Regulating Uniform Zn Deposition via Hybrid Artificial Layer for Stable Aqueous Zn-Ion Batteries

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Aqueous Zn-ion batteries (ZIBs) have great potential as promising candidates for next-generation energy conversion and storage devices, benefiting from competitive theoretical capacity, low cost, and high security. However, further applications of ZIBs are impeded by dendrite generation and side reactions. Herein, considering that Zn dendrites are caused by nonuniform metal deposition, involving uneven electric field and Zn2+ ion flux, a dual-functional carbon-coated NaTi2(PO4)3 (NTP-C) artificial protective layer with large surface area is constructed onto the surface of metallic Zn to stabilize Zn anode and regulate uniform Zn deposition. Benefiting from a synergistic strategy, NTP-C coating not only takes advantages of carbon to provide abundant Zn deposition sites to homogenize nucleation, adjust electric field distribution, and reduce local current density but also utilizes the ionic channel in NTP structure to modulate the distribution of Zn2+ flux at the same time. Consequently, the NTP-C@Zn symmetrical cell exhibits a stable cycling for more than 600 h with a low polarization (18.6 mV) at 1 mA cm−2/1 mAh cm−2. Especially, the NTP-C@Zn symmetrical cell even enables a steady plating/stripping process at a harsh condition (100 mA cm−2) without short circuit, indicating a potential application of high-load electrodes or supercapacitors. Furthermore, the NTP-C@Zn//α-MnO2 full cell also displays enhanced electrochemical performance for 1200 cycles with a capacity retention of 76.6% under 5 C (~1.5 A g−1). This work provides a synergistic strategy combining two protective mechanisms and delivers new inspirations for the improvement of stable Zn anode in aqueous ZIBs.

1. Introduction

Clean energies have attracted increasing attentions recently, owing to the massive energy requirement and serious pollution of fossil fuels [1]. Electrochemical batteries are considered as optimal choices for electrical energy conversion and storage on account of inherent effectiveness, convenience, and reliability [2]. Rechargeable aqueous batteries have attracted research attention due to superior safety, nonnottoxicity, nonflammability, high ionic conductivity (~1 S cm−1), and competitive cost [3, 4]. In recent years, various aqueous metal-ion batteries, including monovalent metal ions based on Li+, Na+, and K+ and multivalent charge carriers based on Zn2+, Mg2+, and Al3+, have been developed [5]. Owing to the multielectron redox reaction mechanism, multivalent ion batteries have potential to provide higher specific capacity and energy density than monovalent metal-ion batteries [6]. Compared with other rechargeable batteries, aqueous Zn-ion batteries (ZIBs) possess several advantages, including abundance, low cost, eco-friendliness, and low toxicity. Zn anode provides competitive gravimetric capacity and volumetric capacity (820 mAh g−1 and 5855 mAh cm−3) with suitable redox potential (~0.762 V versus standard hydrogen electrode) and overpotential in aqueous electrolyte [7–12].

Although metallic Zn anode has such advantages, it is still suffering from many challenges, including Zn dendrite generation and side reactions (hydrogen evolution, Zn corrosion, and passivation) [13]. These issues bring about unstable cycling performance with low Coulombic efficiency (CE), capacity fading, and even short circuit when the dendrite punctures the separator, which limit the further development of ZIBs and impede their practical applications [14].
Until now, a great number of strategies have been proposed for modifying metallic Zn electrodes, such as anode structure design [15, 16], alloying with other metals [17], electrolyte optimization [18, 19], separator modification [20, 21], and building artificial protective layer. Among these strategies, constructing protective coating has arisen widespread interest owing to its inherent merits, such as effective performance enhancement, possibility in large-scale manufacturing, tunability and designability of physical and chemical properties [22, 23]. Up to now, numerous coatings have been reported to stabilize Zn anodes, which exploit different protective mechanisms. Firstly, porous materials like nano-CaCO₃ [24], kaolin [25], Zn-based montmorillonite (MMT) [26], and MOF-based materials [27] can regulate Zn²⁺ flux for stable cycling by the selective channels and pores. For example, a porous nano-CaCO₃ coating was applied on the surface of Zn electrodes by Kang et al. [24], which enables uniform and position-selected Zn plating/striping by the molecular sieving ability. Using carbon-based materials, including reduced graphene oxide (rGO) [28], porous carbon [29], and mesoporous hollow carbon [30], as protective layers can improve the cyclability of ZIBs via increasing the Zn deposition sites, regulating electric field distribution, and reducing local current density. To illustrate, Li et al. [29] designed a carbon-coated Zn anode, in which the porous carbon layer can provide abundant nucleation sites for uniform and dense Zn deposition. Apart from the inorganic protective layers, polyamide with unique hydrogen-bonding network and coordination with metal ions [31], polymer glue [32], ZnF₂, and S/N-rich organic compounds [33], etc., were also developed to stabilize Zn anode and prolong the lifespans, but the introduced polymer components may result in increased polarization and nucleation overpotential. In short, there is still great room for developing functional protective layers for improved Zn anode.

