-magnification TEM images for $Pt_{23}Ni_{77}$.

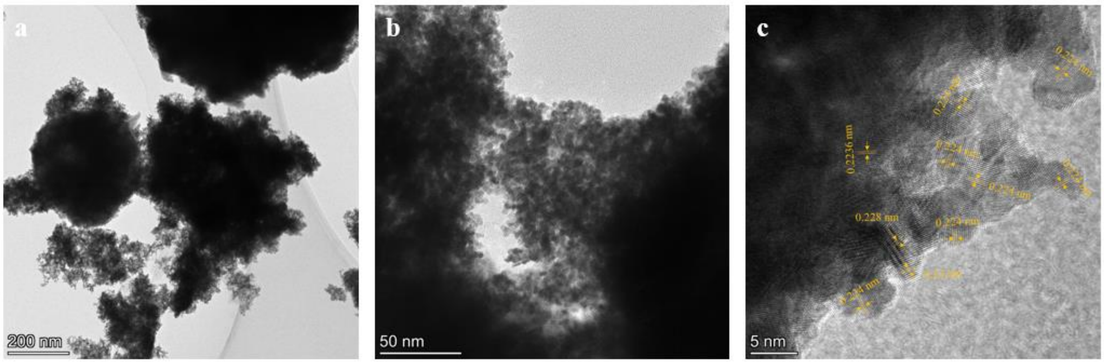

Fig. S8 (a-c) Low-magnification TEM images for $Pt_{42}Ni_{58}$.

