Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary information

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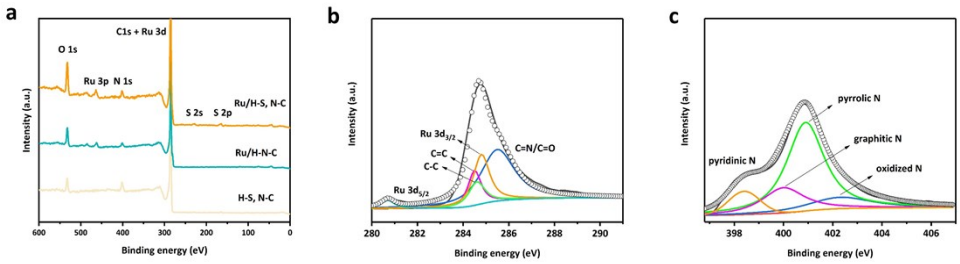

Fig S1 (a) XPS survey of Ru/H-S, N-C, Ru/H-N-C, and H-S, N-C; (b) C 1s and Ru 3d spectra; (c) N 1s spectra

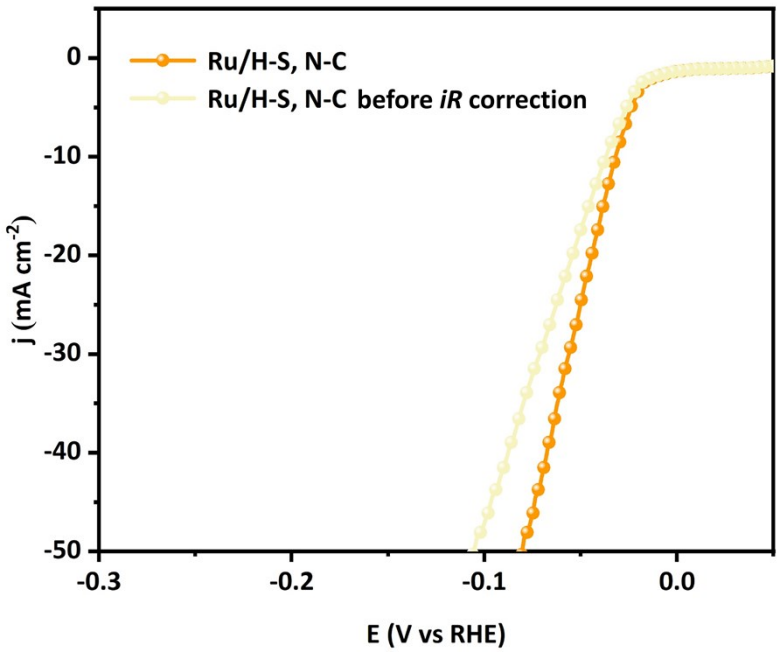

Fig S2 The comparison of LSV curves before and after *iR* correction of Ru/H-S, N-C

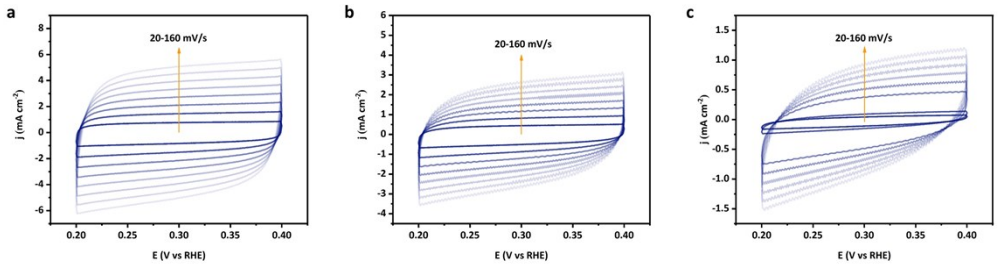

Fig S3 CV curves between 0.30 and 0.40 V of (a) Ru/H-S, N-C, (b) Ru/H-N-C, and (c) H-S, N-C

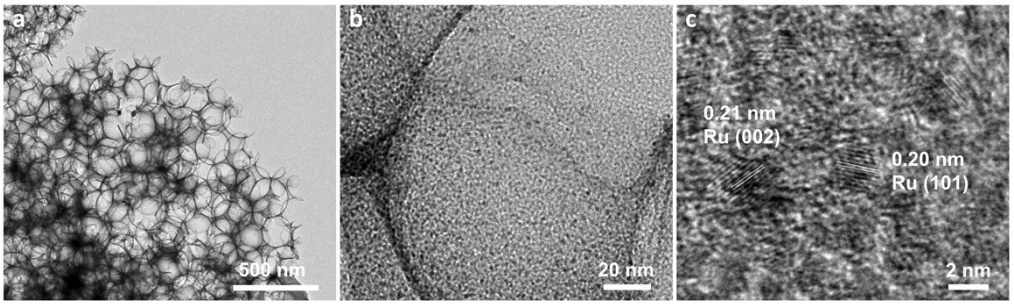

Fig S4 (a) TEM and (b-c) HRTEM images of Ru/H-S, N-C after stability test.

