

Supplementary Material

MOFs-assisted synthesis of octahedral carbon supported PtCu nanoalloy catalysts with efficient hydrogen evolution reaction

Chengtian Zhang,^{a,b} Pengyan Wang,^a Wenqiang Li,^a Zhiwei Zhang,^a Jiawei Zhu,^a
Zonghua Pu,^{*a} Yufeng Zhao^c and Shichun Mu^{*a,b}

^aState Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China.

^bFoshan Xianhu Laboratory of the Advanced Energy Science and Technology Guangdong Laboratory, Xianhu hydrogen Valley, Foshan 528200, China.

^cInstitute for Sustainable Energy/College of Sciences, Shanghai University, Shanghai 200444, China.

*Corresponding authors E-mail: msc@whut.edu.cn (S. Mu), puzonghua@whut.edu.cn (Z. Pu)

Materials and reagent:

All chemicals used in this experiment were analytical grade and used without further purification. Cupric acetate monohydrate ($\text{Cu}(\text{CO}_2\text{CH}_3)_2 \cdot \text{H}_2\text{O}$), L-glutamic acid, Chloroplantinic acid and Ethanol were purchased from Sinopharm Chemical Reagents, China. 1,3,5-benzenetricarboxylic acid (H_3BTC) was obtained from Aladdin Reagents Ltd. Phosphomolybdic acid were from Shanghai Macklin Biochemical Co., Ltd. The commercial Pt/C (20 wt. %) catalyst and Nafion (5 wt. %) were purchased from Sigma-Aldrich. The deionized water used throughout the whole experimental process was ultra-purified (18.25 M Ω).

Preparation of NENU-5:

NENU-5 ($[\text{Cu}_2(\text{BTC})_{4/3}(\text{H}_2\text{O})_2]_6[\text{H}_3\text{PMo}_{12}\text{O}_{40}]$, BTC=benzene-1,3,5-tricarboxylate) is based on a mature Cu-based MOF [HKUST-1: $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$] with Mo-based Keggin-type POMs ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) periodically occupying the largest pores¹. In a typical procedure, 0.6 g of copper (II) acetate monohydrate ($\text{Cu}(\text{CO}_2\text{CH}_3)_2 \cdot \text{H}_2\text{O}$) 220 mg of L-glutamic acid and 0.9 g of phosphomolybdic acid hydrate were mixed in 120 ml of deionized water with stirring at ambient condition for 30 min. And then, 422 mg of H_3BTC were dissolved in 120 ml of ethanol, which was swiftly injected into the above solution in succession. Then, the resulting solution was stirred for 14 h at room temperature. The precipitate was obtained by centrifugation and washed twice with ethanol. Then the NENU-5 powders were dried in vacuum at 70 °C overnight.

Electrochemical Measurements.

The polarization curves were plotted by the formula: $E_{\text{actual}} = E_{\text{test}} - iR_s \times 100\%$. The electrochemically active surface area (ECSA) was evaluated by measuring the charge

associated with Hupd adsorption (Q_H) from CV curves in N_2 -saturated 0.1 M $HClO_4$ solution. The characteristic potential regions of Hupd range is from 0.05 to 0.4V (vs. RHE) and the scan rate was 50 mV/s. The ECSA was calculated based on the

$$ECSA = \frac{Q_H}{m \times q_H}$$

following equation:

Here, Q_H is the charge collected in the hydrogen adsorption region, m is the loading amount of Pt and q_H (0.21 mC cm^{-2}) is the charge required for monolayer adsorption of hydrogen on a Pt surface.

Material characterization and equipment

The phase and crystalline structures of the products were characterized were performed on a Bruker D8 advance XRD system using Cu Ka radiation. X-ray photoelectron spectroscopy (XPS) testing was performed on an ESCALAB 250Xi/ESCALAB 250Xi X-ray photoelectron using a spectrometer Al Ka as the excitation source. The morphology and structure of the as-prepared nanoparticles were characterized by field emission scanning electron microscopy (FE-SEM, Zeiss Ultra Plus) with an acceleration voltage of 5 kV and transmission electron microscopy (TEM, JEM-2100F) with an acceleration voltage of 200 kV. The HAADF-STEM imaging test and the X-ray spectroscopy (EDS) analysis were performed on a Talos F200S. The Inductively Coupled Plasma-Optical Emission spectrometry (ICP-OES) test was performed on Prodigy 7. N_2 adsorption-desorption isotherms were carried out on a Micromeritics ASAP 2020 system.