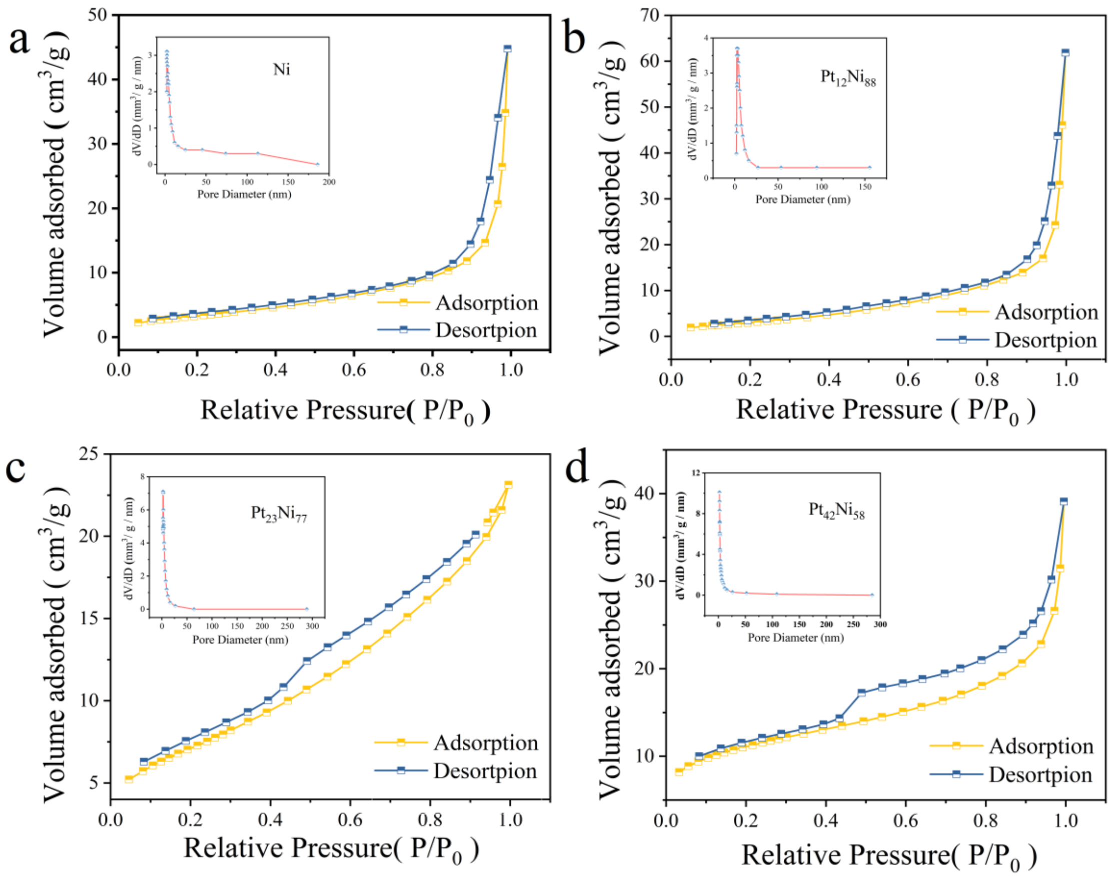

Fig. S9 N_2 adsorption/desorption isotherms and pore size distribution of the (a) Ni, (b) $Pt_{12}Ni_{88}$, (c) $Pt_{23}Ni_{77}$, and (d) $Pt_{42}Ni_{58}$.

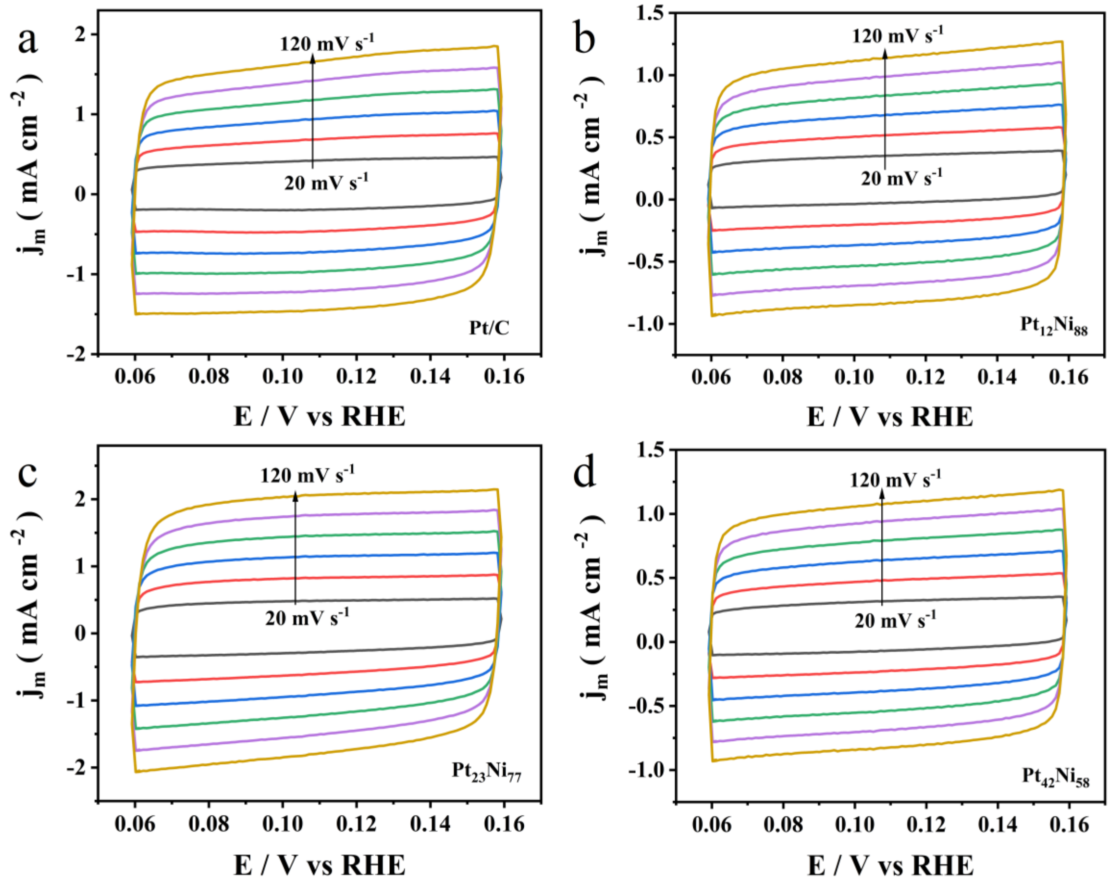

Fig. S10 The CV curves obtained at different scan rates (20-120 mV s^{-1}) a) Pt/C, b) $Pt_{12}Ni_{88}$, c) $Pt_{23}Ni_{77}$, and d) $Pt_{42}Ni_{58}$ in 0.5 M H_2SO_4.