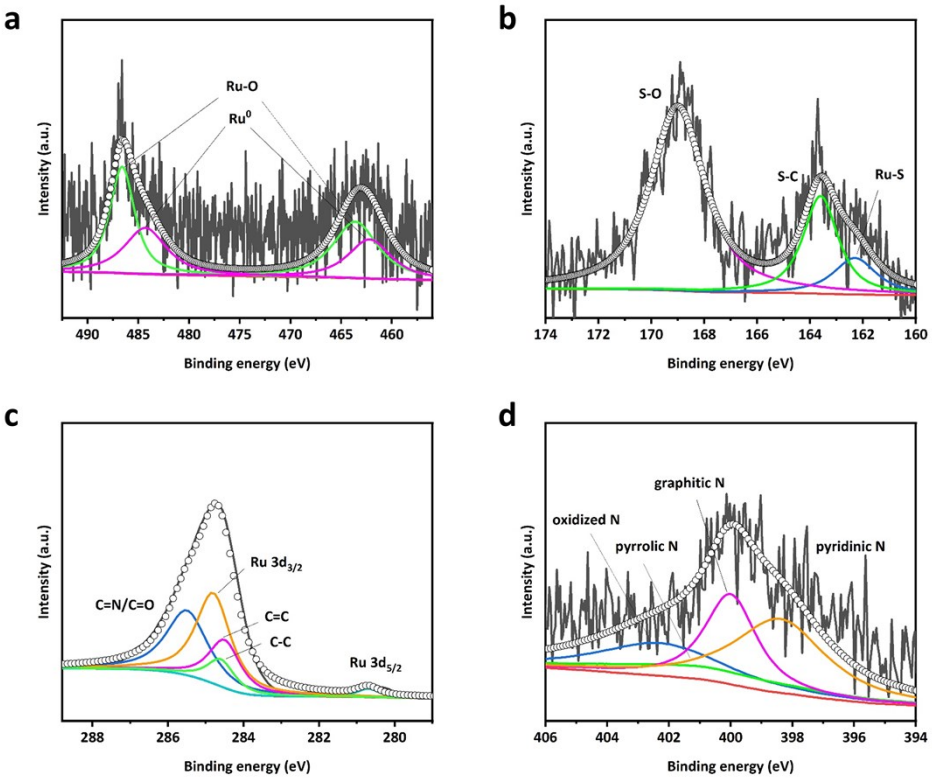

Fig S5 XPS spectra of Ru/H-S, N-C after stability test

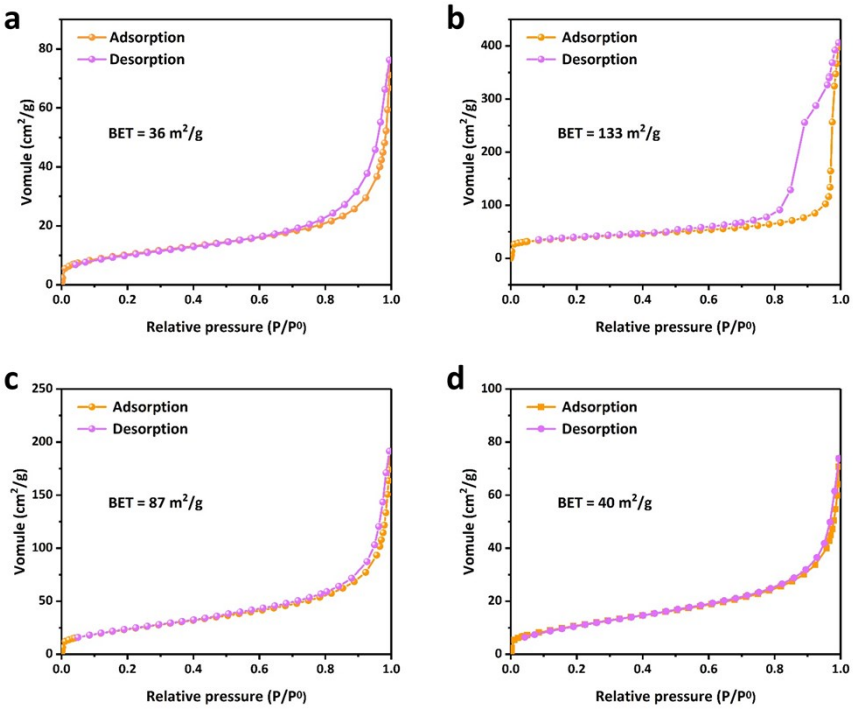

Fig. S6 The N_2 adsorption and desorption measurements (a) Ru-S, N-C and Ru/H-S, N-C with different diameters of SiO_2 as templates (b) 50 nm, (c) 227 nm, and (d) 380nm

