

## Supporting Information

### A Simple Approach Making Acetylene Black Electrocatalytically Active for Flexible Rechargeable Zinc-Air Batteries

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#### Experimental

##### Preparation of the F-ACET-x materials

0.6 g of acetylene black (denoted as ACET, MIT KJ GROUP) was fully ground using moderate isopropanol in a mortar, followed by adding 520  $\mu$ L of PTFE (60 wt.%, Ourchem) to obtain a homogeneous paste. It was rolled into 0.2 mm slices that were further dried at room temperature for 12 hours, leading to the ACET/PTFE composite. Finally, the composite was heated in 100 kPa Ar atmosphere at a selected temperature (200, 400, 450, 500, 550, 600, or 800  $^{\circ}$ C) for 1 hour, producing catalysts denoted as F-ACET-x, where x is the heating temperature. For comparison experiment, F-PTFE was synthesized by directly pyrolyzing 4.8 g PTFE at the 100 kPa Ar atmosphere and 500  $^{\circ}$ C for 1 hour, showing a yield of 14.6%.

##### Materials characterization

The pyrolysis of ACET/PTFE composite was examined by TGA (NETZSCH STA 409C, Germany) with a constant heating rate of 5  $^{\circ}$ C/min in Ar atmosphere. The morphology was observed using a field emission scanning electron microscope (FESEM, ZEISS SUPRA 55VP), coupled with a BRUKER X Flash Detector 5010. High-resolution transmission electron microscopy (HRTEM) images, energy-dispersive X-ray spectra (EDS), and selected area electron diffraction (SAED) patterns were obtained using an FEI Tecnai G2 F20, equipped with a field emission gun, operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo ESCALAB 250Xi spectrometer with a monochromatic Al K $\alpha$  radiation source, and the C 1s peak (284.8 eV) was fixed. Raman spectroscopy was conducted using a Renishaw inVia Raman microscope, equipped with a 532 nm laser. X-ray diffraction (XRD) was carried out using a SHIMADZU XDS-6100 powder X-ray diffractometer, equipped with Cu K $\alpha$  ( $\lambda=1.5406$   $\text{\AA}$ ) radiations. The Brunauer-Emmett-Teller (BET) surface area was determined using nitrogen desorption isotherms, measured at liquid-nitrogen temperature (77 K).

##### Electrochemical measurements

All electrochemical measurements were performed using a METROHM Autolab PGSTAT302N electrochemical workstation at room temperature. The cycle voltammetry (CV) tests for F-ACET were conducted in the potential range of -0.8 ~ 0.2 V (vs. Ag/AgCl) using the sweep

rates of 2, 4, 6, 8, and 10 mV/s. A Pt wire and Ag/AgCl electrode served as the counter and the reference electrode, respectively. The ORR electrocatalytic activity was measured using a rotating disk electrode (RDE GC, 00654867) technique. The disk diameter was 5.00 mm. The glassy carbon electrode was polished and cleaned prior to use. The catalyst (4 mg) was dispersed in ethanol (300  $\mu$ L) with Nafion solution (30  $\mu$ L, 5 wt.%, Sigma-Aldrich). Then, the mixture was ultrasonicated for over 1 h to generate a homogeneous ink. Next, 10  $\mu$ L of dispersion was transferred and uniformly loaded onto the glassy carbon disk. Finally, the as-prepared catalyst film was dried at room temperature over 6 h. Then, 0.1 M KOH solution was used as the electrolyte at room temperature, which was purged with a high-purity O<sub>2</sub> (or N<sub>2</sub>) flow for at least 30 min prior to the measurements and continuously flowed O<sub>2</sub> (or N<sub>2</sub>) above the liquid level during measurements. The linear scan voltammograms (LSV) were obtained at a scan rate of 5 mV/s and a voltage range of 0.2 to -1.0 V (vs. Ag/AgCl) and 0.2 to 1.2 V (vs. Ag/AgCl) at a rotation speed of 1600 rpm, respectively. Voltamperometry measurements were performed at different rotation speeds of (400, 900, 1600, and 2500 rpm) in an O<sub>2</sub>-saturated electrolyte from 0.2 to -1.0 V (vs. Ag/AgCl) and a scan rate of 5 mV/s. The potential was converted to the reversible hydrogen electrode (RHE) potential using the equation <sup>1</sup>:

$$E_{RHE} = E_{Ag/AgCl} + 0.059 pH + 0.209$$

The Koutecky-Levich equation was used to analyze the transferred electron number (n) during the ORR with disk currents.

