

Article

Contents lists available at ScienceDirect

Acta Physico-Chimica Sinica



journal homepage: www.sciencedirect.com/journal/acta-physico-chimica-sinica

Sulfur-doped carbon dots: a novel bifunctional electrolyte additive for high-performance aqueous zinc-ion batteries \star



Qianli Ma, Tianbing Song, Tianle He, Xirong Zhang, Huanming Xiong 🐌

Department of Chemistry, Shanghai Key Laboratory of Electrochemical and Thermochemical Conversion for Resources Recycling, Fudan University, Shanghai, 200438, China

ARTICLE INFO

Keywords: Carbon dot Zinc-ion battery Stable zinc anode Crystal plane regulation Solvation shell

ABSTRACT

Aqueous zinc-ion batteries (AZIBs) have gained considerable attention as next-generation energy storage devices due to their inherent safety, environmental friendliness, and cost-effectiveness. However, their widespread application is severely hampered by uncontrolled zinc dendrite growth and detrimental side reactions (e.g., hydrogen evolution, corrosion, and passivation), which lead to reduced Coulombic efficiency and shortened cycle life. Current strategies to improve zinc anode stability mainly focus on artificial interface coatings, electrode structure design, and electrolyte optimization. Among these approaches, electrolyte additive engineering is considered the most promising for practical applications due to its simplicity, low cost, and excellent scalability. Nevertheless, conventional additives (including metal ions, polymers, and surfactants) typically address only single issues (either dendrite suppression or side reaction mitigation), failing to achieve synergistic effects. In this work, we developed sulfur-doped carbon dots (S-CDs) as a novel bifunctional electrolyte additive to significantly enhance AZIB performance. The carbon dot additive was synthesized via a facile calcination method, followed by systematic characterization of its structure and properties using methods such as fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and density functional theory (DFT) calculations. Comprehensive electrochemical evaluations were conducted to investigate the influence of S-CDs on zinc deposition behavior and overall battery performance. Experimental results demonstrate the successful synthesis of sulfur-doped carbon dots with abundant surface functional groups. During battery operation, the strong binding affinity between S-CDs and Zn^{2+} effectively reconstructs the Zn^{2+} solvation shell, reducing water molecule content and thereby minimizing electrode corrosion and side reactions caused by interfacial active water molecules. Moreover, the S-CDs induce the formation of stable (002) crystallographic planes that continuously renew during plating/stripping cycles, with particularly pronounced effects under high current densities, significantly enhancing the structural stability of the electrode. The synergistic effect of these dual functions leads to remarkable improvement in zinc electrode performance and ultimately endows the battery with ultra-long cycling life. Benefiting from the positive effects of the carbon dot additive, the symmetric cell achieves exceptional stability for nearly 2000 h at a high current density of 10 mA cm⁻², far outperforming conventional electrolyte systems. Furthermore, both Zn||NH₄V₄O₁₀ and Zn||MnO₂ full cells exhibit superior electrochemical performance and significantly enhanced cycling stability, confirming the excellent compatibility of the carbon dot additive with various cathode materials. This study provides novel insights and fundamental theoretical guidance for developing high-performance AZIBs, representing a significant advancement in sustainable energy storage technologies.

1. Introduction

The global energy crisis and environmental issues have compelled countries worldwide to gradually transition towards clean and renewable energy sources. Among these, renewable energies such as wind and solar power are characterized by intermittency and instability, making the development of new large-scale energy storage technologies crucial for their utilization [1,2]. Aqueous zinc-ion batteries have

* Corresponding author. E-mail address: hmxiong@fudan.edu.cn (H. Xiong).

https://doi.org/10.1016/j.actphy.2025.100106

Received 16 April 2025; Received in revised form 13 May 2025; Accepted 22 May 2025 Available online 23 May 2025

1000-6818/© 2025 College of Chemistry and Molecular Engineering, Peking University. Published by Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

 $^{^{\}star}$ The project was supported by the National Natural Science Foundation of China (U24A20565, 21975048).

garnered widespread attention due to their safety, environmental friendliness, and low cost. The zinc electrode boasts an exceptionally high volumetric capacity density (5822 mAh•cm⁻³) and a low price (approximately 1 % of that of lithium electrodes), which is highly advantageous for constructing large-scale energy storage devices [3]. However, current aqueous zinc batteries face challenges such as dendrite growth and various harmful side reactions, which severely impact the cycling stability of the batteries and hinder their commercialization process [4,5].

Constructing a stable zinc anode is a core challenge in the field of aqueous zinc batteries. In previous studies, artificial coatings have been widely used for anode protection, but the external coatings are prone to detachment and failure during cycling. Recent findings indicate that the crystal plane orientation during electrodeposition significantly influences the morphology of zinc deposition [6,7]. In the hexagonal close-packed structure of zinc metal, the (101) plane forms an angle of 30° – 70° with the substrate, while the (100) plane forms an angle of 70° – 90° . These large-angle arrangements are prone to dendrite growth. In contrast, the (002) plane tends to align at small angles of 0° -30°, which helps form a uniform and dense deposition layer, thereby constructing a stable electrode interface. Adjusting the crystal plane orientation of zinc electrodes has evolved into an effective strategy for stabilizing zinc electrodes, with specific methods including acid etching, alloying, plasma sputtering, etc. [8-10]. However, these processes are overly complex and difficult to scale up for mass production. In comparison, introducing electrolyte additives demonstrates significant advantages in feasibility and practicality [11]. Research shows that certain organic or inorganic additives can effectively regulate the directional growth of zinc crystal planes [12–14]. Among them, organic additives typically require high dosages, which not only reduce the energy density of the battery but may also pose safety risks due to the carcinogenicity of certain organic compounds (such as pyridine, 2-methylimidazole, etc.). Inorganic additives (such as indium sulfate, europium chloride, etc.) are often expensive, making cost control challenging.