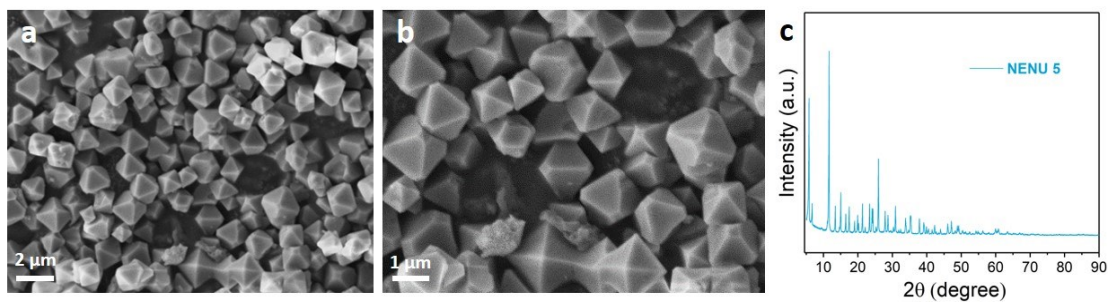


Figure S1. (a, b) SEM images of NENU-5. (c) XRD pattern of NENU-5.

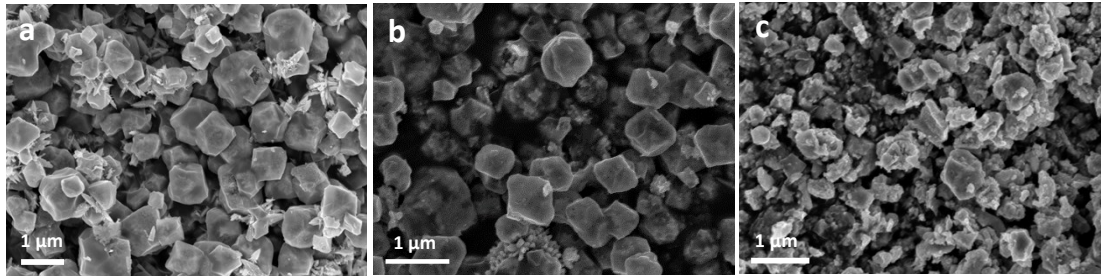


Figure S2. SEM images of (a) PtCu-MoO₂@C-700 °C (b) PtCu-MoO₂@C-800 °C and (c) PtCu-MoO₂@C-900 °C.

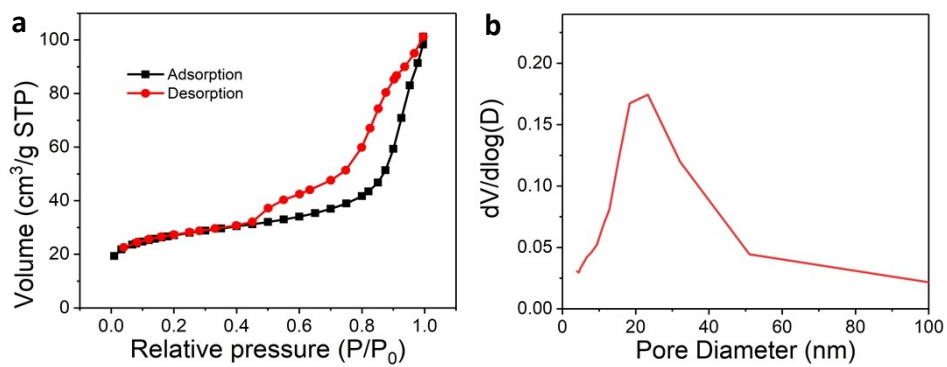


Figure S3. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution curve of PtCu-MoO₂@C.

