# Supporting Information

# Atomically Ordered Ir<sub>3</sub>Ti Intermetallics for pH-Universal Overall Water Splitting

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## Experimental

#### **Reagents and Chemicals**

Iridium (III) chloride hydrate (IrCl<sub>3</sub>·xH<sub>2</sub>O, 99.9%) was purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Platinum (II) acetylacetonate ( $C_{10}H_{14}O_4Pt$ , 97%), Rhodium (III) chloride trihydrate ( $Cl_3H_6O_3Rh$ , 98%) and Titanium (III) trichloride (TiCl<sub>3</sub>, AR) were purchased from Macklin Biochemical Co., Ltd (Shanghai, China). Commercial carbon nanotubes (CNTs) were purchased from Hesen electric co., Ltd (Shanghai, China). All chemicals were used without further purification. Commercial Pt/C was purchased from D&B Laboratory Equipment Co., Ltd (Shanghai, China), and the mass fraction of Pt is 20%. Commercial IrO<sub>2</sub> (99.9% metals basis) was purchased from Aladdin Biochemical Technology Co., Ltd (Shanghai, China).

### Functionalization treatment of carbon nanotubes

The functionalization treatment of CNTs was conducted in nitric acid solution at 160 °C for 6 h. Typically, 900 mg CNTs were added to 200 mL nitric acid solution (1.0 M) in a 250 ml flask and heated the flask at 160 °C for 6 h under stirring and refluxed in an oil bath. After cooling down to room temperature, the black suspension was collected by centrifugation and washed with ultra-pure water for 5~6 times. After the freezing-dry treatment, the water in the product was removed. And the functionalized CNTs support can be obtained.

#### Synthesis of Ir<sub>3</sub>Ti/CNT, Pt<sub>3</sub>Ti/CNT, Rh<sub>3</sub>Ti/CNT, and Ir/CNT

In a typical synthesis, 0.055 mmol  $IrCl_3 xH_2O$ , 0.055 mmol TiCl\_3 were mixed in 2 mL deionized water and sonicated until completely dissolved. Functionalized CNTs (60 mg) were dispersed in the mixture solution, and ultrasonicated for 2 h. After 24 h of freeze-drying treatment, the water was removed to obtain the aerogel of metal precursors loaded on CNTs. Then the  $IrCl_3$ -TiCl\_3/CNT aerogels were annealed in flowing 10 vol% Ar/H<sub>2</sub> at 1000 °C for 6 h with a heating rate of 5 °C min<sup>-1</sup>.

Pt<sub>3</sub>Ti/CNT, Rh<sub>3</sub>Ti/CNT were prepared in the same route, and the same amount of noble metal (0.055 mmol  $C_{10}H_{14}O_4Pt$ , 0.055 mmol  $Cl_3H_6O_3Rh$ ) and CNTs were used.

Ir/CNT was prepared in the same route without the addition of TiCl<sub>3</sub>.

#### **Physicochemical characterizations**

The X-ray powder diffraction (XRD) patterns of prepared materials were collected on a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA with Cu K $\alpha$ radiation ( $\lambda = 0.15406$  nm). The scanning electron microscopy (SEM) images were taken on a TESCAN MIRA LMS scanning electron microscope. Transmission electron microscopy (TEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, and selected area electron diffraction (SAED) patterns were obtained on a Talos F200S transmission electron microscope (200 kV). Aberration-corrected HAADF-STEM images, energy-dispersive X-ray spectroscopy (EDS) elemental mapping images and line scan profiles were obtained on a JEOL JEM-ARM300F Grand ARM transmission electron microscope (300 kV). The X-ray photoelectron spectroscopy (XPS) results were recorded on a Thermo Fisher Scientific photoelectron spectrometer using an Al Kα radiation. All binding energies were calibrated by the C 1s peak energy of 284.4 eV. The Raman spectra were carried out on a Horiba scientific-LabRAM HR evolution spectrometer with a 514 nm laser light. The Brunauer-Emmett-Teller (BET) specific surface area and pore size were measured based on a N<sub>2</sub> adsorption–desorption method using Autosorb-IQ-MP at 77 K. The accurate contents of various elements (except Ir) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Agilent 725 (OES) instrument. The contents of Ir were quantified by thermogravimetric analysis (TGA) on a Netzsch STA449C thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> under the air atmosphere, and the final products (i.e. IrO<sub>2</sub> and TiO<sub>2</sub>) were determined by XRD.

