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Self-assembled ZnO-carbon dots anode materials for high performance nickel-zinc alkaline batteries

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ABSTRACT

The development of high-performance nickel-zinc (Ni-Zn) alkaline batteries is mainly plagued by short life span and poor rate performance of ZnO anode materials. To improve the cycling stability and rate capability of Ni-Zn batteries, carbon dots (CDs) are employed to construct clustered ZnO-CDs nanocomposites, coating ZnO with protective shells of carbon layers and providing electron paths to enhance conductivity of the nanocomposites. Univalent zinc species are found at the interfaces between CDs derivatives and ZnO, which are embedded in the nanoclusters and protected well by carbon coating. Theoretical calculations show univalent zinc species change the electronic structures of ZnO surface, so as to accelerate the charging process of ZnO anode materials. Such ZnO-CDs derived nanocomposites exhibit excellent rate capability (95.3%, 84.7% and 75.0% of capacity retention rate at 2, 5 and 10 A g⁻¹, respectively) and outstanding cycling stability with 92.0% of capacity retention rate from 1 to 10 A g⁻¹ and 71.6% of capacity retention rate after 500 cycles).

1. Introduction

Secondary batteries have changed human life, but none of them is perfect in practical applications. For example, the popular lithium batteries, with excellent energy density and cycling performance, are suffering from flammable organic electrolytes and high production cost [1,2]. While the traditional lead-acid batteries with low cost and excellent stability, are always criticized for poor energy density and environmental pollution [3,4]. Even the Zn-MnO₂ batteries with renewed interests are also restricted by a lower discharge plateau (1.2–1.4 V) [5]. Among commercial batteries, newly launched Ni-Zn alkaline batteries (or Ni-Zn batteries) have a combination of advantages, including higher plateau voltage (1.6 V), abundant raw materials, low production cost, excellent safety performance, no memory effects, environmental benign, etc [6–11]. But they are suffering from short life span and instability of charging-discharging cycles, which mainly arise

from the weak anticorrosion stability and inferior rate capability of ZnO anode materials [12,13]. To solve these problems, various carbon materials have been coated on ZnO to enhance its anti-corrosion ability, inhibit ZnO dissolution in the concentrated alkaline electrolytes and improve the conductivity of the anode materials [13-16]. Unfortunately, the most widely reported carbon materials, especially carbon nanotubes and graphene, are not sufficient for this purpose. In order to protect ZnO sufficiently, these one-dimensional or two-dimensional nanomaterials should be employed in a large scale of 10-30 wt% [17,18]. However, specific capacities of carbon materials, which are mainly generated by ion adsorption behaviors, are so small and negligible that the addition of carbon will decrease the whole specific capacity of the composites. Besides, a large amount of carbon's participation also means a non-uniform coating, unavoidable surface flaking and affected interface reactions [19,20]. Therefore, above contradictions between effective protection and specific capacity indicate a

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bottleneck for the development of ZnO-based anode materials.

As a new kind of zero-dimensional carbon nanomaterials, CDs have been tested for energy storage applications recently [21–24]. Different from the popular carbon nanotubes and graphene, CDs usually have carbon cores doped with hetero elements like O, N, P and S, and defective surfaces with various groups for interfacial adsorption and complexation [25,26]. As a result, a small quantity of CDs will show distinctive merits such as controllable surface structures, good solubility in solvents, homogeneous dispersibility in host materials, and promising electrochemical properties [27–29]. Recent literature indicates that CDs help form efficient interfaces between electrolytes and electrodes, to increase the specific capacity and the cycle stability of electrodes [30]. Thus, when CDs participate in the self-assembly of the composite materials, they will construct compact and uniform surface coating for better anti-corrosion ability and more paths for the rapid ion transfer/ diffusion at the interface [30,31].

