



Enhancing the performance of nanostructured ZnO as an anode material for lithium-ion batteries by polydopamine-derived carbon coating and confined crystallization



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ABSTRACT

Transition metal oxides (TMOs) generally suffer severe capacity degradation as the potential anode materials for lithium-ion batteries, since the large volume changes of TMO anodes during conversion reactions result in the collapse of electrode structures. Fabricating specific nanostructures of TMOs has been demonstrated as a successful approach to partially solve this issue. Besides the concern of capacity retention, our previous work has demonstrated that the specific capacities of TMOs can be improved by enhancing their degrees of crystallinity. Therefore, the TMO nanostructures with high degrees of crystallinity are highly desired to achieve both high specific capacity and good capacity retention. However, the high crystallinity and desired nanostructure are usually contradictory in nanofabrication since the thermal treatment will lead to the collapse of a nanostructure. To overcome the obstacle, herein, the polydopamine coating followed by a thermal treatment in nitrogen is first introduced as a confined crystallization strategy to enhance the degree of crystallinity and simultaneously maintain the nanostructure of ZnO microspheres. Electrochemical performance tests demonstrate that the appropriate coating thickness and heat treatment can enhance the specific capacity from 288.0 mAh g⁻¹ of pristine ZnO to 527.0 mAh g⁻¹ of carbon coated ZnO after 100 cycles. The present work provides a good opportunity to develop TMO anodes with high capacities and superior cycling performances by the polydopamine-derived carbon coating and confined crystallization.

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1. Introduction

Transition metal oxides (TMOs, TM = Fe, Cu, Ni, Co, etc.) have attracted great attentions as alternative high-capacity anode materials to replace the currently used graphite, in order for lithium-ion batteries (LIBs) to achieve higher energy densities. The high capacities of TMOs are based on a reversible conversion reaction mechanism, which is different from the lithium-ion intercalation/deintercalation reactions. The conversion reaction of TMO is presented as the equation $TMO + 2Li^+ \rightleftharpoons TM + Li_2O$, if the transition metal is bivalent [1–3]. In the repeated cycling, TMO electrodes

undergo massive phase transformations accompanied by large volume changes, which will result in electrode disintegrations. On this account, when the active materials gradually lose the electronic contact with current collector during the electrode disintegration, TMO anodes suffer severe capacity fading [4–6]. In addition, TMO anodes often exhibit poor rate performance as well because of their low conductivities [7].

To address these issues, several approaches were successfully applied to enhance the conductivity of TMO electrode and maintain the electrode structure in previous reports. One is fabricating a specific nanostructure of TMOs [7,8]; another is incorporating TMO nanoparticles into nanostructured carbon materials such as porous carbon [9–20], graphene [21–26], and etc. The rationally designed nanostructures or nanocomposites will accommodate the large volume changes occurred during the lithiation and delithiation of metal oxides to mitigate the electrode disintegrations. In these approaches, the structural patterns of TMO nanostructures, namely

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the inner spacing shape and the assembling pattern of building blocks, is an important factor influencing the electrochemical performance [27,28]. For instance, nanostructured ZnO is intensively studied as materials for lithium-ion batteries and other applications including detector [29], solar cell [30], light-emitting diode [31], and etc. because of its low cost and abundant resource. Our previous work compares the performances of the microspheres assembled with tortuous nanosheets, hexagonal nanorods and radial assembly of nanorods of ZnO [27]. The results clearly demonstrated that the ZnO microspheres with the most sufficient inner spacing exhibit the best capacity retention among all three samples. Besides, the results also indicated that the specific capacity of ZnO can be improved by enhancing their degree of crystallinity. Therefore, ZnO nanostructures with high degree of crystallinity are highly desired to achieve both large specific capacity and good capacity retention.

However, the high degree of crystallinity and desired nanostructure are usually contradictory in nanofabrication since the thermal treatment, as a method to enhance the degree of crystallinity, will lead to the collapse of a nanostructure. For example, the nanostructure of ZnO in our previous report collapsed quickly to a nanoparticle packing at 600 °C for only 20 min [27]. To overcome the obstacle, herein, the polydopamine coating followed by a thermal treatment in nitrogen is first introduced as a confined crystallization strategy to enhance the degree of crystallinity and simultaneously maintain the nanostructure of the prepared ZnO microspheres. The primary advantage of polydopamine coating is that it can be easily deposited on virtually all types of inorganic and organic substrates, including superhydrophobic surfaces, with controllable film thickness and durable stability [32]. Hence, the surface of ZnO nanostructures will be fully and evenly covered by a polydopamine thin layer, which mitigates the collapse and aggregation of the nanostructures to some extent during the thermal treatment. In addition, the presence of nitrogen atoms in dopamine results in the nitrogen doping of the derived carbon layer, which would be highly beneficial for improving the performance of electrode materials.