Carbon dots (CDs) have garnered attention in the field of electrochemistry due to their abundant surface groups and structural tunability [15–17]. Environmentally friendly, low-toxicity, and low-cost carbon dots are considered ideal materials for green energy storage systems, and their application in aqueous zinc batteries has been preliminarily explored [18,19]. Zhang et al. [20] introduced graphene quantum dots (GODs) as additives into the electrolyte, where GODs adsorbed on the high-potential tips of the zinc anode reduced the nucleation overpotential through strong binding with Zn^{2+} . GQDs also weakened the reactivity of water molecules by forming hydrogen bonds with them, thereby enhancing the battery's cycling performance. The Li research group [21] developed an additive system based on graphitic carbon nitride dots, which serves as an efficient colloidal ion carrier and participates in constructing a zinc anode protection interface with dynamic self-healing properties. This unique interface structure not only exhibits excellent zinc ion conductivity and transference number but also effectively regulates the zinc ion flux distribution, enabling uniform zinc deposition. Song et al. [22] designed a nitrogen-sulfur co-doped carbon dot additive, where the abundant polar groups on the carbon dot surface can modulate the solvation structure of zinc ions by reducing coordinated active water molecules, thereby guiding uniform zinc deposition and avoiding side reactions. In summary, previously reported carbon dot electrolyte additives primarily focus on adjusting the Zn^{2+} solvation structure or forming an adsorption layer on the electrode surface, thereby reducing the corrosion of active water and providing additional nucleation sites for Zn^{2+} deposition. If a carbon dot-based electrolyte additive could be developed to combine these functions-both regulating the Zn²⁺ solvation structure to reduce the corrosion of the zinc electrode by active water and inducing the formation of a zinc electrode interface dominated by the (002) crystal plane to avoid dendrite formation-it would be a work of profound significance, comprehensively improving the working conditions of the zinc anode.

In this work, to address the instability of aqueous zinc anodes and the severe corrosion of electrodes by active water molecules, sodium *p*-styrenesulfonate was used as a carbon and sulfur source to synthesize sulfur-doped carbon dots through a simple calcination method. These carbon dots were then employed as an electrolyte additive for aqueous zinc batteries. Systematic electrochemical tests were conducted to investigate the influence mechanism of carbon dots on the zinc deposition process and the overall battery performance.

2. Experimental section

2.1. Synthesis of carbon dots

Place 1 g of sodium *p*-styrenesulfonate (90 %, Sinopharm Chemical Reagent) in a tube furnace, and heat it to 400 °C at a heating rate of 5 °C min⁻¹, followed by calcination for 1.5 h. Dissolve the obtained black powder in 50 mL of deionized water, filter it through a 0.22 μ m membrane, and then transfer it into a dialysis bag with a molecular weight cutoff of 3500 D. After dialysis for 24 h, remove the solution and freezedry it to obtain brown powdery carbon dots [23].

2.2. Synthesis of cathode materials

Dissolve 0.32 g of NH₄VO₃ (99 %, Macklin) in 40 mL of deionized water and stir at 60 °C for 1 h. Subsequently, add 0.58 g of $H_2C_2O_4\cdot 2H_2O$ (AR, Aladdin) and stir until completely dissolved. Transfer the resulting emerald green solution to a 100 mL high-pressure reactor and react at 180 °C for 6 h. After the reaction, wash the resulting dark green solid multiple times with deionized water, and then transfer it to a 60 °C oven for thorough drying to obtain NH₄V₄O₁₀.

Dissolve 2.5 g of MnSO₄·H₂O (AR, Aladdin) and 2 mL of 0.5 mol L⁻¹ H₂SO₄ (AR, Adamas) in 80 mL of deionized water with stirring until completely dissolved. Subsequently, add 1.6 g of KMnO₄ (AR, Adamas) and stir for 2 h to form a brown suspension. Transfer the suspension to a 100 mL high-pressure reactor and react at 120 °C for 24 h. After the reaction, filter and wash multiple times with deionized water, then transfer to a 60 °C oven for thorough drying to obtain q-MnO₂.

2.3. Cell assembly

Preparation of electrolyte: Carbon dots were added to a 2 mol L^{-1} ZnSO₄ aqueous solution to prepare electrolytes with different concentrations. According to the amount of carbon dots added (0, 0.2, 0.4, 1 mg mL⁻¹), they were named as: ZS, ZS-CD0.2, ZS-CD0.4, ZS-CD1.

Preparation of electrodes: Clean zinc plates with a thickness of 0.05 mm were cut into 12 mm diameter discs to serve as zinc electrodes. Clean copper plates with a thickness of 0.05 mm were cut into 12 mm diameter discs to serve as copper electrodes. NH₄V₄O₁₀, conductive carbon black, and PVDF were mixed in a mass ratio of 7 : 2: 1, and an appropriate amount of NMP was added, followed by stirring for 4 h to form a uniform slurry. The slurry was evenly coated onto titanium foil (thickness of 0.02 mm) using a coater, dried overnight in an oven at 60 °C, and then cut into 12 mm diameter discs for use. MnO₂ electrode discs were prepared using the same method and ratio.

The CR2016 coin cell casing was used for cell assembly, with the positive and negative electrodes separated by a Whatman GF/D glass fiber separator. Depending on the test, 80 μ L of the aforementioned electrolyte was added. Unless otherwise specified, relevant tests were conducted only after the cell assembly was completed and left to stand for 4 h.

2.4. Characterization and electrochemical testing

The morphology of the materials was observed using transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan) and scanning electron microscopy (SEM) (Phenom Prox, Phenom, Netherlands). The functional groups and crystal structure of the materials were analyzed using Fourier transform infrared spectroscopy (FT-IR) (Nicolet iS10, ThermoFisher, USA), X-ray polycrystalline diffraction (XRD) (D2 PHASER, Bruker, Germany), and X-ray photoelectron spectroscopy (XPS) (Scientific K-Alpha, Thermo, USA). The state of water molecules was characterized using nuclear magnetic resonance spectroscopy (NMR) (AVANCE III HD, Bruker, Switzerland). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronoamperometry (CA), linear sweep voltammetry (LSV), and Tafel curve measurements were performed on an electrochemical workstation (CHI 660E, Chenhua Instruments, Shanghai). The constant current charge-discharge and rate performance tests of Zn||Zn, Zn||Cu, Zn||NH₄V₄O₁₀ and Zn||MnO₂ were conducted on a cell testing system (CT3002A, Land Electronics, Wuhan). All measurements and assembly were carried out at room temperature.

2.5. Theoretical calculation methods

The binding energy can be calculated using the Materials Studio 2023 DMol3 model based on density functional theory (DFT). Spinpolarized calculations were applied to all model systems, and van der Waals corrections were considered using the Tkatchenko-Scheffler method. The binding energy E_b is defined as: $E_b = E_{\text{total}} - E_{\text{sub}} - E_{2n}^2$, where E_{total} is the total energy, E_{sub} is the energy of an empty substrate, and E_{2n}^{2+} is the energy of a single Zn^{2+} .

