Artificial solid-electrolyte interface facilitating uniform Zn deposition by promoting chemical adsorption

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ABSTRACT Zn-air batteries are promising energy storage and conversion systems to replace the conventional lithium-based ones. However, their applications have been greatly hindered by the formation of Zn dendrites and ZnO passivation layer on the Zn anodes. Herein, we report the fabrication of an artificial protective layer comprised of N-doped three-dimensional hollow porous multi-nanochannel carbon fiber with well-dispersed TiO₂ nanoparticles (HMCNF). The incorporated TiO₂ nanoparticles and N dopants improve the ion flux distribution and promote the surface adsorption, facilitating the interfacial pseudocapacitive behaviors during Zn deposition. The hierarchical architecture also induces homogeneous electric field distribution at the anode/electrolyte interface. Accordingly, the deposition behavior of Zn is regulated, giving rise to enhanced utilization and rechargeability of Zn. When integrated in alkaline Zn-air batteries, the HMCNF-coated Zn anodes exhibit improved electrochemical performances relative to those with the bare Zn anodes, demonstrating a versatile strategy to boost energy storage of metal anodes through optimizing surface adsorption properties.

Keywords: regulated Zn deposition, Zn adsorption, artificial solid-electrolyte interface, Zn anode, Zn-air battery

INTRODUCTION

The quest for advanced renewable energy conversion and storage systems has become urgent due to the ever-growing energy need and environmental concerns caused by the world-wide use of fossil fuels. With higher energy density and lower cost, Zn-air batteries (ZABs) have emerged as a promising alternative to lithium-ion batteries (LIBs) to power a wide scope of appliances. More importantly, the better compatibility of Zn with aqueous electrolytes promises better safety compared with that of LIBs which mostly use flammable organic electrolytes [1].

Despite recent progress in optimizing the air cathode part which involves rational design and optimization of the catalyst [2–5] and gas diffusion layer [6,7], the development of the corresponding anode counterpart has lagged behind. Notably, chemical change and structure reformation on the surface of the Zn metal cause the deterioration of the overall cycling stability, which has greatly hindered the large-scale commercialization of

secondary ZABs [8]. Different from the case of nonaqueous LIBs with a solid-electrolyte interface (SEI), the bare Zn anode is directly exposed to the aqueous electrolytes in ZABs and thus prone to degradation due to the absence of a protective layer [9]. Non-uniform dissolution/deposition of the active Zn species leads to Zn dendrite formation and excessive ZnO precipitation on the surface of the Zn anode, causing low Zn utilization, capacity loss and even short circuit in the alkaline electrolyte during repeated charging-discharging processes [10–13]. Numerous efforts have been devoted to addressing the dendrite formation and surface passivation issues of Zn anodes, such as the construction of three-dimensional (3D) Zn architectures [14–18], alloying Zn with heavy metals [19–21], and coating Zn anode with a protective layer [22–24]. Despite these efforts, realizing uniform dissolution/deposition of Zn for advanced electrochemical set-ups, and probing the correlation between structure engineering and performance optimization remain challenging.

According to the Sand's model, the deposition behavior of Zn is mainly underpinned by the electric field/ion concentration distribution over the electrolyte/anode interface, as well as the transport of active Zn species [13,25,26]. The slow Zn mass transport induces a steep concentration gradient towards the electrolyte/anode interface, resulting in uncontrolled Zn deposition [27]. Besides, the inferior adsorbing ability of the substrate for Zn can hardly regulate the ion concentration near the electrode/electrolyte interface [28,29], which is also adverse to the uniform deposition of Zn. Therefore, to achieve the uniform Zn deposition, it is desirable to simultaneously enhance the Zn mass transport and chemical adsorption of Zn, as well as delocalize the current density at the electrolyte/anode interface.

Herein, we report the stabilization of Zn anodes by employing the N-doped 3D hollow porous multi-nanochannel carbon fibers with well-dispersed TiO₂ nanoparticles (HMCNF) as an artificial SEI layer, which simultaneously addresses the Zn dendrite growth and ZnO passivation issues. Experimental results and density functional theory (DFT) simulations indicate that the incorporation of TiO₂ phase and N dopants favors the chemical adsorption of Zn, and the associated pseudocapacitive effect enables uniform Zn deposition. The as-formed multiple well-aligned hollow channels in carbon fibers facilitate the uniform mass transport towards the electrode surface and improve Zn adsorption kinetics, and the porous architecture

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effectively homogenizes the interfacial electric field distribution and decreases the charge-transfer resistance. Moreover, construction of the artificial SEI functions as the 3D continuation of Zn anode that buffers the volume expansion of the Zn metal. Collectively, these favorable traits permit smooth and controllable Zn deposition on the HMCNF layer, bringing high stability of the Zn anode. When integrated into ZABs, the HMCNF-coated Zn anodes exhibit significantly improved cycling performance compared with the bare Zn anodes. Our study demonstrates the feasibility to realize uniform Zn deposition through leveraging the enhanced chemisorption of Zn on the HMCNF-modified Zn anodes. The strategy can be further extended to a broader scope of battery systems based on alkali metal anodes, for which the electrochemical performance is fundamentally underpinned by the electrode/electrolyte interface.