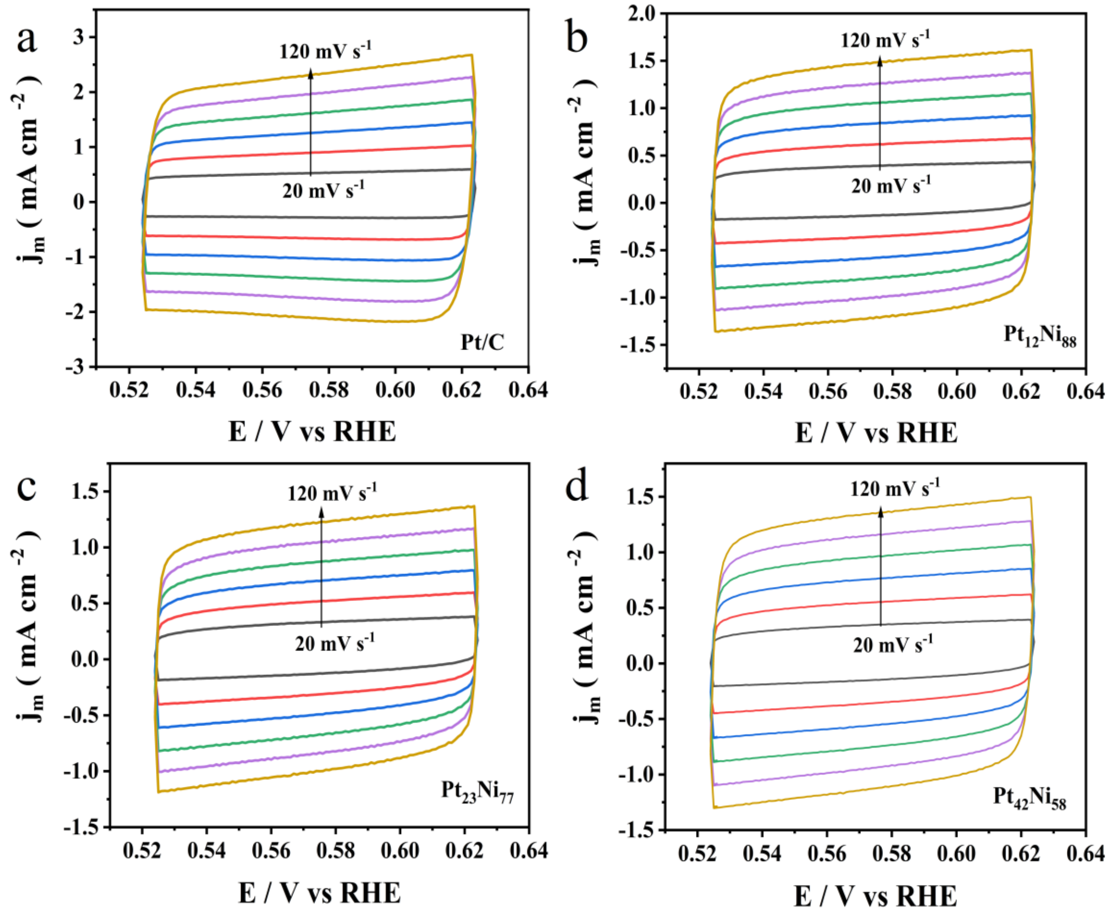

Fig. S11 The CV curves obtained at different scan rates (20-120 mV s^{-1}) a) Pt/C, b) $Pt_{12}Ni_{88}$, c) $Pt_{23}Ni_{77}$, and d) $Pt_{42}Ni_{58}$ in 1.0 M KOH.

