## **Electronic Supplementary Information**

# The volcanic relationship between HER activity and lattice constant of RuCo alloy nanofilm as a high efficient electrocatalyst

Yanyan Wang,<sup>‡</sup> Zhandong Ren,<sup>‡\*</sup> Ning Cong, Yaping Heng, Ming Wang, Ziqian Wang, Zhiqiang Xie, Ye Liu, Juanjuan Han and Yuchan Zhu\*

School of Chemical and Environmental Engineering, Wuhan Polytechnic University, Wuhan, 430023,

P. R. China.

<sup>‡</sup>Y.Y.W. and Z.D.R. contributed equally to this work.

\* Corresponding author:

Zhandong Ren, Professor, School of Chemical and Environmental Engineering, Wuhan Polytechnic University, Wuhan, 430023, P. R. China.

E-mail: renzhandong@163.com. Tel.: 86-27-83943956.

Yuchan Zhu, Professor, School of Chemical and Environmental Engineering, Wuhan Polytechnic

University, Wuhan, 430023, P. R. China.

E-mail: <u>zhuyuchan@163.com</u>. Tel.: 86-27-83943956.

#### 1. Experimental methods

## 1.1 Materials

Ruthenium target (99.99%) and Cobalt target (99.99%) were purchased from Goodwill Metallic Techology Co. Ltd., Beijing, China. Ruthenium chloride (RuCl<sub>3</sub>, AR), sodium acetate (CH<sub>3</sub>COONa·3H<sub>2</sub>O, AR), N-butanol (C<sub>4</sub>H<sub>9</sub>OH, AR), ethanol (C<sub>2</sub>H<sub>5</sub>OH, AR) and titanium foil (Ti, 99.999%) were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Commercial Pt/C (40% loading, 2-5 nm Pt size) is Johnson Matthey Co. Ltd. All reagents were analytical grade and used without further purification. Argon gas (99.999%) and oxygen gas (99.9%) was purchased from Ming-Hui Company. The water (18.25 M $\Omega$  cm<sup>-1</sup>) used in all experiments was prepared by passing through an ultra-pure purification system.

#### 1.2 Preparation of RuCo-ANFs and Ru-NF electrode

With 99.99% Ru and 99.99% Co as sputtering targets and Ti foil as the substrate, RuCo-ANFs electrodes with different proportions were prepared by magnetron sputtering with DC power supply. Before sputtering, the Ti foil was polished with metallographic sandpaper to remove the surface oxide layer. Next, the Ti foil substrate was degreased by ultrasonic cleaning with acetone, 2 mol L<sup>-1</sup> hydrochloric acid and ethanol. After drying, it is installed on the sample stage of the vacuum chamber of the magnetron sputtering instrument. Before the formal sputtering, the vacuum chamber was first evacuated to  $4 \times 10^{-4}$  Pa, and replaced with high-purity argon repeatedly to remove the air in the vacuum chamber. Then introduce high-purity argon, adjust the pressure of the vacuum chamber to 1.0 Pa, and obtain RuCo-ANFs electrodes with different proportions by controlling the DC power supply, as shown in Table S1 (ESI†). The loading of Ru is 35 µg cm<sup>-2</sup>, and the loading of Co is 2, 7, 12, 19 and 45 µg cm<sup>-2</sup>. When preparing Ru-NF electrode, the Co target should be turned off, and the loading of Ru is also 35 µg cm<sup>-2</sup>. In order to increase the stability of the electrode, the electrodes prepared above were roasted in a tubular furnace at 200 °C in argon atmosphere for 1 h.

