Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

A processable Prussian blue analogue-mediated route to promote alkaline electrocatalytic water splitting over bifunctional copper phosphide

Jiahui Chen,[a,b] Yunming Li,*[c] Huangqing Ye,[d] Pengli Zhu,[e] Xian-Zhu Fu,*[a] and Rong Sun[e]

[a] College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China

[b] College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China

[c] School of New Energy Science and Engineering, Xinyu University, Xinyu 338004, China

[d] SZU-NUS Collaborative Innovation Center for Optoelectronic Science & Technology, Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, China.

[e] Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China

* Corresponding authors:

E-mail: 395591748@qq.com (Y. Li)

E-mail: xz.fu@szu.edu.cn (X. -Z. Fu)

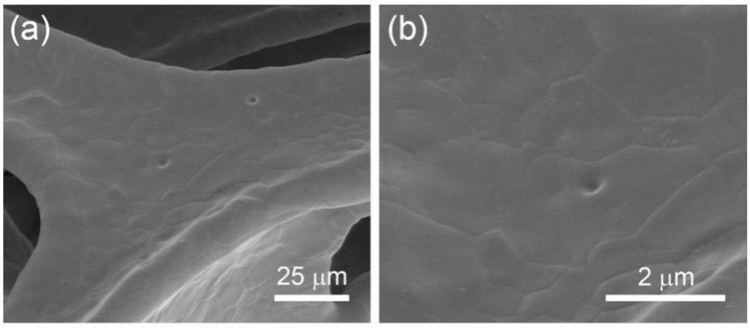

Fig. S1 SEM images of the copper foam in different magnifications.

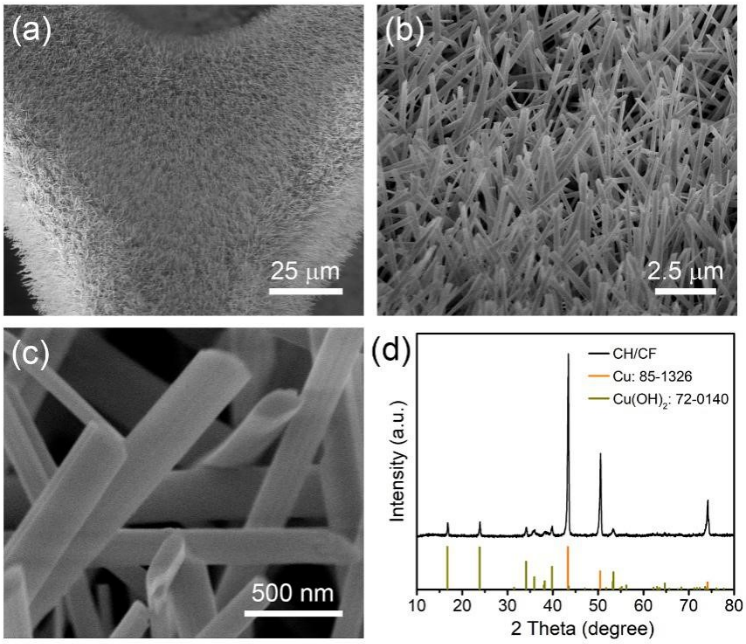

Fig. S2 (a-c) SEM images of CH/CF in different magnifications and (d) XRD pattern of CH/CF.

Table S1 Optimization of the synthetic parameters of CH@PBA/CF.

Samples	H_2O	0.1 M HCl	$K_3[Co(CN)_6]$	Reaction times
CH@PBA/CF-1	40 mL	1 mL	100 mg	4 h
CH@PBA/CF-2	40 mL	0.5 mL	100 mg	4 h
CH@PBA/CF-3	40 mL	1.5 mL	100 mg	4 h
CH@PBA/CF-4	40 mL	1 mL	100 mg	2 h
CH@PBA/CF-5	40 mL	1 mL	100 mg	6 h

