Continuous Carbon Hollow Shell with Zinc Oxide Nanoparticles Embedded as an Anode Material with Excellent Lithium Storage Capability

Yuting Mao, Qin Wang, Xi Wu, Huiqi Xie, Xiaomei Ma, and Min Chen* [a]

Continuous carbon hollow shells with embedded ZnO nanoparticles were synthesized from colloidal polystyrene/ZnO as templates and glucose oligomer as the carbon source followed by calcination. The resulting uniform ZnO/C hollow spheres display a relatively high reversible capacity of 994 mAh g⁻¹ after 100 cycles at 0.1 A g⁻¹ and 812 mAh g⁻¹ after 200 cycles at 1 A g⁻¹, which is superior to most reported ZnO-based anode materials. The excellent electrochemical performance of the ZnO/C hollow spheres may arise from the following aspects: the shortened pathway of Li ions and electrolyte attributed to the unique hollow shell structures, improved electronic conductivity, firm encapsulation of ZnO nanoparticles, and high specific surface area of the products, which together facilitate the ZnO nanoparticles to undergo the alloying reaction completely.

Introduction

Renewable energy sources and new energy sources are important research topics. Lithium-ion batteries (LIBs) are applied widely as power sources not only for portable electronic devices but also for hybrid electric vehicles and electric vehicles because of their high reversible specific capacity and long life span without memory effects. [1–3] However, the current graphite anode cannot meet the increasing demand for energy storage capability because of its limited theoretical capacity (372 mAh g⁻¹). [4]

Transition metal oxides (TMOs) have attracted attention in recent years for their high theoretical capacities and have become potential candidates for the next generation of LIB anode materials. [5–11] Of these, ZnO has drawn wide attention for its abundance, high theoretical capacity (987 mAh g⁻¹), and environmentally benign nature. Unfortunately, the poor electronic conductivity and pulverization of the ZnO bulk results from a large volume expansion (≈228%) during the charge–discharge process that may lead to fast capacity fading, which hinders its practical application. [12]

Downsizing the materials to the nanoscale is a promising method to buffer this drastic volume change. [13–16] especially for hollow structures, which have drawn a lot of attention because of their advantages in that they can accommodate volume expansion, shorten the diffusion path of Li ions, and increase the contact area between the electrode and electrolyte. [17,18] However, nanostructured ZnO tends to agglomerate, because of its high surface area, to result in poor cycle retention. To obtain high electrical conductivity and structural stability, forming composites of carbonaceous materials with ZnO seems to be an effective strategy. Among these carbon sources, graphene is one of the most widely used candidates to fabricate ZnO/C composites, and the reported ZnO nanoparticles anchored on vertically aligned graphene nanosheets (ZnO-VAGNs), [19] ZnO nanocrystals attached to graphene nanosheets (ZnO@GN) hybrid, [20] and self-assembled zinc oxide nanoggregates by using graphene oxides as templates (SAZO@GO) [21] exhibit a good reversible capacity and rate performance with a limited cyclic stability (50–80 cycles). This is because graphene is a 2D material and ZnO nanoparticles (NPs) are practically anchored on the surface; thus, the confinement may not be sufficient to resist the volume change. Other carbon precursors with a low molecular weight include melamine/phenol, [22] polyethylene glycol (PEG-400), [23] and metal–organic frameworks (MOFs). [24] These could form a carbon matrix in which the ZnO NPs are embedded and the carbon content of the ZnO/C composites is relatively high (30–50 wt%), which decreases the specific capacity. Glucose is another cheap and environmentally friendly carbon source with low molecular weight that has been used as a carbon source in other studies. [25–27] Unfortunately, if it is combined with ZnO nanorods at room temperature, it cannot provide complete encapsulation (carbon content ≈3.0 wt%) to maintain cyclic stability (<50 cycles) because of the weak interaction with ZnO. [28]