EXPERIMENTAL SECTION

Materials

Polyacrylonitrile (PAN, $M_w=150,000$) was purchased from Shanghai Jinshan Petrochemical Co., Ltd. Polymethyl methacrylate (PMMA, $M_w=300,000$) was purchased from Heilongjiang New Chemical Industry Co., Ltd. Tetrabutyl titanate (TBT, $\geq 99\%$), *N,N*-dimethylformamide (DMF, $\geq 99.5\%$), hydrochloric acid (HCl, 37%), potassium hydroxide (KOH, $\geq 85\%$), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), and anhydrous ethanol (EtOH, $\geq 99.7\%$) were purchased from Shanghai Sino-pharm Chemical Reagent Co., Ltd. Nafion solution (5%) and 20% Pt/C catalyst were purchased from Shanghai Hesen Electric Co., Ltd. IrO_2 (99.9%) was purchased from Shanghai Macklin Biochemical Co., Ltd. All chemicals were used as received without further purification.

Synthesis

HMCNF was synthesized using a coaxial electrospinning-annealing technique. To prepare the precursor solution for the shell layer, 1.05 g of PAN and 0.45 g of PMMA were dissolved in 9.45 g of DMF under magnetic stirring for 12 h at room temperature. The core layer precursor solution was prepared by dissolving 2.2 g of PMMA in 7.8 g of DMF and stirred for 12 h at room temperature, followed by the addition of 0.24 g of TBT and 0.02 mL of 37 wt% HCl aqueous solution. The shell and core precursor solutions were then injected into two syringes connected with a stainless-steel spinneret at the rate of 0.5 and 0.3 mL h^{-1} , respectively. The spinneret at the connection was made of two coaxial needles with diameters of 18-gauge and 14-gauge, respectively. The distance between the needles and the fiber collector was set at around 15 cm. During the electrospinning process, the applied voltage was 18 kV (25°C and 30% humidity). After the electrospinning, the obtained carbon nanofibers were firstly pre-oxidized at 280°C for 0.5 h in air, and then annealed at 700°C for 2 h under argon (5°C min^{-1}). Pristine hollow porous carbon nanofiber (HPCNF) was also prepared using the same approach for reference, for which no TBT and HCl was added.

Characterizations

Powder X-ray diffraction (XRD) patterns were obtained by a diffractometer (Bruker AXS D8 Advance, $\text{K}\alpha$ radiation, $\lambda = 0.15418 \text{ nm}$). Scanning electron microscopy (SEM) images were

acquired with an SU8010 field-emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, and energy dispersive X-ray spectroscopy (EDS) data were acquired using a JEOL-2010F operated at 200 kV. Nitrogen adsorption analyses were carried out using an Accelerated Surface Area and Porosimetry Analyzer (ASAP 2020; Micromeritics Instrument Corp.). X-ray photoelectron spectroscopy (XPS) experiments were carried out using a PHI-5400 spectrometer equipped with an Al- $\text{K}\alpha$ X-ray source ($h\nu = 1486.6 \text{ eV}$), with the charge calibrated using the CH_x peak in the carbon 1s spectra (284.6 eV). Raman measurements were performed by a Renishaw inVia-Reflex confocal microscope-based Raman spectrometer with 532 nm laser. Thermogravimetric (TG) analyses were conducted using an apparatus (TGA8000). Atomic force microscopy (AFM) test was conducted using a BRUKER Dimension Icon.

Theoretical calculation

DFT analysis, as implemented in the Vienna *Ab initio* Simulation Package (VASP) [30,31], was employed to calculate the binding energies and the differential charge density of the prepared HMCNF sample with Zn. The projector-augmented wave (PAW) method [32,33] was applied to evaluate atom-electron interactions with the cut-off energy of 400 eV. The exchange-correlation functional was represented with the generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) functional [34]. The k points were generated through the Monkhorst-Pack algorithm [35]. The DFT-D3 method was used to better describe the van der Waals interaction between Zn, carbon, nitrogen and TiO_2 . The Brillouin zone was integrated using a $3 \times 3 \times 1$ MP grid, where the energies were calculated to converge to the accuracy of $1.0 \times 10^{-5} \text{ eV}$. The lattice leaved a vacuum region of more than 20 Å in the z direction. The Zn binding energies were calculated as follows:

$$E = E_{\text{total}} - E_0 + E_{\text{Zn}}, \quad (1)$$

where E_{total} is the total energy of one Zn atom binding to carbon (C), graphitic nitrogen (GrN), pyridinic nitrogen (PyN), pyrrolic nitrogen (PrN), and TiO_2 ; E_0 is for each model carbon (C), graphitic nitrogen (GrN), pyridinic nitrogen (PyN), pyrrolic nitrogen (PrN) and TiO_2 without the binding of Zn; and E_{Zn} is for one Zn atom.

