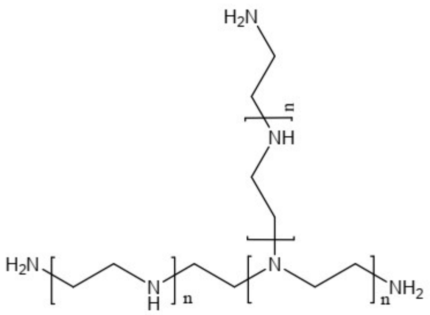
Electronic Supplementary Information



Scheme S1 Molecular structure of PEI.

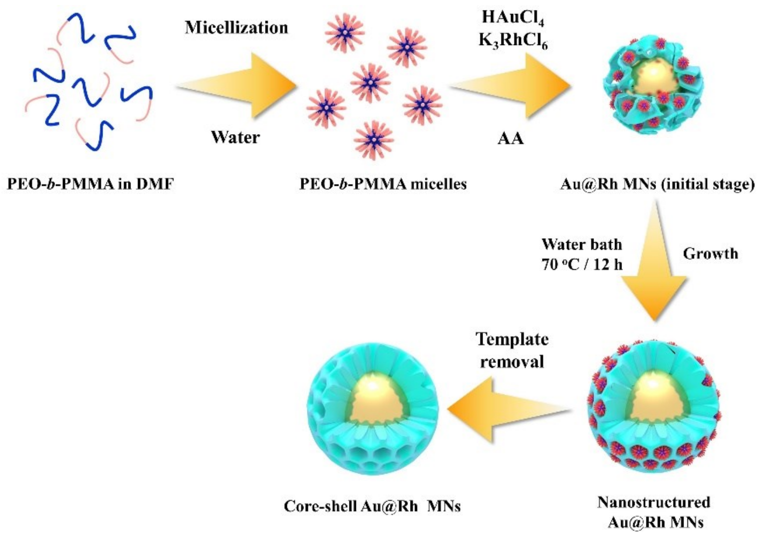


Fig. S1 Schematic showing for the fabrication process of Au@Rh MNs.

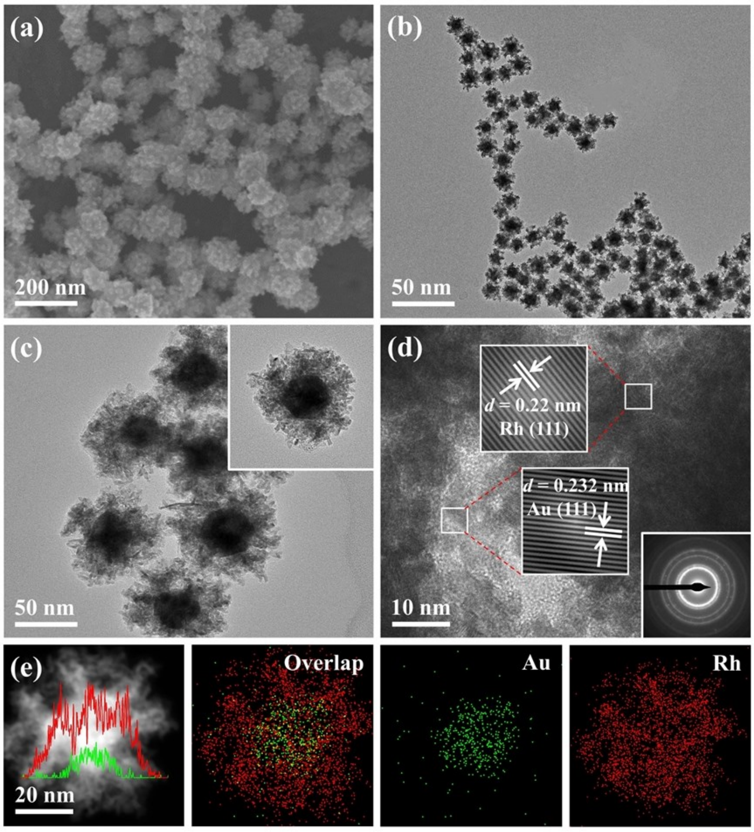
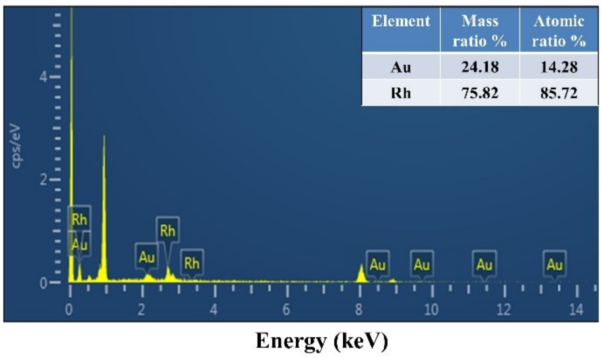