In detail, this work prepared the ZnO microspheres with different carbon coating thicknesses by the confined crystallization strategy. The structural properties and electrochemical performances of the carbon coated ZnO microspheres are studied comparing to the pristine sample. The results demonstrate the enhanced performance of the highly crystallized ZnO nanostructures with the optimized coating thickness. The present work presents an effective way to develop highly crystallized transition metal oxide nanostructures for energy storage and conversion applications.

2. Experimental

2.1. Materials and preparation

The nanostructured ZnO microspheres were prepared via a hydrothermal route according to our previous report [27]. Firstly, the aqueous solutions of 0.01 mol L⁻¹ zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), 0.01 mol L⁻¹ hexamethylenetetramine (HMT, C₆H₁₂N₄), and 0.1 mol L⁻¹ trisodium citrate (Na₃C₆H₅O₇·2H₂O) were prepared respectively. Then, 30 mL of the zinc nitrate solution, 30 mL of the HMT solution, and 2 mL of the trisodium citrate solution were mixed and stirred thoroughly. The mixed solution was transferred to a Teflon-lined autoclave with the capacity of 100 mL for hydrothermal synthesis at 95 °C in an oven for 12 h. After which the autoclave was removed from the oven and allowed to cool to room temperature. The resulting white precipitate in the autoclave was collected and washed with deionized water several

times before being dried in a vacuum oven at 130 °C for 12 h.

For a typical synthesis of carbon coated ZnO, 100 mg of the as-prepared ZnO microspheres was mixed with various amounts of dopamine hydrochloride (20, 30 and 50 mg) in a Tris buffer (75 mL, 10 mmol L⁻¹; pH = 8.5) and then stirred for 24 h. The polydopamine coated samples were collected by centrifugation and washed three times using water. To carbonize the polydopamine coating and enhance the degree of crystallinity of ZnO, the dried powders were placed in a tube furnace and heated under N₂ at 600 °C for 2 h with a heating rate of 2 °C min⁻¹. The resultant products were denoted as ZnO@C–Y, where Y represents the mass of dopamine hydrochloride in mg used in the preparation.

2.2. Physical characterization

The morphologies of the pristine ZnO microspheres and the ZnO@C–Ys were examined with a Zeiss Ultra-Plus field emission scanning electron microscope (FE-SEM). The powder X-ray diffraction (XRD) patterns of all the samples were recorded on a Rigaku D/MAX-RB diffractometer with a CuK α radiation operating at 40 kV, 50 mA. The X-ray photoelectron spectra (XPS) were recorded on a VG Multilab2000X X-ray photoelectron spectrometer with an Al K α excitation source, where binding energies were calibrated by referencing the C 1s peak (284.6 eV) to reduce the sample charge effect. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) images were taken with a JEM 2100 F electron microscope operating at 200 kV, and energy dispersive spectrometer (EDS) mapping was used to analyze the composition and element distribution of the samples. The thermogravimetric and differential thermal analysis (TG-DTA) was carried out on an SDT Q600 thermal analyzer.

2.3. Electrochemical testing

The electrochemical performances of the ZnO samples with and without carbon coating were determined in CR–2032–type coin cells. The ZnO electrodes were prepared by laminating the mixed slurry composed of 80 wt% of ZnO sample, 10 wt% of acetylene black and 10 wt% of polyvinylidene difluoride (PVDF). The mass loading of ZnO samples was about 5 mg cm⁻². The coin cells were assembled in an argon filled glove box with a ZnO electrode as anode, a lithium foil as counter electrode, a Celgard PE membrane as separator, and 1 M LiPF₆ in a 1:1 ethyl carbonate (EC): dimethyl carbonate (DMC) solvent as electrolyte. The cycling and rate performances of the coin cells were tested with constant current charge/discharge on NEWARE BTS battery testers at room temperature. 1C approximately equals to a current density of 1000 mA g⁻¹ according to the theoretical of 988.2 mAh g⁻¹ of ZnO. The cyclic voltammetry (CV) tests were carried out with the scan rate of 0.1 mV s⁻¹ from 0.05 to 3.00 V on a CHI 660D electrochemical workstation (CH Instruments). The electrochemical impedance spectroscopies (EIS) of cycled cells were measured at open circuit potential (OCP) with a 10 mV perturbation in the frequency range of 10⁶–10⁻³ Hz on the CHI 660D electrochemical workstation. All the potentials in the present work refer to Li⁺/Li.

3. Results and discussion

3.1. Materials characterization

Figs. 1 and 2 compare the FE-SEM images and the XRD patterns of the pristine ZnO microspheres and the derived ZnO@C–Ys respectively. As can be seen in Fig. 1A and B, the ZnO microspheres (1.0–2.0 μ m in diameter) assembled with tortuous nanosheets are successfully synthesized by the hydrothermal reaction of

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