In this study, CDs with high yield (more than 80%) and high graphitization are produced hydrothermally from general agents to construct porous ZnO nanoclusters. After annealing, the obtained *Black ZnO Nano Clusters* have few layers (3–5 layers) of carbon coating, low carbon content of 5.6 wt%, tiny spines of 10–20 nm, specific surface areas of 49.8 m² g⁻¹, and univalent zinc (Zn⁺) species which facilitate ion absorption and accelerate electron transfer. As a result, the optimal sample shows an excellent cycling stability with a retention rate of 92% after 5000 cycles, and a striking rate performance of 75% at current densities of 1–10 A g⁻¹. In comparison with those reported ZnO-carbon composites for Ni-Zn batteries, our CDs-ZnO derived anodes exhibit great advantages in their controllable internal structures and surface compositions, which confirms that CDs are promising adjuvant for the next generation of Ni-Zn batteries.

2. Experimental section

2.1. Synthesis of carbon dots (CDs)

On the basis of our previous work [30], 1.0 g of citric acid anhydrous (CA) and 300 μ L of ethylenediamine (EDA), were added into a Teflonlined stainless-steel autoclave, followed by the addition of 500 μ L of distilled water. The sealed autoclave was heated at 160 °C for 5 h. After cooling down to room temperature, 10 mL of water was added into the reactants to form a homogeneous solution. Then, the solution was dialyzed for 24 h against purified water to remove unreacted materials. The CDs were obtained by adding ethanol into the clear solution and collecting the precipitate after centrifugation. The precipitate was washed by ethanol several times and further dried in a vacuum oven at 80 °C for 24 h.

2.2. Synthesis of Black ZnO Nano Clusters and White ZnO Nano Rods

150 mL of $Zn(NO_3)_2$ ·6H₂O solution (4.2 mg mL⁻¹) containing 150 mg of CDs, and 150 mL of hexamethylenetetramine (HMTA) aqueous solution (2.4 mg mL $^{-1}$) were prepared at room temperature, separately. Then, the HMTA solution was heated to 85 °C in a water bath under vigorous stirring. After that, Zn(NO₃)₂·6H₂O solution with CDs was continuously injected into the HMTA solution via a peristaltic pump at an injection rate of 6 mL min^{-1} for 25 min and the final mixed solution was kept at 85 °C for 10 h. After centrifugation, the products were isolated from the supernatant and washed three times by deionized water to remove the unreacted zinc ions, CDs and hydroxide ions. The precipitate was dried in a vacuum at 80°C for 12 h, resulting in the pale brown powder (CDs covered ZnO). At last, as obtained powder was annealed at 600 °C in nitrogen atmosphere for 120 min with a heating/ annealing rate of 1 °C min⁻¹. The final product was named as Black ZnO Nano Clusters. As the control sample, ZnO Nano Rods were synthesized without CDs, and the other processes were the same with the synthesis of Black ZnO Nano Clusters. Correspondingly, the final product was named

as White ZnO Nano Rods.

2.3. Electrochemical measurements

All ZnO based electrodes were fabricated by grounding 75 wt% of active material (ZnO or ZnO composites), 10 wt% of zinc powder, 10 wt % of acetylene black powder and 5 wt% of PTFE binder thoroughly in an agate mortar together with some drops of anhydrous ethanol to form a slurry. The obtained slurry was pasted on a stainless-steel grid (316 L) current collector with an area of 2 cm^2 and then the obtained ZnO based electrodes were pressed under 30 MPa. Subsequently, the as-prepared ZnO based electrodes dried in a vacuum oven at 80 °C for 12 h. The loading mass of the ZnO based electrodes was about 30 mg.

In three-electrode system, (Hg/HgO, 1 M of KOH) electrodes were chosen as the reference electrodes and Zn foils were used as the counter electrodes. The cyclic voltammetry (CV), Tafel plots and electrochemical impedance spectroscopy (EIS) of ZnO based electrodes were measured in the mixed alkaline electrolyte (4 M of KOH, 0.9 M of KF and 0.1 M of LiOH, saturated with ZnO). All the tests were recorded on a CH Instruments 660E electrochemical workstation. In two-electrodes system, Ni(OH)₂ electrodes served as cathodes (80 wt% of Ni(OH)₂ powder, 10 wt% of acetylene black powder and 10 wt% of PTFE binder) whose loading mass was about 250 mg (related capacity was triple to the ZnO based electrode) in the aim of making sure that the capacities of cells was controlled by ZnO based electrodes (served as anodes). When the same mixed alkaline electrolyte was applied in two-electrode devices with micro battery molds, only a limited amount of electrolyte was used to prevent it producing the excessive capacity.[32,33] Ten charge-discharge cycles at 1 A g^{-1} were performed during the pre-activation process. Besides, to ensure that anodes finished charging first, we overcharged our cells by 10% reversible capacity in each cycle, and the cut-off voltage was set as 1.2 V to prevent over-discharge.