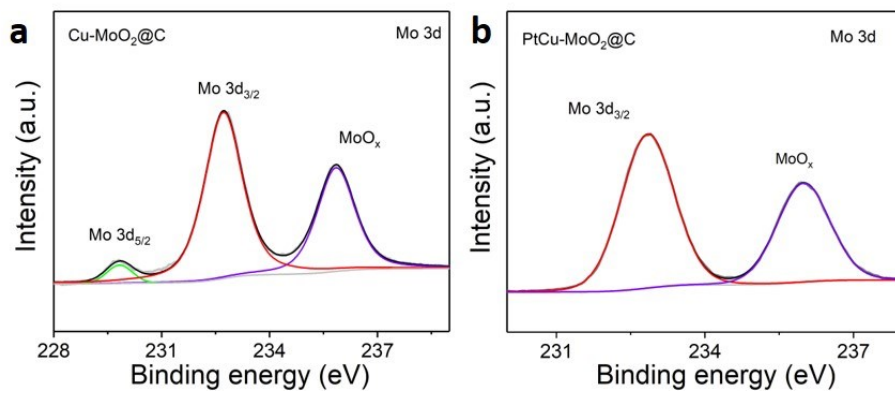


Figure S4. Mo 3d XPS spectrum of (a) Cu-MoO₂@C and (b) PtCu-MoO₂@C.

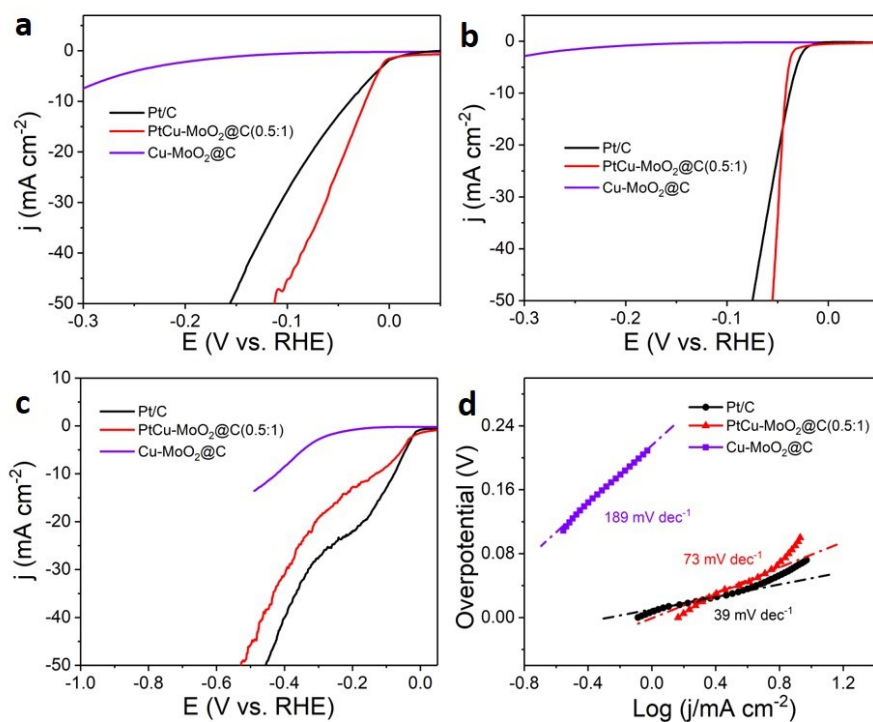


Figure S5. Polarization curves of PtCu-MoO₂@C (0.5:1), Cu-MoO₂@C and Pt/C in (a) 1 M KOH, (b) 0.5 M H₂SO₄ and (c) 1 M PBS. (d) Corresponding Tafel slopes of PtCu-MoO₂@C (0.5:1), Cu-MoO₂@C and Pt/C in 1 M PBS.

