Supporting Information

ZnSe grown on carbon nanofibers derived from ZIF-8 as a zincophilic layer for zinc metal anodes

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Experiment section

Materials

Zn foil (99.99%, 100 μm) was purchased from Tianjin Annuohui New Energy Technology Co., Ltd. Cu foil (Single light 12U * 200MM) was purchased from Fusha Town, Zhongshan City, Wenquan Metal Materials Department. Ti foil (0.02mm) was purchased from Dongguan Jiazhi Metal Products Co., Ltd. Whatman GF/D (CAT No.1823-090) was purchased from Shanghai Tianbang Industrial Co, LTD. 2-Methylimidazole (98%) was bought from Shanghai Macklin Biochemical Technology Co, Ltd. Methanol (AR) was bought from Sinopharm Chemical Reagent. N, N-Dimethylacetamide (DMF, AR), Zinc acetate dihydrate ($(CH_3COO)_2Zn{\cdot}2H_2O$, AR) were bought from Fuchen Chemical Reagent Co., Ltd., China. Polyacrylonitrile (PAN, Mw = 80000) was bought from Kunshan Hongyu Plastic Cement. Polyvinylidene difluoride (PVDF, Mw = 400000) was purchased from Innochem. Carbon black was purchased from Luoen Co., Ltd. N-methyl-2-pyrrolidone (NMP) was purchased from TianJing GuangFu Technology Development Co., Ltd. Ammonium (AR) metavanadate was purchased from Tianjin Damao Chemical Reagent Factory. Zinc sulfate ($ZnSO_4{\cdot}7H_2O{\geq}99.5\%$) was purchased from Tianjin Guangfu Technology Development Co., Ltd. All reagents can be used without further purification.

Characterization

The crystal structures were identified by X-ray diffraction (XRD; Rigaku Ultima IV, Japan). The chemical composition and valence states of the surface were analyzed using X-ray photoelectron spectroscopy (XPS, Escalab 250xi. Thermo Fisher Scientific USA). The morphologies of the samples were observed using scanning electron microscopy (SEM, Phenom, The Netherlands) and transmission electron microscopy (TEM, JEM-2100, JEOL, Japan). The chemical structure was determined using Raman spectroscopy (InVia Microscope Raman, Renishaw, UK). The contact angle was measured using a contact angle meter (SDC-350; Sindin Precision, China).

Synthesis procedures for the materials

Synthesis of (Zn $(Ac)_2$/PAN)

Zinc precursor nanofibers were prepared via electrospinning. Firstly, 0.5 g PAN was added to 4.5 g DMF, and the mixed solution was heated to 80 °C for 8 h to obtain solution A. Zn $(Ac)_2 \cdot 2H_2O$ (0.878 g) was dissolved in 4 g of DMF and stirred for 12 h to obtain solution B. Solutions A and B were mixed in a mass ratio of 5:3 and stirred at room temperature for 12 h to obtain a uniform spinning solution. The spinning solution was electrospinning to obtain $Zn(Ac)_2$/PAN nanofiber membranes. During the electrospinning process, the spinning voltage was 14 kV and the spinning distance was 19 cm.

Synthesis of ZIF-8/PAN

Preparation of ZIF-8/PAN supported composite nanofibers by in situ growth method: 2-methylimidazole (0.0985 g) was dissolved in 30 ml of methanol and stirred at room temperature for 30 min until it was fully dissolved. Weigh 0.100 g of nanofiber membrane Zn $(Ac)_2$/PAN and fully immersed in a 2-methylimidazole solution at room temperature. After standing for 24 h, the nanofiber membrane was removed, filtered, washed three times with a methanol solution, and dried at 80 °C for 24 h. PAN composite ZIF-8/PAN nanofibers loaded with ZIF-8 were obtained.

Synthesis of ZnSe/CNFs

The ZIF-8/PAN composite nanofibers were placed in a porcelain boat, and selenium powder was added to the porcelain boat at a mass ratio of 1:1 to ZIF-8/PAN. The entire process was pyrolyzed at high temperatures in a nitrogen atmosphere. First, the temperature was increased to 150 °C and 250 °C at a rate of 5 °C/min and then increased to 600 °C at a rate of 2 °C/min. ZnSe/CNFs were obtained by holding at 150 °C, 250 °C, and 600 °C for 1 h.