#### **Electrochemical measurements**

All electrochemical measurements were carried out with a three-electrode system on CHI660 electrochemical workstation (Chenhua, Shanghai). A graphite rod and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The catalyst-deposited glassy carbon electrode (diameter: 3 mm, area:  $0.0706 \text{ cm}^2$ ) served as the working electrode. To prepare the catalyst ink, 2 mg of the electrocatalysts were dispersed in a 1 mL mixture solution including 760 µL of ethanol, 190 µL of water and 50 µL of 5 wt.% Nafion solution and sonicated at least 1 h to form

a homogeneous ink. A certain amount of catalyst ink was deposited on the glassy carbon electrode to form a uniform thin film (the loading of noble mental was controlled to be  $6 \mu g$ ).

Polarization curves were then performed in N<sub>2</sub>-saturated 1.0 M KOH and 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolytes, after a continuous cyclic voltammetry. All potentials were calibrated to the reversible hydrogen electrode (RHE). In 1.0 M KOH,  $E_{RHE} = E_{SCE} + 1.0675$  V. In 0.5 M H<sub>2</sub>SO<sub>4</sub>,  $E_{RHE} = E_{SCE} + 0.242$  V. During all electrochemical measurements, 95% *iR* compensation was applied to compensate for the resistance losses due to the electrolytes, and polarization curves were corrected as follows:  $E_{iR-corrected} = E - iR$ . Linear sweep voltammetry (LSV) curves of HER and OER were obtained with a scan rate of 5 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) measurements were carried out within a frequency range spanning from 100 kHz to 0.01 Hz, utilizing an AC amplitude of 10 mV. The electrochemically active surface area (ECSA) was estimated by electrochemical double layer capacitance  $(C_{dl})$  measurements. The  $C_{dl}$  was conducted from CVs at a serious scan rate of 20, 40, 60, 80, 100 and 120 mV s<sup>-1</sup> in non-Faraday potential window and calculated from the slope of the double-layer charging current versus the scan rate. Accelerated degradation tests were measured in the range of -0.2 to 0.0 V for HER (1.4 to 1.6 V for OER) at a sweep rate of 100 mV s<sup>-1</sup> for 10,000 cycles.

The performance of overall water splitting was measured in a two-electrode system with the catalyst-modified carbon paper (area: 0.25 cm<sup>2</sup>) as the cathode and anode

electrodes simultaneously from 1.0 V to 2.0 V. Chronoamperometry measurements were carried out at the voltage that the current density reached 10 mA cm<sup>-2</sup>.

# **Calculation details**

All of the density functional theory (DFT) calculations based on first principle theory were conducted using the Vienna ab-initio Simulation Package (VASP) software.<sup>1</sup> The projector augmented wave (PAW) pseudopotential and the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) were adopted to describe exchange-correlation interactions.<sup>2, 3</sup> Subsequently, Van der Waals interaction was considered by DFT-D3 method.<sup>4, 5</sup> The dipolar correction was incorporated while disabling symmetrization. The vacuum with a length of 15 Å was set along the z-axis to avoid periodic interactions. The plane waves basis cutoff energy was applied to be 500 eV, with the Brillouin zone k-point sampling using  $3 \times 3 \times 1$  a Monkhorst-Pack mesh.<sup>6</sup> To optimize structure, the convergence threshold in structural optimization was set to be  $10^{-5}$  eV for electronic self-consistent iteration and 0.03 eV Å<sup>-1</sup> for residual force. The adsorption Gibbs free energy ( $\Delta G$ ) was calculated as follows:  $\Delta G = \Delta E +$  $\Delta ZPE$  - T $\Delta S$ . in which  $\Delta E$ ,  $\Delta ZPE$ , T and  $\Delta S$  represent reaction energy difference, the difference of the zero-point energy, temperature (298.15 K), and the difference of entropy, respectively.

# **Figures and Tables**



Figure S1. The XRD patterns of Ir<sub>3</sub>Ti/CNT and functionalized CNTs.