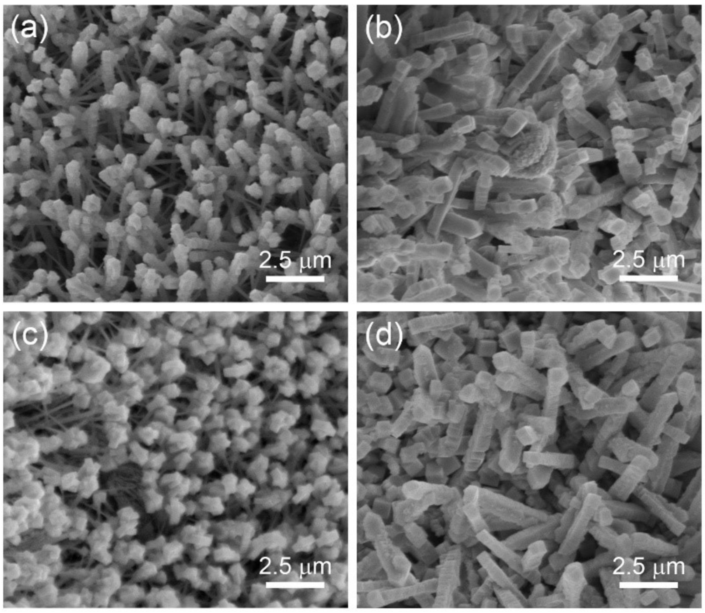

Fig. S3 SEM images of samples obtained by using different synthetic parameters in Table S1: (a) CH@PBA/CF-2, (b) CH@PBA/CF-3, (c) CH@PBA/CF-4 and (d) CH@PBA/CF-5.

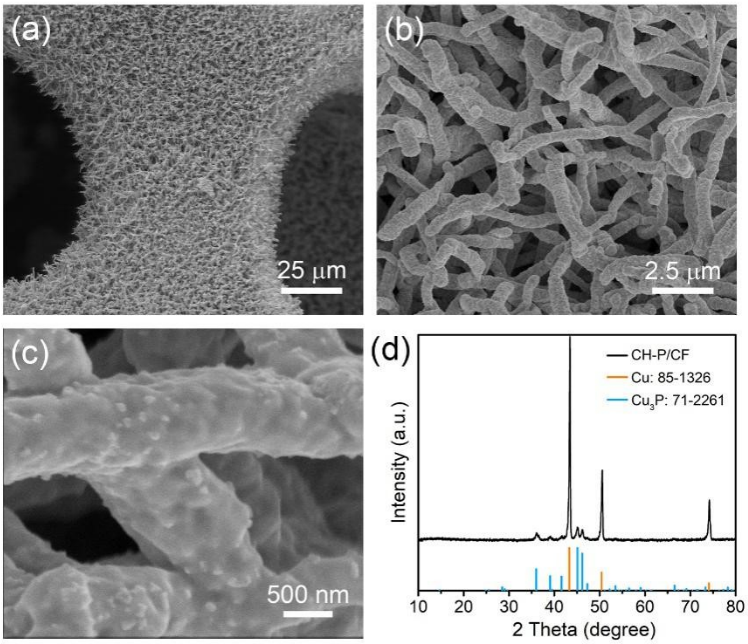

Fig. S4 (a-c) SEM images of CH-P/CF in different magnifications and (d) XRD pattern of CH-P/CF.

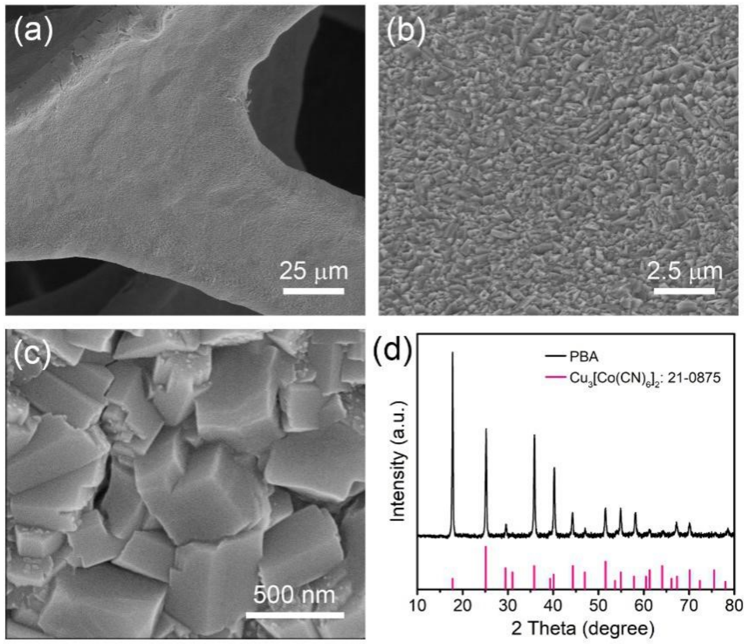

Fig. S5 (a-c) SEM images of PBA/CF in different magnifications and (d) XRD pattern of PBA powder scrapped from the copper foam.