3. Results and discussion

Using a simple one-step pyrolysis method, sodium *p*-styrenesulfonate was converted into sulfur-doped carbon dots. Uniformly dispersed carbon dot particles with a diameter of about 5 nm were observed by TEM (Fig. 1a and b). Higher resolution observation revealed the crystalline carbon core of the carbon dots, with a lattice spacing of 0.21 nm, corresponding to the (100) plane of graphite [24]. Compared to traditional hydrothermal and solvothermal methods, pyrolysis in air avoids the use of hazardous high-pressure reactors, enhances the safety of the synthesis process, and allows for scalable synthesis, which is beneficial for future production. To investigate the surface state of the carbon dots, Fourier-transform infrared spectroscopy (FT-IR) was used to determine the surface functional groups. As shown in Fig. 1c-a broad absorption peak at 3449 cm⁻¹ corresponds to the stretching vibration of the O-H



Fig. 1. Synthesis and structural characterization of CDs

(a) Schematic illustration of CDs synthesis. (b) TEM image, (c)FT-IR and (d) XRD spectra of CDs. (e) XPS survey spectra, and (f-h) high-resolution C 1s, O 1s, S 2p spectra of CDs.

bond. The peaks at 1638, 1388, and 1129 cm⁻¹ correspond to the stretching vibrations of C=C, C-OH, and C-O-C, respectively, while the absorption peak at 623 cm⁻¹ is attributed to the C-S stretching vibration formed by sulfur doping [25,26]. The XRD pattern of the carbon dots shows a broad peak, indicating a core structure dominated by graphite (Fig. 1d) [27]. XPS spectra confirmed the elemental composition of the carbon dots, primarily consisting of C, O, and S (Fig. 1e). The fine spectrum of O 1s can be divided into two peaks at 531.6 and 533.1 eV (Fig. 1f), corresponding to C=O and C-O, respectively [28,29]. The fine spectrum of C 1s consists of three peaks at 288.9, 285.8, and 284.8 eV (Fig. 1g), corresponding to C-S, C-O, and C-C structures, respectively. The fine spectrum of S 2p consists of two peaks at 169.2 and 168.0 eV (Fig. 1h), corresponding to C-SO₄ and -C-SO₃ [23].

Elemental analysis of the carbon dots using energy-dispersive spectroscopy (EDS) (Fig. S1, Supporting Information) showed a strong S element signal, indicating a high S content in the carbon dots, and the mapping spectrum demonstrated the uniformity of S doping. These test results indicate that we have successfully synthesized sulfur-doped carbon dots with abundant surface functional groups. To study the charge characteristics of the carbon dots, the Zeta potential of the carbon dot aqueous solution was tested, showing a low Zeta potential of about -28 mV (Fig. S2), mainly due to the negative charge groups on the surface of the carbon dots, which will facilitate the tight binding of carbon dots with Zn^{2+} [30]. The fluorescence properties of carbon dots often attract researchers' attention. The photoluminescence (PL) spectrum of the carbon dots (Fig. S3) shows that within the excitation wavelength range of 310-370 nm, the carbon dots exhibit an emission peak that shifts with the excitation wavelength. When excited at 340 nm, the emission peak is located at 409 nm. The fluorescence quantum yield of the carbon dots, measured using an integrating sphere, is 19 %.

Subsequent tests were conducted using a $2 \text{ mol } L^{-1} \text{ ZnSO}_4$ electrolyte with the addition of carbon dots at different concentrations. To

characterize the state of water molecules in the zinc sulfate electrolyte, the ²H NMR spectra of the zinc sulfate electrolyte was tested. The results (Fig. 2a) showed that the 2 H peak of pure D₂O was at 4.705, while in the $2 \text{ mol } L^{-1}$ ZnSO4 solution, a broad peak with a maximum at 4.785 was observed. This indicates that in the ZnSO₄ environment, due to the strong coordination between Zn²⁺ and D₂O, the electron density around D⁺ decreases, leading to a reduction in the shielding effect on the proton, causing the peak signal to shift to a lower field. Additionally, the varying degrees of binding between water molecules and Zn²⁺ result in a broad peak. After adding 0.4 mg mL⁻¹ of carbon dots, the peak shifted back to 4.769, and the peak width significantly decreased, indicating that some bound D₂O molecules were released back into the environment. Furthermore, if only 0.4 mg mL⁻¹ of carbon dots were added to D₂O, the peak position was at 4.720, showing that the addition of carbon dots alone does not reduce the chemical shift of the peak. The aforementioned peak shift back is due to the preferential binding of carbon dots with Zn²⁺. This indicates that carbon dots can effectively bind with Zn^{2+} , thereby weakening the interaction between Zn^{2+} and water molecules, ultimately altering its solvation structure [31-33]. Consistent conclusions were also drawn from the FT-IR spectra (Fig. 2b). After adding 0.4 mg mL⁻¹ and 1 mg mL⁻¹ of carbon dots to the 2 mol L⁻¹ ZnSO₄ aqueous solution, the O-H stretching vibration peak gradually shifted from 3218 cm⁻¹ to 3228 and 3233 cm⁻¹ with increasing concentration, further indicating that the addition of carbon dots weakens the interaction between Zn^{2+} and water molecules [34].

To further elucidate the mechanism of interaction between carbon dots and Zn^{2+} , we used DFT calculations to evaluate the binding ability of surface groups on carbon dots with Zn^{2+} (Fig. 2c). The results showed that the binding energy of water molecules was -4.87 eV, hydroxyl groups was -11.96 eV, carboxyl groups was -11.74 eV, and sulfonic acid groups was -12.38 eV. It can be seen that, compared to the conventional hydroxyl and carboxyl groups on the surface of carbon dots



Fig. 2. Various spectra and electrochemical tests for the ZS-CD electrolyte system

(a) ²H NMR spectra of H₂O from 2 mol L⁻¹ ZnSO₄, 2 mol L⁻¹ ZnSO₄ with 0.4 mg mL⁻¹ CDs and 0.4 mg mL⁻¹CDs. (b) FTIR spectra for 2 mol L⁻¹ ZnSO₄, 2 mol L⁻¹ ZnSO₄ with 0.4 mg mL⁻¹CDs. (c) Binding energies of Zn²⁺ absorbed on different function groups by DFT calculations; (d) LSV curves at scan rate of 1 mV s⁻¹ reflecting HER and OER performance of the system; (e) Tafel plots representing corrosion behaviors; (f) CA curves indicating Zn²⁺ diffusion process of Zn electrode in ZS and ZS-CD0.4 electrolytes.

and water molecules in the electrolyte, sulfonic acid groups have the strongest binding ability. The abundant sulfonic acid groups introduced by sulfur doping serve as effective binding sites, enhancing the interaction between carbon dots and Zn^{2+} , thereby regulating the solvation shell of Zn^{2+} . In conventional zinc sulfate electrolytes, the solvated [Zn $(H_2O)_6$]²⁺ not only needs to overcome the energy barrier of the desolvation process (hindering deposition kinetics) but also causes severe corrosion of the electrode by active water molecules. The reconstruction of the Zn^{2+} solvation shell by carbon dot additives will significantly reduce these adverse effects, making the electrode more stable during the deposition process.