Electrochemical measurements

Fabrication of HMCNF-coated Zn foil (HMCNF-Zn) and HPCNF-coated Zn foil (HPCNF-Zn): A slurry was prepared by mixing HMCNF and 5 wt% Nafion in a weight ratio of 8:2 in ethanol, followed by 0.5 h of ultrasonication. The slurry was then sprayed on Zn foil and dried in vacuum at 60°C for 8 h to obtain HMCNF-Zn. The HPCNF-Zn was prepared using the same protocol for comparison.

Assembly of ZABs: The ZABs were assembled using a catalyst-loaded carbon paper as the cathode, a Zn anode (HMCNF-Zn, HPCNF-Zn and bare Zn), and the aqueous electrolyte containing 6 mol L^{-1} of KOH and 0.2 mol L^{-1} of $\text{Zn}(\text{CH}_3\text{COO})_2$. To prepare the catalyst ink, 0.5 mg of 20% Pt/C and 0.5 mg of IrO_2 powder were added into the solution containing 1 mL of ethanol and 25 μL of 5 wt% Nafion, and ultrasonicated for 0.5 h. The catalyst ink was sprayed onto the carbon paper to achieve a catalyst loading of about 1 mg cm^{-2} . The cell was assembled

under ambient conditions, where stationery electrolyte and air with the atmospheric pressure as the cathode gas were applied, as shown in in Fig. S1.

Galvanostatic charge-discharge tests were performed using a Neware test system. For each cycle, the ZABs were discharged/charged at the current densities of 10 and 20 mA cm⁻² for 10 min (5 min of discharge and 5 min of charge). Discharge curves for the ZABs were carried out at the current density of 10 mA cm⁻². Cyclic voltammetry (CV), chronoamperogram (CA) and electrochemical impedance spectroscopy (EIS) were carried out with a CHI760E electrochemical workstation in a three-electrode configuration. Bare Zn or HMCNF-Zn was used as the working electrode, with the Pt foil as the counter and the saturated calomel electrode (SCE) as the reference. CV measurements were performed in the range of -0.9 to -2.0 V at different scan rates of 5, 10 and 20 mV s⁻¹. CA curves were obtained at the overpotential of -150 mV. EIS spectra were measured with an alternating current amplitude of 10 mV in the frequency range from 10⁵ to 10⁻² Hz for the pristine anode and the one after 10 discharge-charge cycles. *In situ* optical microscope tests were conducted in a two-electrode configuration, with the anode of bare Zn or HMCNF-Zn and the air cathode of catalyst-loaded carbon paper.

RESULTS AND DISCUSSION

Syntheses and characterizations

Coaxial electrospinning-annealing technique provides a versatile approach to fabricating carbon fiber layers with delicate control in morphology, composition, and structure. Optimizing the composition of the core and shell precursors and tailoring the parameters of the annealing process allow tuning of the porous and hollow carbon fiber structures. In this work, the precursor solutions for the shell and core layer were prepared by dissolving PAN and PMMA in DMF, and dissolving PMMA, TBT and HCl aqueous solution in DMF, respectively. HCl was added to inhibit the fast hydrolysis of TBT [36–38]. During the electrospinning process, hydrolysis of TBT produces TiO₂ nanoparticles, which become well dispersed in the precursor solution for the core layer due to its low surface energy, and align along the direction of the electric field in the PMMA fibers during the electrospinning process because of its semiconductor characteristic, inducing directed assembly and formation of the desired 3D fiber-based skeleton. PAN acts as the carbon precursor, while PMMA functions as the sacrificial agent and decomposes during the high-temperature carbonization, ultimately yielding the 3D hollow porous multi-nanochannel carbon fiber anchored with well-dispersed TiO₂ nanoparticles. Without adding TBT and HCl, single-channel hollow porous carbon nanofibers would form along the decomposition of PMMA. In this way, the TiO₂ loading densities can be readily adjusted by tuning the concentration of TBT and HCl in the precursor solutions.

As shown by the SEM images in Fig. 1a and Fig. S2, the as-prepared HMCNF exhibits a 3D architecture with hollow multi-nanochannels, whereas the hollow porous nanofibers are formed for the HPCNF without adding TBT and HCl. This highlights the importance of TiO₂ in creating and tuning the multichannel structures. The diameter of the fiber decreases with the increase of TBT (700 nm for HPCNF, and 470 nm for HMCNF). TEM images show a lotus-root-like porous architecture at the end of the fibers, indicating that nanopores are formed in the wall of

