

Supporting information

Surface modulation of zinc anodes by foveolate ZnTe nanoarrays for dendrite-free zinc ion batteries

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1. Supplemental Experimental Details

1.1 Materials. Zn foil (~0.1 mm), Ti foil (~0.01 mm) and Graphite rod were purchased from Haoxuan Metal Material Co. , Ltd. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (>99.0%), saturated calomel electrode, Tellurium dioxide powder (>99.99%) and V_2O_5 powder (>99.99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All other reagents were analytical grade and used directly without further purification. Deionized water was used to prepare all aqueous electrolytes.

1.2 Materials Preparation:

Synthesis of Zn@ZnTe: The commercial Zn foil was cut into Zn ribbons (4 cm × 4 cm), and then one side of the Zn ribbon was carefully polished with sandpaper to remove the passivation layer. The working solution of tellurium (Te^{4+}) was obtained by dissolving 20 mg of TeO_2 (99.99% Merck) in 250 mL of deionized water. The 5 cc of 98% concentrated H_2SO_4 was introduced into the working solution and heated for 30 min to obtain a clear 0.5 mM solution of Te^{4+} . The second working solution of Zn^{2+} was prepared by dissolving 10.8 g ZnSO_4 (99.99% Merck) in 250 mL distilled water to obtain a 0.15 M solution. During using an electrochemical workstation (CHI660E, Shanghai, China), the treated Zn foil was used as the working electrode, while Graphite rod and saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode, respectively. The deposition was performed for 3,200 s under the static potential of -1.2 V (vs. SCE). The material was taken out and rinsed with deionized water and ethanol several times. The resulting Zn foil was dried at 60 °C for 1 h in a vacuum oven.

1.3 Materials Characterization:

The micromorphology of the samples was observed using scanning electron microscopy (SEM, FEI-Quanta 250, USA). The elemental analysis of the samples was characterized using a scanning electron microscope (FE-SEM, JSM-7500, Japan) equipped with corresponding energy-dispersive X-ray (EDX) elemental mapping. The crystal structure of the samples was characterized through the X-ray diffraction

analysis (XRD, Smart Lab, Rigaku, Japan) with Cu-K α ($\lambda = 1.540598 \text{ \AA}$, Smart Lab) source (scan rate of 2° min^{-1}) in the 2θ range of $10^\circ \sim 80^\circ$. The surface element analysis of the samples was carried out by a PHI 5000 VersaProbe XPS instrument (XPS, Thermo ESCALAB 250XI, USA) and Fourier transform infrared spectrum (FTIR, NICOLET iS50, USA).

1.4 Electrochemical Tests:

Electrochemical characterization of symmetrical Zn//Zn, Zn@ZnTe//Zn@ZnTe cells were conducted using both transparent cells and 2032-type coin cells. Electrochemical impedance spectroscopy (EIS) of these cells was conducted on an electrochemical workstation (CHI660E, Shanghai, China) over the frequency range of 100 kHz to 1 Hz. The Zn@ZnTe//V₂O₅ coin cells were galvanostatically charged/discharged in the voltage range of 0.2–1.5 V vs. Zn/Zn²⁺ at different current densities on a Land CT5001A battery tester, and specific capacities were calculated based on the active mass of ZnTe cathode. The mass of ZnTe and Zn foil are approximately 1.4 mg and 100 mg, respectively. The width of Zn, Zn@ZnTe and separator are 14 mm, 14 mm, and 18 mm, respectively.

1.5 Transparent Zn@ZnTe Cell and In Situ Dendrite Observation:

A transparent Zn@ZnTe//Zn@ZnTe cell was designed to observe the Zn dendrite growth. Specifically, a transparent glass dish, two sheets of zinc telluride electrodeposited ($0.5 \text{ cm} \times 3 \text{ cm}$), and two plastic clamps form a pool for observing the Zn dendrites. The transparent glass dish is used to store the electrolyte. The Zn dendrite growth was in situ observed by an optical microscope equipped with a digital camera. Meanwhile the transparent Zn cell was tested for Zn stripping/plating using an electrochemical workstation (CHI660E).

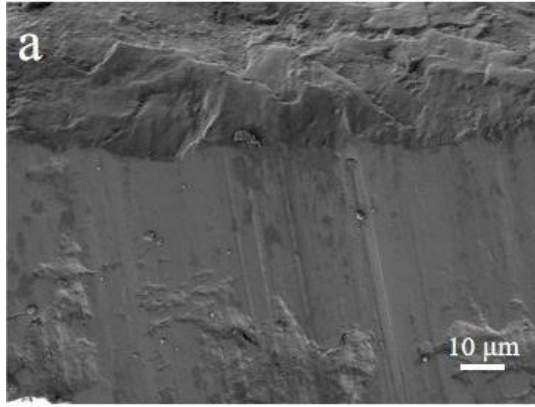


Fig. S1. cross-sectional image of Zn@ZnTe electrode, showing that the thickness of the ZnTe is $\approx 12 \mu\text{m}$.