3. Results and discussion

The preparation procedure of *Black ZnO Nano Clusters* is shown in Scheme 1. Briefly, CDs derived from a hydrothermal synthesis were added in $Zn(NO_3)_2$ aqueous solution. Then, the mixed solution was continuously injected into a hot hexamethylenetetramine solution and kept at 85 °C for 10 h. The yellow precipitate was collected and named as *Yellow ZnO Nano Clusters*. After annealing in nitrogen atmosphere, *Yellow ZnO Nano Clusters* turned into the final product *Black ZnO Nano Clusters*, in which CDs were found in the internal nanoclusters and the external carbon shells. As control, *White ZnO Nano Rods* were also prepared through the same procedure without adding CDs (Scheme S1 in Supporting Information, SI).

The field-emission transmission electron microscope (FETEM) image of CDs is shown in Fig. 1A with an inset of the high-resolution transmission electron microscope (HRTEM) image. Obviously, CDs are monodispersed and have uniform particle sizes with diameters of 2-4 nm. The lattice fringe spacing of CDs is measured to be 0.34 nm, which is consistent with the lattice spacing of graphite (002), indicating that the as-synthesized CDs have an obvious characteristic of graphitization [25]. Fig. 1B and C show the FESEM images of White ZnO Nano Rods and Black ZnO Nano Clusters, respectively. It is interesting that after addition of CDs, the product morphology changed from nanorods with diameters of about 100 nm to nanoclusters with numerous burrs of 10-20 nm, indicating that CDs are able to control ZnO growth effectively. Under the same condition, White ZnO Nano Rods were obtained without CDs, because ZnO is apt to grow into one dimensional morphology (Fig. 1D). Such White ZnO Nano Rods have porous structures, which may result from the decomposition of the template hexamethylenetetramine (Fig. 1E). Our previous research has shown that metal ions are apt to adhere on CDs surfaces, and thus, CDs will adhere on the newborn metal oxides and influence the final morphologies of the products [30]. It is more crucial that the growth of metal oxides with the capping agent CDs



Hexamethylenetetramine

Scheme 1. Synthetic route of Black ZnO Nano Clusters.



Fig. 1. (A) FETEM image and the inset HRTEM image of CDs. FESEM images of (B) White ZnO Nano Rods and (C) Black ZnO Nano Clusters, respectively. FETEM images of (D and E) White ZnO Nano Rods and (F, G and H) Black ZnO Nano Clusters with different magnifications, respectively. (I) SAED images of Black ZnO Nano Clusters.

on their surface will produce CDs-based shell structures [34]. In this way, CDs and metal oxide nanoparticles will assemble together to form multiple complex structures (Fig. 1F). After annealing, the CDs on ZnO surfaces turned into continuous compact carbon layers as shells with a thickness of about 4 nm (3-5 layers, marked as white dotted lines, Fig. 1G and H), which passivated ZnO nanomaterials, hindered zincate dissolution, and improved the cycle life of Zn anode significantly [6]. This result is in accord with the element mapping (Fig. S1, SI) that shows in the surface layers, C and O are the main elements while Zn is negligible. It also should be mentioned that the ZnO crystal lattices are not influenced by carbon coating and annealing. Shown as the figure of the selected area electron diffraction (SADE, Fig. R5C), it indicates that the Black ZnO Nano Clusters still possess high crystallinity and a hexagonal wurtzite structure, in which the six diffraction rings are perfectly indexed to the same positions as those from typical bulk ZnO (space group P63mc, JCPDS card No. 36-1451) [35].