We assembled Zn||Zn symmetric cells and conducted a series of electrochemical tests. First, the stability of the zinc electrode was tested. The nucleation overpotential plot (Fig. S4) shows that the nucleation overpotential of the symmetric cell using 2 mol L^{-1} ZnSO4 is 85 mV, while the overpotential of the symmetric cell using ZS-CD0.4 electrolyte with 0.4 mg mL⁻¹ carbon dots decreases to 76 mV. This indicates that the nucleation barrier of Zn^{2+} is reduced due to the adjustment of the Zn^{2+} solvation shell by carbon dots, which is beneficial for forming uniform deposition and avoiding the issues of dead zinc and short circuits caused by dendrite growth [35]. From the LSV curve of the cell (Fig. 2d), it can be seen that the onset potentials of hydrogen evolution reactions (HER) and oxygen evolution reactions (OER) for the symmetric cell using ZS-CD0.4 electrolyte are higher than those for the cell using ZS electrolyte, indicating that the carbon dot additive can suppress the kinetics of HER and OER, thereby achieving a wider electrochemical stability window [36]. Additionally, the Tafel curve of the symmetric cell was obtained at a scan rate of 1 mV s⁻¹ (Fig. 2e). The corrosion current of the symmetric cell using ZS electrolyte is 2.4 mA, while that of the symmetric cell using ZS-CD0.4 electrolyte is significantly reduced to 0.158 mA, meaning that the carbon dot additive reduces the occurrence of corrosion side reactions, increasing the stability of the electrode during cycling and making it less susceptible to corrosion and the generation of by-products [37].

The fluctuation of the current-time curve can reflect changes in the electrode surface morphology during deposition. The CA test results (Fig. 2f) show that when an overpotential of -150 mV is applied, the current of the symmetric cell using ZS electrolyte continues to increase during the 200 s test period, indicating a prolonged and unconstrained 2D diffusion process and rough deposition growth. Zn²⁺ diffuses laterally along the electrode surface to find the most energetically favorable charge transfer sites. To reduce surface energy and exposed area, Zn^{2+} tends to aggregate and form dendrites [37]. In contrast, the symmetric cell using ZS-CD0.4 electrolyte rapidly transitions from an initial disordered 2D diffusion process lasting about 70 s to a uniform and stable 3D diffusion process, indicating that Zn²⁺ is locally reduced to Zn under constrained 2D surface diffusion [38]. This change is due to the coordination interaction between the oxygen-containing functional groups on the carbon dot surface and Zn^{2+} , which constrains the 2D diffusion of Zn^{2+} on the electrode surface. Zn^{2+} is forced to deposit very close to the initial adsorption site, avoiding concentrated deposition at a few low surface energy sites, thereby forming more small-sized nucleation sites. Combined with the low nucleation barrier brought by the carbon dot-adjusted solvation shell, the uniformity of subsequent deposition is effectively enhanced [20,39]. Overall, these tests demonstrate the ability of the carbon dot additive to suppress side reactions and promote uniform zinc deposition, which will help maintain the stability of the battery during long cycling and extend its working life.

The symmetric cells were subjected to EIS (Fig. 3a). The results from equivalent circuit fitting revealed that the initial charge transfer resistance (R_{ct}) of the symmetric cell using ZS electrolyte reached 872 Ω . However, with the introduction of carbon dot additives, the R_{ct} of the Zn||Zn symmetric cell significantly decreased to 270 Ω . The reduced impedance indicates that the carbon dot additives facilitate desolvation and efficient charge transfer processes, enabling faster deposition kinetics [40]. The cycling performance of symmetric cells with different concentrations of carbon dot additives was tested at a current density of 1 mA cm⁻² (Fig. 3b and Fig. S5). As a control, the symmetric cell using



Fig. 3. Cyclic performance of Zn||**Zn symmetric cells using ZS and ZS-CD0.4 electrolytes** (a) Initial EIS profiles and (b–e) long-term galvanostatic charging/discharging under different current densities.

ZS electrolyte failed rapidly after only 96 h of cycling. In contrast, all cells with carbon dot additives exhibited significantly improved cycling lifetimes. The symmetric cell using ZS-CD0.4 electrolyte performed the best, achieving a cycling lifetime of 1230 h with a polarization voltage of only 34.7 mV, indicating better reversibility of zinc deposition and stripping in the presence of carbon dots. The cycling behavior of the cells was tested within a current density range of 1 mA cm⁻² to 10 mA cm⁻² (Fig. 3c and Fig. S6). Even at a high current density of 10 mA cm⁻², the symmetric cell using ZS-CD0.4 electrolyte maintained a small

polarization voltage, while the control group exhibited significant voltage fluctuations due to side reactions and dendrite growth. Based on the preceding tests, we found that the electrolyte with 0.4 mg mL⁻¹ carbon dots provided the best cycling performance. Therefore, we selected the ZS-CD0.4 electrolyte for subsequent cell assembly and testing.