Taking account of Zn dendrites are caused by nonuniform metal deposition, involving uneven electric fields and Zn²⁺ ion flux, in this work, we combine two mechanisms and construct a protective layer composed of NaTi₂(PO₄)₃ with carbon coating (NTP-C) onto the surface of Zn metal anode to regulate Zn deposition behavior for stable aqueous ZIBs. Since the carbon-coated NTP particles are imbedded in the carbon matrix, the protective layer can not only increase the Zn deposition sites for homogeneous nucleation, and uniform electric field for reduced local current density, but also regulate the distribution of Zn²⁺ flux simultaneously. In such way, the generation of Zn dendrites and side reactions can be suppressed (Figure 1(a)). The NTP-C@Zn symmetrical cell exhibits a stable cycling performance during Zn plating/striping with a lifespan over 600 h at 1 mA cm⁻²/1 mAh cm⁻², which is 6 times and 2 times longer than that of unmodified Zn and NTP@Zn symmetrical cell, respectively. Moreover, the critical current density of NTP-C@Zn symmetrical cell, at which the cell undergoes short circuit, is above 100 mA cm⁻². Furthermore, the full cell based on NTP-C-modified anode and α-MnO₂ cathode exhibits a stable long-term cycling performance and a superior capacity retention for 1200 cycles under 5 C, among which 1 C equals to 308 mAg⁻¹.

2. Materials and Methods

2.1. Raw Materials. The materials used are as follows: citric acid (99.5%, Shanghai D&B Biological Science and Technology Co., Ltd.), sodium acetate (CH₃COONa·3H₂O, 99.0%, YongDa Chemical), titanium butoxide (TBOT, 99.0%, Macklin), phosphoric acid (85 wt% solution of H₃PO₄ in H₂O, Meryer), zinc sulfate (ZnSO₄, 99.5%, Aladdin), manganese sulfate monohydrate (MnSO₄·H₂O, 99.0%, Aladdin), potassium permanganate (KMnO₄, GR, Sinopharm Chemical Reagent Co., Ltd.), and hydrochloric acid (HCl, 36.0–38.0 wt%, AR, Beijing Tongguang Fine Chemical Company). Zn foils (99.95%) with the thickness of 0.1 mm were purchased from Bodun Metal.

2.2. Synthesis of NTP and NTP-C. NTP and NTP-C were obtained by a simple sol-gel method [34]. Firstly, 2 mmol citric acid, 2 mmol titanium butoxide (TBOT), 1 mmol CH₃COONa·3H₂O, and 3 mmol H₃PO₄ were dissolved in 20, 20, 10, and 10 mL ethyl alcohol, respectively. Then, the last three solutions were added to the first one sequentially. After mixing the solution at 80°C by magnetic stirring at 500 rpm, a gel-like product was obtained. Then, the gel-like product was dried at 80°C overnight under vacuum. At last, the dry gel was ground and annealed to form NTP and NTP-C. NTP was obtained after annealing at 350°C for 4 hours and then at 750°C for 8 hours in muffle oven with a heating rate of 2°C per minute, while NTP-C was generated with the same annealing procedure in the tube furnace with argon atmosphere protection.

2.3. Preparation of NTP@Zn and NTP-C@Zn. Zn foil with a thickness of 0.1 mm was cleaned with ethanol before using. The slurries were prepared by mixing 180 mg of NTP or NTP-C and 20 mg of polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) at 300 rpm for 8 hours by magnetic stirring, in which the amount of NMP was 320 μL or 600 μL, respectively. Then, the slurry was blended onto Zn foil and dried at 80°C overnight in the vacuum oven to obtain the NTP@Zn or NTP-C@Zn.

2.4. Synthesis of α-MnO₂. α-MnO₂ was prepared by a simple hydrothermal method [35]. At first, 0.6078 g KMnO₄ was dissolved in 78.3 mL deionized water. Then, 1.7 mL HCl was added into the solution. After stirring for 10 minutes, the above solution was transferred into a 100 mL Teflon-lined autoclave and then heated at 140°C for 12 h. After cooling down to room temperature, the sample was separated via centrifugation and washed with deionized water for 5-7 times until obtaining neutral liquid supernatant. Finally, the α-MnO₂ was collected after drying in the vacuum oven overnight.

2.5. Characterizations. X-ray diffraction (XRD) patterns were recorded by using a Rigaku X-ray diffractometer (Smartlab SE, Japan) with Cu-Ka radiation (λ = 1.54182 Å) and a scan rate of 5°/min between 5° and 80°. The morphologies and EDS mapping of power samples and electrodes were obtained from a field-emission scanning electron microscope (Zeiss Supra55, Germany). The TEM, HRTEM,
and elemental mapping images were acquired by a transmission electron microscope (JEM-2100F, Japan). The nitrogen adsorption-desorption tests were carried out by NOVA2000e to investigate the surface area and average pore diameter of NTP and NTP-C powder samples. TGA data was obtained from 50 to 800°C at a heating speed of 10°C min⁻¹ on TGA/DSC 3+ manufactured by Mettler Toledo. Elemental analysis was performed by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent ICP OES730, USA). Contact angle was tested on a contact angle measuring equipment manufactured by Surfatech Co., Ltd.