Fig. S2 (a) SEM image, (b and c) TEM images and (d) HRTEM image and the lattice fringes of the corresponding areas. The inset in (d) is the SAED pattern. (e) HAADF-STEM image, compositional line profiles and corresponding element mappings of Au and Rh for Au@Rh MNs.



Element	Mass ratio %	Atomic ratio %
Au	24.18	14.28
Rh	75.82	85.72

Fig. S3 SEM-EDX spectrum of Au@Rh MNs.

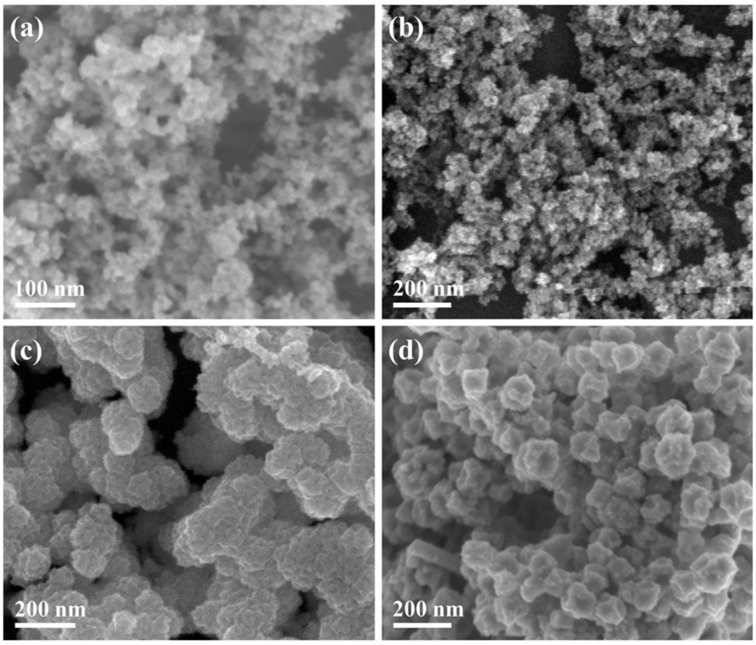


Fig. S4 SEM images of Au@Rh MNs obtained by replacing AA with (a) $NaBH_4$, (b) HCOOH, (c) NaH_2PO_2 and (d) C_2H_5OH.

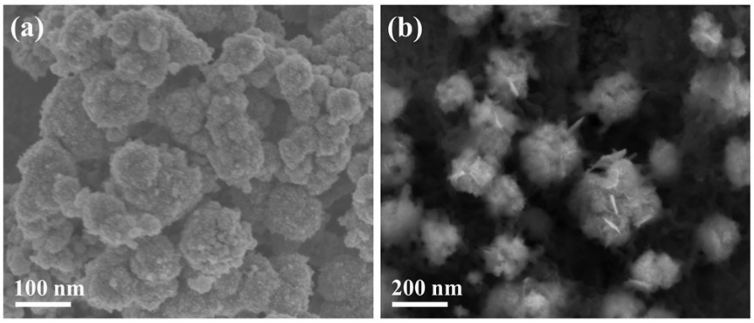


Fig. S5 SEM images of Au@Rh MNs obtained (a) without any surfactant and (b) with PS_{18000}-*b*-PEO_{7500}.