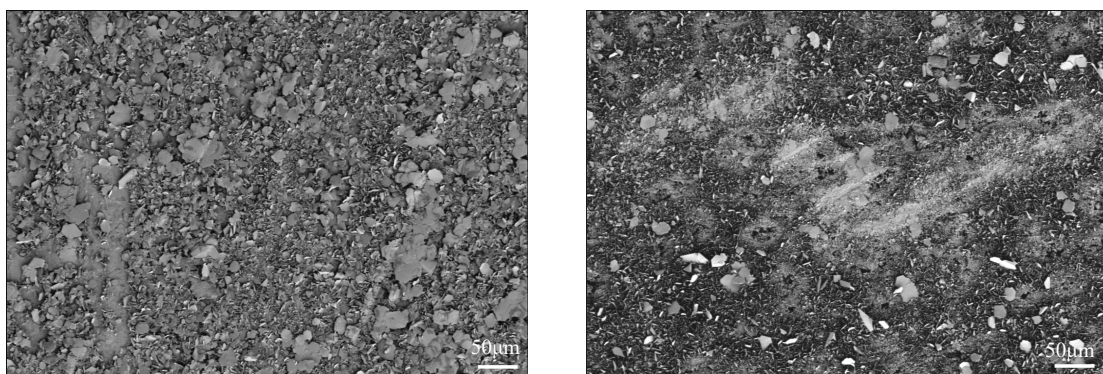


Fig. S2. SEM images of bare Zn and Zn@ZnTe electrodes soaked in ZnSO₄ electrolyte after 7 days.

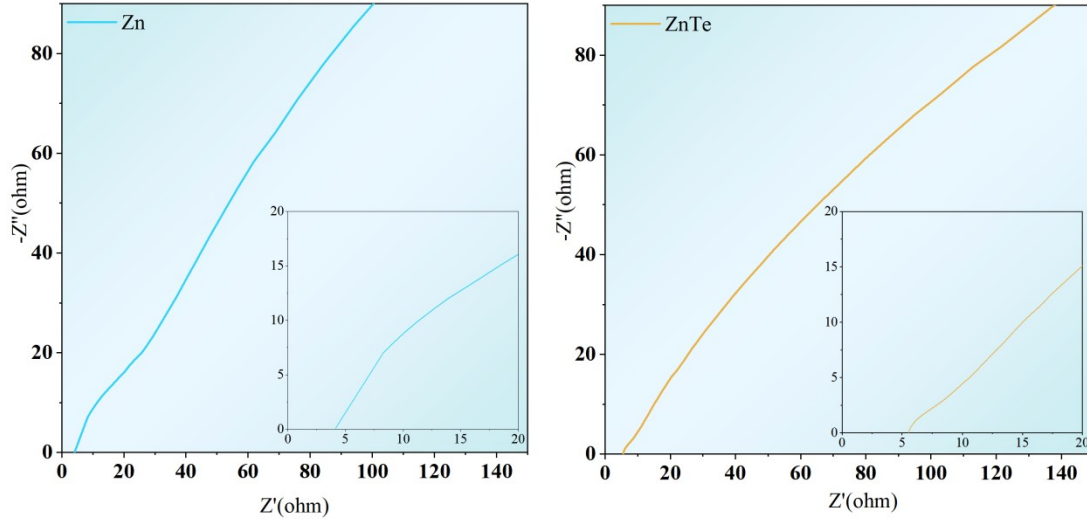


Fig. S3. Nyquist plots collected at open circuit voltage (OCV) over the frequency range of 100kHz to 1Hz.) Zn symmetric cell with glass fibre as separator (inset: enlargement of indicated range) ZnTe coated Zn symmetrical cell with glass fibre as separator (inset: enlargement of indicated range).