2.6. Cell Assembly and Electrochemical Measurements. CR-2025 type coin cells were used for all electrochemical measurements. The symmetrical cells were assembled with two identical electrodes with a diameter of 11 mm, glass fiber separator with a diameter of 19 mm, and moderate amount of 2 M ZnSO₄ and 0.2 M MnSO₄ electrolyte. The full cells used α-MnO₂ as cathode, bare Zn, NTP@Zn, or NTP-C@Zn as anode, glass fiber as separator, and 2 M ZnSO₄ and 0.2 M MnSO₄ as electrolyte. Of note, α-MnO₂ electrodes were fabricated by a simple drop casting approach. The cathode slurry was composed of the as-prepared α-MnO₂, super P, and PVDF with a weight ratio of 70: 20:10. After mixing in NMP at 300 rpm for 8 hours by magnetic stirring, the slurry was dropped onto carbon cloth disks with a diameter of 11 mm and dried under vacuum at 80°C overnight. The mass loading of α-MnO₂ was ~0.6 mg cm⁻². The galvanostatic Zn plating/stripping tests of symmetrical cells and the charge/discharge capacity and cyclic stability of full cells were investigated on LAND CT2001A. Electrochemical impedance spectra (EIS) was tested via CHI660E electrochemical workstation with frequency from 0.01 Hz to 100 kHz and an amplitude of 5 mV. Cyclic voltammetry (CV) was carried out on CHI660E electrochemical workstation between 0.8 and 1.8 V (vs. Zn/Zn²⁺). For evaluating corrosion performance, a three-electrode system was used to perform Tafel tests on CHI660E electrochemical workstation, with bare Zn, NTP@Zn, or NTP-C@Zn as working electrode, Pt as counter electrode, and Ag/AgCl as reference electrode. Chronoamperometry (CA) tests were conducted to investigate the Zn deposition behavior on different electrodes in symmetrical cells at a constant overpotential of ~150 mV within 120 s.

3. Results and Discussion

3.1. Material Characterization. The fabrication processes about NTP and NTP-C samples are depicted in Figure 1. NTP sample is represented by the white powder and the black dots stand for NTP-C sample. The crystal structure in Figure 1 shows that the as-synthesized NTP is constructed from octahedral TiO₆ and tetrahedral PO₄ through corner sharing [36], and previous studies have shown that Zn²⁺ migration can take place in the voids formed by eight oxygen atoms [37]. Owing to the dual-function protective layer, the distribution of electric field and Zn²⁺ flux can be regulated simultaneously.
To analyze the crystalline structures of as-prepared samples, X-ray diffraction (XRD) measurement was performed. As illustrated in Figure 2(a), the sharp diffraction peaks can be assigned to NaTi$_2$(PO$_4$)$_3$ (JCPDS No. 33-1296), suggesting the successful synthesis of the NASICON materials with R-3c space group [38]. The peak positions of the NTP and NTP-C samples are identical, indicating that the introduced carbon does not affect the crystalline structure of NaTi$_2$(PO$_4$)$_3$. According to the TGA result, the carbon content in the NTP-C sample is about 7.25 wt% (Figure 2(b)).

To analyze the elemental content of the as-prepared samples, inductively coupled plasma optical (ICP-OES) was conducted. As shown in Table S1, the mass percentages of Na, Ti, and P are 5.7377%, 22.3457%, and 22.8807%, respectively, and the stoichiometry of NTP can be determined as NaTi$_2$(PO$_4$)$_3$. For the elemental analysis of NTP-C (Table S2), the mass percentages of Na, Ti, and P are 3.6387%, 15.0159%, and 15.8130%, respectively, which can also be assigned to NaTi$_2$(PO$_4$)$_3$. The graphitization degree of the carbon coating was analyzed by Raman. The Raman spectra of NTP-C (Figure 2(c)) displays two characteristic peaks at 1332 cm$^{-1}$ and 1596 cm$^{-1}$, which corresponds to D band and G band of carbon as previous report [39], respectively. Typically, the D band is ascribed to disordered amorphous carbon with defects, and the G band is attributed to crystalline graphitic carbon [40, 41]. The relative intensity ratio of D band and G band ($I_D/I_G$) of NTP-C is about 1.016, which implies that the carbon coating and matrix from NTP-C powder have a mixed crystalline and amorphous property. Since carbon-based materials, especially the materials with defects enable energetically favorable nucleation sites [42], the NTP-C protective layer possesses the potential to provide abundant Zn deposition sites. The nitrogen adsorption-desorption isotherms as displayed in Figure 2(d) demonstrate that the specific surface area of NTP is 15.7 m$^2$g$^{-1}$. Moreover, the pore size distribution curves (BJH image) in Figure 2(e) describe that the NTP nanoparticles possess typical mesoporous structure with an average pore diameter of 32.9 nm. NTP-C exhibits a larger specific surface area of 131.637 m$^2$g$^{-1}$ and a smaller pore diameter of 9.7 nm, which may be associated with the formation of carbon coating and beneficial to reduce the local current density.