Subsequently, long-term cycling tests at high current densities of 5 mA cm⁻² and 10 mA cm⁻² were conducted. The symmetric cell using ZS-CD0.4 electrolyte stably cycled for over 2000 h at 5 mA cm⁻² and 0.5



Fig. 4. Morphology characterization of Zn electrode

(a) XRD patterns of Zn electrode after 50 and 100 cycles in ZS and ZS-CD0.4 electrolyte, respectively. (b) XRD patterns of Zn electrode at different cycling stages (0, 10, 20, 50, and 100 cycles) in ZS-CD0.4 electrolyte. SEM image and EDS mapping of Zn electrode after 50 cycles in (c) ZS and (d) ZS-CD0.4 electrolyte. (e) Schematic illustration of the bifunctional mechanism of CDs.

mAh•cm⁻² (Fig. 3d). Moreover, when the current density was further increased to 10 mA cm⁻² (Fig. 3e), the cell still maintained excellent cycling performance, achieving an ultra-long lifespan of 1961 h (nearly 20,000 cycles). From the enlarged detail graphs, it can be observed that the cell exhibited smooth voltage curves during the initial stage (5th-10th cycles), mid-term (10000th-10005th cycles), and final stage (15000th-15005th cycles) of cycling, reflecting a stable internal working state. This demonstrates strong competitiveness compared to other anode protection strategies recently reported by researchers (Table S1), proving that the carbon dot additive can effectively enhance the cycling capability of the cell at high current densities.

The symmetric cells cycled in ZS and ZS-CD0.4 electrolytes for 50 and 100 h, respectively, were disassembled, and the zinc electrode surfaces were examined using XRD (Fig. 4a). The test results showed that the signal of the byproduct Zn₄SO₄(OH)₆·4H₂O on the electrode surface of the symmetric cell using ZS electrolyte continuously increased with cycling time, while no related signal was observed on the electrode of the symmetric cell using ZS-CD0.4 electrolyte, proving the additive's ability to suppress side reactions. Additionally, we found that the zinc metal in the symmetric cell using ZS electrolyte was dominated by the (101) crystal plane, whereas the (002) crystal plane of zinc metal in the symmetric cell using ZS-CD0.4 electrolyte had a high proportion and continuously increased with cycling time. The (002) plane zinc, arranged at a small angle to the substrate, deposited more densely and uniformly, exhibiting higher stability in the electrolyte and being less susceptible to corrosion. This indicates that the carbon dot additive also has the ability to induce the formation of specific crystal planes on the electrode. To confirm this hypothesis, the electrodes of the cell using ZS-CD0.4 electrolyte after 10, 20, 50, and 100 cycles were examined using XRD (Fig. 4b), and the results were consistent with the previous findings, showing that the signal of the (002) crystal plane of the zinc electrode continuously strengthened with the increase in cycle number. The zinc deposition in the cell using ZS electrolyte did not show selectivity for the (002) crystal plane (Fig. S7), but rather deposited randomly and disorderly, with the surface-deposited zinc mainly in the (101) plane, which is prone to corrosion and dendrite growth, unfavorable for the cell's stability during long-term cycling. This also explains why the symmetric cell is more stable at high current densities. When cycling at high current densities, carbon dots can help the electrode quickly construct and renew the (002) crystal plane, thereby maintaining the electrode's stability, whereas at low currents, due to the slow deposition rate, the electrode is more significantly affected by side reactions, leading to poor cycling performance.

The electrode sheets of the symmetric cells cycled at 1 mA cm $^{-2}$, 0.5 mAh•cm⁻² for 50 h were observed using SEM, yielding results consistent with the aforementioned XRD tests. As seen in Fig. 4c and d, the electrode sheet surface of the cell using ZS electrolyte had a large number of flaky byproducts and loose, disordered zinc, while the electrode sheet surface of the cell using ZS-CD0.4 electrolyte was uniformly flat with few byproducts. EDS elemental analysis showed that the oxygen element content on the electrode surface of the cell using ZS electrolyte reached 35.28 %, and the sulfur element content was 0.95 %, indicating a high content of byproducts on the surface, whereas the oxygen and sulfur element contents on the electrode surface of the cell using ZS-CD0.4 electrolyte were only 2.14 % and 0.12 %, respectively. The comparison of electrodes after 100 cycles was even more pronounced (Fig. S8), with the electrode sheet surface in ZS electrolyte showing a large number of vertically arranged byproducts, while the electrode sheet surface in ZS-0.4 electrolyte remained flat and dense.

In addition, we continuously monitored the pH changes of the Zn||Zn symmetric cell during 50 cycles at 1 mA cm⁻² and 0.5 mAh•cm⁻² (Fig. S9). During the monitored 50 cycles, the pH of the electrolyte in the symmetric cell system using ZS electrolyte rapidly increased from the initial state of 3.13–5.23. Notably, the pH at the anode/electrolyte interface was significantly higher than that of the bulk electrolyte [41], indicating that severe HER occurred on the zinc anode surface, leading

to the formation of a large amount of by-products [42]. In contrast, the symmetric cell using ZS-CD0.4 electrolyte, due to the positive effect of carbon dots, exhibited a slower increase in pH, rising only from the initial state of 3.16-4.52, suggesting that the HER was suppressed, and the formation of by-products was correspondingly reduced. These test results indicate that after the addition of carbon dots, the side reactions on the electrode surface were significantly reduced due to the formation of the stable (002) crystal plane. Bravais' law states that the ultimately exposed crystal plane has the lowest growth rate (the growth direction of a crystal plane is defined as the direction perpendicular to that plane) [43]. The ability of carbon dots to induce the formation of the (002) crystal plane on the zinc electrode surface stems from the preferential adsorption of carbon dots on the zinc (002) crystal plane, which hinders the rapid growth of zinc atoms on this plane. Consequently, the area proportion of the faster-growing (100) and (101) crystal planes gradually decreases, while the area proportion of the slowest-growing (002) crystal plane continuously increases. After a period of deposition, the zinc electrode surface exhibits a structure dominated by the (002) crystal plane.

The experimental results above reveal the mechanism of carbon dots as a bifunctional electrolyte additive (Fig. 4e): on one hand, the solvated $[Zn(H_2O)_6]^{2+}$ in conventional ZnSO₄ electrolyte generates a large number of active water molecules at the electrode-electrolyte interface during deposition, which corrodes the electrode and produces insulating by-products. Carbon dots, through their strong binding ability with Zn^{2+} , reconstruct the solvation shell of Zn^{2+} , reducing the content of water molecules, thereby avoiding electrode corrosion and side reactions caused by active water molecules at the interface during deposition. On the other hand, zinc electrodes working in conventional electrolytes tend to form unstable (101) and (001) crystal planes, which are prone to dendrite growth and side reactions during cycling. Our carbon dots can induce the formation of stable (002) crystal planes and continuously renew them during the deposition-stripping cycle, which is particularly effective under high current conditions, significantly enhancing the structural stability of the electrode itself. Under the combined effect of these two functions, the performance of the zinc electrode is significantly improved, ultimately endowing the battery with an ultra-long cycle life.