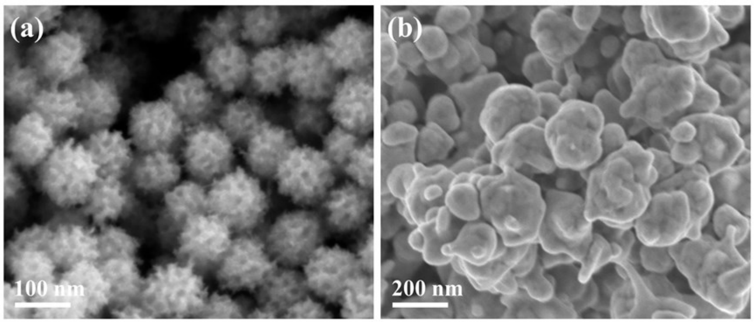


Fig. S6 SEM images of (a) Rh MNs and (b) Au NPs.

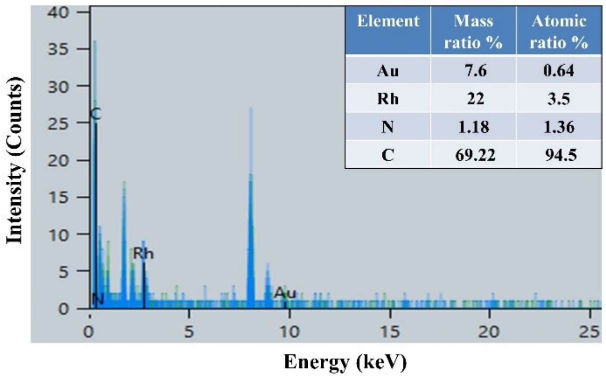


Fig. S7 TEM-EDX spectrum of Au@Rh@PEI MNs.

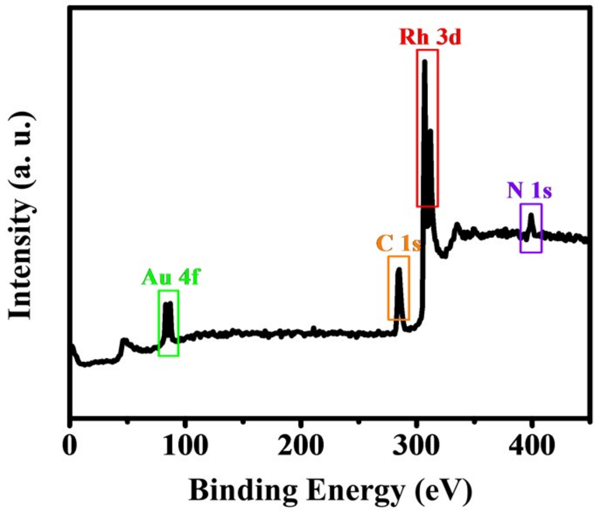


Fig. S8 XPS survey spectrum of Au@Rh@PEI MNs.

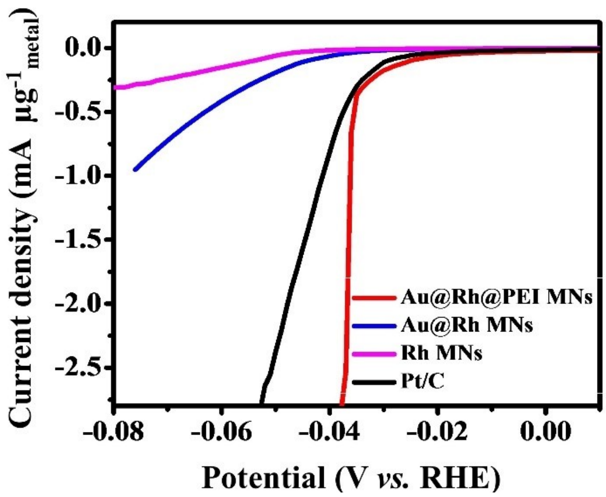


Fig. S9 Metal mass-normalized LSV curves of different catalysts for HER in 0.5 M H_2SO_4.

