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# Nano-$MnO_2$@$TiO_2$ microspheres: A novel structure and excellent performance as anode of lithium-ion batteries

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## HIGHLIGHTS

- $MnO_2$ microspheres consisting of compact nanoparticles were coated with $TiO_2$.
- Resulting product exhibits excellent performance as anode of lithium ion battery.
- $TiO_2$ stabilizes $MnO_2$ morphology and facilitates lithium insertion/extraction.

## ARTICLE INFO

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## ABSTRACT

A structurally hierarchical $MnO_2/TiO_2$ composite (Nano-$MnO_2$@$TiO_2$) is fabricated by calcining $MnCO_3$ microspheres and coating a thin layer of $TiO_2$ through the heat decomposition of tetrabutyl titanate, and evaluated as anode of gravimetrically and volumetrically high energy density lithium ion battery. The characterizations from FESEM, TEM, HRTEM and XRD, indicate that the resulting Nano-$MnO_2$@$TiO_2$ takes a spherical morphology with a core of about 2 μm in diameter, consisting of compact $MnO_2$ nanoparticles, and a shell of 60 nm thick, consisting of smaller $TiO_2$ nanoparticles. The charge/discharge tests demonstrate that Nano-$MnO_2$@$TiO_2$ exhibits excellent performance as anode of lithium ion battery, delivering a capacity of 938 mAh $g^{-1}$ at 300 mA $g^{-1}$ after 200 cycles, compared to the 103 mAh $g^{-1}$ of the uncoated sample. The microsphere consisting of compact nanoparticles provides Nano-$MnO_2$@$TiO_2$ with high specific gravity. The dimensionally and structurally stable $TiO_2$ maintains the integrity of $MnO_2$ microspheres and facilitates lithium insertion/extraction. This unique structure yields the excellent cyclic stability and rate capability of Nano-$MnO_2$@$TiO_2$.

## 1. Introduction

Next-generation lithium-ion batteries (LIBs) with high power and energy density and excellent cyclic stability are needed to power future advanced devices such as communication products and electric vehicles [1–3]. As the anode first introduced in the commercial market of LIBs, however, graphite has a low specific capacity (372 mAh $g^{-1}$) and cannot meet the increasing energy density demand of the advanced devices. Recently, various metal oxides, such as manganese oxides (MnO, $MnO_2$, $Mn_2O_3$, and $Mn_3O_4$) and tin oxides (SnO, $SnO_2$), have been extensively studied as anodes for high energy density LIBs, because they can provide far larger specific capacities than graphite, which are based on the reactions [4–12]:

$$M_xO_y + 2yLi^+ + 2ye^- = xM + yLi_2O \tag{1}$$

Among these oxides, manganese-based oxides are most attractive because of the abundance and the environmental friendliness of manganese [13,14]. Compared with other manganese oxides, $MnO_2$ is most easily prepared and provides the largest specific capacity [15–17]. Based on equation (1), the calculated theoretical specific capacity of $MnO_2$ is 1233 mAh $g^{-1}$, compared to the 756 mAh $g^{-1}$ of MnO, 937 mAh $g^{-1}$ of $Mn_3O_4$, and 1019 mAh $g^{-1}$ of $Mn_2O_3$. Like other manganese oxides, however, $MnO_2$ exhibits poor cyclic stability due to the large volume change during lithium insertion/extraction [18].

To buffer the volume change of the electrode materials that have larger lithium insertion capacity, various porous- and nano-structured materials have been developed, including nanoparticles [19],

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nanosheets [20–22], hollow or porous nanostructures [23–26], and nanowires or nanorods [27–29]. The space in pores or among nanoparticles can buffer the volume change during lithium insertion/extraction, ameliorating the cyclic stability of the electrode materials. However, porous- and nano-structured materials have a larger surface area than their micro-size counterpart, which might cause the electrode material dissolution and the electrolyte decomposition [30]. In Addition, porous configuration and nanostructure that can provide space for buffering volume change yield low specific gravity of the electrode that leads to volumetrically low energy density of LIBs.

Comparatively, coating a layer of stable transition metal oxides on electrode materials is generally considered as an effective way to improve the cyclic stability of electrode materials. The coating layer not only confines the oxide structure but also separates the oxide from direct contact of electrolyte that might cause metal ion dissolution from the oxides and electrolyte decomposition [31–33]. Titanium dioxide ($TiO_2$) is ideal for coating due to its advantages of structural and dimensional stability (less than 4% volume expansion), nontoxicity, and low cost [34–40]. Besides its protection for the structural integrity of the electrode materials, $TiO_2$ coated on electrode materials can accelerate the lithium insertion/extraction kinetics due to its activity for lithium insertion/extraction, which benefits the rate capability of the electrode materials. In a previous report,[6] a composite of $Mn_2O_3$@$TiO_2$ by coating $TiO_2$ on porous nano-$Mn_2O_3$ cubes was found to exhibit good cyclic stability and rate capability. However, the maximum reversible capacity of the $Mn_2O_3$@$TiO_2$ was maintained only for 100 cycles at a current rate of 200 $mAg^{-1}$. This performance suggests that $TiO_2$ cannot provide an effective protection for the structural integrity of electrode materials that have porous configurations.

