Supplementary Information

Long-life sodium-sulfur batteries enabled by super-sodiophilic seeds

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Methods

Preparation of Na@CNT-BiF_3 composite: First, BiF_3 particles were uniformly dispersed on the surface of the CNT material by simply mixing with ethanol, and then the self-supported CNT-BiF_3 electrode was obtained by a simple filtration. Then, Na disks were heated to 150 °C in a stainless-steel container. After melting, a pair of stainless-steel tweezers was used to remove the impurities until the molten sodium exhibited a shiny metallic luster. Finally, the self-supported CNT-BiF_3 electrode was soaked in molten sodium to obtain the Na@CNT-BiF_3 composite. The whole process was carried out inside an Ar-filled glove box with O_2 and H_2O contents of < 0.1 ppm.

Preparation of Na@Cu-BiF_3 composite: First, different contents of BiF_3 and PVDF were added to N-methyl-2-pyrrolidone (NMP) to form a slurry. The slurry was then coated onto a copper foil and dried in a vacuum oven at 60 °C. Then, the Cu-BiF_3 electrode was soaked in molten sodium to obtain the Na@Cu-BiF_3 composite. The whole process was carried out inside an Ar-filled glove box with O_2 and H_2O content of < 0.1 ppm.

Preparation of sulfur cathode. The sulfur cathode was prepared by a conventional melt-diffusion method. Specifically, Ketjen Black carbon and sublimed sulfur in a weight ratio of 1 : 9 were evenly mixed and heated at 155 °C in a sealed vial under an Ar atmosphere for 12 h to achieve a homogeneous sulfur distribution. Then, the as-obtained composite was heated at 200 °C for 30 min to eliminate the excess sulfur from the surface. The sulfur weight in the composite was close to ~ 87 wt%, which was confirmed by comparing the weight of the composites before and after the melt-diffusion process. Furthermore, the 80 wt.% C/S composite, 10 wt.% sodium carboxymethyl cellulose (CMC) binder, 5 wt.% multi-walled carbon nanotubes, and 5 wt.% Super-P were mixed in NMP to form a slurry. The slurry was coated onto a carbon-coated aluminum foil and dried in a vacuum oven at 60 °C. Finally, the dried foil was punched into 10 mm disk electrodes with an areal mass loading of 3 mg cm^{-2}.

Preparation of the electrolyte. Sodium bis(fluorosulfonyl)imide (NaFSI) was dried in a vacuum oven for 24 h at 60 ^{o}C. 1,2-dimethoxyethane (DME) was dried with molecule sieves for 72 h. The electrolyte was prepared inside an Ar-filled glove box. Particularly, DME was mixed with NaFSI at a molar ratio of 1 : 1.2 and stirred over 3 h to obtain a transparent solution. Then, 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE) was added to the above solution with the same molar amount as NaFSI.

Characterizations. The morphology characterization was carried out with a scanning electron microscope (FEI Quanta 650 SEM running at 20 kV) equipped with an energy dispersive X-ray (EDX) spectrometer to study the elemental distribution. Monochromatic Al Kα (1,486.6 eV) radiation was used for XPS examination with a Kratos Analytical spectrometer.

Synchrotron X-ray diffraction (XRD). Synchrotron *in-operando* XRD tests were carried out at the 11-ID-C beamline with the Advanced Photon Source (APS) at Argonne National Laboratory. The beam spot size was 0.5 mm x 0.5 mm with the X-ray energy at 105.7 keV. The 2D diffraction images were captured with a Perkin Elmer area detector. The sample-to-detector distance was calibrated with a CeO_2 standard and the images were combined into 1D diffraction patterns with the use of the GSAS-II tool. XRD data were continually acquired by rastering back and forth between cells for a duration of 2 min per pattern.

Throughout this time, the cells were cycled at a rate of 0.1C rate from 0.8 to 2.8 V for a complete cycle of charge and discharge. CR2032-style window coin cells were put together inside a glovebox with < 1 ppm of O_2 and H_2O. To enable X-ray penetration, a 3 mm window was punched through both the top and bottom casings. The windows were sealed with Cu foil (9 µm thick) and Al foil (12 µm thick), respectively, on the anode side and the cathode side. An epoxy composed of Catalyst 15 and Eccobond 45 with a volume ratio of 1: 1 was applied to the foils as a reliable sealing. To ensure optimal mechanical contact between the CNT/CNT-BiF_3 electrode and the ion source, two Na metal discs were employed as a spacer. These house-built cells were assembled in our laboratory and shipped to APS for characterization.