Briefly, an ideal ZnO/C composite material for an anode is composed of ZnO NPs encapsulated within a robust and continuous carbon layer with an appropriate weight percentage, which is designed not only to ensure high electrical conductivity but also realize sufficient utilization of ZnO and, consequently, exhibit a relatively high specific capacity. Hence, in this study, glucose oligomers acquired from hydro-

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thermal pretreatment were used as a carbon source to form continuous carbon hollow shells embedded with ZnO NPs (with a carbon content of 20.6 wt%) by employing colloidal polystyrene (PS)/ZnO core–shell spheres as the templates. In the synthesis, the glucose oligomer solution first penetrated into the gaps between the primary ZnO NPs and then gradually encapsulated them to form continuous carbon shells.

This unique structure and synthesis technique has several advantages compared with those used in previous studies. First, compared to other low-molecular-weight carbon sources, the glucose oligomer with a higher molecular weight could be tangled easily onto the primary ZnO NPs to result in firm and complete encapsulation by carbon after calcination. This unique structure prevents direct contact between ZnO and the electrolyte, and the continuous carbon shell provides an electrical highway to improve the electrochemical kinetics, which results in an enhanced capacity and rate performance. Second, the inside void spaces derived from the hollow structure and the outside elastic carbon shells buffer the drastic volume change effect during lithiation/delithiation and shorten the ion diffusion pathways, which contribute to outstanding cycling stability. As a result, the continuous carbon hollow shells embedded with ZnO NPs exhibit a good Li storage capacity, excellent rate performance, and long cycle life.

Results and Discussion

Synthesis and characterization of ZnO/C hollow spheres

Continuous carbon hollow shells with embedded ZnO NPs were fabricated using sulfonated polystyrene (SPS) spheres as templates and glucose oligomer as the carbon source followed by calcination (Scheme 1). Negatively charged polystyrene (PS) spheres modified with –SO$_3$H groups (SPS) were achieved by sulfonation followed by Zn ion absorption onto the surface of the SPS by electrostatic interactions. The ZnO shells were formed gradually by adding the NaOH. The SPS/ZnO core–shell spheres were uniform with an average size of 300 nm (Figure 1a,d). The SPS/ZnO composite spheres were calcined at 500 °C for 0.5 h in Ar to remove the inner cores. The relatively low temperature of the combustion under an inert atmosphere resulted in approximately 6 wt% residual carbon, which contributed to the intact hollow structure because of the poor mechanical properties of pure ZnO. During the combustion process, the ZnO nanocrystals grew bigger and the gaps increased significantly in the shell (Figure 1b,e). Next, the ZnO hollow spheres were immersed in the glucose oligomer aqueous solution, which led to an increase of the viscosity and molecular weight because of polymerization.$^{[29,30]}$ If we compare this process with that with a conventional low-molecular-weight carbon source, the polymer chains are tangled much more easily onto the primary ZnO NPs to result in firm encapsulation by carbon after calcination at 500 °C for 4 h in Ar. The hollow nature of the final ZnO/C products with an intact spherical structure is shown in Figure 1c,f. Compared with that of the SPS/ZnO templates, the morphologies of the ZnO/C final products show no apparent changes except that the size of the spheres became smaller because of the shrinkage of the carbon shell during annealing.$^{[26]}$ Additionally, a small number of spheres were broken as a result of the two-step calcination process.