Zn||Cu half-cells were assembled to further investigate the influence of carbon dot additives on the deposition/stripping processes at the electrode surface. After the initial few cycles of reshaping zinc coordination, the half-cells entered a stable working state, and the Coulombic efficiency (CE) also maintained a consistently high value. However, due to dendrite growth and byproduct accumulation during cycling in the half-cell using ZS electrolyte, it failed to function properly after 137 cycles, experiencing severe overcharging. In contrast, the half-cell using ZS-CD0.4 electrolyte benefited from the positive effects of carbon dots, maintaining a stable working state over 500 cycles and achieving an average CE of 97.38 % (Fig. 5a). From the polarization voltage curves (Fig. 5b and c), it can also be observed that the CE of the half-cell using ZS electrolyte fluctuated significantly, indicating a disordered deposition process, while the half-cell using ZS-CD0.4 electrolyte operated smoothly, demonstrating the positive role of carbon dots in promoting uniform zinc deposition.

We synthesized the NH₄V₄O₁₀ (NVO) cathode material according to the method reported in the literature [44], and assembled Zn||ZS||NVO full cells and Zn||ZS-CD0.4||NVO full cells. The full cells using the ZS electrolyte and those using the ZS-CD0.4 electrolyte exhibited similar CV curves (Fig. 5d), indicating that the introduction of carbon dot additives does not alter the redox reaction type of the full cells. After cycling the full cells for 5 cycles at a current density of 0.2 A g⁻¹, EIS was performed, and the results were fitted with an equivalent circuit (Table S2 and Fig. S10). Firstly, the Nyquist plots of the full cells consist of a semicircle in the high-frequency region and a straight line with a slope close to 1 in the low-frequency region, indicating that the electrode process is jointly controlled by charge transfer and diffusion



Fig. 5. Electrochemical performances of Zn||Cu half cells, Zn||NVO full cells and Zn||MnO₂ full cells with different electrolytes Comparison of (a) coulombic efficiency measurements and (b, c) the corresponding voltage profiles at selected cycles of Zn||Cu cells. Electrochemical performances of Zn||NVO cells: (d) CV curves at a scan rate of 0.5 mV s^{-1} ; (e) rate capability under different current densities and (f) long-term cycling performance and corresponding CE at a current density of $3A \cdot g^{-1}$. Electrochemical performances of Zn||MnO₂ cells: (g) CV curves at a scan rate of 0.5 mV s^{-1} ; (h) rate capability under different current densities and (i) long-term cycling performance and corresponding CE at a current density of 0.2 A g^{-1} .

processes. The slopes of the straight lines in the low-frequency region for full cells with and without carbon dot additives are similar, representing comparable diffusion behaviors, and the addition of carbon dots does not significantly affect the diffusion process. However, it is noteworthy that the interfacial charge transfer resistance (R_{cl}) of the full cells shows a significant difference after the addition of carbon dot additives. For Zn||NVO using the ZS electrolyte, the R_{ct} is 70.0 Ω , which decreases significantly to 45.0 Ω when using the ZS-CD0.4 electrolyte. This phenomenon indicates that the ZS-CD0.4 electrolyte can effectively reduce side reactions within the cells, suppress the formation of passivation layers on the electrode surface, thereby ensuring rapid charge transfer processes and reducing the R_{ct} of the cells [45,46].

The rate performance of the full cells was tested at different discharge rates of 0.2, 0.5, 1, 2, 3, and 5 A g⁻¹ (Fig. 5e). The full cells using the ZS-CD0.4 electrolyte exhibit higher specific capacities than those using the ZS electrolyte under all current conditions, and when the current is returned to 0.2 A g⁻¹, the specific capacity of the full cells using the ZS-CD0.4 electrolyte essentially recovers to the initial state. This demonstrates the excellent performance of the carbon dot additives under various current conditions, even at high currents, helping to achieve rapid redox kinetics and stable interfacial charge transfer. We tested the long-term operational capability of the full cell under fast charge-discharge conditions at 3 A g⁻¹ (Fig. 5f). The full cell using ZS-

CD0.4 electrolyte achieved a specific capacity of 299.6 mAh•g⁻¹ after 5 cycles of activation, significantly higher than the 249.5 mAh \bullet g⁻¹ specific capacity of the full cell using ZS electrolyte. Moreover, in subsequent cycles, due to the suppression of side reactions and enhanced electrode stability by the carbon dot additive, the latter exhibited excellent capacity retention, maintaining 90.3 % after 500 cycles, while the full cell using ZS electrolyte had a capacity retention of only 72.1 %. The charge-discharge curves of the full cell during cycling also confirmed this (Fig. S11). Compared to the full cell using ZS electrolyte, the full cell using ZS-CD0.4 showed better cycling reversibility and lower polarization. To verify the compatibility of the carbon dot additive with different cathode materials, we also selected another commonly used cathode material, MnO₂, for corresponding tests. The Zn||MnO₂ full cells using ZS electrolyte and ZS-CD0.4 electrolyte had similar cyclic voltammetry curves (Fig. 5g). In subsequent impedance and cycling tests, the introduction of the carbon dot additive also brought significant performance improvements to the Zn||MnO₂ full cell, with relatively smaller impedance (Fig. S12) and higher capacity retention after long-term cycling at 0.2 A g^{-1} (61.2 % vs. 17.8 %) (Fig. 5h,i and Fig. S13). These results lead to the same conclusion as the aforementioned Zn|| NVO full cell, demonstrating the excellent compatibility of the carbon dot additive. The full cell tests fully proved that the carbon dot additive has the comprehensive ability to protect the zinc anode, be compatible with different cathode materials, and optimize battery performance.

4. Summary

This study investigated the synthesis of carbon dots using sodium pstyrenesulfonate as a raw material through a simple one-step pyrolysis method, and their application as an electrolyte additive in aqueous zincion batteries. Due to the strong binding ability of carbon dots with Zn^{2+} . the interaction between Zn^{2+} and water molecules was weakened, leading to the reconstruction of the solvation shell of hydrated Zn^{2+} . This significantly reduced the corrosion of the electrode by active water molecules and lowered the nucleation energy barrier of Zn^{2+} , resulting in more uniform deposition. Additionally, it was found that carbon dots could induce the formation of dense (002) crystal planes during the deposition of Zn^{2+} , further enhancing the stability of the electrode. Benefiting from the synergistic effects of carbon dot additives in reconstructing the solvation shell and inducing stable crystal plane growth, the Zn||ZS-CD0.4||Zn symmetric cell achieved a stable cycle of nearly 2000 h at 10 mA cm⁻². The carbon dot additive also effectively improved the performance of full cells and demonstrated good compatibility with different cathode materials: the Zn||NVO full cell exhibited a specific capacity of 299.6 mAh•g⁻¹ and a capacity retention rate of 90.3 % over 500 cycles; the Zn||MnO₂ full cell showed a specific capacity of 170.3 mAh•g⁻¹ and a capacity retention rate of 61.2 % over 500 cycles. This work demonstrates the positive role of sulfur-doped carbon dot additives in the electrolyte of aqueous zinc-ion batteries, providing an efficient solution for anode protection in aqueous zinc batteries.