## 1.3 Preparation of Ru/C electrode

Add 0.2449 g CH<sub>3</sub>COONa·3H<sub>2</sub>O to 30 mL 0.02 mol L<sup>-1</sup> RuCl<sub>3</sub>-n-butanol solution and disperse evenly by ultrasound. Then add an appropriate amount of n-butanol solution to ensure that the filling degree of the inner tank of the reactor is 60%. Put the autoclave into a constant temperature drying oven, set the temperature to 180 °C and the time to 6h. After the hydrothermal reaction, the samples were washed with absolute ethanol and ultrapure water respectively. Then, the sample was put into a vacuum drying oven and dried at 40 °C. After drying, carbon powder of the same quality was added to the Ru sample, and 50 wt% Ru/C sample was obtained after fine grinding. 1 mg 50 wt% Ru/C powders were mixed with 1 ml 0.05 wt% nafion ethanol solution respectively to prepare catalyst ink. After ultrasonic mixing, 21  $\mu$ L of Ru/C ink was added dropwise to the Ti foil substrate with a loading of 35  $\mu$ g cm<sup>-2</sup>.

#### 1.4 Preparation of Pt/C electrode

1 mg 40 wt% Pt/C powders (Johnson Matthey) was mixed with 1 ml 0.05 wt% nafion-ethanol solution respectively to prepare catalyst ink. After ultrasonic mixing, 26  $\mu$ L of Pt/C ink was added dropwise to the Ti foil substrate with a loading of 35  $\mu$ g cm<sup>-2</sup>.

#### 1.5 Material characterization

X-ray diffraction (XRD) patterns were acquired on an XRD-7000 X-ray diffractometer (Shimadzu, Japan). Transmission Electron Microscopy (TEM) were conducted on an JEM-2100F (JEOL, Japan). Scanning Electron Microscope (SEM) images were taken with a  $\Sigma$ IGMA fieldemission SEM (Zeiss, Germany). X-ray photoelectron spectrometry (XPS: ESCLAB 250Xi, Thermo Fisher Scientific, The United States) with monochromatized Al Ka radiation was used to analyze the electronic properties. Analysis of the composition of the electrode was carried out by X-ray fluorescence (XRF: EDX-7000, Shimadzu, Japan).

#### 1.6 Electrochemical measurements

The electrochemical experiments were carried out in a typical three-electrode electrochemical cell with a carbon paper as a counter electrode (TGP-H-090, Toray, Japan) and Hg/HgO/KOH(1.0 M) as the reference electrode (R0501, Tianjin Aida Hengsheng Technology Development Co., Ltd, China). The working electrodes are RuCo-ANFs electrodes with different proportions with an area of 0.3 cm<sup>2</sup>. Cyclic voltammetry (CV) measurements were performed in Ar-saturated 1.0 M KOH solution at the scan rate of 100 mV s<sup>-1</sup>. The activity of hydrogen evolution reaction (HER) was characterized by linear voltammetry scanning (LSV) in 1.0 M KOH solution at a scan rate of 5 mV s<sup>-1</sup>. All potentials were corrected with iR to the reversible hydrogen electrode (RHE). The analysis of electrochemical surface area (ECSA) is calculated by double-layer capacitance ( $C_{dl}$ ). At first, CV scanning is performed at different scanning speeds (10, 20, 40, 50, 60, 70, 80, 100 mV s<sup>-1</sup>) to obtain the current of  $C_{dl}$ . Secondly, the double-layer current at 0.77 V is linearly fitted to the scanning rate, and its slope is the  $C_{dl}$ . Further divide the  $C_{dl}$  by the capacitance constant ( $C_{ref}$ , 60 mC cm<sup>-2</sup>) to obtain ECSA. Electrochemical stability testing is performed by two methods. One test method is to determine electrochemical stability by comparing HER activity before and after CV by a continuous scan of 1000 cycles. Another stability test method is to continuously test the HER activity at a fixed potential for 6 h after the above 1000 CV scans. Electrochemical impedance spectroscopy (EIS) was recorded under the condition of frequency of 100 mHz  $\sim$  100 kHz and ac voltage amplitude of 50 mV.