Scanning electron microscopy (SEM) and transmission electron microscope (TEM) were applied to characterize the morphologies of NTP and NTP-C. Uniform sphere-like NTP nanoparticles with diameters of 80-100 nm are observed, as shown in Figure 3(a). Because the citric acid used in the synthesis process not only acts as a chelating agent to control particles growth but also acts as a carbon source to contribute to the formation of 3D carbon matrix [36], the NTP-C nanoparticles are evenly distributed onto the carbon matrix with a particle diameter of about 30 nm (Figure 3(b)). The uniform distribution of the composite
elements of NTP and NTP-C is confirmed by EDS mapping, as shown in Figure S1 and Figure S2. Moreover, the TEM images of NTP and NTP-C in Figure S3 and Figure 3(c) also display that the microsphere particles are in the sizes about 100 nm and 30 nm, respectively. The high-resolution TEM image of NTP-C as shown in Figure 3(e) exhibits that the nanoparticles are distributed into the amorphous carbon matrix and encapsulated by a homogeneous carbon coating with a thickness about 5 nm. Furthermore, the lattice fringes of NTP and NTP-C are measured as 0.436 and 0.435 nm (Figures 3(d) and 3(e)), which can be assigned to the interplanar spacing of the (104) plane of hexagonal NaTi2(PO4)3 [36]. The elemental mapping images in Figure S3 and Figure 3(f) also demonstrate the uniform distribution of elements Na, Ti, O, and P and Na, Ti, O, P, and C for NTP and NTP-C.

3.2. Electrochemical Performance and Protective Mechanisms of Artificial Layers. To demonstrate the function of the NTP-C protective layer in regulating Zn deposition, we bladed NTP and NTP-C slurries onto the surface of Zn foils as described in Materials and Methods. The cross-sectional SEM images in Figures 4(a) and 4(b) show that the average thickness of the both protective layers is about 30 μm, therefore the difference of the electrochemical properties of the electrodes is mainly caused by the inherent properties of the applied artificial layers, without the influence of thickness. To evaluate the wetting performance of electrolyte on different substrates, the contact angles were measured by dropping 2 M ZnSO4+0.2 M MnSO4 electrolyte onto the surface of bare Zn, NTP@Zn, and NTP-C@Zn. As shown in Figures 4(c)–4(e), the contact angles of the electrolyte drops on bare Zn, NTP@Zn, and NTP-C@Zn are 85°, 24°, and 108°, respectively. The large value of the contact angle of NTP-C@Zn indicates that the NTP-C protective layer provides an isolation function between water and Zn. Therefore, the NTP-C layer can reduce the direct contact between water and Zn. Furthermore, to analyze the ability of NTP-C on preventing corrosion, linear polarization measurements were performed on a three-electrode system with an electrolyte of 2 M ZnSO4. In Figure 4(f), NTP-C@Zn exhibits the highest corrosion potential (−0.987 V vs. Ag/AgCl) among all the three kinds of electrodes, while the corrosion potentials of bare Zn or NTP@Zn electrodes are −1.008 V and −1.006 V, respectively. According to previous report [43], the higher corrosion potential represents the less tendency
to occur corrosion reaction. It clearly verifies that the NTP-C coating can suppress corrosion and protect Zn anode owing to its isolation function.

To evaluate the electrochemical performance of the modified Zn anodes, galvanostatic cycling was conducted on the symmetrical cells with bare Zn, NTP@Zn, and NTP-C@Zn electrodes at 1 mA cm\(^{-2}\)/1 mAh cm\(^{-2}\). Demonstrated in Figure 5(a), the symmetrical cell with NTP-C@Zn electrodes displays superior stability with a cycle life of over 600 h, while the lifespans of the symmetrical cell with bare Zn and NTP@Zn electrodes are less than 100 h and 250 h, respectively. Figures 5(c)–5(e) exhibit the detailed voltage profiles during different cycle numbers, and there are no significant changes of the voltage profiles of NTP-C@Zn symmetrical cell in different cycle periods, further indicating that the NTP-C artificial layer has the ability to improve the cyclability of Zn anode. In addition, the carbon-coated NTP protective layer plays an important role in reducing polarization. As shown in the partially enlarged voltage profiles of the first charge/discharge cycle of all the three symmetrical cells (Figure 5(b)), the NTP-C@Zn symmetrical cell demonstrates an ultralow nucleation overpotential of 37.2 mV, which is represented by the gap between the sharp tip and the platform [44], whereas the corresponding values of bare Zn and NTP@Zn are 61.3 mV and 45.6 mV, respectively. In addition, the mass transfer overpotential is represented by the voltage value at platform position [44]. The overpotentials of bare Zn, NTP@Zn, and NTP-C@Zn symmetrical cells are 45.0 mV, 26.0 mV, and 22.3 mV, respectively, indicating that NTP-C can provide a better zincophilicity and superior interfacial properties, reducing the energy barrier for Zn deposition [44]. Moreover, the capacity-voltage profiles of bare Zn, NTP@Zn, and NTP-C@Zn symmetrical cells at the 25th cycle in galvanostatic cycling are depicted in Figures 5(f)–5(h). The NTP-C@Zn symmetrical cell demonstrates a superior plating/stripping polarization (18.9 mV), lower than those of bare Zn and NTP@Zn symmetrical cells (38.4 mV and 21.4 mV, respectively), suggesting an improved Zn\(^{2+}\) transport kinetics [45] during Zn\(^{2+}\) plating and stripping process in NTP-C layer. Furthermore, the cycling performance of graphite@Zn symmetrical cell at the same current density and areal capacity was also investigated to illustrate the protective ability of carbon material by itself. As shown in Figure S4(a), the lifespan of the graphite-protected electrode is less than 200 h, indicating that the
enhancement of the electrochemical performance in NTP-C@Zn symmetrical cell is due to the synergistic function of NTP and carbon coating.