CRediT authorship contribution statement

Qianli Ma: Writing – original draft, Visualization, Validation, Software, Methodology, Formal analysis, Data curation. Tianbing Song: Validation, Software, Methodology, Formal analysis. Tianle He: Visualization, Software, Formal analysis, Data curation. Xirong Zhang: Visualization, Validation, Software. Huanming Xiong: Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Huanming Xiong reports financial support was provided by National Natural Science Foundation of China. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.actphy.2025.100106.

References

- Y.H. Li, H. Yao, X.J. Liu, X.T. Yang, D. Yuan, Nano Res. 16 (2023) 9179–9194, https://doi.org/10.1007/s12274-023-5637-7.
- [2] J.D. Huang, Y.H. Zhu, Y. Feng, Y.H. Han, Z.Y. Gu, R.X. Liu, D.Y. Yang, K. Chen, X. Y. Zhang, W. Sun, et al., Acta Phys. Chim. Sin. 38 (2022) 2208008, https://doi.org/ 10.3866/PKU.WHXB202208008.
- [3] M. Song, H. Tan, D.L. Chao, H.J. Fan, Adv. Funct. Mater. 28 (2018) 1802564, https://doi.org/10.1002/adfm.201802564.
- [4] Z.H. Yi, G.Y. Chen, F. Hou, L.Q. Wang, J. Liang, Adv. Energy Mater. 11 (2020) 2003065, https://doi.org/10.1002/aenm.202003065.
- [5] B. Qiu, L.Z. Xie, G.Q. Zhang, K.J. Cheng, Z.W. Lin, W. Liu, C.X. He, P.X. Zhang, H. W. Mi, Chem. Eng. J. 449 (2022) 137843, https://doi.org/10.1016/j. cej.2022.137843.