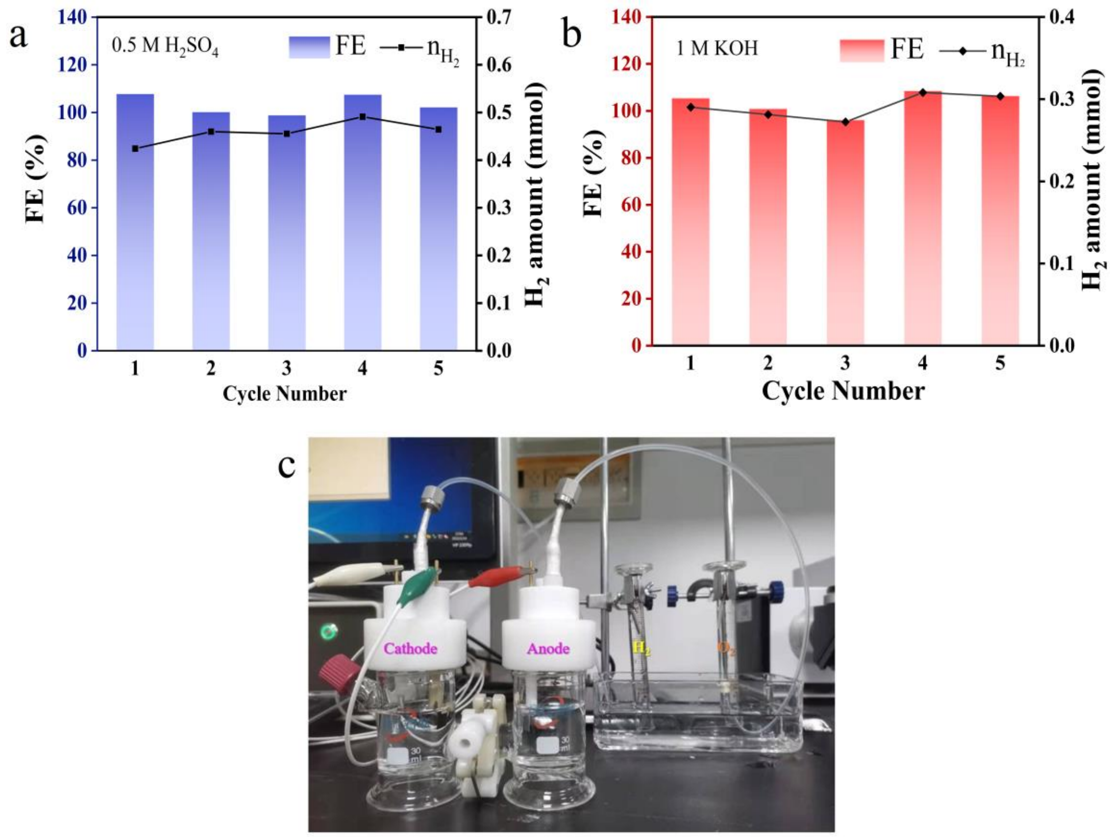

Fig. S12 Amount of H_2 and FEs during recycling tests for 5 cycles with an overpotential of 100 mV and 10 min in (a) 0.5 M H_2SO_4 and (b) 1.0 M KOH. (c) Diagram of the device for collecting hydrogen and oxygen using the drainage gas collection method.