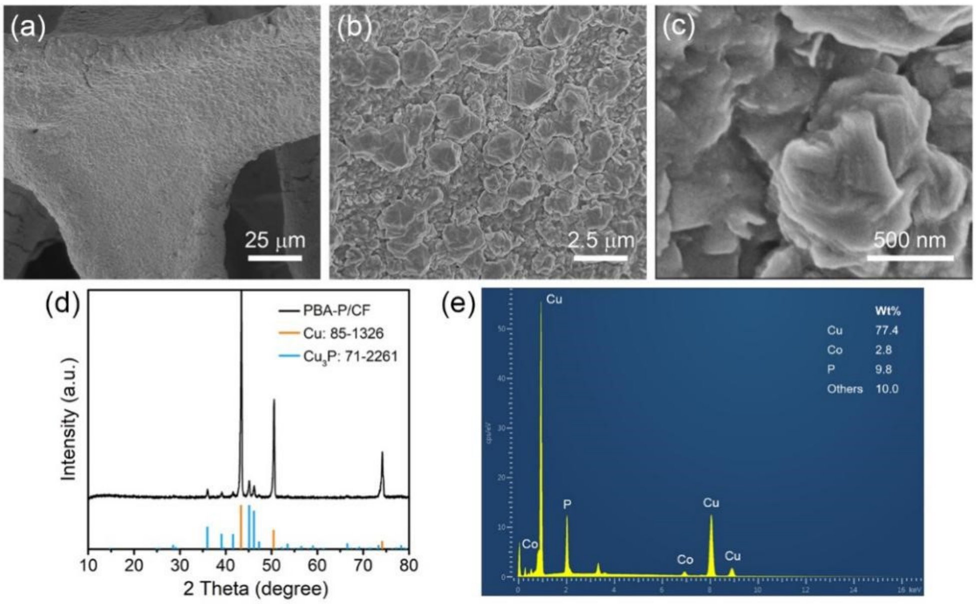

Fig. S6 (a-c) SEM images in different magnifications, (d) XRD pattern and (e) SEM EDS spectrum of PBA-P/CF.

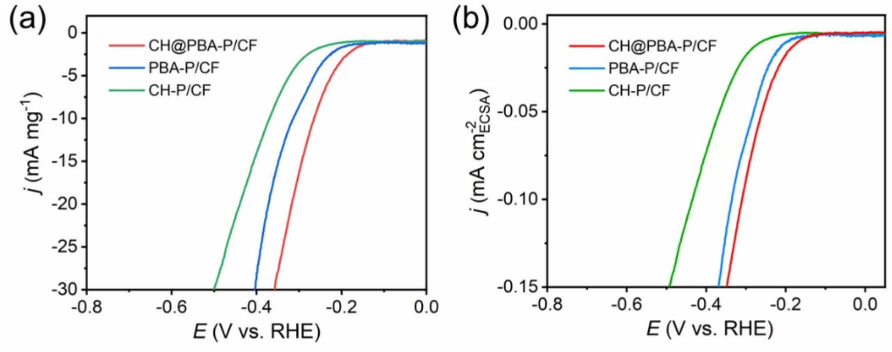

Fig. S7 The LSV curves normalized to (a) mass loading and (b) ECSA.