To confirm the integrity of the carbon shell, the ZnO/C–160 °C composite spheres were washed with 1 M HCl solution for 2 h to remove the ZnO NPs. The residual carbon shell was intact and crumpled, and the bubble-like cavities showed that the ZnO NPs were encapsulated well (Figure 2a). In stark contrast, the carbon shell of the ZnO/C–25 °C after HCl treatment was almost broken (Figure S1, Supporting Information) because of the weak interaction of the glucose monomer with ZnO NPs that led to incomplete encapsulation. Moreover, the immersion of ZnO hollow spheres in the glucose oligomer solution was performed at room temperature. In contrast to the conventional method that distributes ZnO hollow spheres into a glucose monomer solution followed by hydrothermal reaction (Figure S2, Supporting Information), the mild experimental conditions used in this study also prevent ZnO nanocrystals from falling off the carbon skeleton and thus lead to the formation of a complete ZnO/C shell structure.
In addition, the carbon layer and adsorption–desorption isotherms of the samples arise from disordered edges, or other structural defects, and the G band at \( \tilde{\nu} = 1584 \text{ cm}^{-1} \) is attributed to the vibration mode in graphite-like carbon.\[^{[22]}\] The partially graphitized carbon shell endows ZnO/C-160°C with the potential for excellent electronic conductivity and ion transport properties.

The selected area electron diffraction (SAED) pattern presented in Figure 2b (inset) shows the polycrystalline structure of ZnO/C-160°C.\[^{[31]}\] In addition, the carbon layer and ZnO NPs can be distinguished easily in the high-resolution transmission electron microscopy (HR-TEM) image (Figure 2c) by their different contrasts. The lattice fringes observed in the different parts are clear, and the inner d-spacing values of 0.25, 0.26, and 0.28 nm are assigned to the (101), (002), and (100) planes of crystalline ZnO, respectively.\[^{[32]}\] The outer lattice spacing of 0.34 nm corresponds to the (002) plane of the partially graphitic carbon layer.\[^{[23]}\]

Powder XRD patterns of the as-prepared ZnO NPs, ZnO hollow spheres (HS), ZnO/C-25°C, and ZnO/C-160°C are shown in Figure 3a. All diffraction peaks are indexed to the Wurtzite phase of hexagonal ZnO (JCPDS No. 36-1451). Furthermore, the average crystallite sizes estimated by the Scherrer formula were 39.0, 14.9, 14.7, and 14.1 nm, respectively. This indicates that the confinement of the carbon skeleton could suppress the growth of ZnO NPs, which is beneficial to accommodate the volume change in the cyclic lithiation/delithiation process.\[^{[33]}\] There is no clear diffraction peak related to amorphous carbon at \( 2\theta = 23^\circ \) in the pattern of ZnO/C, which is probably because of the relatively weak peak intensity compared to the pattern of the ZnO crystal.\[^{[33]}\]

The carbon contents of all the samples were investigated by using thermogravimetric analysis (TGA). No apparent weight loss for ZnO NPs was observed (Figure 3b). In contrast, ZnO HS, ZnO/C-25°C, and ZnO/C-160°C show a clear weight loss from 300 to 650°C that can be ascribed to the decomposition of carbon. As a result, the carbon contents of ZnO HS, ZnO/C-25°C, and ZnO/C-160°C are approximately 6.26, 11.50, and 20.61 wt\%, respectively. We suspect that the oligomer chains are tangled easily on the ZnO NPs to result in complete encapsulation compared with the glucose monomer, which was verified by using TEM (Figure S1, Supporting Information).

The Raman spectra of ZnO/C-160°C in the range of 750–2000 cm\(^{-1}\) are shown in Figure 3c. There are two distinct peaks: the D band at \( \tilde{\nu} = 1340 \text{ cm}^{-1} \) arises from disordered carbon, edges, or other structural defects, and the G band at \( \tilde{\nu} = 1584 \text{ cm}^{-1} \) is attributed to the vibration mode in graphite-like carbon.\[^{[22]}\] The partially graphitized carbon shell endows ZnO/C-160°C with the potential for excellent electronic conductivity and ion transport properties.