- [6] B. Qiu, K.Y. Liang, W. Huang, G.Q. Zhang, C.X. He, P.X. Zhang, H.W. Mi, Adv. Energy Mater. 13 (2023) 2301193, https://doi.org/10.1002/aenm.202301193.
- [7] Z. Zhao, R. Wang, C. Peng, W. Chen, T. Wu, B. Hu, W. Weng, Y. Yao, J. Zeng, Z. Chen, et al., Nat. Commun. 12 (2021) 6606, https://doi.org/10.1038/s41467-021-26947-9.
- [8] X. Wang, J.P. Meng, X.G. Lin, Y.D. Yang, S. Zhou, Y.P. Wang, A.Q. Pan, Adv. Funct. Mater. 31 (2021) 2106114, https://doi.org/10.1002/adfm.202106114.
- [9] Z. Yi, J. Liu, S. Tan, Z. Sang, J. Mao, L. Yin, X. Liu, L. Wang, F. Hou, S.X. Dou, et al., Adv. Mater. 34 (2022) e2203835, https://doi.org/10.1002/adma.202203835.
 [10] H. Lu, Q. Jin, X. Jiang, Z.M. Dang, D. Zhang, Y. Jin, Small (Weinh.) 18 (2022)
- e2200131, https://doi.org/10.1002/smll.202200131. [11] Y.E. Qi, Y.Y. Xia, Acta Phys. Chim. Sin. 39 (2023), https://doi.org/10.3866/Pku. Whxb202205045.
- [12] X.C. Liang, X.F. Chen, Z.X. Zhai, R.S. Huang, T.Q. Yu, S.B. Yin, Chem. Eng. J. 480 (2024) 148040, https://doi.org/10.1016/j.cej.2023.148040.
- [13] J. Cao, M. Sun, D. Zhang, Y. Zhang, C. Yang, D. Luo, X. Yang, X. Zhang, J. Qin, B. Huang, et al., ACS Nano 18 (2024) 16610–16621, https://doi.org/10.1021/ acsnano.4c00288.
- [14] R.X. Zhang, Y.X. Cui, L.L. Liu, S.M. Chen, J. Power Sources 602 (2024) 234351, https://doi.org/10.1016/j.jpowsour.2024.234351.
- [15] C. Xia, S. Zhu, T. Feng, M. Yang, B. Yang, Adv. Sci. 6 (2019) 1901316, https://doi. org/10.1002/advs.201901316.
- [16] L. Ai, R. Shi, J. Yang, T. Zhang, S. Lu, Small (Weinh.) 17 (2021) e2007523, https:// doi.org/10.1002/smll.202007523.
- [17] J. Gao, M.M. Zhu, H. Huang, Y. Liu, Z.H. Kang, Inorg. Chem. Front. 4 (2017) 1963–1986, https://doi.org/10.1039/c7qi00614d.
- [18] M.G. Yi, M.J. Jing, Y.C. Yang, Y.J. Huang, G.Q. Zou, T.J. Wu, H.S. Hou, X.B. Ji, Adv. Funct. Mater. 34 (2024) 2400001, https://doi.org/10.1002/ adfm.202400001.
- [19] R.T. Guo, L. Li, B.W. Wang, Y.G. Xiang, G.Q. Zou, Y.R. Zhu, H.S. Hou, X.B. Ji, Energy Storage Mater. 37 (2021) 8–39, https://doi.org/10.1016/j. ensm.2021.01.020.
- [20] H. Zhang, R.T. Guo, S. Li, C. Liu, H.Y. Li, G.Q. Zou, J.G. Hu, H.S. Hou, X.B. Ji, Nano Energy 92 (2022) 106752, https://doi.org/10.1016/j.nanoen.2021.106752.
- W. Zhang, M. Dong, K. Jiang, D. Yang, X. Tan, S. Zhai, R. Feng, N. Chen, G. King, H. Zhang, et al., Nat. Commun. 13 (2022) 5348, https://doi.org/10.1038/s41467-022-32955-0.
- [22] T.B. Song, Z.H. Huang, X.R. Zhang, J.W. Ni, H.M. Xiong, Small (Weinh.) 19 (2023) e2205558, https://doi.org/10.1002/smll.202205558.
- [23] Q. Luo, H. Ding, X. Hu, J. Xu, A. Sadat, M. Xu, F.L. Primo, A.C. Tedesco, H. Zhang, H. Bi, Dalton Trans. 49 (2020) 6950–6956, https://doi.org/10.1039/d0dt01187h.
- [24] S.J. Mohammed, K.M. Omer, F.E. Hawaiz, RSC Adv. 13 (2023) 14340–14349, https://doi.org/10.1039/d3ra01646c.
- [25] P.P. Zhu, Z. Cheng, L.L. Du, Q. Chen, K.J. Tan, Langmuir 34 (2018) 9982–9989, https://doi.org/10.1021/acs.langmuir.8b01230.
- [26] J. Duan, J. Yu, S. Feng, L. Su, Talanta 153 (2016) 332–339, https://doi.org/ 10.1016/j.talanta.2016.03.035.
- [27] L. Li, Y. Li, Y. Ye, R. Guo, A. Wang, G. Zou, H. Hou, X. Ji, ACS Nano 15 (2021) 6872–6885, https://doi.org/10.1021/acsnano.0c10624.
- [28] Y. Park, J. Yoo, B. Lim, W. Kwon, S.W. Rhee, J. Mater. Chem. A 4 (2016) 11582–11603, https://doi.org/10.1039/c6ta04813g.
- [29] P. Boulanger, J. Riga, J. Delhalle, J.J. Verbist, Polymer 29 (1988) 797–801, https://doi.org/10.1016/0032-3861(88)90135-8.
- [30] W.W. Liu, M. Li, G.P. Jiang, G.R. Li, J.B. Zhu, M.L. Xiao, Y.F. Zhu, R. Gao, A.P. Yu, M. Feng, et al., Adv. Energy Mater. 10 (2020) 2001275, https://doi.org/10.1002/ aenm.202001275.
- [31] X. Fan, L. Chen, Y. Wang, X. Xu, X. Jiao, P. Zhou, Y. Liu, Z. Song, J. Zhou, Nano-Micro Lett. 16 (2024) 270, https://doi.org/10.1007/s40820-024-01475-5.
- [32] J. Hao, L. Yuan, C. Ye, D. Chao, K. Davey, Z. Guo, S.Z. Qiao, Angew. Chem. Int. Ed. Engl. 60 (2021) 7366–7375, https://doi.org/10.1002/anie.202016531.
- [33] N.N. Chang, T.Y. Li, R. Li, S.N. Wang, Y.B. Yin, H.M. Zhang, X.F. Li, Energy Environ. Sci. 13 (2020) 3527–3535, https://doi.org/10.1039/d0ee01538e.
- [34] Z. Cao, X. Zhu, S. Gao, D. Xu, Z. Wang, Z. Ye, L. Wang, B. Chen, L. Li, M. Ye, et al., Small (Weinh.) 18 (2022) e2103345, https://doi.org/10.1002/smll.202103345.
- [35] F.X. Xie, H. Li, X.S. Wang, X. Zhi, D.L. Chao, K. Davey, S.Z. Qiao, Adv. Energy Mater. 11 (2021) 2003419, https://doi.org/10.1002/aenm.202003419.
- [36] J.L. Cong, X. Shen, Z.P. Wen, X. Wang, L.Q. Peng, J. Zeng, J.B. Zhao, Energy Storage Mater. 35 (2021) 586–594, https://doi.org/10.1016/j.ensm.2020.11.041.
- [37] Z.M. Zhao, J.W. Zhao, Z.L. Hu, J.D. Li, J.J. Li, Y.J. Zhang, C. Wang, G.L. Cui, Energy Environ. Sci. 12 (2019) 1938–1949, https://doi.org/10.1039/c9ee00596j.
- [38] G.D. Wilcox, P.J. Mitchell, J. Power Sources 28 (1989) 345–359, https://doi.org/ 10.1016/0378-7753(89)80064-3.
- [39] M. Chen, Y. Gong, Y. Zhao, Y. Song, Y. Tang, Z. Zeng, S. Liang, P. Zhou, B. Lu, X. Zhang, et al., Natl. Sci. Rev. 11 (2024) nwae205, https://doi.org/10.1093/nsr/ nwae205.
- [40] W.Y. Chen, S. Guo, L.P. Qin, L.Y. Li, X.X. Cao, J. Zhou, Z.G. Luo, G.Z. Fang, S. Q. Liang, Adv. Funct. Mater. 32 (2022) 2112609, https://doi.org/10.1002/adfm.202112609.
- [41] D.L. Han, Z.X. Wang, H.T. Lu, H. Li, C.J. Cui, Z.C. Zhang, R. Sun, C.N. Geng, Q. H. Liang, X.X. Guo, et al., Adv. Energy Mater. 12 (2022) 2102982, https://doi.org/ 10.1002/aenm.202102982.
- [42] K. Ouyang, S. Chen, W. Ling, M. Cui, Q. Ma, K. Zhang, P. Zhang, Y. Huang, Angew. Chem. Int. Ed. Engl. 62 (2023) e202311988, https://doi.org/10.1002/ anie.202311988.
- [43] M. Qiu, P. Sun, Y. Wang, L. Ma, C. Zhi, W. Mai, Angew. Chem. Int. Ed. Engl. 61 (2022) e202210979, https://doi.org/10.1002/anie.202210979.

Q. Ma et al.

- [44] D. Xu, Z. Wang, C. Liu, H. Li, F. Ouyang, B. Chen, W. Li, X. Ren, L. Bai, Z. Chang, et al., Adv. Mater. 36 (2024) e2403765, https://doi.org/10.1002/adma.202403765.
 [45] Y.H. Tao, Y.J. Cui, H.X. Wang, Z.L. Li, Z.J.S. Qian, P.P. Zhang, H.J. Zhou, M.J. Shi, Adv. Funct. Mater. 35 (2024) 2414805, https://doi.org/10.1002/ adfm.202414805.
- [46] Y.H. Tao, J. Jin, Y.J. Cui, H.X. Wang, Z.J.S. Qian, M.J. Shi, ACS Sustain. Chem. Eng. 12 (2024) 16434-16443, https://doi.org/10.1021/acssuschemeng.4c06939.