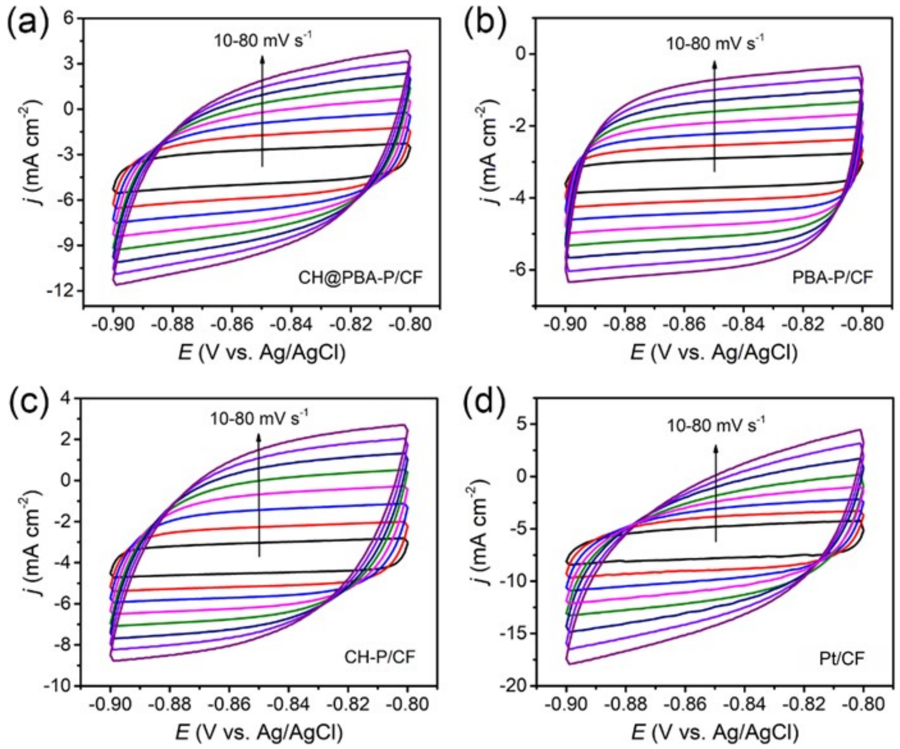

Fig. S8 Cyclic voltammetry curves of the electrocatalysts in the region of -0.8~-0.9 V vs. Ag/AgCl at various scan rates: (a) CH@PBA-P/CF, (b) PBA-P/CF, (c) CH-P/CF and (d) Pt/CF.

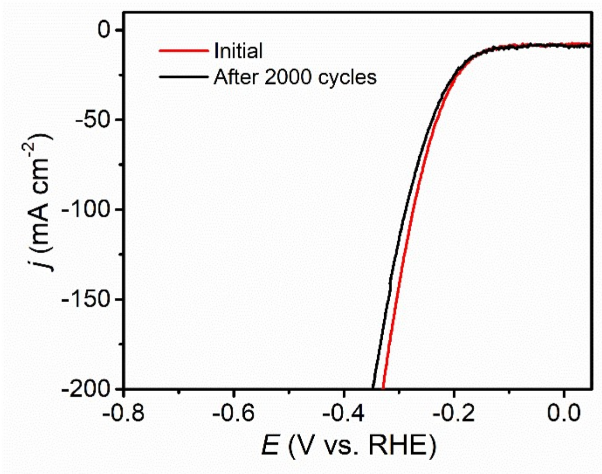

Fig. S9 The LSV curves before and after 1000 CV cycles in 1 M KOH.

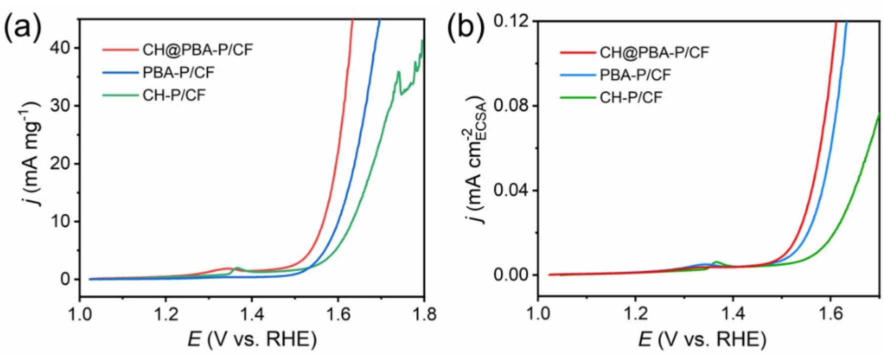

Fig. S10 The LSV curves normalized to (a) mass loading and (b) ECSA.