fibers (Fig. 1b), bridging the interior and exterior of the nanofibers and producing an interconnected hierarchical architecture. It is also worth mentioning that no additional chemical etching is required to induce the formation of the hollow architecture, which is advantageous considering the large-scale potential. The TiO₂ nanoparticles with the size range of 3–6 nm uniformly distribute throughout the nanofibers (Fig. 1c–g), consistent with the STEM-EDS element maps in Fig. 1h. The captured lattice fringe of 0.35 nm matching well with the (101) plane of anatase TiO₂ (JCPDS No. 21-1272) [39] was further corroborated by the XRD pattern in Fig. 2a. The diffraction peak corresponding to the (101) plane of the TiO₂ appears for HMCNF. The broad diffraction peaks can be attributed to the low crystallinity of the carbon nanofibers as well as the small size of the TiO₂ nanoparticles [40,41]. The TiO₂ content in the HMCNF is 9.0 wt% according to the TG data (Fig. S3). Raman spectrum was applied to evaluate the crystallinity of the carbon skeleton. The intensity ratio of the D band to G band (Fig. S4), which is an indicator of carbon disorders and defects [42], was calculated to be ~1.06 for both HPCNF and HMCNF. This indicates the carbon nanofibers maintain the low crystallinity upon incorporation of the TiO₂ nanoparticles.

XPS was conducted to probe the surface chemical environments of C, N, O and Ti in HPCNF and HMCNF (Fig. S5). The Ti 2p_{3/2} and Ti 2p_{1/2} are located at 458.6 and 464.3 eV, respectively (Fig. 2b), confirming the formation of the TiO₂ phase in HMCNF [43]. As shown in Fig. 2c, the N 1s spectrum can be deconvoluted to four peaks, corresponding to the pyridinic nitrogen (398.5 eV), pyrrolic nitrogen (399.7 eV), graphitic nitrogen (400.2 eV), and oxidized nitrogen (403.3 eV) [44], respectively, which indicates successful nitrogen doping into the carbon nanofibers. Nitrogen adsorption isotherm was measured to determine the pore structure and the Brunauer-Emmett-Teller (BET) surface area of the sample (Fig. 2d). HMCNF mainly possesses two types of pore sizes with 2 and 4 nm in diameter, with the BET surface area of 48.7 m² g⁻¹.

Zn dissolution/deposition behavior at the anode/electrolyte interface

To investigate the effect of HMCNF coating on the Zn dissolution/deposition behaviors, CV rate scanning was conducted in a three-electrode configuration between -2.0 and -0.9 V vs. the SCE. As shown in Fig. 3a–f, bare Zn and HMCNF-Zn show similar CV curves, indicating the addition of the HMCNF layer does not alter the intrinsic electrochemical reaction of the Zn anodes during cycling. For HMCNF-Zn at the scanning rate of 10 mV s⁻¹, a pair of anodic (P_a) and cathodic (P_c) peaks located at -1.123 and -1.635 V are corresponding to the electrochemical reaction of Zn + 4OH⁻ = Zn(OH)₄²⁻ + 2e⁻ [8]. An additional anodic peak (-1.139 V) during the negative scan is caused by the oxidation of the exposed Zn metal [45]. In addition, the P_c and P_a of bare Zn exhibit a negative and positive shift, respectively, compared with the cathodic and anodic peaks of HMCNF-Zn at the same scanning rate. The shift of P_c and P_a in opposite directions for bare Zn compared with HMCNF-Zn brings a larger voltage difference (ΔE_p) between E_{p,c} and E_{p,a} (Tables S1, 2), which unarguably demonstrates the efficacy of the HMCNF layer in mitigating the repeated formation/dissolution of the passivation layer (Zn(OH)₄²⁻ = ZnO + 2OH⁻ + H₂O) [8], giving rise to better reversibility of the Zn dissolution/deposition process.

Figure 1 (a) Top-view SEM image of HMCNF, with the inset showing the corresponding cross-sectional SEM image. (b) TEM image of HMCNF, with the insets highlighting the through-hole pores and hollow multi-channels. (c) TEM image of a single HMCNF. (d–g) HRTEM images of HMCNF. The enlarged regions in the insets exhibit the lattice fringe that matches well with the (101) plane of anatase TiO_2 . (h) STEM-EDS element maps of HMCNF.

To further study the Zn adsorption kinetics on the bare and HMCNF-coated Zn anodes, surface- and diffusion-controlled processes were decoupled and analyzed with the assist of the CV rate scanning test. As shown in Fig. 3a–f, increasing the scanning rate from 5 to 20 mV s^{-1} results in the increase of the I_{Pa} and I_{Pc} values for both bare Zn and HMCNF-Zn anodes. The power law depicts the correlation between the redox peak current (I) and the scan rate (ν) [28]:

$$\log(I) = b \log(\nu) + \log(a), \quad (2)$$

where a and b are constants. The electrochemical behavior is dominated by the diffusion-controlled process with b approaching 0.5, or by the surface-controlled process with b approaching 1. As shown in Fig. 3g, h, the b values for the Pc of bare Zn approaches 0.5, while the value for HMCNF-Zn is calculated to be around 1, suggesting that the uniform Zn adsorption greatly influences the Zn deposition behavior, and the Zn plating process is mainly surface-controlled for HMCNF-Zn. While for the Pa of HMCNF-Zn and bare Zn, the b values approach 0.5, suggesting that the Zn dissolution process is primarily diffusion-controlled. The behavior of the current can be depicted in a more precise manner by decoupling the diffusion-controlled and capacitive contributions at a set potential using the equation below:

$$I = k_1 \nu + k_2 \nu^{1/2}, \quad (3)$$

where I , $k_1 \nu$, $k_2 \nu^{1/2}$ represent the whole current, current from the

surface-controlled process and current from the diffusion-controlled process, respectively. By plotting $I/\nu^{1/2}$ as a function of $\nu^{1/2}$, the values of k_1 and k_2 can be estimated through linear fitting (Fig. 3i and Fig. S6). For the Pc , the fractions of surface capacitive contribution for HMCNF-Zn are 70.3%, 77.0% and 82.5% at the scanning rate of 5, 10 and 20 mV s^{-1} , respectively, which are much higher than that of 12.3%, 16.5% and 21.8% for bare Zn. This difference in the pseudocapacitive contributions of the bare Zn and HMCNF-coated Zn anodes reveals that Zn is more readily adsorbed and deposited with the HMCNF protective layer.

We performed DFT calculations to understand the interactions between the as-deposited Zn metals and the TiO_2 -incorporated nitrogen-doped carbon nanofibers. As summarized in Fig. 4a–f, the interaction between Zn atoms and graphite ($E_{\text{BE}} = -0.52 \text{ eV}$) is weak, whereas the binding energy of Zn atoms on TiO_2 is much stronger ($E_{\text{BE}} = -7.89 \text{ eV}$), facilitating the adsorption of Zn and consequent control of the Zn deposition behavior. In addition, for the three different types of nitrogen atoms, pyrrolic (PrN) and pyridinic (PyN) nitrogen exhibit stronger Zn adsorption abilities with higher binding energies relative to that for the pure graphite. Hence, super-zincophilic TiO_2 nanoparticles uniformly embedded in carbon fibers with PrN and PyN atoms greatly strengthen the adsorption and capturing of Zn during cycling. The differential charge density of

Figure 2 (a) XRD patterns of HPCNF and HMCNF, and the reference pattern of anatase TiO₂ (JCPDS No. 21-1272). High-resolution XPS spectra of HMCNF showing the (b) Ti 2p and (c) N 1s regions. (d) BJH pore size distribution of HMCNF with the inset showing the N₂ adsorption/desorption isotherms.

Zn adsorbed on TiO₂, graphite, and nitrogen atoms were also identified (Fig. 4g and Fig. S7). The charge transfer between Zn and TiO₂ (isovalue: 0.01), as well as that between PrN/PyN and TiO₂ (isovalue: 0.0025) is notably higher relative to that between Zn and carbon (isovalue: 0.000055). These results indicate that TiO₂ anchoring and N doping collectively promote Zn deposition by providing the thermodynamically favorable active sites. Accordingly, the surface affinity towards Zn is greatly enhanced upon the addition of the HMCNF layer, allowing homogeneous Zn deposition with better electrochemical performances during cycling.

Electrochemical performance

To evaluate the efficacy of the fabricated artificial SEI layer, we assembled aqueous ZABs by employing HMCNF-Zn or bare Zn as the anode, catalyst-coated carbon paper as the air cathode and 6 mol L⁻¹ KOH aqueous solution containing 0.2 mol L⁻¹ zinc acetate as the electrolyte. The cycling stability of ZABs were examined at different current densities with each cycle being 10 min. Round-trip efficiency was calculated to assess the reversibility of the electrochemical reactions with the bare or protected Zn anodes. As shown in Fig. 5a, when cycled at the current density of 10 mA cm⁻², the discharge and charge voltage of HMCNF-based battery are 1.21 and 2.01 V, respectively, in the 1st cycle, delivering a round-trip efficiency of 60.2%. After more than 150 cycles, the battery with HMCNF-Zn anode only displays a slight efficiency decrease, exhibiting the round-trip efficiency of 57.9%. In contrast, the ZAB with the anode of HPCNF-Zn or bare Zn brings a lower round-trip efficiency of

58.5% and 58.2% in the 1st cycle, and 55.6% and 51.1% in the 150th cycle, respectively. Moreover, the ZAB with the HMCNF-Zn anode still maintains a higher round-trip efficiency of 54.6% than that of the cell with HPCNF anode (53.0%) when tested for 300 cycles. The outstanding cycling stability for the ZAB with the HMCNF-Zn anode is further demonstrated by the 52.7% round-trip efficiency retention after 485 cycles (81 h). However, the ZAB with the bare Zn anode or HPCNF anode exhibits severe voltage polarization augment at 180th cycle (30 h) and 330th cycle (55 h), which can be attributed to the nonuniform dissolution/deposition of Zn species (Fig. 5b). That is to say, the cycling life of the HMCNF-based ZAB could be prolonged by >2.5 times by the treatment of HMCNF coating on Zn anode. The remarkably improved cycling stability of the HMCNF-coated Zn cell was also observed at a higher current density (20 mA cm⁻²), as illustrated in Fig. 5c, d. The battery based on HMCNF produces an initial discharge potential of 1.18 V and charge potential of 2.00 V with a round-trip efficiency of 58.8%. After over 250 times of cycles (42 h), the battery only exhibits a slight voltage loss (49.9%), revealing the wide applicability of the HMCNF layer in promoting sustainable performances. For the ZAB comprised of the bare Zn anode, the round-trip efficiency drops from 54.3% in the 1st cycle to 38.6 % after 150 cycles (25 h). The round-trip efficiency of the ZAB equipped with different anodes is summarized in Fig. 5e, f.