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}$$

$$B = 0.2nFC_{O_2}D_{O_2}^{2/3}v^{-1/6}$$

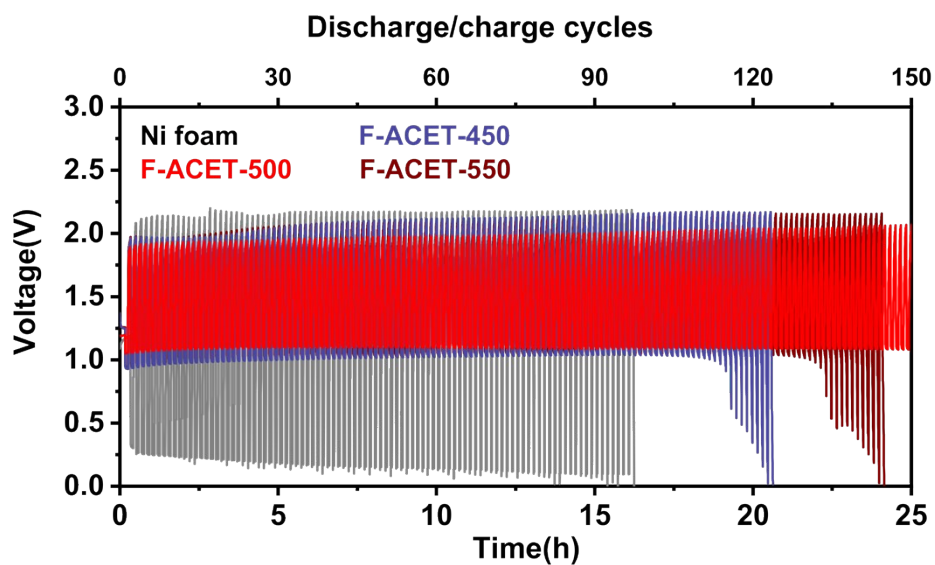
Here,  $j$  is the overall current density (mA/cm<sup>2</sup>),  $j_L$  is the diffusion-limiting current density (mA/cm<sup>2</sup>),  $j_K$  is the kinetic current density (rpm),  $\omega$  is the rotation speed (mA/cm<sup>2</sup>),  $F$  is the Faraday constant (96485 C/mol),  $C_{O_2}$  is the bulk concentration of O<sub>2</sub> ( $1.2 \times 10^{-6}$  mol/cm<sup>3</sup>),  $D_{O_2}$  is the diffusion coefficient of O<sub>2</sub> ( $1.9 \times 10^{-5}$  cm<sup>2</sup>/s),  $v$  is the kinematics viscosity of the electrolyte (0.01 cm<sup>2</sup>/s), and  $n$  denotes the number of transferred electrons in the ORR.