All potentials refer to that of the reversible hydrogen electrode (RHE) transformation. E(vs. RHE) = E(vs. Hg/HgO) + 0.0591pH + 0.0977V = E(vs. Hg/HgO) + 0.926V

## 1.7 DFT calculations

First-principles calculations were performed using the Vienna Ab Initio Simulation Package (VASP, version 5.4.4) within a PBE (Perdew Burke Ernzerhof) generalized gradient approximation (GGA) to the exchange and correlation functional. A projector augmented wave (PAW) basis along with a plane-wave kinetic energy cutoff of 520 eV was employed for all computations. For the calculation of surface and chemisorption systems, a  $p(3\times3)$  surface unit cell was used, which is correspond to 1/9 surface coverage. A four-layer metal slab and repeated cell geometry with successive slabs separated by a vacuum region equivalent to four metal layers, and the Brillouin zone was sampled using a  $4\times4\times1$  Monkhorst-Park mesh. During the geometry optimization, the adsorbate layer and the top two layers of the slab were allowed to relax. The energies were converged to  $1\times10^{-4}$  eV per atom and ionic relaxations were allowed until the absolute value of force on each atom was below 0.02 eV/A.



Figure S1 XRD patterns of Ru-NF (a),  $Ru_{63}Co_{37}$ -ANF (b) and Co-NF (c).



Figure S2 XRD patterns of RuCo-ANFs with different ratios.



Figure S3 TEM images of Ru<sub>63</sub>Co<sub>37</sub>-ANF.



Figure S4 HRTEM images of  $Ru_{63}Co_{37}$ -ANF with lattice vacancies (a) and dislocation (b).



Figure S5 SEM image (a) and mapping (b-c) of Ru<sub>63</sub>Co<sub>37</sub>-ANF.



Figure S6 The C 1s spectra of Ru-NF, Ru<sub>93</sub>Co<sub>7</sub>-ANF, Ru<sub>75</sub>Co<sub>25</sub>-ANF and Ru<sub>63</sub>Co<sub>37</sub>-ANF.



Figure S7 The Ru 3p spectra of Ru-NF,  $Ru_{93}Co_7$ -ANF,  $Ru_{75}Co_{25}$ -ANF and  $Ru_{63}Co_{37}$ -ANF.



Figure S8 The Co 2p spectra of  $Ru_{63}Co_{37}$ -ANF and Co-NF.



Figure S9 The XPS core-level spectra of O 1s of Ru<sub>63</sub>Co<sub>37</sub>-ANF (a) and Ru-NF (b).

At last, there are three forms of oxygen atoms on the surface of Ru-NF, namely  $O^{2-}$  (530.2 eV),  $OH^{-}$  (531.3 eV) and  $H_2O$  (532.4 eV) in Fig. S8 (ESI<sup>†</sup>). While for Ru<sub>63</sub>Co<sub>37</sub>-ANF, it mainly exists in the form of  $OH^{-}$  (531.6 eV), which can prove that there are many defects on the surface of Ru<sub>63</sub>Co<sub>37</sub>-ANF.



Figure S10 The mass activities of Ru-NF,  $Ru_{63}Co_{37}$ -ANF, 50 wt% Ru/C and 40 wt% Pt/C at the overpotential of 50 mV (a). The mass activities of RuCo-ANFs with different ratios at the overpotential of 50 mV (b).



Figure S11 The double-capacitance curves of Ru-NF (a),  $Ru_{63}Co_{37}$ -ANF (b) and 50 wt% Ru/C (c) with different sweeping speeds. The double layer capacitance fitting curves of Ru-NF,  $Ru_{63}Co_{37}$ -ANF and 50 wt% Ru/C (d). The cyclic voltammetry curves of 40 wt% Pt/C (e). The electrochemical surface area (ECSA) of Ru-NF,  $Ru_{63}Co_{37}$ -ANF, 50 wt% Ru/C and 40 wt% Pt/C (f).