**Figure S2.** (a) HAADF-STEM image and (b) EDS line scan profile of an individual Ir<sub>3</sub>Ti NP.



Figure S3. EDS spectrum of an individual Ir<sub>3</sub>Ti NP.



**Figure S4.** (a) TEM image and (b) the corresponding particle size distribution histogram of Ir/CNT. (c) XRD pattern of Ir/CNT.



Figure S5. (a) TEM image and (b) the corresponding particle size distribution histogram of  $Pt_3Ti/CNT$ . (c) XRD pattern of  $Pt_3Ti/CNT$ .



Figure S6. (a) TEM image and (b) the corresponding particle size distribution histogram of  $Rh_3Ti/CNT$ . (c) XRD pattern of  $Rh_3Ti/CNT$ .



Figure S7. SEM images of (a) Ir<sub>3</sub>Ti/CNT and (b) functionalized CNTs. (c) TEM image

of functionalized CNTs.



Figure S8. (a)  $N_2$  adsorption-desorption isotherms and (b) the corresponding pore size distribution curve of Ir/CNT.



Figure S9. XRD patterns of (a) Ir<sub>3</sub>Ti/CNT and (b) Ir/CNT after TGA measurements.



**Figure S10.** Cyclic voltammetry curves of (a)  $Ir_3Ti/CNT$ , (b) Ir/CNT and (c) Pt/C for HER at different scan rates in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (d) The calculated  $C_{dl}$  values.



**Figure S11.** Cyclic voltammetry curves of (a)  $Ir_3Ti/CNT$ , (b) Ir/CNT and (c)  $IrO_2$  for OER at different scan rates in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (d) The calculated  $C_{dl}$  values.



Figure S12. Nyquist plots for (a) HER and (b) OER in 0.5 M  $H_2SO_4$ . The insets are the equivalent electrical circuits.



**Figure S13.** (a) TEM image, (b) HRTEM image and (c) SAED pattern of  $Ir_3Ti/CNT$  as cathode for overall water splitting after the CP test in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



**Figure S14.** (a) TEM image, (b) HRTEM image and (c) SAED pattern of  $Ir_3Ti/CNT$  as anode for overall water splitting after the CP test in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



**Figure S15.** Cyclic voltammetry curves of (a)  $Ir_3Ti/CNT$ , (b) Ir/CNT and (c) Pt/C for HER at different scan rates in 1.0 M KOH. (d) The calculated  $C_{dl}$  values.



**Figure S16**. Cyclic voltammetry curves of (a)  $Ir_3Ti/CNT$ , (b) Ir/CNT and (c)  $IrO_2$  for OER at different scan rates in 1.0 M KOH. (d) The calculated  $C_{dl}$  values.



**Figure S17.** Nyquist plots for (a) HER and (b) OER in 1.0 M KOH. The insets are the equivalent electrical circuits.



Figure S18. The structural models of (a)  $Ir_3Ti$  (111) and (b) Ir (111).



Figure S19. The average Bader charge of Ir and Ti atoms for Ir<sub>3</sub>Ti (111).



Figure S20. Structural models of \*H intermediate on  $Ir_3Ti$  (111) and Ir (111) for the acidic HER process.



Figure S21. (a) Predicted water dissociation energy barriers on  $Ir_3Ti$  (111) and (b) the corresponding structural models.



**Figure S22.** (a) Predicted water dissociation energy barriers on Ir (111) and (b) the corresponding structural models.



Figure S23. Structural models of intermediates on  $Ir_3Ti$  (111) in the OER process.



Figure S24. Structural models of intermediates on Ir (111) in the OER process.

Ir <sub>3</sub> Ti (JCPDS N	o. 01-071-9323)	Calculated
Space group	Pm3m	-
a	3.845 Å	3.832 Å
b	3.845 Å	3.832 Å
с	3.845 Å	3.832 Å
α	90°	90°
β	90°	90°
γ	90°	90°

**Table S1.** Lattice parameters of  $Ir_3Ti$ , as determined from the Rietveld refinementanalysis and compared with the theoretical values of  $Ir_3Ti$  IMCs from ICSD.