Fig. 2A shows the X-ray diffraction (XRD) patterns of *White ZnO Nano Rods* and *Black ZnO Nano Clusters*, where the characteristic diffraction

peaks are consistent with the standard JCPDS data of ZnO wurtzite structure. The peaks of *Black ZnO Nano Clusters* at $2\theta = 31.87^{\circ}$, 34.50° , 36.34°, 47.59°, 56.63° and 62.92° are attributed to the (100), (002), (101), (102), (110), and (103) crystal planes of hexagonal phase ZnO (JCPDS No. 36-1451), respectively. There are no discernible peaks assigned to CDs or CDs derivatives because of their low content and crystallinity of CDs [30]. Fig. 2B compares the Fourier transform infrared (FTIR) spectra of these two samples, where the bands at 3440 and 1628 cm⁻¹ are assigned to the O-H stretching vibration and the H-O-H bending vibration of the atmospheric water absorbed on the surface, respectively.[36] Such bands are weaker in the white sample, because its surface area is smaller than that of the black one. A significant difference between White ZnO Nano Rods and Black ZnO Nano Clusters lies in the FTIR absorption band of Zn-O stretching vibration, which locates at 533.2 and 459.5 cm⁻¹, respectively. Zn-O infrared absorption band of Black ZnO Nano Clusters lies in the lower wavenumbers because the abundant defects in Black ZnO Nano Clusters weaken the strength of Zn-O bond [37]. Fig. 2 C displays solid



Fig. 2. (A) XRD patterns, (B) FTIR spectra, (C) powder UV–Vis absorption curves, (D) Nitrogen adsorption-desorption isotherms and (E) Pore size distributions calculated by the DFT method for White ZnO Nano Rods and Black ZnO Nano Clusters, respectively. (F) TG analysis of Black ZnO Nano Clusters.

ultraviolet-visible (UV-Vis) absorption spectra of two samples. In contrast with White ZnO Nano Rods, Black ZnO Nano Clusters exhibit a strong absorption in the whole visible region besides the characteristic band of ZnO at 367 nm [38], indicating that black carbon layers have coated ZnO matrixes completely. Surface areas and porous features of the products are evaluated by nitrogen adsorption measurements, and the corresponding results are shown in Fig. 2 D and E, respectively, as well as in Table S1 (SI). The specific surface area of the Black ZnO Nano *Clusters* (49.8 m² g⁻¹) is about 10 times larger than that of the *White ZnO* Nano Rods (4.7 m² g⁻¹), indicating that microstructures constructed by CDs will greatly improve the contact area between the electrode and the electrolyte. Since Black ZnO Nano Clusters have much more porous structures than White ZnO Nano Rods, the former facilitates the fast transfer of charges and ions [39]. Fig. 2F presents the thermogravimetric analysis (TGA) curve of Black ZnO Nano Clusters. The sample's weight drops slowly at the first stage from room temperature to 300 °C, which can be ascribed to water evaporation. As temperature increases, the weight of the sample decreases gradually until 800 °C and keeps unchanged subsequently, indicating that the carbon material in the sample has been decomposed or burned out in air. The corresponding weight loss is 5.6 wt%, which is much lower than those reported carbon contents in other ZnO-Carbon composites [12,13,15,16,40]. This result proves the outstanding advantage of CDs with respect to carbon coating, that as few as 5 wt% of CDs is enough for protecting ZnO.

X-ray photoelectron spectroscopy (XPS) measurement results in Fig. S2 A (SI) confirm the existing states of zinc, oxygen, nitrogen and carbon in Black ZnO Nano Clusters. The C 1 s band in Fig. S2 B can be deconvoluted into three peaks at 284.2, 285.4 and 287.5 eV, corresponding to the graphitic carbon, the hydroxyl groups and the carboxyl groups on the surface carbon coating, respectively [21]. The spectra of Zn 2p in Fig. S2 C include two peaks at 1023.5 and 1046.7 eV, corresponding to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively. The difference between these two peaks is the spin orbital splitting energy of Zn 2p, which is often observed in ZnO based materials [15]. Fig. S2 D displays the highresolution spectrum for O species, including three types of oxygen in *Black ZnO Nano Clusters*. The peak at 530.8 eV is attributed to O^{2-} in the ordered hexagonal ZnO, while the peak at 533.0 eV results from the water adsorbed on the surface [30]. Particularly, the peak at 531.8 eV corresponds to the hydroxyl groups (C-OH) from carbon part [30], which is consistent with the result of C1s high-resolution spectra. The more important concern is the atomic percentage of different elements in Fig. S2A, where C1s (68.90 at.%) is far beyond Zn2p (1.75 at.%). Such a huge disparity of the element distribution verifies that the carbon is the

main surface composition, and it is consistent with the carbon surface coating structures proved by HRTEM (Fig. 1 H) and elemental mappings (Fig. S1, SI) results.