Figure S12 The double-capacitance curves of Ru-ANF (a),  $Ru_{93}Co_7$ -ANF (b),  $Ru_{75}Co_{25}$ -ANF (c),  $Ru_{63}Co_{37}$ -ANF (d),  $Ru_{52}Co_{48}$ -ANF (e) and  $Ru_{31}Co_{69}$ -ANF (f) with different sweeping speeds. The double layer capacitance fitting curves of RuCo-ANFs with different ratios (g). The electrochemical surface area (ECSA) of RuCo-ANFs with different ratios (h).



Figure S13 The specific activities of Ru-NF,  $Ru_{63}Co_{37}$ -ANF, 50 wt% Ru/C and 40 wt% Pt/C at the overpotential of 50 mV (a). The specific activities of RuCo-ANFs with different ratios at the overpotential of 50 mV (b).



Figure S14 The EIS measurements of Ru<sub>63</sub>Co<sub>37</sub>-ANF and Ru-NF at  $\eta = 50$  mV.

In addition, the  $R_{ct}$  of Ru<sub>63</sub>Co<sub>37</sub>-ANF (8.2  $\Omega$  cm<sup>2</sup>) is smaller than that of Ru-NF (15.8  $\Omega$  cm<sup>2</sup>) in Fig. S13 (ESI<sup>†</sup>), which indicates that the charge transfer is faster in the HER process.



Figure S15 Accelerated life test of  $Ru_{63}Co_{37}$ -ANF through the consecutive CV scan measurements (a). Long-time stability tests of  $Ru_{63}Co_{37}$ -ANF at the overpotential of 50 mV.

After 1000 cycles of CV scanning, the HER activity of  $Ru_{63}Co_{37}$ -ANF electrode not only did not decrease, but increased slightly in Fig. S14 (ESI†). The chronoamperometric test was conducted at the overpotential of 50 mV. The HER activity of  $Ru_{63}Co_{37}$ -ANF electrode increased first and then decreased slightly, with an overall decline rate of 5%.



Figure S16 TEM image (a-before, b-after), SEM image (c-before, d-after) and XRD pattern (e) of  $Ru_{63}Co_{37}$ -ANF before and after the long-time stability test for 6h.

As shown by TEM and SEM images, the morphology of  $Ru_{63}Co_{37}$ -ANF electrode has not changed obviously before and after the stability test.

At the same time, the lattice structure of  $Ru_{63}Co_{37}$ -ANF remains unchanged, and the position of the characteristic diffraction peak does not move in the XRD pattern.



Figure S17 DFT calculations of  $\Delta G_{H^*}$  for the  $Ru_2Co_1$  and  $Ru_1Co_2.$ 



Figure S18 The cyclic voltammetry curves of Ru-NF (a) and  $Ru_{63}Co_{37}$ -ANF (b).



Figure S19 The cyclic voltammetry curves of RuCo-ANFs with different ratios.

RuCo-ANFs -	Sputtering power / W		Content / mol%		Loading / $\mu g \ cm^{-2}$	
	Ru	Co	Ru	Со	Ru	Со
Ru	30	0	100	0	35	0
Ru <sub>93</sub> Co <sub>7</sub>	30	10	92.81	7.19	35	2
Ru <sub>75</sub> Co <sub>25</sub>	30	30	74.69	25.41	35	7
Ru <sub>63</sub> Co <sub>37</sub>	30	50	63.18	36.82 <sup>2</sup>	35	12
			41.62	58.38b		
Ru <sub>63</sub> Co <sub>37</sub>		~	70.92	29.082	25	8.5
(aner stability test)	~		51.39	48.61 <sup>b</sup>	55	
Ru <sub>52</sub> Co <sub>48</sub>	30	100	52.15	47.85	35	19
Ru <sub>31</sub> Co <sub>69</sub>	30	120	31.13	68.87	35	45

Table S1 Composition analysis of RuCo-ANFs with different ratios by XRF and SEM-Mapping.

Note: <sup>a</sup> analysis by XRF; <sup>b</sup> analysis by SEM-Mapping.