Catalyst	Electrolyte	HER $\eta^a$ (mV)	<b>OER</b> $\eta^b$ (mV)	Reference
Ir <sub>3</sub> Ti/CNT	0.5 M H <sub>2</sub> SO <sub>4</sub>	21	245	This work
Ir/NSC#	0.1 M HClO <sub>4</sub>	17	275	7
IrTe <sub>2</sub> HNSs#	$0.5 \text{ M} \text{ H}_2\text{SO}_4$	20	275	8
RhCu NTs	$0.5 \text{ M} \text{ H}_2\text{SO}_4$	12	345	9
Ru-Ni NAs	$0.5 \text{ M} \text{ H}_2\text{SO}_4$	39	252	10
RuTe <sub>2</sub> PNR#	$0.5 \ M \ H_2 SO_4$	35	245	11
IrW NDs#	0.1 M HClO <sub>4</sub>	12	285	12
RuNi-NCNFs	$0.5 \mathrm{~M~H_2SO_4}$	23	290	13
IrO <sub>x</sub> -500	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	40	282	14
Ir-SA@Fe@NCNT	$0.5 \mathrm{~M~H_2SO_4}$	26	250	15
$RuB_2$	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	52	223	16
Li-IrSe <sub>2</sub> #	$0.5 \mathrm{~M~H_2SO_4}$	55	220	17
PtCo/Ir FBNWs	0.1 M HClO <sub>4</sub>	14	308	18
Pt-RuO <sub>2</sub> HNSs	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	26	228	19
Ir WNWs	0.1 M HClO <sub>4</sub>	15.4	270	20
IrCo <sub>0.65</sub> ND	0.1 M HClO <sub>4</sub>	17	281	21
Ir <sub>6</sub> Ag <sub>9</sub> NTs/C	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	20	285	22
IrCo PHNCs#	0.1 M HClO <sub>4</sub>	35	310	23
IrCoNi PHNCs#	0.1 M HClO <sub>4</sub>	55	303	23
Ir-NR/C	0.5 M H <sub>2</sub> SO <sub>4</sub>	28	290	24
Ir/cucurbit[6]uril#	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	52	270	25

**Table S2.** Comparisons of HER and OER activities for  $Ir_3Ti/CNT$  and various noblemetal-based electrocatalysts reported recently in acidic electrolytes.

#: data are read from figures in literatures.

a: Unless otherwise specified,  $\eta$  refers to overpotentials required to reach current density of 10 mA cm<sup>-2</sup> in HER.

b: Unless otherwise specified,  $\eta$  refers to overpotentials required to reach current

density of 10 mA cm<sup>-2</sup> in OER.

Table S3. Comparison of the overall water splitting electrocatalytic performance for
Ir <sub>3</sub> Ti/CNT and various noble metal-based electrocatalysts reported recently in acidic
electrolytes.

Catalwat	Electrolyte	Cell Voltage (V) @10 mA cm <sup>-</sup>	Referenc
		2	e
Ir <sub>3</sub> Ti/CNT	$0.5 \text{ M H}_2\text{SO}_4$	1.51	This work
IrCoNi PHNCs	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	1.65	23
Ir@Ni-NDC	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	1.54	26
Au@AuIr <sub>2</sub>	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	1.55	27
Ir-doped WO <sub>3</sub>	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	1.56	28
Ir-NR/C	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	1.55	29
Ir/MoS <sub>2</sub> NFs	0.1 M HClO <sub>4</sub>	1.55	30
RuO <sub>2</sub> -WC NPs	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	1.66	31
Ir@Sr-p-TiO <sub>2</sub> NWs	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	1.52	32
$Au@Au_{0.43}Ir_{0.57}$	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	1.52	33
Ir <sub>6</sub> Ag <sub>9</sub> NTs/C	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	1.55	34
IrW/WO <sub>3-x</sub> @NC/CP	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	1.52	35
Ir <sub>3</sub> CeO <sub>x</sub> /C	0.5 M H <sub>2</sub> SO <sub>4</sub>	1.64	36