Electron paramagnetic resonance (EPR) measurements were carried out to investigate the detailed information of ZnO surface states. In Fig. 3 A and Fig. S3 (SI), both the *Commercial ZnO* powder and the Yellow ZnO Nano Clusters have no EPR signals, while the *White ZnO Nano*

Rods and the Black ZnO Nano Clusters show much different signals. For White ZnO Nano Rods, the g value is 1.959, corresponding to the typical oxygen vacancies (Vo⁺). For Black ZnO Nano Clusters, the above signal disappears but a strong signal at g = 2.002 emerges [41,42]. This phenomenon present two important signals. One is that the oxygen vacancies on ZnO surfaces are passivated by the organic groups of CDs derivatives, confirming the tight protection on ZnO by CDs derivatives. The other is that the new born EPR signal may be ascribed to univalent zinc (Zn⁺) structures. Moreover, X-ray absorption spectroscopy (XAS), UV–Vis absorption curves based on diffuse reflectance (DR) spectroscopy [43–45] and optimized Zn⁺/ZnO DFT model also prove the existence of Zn⁺ sites (Fig. S4 and Fig. S5 in SI).

According to previous studies [42,46], Zn^+ can form by substitution of Brønsted acid site when ZnO is calcined at high temperature with reductive substances. In order to explore the origin of Zn⁺ in Black ZnO Nano Clusters, an analog computation was carried out and the results are shown in Fig. 3 B and C. In detail, the as-prepared CDs have negative surface charges based on carboxyl and hydroxyl groups, which are apt to adsorb Zn²⁺ ions when Yellow ZnO Nano Clusters are synthesized, as proved by the Zeta potential measurements in Fig. S6. When CDs and ZnO nanoclusters combine together, the hydroxyl groups of CDs derivatives may attract the O atoms of ZnO to form Brønsted acid sites. During annealing, such Brønsted acid sites may be substituted by those Zn^{2+} adsorbed on CDs previously. In this way, Zn^{2+} ions obtain electrons from the negatively charged CDs or CDs derivatives and change to be Zn⁺ species which are stabilized in the interfaces between CDs derivatives and ZnO. It should be mentioned that XPS measurements did not show Zn⁺ signals, indicating that Zn⁺ species are embedded in the nanoclusters (see Scheme S2 in SI). Further calculations (as shown in Scheme S3 in SI) imply that the chemisorption energy (ΔE_{ads}) of a ZnO cluster towards an OH⁻ ion is 1.820 eV. After binding a Zn^+ , the ΔE_{ads} increases to 1.894 eV, which accelerates the decisive step of the charging process, i.e., $ZnO + 2OH^- + H_2O \Rightarrow Zn(OH)_4^2$. Obviously, plenty of Zn^+ sites will endow ZnO with a favorable electronic structure for energy storage [47,48]. Furthermore, density functional theory (DFT) calculations were carried out to investigate the difference in density of states



Fig. 3. (A) EPR curves for the White ZnO Nano Rods and the Black ZnO Nano Clusters. (B) The B3LYP hybrid exchange–correlation optimized geometry of the adsorbed hydroxyl ion by Zn^+ active site. (C) The models of CDs derivatives and ZnO crystals (100). When combination happens, a Brønsted acid site of CDs derivatives is substituted by a Zn^{2+} ion which changes to be Zn^+ . DOS of (D) pure ZnO and (E) Black ZnO Nano Clusters.

(DOS) between pure ZnO (Fig. 3 D) and *Black ZnO Nano Clusters* (Fig. 3 E). In comparison with ZnO, *Black ZnO Nano Clusters* exhibit a narrowed bandgap resulted from carbon coating, which means charge carriers can be easily excited to the conduction band. In fact, *Black ZnO Nano Clusters* have a higher conductivity than ZnO as observed in experiments [48].