The composition and loading of Ru<sub>63</sub>Co<sub>37</sub>-ANF sample after the stability test are analyzed by XRF and SEM-mapping. Compared with the Ru<sub>63</sub>Co<sub>37</sub>-ANF sample before the stability test, the loading of Ru element is almost unchanged, while the loading of Co element is reduced. Therefore, the mole fraction of Ru increases (XRF: from 63.18 to 70.92 mol%; SEM mapping: from 41.62 to 51.39 mol%). In addition, the lattice structure of Ru<sub>63</sub>Co<sub>37</sub>-ANF does not change before and after the stability test through the XRD diffraction (Fig. S16 e). This indicates that some Co elements on the electrode surface will be lost during the stability test. However, it does not affect the important structure of the electrode and thus can not reduce HER activity.

Catalyst	Electrolyte	Loading	n <sub>10</sub>	Tafel	References	
	J	(ug cm <sup>-2</sup> )	(mV)	slone		
		(PB )	()	mV dec <sup>-1</sup>		
Ru <sub>62</sub> C0 <sub>27</sub> -ANF	1.0 M KOH	47	43	42.4	This work	
- 05 57			-		80% iR-compensation	
RuCo@NC-600	1.0 M KOH	255	34	36	<i>J. Mater. Chem. A</i> , 2020, 8, 12810–12820. (1) with iR-compensation	
Co-substituted	1.0 M KOH	153	13	29	Nat. Commun., 2018, 9, 4958.	
Ru					(2) 100% iR-compensation	
RuCo@NC-750	1.0 M KOH	433	25	37	<i>Electrochim. Acta</i> , 2019, 327, 134958. (3) without iR-compensation	
Ru@Co-NC	1.0 M KOH	764	23	58.1	<i>Appl. Surf. Sci.</i> , 2019, 494, 101–110. <b>(4)</b> with iR-compensation	
RuCo@HCSs	1.0 M KOH	433	21	32	ACS Sustainable Chem. Eng., 2019, 7, 18744–18752. (5)	
RuCo@NC(S-4)	1.0 M KOH	275	28	31	<i>Nat. Commun.</i> , 2017, 8, 14969. <b>(6)</b>	
CF@Ru-CoCH	1.0 M KOH	~	66	65	<i>Electrochim. Acta</i> , 2020, 331, 135367. (7) with iR-compensation	
Ru/CoO hybrid	1.0 M KOH	~	55	70	J. Energy Chem., 2019, 37, 143–147. (8)	
Ru <sub>1</sub> Co <sub>2</sub> NPs	1.0 M KOH	780	188	66.5	ACS Applied Energy Materials, 2020, 3, 1869-1874. (9)	
RuCo ANSs	1.0 M KOH	142	10	20.6	Angew. Chem. Int. Ed., 2022, 61, e202113664.	
M-Co NPs@Ru SAs/NC	1.0 M KOH	337	34	55	Small, 2021, 2105231. (11)	
Co <sub>1-x</sub> Ru <sub>x</sub> /GC	1.0 M KOH	500	14	71.7	Chem. Eng. J., 2021, 417, 128047. (12)	
Ru@Co/N-CNTs	1.0 M KOH	~	48	33	ACS Sustainable Chem. Eng., 2020, 8, 9136-9144. (13)	

Table S2 Comparison of HER activities between Ru<sub>63</sub>Co<sub>37</sub>-ANF with other RuCo composite and RuM allov electrocatalysts in literatures.