To further comprehend the impact of protective layers on Zn deposition, the morphological evolution of Zn plating/striping on electrodes, including bare Zn, NTP@Zn, and NTP-C@Zn in symmetrical cells, was investigated via SEM. To avoid the influence of glass fiber separator, the cycled electrodes were rinsed by deionized water for 3-5 times and then vacuum dried. Figure 6(a), I exhibits the pristine Zn surface before cycling. As shown in Figure 6(a), II, the surface of the bare Zn foils after 20 cycles is messy, with the morphology of loose packed hexagonal thin plate. Prolongating the cycle number to 50, irregular and stacked dendrites can be detected in Figure 6(a), III. The larger dendrites and by-products occupy the surface of metallic Zn, which can puncture the separator and cause cell failure eventually. On the other hand, by-products are confirmed by EDS mapping, as shown in Figure S5. The bare Zn electrode after cycling exhibits uniform elements distributions, containing Zn, O, and S, indicating the formation of by-products composed of Zn₅SO₄(OH)ₓ·xH₂O. They may increase the tortuosity and irregularity of the anode/electrolyte interface, which can lead to more serious hydrogen evolution reaction and even resulting in cell expansion failure [46].

Figure 5: (a) Galvanostatic cycling performance about different symmetrical cells (Zn//Zn, NTP@Zn//NTP@Zn, and NTP-C@Zn//NTP-C@Zn) at 1 mA cm⁻²/1 mAh cm⁻². (b) Comparison of the first cycle voltage patterns in different symmetrical cells. (c–e) Detailed voltage profiles during different cycling periods. The curve of bare Zn cell is not displayed in (c), and the profiles of bare Zn and NTP@Zn cells are not displayed in (d), due to the short circuit. The capacity-voltage profiles of (f) bare Zn, (g) NTP@Zn, and (h) NTP-C@Zn symmetrical cells at a 1 mA cm⁻²/1 mAh cm⁻² at the 25th cycle.
Figure 6: (a) SEM images of electrodes: (I) bare Zn, (II) bare Zn after 20 cycles, (III) bare Zn after 50 cycles, (IV) bare Zn after short circuit, (V) pristine NTP@Zn, (VI) the surface of NTP@Zn after 20 cycles, (VII) the surface of NTP@Zn after 50 cycles, (VIII) the surface of Zn foil after removing NTP coating (NTP@Zn electrode was collected after 20 cycles), (IX) pristine NTP-C@Zn, (X) the surface of NTP-C@Zn after 20 cycles, (XI) the surface of NTP-C@Zn after 50 cycles, and (XII) the surface of Zn foil after removing NTP-C coating (NTP-C@Zn electrode was collected after 20 cycles). (b) Schematic illustrations of the Zn deposition process on bare Zn, NTP@Zn and NTP-C@Zn foils. (c) SEM and EDS images of (I) NTP@Zn and (II) NTP-C@Zn after 50 cycles at a low magnification. The labeled part by the red circle in (I) is aggregated protrusion.

The SEM images of NTP@Zn electrodes in different states are shown in Figure 6(a), V–VIII. In Figure 6(a), V, NTP nanoparticles were coated evenly on the surface of metallic Zn before cycling. After 20 cycles, the surface of the electrode became fluctuated as shown in Figure 6(a), VI without the irregular Zn deposition. Compared with the deposited Zn on bare Zn anode, a relatively flat surface with grain boundary which is different from the original Zn morphology can be observed after removing the NTP coating layer (Figure 6(a), VIII), implying that the artificial layer enables refined and uniform Zn^{2+} flux to modulate Zn deposition by the ionic channels of NTP [37]. Figure 6(c), I exhibits the morphology of NTP@Zn after 50 cycles at a low magnification. It is evident to see that the deposited Zn agglomerates and forms protrusions on the NTP surface due to the limited mechanical properties and the increased Zn deposition loadings, which lead to NTP coating collapse and the absence of the protective function. The elemental mapping images in Figure 6(c), I show that the protrusion contains Zn, O, and S elements. However, in the flat region of the electrode, negligible Zn signal can be observed and the P and Ti elements are uniformly distributed, indicating the formation of Zn dendrites and by-products on the NTP@Zn after cycling. Furthermore, the partially enlarged picture of the protrusion shown in Figure 6(a), VII displays chaotic Zn deposition. In brief, the above images demonstrate that Zn deposition mainly occurs between the metal foils and the NTP coating. However, once a large amount of Zn is deposited beneath the coating, the protective effect of NTP is destroyed.