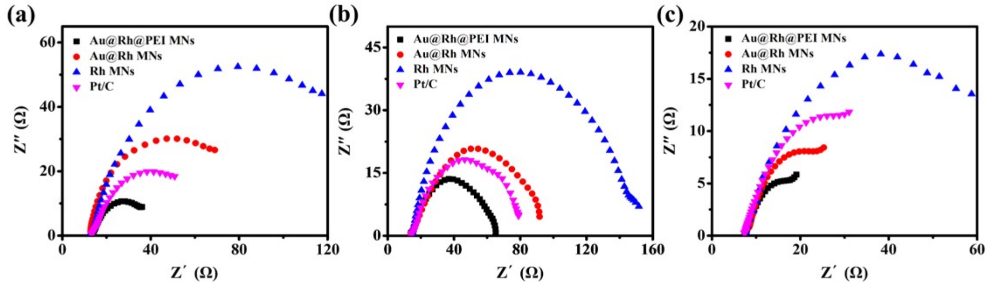


Fig. S10 EIS spectra of various catalysts in (a) 0.5 M H_2SO_4, (b) 1 M KOH and (c) 1 M PBS. The applied potentials in 0.5 M H_2SO_4, 1 M KOH and 1 M PBS are -0.073 V (*vs*. RHE), -0.276 V (*vs*. RHE) and -0.136 V (*vs*. RHE), respectively.

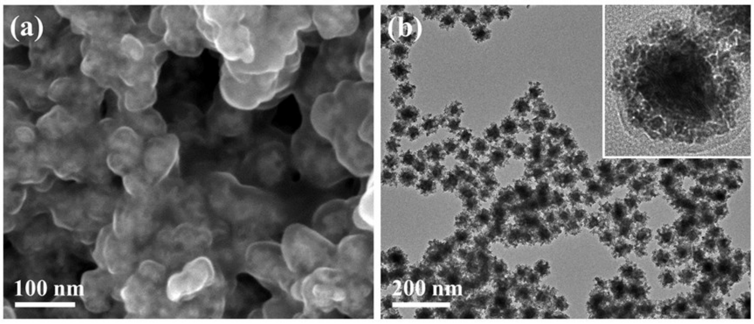


Fig. S11 (a) SEM image and (b) TEM images of Au@Rh@PEI MNs in neutral media after 24 h *V-t* test.

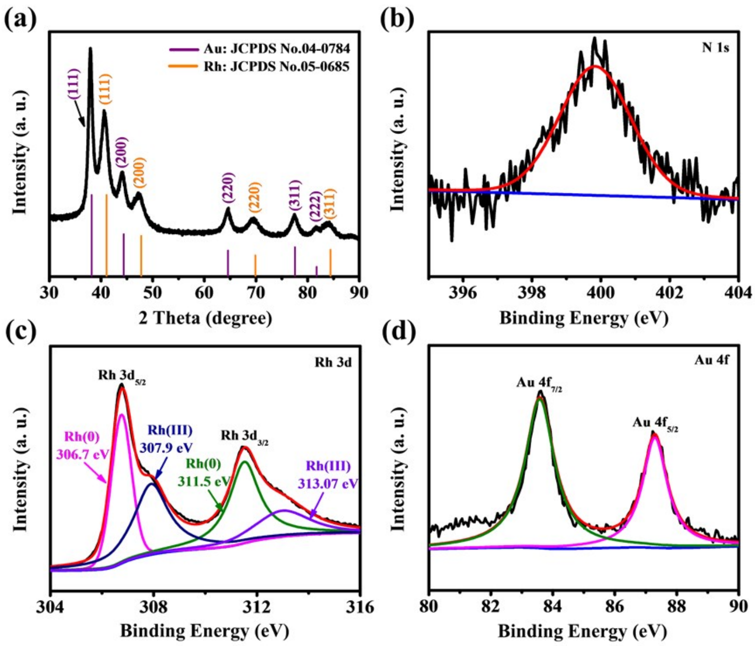


Fig. S12 (a) XRD pattern, high-resolution (b) N 1s, (c) Rh 3d and (d) Au 4f XPS spectra of Au@Rh@PEI MNs in neutral media after HER stability testing.