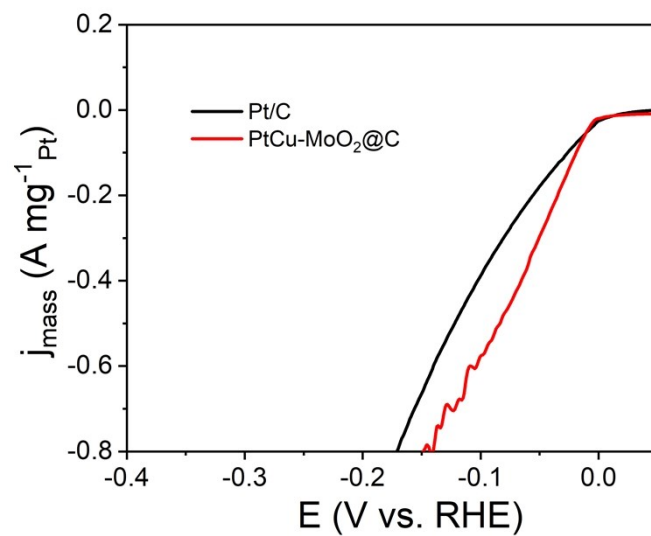


Figure S6. Mass activity curves of PtCu-MoO₂@C and Pt/C in 1 M KOH (Normalized to Pt loading).

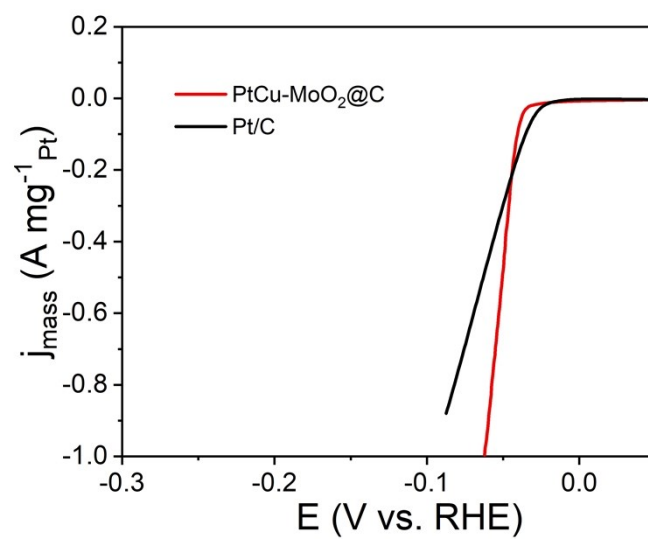


Figure S7. Mass activity curves of PtCu-MoO₂@C and Pt/C in 0.5 M H₂SO₄ (Normalized to Pt loading).

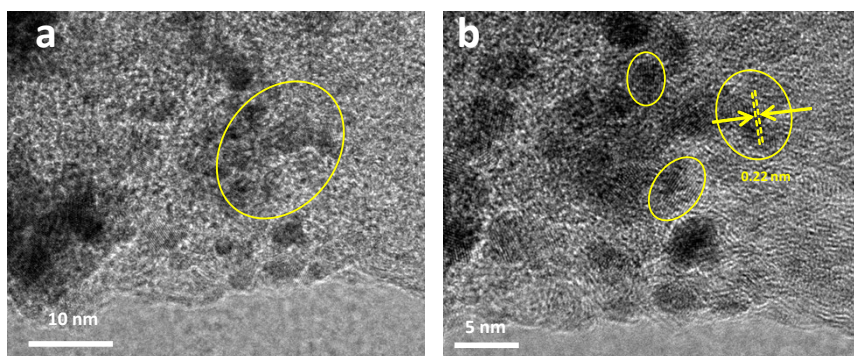


Figure S8. (a) and (b) HR-TEM images for PtCu-MoO₂@C catalysts after 3,000 potential sweeps in 1 M KOH.