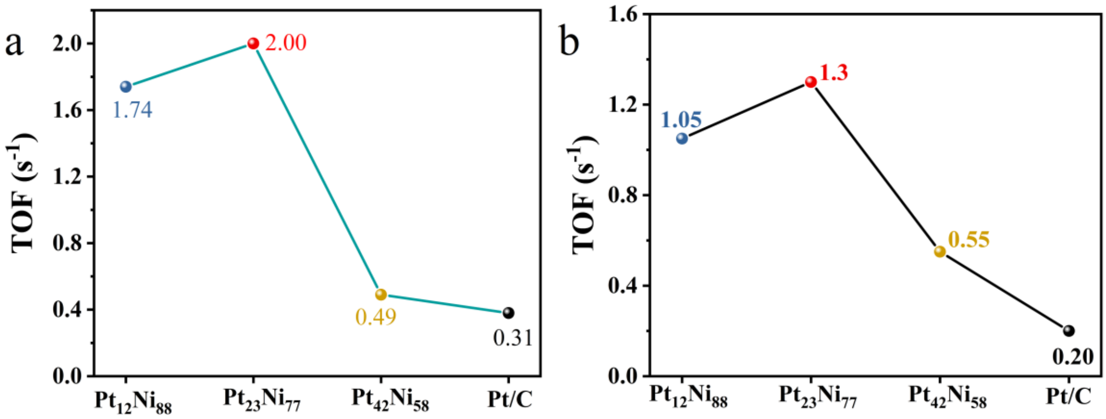

Fig. S13 (a) Comparison of potential-dependent TOF at -0.05 V vs. RHE in 0.5M H_2SO_4. (b) Comparison of potential-dependent TOF at -0.07 V vs. RHE in 1.0 M KOH.

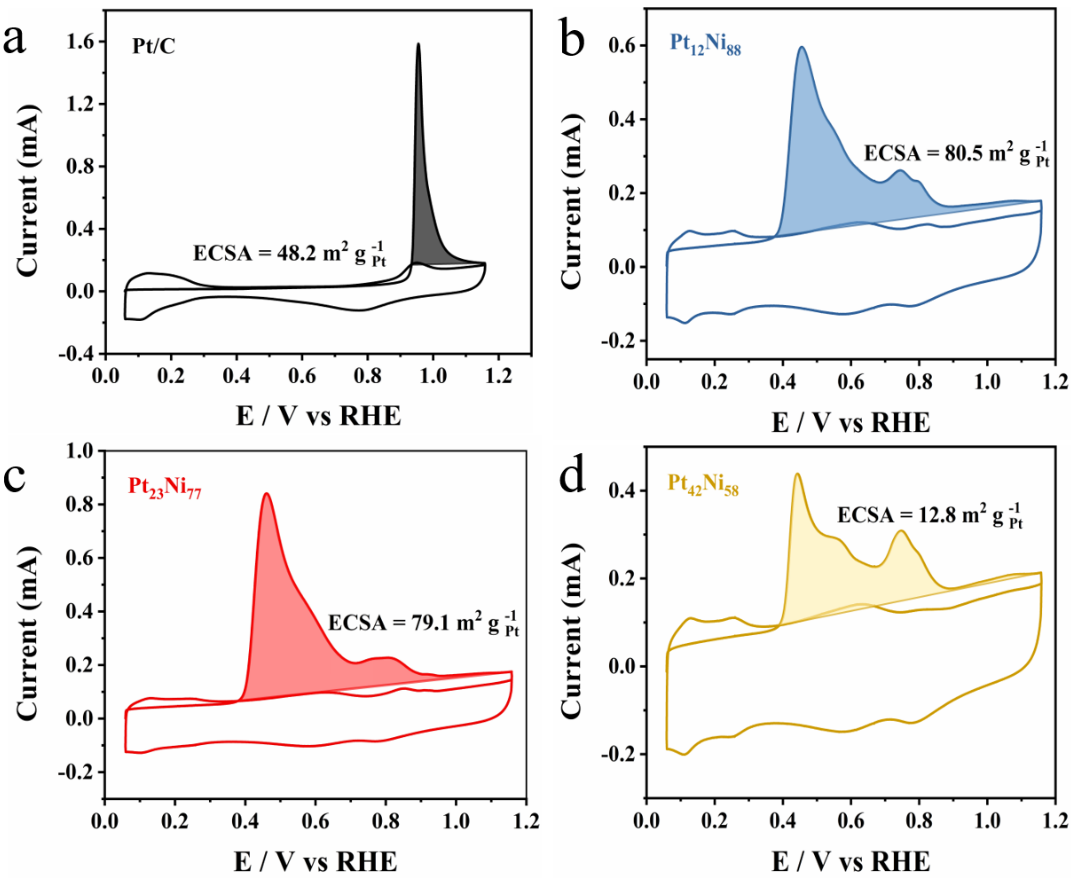

Fig. S14 CO stripping that quantifies the surface area of catalysts at 50 mV s^{-1} in N_2-saturated 0.5 M H_2SO_4.

Table S1. ICP-MS analysis of catalysts.