The \( \text{N}_2 \) adsorption–desorption isotherms of the samples are presented in Figure 3d (the pore size and distributions of the samples are shown in Figure S3, Supporting Information). The Brunauer–Emmett–Teller (BET) specific surface area of ZnO/C-160°C is \( 143.3 \text{ m}^2\text{g}^{-1} \), which is much higher than that of ZnO/C-25°C (73.9 m\(^2\)g\(^{-1}\)), ZnO HS (63.6 m\(^2\)g\(^{-1}\)), and ZnO NPs (10.9 m\(^2\)g\(^{-1}\)). The high BET surface area of ZnO/C-160°C may arise from the hollow structure as well as the presence of pores and structural defects in the carbon layer after calcination. This is beneficial to accommodate extra Li ions at the electrode surface and to reduce the ion transport path length.\[^{[34]}\] In addition, our X-ray photoelectron spectroscopy (XPS) results indicate that ZnO/C-160°C is composed of C, Zn, and O as expected (Figure S4, Supporting Information).

**Electrochemical performance**

The electrochemical properties of all the samples were investigated over the potential range of 0.001–3 V. The specific capacities are calculated based on the total mass of the active materials. The cyclic voltammograms (CVs) of ZnO/C-160°C over the first four cycles at a sweep rate of 0.1 mVs\(^{-1}\) are shown in Figure 4a. The initial cathodic scan shows an intense peak at 0.43 V that corresponds to the decomposition of the electrolyte and the formation of a solid-electrolyte interface (SEI) layer, which led to the irreversible capacity and
weakened significantly in subsequent cycles.\cite{35} The peak at 0.6–0.9 V may originate from the reduction of ZnO to Zn and the formation of the Li$_2$Zn$_x$ alloy.\cite{36} Another relatively weak peak below 0.1 V is caused by the intercalation of Li$^+$ into the carbon as reported previously.\cite{23} In addition, several adjacent oxidation peaks below 0.75 V may be assigned to the multiple delithiation reactions of a lithium–zinc alloy and the decomposition of the SEI layer.\cite{37,38} A broad peak near 1.25 V arises from the reaction between Zn and Li$_2$O to form ZnO.\cite{36} The curves are generally quite similar to each other except the first one, which indicates the reversible reaction kinetics and stability of the Li storage capacity of the ZnO/C-160°C electrode.

Selected galvanostatic discharge and charge profiles of the ZnO/C-160°C electrode at a current density of 1 Ag$^{-1}$ are depicted in Figure 4b. The initial discharge and charge capacities are 1445 and 775 mAhg$^{-1}$ with a Coulombic efficiency of 54%. However, the discharge/charge values for ZnO/C-25°C, ZnO HS, and ZnO NPs are 1054/614, 1136/690, and 1010/621 mAhg$^{-1}$, respectively (Figure S5b,d,f, Supporting Information). The increased Li storage capacity of ZnO/C-160°C may arise from the increased specific surface area from the introduction of the complete carbon shell (Figure S1, Supporting Information, and Figure 3d), which increases the contact area between the electrode and electrolyte and, consequently, leads to more active sites for Li storage.\cite{23} The irreversible capacity loss and low Coulombic efficiency are due to of the formation of the SEI film and the degradation of the electrolyte as indicated by the plateau at approximately 0.45 V in the first discharge profile, which is in accord with the corresponding CV profile. Moreover, the specific capacity of the ZnO/C-160°C electrode increases swiftly after the first 10 cycles. This phenomenon could be explained by the reversible formation of a polymer-like film.
that arises from the kinetically activated degradation of electrolyte, which has been observed in other nanostructured TMO electrodes.\cite{39–41} The discharge–charge capacities tend to be stable after 100 cycles, and the electrode maintained a high capacity along with excellent reversible properties in subsequent cycles.