Table S1. Statistic data of yield after each synthesis procedure of Ru/H-S, N-C

Procedure	**Weight (mg)**	**Yield (%)**
Weighing	127.06	-
Self-assembly & Oil bath	107.02	84.23
Pyrolysis	78.53	73.38
HF etching	6.71	8.54

Table S2. Element composition of Ru/H-S, N-C and Ru/H-N-C on the basis of TEM-EDS

Sample	Element	Wt%
Ru/H-S, N-C	Ru	16.76
	S	2.29
	N	1.12
	C	79.83
Ru/H-N-C	Ru	13.12
	N	0.43
	C	86.45

Table S3. The comparison of HER performance between Ru/H-S, N-C and other Ru-based catalysts

Catalysts	Electrolyte	η_{10} (mV)	Tafel slope (mV dec^{-1})	loading (mg cm^{-2})	Ref.
Ru/H-S, N-C	1.0 M KOH	32	24	0.35	This work
Pt/C	1.0 M KOH	40	42	0.35	This work
Ru^0/CeO_2	1.0 M KOH	47	41	0.197	1
Ru-MoO_2	1.0 M KOH	29	31	0.285	2
$Cu_{2-x}S$@Ru	1.0 M KOH	82	48	0.23	3
NiO/Ru@Ni	1.0 M KOH	39	75	-	4
RuP_2@NPC	1.0 M KOH	52	69	1.0	5
S-4	1.0 M KOH	28	31	0.275	6
Ru_2Ni_2 SNs/C	1.0 M KOH	40	23.4	0.1	7
Ru@SC-CDs 2:10	1.0 M KOH	29	57	0.42	8
Ru_2P@PNC/CC-900	1.0 M KOH	50	66	1.5	9
Ni@Ni_2P-Ru HNRs	1.0 M KOH	41	31	-	10
SA-Ru-MoS_2	1.0 M KOH	76	21	0.285	11
Ru-MoS_2/CNT	1.0 M KOH	50	62	1.0	12
RuS_x/S-GO	1.0 M KOH	58	56	1.0	13

$Ru_{0.33}Se$ @ TNA	1.0 M KOH	57	50	0.2	14

Table S4. The calculation of the atomic ratio of Ru 3p to N 1s of Ru/H-S, N-C before and after the stability test.

Sample	Element	Peak Area	Sensitivity Factor	Normalized Area	Atomic Ratio
Before stability test	Ru 3p	16007.3	13.262	1207.0	0.302
	N 1s	6693.6	1.676	3993.8	
After stability test	Ru 3p	7693.1	13.262	580.1	0.305
	N 1s	3190.6	1.676	1903.7	

Reference:

1. E. Demir, S. Akbayrak, A. M. Onal and S. Ozkar, *ACS Appl. Mater. Interfaces*, 2018, **10**, 6299-6308.
2. P. Jiang, Y. Yang, R. Shi, G. Xia, J. Chen, J. Su and Q. Chen, *J. Mater. Chem. A*, 2017, **5**, 5475-5485.
3. D. Yoon, J. Lee, B. Seo, B. Kim, H. Baik, S. H. Joo and K. Lee, *Small*, 2017, **13**, 1700052.
4. C. Zhong, Q. Zhou, S. Li, L. Cao, J. Li, Z. Shen, H. Ma, J. Liu, M. Lu and H. Zhang, *J. Mater. Chem. A*, 2019, **7**, 2344-2350.
5. Z. Pu, I. S. Amiinu, Z. Kou, W. Li and S. Mu, *Angew. Chem. Int. Ed.*, 2017, **56**, 11559-11564.
6. J. Su, Y. Yang, G. Xia, J. Chen, P. Jiang and Q. Chen, *Nat. Commun.*, 2017, **8**, 14969.
7. J. Mahmood, F. Li, S. M. Jung, M. S. Okyay, I. Ahmad, S. J. Kim, N. Park, H. Y. Jeong and J. B. Baek, *Nat. Nanotechnol.*, 2017, **12**, 441-446.
8. Y. Liu, Y. Yang, Z. Peng, Z. Liu, Z. Chen, L. Shang, S. Lu and T. Zhang, *Nano Energy*, 2019, **65**, 104023.
9. T. Liu, B. Feng, X. Wu, Y. Niu, W. Hu and C. M. Li, *ACS Appl. Energy Mater.*, 2018, **1**, 3143-3150.
10. Q. Liu, L. Wang, X. Liu, P. Yu, C. Tian and H. Fu, *Sci. China Mater.*, 2018, **62**, 624-632.
11. J. Zhang, X. Xu, L. Yang, D. Cheng and D. Cao, *Small Methods*, 2019, **3**, 1900653.
12. X. Zhang, F. Zhou, S. Zhang, Y. Liang and R. Wang, *Adv. Sci.*, 2019, **6**, 1900090.
13. W. Fang, H. Hu, T. Jiang, G. Li and M. Wu, *Carbon*, 2019, **146**, 476-485.
14. K. Wang, Q. Chen, Y. Hu, W. Wei, S. Wang, Q. Shen and P. Qu, *Small*, 2018, **14**, e1802132.