Synthesis of V_2O_5

1.0 g of NH_4VO_3 powder was put into a crucible and annealed to 400°C for 2 h. After cooling, the resulting V_2O_5 was collected and ground.

Preparation of ZnSe/CNFs@Zn anode

The ZnSe/CNF @Zn electrode was prepared by mixing polyvinylidene fluoride (PVDF) with ZnSe/CNFs at a weight ratio of 2:8 in a moderate amount of N-methylpyrrolidone (NMP) solvent by grinding. Commercial zinc foil with an initial thickness of 100 μm was first polished using sandpapers of varying grit sizes, reducing its thickness to approximately 90.29 μm. Subsequently, the prepared slurry was coated onto the polished Zn foil via the doctor-blading method. The coated foil was then vacuum-dried at 60 °C for 24 h. The ZnSe/CNF @Zn foils were then punched into 12 mm diameter anodes. The bare Zn foil was punched into discs, which were recorded as the bare Zn anodes.

Preparation of V_2O_5 cathode

The cathode was composed of V_2O_5, acetylene black, and polyvinylidene fluoride (PVDF) in a weight ratio of 7:2:1, which was mixed with a moderate amount of N-methylpyrrolidone (NMP) solvent under grinding. Then, the slurry was evenly cast on the surface of a Ti foil with a diameter of 12 mm and dried under vacuum at 80°C for 8 h. The loading mass of V_2O_5 active material in the electrodes was approximately 1.4 mg cm^{-2}.

Electrochemical test

The CR2032 coin batteries were assembled in air and subjected to the Zn||Zn batteries, ZnSe/CNFs@Zn||ZnSe/CNFs@Zn batteries, Zn and ZnSe/CNFs@Zn||Cu batteries, Zn and ZnSe/CNFs@Zn||V_2O_5 batteries, a 2 M $ZnSO_4$ aqueous solution and glass fiber separator served as electrolyte and separators, respectively. The variable temperature impedance (EIS) of symmetrical batteries was tested, and the applied frequency range was from 100 kHz to 0.1 Hz with an AC amplitude of 5 mV (CHI760E, Shanghai). Chronoamperometry (CA) of the Zn||Zn and ZnSe/CNFs@Zn||ZnSe/CNFs@Zn batteries at a stable potential -150 mV (CHI760E, Shanghai). Linear Sweep Voltammetry（LSV）at a scan rate of 10 mV s^{-1} and Tafel at a scan rate of 10 mV s^{-1} were performed using an electrochemical workstation (CHI760E, Shanghai) with a three-electrode system, and the electrolyte was a 2M $ZnSO_4$ aqueous solution. The three-electrode system used Ag/AgCl as the reference electrode and platinum mesh as the counter electrode. The CV curves of the Zn and ZnSe/CNFs@Zn||Cu batteries at a scan rate of 5 mV s^{-1} in the voltage range of -0.2-0.6V, and the CV curves of the Zn and ZnSe/CNFs@Zn||V_2O_5 batteries at a scan rate of 0.1 mV s^{-1} in the voltage range of 0.2-1.6 V. The EIS test of the Zn and ZnSe/CNFs@Zn||V_2O_5 battery was 100 kHz-0.01 Hz.

DOD calculation method

The depth of discharge (DOD) is the percentage of the capacity involved in the electrode reaction relative to the overall capacity of the Zn metal anode. The DOD can be calculated using the following formula: DOD= y/(C_(Zn,mass)×m) ×100%, where y (mAh) is the Zn capacity used during electrochemical testing, C_ (Zn, mass) is the theoretical mass capacity of Zn, m is the weight of Zn metal anode.