The cycling performance and stability of the four electrodes at a current density of 1 A g\(^{-1}\) are shown in Figure 4c. The discharge specific capacity of the ZnO NPs electrode fades quickly during the first 10 cycles, and it retains a discharge capacity of 61 mAh g\(^{-1}\) after 200 cycles, which is only 6% of the initial capacity. Conversely, the other three electrodes with hollow structures exhibit outstanding cycling stability. It is accepted that the special void spaces derived from unique hollow structures may accommodate the drastic volume change efficiently during the lithiation/delithiation reactions and prevent the active materials from pulverization. Moreover, the ZnO/C-160°C anode maintains a discharge specific capacity of 812 mAh g\(^{-1}\), which is superior to that of ZnO/C-25°C (607 mAh g\(^{-1}\)) and ZnO HS (514 mAh g\(^{-1}\)). This can be ascribed to the introduction of the continuous carbon shell. The improved electronic conductivity makes the transportation of Li ions and electrons easier, which leads to better utilization of the active ZnO NPs.\cite{42} Moreover, the carbon shell contributes extra active sites for Li storage. To verify this hypothesis, the hollow carbon spheres derived from the dissolution of ZnO from ZnO/C-160°C composites with 1 M HCl were tested to measure their capacity performance at a current density of 1 A g\(^{-1}\). The obtained hollow carbon spheres maintain the discharge specific capacity of 450 mAh g\(^{-1}\) after 200 cycles, which is higher than the theoretical specific capacity of a graphite anode (Figure S6, Supporting Information). We believe that the high specific surface area plays an important role to accommodate more Li ions, and similar results have been reported previously.\cite{43,44}

The rate performance of ZnO/C-160°C is presented in Figure 4d. The discharge specific capacities are 810, 789, 751, 688, 613, and 475 mAh g\(^{-1}\) at current densities of 0.1, 0.2, 0.5, 1, 2, and 5 A g\(^{-1}\), respectively. This rate performance is not only better than that of ZnO NPs, ZnO HS, and ZnO/C-25°C electrodes but also superior to most reported ZnO/C composite electrodes (Table 1). If the current density is brought back to 0.1 A g\(^{-1}\), the discharge capacity recovers immediately to 819 mAh g\(^{-1}\) and then increases to 994 mAh g\(^{-1}\) after 100 cycles (Figure 4e).

To further analyze the interfacial and ion diffusion kinetics of the four electrodes before cycling, electrochemical impedance spectroscopy (EIS) was performed at room temperature. The Nyquist plots of all the samples have similar patterns (Figure 5). The semicircles in the medium-high frequency region relate to the SEI film and the charge-transfer resistance of Li ion insertion, and the inclined lines in the low-frequency region correspond to the diffusion of Li\(^+\) in the electrodes.\cite{39,46,49} It is clear that the charge-transfer resistance of the ZnO/C-160°C electrode is much lower than that of the other electrodes before cycling.

![Figure 5. Nyquist plots of the ZnO NPs, ZnO HS, ZnO/C-25°C, and ZnO/C-160°C electrodes before cycling.](image)

Table 1. Comparison of cycling performance among ZnO/C composite anodes.

<table>
<thead>
<tr>
<th>Material</th>
<th>Carbon content [wt%]</th>
<th>Rate [1 C = 987 mA g(^{-1})]</th>
<th>Reversible capacity [mAh g(^{-1})] (after n cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/ZnO nanorod array\cite{28}</td>
<td>~3.0</td>
<td>0.25 C</td>
<td>330 (50 cycles)</td>
</tr>
<tr>
<td>ZnO/VAGNs\cite{29}</td>
<td>32.0</td>
<td>80 mA g(^{-1})</td>
<td>810 (100 cycles)</td>
</tr>
<tr>
<td>SSL ZnO/C NPs\cite{39}</td>
<td>20.3</td>
<td>100 mA g(^{-1})</td>
<td>813 (100 cycles)</td>
</tr>
<tr>
<td>ZnO NPs/3D CF\cite{28}</td>
<td>18.6</td>
<td>100 mA g(^{-1})</td>
<td>850 (200 cycles)</td>
</tr>
<tr>
<td>ZnO NS/graphite\cite{28}</td>
<td>13.7</td>
<td>1 A g(^{-1})</td>
<td>600 (100 cycles)</td>
</tr>
<tr>
<td>ZnO@GAs\cite{40}</td>
<td>10.6</td>
<td>1.6 Ag g(^{-1})</td>
<td>445 (500 cycles)</td>
</tr>
<tr>
<td>ZnO NP/nanocarbon\cite{40}</td>
<td>10.6</td>
<td>5 Ag g(^{-1})</td>
<td>280</td>
</tr>
<tr>
<td>ZnO NP/porous carbon\cite{40}</td>
<td>10.6</td>
<td>0.98 Ag g(^{-1})</td>
<td>705 (100 cycles)</td>
</tr>
<tr>
<td>ZnO/C HS (this work)</td>
<td>20.6</td>
<td>4.9 Ag g(^{-1})</td>
<td>~480</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 C</td>
<td>650 (200 cycles)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 C</td>
<td>375</td>
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<tr>
<td></td>
<td></td>
<td>100 mA g(^{-1})</td>
<td>994 (100 cycles)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 A g(^{-1})</td>
<td>812 (200 cycles)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 A g(^{-1})</td>
<td>475</td>
</tr>
</tbody>
</table>