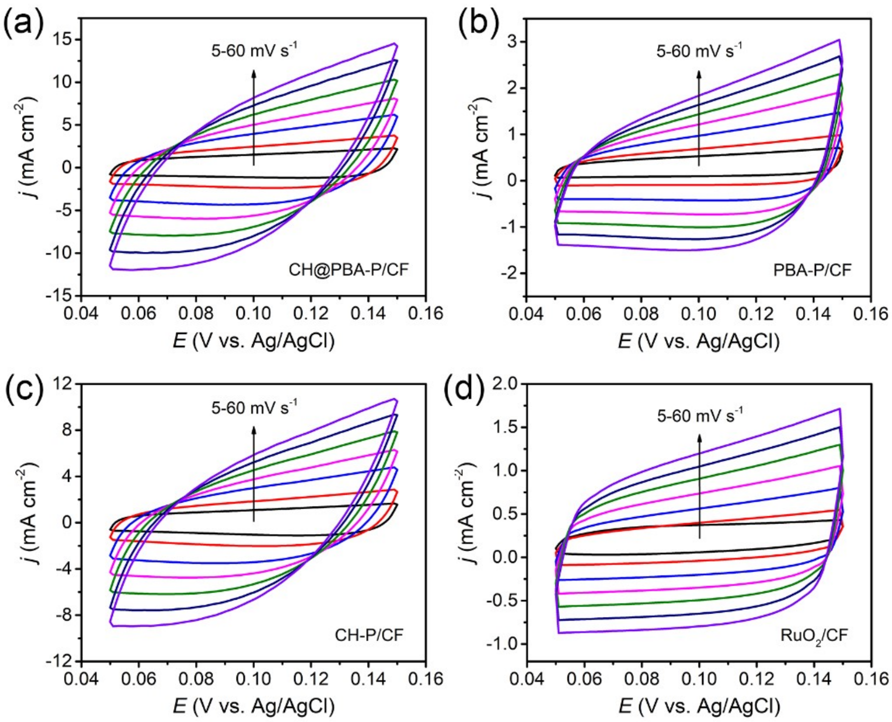

Fig. S11 Cyclic voltammetry curves of the electrocatalysts in the region of 0.05~0.15 V vs. Ag/AgCl at various scan rates: (a) CH@PBA-P/CF, (b) PBA-P/CF, (c) CH-P/CF and (d) RuO_2/CF.

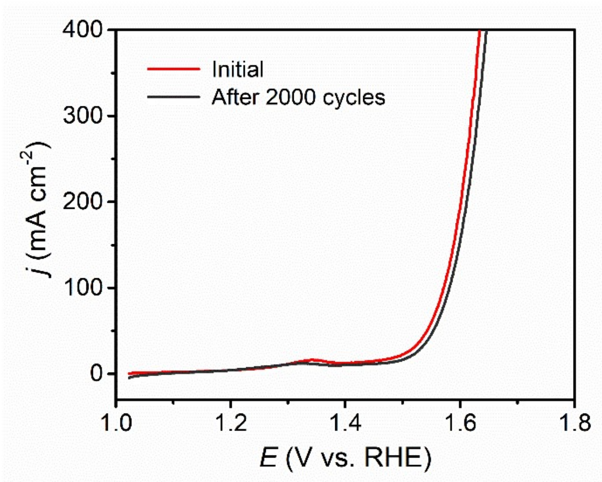

Fig. S12 The LSV curves before and after 1000 CV cycles in 1 M KOH.

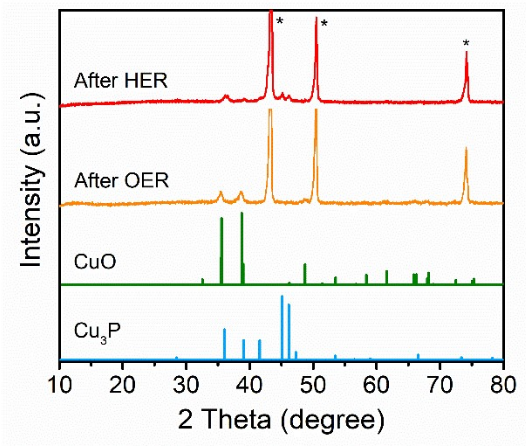

Fig. S13 XRD patterns of CH@PBA-P/CF after chronoamperometry measurements for overall water splitting.