### **Fabrication and characterization of flexible zinc-air batteries**

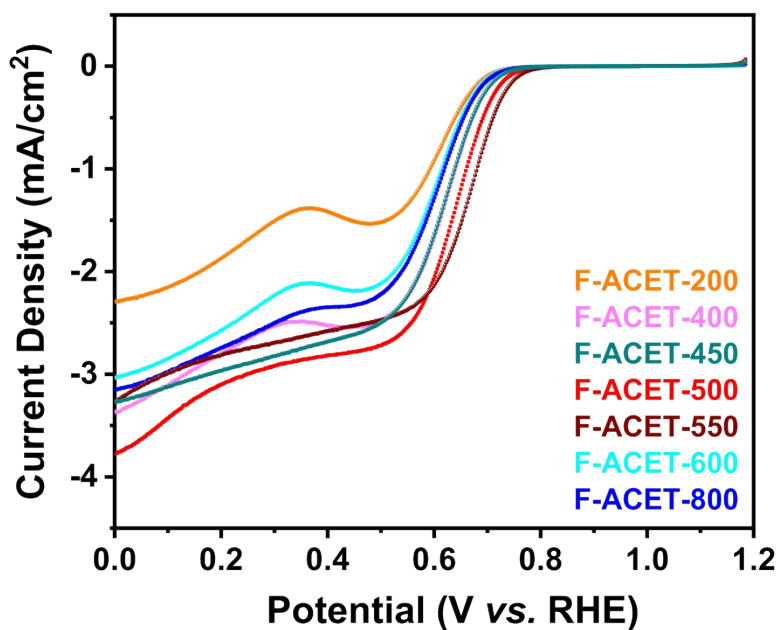
A home-made solid-state ZAB was assembled using the layer-by-layer method. A polished zinc foil (0.15~0.25 mm, 99.9%, SCR) was placed against the polyvinyl alcohol (PVA, 145000, Aladdin) gelled membrane and air electrode. The air electrode consisted of the catalytic layer and the current collector, with an effective area of 1.76 cm<sup>2</sup>, to allow O<sub>2</sub> (from ambient air) to reach the catalyst. To obtain the catalytic layer, 0.15 g of catalyst was ball-milled in isopropyl alcohol for 2 h (for F-PTFE electrode, 0.3 g F-PTFE and 1.2 g ACET was mixed and then well ball-milled), and, subsequently mixed with 230  $\mu$ l of polytetrafluoroethylene (PTFE, 60 wt.%) to yield a homogeneously mixed paste. After rolling into 0.2 mm slices, the catalytic layer was pressed on Ni foam (surface density: 350 g/m<sup>2</sup>; MIT KJ GROUP) using the uniaxial pressure of 10 mPa. The mass loading was approximately 5 mg/cm<sup>2</sup>. The as-prepared electrode was vacuum dried at 180 °C for 8 h. The PVA gel electrolyte was prepared by dissolving 5 g of PVA powder in 50 ml of deionized

water at 95 °C and stirring for 2 hours. Then, 5 ml of 18 M KOH solution was added into the above mixture and stirred for another 20 min. The solution was poured on a glass plate to form a thin film, which was subsequently frozen at -25 °C for 3 hours and stored at 5 °C.

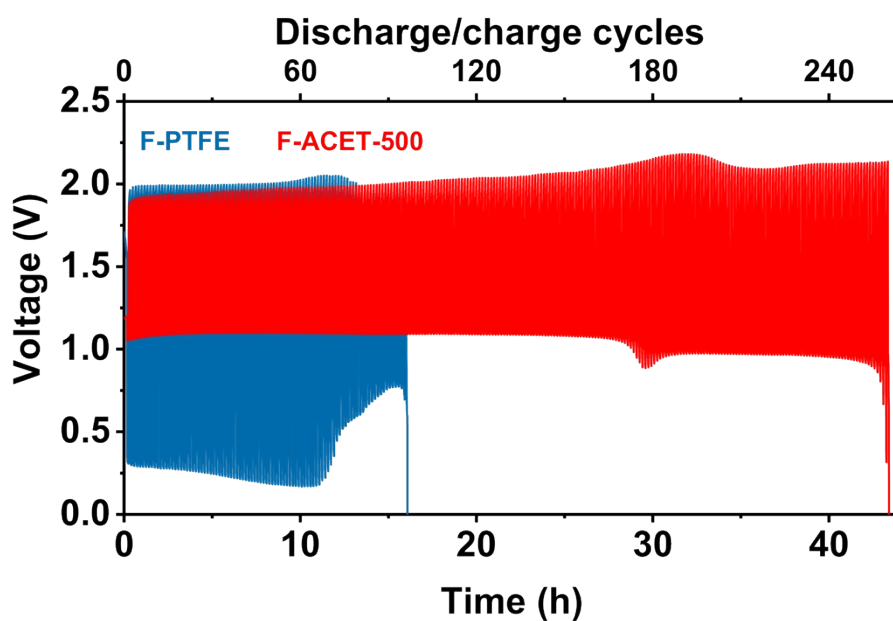
Linear sweep voltammetry (LSV) was carried out using the METROHM Autolab PGSTAT302N electrochemical workstation. LSV was carried out at a scan rate of 1.0 mA/s, with a cut-off voltage of 0.5 V and 2.5 V (vs. Zn/Zn<sup>2+</sup>) during discharge and charge, respectively. The galvanostatic discharge and charge/discharge data were collected using a LAND CT2001A battery tester.



**Fig S1.** Discharge/charge properties of F-ACET-450, F-ACET-550, F-ACET-550 and Ni foam-based flexible ZABs at a current density of 2 mA/cm<sup>2</sup> with a 10 min/cycle.