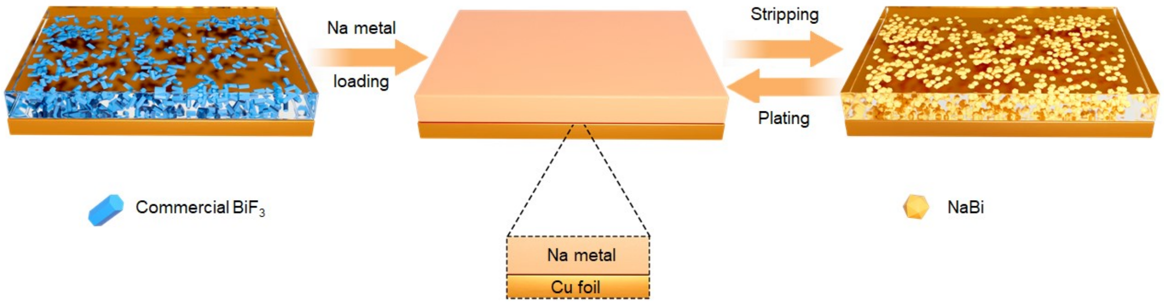

Fig. S1. Illustration of the synthetic route and mechanism during the cycling of Na@Cu-BiF$_3$.

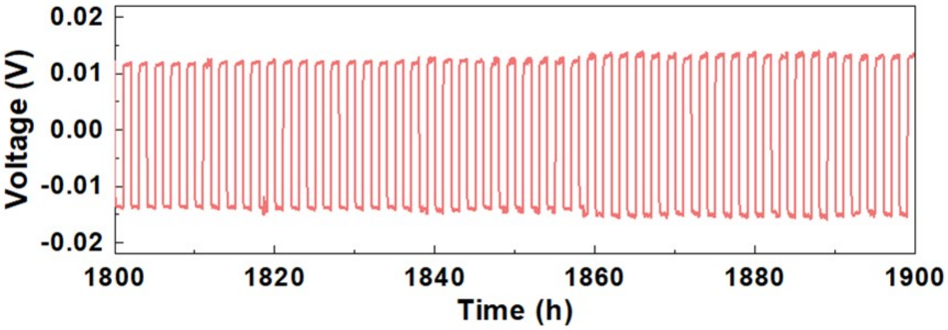

Fig. S2 Enlarged Voltage profiles of the Na@CNT-BiF$_3$ || Na@CNT-BiF$_3$ cells measured at 2 mA cm^{-2} for 1,800 - 1,900 h.

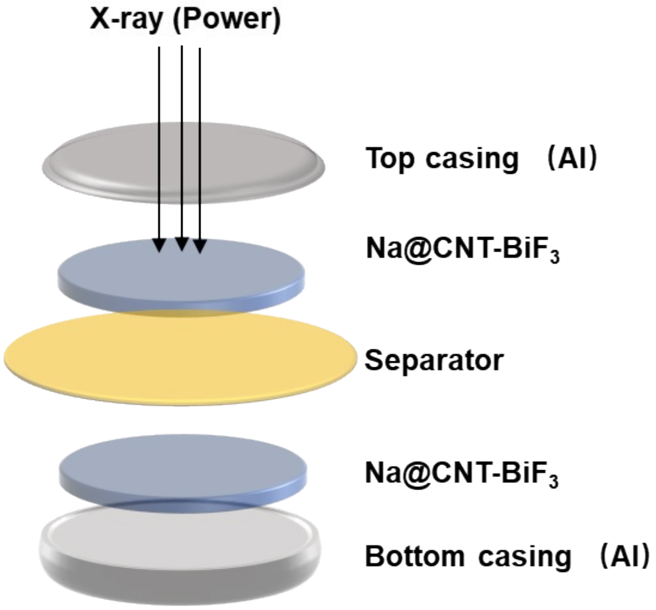

Fig. S3. Schematic diagram of *in-situ* XRD test.

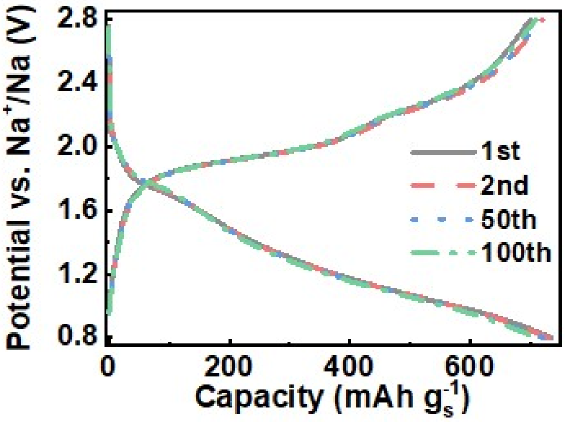

Fig. S4 Voltage profiles of Na@Cu-BiF_3 at various cycles.