Table S2 Comparison of the catalytic activity of CH@PBA-P/CF with other reported copper-based electrocatalysts.

Catalysts	Substrate*	HER (mV)		OER (mV)		References
		η_{50}	η_{100}	η_{50}	η_{100}	
CH@PBA-P/CF	CF	231	274	312	341	This work
CuNiS	NF	151	225	398	426	1
CoMoS	NF	213	238	350	395	2
Mn/Ni-doped Cu_2S	Monolith	136	160	317	330	3
CuNi@NiFeCu	CP	185	~200	285	297	4
Cu_3P/Ni_2P	CF	~180	~220	330	400	5
Co-Cu-P	NF	153	182	343	365	6
CuNiFeCrCo	NF	~170	180	~295	315	7
$Cu_2S/Co(OH)_2$	CF	241	/	268	/	8
Cu_2S@CoS	CF	235	/	275	/	9
Cu-Co-P	Cu foil	288	/	425	/	10
Cu_3P@NiFeMOF	CF	350	/	345	/	11
NiCu/NiCuN@NC	NF	/	149	/	295	12
Cu_3N/CuO	NF	/	280	/	425	13
CuNiS	CP	/	~300	/	~410	14
CoNiS@CuO	CF	/	~175	/	314	15
NiCu	Cu foil	/	167	/	~390	16

Note: * CF = copper foam, NF = nickel foam, CP = carbon paper.

Reference

1 D. Chinnadurai, R. Rajendiran and P. Kandasamy, *J. Colloid Interface Sci.*, 2022, **606**, 101-112.

2 A. Sajeev, V. K. Mariappan, D. Kesavan, K. Krishnamoorthy and S.-J. Kim, *Mater. Adv.*, 2021, **2**, 455-463.

3 H. Yuan, S. Zheng, S. Sang, J. Yang, J. Sun, Z. Ma and X. Wang, *Int. J. Hydrogen Energy*, 2022, **47**, 11827-11840.

4 D. Cao, H. Xu and D. Cheng, *Appl. Catal. B: Environ.*, 2021, **298**, 120600.
5 H. Liu, J. Gao, X. Xu, Q. Jia, L. Yang, S. Wang and D. Cao, *Chem. Eng. J.*, 2022, **448**, 137706.
6 Y. Liu, Y. Yang, B. Chen, X. Li, M. Guo, Y. Yang, K. Xu and C. Yuan, *Inorg. Chem.*, 2021, **60**, 18325-18336.
7 B. Nourmohammadi Khiarak, M. Mojaddami, Z. Zamani Faradonbeh, A. O. Zekiy and A. Simchi, *Energy Fuels*, 2022, **36**, 4502-4509.
8 D. Wang, J. Li, Y. Zhao, H. Xu and J. Zhao, *Electrochim. Acta*, 2019, **316**, 8-18.
9 Q. Zhou, T.-T. Li, J. Wang, F. Guo and Y.-Q. Zheng, *Electrochim. Acta*, 2019, **296**, 1035-1041.
10 R. N. Wasalathanthri, S. Jeffrey, R. A. Awni, K. Sun and D. M. Giolando, *ACS Sustainable Chem. Eng.*, 2019, **7**, 3092-3100.
11 E. Li, Q. Mou, Z. Xu, J. Ma, X. Liu, G. Cheng, P. Zhao and H. Li, *Catal. Lett.*, 2022, DOI: 10.1007/s10562-021-03865-5.
12 J. Hou, Y. Sun, Z. Li, B. Zhang, S. Cao, Y. Wu, Z. Gao and L. Sun, *Adv. Funct. Mater.*, 2018, **28**, 1803278.
13 C. Panda, P. W. Menezes, M. Zheng, S. Orthmann and M. Driess, *ACS Energy Lett.*, 2019, **4**, 747-754.
14 D. Cao and D. Cheng, *Chem. Commun.*, 2019, **55**, 8154-8157.
15 J. Yang, H. Xuan, G. Zhang, R. Wang, J. Yang, X. Liang, Y. Li and P. Han, *Appl. Surf. Sci.*, 2021, **570**, 151181.
16 J. Niu, Y. Yue, C. Yang, Y. Wang, J. Qin, X. Zhang and Z.-S. Wu, *Appl. Surf. Sci.*, 2021, **561**, 150030.