					85% iR-compensation
RuCoP clusters	1.0 M KOH	300	23	37	Energy Environ. Sci., 2018,
					11, 1819-1827. <b>(14)</b>
					85% iR-compensation
Ni <sub>1.5</sub> Co <sub>1.4</sub> P@Ru	1.0 M KOH	283	52	50	Chem. Commun., 2017, 53,
					13153-13156. <b>(15)</b>
Ru-CoNi@NC-2	1.0 M KOH	~	268	63	ACS Sustainable Chem. Eng.,
					2019, 7, 17227-17236. (16)
					without iR compensation
RuNi NSs	1.0 M KOH	27 (Ru)	15	28	Nano Energy, 2019, 66,
					104173. <b>(17)</b>
NiRu@N–C	1.0 M KOH	273	32	64	J. Mater. Chem. A, 2018, 6,
					1376-1381. <b>(18)</b>
					with iR compensation
NiRu <sub>2</sub> @NC-600	1.0 M KOH	273	53	37.95	Dalton Trans., 2020, 49,
					13647-13654. <b>(19)</b>
Cu <sub>53</sub> Ru <sub>47</sub>	1.0 M KOH	306	15	30	ACS Energy Lett., 2020, 5,
					192-199. <b>(20)</b>
					with iR-compensation
MoRu/C	1.0 M KOH	127	27.1 ( <i>η</i> <sub>5</sub> )	51	Chem. Commun., 2020, 56,
					14475-14478. <b>(21)</b>
					80% iR-compensation
RuW	1.0 M KOH	78 (Ru)	~70	59.1	ACS Appl. Energy Mater.,
					2021, 4, 2348-2356. (22)
<i>h</i> -RuSe <sub>2</sub>	1.0 M KOH	300	34	95	Angew. Chem. Int. Ed., 2021,
					60, 7013-7017. <b>(23)</b>
Ru <sub>0.33</sub> Se@TNA	1.0 M KOH	200	57	50	Small, 2018, 14, 1802132. (24)
					90% iR-compensation
Ru <sub>x</sub> Se-400	1.0 M KOH	1000	45	31.4	Nanoscale, 2020, 12, 23740-
					23747. <b>(25)</b>
					90% iR-compensation
RuAu single-atom	1.0 M KOH	280	24	27	Adv. Energy Mater., 2019, 9,
alloy					1803913. <b>(26)</b>
					with iR-compensation
Pd <sub>3</sub> Ru	1.0 M KOH	15	42	~	ACS Catal., 2019, 9, 9614-
					9621. <b>(27)</b>
RuRh <sub>2</sub>	1.0 M KOH	283	24	31	Adv. Sci., 2021, 8, 2002341.
					(28)

# References

1. F. Zhang, Y. Zhu, Y. Chen, Y. Lu, Q. Lin, L. Zhang, S. Tao, X. Zhang and H. Wang, *J. Mater. Chem. A*, 2020, 8, 12810–12820.

2. J. Mao, C.-T. He, J. Pei, W. Chen, D. He, Y. He, Z. Zhuang, C. Chen, Q. Peng, D. Wang and Y. Li, *Nat. Commun.*, 2018, 9, 4958.

3. C. Gao, H. Wang, S. Li, B. Liu, J. Yang, J. Gao, Z. Peng, Z. Zhang and Z. Liu, *Electrochim. Acta*, 2019, 327, 134958.

4. H. Gao, J. Zang, X. Liu, Y. Wang, P. Tian, S. Zhou, S. Song, P. Chen and W. Li, *Appl. Surf. Sci.*, 2019, 494, 101–110.

5. H. Wang, C. Gao, R. Li, Z. Peng, J. Yang, J. Gao, Y. Yang, S. Li, B. Li and Z. Liu, *ACS Sustainable Chem. Eng.*, 2019, 7, 18744–18752.

6. J. Su, Y. Yang, G. Xia, J. Chen, P. Jiang and Q. Chen, Nat. Commun., 2017, 8, 14969.

7. J. Li, Q. Zhou, Z. Shen, S. Li, J. Pu, C. Zhong, M. Cao, X. Jin, H. Zhang, Y. Wang, H. Ma, *Electrochim. Acta*, 2020, 331, 135367.