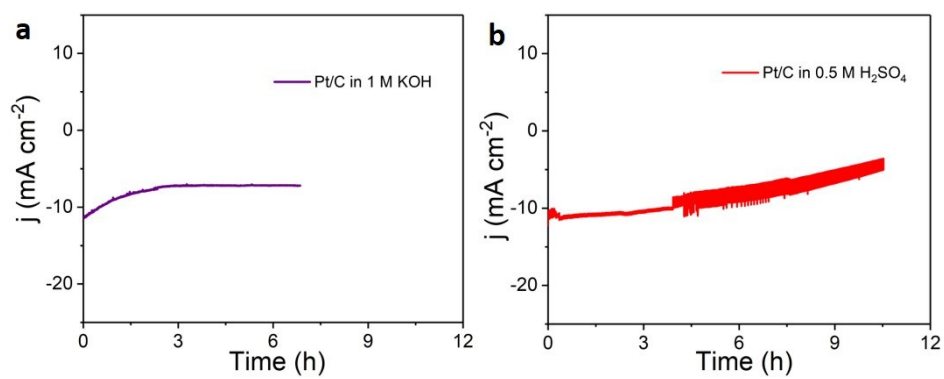


Figure S9. Long-term durability tests of Pt/C in (a) 1 M KOH and (b) 0.5 M H₂SO₄.

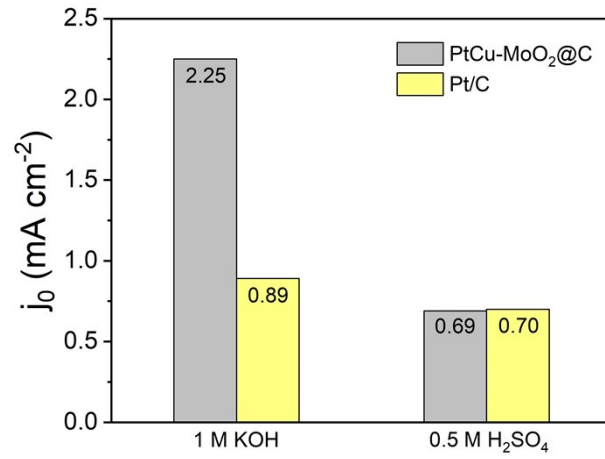


Figure S10. Exchange current density (j_0) of PtCu-MoO₂@C (0.5:1) and Pt/C in different media.

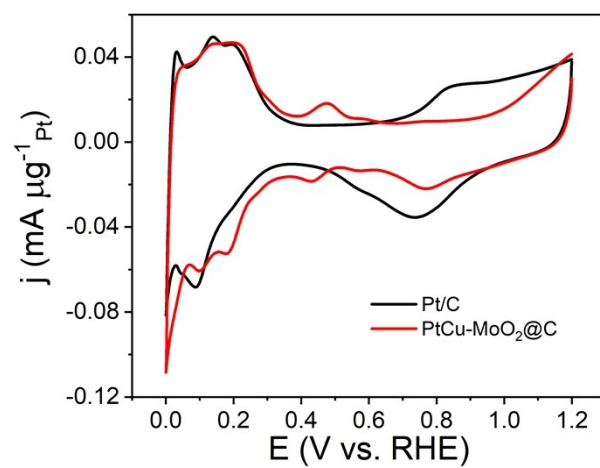


Figure S11. Cyclic voltammetry curves of PtCu-MoO₂@C and Pt/C catalysts in N₂-saturated 0.1 M HClO₄ solution with a sweep rate of 50 mV/s.