Figure 6(a), IX–XII reveal the morphology revolution of NTP-C@Zn electrodes. Figure 6(a), IX shows that NTP-C artificial layer covered the surface of metallic Zn before cycling, which consisted of aggregated NTP nanoparticles. After 20 cycles, the NTP-C coating maintained stable and showed a similar morphology to that before cycling with a small amount of deposited Zn (Figure 6(a), X). Removing the NTP-C coating layer after 20 cycles, Figure 6(a), XII presents a smooth and dense Zn deposition layer, implying part of the Zn^{2+} flux is homogenized by the ionic channels of NTP and guided to the surface of Zn metal, on which the reduction reaction occurs. Observing the morphology at a low magnification, there are no aggregated Zn bumps on NTP-C surface, and the EDS images in Figure 6(c), II show uniform element distribution. As depicted in Figure 6(a), XI, under high magnification, Zn was deposited on the surface of NTP-C nanoparticles and generated a comparable flat surface with smaller size and horizontally grown dendrites, which is due to the abundance nucleation sites delivered by NTP-C. In addition, NTP-C provides increased surface area and defects from the introduced carbon coating and adjusts the electric field distribution and induces Zn deposition onto
the particles surface. Therefore, the synergistic strategy combining the protective functions of NTP and carbon enables dual uniform Zn deposition layers above and below the coating.

In order to clarify the protective effect of carbon material, Figure S4(b) and S4(c) show the morphologies of the graphite-coated electrodes before and after cycling. In Figure S4(b), the graphite layer is uniformly built on the surface of metallic Zn. After cycling, a large number of dendrites and by-products can be observed on the electrode surface (Figure S4(c)), suggesting that the performance improvement by only graphite coating is insufficient.

Based on the observations of the SEM images, we proposed the illustrations of Zn deposition process on different electrodes, including bare Zn, NTP@Zn, and NTP-C@Zn shown in Figure 6(b). Without the protective layers, Zn dendrites grow on the surface of Zn foil uniformly and loosely, leading to short circuit ultimately. NTP can suppress the Zn dendrites to an extent via homogenizing Zn$^{2+}$ flux. Unfortunately, the lifespan under the NTP protection is limited to 250 h due to the Zn protrusion and the collapse of NTP coating. By combining the advantages of NTP and carbon, NTP-C provides dual Zn deposition layers and further prolongs the lifespan of symmetrical cell to more than 600 h.

In order to further reveal the mechanisms of NTP-C@Zn in suppressing dendrites growth, the structures of bare Zn and NTP-C@Zn anodes before and after 20 cycles were investigated by XRD. In Figure 7(a), the peaks in the XRD pattern of bare Zn before cycling can be assigned to the standard card of Zinc (JCPDS No. 04-0831). After 20 cycles, strong signals at 8.1 degrees of Zn$\text{SO}_4\text{(OH)}_6\cdot3\text{H}_2\text{O}$ (JCPDS No. 39-0688) are detected in the XRD pattern, implying the formation of by-products, which is consistent with the EDS mapping results (Figure S5). Furthermore, the reaction on the anode surface can be explained by the following equations [45]:

\[
\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad (1)
\]

\[
\text{H}_2\text{O} + e^- \rightarrow \frac{1}{2}\text{H}_2(g) + \text{OH}^- \quad (2)
\]
4Zn^{2+} + 6OH^{-} + SO_4^{2-} + xH_2O \rightarrow Zn_4SO_4(OH)_{6+x}H_2O \ (3)

The XRD pattern of pristine NTP-C@Zn (Figure 7(b)) confirms the successful construction of NTP-C layer on the surface of Zn foils. After 20 cycles, there are no significant changes in the peak positions, and only a new weak diffraction peak at 9.5 degrees of Zn_4SO_4(OH)_{6+x}H_2O (JCPDS No. 39-0689) can be observed. Compared with the intense characteristic peak of Zn_4SO_4(OH)_{6+5}H_2O in the XRD pattern of the cycled bare Zn anode, the weak by-product peak on the cycled NTP-C@Zn surface shows that the NTP-C protective layer is able to suppress the occurrence of side reactions. To evaluate the surface of Zn metal in the cycled NTP-C@Zn, the NTP-C protective layer was removed and XRD measurement was performed on the exposed surface to detect the crystalline structure.

Figure 7(b) shows that the diffraction peaks of the XRD pattern of the newly exposed surface are assigned to pure Zn metal, without any diffractions of NASICON structure and by-products, indicating that NTP-C can reduce side reactions by isolating water from the Zn metal surface. The XRD patterns of NTP-C@Zn with different deposited capacities of 0, 0.05, 0.1, 0.2, and 0.5 mAh cm\(^{-2}\) further confirm the stability of NTP-C@Zn. As presented in Figure 7(c), besides the characteristic peaks that can be indexed into NTP, there are also peaks of Zn substrate located around 39 degrees. No obvious peaks of by-products were detected in these patterns, indicating that the structure of NTP-C@Zn can remain stable under different deposited capacities.