**Fig S2.** Linear sweep curves of different F-ACET-x catalysts in O<sub>2</sub>-saturated 0.1 M KOH with a rotation rate of 1600 rpm and a scan rate of 5 mV/s.

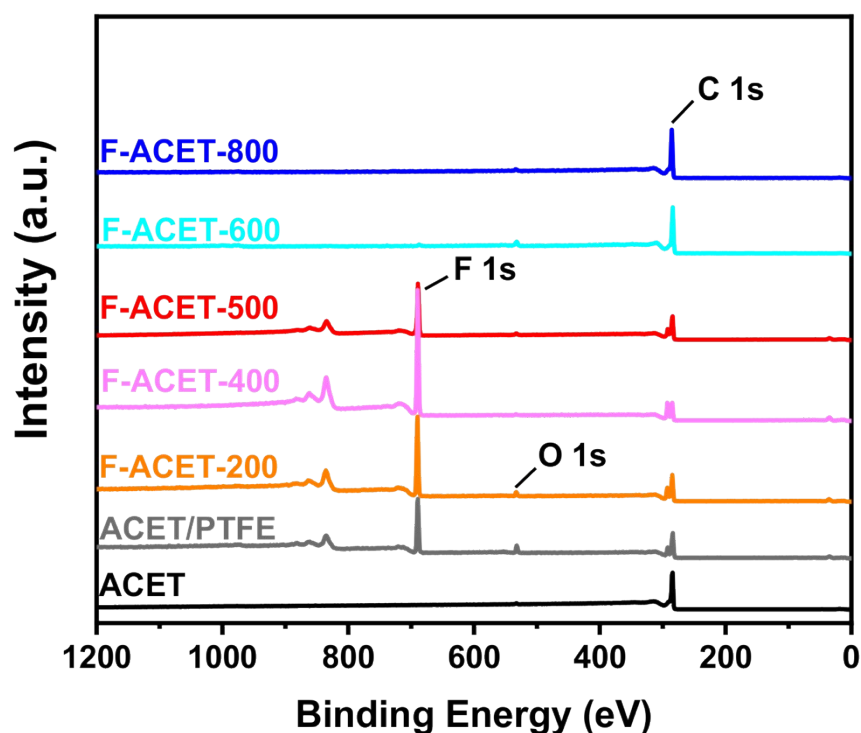


**Fig S3.** Discharge/charge properties of F-ACET and F-ACET-500-based flexible ZABs at a current density of 2 mA/cm<sup>2</sup> with a 10 min/cycle.

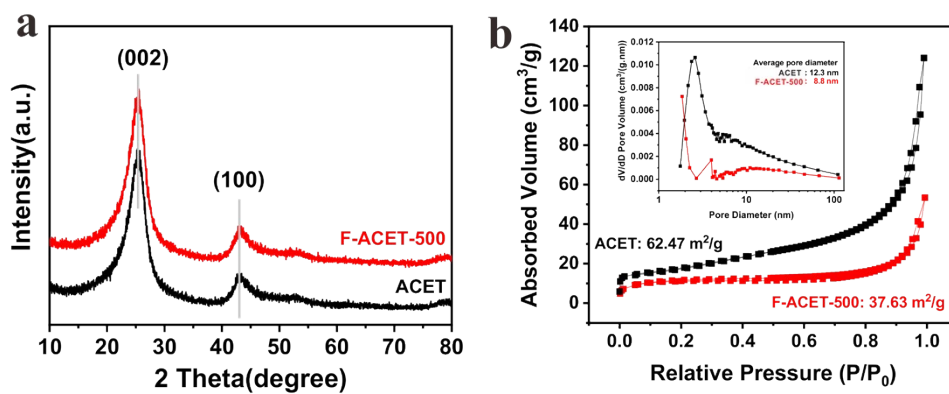
**Table S1.** Performance comparison of the solid-state SMG-ZAB with reported solid-state ZABs