[a] VAGNs: vertically aligned graphene nanosheets. SSL ZnO/C NPs: solid-solution-like ZnO/C composite nanofibers. ZnO NPs/3D CF: ZnO nanoparticles/3D carbon framework. ZnO NS/graphite: ZnO nanosheets/graphite. ZnO@GAs: ZnO@ graphene aerogels. ZnO NP: ZnO nanoparticle.

Figure 5. Nyquist plots of the ZnO NPs, ZnO HS, ZnO/C-25°C, and ZnO/C-160°C electrodes before cycling.
Experimental Section

Materials

Styrene (St, 99%) obtained from Sinopharm Chemical Reagent Co. Ltd. (China), was purified with 5 wt% aqueous NaOH solution to remove inhibitors and dried over anhydrous CaCl₂ before use. Sodium dodecylsulfate (SDS) and potassium persulfate (KPS) were supplied by Sigma–Aldrich (Shanghai). Ethanol, zinc acetate dihydrate [Zn(AC)₂·2H₂O], NaOH, dextrose monohydrate (C₆H₁₂O₆·H₂O), and H₂SO₄ (98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized water (≈17 MΩ·cm⁻¹) was used throughout the experiments.

Synthesis of SPS/ZnO composite spheres

The sulfonated PS core–shell sphere templates (SPS) were fabricated according to our previous method. Firstly, monodisperse positively charged PS colloids were synthesized by emulsion polymerization as follows: styrene (6 g), SDS (0.08 g), and H₂O (94 g) were introduced into a 250 mL four-neck round-bottomed flask equipped with a mechanical stirrer, a thermometer with a temperature controller, a N₂ inlet, an Allihn condenser, and a heating mantle. The reactant was stirred constantly and degassed by N₂ at RT for approximately 30 min and then heated to 70 °C. KPS aqueous solution (0.2 g of KPS dissolved in 10 g of water) was added, and the mixture was heated at 70 °C for another 10 h, then centrifuged, washed, and dried to obtain PS powders. The dried PS powder (4.0 g) was distributed in concentrated H₂SO₄ (98%, 40 mL) and stirred at 40 °C for 4 h to form sulfonated PS core–shell gel spheres, which were separated by centrifugation, washed with a large excess of ethanol, and then dispersed in ethanol for subsequent use.

In a typical procedure to prepare SPS/ZnO composite spheres, Zn(AC)₂·2H₂O (0.36 g) and the as-prepared SPS–ethanol dispersion (5.04 g, 1.40 wt%) were dispersed in ethanol (60 mL) ultrasonically to form a well-distributed mixture and heated to 60 °C for 0.5 h under magnetic stirring. Then, a NaOH ethanol solution (40 g, 0.32 wt%) was added dropwise over 2 h, and the mixture was stirred at 60 °C for another 3 h. The obtained milky suspension was centrifuged and washed with ethanol three times and dried at 80 °C. ZnO NPs used as a control were prepared under the same conditions in the absence of SPS.