For the Zn/Zn cell with glass fibre, the ionic conductivity of the glass fibre separator could be calculated from the bulk electrolyte resistance by the following equation:

$$\sigma = \frac{L}{RS}$$

Where L is the thickness of the glass fibre separator (0.675mm), S is the contact area (1cm²), and R_{ZnTe(glass fibre)} ≈ 4.1 ohm at room temperature. Thus, $\sigma_{\text{glass fibre}} = 1.64 \times 10^{-2} \text{ S cm}^{-1}$. For the ZnTe coated Zn symmetrical cell, R(ZnTe) = R_{ZnTe} - R_{ZnTe(glass fibre)}} = 5.6 ohm. Therefore, the ionic conductivity of the ZnTe film can be evaluated as $\sigma_{\text{ZnTe}} = \sim 2.14 \times 10^{-4} \text{ S cm}^{-1}$.

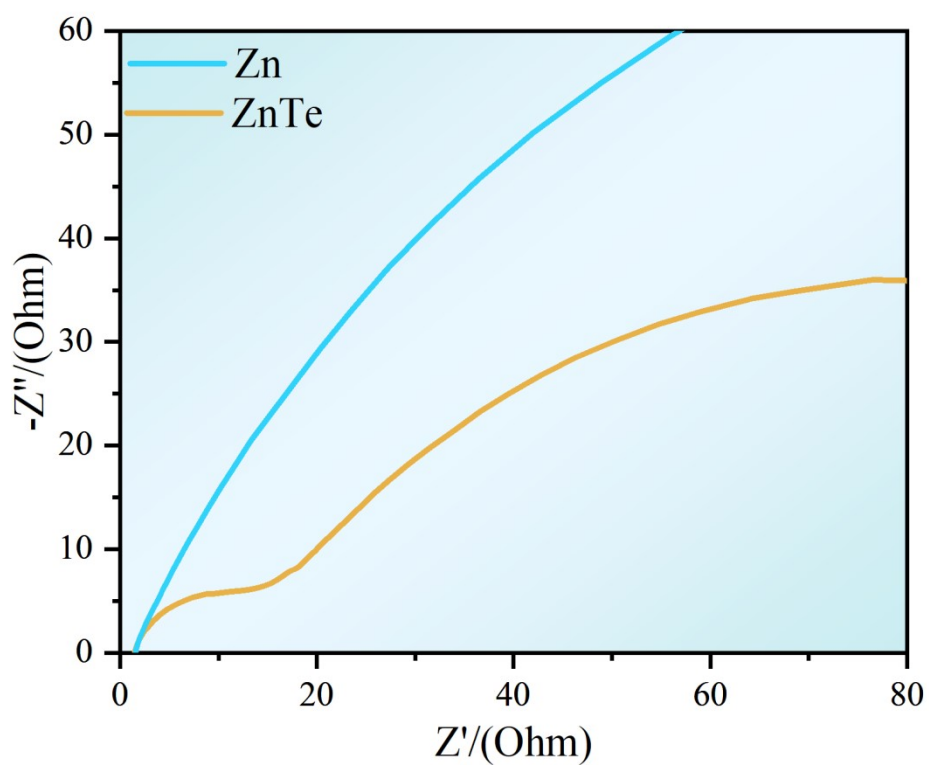


Fig. S4. Electrochemical impedance spectroscopy measurements of bare Zn and Zn@ZnTe symmetric cells.

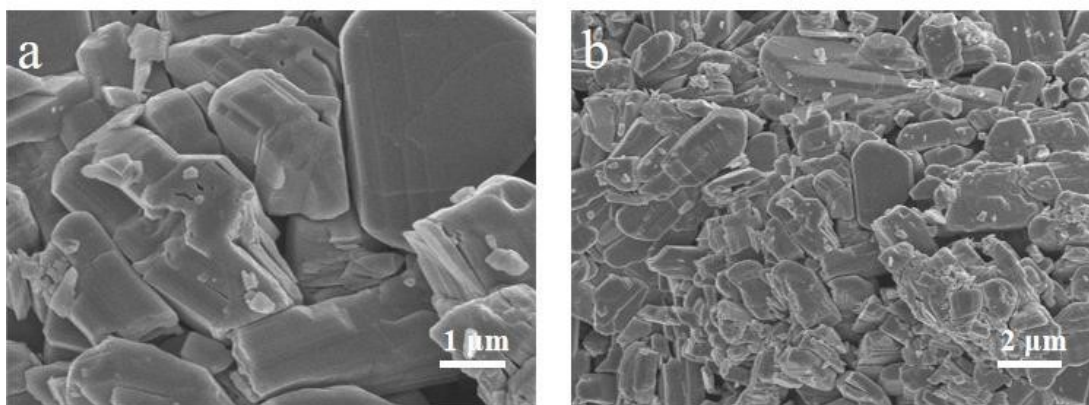


Fig. S5. SEM images of V₂O₅ at different magnifications.