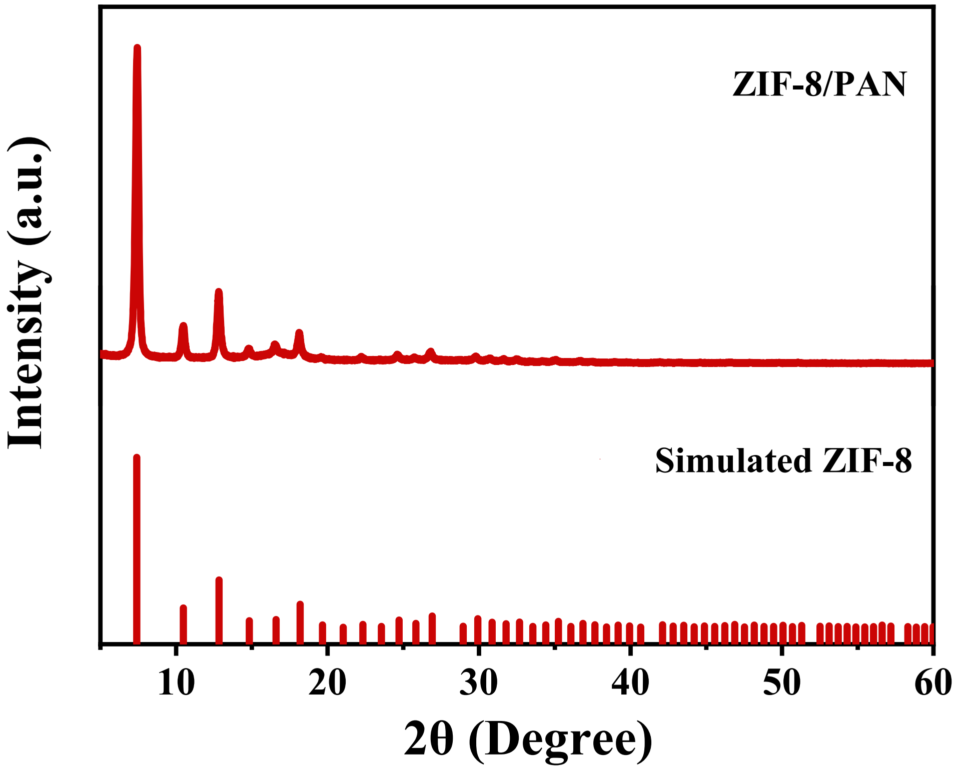


Figure S1. XRD pattern of ZIF-8/PAN.

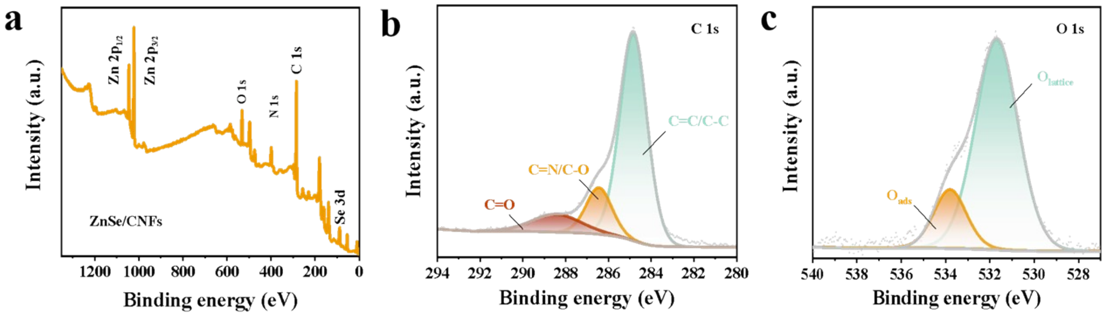
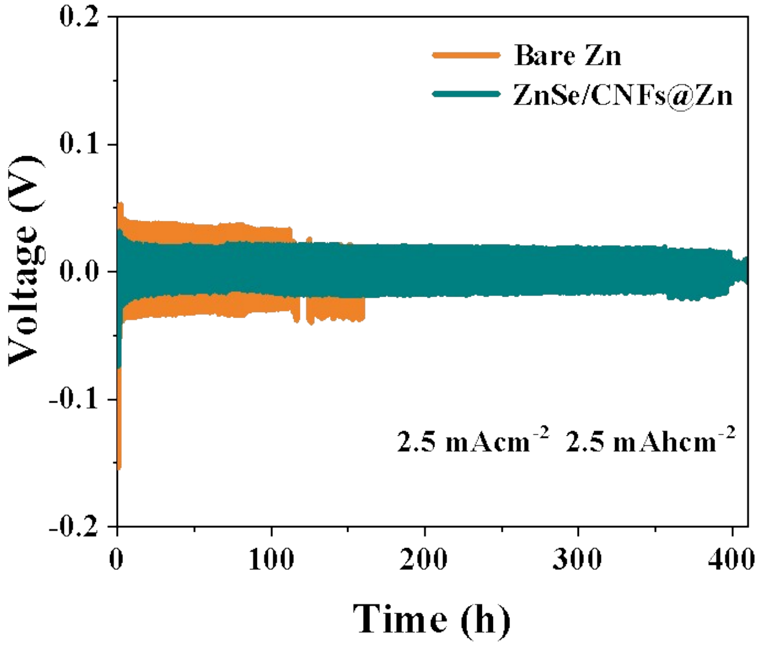