Catalyst	Pt loading (wt. %)	Ni loading (wt. %)	Molar ratio of Pt : Ni
$Pt_{12}Ni_{88}$	12	88	0.03941
$Pt_{23}Ni_{77}$	23	77	0.09184
$Pt_{42}Ni_{58}$	42	58	0.22180

Table S2. Porosity Parameters of the Ni, $Pt_{12}Ni_{88}$, $Pt_{23}Ni_{77}$, and $Pt_{42}Ni_{58}$ catalysts.

Sample	Ni	$Pt_{12}Ni_{88}$	$Pt_{23}Ni_{77}$	$Pt_{42}Ni_{58}$
S_{BET} [a]	17.6104	21.4322	27.8802	26.4335
D_{pore} [b]	16.6038	18.9621	5.4376	8.4741
V_{pore} [c]	0.0731	0.1016	0.0379	0.0560

[a] BET surface areas (m^2/g). [b] Average pore size (nm). [c] Single-point adsorption total pore volume of pores (cm^3/g).

Table S3. Summary of the HER Properties of $Pt_{23}Ni_{77}$ and other representative catalysts in literature at 1.0 M KOH.

Catalysts	**Overpotential (mV vs. RHE) at 10 mA cm^{-2}**	**Ref.**
$Pt_{23}Ni_{77}$	32	This work
Pt_1/N-C	46	1
Pt/NiRu-OH	38	2
Pt-Ni NWs/NiO_x	40	3
Pt_3Ni_2-NWs-S	42	4
A-CoPt-NC	50	5
Pt-Ni-O	40	6
RhPd-H	40	7
Pt/MOF-O	66	8
Pt/np-$Co_{0.85}Se$	58	9
Pt-$Co(OH)_2$/C	32	10
RuTeP	35	11
Ru_1Ni_1-NCNFs	35	12
Pd_3Ru/C	42	13
$Pt_{3.6}$Ni-S NWs	38	14
Pt/MgO	39	15

Table S4. Summary of the HER Properties of $Pt_{23}Ni_{77}$ and other representative catalysts in literature at 0.5 M H_2SO_4.

Catalysts	**Overpotential (mV vs. RHE) at 10 mA cm^{-2}**	**Ref.**
$Pt_{23}Ni_{77}$	21.2	This work
Pt_1Ru_1/NMHCS-A	22	16
Pt-SAs/WS_2	32	17
1% PtW_6O_{24}/C	22	18
Pt_1/OLC	38	19
PtN_x/TiO_2	67	20
Pt/MOF-O	28	8
$PtTe_2$ NSs	~40	21
PtRu/RFCS	46.6	22
Pt/C-40%	45	23
Pt_3Ni_4 NWs/C	40	4
Pt@NHPCP	56	24
Pt@MTO-S	73	25
ALD50 Pt/NGNs	39	26
PtSi	22	27

Table S5. Comparison of the MOR activity of different Pt electrocatalysts in acid solution.

Catalysts	Electrolytes	Onset potential (V vs. RHE)	Mass activity (mA mg^{-1})	Ref.
$Pt_{23}Ni_{77}$	0.5 M H_2SO_4 + 0.5 M Methanol	0.60	2470	This work
CeO_x/PtCu/$CeCuO_x$/C	0.5 M H_2SO_4 + 0.5 M Methanol	0.52	889	28
Ce-modified Pt NPs/C	0.5 M H_2SO_4 + 1.0 M Methanol	0.55	1470	29
CuWPt-1	0.1 M $HClO_4$ + 1.0 M Methanol	0.60	2110	30
GDY@PtCu	0.5 M H_2SO_4 + 1.0 M Methanol	0.64	700	31
Ru-ca-PtNi	0.1 M $HClO_4$ + 0.5 M Methanol	0.60	2010	32
$Pt_3Co–CoP_2$	0.1 M $HClO_4$ + 1.0 M Methanol	0.59	1400	33
Pt/CeO_2-P	0.5 M H_2SO_4 + 1.0 M Methanol	0.60	714	34
PtCo @NC	0.1 M $HClO_4$ + 1.0 M Methanol	0.45	2300	35
PtTe PNCs	0.5 M H_2SO_4 + 1.0 M Methanol	0.54	1020	36

References

[1] S. Fang, X. Zhu, X. Liu, J. Gu, W. Liu, D. Wang, W. Zhang, Y. Lin, J. Lu, S. Wei, Y. Li and T. Yao, *Nat Commun*, 2020, **11**, 1029.