Discharge curves for the ZABs based on the bare Zn and HMCNF-Zn anodes at the current density of 10 mA cm⁻² are presented in Fig. 5g. The cell with the HMCNF-Zn anode delivers a much longer discharge time (120 h) compared with

Figure 3 CV rate scanning (5, 10, 20 mV s⁻¹) of (a–c) the HMCNF-Zn and (d–f) bare Zn anodes. (g) Plots of log(*I*) as a function of log(*v*) for the HMCNF-Zn and bare Zn anodes. (h) Values of *b* in power-law relationship for the HMCNF-Zn and bare Zn anodes. (i) Contributions of surface-controlled pseudocapacitive currents at different scanning rates for the redox P_c for the HMCNF-Zn and bare Zn anodes.

Figure 4 DFT calculation results of the interaction between Zn and (a) carbon (C), (b) graphitic nitrogen (GrN), (c) pyridinic nitrogen (PyN), (d) pyrrolic nitrogen (PrN), and (e) TiO₂. The grey, light blue, brown, red and blue balls donate Zn, N, C, O and Ti atoms, respectively. (f) Binding energy of Zn with each component in HMCNF. (g) The differential charge density of Zn adsorbed on TiO₂. The yellow and green color represent charge accumulation and depletion, respectively (isovalue: 0.01).

Figure 5 (a, b) Galvanostatic cycling curves of ZABs with the bare Zn, HPCNF-Zn and HMCNF-Zn anodes at the current density of 10 mA cm^{-2} . (c, d) Galvanostatic cycling curves of ZABs with the bare Zn and HMCNF-Zn anodes at the current density of 20 mA cm^{-2} . Comparison of round-trip efficiency of ZABs with different anodes during cycling at the current density of (e) 10 mA cm^{-2} , and (f) 20 mA cm^{-2} . (g) Discharge profiles of ZABs with the bare Zn and HMCNF-Zn anodes at the current density of 10 mA cm^{-2} . The corresponding overpotential profiles during discharge for (h) the HMCNF-Zn and (i) the bare Zn anodes, with the linear regions highlighted to calculate the resistivity values.

that of the cell with the bare Zn anode (27 h), demonstrating the compelling discharge stability enabled by incorporating the HMCNF layer. We further transformed the discharge curve into a polarization curve (cell overpotential vs. depth of discharge) to understand the discharge behavior. Since the ohmic over-

potential that evolves almost linearly with time is caused by the increased internal resistance of the cell, the slope of the linear region can be used to estimate the resistivity of the newly formed interfacial electrolyte/Zn layer [8]. As highlighted in Fig. 5h, i, the slope of the bare Zn anode (0.109 V) is higher than that of

the HMCNF-Zn (0.061 V), and the calculated resistivity for the bare Zn and HMCNF-Zn anode is 10.9 and 6.1 $\Omega \text{ cm}^2$, respectively. The observed higher cell resistance can be ascribed to the formation of the dendrites that leads to poor contact between the electrode and the electrolyte, as well as the formation of ZnO ($\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + 2\text{OH}^- + \text{H}_2\text{O}$) on the Zn anode that dramatically lowers the electrical conductivity [46].

Multiple characterization techniques were applied to further probe the origin accounting for the enhanced electrochemical performance of the Zn anode with the HMCNF protective layer, which can be mainly divided into two aspects: uniform Zn deposition with mitigated dendrite formation, and regulation of the ZnO passivation layer.

To understand the role of the HMCNF coating in suppressing dendrite growth, we turned to SEM to compare the surface structural features of the bare Zn and HMCNF-Zn anodes after cycling. As shown in Fig. 6a, b and Fig. S8a, significant mor-

phological changes were observed for the bare Zn anode after 150 cycles at the current density of 10 mA cm^{-2} . Emergence of irregular micro-sized polyhedrons and flakes on the surface of the bare Zn foil reflects an unregulated metal dissolution/deposition process. The cross-sectional SEM image of the bare Zn anode shows Zn protrusions that are detached from the Zn foil, as highlighted by white arrows in Fig. 6b. This type of detachment induces the formation of the “dead” Zn that are irreversible and can hardly be utilized during the following electrochemical cycling [47]. The HMCNF-Zn anode, on the other hand, preserves the porous fiber layer without observable formation of the Zn dendrites after 150 cycles at 10 mA cm^{-2} (Fig. 6c and Fig. S8b, c). The corresponding cross-sectional SEM image (Fig. 6d) suggests Zn is plated on the HMCNF/Zn anode interface as a dense uniform layer of microflakes, in contrast to the irregular deposition on the bare Zn anode. Since the electrical conductivity of the HMCNF layer is lower than that of the