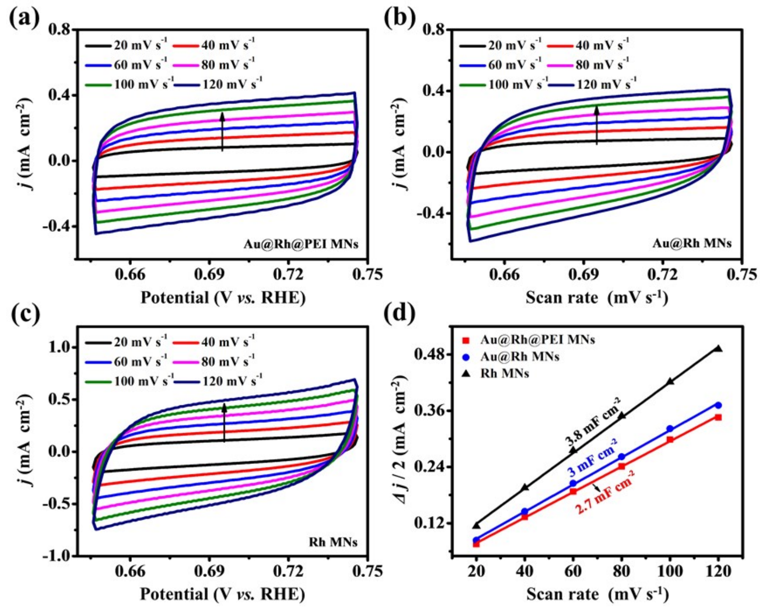


Fig. S13 CV curves at various scan rates of (a) Au@Rh@PEI MNs, (b) Au@Rh MNs and (c) Rh MNs with potential ranges from 0.646 to 0.746 V (*vs*. RHE) in 1 M PBS solution. (d) The corresponding capacitive current densities of different catalysts at 0.696 V (*vs*. RHE).

Table S1. HER performance comparison in acidic media between the Au@Rh@PEI MNs and some other reported electrocatalysts.

Electrocatalysts	Electrolytes	Electrode substrate	Overpotential @ 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Ref.
Au@Rh@PEI MNs	**0.5 M H_2SO_4**	**glassy carbon electrode (GCE loading ~ 0.05 mg cm^{-2})**	**30**	**30**	**This work**
RhCoB aerogels	0.5 M H_2SO_4	GCE (loading ~ 0.085 mg cm^{-2}	12	30.7	1
boron-doped RhFe alloy	0.5 M H_2SO_4	rotating disk electrode (RDE: loading ~ 0.51 mg cm^{-2})	25	32	2
Rh_2S_3 hexagonal nanoprisms	0.5 M H_2SO_4	RDE (loading ~ 0.153 mg cm^{-2})	117	44	3
Rh_2P/XC-72	0.5 M H_2SO_4	GCE (loading ~ 0.0225 mg cm^{-2})	14	31.7	4
Rh-MoS_2	0.5 M H_2SO_4	GCE (loading ~ 0.309 mg cm^{-2})	47	24	5
Rh_xP/NPC	0.5 M H_2SO_4	GCE (loading ~ 0.0017 mg cm^{-2})	19	36	6
Rh Hollow nanoparticle/C	0.5 M H_2SO_4	GCE (loading ~ 0.018 mg cm^{-2})	28.1	24	7
Rh-Ag-Si ternary composites	0.5 M H_2SO_4	(RDE: loading ~ 0.140 mg cm^{-2})	120	51	8
Rh-Au-Si nanocomposite	0.5 M H_2SO_4	GCE (loading ~ 0.255 mg cm^{-2})	60	24	9
rGO/CoP-Rh catalysts	0.5 M H_2SO_4	GCE (loading ~ 0.218 mg cm^{-2})	72	43	10
PtRh DNAs	0.5 M H_2SO_4	GCE (loading ~ 0.225 mg cm^{-2})	27	30	11
$Rh_{50}Ru_{50}$@UiO$_{-66}$-NH_2	0.5 M H_2SO_4	GCE (loading ~ 0.343 mg cm^{-2})	77	79	12

Table S2. HER performance comparison in alkaline media between the Au@Rh@PEI MNs and some other reported electrocatalysts.