Synthesis of ZnO/C hollow spheres

First, the as-prepared SPS/ZnO composite spheres were calcined under an Ar atmosphere at 500 °C for 0.5 h to remove the internal SPS templates. Then, the obtained black powder (0.05 g) was immersed in 0.4 M glucose solution (40 mL), which was pretreated hydrothermally at 160 °C for 4 h and stirred at RT vigorously overnight. The resulting product was harvested by centrifugation and washed thoroughly with deionized water several times. After it was dried at 80 °C, a certain amount of the as-obtained powder was loaded into a tube furnace and annealed under an Ar flow at 500 °C for 4 h with a ramp rate of 1 °C·min⁻¹ over the range of 400–500 °C. The final product was denoted as ZnO/C-160 °C. For comparison, the same mass of ZnO hollow spheres was immersed in glucose solution without hydrothermal pretreatment at RT (25 °C) and then calcined to obtain ZnO/C-25 °C. Similarly, ZnO hollow spheres and ZnO NPs were calcined under the same conditions and labeled as ZnO HS and ZnO NPs, respectively.

Conclusions

We designed and fabricated continuous carbon hollow shells with embedded ZnO nanoparticles by using a glucose oligomer as the carbon source. The abundant polymer chains of the glucose oligomers can tangle easily on the primary ZnO nanoparticles to form continuous carbon. The as-obtained composite electrode displays a relatively high reversible capacity of 994 mAh·g⁻¹ after 100 cycles at 0.1 Ag⁻¹ and 812 mAh·g⁻¹ after 200 cycles at 1 Ag⁻¹, which is superior to that of most ZnO/C composites reported previously. The unique hollow structure, improved electronic conductivity, appropriate ZnO mass ratio, and high specific surface area contribute to its notable electrochemical performance. Finally, we believe that this glucose-oligomer-assisted immersion method can be extended to fabricate other high-performance transition metal oxide/C composite electrode materials for advanced lithium-ion batteries.
Characterization

The morphologies of these products were analyzed by using FE-SEM (Ultra 55) and TEM (Tecnai G2 20 TWIN & Tecnai G2 F20 S-Twin). The crystal structures of the as-synthesized samples were observed by using powder XRD (Bruker, D8 Advance X-ray diffractometer) using CuKα radiation (λ = 0.15408 nm) with a scanning rate of 10° min⁻¹ in the range of 2θ = 10–80°. The carbon content of the samples was tested by using TGA (Q500) at a heating rate of 20° C min⁻¹ in pure air (40 mL min⁻¹) of gas flow from RT to 800°C. XPS was performed by using an AXIS Ultra DLD spectrometer (Kratos) to characterize the surface composition. Raman spectra were recorded by using an Invia instrument with a 520 nm Ar-ion laser. The specific surface area of the samples was estimated from the N₂ adsorption (Quadrasorb evo).

Electrochemical measurements

The working electrode was obtained by pasting the slurry, which was a mixture of the as-prepared samples, carbon black (super P), and polyvinylene fluoride (PVDF) binder using an electrochemical workstation (CHI 660B) over the potential range of 2.0 V. The capacities of the electrodes was approximately 1 mg cm⁻². Electrochemical measurements were performed using 2032-type coin cells assembled in an Ar-filled glovebox (H₂O, O₂ < 0.1 ppm) with Li foil as the counter electrode. The electrolyte was 1.0 M LiPF₆ in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 v/v). The capacities and cycle properties were tested by using a Land battery tester (CT2001A model) at different current densities in a voltage window between 0.001 and 3.0 V versus Li/Li⁺. CV was recorded using an electrochemical workstation (CHI 660B) over the potential range of 0.001–3 V at a scanning rate of 0.1 mV s⁻¹. EIS measurements of the electrodes were measured by using the same instrument over the frequency range between 100 kHz and 0.01 Hz.

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Conflict of interest

The authors declare no conflict of interest.

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