Comparison of Bader charges between a pure ZnO model and a carbon covered ZnO model (Table S2, Table S3 and Scheme S4 in SI) also proves that oxygen groups from the carbon part could help electrons transport from carbon shells to ZnO matrixes, and thus, *Black ZnO Nano Clusters* have a stronger ability to obtain electrons from external electric



Fig. 4. Electrochemical performances in the three-electrode systems: (A) CV curves of different samples at a scan rate of 10 mV s^{-1} ; (B) CV curves of White ZnO Nano Rods based anodes at different scan rates; (C) CV curves of Black ZnO Nano Clusters based anodes at different scan rates; (D) Relationship between the oxidation peak current densities and the square root of the scan rate for White ZnO Nano Rods and Black ZnO Nano Clusters based anodes, respectively; (E) Tafel plots for three samples; (F) Nyquist plots of three samples.

field [49].

The structural advantages of *Black ZnO Nano Clusters* based anodes are manifested in their electrochemical performances, after comparing that of *Commercial ZnO* and *White ZnO Nano Rods* used as the control samples. In comparison with the control, *Black ZnO Nano Clusters* based anodes have more prominent oxidation/reduction peaks in cyclic voltammetry (CV) measurements (Fig. 4 A), as well as the better electrochemical reactive activity and reversibility [47]. Moreover, the CV curves of *White ZnO Nano Rods* based anodes show significant polarization and a serious side reaction (like hydrogen evolution) as the sweep rate increases (Fig. 4 B), while *Black ZnO Nano Clusters* based anodes exhibit good CV curves at high sweep rates (Fig. 4 C), which can

be ascribed to more efficient mass and electron transfer paths constructed by CDs [6]. Accordingly, CV results indicate that CDs derivative carbon coating and active Zn(OH)²/₄ intermediates closely related to Zn⁺ sites can effectively enhance the reversibility of the ZnO anodes and reduce side reactions at the same time [51]. In Fig. 4 D, the relationship plots between peak currents and sweep rates illustrate the electrochemical kinetics behaviors of both *White ZnO Nano Rods* and *Black ZnO Nano Clusters* based anodes. The higher slope rate for the data of Black ZnO Nano Clusters based anodes verifies the advantage in ions diffusion rate which is based on the tiny microstructures of this sample [52].

Tafel plots are employed to further investigate the corrosion resistance of related ZnO based anodes. As shown in Fig. 4 E and Table S4 (SI), the corrosion current density and the corresponding potential of Black ZnO Nano Clusters are 2.17 \times 10⁻³ mA cm⁻² and -1.299 V, respectively. In contrast, the Commercial ZnO and White ZnO Nano Rods based anodes present more negative corrosion potential and higher corrosion current density (Table S4), i.e., their corrosion resistances are weaker than Black ZnO Nano Clusters based anodes. Such difference confirms the crucial role of carbon coating constructed by CDs derivatives. Fig. 4 F displays Nyquist curves of different samples used as electrodes. The fitted results show that charge-transfer resistance of Black ZnO Nano Clusters based anodes is only 2.03 Ω and much smaller than those of Commercial ZnO (7.95 Ω) and White ZnO Nano Rods (3.01 Ω) based anodes (more constant parameters and equivalent circuit are shown in Table S4 in SI). These results support the electron flow model, in which oxygen containing functional groups derived from CDs derivatives as bridges of charge transfer help increase the utilization ratio of ZnO matrixes and restrain electrochemical polarization, so as to render both higher rate capability and coulombic efficiency in Ni-Zn batteries [53].