Figure S2. XPS spectra of ZnSe/CNFs (a) XPS survey spectrum (b) C 1s spectrum, and (c) O 1s spectrum.



FigureS3. Cycling performance of symmetric batteries at 2.5 mA cm^{-2} and 2.5 mAh cm^{-2}.

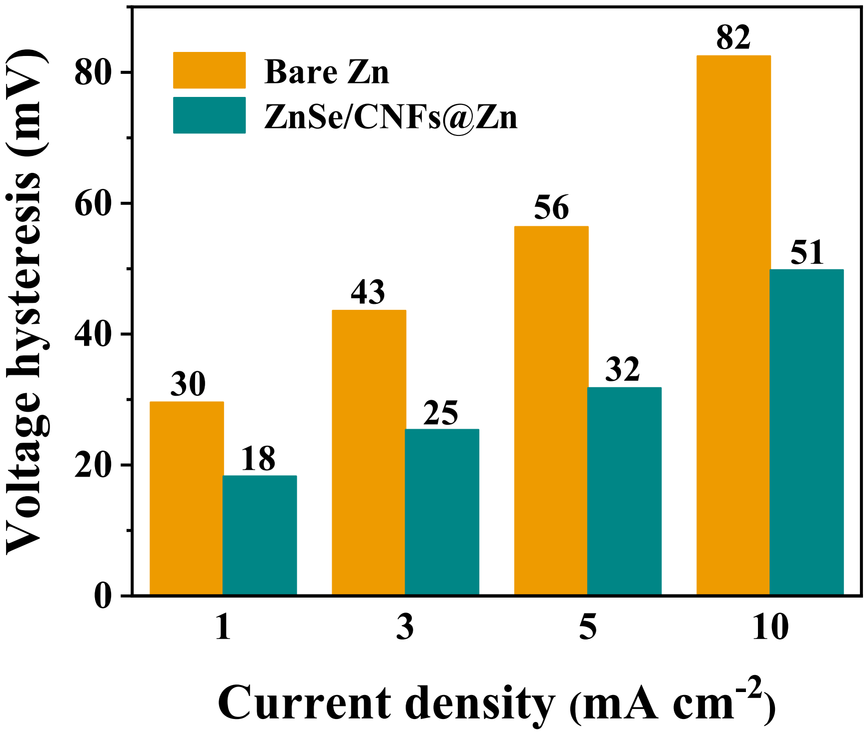


Figure S4. Corresponding voltage hysteresis at various current densities from 1-10 mA cm^{-2}.