Catalyst	Electrolyte	HER $\eta^a$ (mV)	<b>OER</b> $\eta^b$ (mV)	Reference
Ir <sub>3</sub> Ti/CNT	1.0 M KOH	15	268	This work
Ir/NSC#	1.0 M KOH	18.5	266	7
IrTe <sub>2</sub> HNSs#	1.0 M KOH	54	298	8
RhCu NTs	1.0 M KOH	8	315	9
Ru-Ni NAs	1.0 M KOH	39	304	10
RuTe <sub>2</sub> PNR#	1.0 M KOH	32	285	11
IrW NDs#	1.0 M KOH	29	320	12
RuNi-NCNFs	1.0 M KOH	35	290	13
Ir-NR/C	1.0 M KOH	42	296	29
Ru/Cu-RuO <sub>2</sub>	1.0 M KOH	28	241	37
Ru/Co-N-C	1.0 M KOH	19	276	38
$Ir_xW_y$	0.1 M KOH	29	281	39
RuCoP@CN#	1.0 M NaOH	24	260	40
Ir-NSs	1.0 M KOH	50	266	41
Ir@N-G-750	1.0 M KOH	43	270	42
Ru <sub>2</sub> Ni <sub>2</sub> SNs/C#	1.0 M KOH	40	310	43
Ru/N-BP2000	1.0 M KOH	15	285	44

**Table S4.** Comparisons of HER and OER activities for Ir<sub>3</sub>Ti/CNT and various noble metal-based electrocatalysts reported recently in alkaline electrolytes.

#: data are read from figures in literatures.

a: Unless otherwise specified,  $\eta$  refers to overpotentials required to reach current density of 10 mA cm<sup>-2</sup> in HER.

b: Unless otherwise specified,  $\eta$  refers to overpotentials required to reach current density of 10 mA cm<sup>-2</sup> in OER.

Table S5. Comparison of the overall water splitting electrocatalytic performance for
Ir <sub>3</sub> Ti/CNT and various noble metal-based electrocatalysts reported recently in alkaline
electrolytes.

Catalyst	Electrolyte	Cell Voltage (V) @10 mA cm <sup>-</sup>	Referenc
		2	e
Ir <sub>3</sub> Ti/CNT	1.0 M KOH	1.52	This work
Ir-NR/C	1.0 M KOH	1.57	29
Ir <sub>n</sub> -CoMoPO <sub>x</sub>	1.0 M KOH	1.53	45
Pt/VC-2.84	1.0 M KOH	1.59	46
$Pt-Ni_2Fe_1-24$	1.0 M KOH	1.65	47
Rh-Co <sub>x</sub> P	1.0 M KOH	1.57	48
Ir <sub>1</sub> @Co/NC	1.0 M KOH	1.60	49
2.4% Ir-CoSe <sub>2</sub>	1.0 M KOH	1.57	50
RhP <sub>x</sub> /CoNiP <sub>4</sub> O <sub>12</sub> /CC	1.0 M KOH	1.57	51
Pt/Ni <sub>3</sub> Fe/rGO	1.0 M KOH	1.55	52
IrO2@MnO2/rGO	1.0 M KOH	1.60	53
Ru/CoOOH@NF	1.0 M KOH	1.54	54