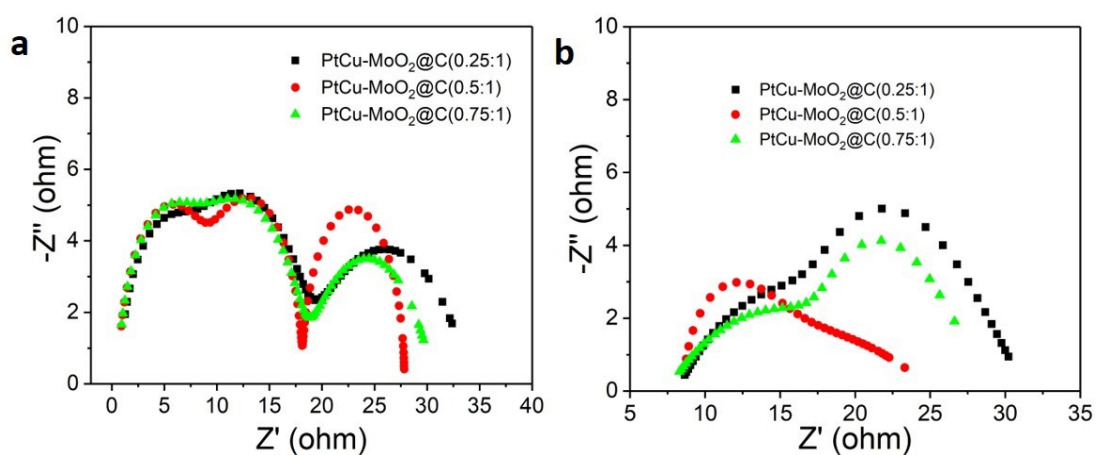


Figure S12. Comparison and fitting of Nyquist plots of different samples modified electrodes at same overpotential of (a) 50 mV in 1 M KOH. (b) 35 mV in 0.5 M H₂SO₄.

Table S1 Comparison of HER performance in both basic and acidic media for the PtCu-MoO₂@C and other electrocatalysts

Catalyst	electrolyte	Pt loading (mg cm ⁻²)	Overpotential @j (mV@mA cm ⁻²)	Tafel slop (mV dec ⁻¹)	Ref.
PtCu-MoO ₂ @C	1 M KOH	0.078	24@10	37	This work
	0.5 M H ₂ SO ₄	0.078	42@10	36	
Pd-Pt-S	1 M KOH	0.02	71@10	31	2
Pt-Ni octahedra	0.1 M KOH	0.024	~60@10	59	3
Mo ₂ C@NC@Pt	0.5 M H ₂ SO ₄	—	27@10	28	4
	1 M KOH	—	47@10	57	
PtRh DNAs	0.5 M H ₂ SO ₄	—	27@10	40	5
	1 M KOH	—	28@10	47	
Pt ₁₃ Cu ₇₃ Ni ₁₄ /CNF@CF	1 M KOH	—	150@5	54	6
Pt NWs/SL-Ni(OH) ₂	1 M KOH	0.016	70@10	72	7
Pt-CoS ₂ /CC	1 M KOH	~0.04	24@10 112@100	82	8
Pt-Co(OH) ₂ /CC	1 M KOH	~0.39	32@10	70	9
			54@20		
			122@100		
Pt/Ni ₃ N	1 M KOH	~0.3	40@10	36.5	10
Pt-NiFe	1 M KOH	—	27@10	51	11
Pt-Ni	1 M KOH	0.0075	65@10	78	12
Pt-Ni ASs	1 M KOH	0.017	27.7@10	27	13
			53.8@30		
Pt-MoS ₂	0.5 M H ₂ SO ₄	0.036	60@10	96	14
Pt-MoO ₂ @PC	0.5 M H ₂ SO ₄	0.012	20@10	22	15
Ru-MoO ₂	0.5 M H ₂ SO ₄	0.045	55@10	44	16
	1 M KOH	0.045	29@10	31	
Pt-MoO ₂ /CNTs	0.5 M H ₂ SO ₄	0.002	60@10	43	17
Pt/MoO ₂	0.5 M H ₂ SO ₄	0.018	47@10	32.6	18
Pd@PdPt	0.5 M H ₂ SO ₄	0.06	39@10	38	19
PtCoNi FNs	0.5 M H ₂ SO ₄	0.085	41@10	37	20
Pt ₂ Co ₈ @N-C	0.5 M H ₂ SO ₄	0.2	47@20	48	21