Fig. 5A, B and C show the charging-discharging curves of Ni-Zn

batteries assembled by different samples at various current densities, respectively. Compared with Commercial ZnO and White ZnO Nano Rods, Black ZnO Nano Clusters based anodes have a lower charging voltage platform but a higher discharging voltage platform, which implies that Black ZnO Nano Clusters can reduce the polarization voltage so as to improve the energy conversion efficiency of the Ni-Zn batteries. After reconstruction with CDs, the rate performance of Black ZnO Nano Clusters based anodes in Fig. 5D manifests that this sample has a better discharge specific capacity at various current densities that are 559, 532, 467, and 421 mAh g $^{-1}$ at 1, 2, 5 and 10 A g $^{-1}$, respectively (1.5C-15C, with retention rates up to 75.0%). In comparison with White ZnO Nano Rods based anodes (retention rate of 59.1%), Commercial ZnO based anodes (retention rate of 39.1%) and other ZnO composites-based anodes (see Table S5 in SI) [12,13,15,16,40,50,52,53], Black ZnO Nano Clusters exhibit much better performances. Our results realize a balance between the specific capacity and the rate performance, suggesting that CDs will play an important role in the practical Ni-Zn batteries.

The cycling performances of three samples are also studied in Ni-Zn batteries. In Fig. 5E at a current density of 1 A g⁻¹, Black ZnO Nano Clusters based anodes perform much better than Commercial ZnO and White ZnO Nano Rods based anodes, whose retention rate even remains 91% after 500 cycles. In contrast, the retention rate of White ZnO Nano Rods based anodes reduces to 72% after 300 cycles and the performance of Commercial ZnO based anodes is much worse. For practical application, the cycling stability tests of Black ZnO Nano Clusters based anodes at high current densities are carried out over 5000 cycles. In Fig. 5F, the discharge specific capacity of Black ZnO Nano Clusters based anodes undergoes a fluctuant trend and grows gradually in the initial 200 cycles. This phenomenon can be ascribed to the carbon layer which retards the over quick pervasion rate of electrolyte into the inner structures at the initial stage. When more charging and discharging cycles are completed, the bulk of electrode is gradually activated and its performance becomes stable. After 5000 cycles, the capacity retentions of Black ZnO Nano Clusters based anodes remain above 92% at a current density of 5 A g^{-1} (7.5C) and 87% at a current density of 10 A g^{-1} (15C), respectively, which are far better than most previous reports (see Table S5 in SI) [12,13,15,16,40,50,52,53]. Previous studies have shown that reversibility of anodic reactions, electron transfer efficiency, corrosion resistance of ZnO and other factors will bring a huge influence to the final cycling stability [54]. Therefore, CDs' participation has improved performances of original ZnO materials in all the above aspects.



Fig. 5. For Ni-Zn batteries, galvanostatic charge–discharge curves of (A) *Commercial ZnO*, (B) *White ZnO Nano Rods* and (C) *Black ZnO Nano Clusters* based anodes at different current densities. (D) Rate performances of the different samples at various current densities, respectively. Cycling stability of (E) different samples at 1 A g⁻¹ and (F) *Black ZnO Nano Clusters* based anodes at various current densities, respectively.

In this research, 1 mg mL^{-1} CDs aqueous solution as the precursor for

Black ZnO Nano Clusters is much excessive. To further investigate the role of the amount of CDs in the improvement of the stability and rate performance, we also use 0.1, and 0.01 mg mL⁻¹ CDs aqueous solution as the precursor to prepare ZnO materials without enough protection from CDs. As shown in Fig. S7 (SI), the huge performance gap in cycling stability and rate stability between Black ZnO Nano Clusters and ZnO samples with fewer CDs is directly related to micromorphology. And related results further demonstrate the crucial functions of CDs in optimizing the surface structures and constructing surface protective layers.

4. Conclusions

In summary, *Black ZnO Nano Clusters* constructed by ZnO nanorods and CDs were prepared via a facile sol–gel method and a subsequent annealing process. The incorporation of CDs changed ZnO morphology, enlarged the specific surface area, produced continuous carbon coating layers and generated univalent zinc sites at the carbon-ZnO interfaces. Different from many other carbon materials, only a small amount (about 5 wt%) of CDs can modify ZnO and improve the composite properties significantly, including conductivity and anti-corrosion ability. More importantly, the novel univalent zinc species also made significant contribution to the electrochemical storage process, as proved by the theoretical calculations. Therefore, CDs are promising additives to make up inherent deficiencies of ZnO materials, which push forward ZnO anodes into practical applications for Ni-Zn batteries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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