# References

- 1 G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, 6, 15-50.
- 2 P. E. Blöchl, *Physical Review B*, 1994, **50**, 17953-17979.
- J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, 77, 3865-3868.
- 4 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics*, 2010, **132**.
- 5 J. Klimeš, D. R. Bowler and A. Michaelides, *Physical Review B*, 2011, **83**, 195131.
- 6 H. J. Monkhorst and J. D. Pack, *Physical Review B*, 1976, **13**, 5188-5192.
- 7 Q. Wang, C.-Q. Xu, W. Liu, S.-F. Hung, H. Bin Yang, J. Gao, W. Cai, H. M. Chen, J. Li and B. Liu, *Nature Communications*, 2020, **11**, 4246.
- 8 Y. Pi, Y. Xu, L. Li, T. Sun, B. Huang, L. Bu, Y. Ma, Z. Hu, C.-W. Pao and X. Huang, *Advanced Functional Materials*, 2020, **30**, 2004375.
- 9 D. Cao, H. Xu and D. Cheng, *Advanced Energy Materials*, 2020, **10**, 1903038.
- 10 J. Yang, Q. Shao, B. Huang, M. Sun and X. Huang, *iScience*, 2019, **11**, 492-504.
- 11 J. Wang, L. Han, B. Huang, Q. Shao, H. L. Xin and X. Huang, *Nature Communications*, 2019, **10**, 5692.
- 12 F. Lv, J. Feng, K. Wang, Z. Dou, W. Zhang, J. Zhou, C. Yang, M. Luo, Y. Yang, Y. Li, P. Gao and S. Guo, *ACS Central Science*, 2018, **4**.
- 13 M. Li, H. Wang, W. Zhu, W. Li, C. Wang and X. Lu, *Advanced Science*, 2020, 7, 1901833.
- 14 W. Quan, Y. Hou, Y. Lin, Z. Hong, R. Yang, H. Yao and Y. Huang, *Inorganic Chemistry*, 2023, **62**, 4011-4019.
- 15 F. Luo, H. Hu, X. Zhao, Z. Yang, Q. Zhang, J. Xu, T. Kaneko, Y. Yoshida, C. Zhu and W. Cai, *Nano Letters*, 2020, **20**, 2120-2128.
- 16 D. Chen, T. Liu, P. Wang, J. Zhao, C. Zhang, R. Cheng, W. Li, P. Ji, Z. Pu and S. Mu, ACS Energy Letters, 2020, 5, 2909-2915.
- 17 T. Zheng, C. Shang, Z. He, X. Wang, C. Cao, H. Li, R. Si, B. Pan, S. Zhou and J. Zeng, *Angewandte Chemie International Edition*, 2019, **58**, 14764-14769.
- 18 Y. Sun, B. Huang, Y. Li, Y. Xing, M. Luo, N. Li, Z. Xia, Y. Qin, D. Su, L. Wang and S. Guo, *Chemistry of Materials*, 2019, **31**, 8136-8144.
- 19 J. Wang, H. Yang, F. Li, L. Li, J. Wu, S. Liu, T. Cheng, Y. Xu, Q. Shao and X. Huang, *Science Advances*, 2022, **8**, eabl9271.
- 20 L. Fu, F. Yang, G. Cheng and W. Luo, *Nanoscale*, 2018, **10**, 1892-1897.
- L. Fu, X. Zeng, G. Cheng and W. Luo, ACS Applied Materials & Interfaces, 2018, 10, 24993-24998.
- 22 M. Zhu, Q. Shao, Y. Qian and X. Huang, Nano Energy, 2018, 56.
- 23 J. Feng, F. Lv, W. Zhang, P. Li, K. Wang, C. Yang, B. Wang, Y. Yang, J. Zhou, F. Lin, G. Wang and S. Guo, *Advanced Materials*, 2017, 29, 1703798.
- 24 F. Luo, L. Guo, Y. Xie, J. Xu, K. Qu and Z. Yang, *Applied Catalysis B-environmental*, 2020, **279**, 119394.
- 25 H. You, D. Wu, Z.-n. Chen, F. Sun, H. Zhang, Z. Chen, M. Cao, W. Zhuang and