Table S1. Electrochemical performance comparison with some reported representative Na-S batteries work

Material	**S loading (mg cm^{-2})**	**Cycling performance (mA h g^{-1})**	**Cycling performance (mA h g^{-1})**	**pouch cell (mA h g^{-1})**	**Refs.**
Na@CNT-BiF_3 || C/S	**3**	**862@0.1 C/200 cycles** **862@0.17 A g^{-1}/200 cycles**	**674@1C/700 cycles** **674@1.17 A g^{-1}/700 cycles**	**/**	**This work**
Na@Cu-BiF_3 || C/S	**2**	**/**	**/**	**661@0.1C /50 cycles**	**This work**
Na | PZM@LE | S	~0.5	/	~300@0.5C/800 cycles	/	S1
S@MHCS-3	5	701@0.1 C/100 cycles	~300@1C/1000 cycles	/	S2
Zn-N_2/CF/S	1	838.5@0.1 A g^{-1}/100 cycles	672.7@1.0 A g^{-1}/1100 cycles	/	S3
S/MoS_2/NCS	1.5	711.6@0.5 A g^{-1}/100 cycles	360.7@1.0 A g^{-1}/2800 cycles	/	S4
S@Co_1–CoS_2/NC	1.6	642@0.2 A g^{-1}/150 cycles	357@5.0 A g^{-1}/5000 cycles	/	S5

Na//S/TiN-TiO$_2$@MCCFs	1.08	640.4@0.1 A g^{-1}/100 cycles	490.5@1.0 A g^{-1}/500 cycles	/	S6
S/Mo$_5$N$_6$	1.2	180@0.2C/3000 cycles	290@1C/1000 cycles	/	S7
S@MoS$_2$-Mo$_1$/SGF	0.96	/	505 @1.0 A g^{-1}/1000 cycles	/	S8
Cu SA/NOC/S-2	4	776@0.1 A g^{-1}/100 cycles	~600@1.0 A g^{-1}/1000 cycles	/	S9
SCC	0.5-0.8	422@0.2C/200 cycles	/	/	S10

Table S2. Comparison of the electrochemical performances of the Na@CNT-BiF$_3$ symmetric cells in this work with previously reported works

Anode	**Electrolyte**	**Current/Capacity (mA cm^{-2}/mAh cm^{-2})**	**Lifespan (h)**	**Overpotential (mV)**	**Refs.**
Na@CNT-BiF$_3$	**LHCE**	**2/2**	**2000**	**13.5**	**This work**
NaIn	1 M NaPF$_6$ in DME	2/2	790	11	S1
Na/SnSe	1 M NaClO$_4$ in EC/PC with 5% FEC	1/1	900	/	S2
NaBrP/Na	1M NaPF$_6$ in EC/DEC with 5% FEC	2/2	240	/	S3
IOHL-Na	1 M NaClO$_4$ in EC/DEC with 5% FEC	1/1	770	65	S4
NaF/Co/Na	1 M NaClO$_4$ in EC/DEC with 5% FEC	1/1	1000	<100	S5

Na@Na$_2$Se/V	1 M NaClO$_4$ in EC/DEC with 5% FEC	0.5/1	1800	40	S6
Na/NST	1 M NaPF$_6$ in EC/DEC with 5% FEC	1/1	1390	/	S7
Na/In/C	1 M NaClO$_4$ in EC/PC with 5% FEC	2/1	710	/	S8
MXene@gC$_3$N$_4$@Na	1 M NaPF$_6$ in DIG	1/1	700	11	S9
Sb@HPCNF-Na	1 M NaPF$_6$ in DIG	2/2	1000	13	S10
VP-Na	1 M NaClO$_4$ in EC/DEC with 5% FEC	1/1	1200	~100	S11
NPCC-Ag-Na	1 M NaClO$_4$ in EC/PC with 5% FEC	1/1	800	70	S12
Na$_3$P@Na	1 M NaTFSI in FEC/EMC	1/1	780	80	S13
Protected Na	1 M NaPF$_6$ in TEG/DME	2/1	380	~50	S14

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