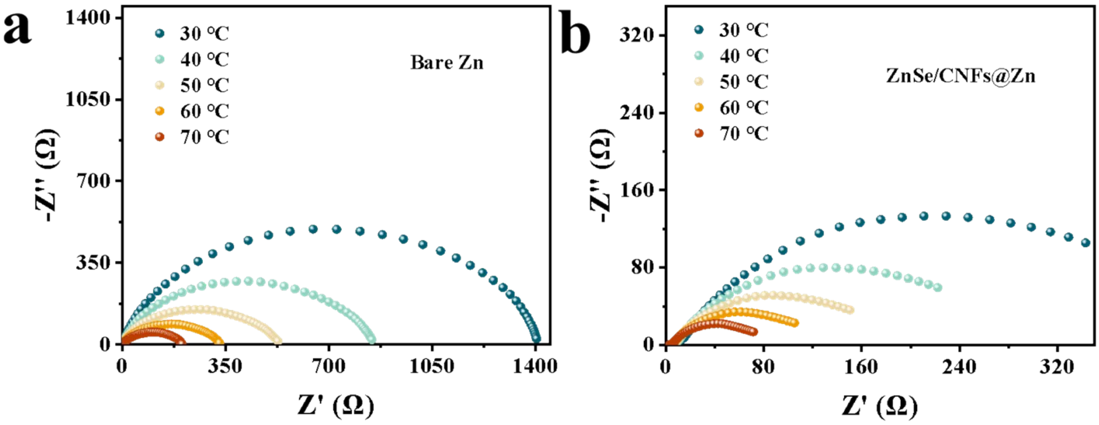


Figure S5. Nyquist plots at different temperatures for (a) bare Zn and (b) ZnSe/CNFs@Zn.

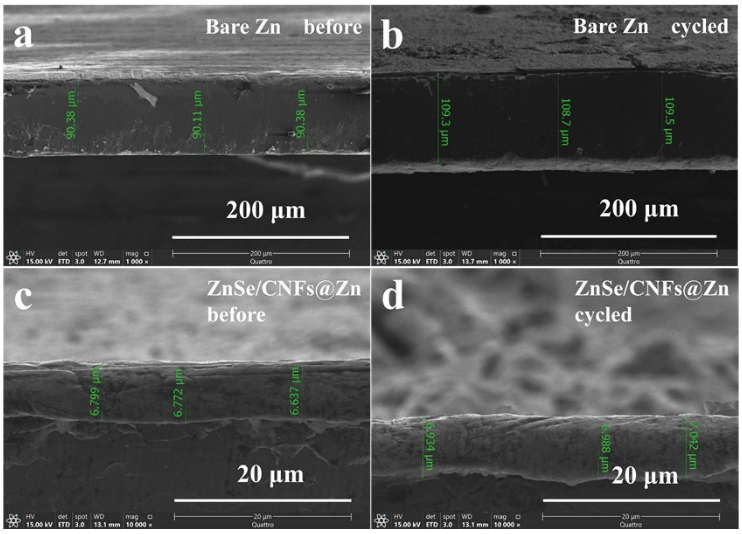


Figure S6. The side-view SEM image of (a, b) Bare Zn, (c, d) ZnSe/CNFs@Zn before and after 50 cycles at 1.0 mA cm^{-2} with a capacity of 1.0 mAh cm^{-2}.

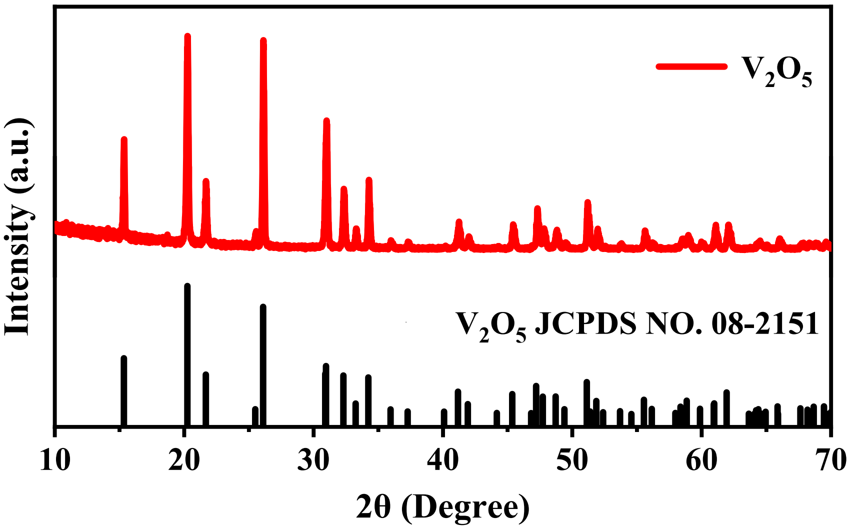


Figure S7. XRD pattern of V_2O_5.