[2] D. Li, X. Chen, Y. Lv, G. Zhang, Y. Huang, W. Liu, Y. Li, R. Chen, C. Nuckolls and H. Ni, *Appl. Catal. B*, 2020, **269**, 118824.

[3] P. Wang, K. Jiang, G. Wang, J. Yao and X. Huang, *Angew. Chem. Int. Ed*, 2016, **55**, 12859-12863.

[4] P. Wang, X. Zhang, J. Zhang, S. Wan, S. Guo, G. Lu, J. Yao and X. Huang, *Nat Commun*, 2017, **8**, 14580.

[5] L. Zhang, Y. Jia, H. Liu, L. Zhuang, X. Yan, C. Lang, X. Wang, D. Yang, K. Huang, S. Feng and X. Yao, *Angew. Chem. Int. Ed*, 2019, **58**, 9404-9408.

[6] Z. Zhao, H. Liu, W. Gao, W. Xue, Z. Liu, J. Huang, X. Pan and Y. Huang, *J Am Chem Soc*, 2018, **140**, 9046-9050.

[7] J. Fan, J. Wu, X. Cui, L. Gu, Q. Zhang, F. Meng, B. H. Lei, D. J. Singh and W. Zheng, *J Am Chem Soc*, 2020, **142**, 3645-3651.

[8] M. Wang, Y. Xu, C.-K. Peng, S.-Y. Chen, Y.-G. Lin, Z. Hu, L. Sun, S. Ding, C.-W. Pao, Q. Shao and X. Huang, *J. Am. Chem. Soc*, 2021, **143**, 16512-16518.

[9] K. Jiang, B. Liu, M. Luo, S. Ning, M. Peng, Y. Zhao, Y. R. Lu, T. S. Chan, F. M. F. de Groot and Y. Tan, *Nat Commun*, 2019, **10**, 1743.

[10] Z. Xing, C. Han, D. Wang, Q. Li and X. Yang, *ACS Catalysis*, 2017, **7**, 7131-7135.

[11] M. Liu, Y. Xu, S. Liu, S. Yin, M. Liu, Z. Wang, X. Li, L. Wang and H. Wang, *J. Mater. Chem. A*, 2021, **9**, 5026-5032.

[12] M. Li, H. Wang, W. Zhu, W. Li, C. Wang and X. Lu, *Adv Sci (Weinh)*, 2020, **7**, 1901833.

[13] X. Qin, L. Zhang, G.-L. Xu, S. Zhu, Q. Wang, M. Gu, X. Zhang, C. Sun, P. B. Balbuena, K. Amine and M. Shao, *ACS Catalysis*, 2019, **9**, 9614-9621.

[14] Z. Liu, J. Qi, M. Liu, S. Zhang, Q. Fan, H. Liu, K. Liu, H. Zheng, Y. Yin and C. Gao, *Angew. Chem. Int. Ed*, 2018, **57**, 11678-11682.

[15] H. Tan, B. Tang, Y. Lu, Q. Ji, L. Lv, H. Duan, N. Li, Y. Wang, S. Feng, Z. Li, C. Wang, F. Hu, Z. Sun and W. Yan, *Nat Commun*, 2022, **13**, 2024.

[16] W. Zhao, C. Luo, Y. Lin, G.-B. Wang, H. M. Chen, P. Kuang and J. Yu, *ACS Catalysis*, 2022, **12**, 5540-5548.

[17] Y. Shi, Z. R. Ma, Y. Y. Xiao, Y. C. Yin, W. M. Huang, Z. C. Huang, Y. Z. Zheng, F. Y. Mu, R. Huang, G. Y. Shi, Y. Y. Sun, X. H. Xia and W. Chen, *Nat Commun*, 2021, **12**, 3021.

[18] F. Y. Yu, Z. L. Lang, L. Y. Yin, K. Feng, Y. J. Xia, H. Q. Tan, H. T. Zhu, J. Zhong, Z. H. Kang and Y. G. Li, *Nat Commun*, 2020, **11**, 490.