Notes and references

1. C. Sun, S. Liu, D. Liang, K. Shao, Y. Ren and Z. Su, *J. Am. Chem. Soc.*, 2009, **131**, 1883-1888.
2. J. Fan, K. Qi, L. Zhang, H. Zhang, S. Yu and X. Cui, *ACS Appl. Mater. Inter.*, 2017, **9**, 18008-18014.
3. R. Kavian, S. I. Choi, J. Park, T. Liu, H. Peng, N. Lu, J. Wang, M. Kim, Y. Xia and S. Lee, *J. Mater. Chem. A*, 2016, **4**, 12392-12397.
4. J. Chi, J. Xie, W. Zhang, B. Dong, J. Qin, X. Zhang, J. Lin, Y. Chai and C. Liu, *ACS Appl. Mater. Inter.*, 2019, **11**, 4047-4056.
5. Z. Han, R. Zhang, J. Duan, A. Wang, Q. Zhang, H. Huang and J. Feng, *Int. J. Hydrogen Energ.*, 2020, **45**, 6110-6119.
6. Y. Shen, A. C. Lua, J. Xi and X. Qiu, *ACS Appl. Mater. Inter.*, 2016, **8**, 3464-3472.
7. H. Yin, S. Zhao, K. Zhao, K. Abdul, H. Tang, L. Chang, H. Zhao, Y. Gao and Z. Tang, *Nat. Commun.*, 2015, **6**, 6430.
8. X. Han, X. Wu, D. Yida, J. Liu, J. Lu, C. Zhong and W. Hu, *Adv. Energy Mater.*, 2018, **8**, 1800935.
9. Z. Xing, C. Han, D. Wang, Q. Li and X. Yang, *ACS Catal*, 2017, **7**, 7131-7135.
10. Y. Wang, L. Chen, X. Yu, Y. Wang and G. Zheng, *Adv. Energy Mater.*, 2016, **7**, 1601390.
11. S. Anantharaj, K. Karthick, M. Venkatesh, T. V. S. V. Simha, A. S. Salunke, L. Ma, H. Liang and S. Kundu, *Nano Energy*, 2017, **39**, 30-43.
12. Z. Cao, Q. Chen, J. Zhang, H. Li, Y. Jiang, S. Shen, G. Fu, B. Lu, Z. Xie and L. Zheng, *Nat. Commun.*, 2017, **8**, 15131.
13. Z. Zhang, G. Liu, X. Cui, B. Chen, Y. Zhu, Y. Gong, F. Saleem, S. Xi, Y. Du, A. Borgna, Z. Lai, Q. Zhang, B. Li, Y. Zong, Y. Han, L. Gu and H. Zhang, *Adv. Mater.*, 2018, **30**, 1801741.
14. J. Deng, H. Li, J. Xiao, Y. Tu, D. Deng, H. Yang, H. Tian, J. Li, P. Ren and X. Bao, *Energy Environ. Sci.*, 2015, **8**, 1594-1601.
15. Y. Jiang, M. Yang, M. Qu, Y. Wang, Z. Yang, Q. Feng, X. Deng, W. Shen, M. Li and R. He, *J Mater Chem A*, 2020, **8**, 10409-10418.
16. P. Jiang, Y. Yang, R. Shi, G. Xia, J. Chen, J. Su and Q. Chen, *J. Mater. Chem. A*, 2017, **5**, 5475-5485.
17. X. Xie, Y. Jiang, C. Yuan, N. Jiang, S. Zhao, L. Jia and A. Xu, *J. Phys. Chem. C*, 2017, **121**, 24979-24986.
18. X. Li, J. Yu, J. Jia, A. Wang, L. Zhao, T. Xiong, H. Liu and W. Zhou, *Nano Energy*, 2019, **62**, 127-135.
19. Y. Liu, S. Liu, Z. Che, S. Zhao, X. Sheng, M. Han and J. Bao, *J. Mater. Chem. A*, 2016, **4**, 16690-16697.
20. M. Liu, L. Chen, A. Wang, K. Fang and J. Feng, *Int. J. Hydrogen Energ.*, 2017, **42**, 25277-25284.
21. W. Ren, W. Zang, H. Zhang, J. Bian, Z. Chen, C. Guan and C. Cheng, *Carbon*, 2019, **142**, 206-216.