According to the previous study [47], the dendritic issues and side reactions will take place severely when the current...
density is increased, which may cause shortened lifespan and enlarged voltage hysteresis. To investigate the protective function of the NTP-C coating at high current density, we tested symmetrical cells with NTP-C@Zn electrodes under the current density of 5, 10, 20 mA cm$^{-2}$ with areal capacity of 1 mAh cm$^{-2}$, respectively. Displayed in Figure 8(a), the NTP-C@Zn symmetrical cell exhibits a lifespan of about 400 h at 5 mA cm$^{-2}$. Furthermore, the NTP-C@Zn symmetrical cell can work over 200 h at 10 mA cm$^{-2}$ (Figure 8(b)). Even at a high current density of 20 mA cm$^{-2}$, the NTP-C@Zn symmetrical cell still presents a stable cycling with a lifespan of 160 h (Figure 8(c)) owing to the synergistic contribution of NTP and the introduced carbon. For the cells cycled with current densities above 5 mA cm$^{-2}$, the polarization voltage of the cells first increased and then decreased. As shown in Figure 8(a), the symmetrical cell exhibits relatively stable cycling performance at the initial stage, and the stable cycling process can last for nearly 300 h at 5 mA cm$^{-2}$. With the increase of the cycling time, the polarization voltage shows an increasing trend, but the cell can continue to work without the occurrence of short circuit failure until about 417 h (as shown in Figure S6d). Similar cycling processes can also be observed at higher current densities (10 mA cm$^{-2}$ and 20 mA cm$^{-2}$). The NTP-C@Zn symmetrical cells can maintain stable cycling within 200 h and 160 h at 10 mA cm$^{-2}$ and 20 mA cm$^{-2}$, respectively, followed by significant polarization increase. The phenomenon of the voltage increasing has also been observed and reported in the previous articles [48–50], which is mainly attributed to the occurrence of side reactions [51]. As for the cycling performance at a low current density, a stable cycling of Zn plating/stripping lasts over 860 h with a low overpotential (20 mV) at 0.5 mA cm$^{-2}$/0.5 mAh cm$^{-2}$, as shown in Figure 8(d). Figure S6g and h demonstrate that the polarization voltage of the cell is relatively stable and the failure of the cell is mainly due to short circuit. Compared with previous reported modification strategies [21, 23, 24, 28, 37, 52–59], NTP-C@Zn symmetrical cell possess satisfying performance, as displayed in Figure 8(e). Since the protective strategy adopted in this work is not the best in cycling time (Table S3), there is still a room to further improve the lifespan of NTP-C@Zn symmetrical cells. The dendrite suppression ability of NTP-C coating layer was also tested under higher current densities, which are 1, 2, 5, 10, 20, 40, 60, 80, and 100 mA cm$^{-2}$ with areal capacity of 1 mAh cm$^{-2}$. The voltage profile shown in Figure 8(f) suggests that the NTP-C protective layer can help achieve a stable
cycling even at 100 mA cm\(^{-2}\) with a polarization voltage of about 490 mV. When the current density is gradually decreased, the cycling performance of the NTP-C@Zn symmetrical cell can return to the original state. In addition, based on a method reported by Adams et al. [60], the CE was tested on Zn//Cu cells to investigate the utilization of Zn during the process of Zn plating/stripping. As illustrated in Figure 8(g), the CE of the NTP-C@Zn//Cu cell is 92.8% at 0.38 mA cm\(^{-2}\), while the values of bare Zn//Cu and NTP@Zn//Cu is 90.2% and 91.0%, respectively. These results demonstrate that NTP-C provides an effective protective layer for stable Zn plating/stripping under high current density and benefits for the utilization of Zn during cycling.

In Figure 9(a), the impedance of the Zn//Zn symmetrical cell is nearly 5 times larger than that of the NTP-C@Zn//NTP-C@Zn symmetrical cell before cycling, which is due to the severe side reactions that bring about the generation of electron-insulating metal oxide/hydroxide. Furthermore, chronoamperometry (CA) tests were conducted to study the Zn deposition behavior on bare Zn and NTP-C@Zn at a constant overpotential of \(-150\) mV within 120 s. The changes in current density with time can reflect the surface variation and the process of nucleation [61]. As exhibited in Figure 9(b), the current density keeps increasing for 120 s in the Zn//Zn symmetrical cell, implying the increase of effective electrode area under rampant 2D diffusion. In order to reduce the surface energy, the absorbed \(\text{Zn}^{2+}\) is inclined to aggregate and form rough and dendritic Zn deposits due to the tip effect during the lateral diffusion process (Figure 9(c)). In contrast, the NTP-C coated Zn electrode displays a short nucleation and 2D diffusion period within 10 s, followed by a 3D diffusion process represented by a stable current density (Figure 9(b)). The constrained 2D diffusion brings about a unaggregated interface shown in Figure 9(d), suggesting the adsorbed \(\text{Zn}^{2+}\) ions appear to be locally reduced to \(\text{Zn}^0\) with constrained 2D behavior [31], which is due to the increased energy barrier for \(\text{Zn}^{2+}\) lateral migration and the abundant nucleation sites of the introduced NTP-C coating.