Catalyst	Peak power density	Recharge ability	Discharge-charge voltage	Ref.
F-ACET-500	52 mW/cm <sup>2</sup>	2 mA/cm <sup>2</sup> , 10 min/cycle for 252 cycles, 42 h	1.10 V – 1.90 V (gap=0.8 V)	This work
N-CNTs–HGF	8.5 mW/cm <sup>2</sup>	2 mA/cm <sup>2</sup> , 10 min/cycle for 78 cycles, 13 h	1.0 V - 2.0 V (gap=1.0 V)	2
Co/N/O tri-doped graphene	29 mW/cm <sup>2</sup> *	1 mA/cm <sup>2</sup> , 60 min/cycle, for 18 cycle, 18 h	1.19 V - 1.89 V (gap=0.7 V)	3
o-CC-H <sub>2</sub>	— —	1 mA/cm <sup>2</sup> , 2 min/cycle for 40 cycles, 1.33 h	1.04 V - 2.01 V (gap=0.97 V)	4
Co-doped np-graphene	83.8 mW/cm <sup>2</sup>	2 mA/cm <sup>2</sup> , 10 min/cycle for 258 cycles, 43 h	1.20 V - 1.97 V (gap=0.77 V)	5
NCNF-1000 fibers	— —	2 mA/cm <sup>2</sup> , 10 min/cycle for 36 cycles, 6 h	1.0 V - 1.78 V (gap=0.78 V)	6
Co <sub>3</sub> O <sub>4</sub> /N-rGO	— —	3 mA/cm <sup>2</sup> , 20 min/cycle for 75 cycles, 25 h	1.2 V – 2.0 V (gap=0.8 V)	7
MnOx-GCC	32 mW/cm <sup>2</sup>	0.7 mA/cm <sup>2</sup> , 20 min/cycle for 175 cycles, 58 h	1.3 V – 1.9 V (gap=0.6 V)	8