R. Cao, ACS Energy Letters, 2019, 4, 1301-1307.

- 26 J. Yang, Y. Shen, Y. Sun, J. Xian, Y. Long and G. Li, *Angewandte Chemie International Edition*, 2023, **62**, e202302220.
- 27 H. Wang, Z. Chen, D. Wu, M. Cao, F. Sun, H. Zhang, H. You, W. Zhuang and R. Cao, *Journal of the American Chemical Society*, 2021, 143, 4639-4645.
- 28 P. Li, X. Duan, Y. Kuang and X. Sun, *Small*, 2021, **17**, 2102078.
- 29 F. Luo, L. Guo, Y. Xie, J. Xu, K. Qu and Z. Yang, *Applied Catalysis B:* Environmental, 2020, **279**, 119394.
- 30 C. Wang, L. Yu, F. Yang and L. Feng, *Journal of Energy Chemistry*, 2023, **87**, 144-152.
- 31 S. Sun, H. Jiang, Z. Chen, Q. Chen, M. Ma, L. Zhen, B. Song and C. Xu, *Angewandte Chemie International Edition*, 2022, **61**, e202202519.
- 32 H. Zhu, Y. Wang, Z. Jiang, B. Deng, Y. Xin and Z. Jiang, *Advanced Energy Materials*, 2024, 14, 2303987.
- 33 H. Wang, Z. Chen, Y. Wang, D. Wu, M. Cao, F. Sun and R. Cao, *National Science Review*, 2024, **11**.
- 34 M. Zhu, Q. Shao, Y. Qian and X. Huang, *Nano Energy*, 2019, **56**, 330-337.
- 35 W. Zhang, X. Zhong, H. Qin, W. Peng, W. Li, Y. Lu, J. He, D. Zhou and W. Hu, *Electrochimica Acta*, 2024, **482**, 144000.
- 36 X. Zhao, Y. Chang, X. He, H. Zhang, J. Jia and M. Jia, *Journal of Rare Earths*, 2023, **41**, 208-214.
- 37 K. Yang, P. Xu, Z. Lin, Y. Yang, P. Jiang, C. Wang, S. Liu, S. Gong, L. Hu and Q. Chen, *Small*, 2018, 14, 1803009.
- 38 C. Rong, X. Shen, Y. Wang, L. Thomsen, T. Zhao, Y. Li, X. Lu, R. Amal and C. Zhao, Advanced Materials, 2022, 34, 2110103.
- 39 L. Fu, X. Hu, Y. Li, G. Cheng and W. Luo, *Nanoscale*, 2019, 11, 8898-8905.
- 40 B. Yang, Y. Du, M. Shao, D. Bin, Q. Zhao, Y. Xu, B. Liu and H. Lu, *Journal of Colloid and Interface Science*, 2022, **616**, 803-812.
- 41 Z. Cheng, B. Huang, Y. Pi, L. Li, Q. Shao and X. Huang, *National Science Review*, 2020, 7, 1340-1348.
- X. Wu, B. Feng, W. Li, Y. Niu, Y. Yu, S. Lu, C. Zhong, P. Liu, Z. Tian, L. Chen,
   W. Hu and C. M. Li, *Nano Energy*, 2019, 62, 117-126.
- 43 J. Ding, Q. Shao, Y. Feng and X. Huang, *Nano Energy*, 2018, 47, 1-7.
- 44 H. Hu, F. M. D. Kazim, Q. Zhang, K. Qu, Z. Yang and W. Cai, *ChemCatChem*, 2019, **11**, 4327-4333.
- 45 R. Wei, M. Liao, L. Sun, Q. Zhang, H. Zhang, L. Zhang and Z. Song, *ACS Applied Materials & Interfaces*, 2024, **16**, 7141-7151.
- 46 N. Wang, X. Bo and M. Zhou, ACS Applied Materials & Interfaces, 2022, 14, 23332-23341.
- 47 L. Wang, L. Zhang, W. Ma, H. Wan, X. Zhang, X. Zhang, S. Jiang, J. Y. Zheng and Z. Zhou, *Advanced Functional Materials*, 2022, **32**, 2203342.
- 48 S. Perumal and J. Seo, *International Journal of Hydrogen Energy*, 2023, **48**, 22009-22020.
- 49 W. Lai, L. Zhang, W. Hua, S. Indris, Z. Yan, Z. Hu, B. Zhang, Y. Liu, L. Wang,

M. Liu, R. Liu, Y. Wang, J. Wang, Z. Hu, H. Liu, S. Chou and S. Dou, *Angewandte Chemie International Edition*, 2019, **58**, 11868-11873.

- 50 L. An, J. Zhu, J. Yang and D. Wang, *Nano Materials Science*, 2024.
- 51 B. Guo, J. Zhao, Y. Xu, X. Wen, X. Ren, X. Huang, S. Niu, Y. Dai, R. Gao, P. Xu and S. Li, *ACS Applied Materials & Interfaces*, 2024, **16**, 8939-8948.
- 52 Y. Ni, W. Zhang, Y. Li, S. Hu, H. Yan and S. Xu, *Nanoscale*, 2024, 16, 7626-7633.
- 53 S. C. Karthikeyan, R. Santhosh Kumar, S. Ramakrishnan, S. Prabhakaran, A. R. Kim, D. H. Kim and D. J. Yoo, ACS Sustainable Chemistry & Engineering, 2022, 10, 15068-15081.
- 54 Y. Ma, Y. Ha, L. Chen, Z. An, L. Xing, Z. Wang and Z. Li, *Small*, 2024, 2311884.