### 3.3. Electrochemical Performance in Full Cells.

To evaluate the practical protective effect of NTP-C in the full cell, the bare Zn and NTP-C@Zn anodes were matched with \(\alpha\)-MnO\(_2\), and the electrochemical performance was investigated. The electrolyte used in the full cell consists of 2 M ZnSO\(_4\) and 0.2 M MnSO\(_4\), in which MnSO\(_4\) was added to inhibit the dissolution of Mn\(^{2+}\) from \(\alpha\)-MnO\(_2\) [62]. \(\alpha\)-MnO\(_2\) was prepared by a facile hydrothermal method from a previous report [35]. Furthermore, the purity of synthesized material was verified by XRD characterization as shown in Figure S7. Figure 10(a) displays two similar cyclic

![Figure 10](image-url)
voltammetry (CV) curves with 2 couples of obvious redox peaks, indicating that the constructed protective layer does not induce new side reactions [63]. Moreover, the NTP-C@Zn//α-MnO₂ full cell exhibits higher current than bare Zn//α-MnO₂ cell, representing a higher electrochemical reactivity [13]. Compared with bare Zn//α-MnO₂, NTP-C@Zn//α-MnO₂ full cell exhibits higher reduction voltages and lower oxidation voltages with smaller overpotential gaps. The artificial NTP-C provides a higher electrochemical reactivity and smaller polarization, suggesting the enhanced reaction kinetics in NTP-C@Zn//α-MnO₂ cells [64]. It is in accordance with the EIS results, as demonstrated in Figure 10(d). NTP-C@Zn//α-MnO₂ full cell provides the lower charge-transfer resistance ($R_Ω$), which is attributed to the stabilized NTP-C interface with less by-products [13].

Figure 10(b) shows the rate performance of full cells composed of Zn and NTP-C@Zn anodes, respectively, at the current density from 1 C to 30 C and back to 1 C eventually (1 C = 308 mA g⁻¹). The NTP-C@Zn//α-MnO₂ cell delivers a series of higher average discharge capacities of 209, 201, 170, 138, 111, and 94 mA h g⁻¹ at different current density of 1 C, 2 C, 5 C, 10 C, 20 C, and 30 C, respectively. After the current density returning to 1 C, the discharge capacity returns to above 200 mA h g⁻¹, confirming a satisfied reversibility contributed by the smaller charge-transfer resistance of NTP-C, while the capacity of bare Zn//α-MnO₂ cell decays fast especially in high rate because of the limited charge-transfer ability [37]. Figure 7(c) compares the charge/discharge curves of bare Zn//α-MnO₂ and NTP-C@Zn//α-MnO₂ full cells at the 10th cycle under 1 C. The charge/discharge curves with protective layer are nearly the same with the curve of bare Zn//α-MnO₂ cell, while the voltage hysteresis is reduced after introducing NTP-C.

Figure 10(e) demonstrates the long cycle performance of full cells at 5 C for 1200 charge/discharge cycles, among which 1 C equals to 308 mA g⁻¹. The NTP-C@Zn//α-MnO₂ full cell delivers a superior capacity of 116.3 mA h g⁻¹ after 1200 cycling with a capacity retention of 76.6%. Furthermore, the CE of NTP-C@Zn//α-MnO₂ is nearly 100%, while the capacity of bare Zn//α-MnO₂ full cell decays below 50 mA h g⁻¹ within 300 cycles due to the continuous side reactions and corrosion.

4. Conclusions

In summary, a protective layer composed of carbon-coated NTP particles with a large specific surface area was constructed onto the surface of Zn foil to regulate Zn deposition, which can effectively suppress the generation of Zn dendrites and side reactions. Considering that Zn dendrites are caused by nonuniform metal deposition under uneven electric fields and Zn²⁺ ion flux, NTP-C layer offers abundant Zn deposition sites for homogeneous nucleation and regulates the distribution of electric field and Zn²⁺ flux simultaneously during the Zn plating/striping process. Combining a synergistic strategy based on two protective mechanisms from carbon and NTP, the NTP-C@Zn symmetrical cell demonstrates a prolonged lifespan over 600 h (6 times and 2 times longer than bare Zn and NTP@Zn symmetrical cell, respectively) and a reduced nucleation overpotential of 37.2 mV and plating/striping polarizations of 18.6 mV at 1 mA cm⁻²/1 mAh cm⁻². Furthermore, it still can achieve stable cycling even at a harsh condition (100 mA cm⁻²). Moreover, the full cell with NTP-C-modified anode and α-MnO₂ cathode enables 1200 cycles under 5 C (1 C = 308 mA g⁻¹) with a capacity retention of 76.6%, which also confirms the advantages from NTP-C. This work combines two protective mechanisms and offers a new inspiration for the practical applications of Zn metal anode in ZIBs.

Data Availability

All data presented in the paper and the supporting information are available from the corresponding author upon reasonable request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Authors’ Contributions

J.J.Y., R.Z., Y.B., and C.W. proposed the research idea and designed the experimental scheme. J.J.Y conducted the experiments and analyzed the data. Y.H.W synthesized α-MnO₂ and participated in the scientific discussions. R.Z., Y.B., and C.W. supervised the research work. The manuscript was written by J.J.Y under the assistance of R.Z., Y.B., and C.W. All authors discussed the results and have given approval to the manuscript.

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Supplementary Materials

EDS images of NTP; EDS images of NTP-C; elemental contents of NTP from ICP results; elemental contents of NTP-C from ICP results; TEM and elemental mapping images of NTP; galvanostatic cycling performance at 1 mA cm⁻²/1 mAh cm⁻² in graphite@Zn//graphite@Zn symmetrical cell and SEM images of graphite@Zn electrodes: before cycling and after cycling; the EDS images of bare Zn electrode after cycling; XRD patterns of α-MnO₂; and comparison of cycling performance between NTP-C protective layer and previous reported modification strategies in symmetrical cell (Supplementary Materials). (Supplementary Materials)

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