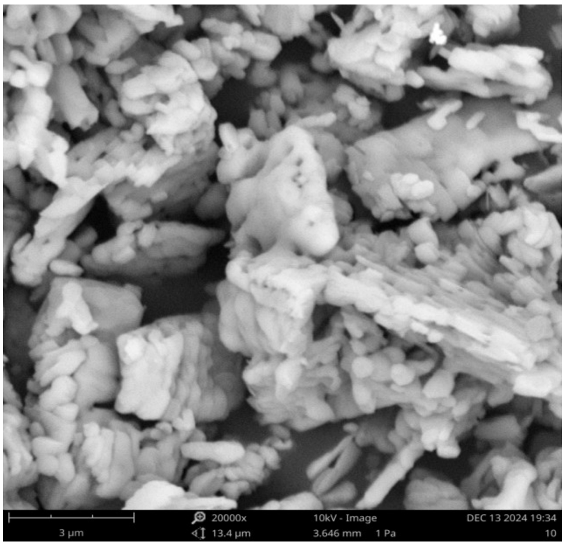


Figure S8. SEM image of V_2O_5 cathode material.

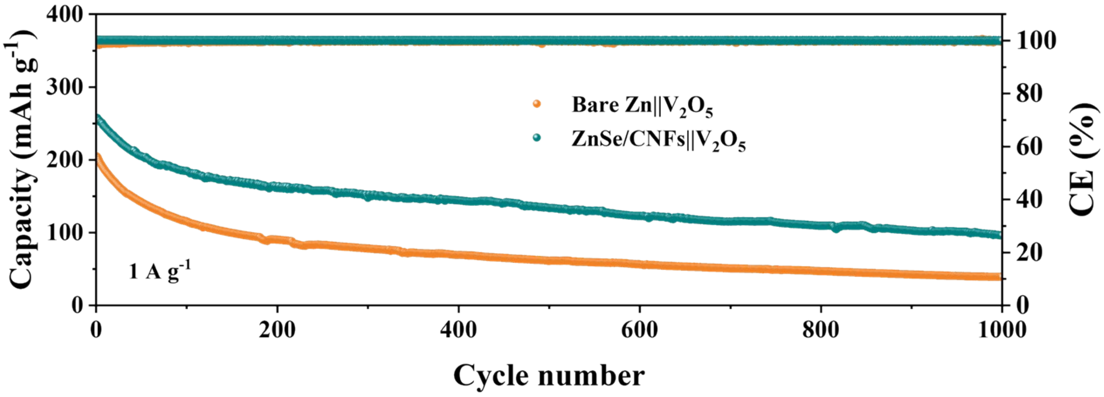


Figure S9. Cycling performance at 1 A g^{-1}.

Table S1 Comparison of cycling performance of ZnSe/CNFs@Zn anode and other metal-based material modified Zn anode in symmetric batteries.

Coating Materials	**Current density (mA·cm^{-2})**	**Areal Capacity (mAh·cm^{-2})**	**Cycling time (h)**	**Reference**
MX-ZSO	5	1	1000	[1]
PZ-8	1	1	800	[2]
PAN/PMMA	2	1	800	[3]
CZn	1	1	600	[4]
MXene/ZnSe	2	1	1300	[5]
ZnO	5	1.25	800	[6]
CSCF	0.5	0.5	1600	[7]
ES-Cm	1	1	1280	[8]
BH-Zn	1	0.5	1000	[9]
PZn	0.5	0.5	400	[10]
ZnSe/CNFs@Zn	1	1	1763	This work

Table S2 Parameters of activation energy

Temperature (°C)	**Kelvin (K)**	**K^{-1}**	**R$_{ct}$**	**lnR$_{ct}^{-1}$（Pre-protection）**	**R$_{ct}$**	**lnR$_{ct}^{-1}$（Post-protection）**
30	303.15	0.003298697	1404	-7.247080585	343	-5.837730447
40	313.15	0.003193358	846.2	-6.740755738	222.2	-5.403577877
50	323.15	0.003094538	527.6	-6.268338421	150.5	-5.013963084
60	333.15	0.003001651	330.2	-5.799698531	105.1	-4.654912278

70	343.15	0.002914177	202.7	-5.311727053	71.54	-4.270256734

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