Electrocatalysts	Electrolytes	Electrode substrate	Overpotential @ 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Ref.
Au@Rh@PEI MNs	**1M KOH**	**GCE (loading ~ 0.05 mg cm^{-2})**	**29**	**31**	**This work**
RhCoB aerogel	1M KOH	GCE (loading ~0.085 mg cm^{-2})	43	40.5	1
Rh_2P/XC-72	1M KOH	GCE (loading ~0.0225 mg cm^{-2})	30	50	4
PtRh DNAs	1M KOH	GCE (loading ~0.225 mg cm^{-2})	28	47	11
$Rh_{50}Ru_{50}$@UiO-66-NH_2	1M KOH	GCE (loading ~0.343 mg cm^{-2})	176	112	12
RuP_2@NPC	1M KOH	GCE (loading ~1.0 mg cm^{-2})	52	69	13
Rh NSs/CNTs	1M KOH	GCE (loading ~0.015 mg cm^{-2})	43	107	14
IrRh NAs	1M KOH	GCE (loading ~0.281 mg cm^{-2})	35	48.4	15
Rh-Rh_2O_3-NPs/C	1M KOH	GCE (loading ~0.028 mg cm^{-2})	63	70	16
MoP_2 NS/CC	1M KOH	CC (loading ~7.8 mg cm^{-2})	85	70	17
Mn-CoP/Ti	1M KOH	Ti (loading ~5.61 mg cm^{-2})	76	52	18
NiRu@N-C	1M KOH	GCE (loading ~0.273 mg cm^{-2})	50	36	19

Table S3. HER performance comparison in neutral media between the Au@Rh@PEI MNs and some other reported electrocatalysts.

Electrocatalysts	Electrolytes	Electrode substrate	Overpotential @ 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Ref.
Au@Rh@PEI	**1 M PBS**	**GCE (loading ~ 0.05 mg cm^{-2})**	**24**	**39**	**This work**
RhCoB aerogel	1 M PBS	GCE (loading ~0.085 mg cm^{-2})	113	149.1	[1]
Rh_2P-based electrocatalyst	1 M PBS	GCE (loading ~0.0225 mg cm^{-2})	38	46	[4]
PtRh DNAs	1 M PBS	GCE (loading ~0.225 mg cm^{-2})	23	87	[11]
$Rh_{50}Ru_{50}$@UiO-66-NH_2	1 M PBS	GCE (loading ~0.343 mg cm^{-2})	111	93.4	[12]
RuP_2@NPC	1 M PBS	GCE (loading ~1.0 mg cm^{-2})	57	87	[13]
OsP_2@NPC	1 M PBS	GCE (loading ~0.43 mg cm^{-2})	54	82	[20]
Ni−Co−P−H microflowers	1 M PBS	GCE (loading ~0.4 mg cm^{-2})	157	84	[21]
CoP-400	1 M PBS	GCE (loading ~0.43 mg cm^{-2})	161	81	[22]
Ru@Co-SAs/N-C	1 M PBS	GCE (loading ~0.285 mg cm^{-2})	55	82	[23]
RhCu nanotubes	0.1 M PBS	GCE (loading ~0.24 mg cm^{-2})	57	95	[24]