[19] D. Liu, X. Li, S. Chen, H. Yan, C. Wang, C. Wu, Y. A. Haleem, S. Duan, J. Lu, B. Ge, P. M. Ajayan, Y. Luo, J. Jiang and L. Song, *Nature Energy*, 2019, **4**, 512-518.

[20] X. Cheng, Y. Lu, L. Zheng, Y. Cui, M. Niibe, T. Tokushima, H. Li, Y. Zhang, G. Chen, S. Sun and J. Zhang, *Nano Energy*, 2020, **73**, 104739.

[21] X. Li, Y. Fang, J. Wang, H. Fang, S. Xi, X. Zhao, D. Xu, H. Xu, W. Yu, X. Hai, C. Chen, C. Yao, H. B. Tao, A. G. R. Howe, S. J. Pennycook, B. Liu, J. Lu and C. Su, *Nat Commun*, 2021, **12**, 2351.

[22] K. Li, Y. Li, Y. Wang, J. Ge, C. Liu and W. Xing, *Energy Environ. Sci*, 2018, **11**, 1232-1239.

[23] L. Zhu, H. Lin, Y. Li, F. Liao, Y. Lifshitz, M. Sheng, S. T. Lee and M. Shao, *Nat Commun*, 2016, **7**, 12272.

[24] J. Ying, G. Jiang, Z. Paul Cano, L. Han, X.-Y. Yang and Z. Chen, *Nano Energy*, 2017, **40**, 88-94.

[25] P. Bhanja, B. Mohanty, A. K. Patra, S. Ghosh, B. K. Jena and A. Bhaumik, *ChemCatChem*, 2018, **11**, 583-592.

[26] N. Cheng, S. Stambula, D. Wang, M. N. Banis, J. Liu, A. Riese, B. Xiao, R. Li, T. K. Sham, L. M. Liu, G. A. Botton and X. Sun, *Nat Commun*, 2016, **7**, 13638.

[27] Z. Pu, T. Liu, G. Zhang, Z. Chen, D. S. Li, N. Chen, W. Chen, Z. Chen and S. Sun, *Adv. Energy Mater*, 2022, **12**, 2200293.

[28] Y. Wang, Z. Li, X. Zheng, R. Wu, J. Song, Y. Chen, X. Cao, Y. Wang and Y.

Nie, *Appl. Catal. B*, 2023, **325**, 122383.

[29] L. Chen, X. Liang, X. Li, J. Pei, H. Lin, D. Jia, W. Chen, D. Wang and Y. Li, *Nano Energy*, 2020, **73**, 104784.

[30] D. Liu, Q. Zeng, C. Hu, D. Chen, H. Liu, Y. Han, L. Xu, Q. Zhang and J. Yang, *Nano Research Energy*, 2022, **1**.

[31] H. Pan, Z. Jiang, Z. Zuo, F. He, F. Wang, L. Li, Q. Chang, B. Guan and Y. Li, *Nano Today*, 2021, **39**, 101213.

[32] F. Kong, X. Liu, Y. Song, Z. Qian, J. Li, L. Zhang, G. Yin, J. Wang, D. Su and X. Sun, *Angew. Chem. Int. Ed*, 2022, **61**, 202207524.

[33] N. Yang, D. Chen, P. Cui, T. Lu, H. Liu, C. Hu, L. Xu and J. Yang, *SmartMat*, 2021, **2**, 234-245.

[34] L. Tao, Y. Shi, Y.-C. Huang, R. Chen, Y. Zhang, J. Huo, Y. Zou, G. Yu, J. Luo, C.-L. Dong and S. Wang, *Nano Energy*, 2018, **53**, 604-612.

[35] G. Hu, L. Shang, T. Sheng, Y. Chen and L. Wang, *Adv. Funct. Mater*, 2020, **30**, 2002281.

[36] Q. Zhang, T. Xia, H. Huang, J. Liu, M. Zhu, H. Yu, W. Xu, Y. Huo, C. He, S. Shen, C. Lu, R. Wang and S. Wang, *Nano Research Energy*, 2023, **2**, 9120041.