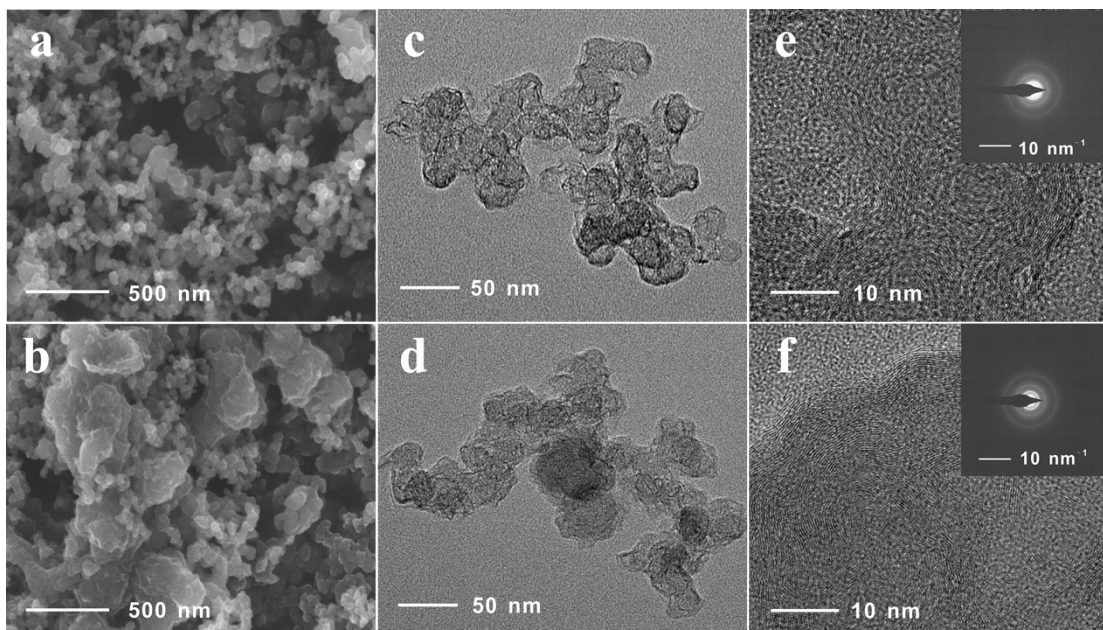
\* Values estimated from graphs



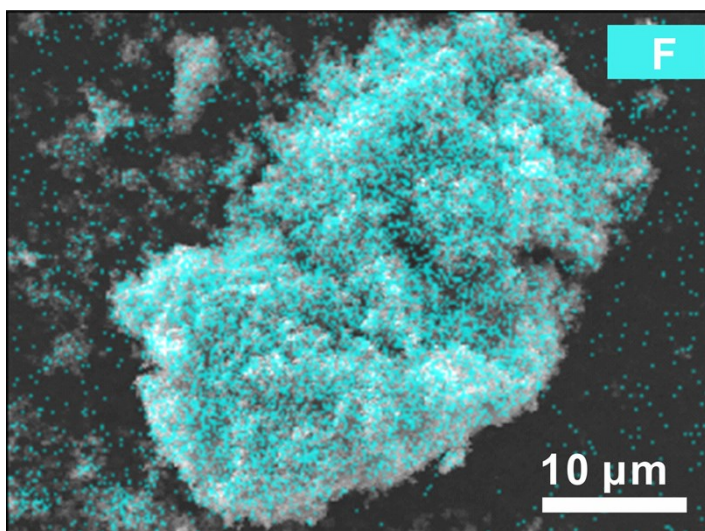
**Fig S4.** Survey scans of ACET, ACET/PTFE, and F-ACET-x.



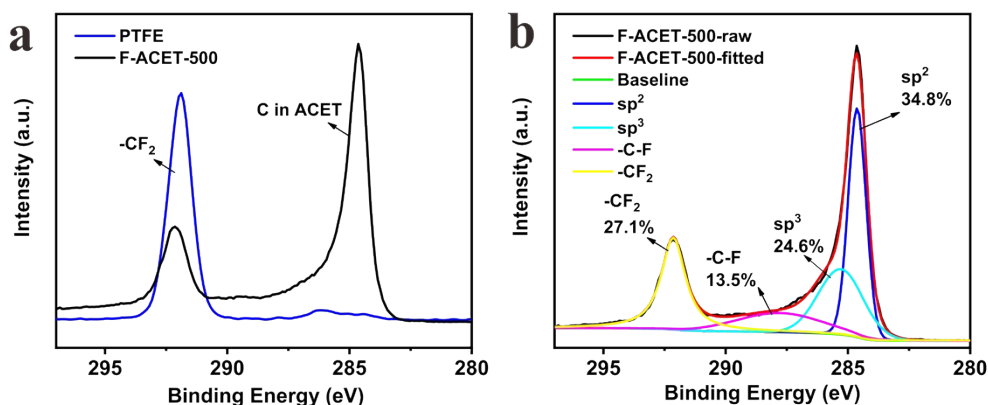
**Fig S5.** (a) XRD patterns of F-ACET-500 and ACET, and (b) N<sub>2</sub> adsorption/desorption isotherms of F-ACET-500 and ACET.



**Fig. S6.** Morphological characterization of F-ACET-500 and ACET: (a, b) SEM image; (c, d) TEM images; (e, f) HRTEM images (inset: SEAD patterns).



**Fig. S7.** EDS elemental mapping of F for F-ACET-500.



**Fig. S8.** (a, b) High-resolution XPS spectrum of C 1s for PTFE and F-ACET-500

## References

- 1 C. Guan, A. Sumboja, H. J. Wu, W. N. Ren, X. M. Liu, H. Zhang, Z. L. Liu, C. W. Cheng, S. J. Pennycook, J. Wang, *Adv. Mater.*, 2017, **29**, 1704117
- 2 Z. H. Cheng, Q. Fu, C. X. Li, X. P. Wang, J. Gao, M. H. Ye, Y. Zhao, L. J. Dong, H. X. Luo, L. T. Qu, *J. Mater. Chem. A*, 2016, **4**, 18240-18247.
- 3 C. Tang, B. Wang, H. F. Wang, Q. Zhang, *Adv. Mater.*, 2017, **29**, 1703185
- 4 H.-F. Wang, C. Tang, B. Wang, B.-Q. Li, X. Cui, Q. Zhang, *Energy Storage Mater.*, 2018, **15**, 124-130.
- 5 H. J. Qiu, P. Du, K. L. Hu, J. J. Gao, H. L. Li, P. Liu, T. Ina, K. Ohara, Y. Ito, M. W. Chen, *Adv. Mater.*, 2019, **31**, 1900528.
- 6 Q. Liu, Y. B. Wang, L. M. Dai, J. N. Yao, *Adv. Mater.*, 2016, **28**, 3000-3006.
- 7 Y. Li, C. Zhong, J. Liu, X. Zeng, S. Qu, X. Han, Y. Deng, W. Hu, J. Lu, *Adv. Mater.*, 2017, **30**, 1703657
- 8 A. Sumboja, M. Lubke, Y. Wang, T. An, Y. Zong, Z. L. Liu, *Adv. Energy Mater.*, 2017, **7**, 1700927