References

1. K. Deng, T. Ren, Y. Xu, S. Liu, Z. Dai, Z. Wang, X. Li, L. Wang and H. Wang, *J. Mater. Chem.A*, 2020, **8**, 5595-5600.
2. L. Zhang, J. Lu, S. Yin, L. Luo, S. Jing, A. Brouzgou, J. Chen, P. K. Shen and P. Tsiakaras, *Appl. Catal., B*, 2018, **230**, 58-64.
3. D. Yoon, B. Seo, J. Lee, K. S. Nam, B. Kim, S. Park, H. Baik, S. Hoon Joo and K. Lee, *Energy Environ. Sci.*, 2016, **9**, 850-856.
4. F. Yang, Y. Zhao, Y. Du, Y. Chen, G. Cheng, S. Chen and W. Luo, *Adv. Energy Mater.*, 2018, **8**, 1703489.
5. Y. Cheng, S. Lu, F. Liao, L. Liu, Y. Li and M. Shao, *Adv. Funct. Mater.*, 2017, **27**, 1700359.
6. Q. Qin, H. Jang, L. Chen, G. Nam, X. Liu and J. Cho, *Adv. Energy Mater.*, 2018, **8**, 1801478.
7. J. Du, X. Wang, C. Li, X.-Y. Liu, L. Gu and H.-P. Liang, *Electrochim. Acta*, 2018, **282**, 853-859.
8. B. Jiang, Y. Sun, F. Liao, W. Shen, H. Lin, H. Wang and M. Shao, *J. Mater. Chem.A*, 2017, **5**, 1623-1628.
9. B. Jiang, L. Yang, F. Liao, M. Sheng, H. Zhao, H. Lin and M. Shao, *Nano Res.*, 2017, **10**, 1749-1755.
10. H. Zheng, X. Huang, H. Gao, W. Dong, G. Lu, X. Chen and G. Wang, *J. Energy Chem.*, 2019, **34**, 72-79.
11. Y. Liu, X. Li, Q. Zhang, W. Li, Y. Xie, H. Liu, L. Shang, Z. Liu, Z. Chen, L. Gu, Z. Tang, T. Zhang and S. Lu, *Angew. Chem., Int. Ed. Engl.*, 2020, **59**, 1718-1726.
12. Z. Ding, K. Wang, Z. Mai, G. He, Z. Liu and Z. Tang, *Int. J. Hydrogen Energy*, 2019, **44**, 24680-24689.
13. Z. Pu, I. S. Amiinu, Z. Kou, W. Li and S. Mu, *Angew. Chem., Int. Ed.*, 2017, **56**, 11559-11564.
14. N. Zhang, Q. Shao, Y. Pi, J. Guo and X. Huang, *Chem. Mater.*, 2017, **29**, 5009-5015.
15. C. Li, Y. Xu, S. Liu, S. Yin, H. Yu, Z. Wang, X. Li, L. Wang and H. Wang, *ACS Sustain. Chem. Eng.*, 2019, **7**, 15747-15754.
16. M. K. Kundu, R. Mishra, T. Bhowmik and S. Barman, *J. Mater. Chem. A*, 2018, **6**, 23531-23541.
17. W. Zhu, C. Tang, D. Liu, J. Wang, A. M. Asiri and X. Sun, *J. Mater. Chem.A*, 2016, **4**, 7169-7173.
18. T. Liu, X. Ma, D. Liu, S. Hao, G. Du, Y. Ma, A. M. Asiri, X. Sun and L. Chen, *ACS Catal.*, 2017, **7**, 98-102.
19. Y. Xu, S. Yin, C. Li, K. Deng, H. Xue, X. Li, H. Wang and L. Wang, *J. Mater. Chem.A*, 2018, **6**, 1376-1381.
20. L. Fang, Y. Wang, X. Yang, H. Zhang and Y. Wang, *J Catal*, 2019, **370**, 404-411.
21. X. Liu, S. Deng, D. Xiao, M. Gong, J. Liang, T. Zhao, T. Shen and D. Wang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 42233-42242.
22. H. Li, X. Zhao, H. Liu, S. Chen, X. Yang, C. Lv, H. Zhang, X. She and D. Yang, *small*, 2018, **14**, e1802824.
23. S. Yuan, Z. Pu, H. Zhou, J. Yu, I. S. Amiinu, J. Zhu, Q. Liang, J. Yang, D. He, Z. Hu, G. Van Tendeloo and S. Mu, *Nano Energy*, 2019, **59**, 472-480.
24. D. Cao, H. Xu and D. Cheng, *Adv. Energy Mater.*, 2020, **10**, 1903038.