Figure 6 Top-view and cross-sectional SEM images of Zn deposition on (a, b) the bare Zn anode, (c, d) the HMCNF-Zn anode, and (e, f) the HMCNF-Zn anode with the protective layer being peeled off after 150 cycles at the current density of 10 mA cm^{-2} . Cross-sectional Zn deposition morphology on (g) the bare Zn anode and (h) the HMCNF-Zn anode during cycling at the current density of 10 mA cm^{-2} using an *in situ* optical microscope. (i) Current-time profiles of the bare Zn and HMCNF-Zn anodes at the overpotential of -150 mV . XRD patterns of (j) the bare Zn anode and (k) the HMCNF-Zn anode before and after cycling, respectively, as well as the Zn and ZnO reference patterns.

underlying Zn metal, Zn deposition will preferentially take place on the Zn metal surface upon contact with the electrolyte [48]. The as-deposited Zn microflakes are stabilized between the HMCNF protective layer and the underlying Zn foil, suggesting a low content of “dead” Zn after cycling. This is further supported by the cross-sectional SEM images depicting a close-grained uniform inner structure of the deposition upon peeling off the protective layer (Fig. 6e, f).

It is worth noting that the thickness of the protective layer is only 8 μm with the mass loading as low as 0.6 mg cm^{-2} , which enables retention of the high energy density for the whole cell. In addition, the good mechanical strength and flexibility of the HMCNF layer buffer the large mechanical deformation during the Zn dissolution/deposition process. Incorporation of the as-formed TiO_2 nanoparticles enhances the mechanical strength, as the Young's modulus of HMCNF-Zn (2–4 GPa) is higher than that of HPCNF-Zn (0.75–1.5 GPa), as illustrated in Fig. S9. Therefore, The HMCNF protective layer collectively mitigates fracture and dendrite penetrations of the Zn anodes through accommodating the volumetric variation during cycling.

Besides comparing the *ex-situ* SEM images, *in situ* optical microscopy was also applied to monitor the evolution of the Zn dendrites with and without the protective layer during the discharging-charging processes. Zn deposition on the bare Zn anode produces black spots after 1 cycle (Fig. 6g), and multiple noticeable protuberances emerge after 150 cycles and continuously grow into dendritic Zn. In stark contrast, the HMCNF-coated Zn brings a smooth surface without forming visible dendrites during the whole plating process (Fig. 6h), which further corroborates the efficacy of the protective layer in introducing homogeneous Zn deposition for enhanced electrochemical performances. The Zn deposition processes on the bare Zn and HMCNF-Zn anodes were further compared using the chronoamperometry study (Fig. 6i). The electrode surface area increases as the dendrites form, which tends to increase the cathodic current at a constant cathodic potential [49,50]. When an overpotential of -150 mV was applied, the increase of the current is higher for the bare Zn anode (78.4 mA) than that of the HMCNF-Zn anode (55.6 mA), suggesting that the HMCNF coating effectively inhibits the dendrite formation.

XRD and XPS were employed to investigate the impact of the HMCNF layer on the regulation of the ZnO passivation layer. Fig. 6j, k present the XRD patterns of the bare Zn and HMCNF-Zn anodes after cycling. The XRD pattern of the HMCNF-Zn anode is well indexed to metal Zn (JSPDS No. 04-0831) after 150 cycles despite minor diffraction peaks of ZnO (JSPDS No. 36-1451). In contrast, the XRD pattern of the bare Zn anode indicates a much higher content of ZnO after cycling. The formation of ZnO with low conductivity and reversibility greatly shortens the cell life of the bare Zn anode. The results were further supported by the XPS study. The XPS survey given in Fig. S10a clearly shows the presence of Zn in the pristine Zn anode. The XPS high-resolution spectra of Zn 2p (Fig. S10b, c) reveal two characteristic peaks (Zn 2p_{1/2} at 1045.2 eV and Zn 2p_{3/2} at 1022.2 eV) [48] for pristine Zn and HMCNF-Zn anodes. After cycling, two additional Zn 2p peaks centered at 1046.4 and 1023.5 eV corresponding to ZnO [51] emerge for the bare Zn anode. For the HMCNF-Zn anode, the Zn 2p_{1/2} and Zn 2p_{3/2} peaks are only slightly shifted ($<0.4\text{ eV}$) to lower binding energies, implying mitigated ZnO passivation.