8. J.-X. Guo, D.-Y. Yan, K.-W. Qiu, C. Mu, D. Jiao, J. Mao, H. Wang, T. Ling, J. Energy Chem., 2019, 37, 143–147.

9. Y. Bao, J. Dai, J. Zhao, Y. Wu, C. Li, L. Ji, X. Zhang, F. Yang, ACS Appl. Energ. Mater., 2020, 3, 1869-1874.

10. C. Cai, K. Liu, Y. Zhu, P. Li, Q. Wang, B. Liu, S. Chen, H. Li, L. Zhu, H. Li, J. Fu, Y. Chen, E. Pensa, J. Hu, Y.-R. Lu, T.-S. Chan, E. Cortés, M. Liu, *Angew. Chem. Int. Ed.*, 2022, 61, e202113664.

 H. Zhang, H. Su, M. A. Soldatov, Y. Li, X. Zhao, M. Liu, W. Zhou, X. Zhang, X. Sun, Y. Xu, P. Yao, S. Wei, Q. Liu, Small, 2021, 2105231.

12. S. Zhang, Y. Rui, X. Zhang, R. Sa, F. Zhou, R. Wang, X. Li, Chem. Eng. J., 2021, 417, 128047.

13. Z. Liu, X. Yang, G. Hu, L. Feng, ACS Sustainable Chem. Eng., 2020, 8, 9136-9144.

14. J. Xu, T. Liu, J. Li, B. Li, Y. Liu, B. Zhang, D. Xiong, I. Amorim, W. Li, L. Liu, *Energy Environ. Sci.*, 2018, 11, 1819-1827.

15. S. Liu, Q. Liu, Y. Lv, B. Chen, Q. Zhou, L. Wang, Q. Zheng, C. Che, C. Chen, *Chem. Commun.*, 2017, 53, 13153-13156.

16. W. Wang, S. Xi, Y. Shao, W. Sun, S. Wang, J. Gao, C. Mao, X. Guo, G. Li, *ACS Sustainable Chem. Eng.*, 2019, 7, 17227-17236.

17. G. Liu, W. Zhou, B. Chen, Q. Zhang, X. Cui, B. Li, Z. Lai, Y. Chen, Z. Zhang, L. Gu, H. Zhang, *Nano Energy*, 2019, 66, 104173.

18. Y. Xu, S. Yin, C. Li, K. Deng, H. Xue, X. Li, H. Wang, L. Wang, J. Mater. Chem. A, 2018, 6, 1376-1381.

19. S. Xu, Z. Li, K. Chu, G. Yao, Y. Xu, P. Niu, F. Zheng, Dalton Trans., 2020, 49, 13647-13654.

20. Q. Wu, M. Luo, J. Han, W. Peng, Y. Zhao, D. Chen, M. Peng, J. Liu, F. M. F. de Groot, Y. Tan, *ACS Energy Lett.*, 2020, 5, 192-199.

21. S. Okazoe, K. Kusada, D. Wu, T. Yamamoto, T. Toriyama, S. Matsumura, S. Kawaguchi, Y. Kubotae, H. Kitagawa, *Chem. Commun.*, 2020, 56, 14475-14478.

22. L. Tan, N. Cong, H. Chen, C. Zhai, J. Han, H. Fang, X. Zhou, Z. Ren, Y. Zhu, ACS Appl. Energy Mater., 2021, 4, 2348-2356.

23. Y. Zhao, H. Cong, P. Li, D. Wu, S. Chen, Wei Luo, Angew. Chem. Int. Ed., 2021, 60, 7013-7017.

24. K. Wang, Q. Chen, Y. Hu, W. Wei, S. Wang, Q. Shen, P. Qu, Small, 2018, 14, 1802132.

25. K. Wang, B. Li, W. Wei, J.Wang, Q. Shen, P. Qu, Nanoscale, 2020, 12, 23740-23747.

26. C.-H. Chen, D. Wu, Z. Li, R. Zhang, C.-G. Kuai, X.-R. Zhao, C.-K. Dong, S.-Z. Qiao, H. Liu, X.-W. Du, *Adv. Energy Mater.*, 2019, 9, 1803913.

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

28. X. Mu, J. Gu, F. Feng, Z. Xiao, C. Chen, S. Liu, S. Mu, Adv. Sci., 2021, 8, 2002341.