The uniform Zn deposition with mitigated dendrite forma-

tion, and controlled ZnO passivation layer formation, which are both realized through the incorporation of the HMCNF protective layer, give rise to favorable Zn dissolution/deposition processes for the HMCNF-Zn anode. This synergistic effect was further corroborated using the impedance measurement (Fig. 7a–d). Before cycling, the intermediate-frequency semicircle in the Nyquist plot is related to charge transfer resistance (R_{ct}), while the low-frequency tail is associated with the ion diffusion process [40]. The equivalent circuit for this case is illustrated in Fig. 7a. Compared with the bare Zn anode, the pristine HMCNF-Zn possesses a higher R_{ct} value due to the relative larger impedance for introducing the less conductive coating layer (Fig. 7c, d). After cycling, the R_{ct} of HMCNF-Zn decreases while that of bare Zn increases, indicating the barrier of the charge transfer is lower compared with that of the bare Zn due to the promoted Zn adsorption [46]. Besides, an additional high-frequency semicircle attributed to the charge transfer resistance (R_{int}) in the newly formed interfacial electrolyte/Zn layer was observed [52]. Noticeably, the HMCNF-Zn cell exhibits a smaller R_{int} (0.25 Ω) compared with that of the cell using the bare Zn anode (0.43 Ω), which reflects the smooth and stable Zn dissolution/deposition reactions enabled by the HMCNF coating at the Zn/electrolyte interface. The equivalent circuit for this case is illustrated in Fig. 7b.

As illustrated in Fig. 7e, for the bare 2D planar Zn anode where metal ions are centralizingly distributed under high local current density, nonuniform dissolution of Zn takes place during the discharging process ($\text{Zn} + 4\text{OH}^- \rightarrow \text{Zn}(\text{OH})_4^{2-} + 2\text{e}^-$) [8], resulting in a rough electrode surface. During the following electroplating process, the nonuniform mass transport and charge transfer bring uncontrolled depletion of $\text{Zn}(\text{OH})_4^{2-}$ ions, which prefer to nucleate and accumulate at the top ends of the electrode, and consequently induce the formation of the Zn dendrites as well as the ZnO passivation layer, as proved by the microscopic images and phase analyses. By comparison, the 3D HMCNF conductive networks directly facing the Zn anode homogenize the electric field distribution and lower the local current density. In addition, the TiO_2 and N dopants in the HMCNF with interconnected nanochannels promote the uniform ion transport and adsorption to the electrode and thus also facilitate a relatively uniform manner of Zn deposition.

CONCLUSIONS

In conclusion, an artificial SEI layer of HMCNF is applied on the Zn anode to access stable Zn anodes in alkaline aqueous ZABs. The unique hollow multi-nanochannel and 3D connected through-hole pores, as well as the well-dispersed TiO_2 nanoparticles embedded in HMCNF provide advantageous surface sites for efficient ion transfer/adsorption and uniform electric field distribution at the side of Zn anode. As a result, the well-regulated Zn deposition simultaneously resolves the issues of Zn dendrite formation and excessive ZnO passivation of the Zn anode. Furthermore, the flexible HMCNF layer accommodates the volume change during repeated discharging/charging, greatly enhancing the mechanical stability of the metal electrode. Benefited from these favorable properties, a stable ZAB cycling performance was achieved with the HMCNF-protected Zn anode for over 485 cycles at the current density of 10 mA cm^{-2} , which notably outperform the ZAB equipped with the bare Zn electrode. The methodology reported in this study presents a new route to accessing high-performance, safe, and stable aqu-

Figure 7 Equivalent circuit models at different status: (a) before cycling and (b) after cycling. EIS of ZABs with (c) the bare Zn anode and (d) the HMCNF-Zn anode before and after cycling (10^{th}). The symbols and lines correspond to experimental and simulated data, respectively. (e) Schematic illustration showing the Zn deposition mechanism on the bare Zn anode and HMCNF-Zn anode. Adding the protective layer promotes homogeneous electric field distribution and uniform ion transport and adsorption, which collectively lead to controlled Zn deposition behaviors.

eous ZABs, which can be further extended to other metal battery systems.

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Author contributions Zhang J designed the experiments and carried out

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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构筑具有高效化学吸附作用的人工固体电解质界面层促进金属锌负极的均匀沉积

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摘要 目前, 锌-空气电池的商业化应用受限于锌枝晶的生长和氧化锌钝化层的形成. 本文通过构筑三维多孔多纳米通道碳复合纤维(HMCNF)作为锌负极人工固体电解质界面层来解决这一问题. 其中, 均匀负载的TiO₂纳米颗粒和氮掺杂基团有效改善了锌的分布和吸附过程, 从而有利于锌沉积过程中界面类电容行为的发生; 同时, 三维多孔多纳米通道的微观结构也使得电场在电极/电解液界面得以均匀分布. 因此, 锌的沉积溶解过程得到有效调控. 与未添加人工界面层的锌负极相比, 基于HMCNF界面层的锌负极的碱性锌-空气电池的电化学性能得到明显提升. 这种基于优化表面吸附来调控金属沉积溶解动力学的策略也可进一步推广至其他金属负极体系来提高其电化学性能.