In this work, we reported a novel composite, $MnO_2$ microspheres coated with a thin layer of $TiO_2$ (Nano-$MnO_2$@$TiO_2$), as anode of lithium ion battery. $MnO_2$ microspheres were developed by calcining $MnCO_3$ microspheres without using any template and then coated with $TiO_2$ from heat decomposition of tetrabutyl titanate. The synthesis is facile and cost-effective. Most importantly, the resulting microspheres consist of compact nanoparticles. The nanoparticles provide short paths for lithium transportation in the particles. The microspheric configuration reduces surface area and ensures the volumetrically high energy density of lithium ion batteries. The $TiO_2$ layer provides a protection of the structural stability and facilitates the lithium insertion/extraction of $MnO_2$. Therefore, the resulting Nano-$MnO_2$@$TiO_2$ exhibits excellent cyclic stability and rate capability.

## 2. Experimental section

### 2.1. Materials synthesis

All the reagents used were analytical reagents. The microspheric $MnCO_3$ was synthesized via a precipitation reaction [41]. Specially, $MnSO_4$ (2 mmol) and $NH_4HCO_3$ (20 mmol) were dissolved in deionized water (100 mL), separately. Anhydrous ethanol (20 mL) was then added into the $MnSO_4$ solution under stirring. The $NH_4HCO_3$ solution was then quickly added into the mixture. The resulting precipitation was harvested by centrifuging, washing with deionized water and ethanol, and drying under vacuum at 80 °C.

The resulting $MnCO_3$ was sintered at 500 °C for 2 h with a rate of 2 °C $min^{-1}$, denoted as Nano-$MnO_2$. 100 mg Nano-$MnO_2$ was dispersed into 100 mL of anhydrous ethanol. 0.40 mL of 28% ammonium hydroxide solution was added into the solution under sonication. Then, 0.75 mL tetrabutyl titanate (TBOT) solution was added into the above mixture under stirring. The obtained mixture was transferred into a round-bottom Flask and refluxed at 45 °C for 18 h in an oil bath, followed by filtering, drying at 80 °C overnight, and annealing at 500 °C in air for 2 h with a slow heating rate of 1 °C $min^{-1}$. The resulting composite of $MnO_2$ and $TiO_2$ was denoted as Nano-$MnO_2$@$TiO_2$.

### 2.2. Materials characterizations

The morphology of the samples was observed with a field-emission scanning electron microscope (FESEM, JEOL JSM-6380), transmission electron microscope (TEM, JEOL JEM-2100HR) and high-resolution TEM (HRTEM). The element contents were analyzed by energy dispersive X-ray spectroscopy (EDS) on a JEOL-5900 SEM. The surface area was determined by the Brunauer-Emmett-Teller method (BET, Micromeritics ASAP 2020 M) at liquid nitrogen temperature (77 K). The crystal structure of the samples was analyzed by X-ray diffraction (XRD, BRUKER D8 ADVANCE) with Cu Ka radiation. FTIR (Bruker Tensor 27, Germany) were used to identify the electrolyte decomposition on the electrodes after cycling. The apparent density of the samples was measured by putting the samples into a volumetric cylinder and vibrating the cylinder until the volume of the samples keeps unchanged.

### 2.3. Electrochemical measurements

The electrode for electrochemical measurements was prepared by mixing 70 wt% of active material, 20 wt% of acetylene black and 10 wt % of polyvinylidene difluoride (PVDF) binder, coating the mixture on a copper sheet and then cutting the sheet into pieces of 12.5 mm in diameter. CR2025 coin cell was assembled in an Ar-filled MBraun glove box by using the prepared electrode as the working electrode, a lithium film as the counter and reference electrode, Celgard 2400 as the separator, and 1 M $LiPF_6$ in EC:EMC:DEC (3:5:2 by volume) as the electrolyte.

The charge-discharge tests were performed in CR2025 coin cells on a Land cell test system (Land CT2001A, China). Cells were cycled between 3 V and 0.01 V (vs. $Li/Li^+$) at 25 °C. Cyclic voltammetry was performed using a Solartron 1470E at 25 °C between 0.01 V and 3.0 V at a sweep rate of 0.1 $mV\,s^{-1}$.

## 3. Results and discussions

### 3.1. Morphology and structure

The morphology and detailed structure of the resulting $MnCO_3$, Nano-$MnO_2$ and Nano-$MnO_2$@$TiO_2$ were characterized by FESEM. The obtained results are presented in Fig. 1. As shown in Fig. 1A, $MnCO_3$ takes a microspherical morphology with an average diameter of 2 μm. After heat treatment, this morphology remains in the product Nano-$MnO_2$, as shown in Fig. 1B. Apparently, the synthesis of $MnO_2$ is facile and its morphology can be controlled simply through inheriting that of the precursor. Nano-$MnO_2$@$TiO_2$ was obtained from the hydrolysis of TBOT and the subsequent heterogeneous nucleation and growth of $TiO_2$ on the surface of Nano-$MnO_2$. As shown in Fig. 1C, the spherical morphology of Nano-$MnO_2$ is maintained after $TiO_2$ coating. The surface of Nano-$MnO_2$@$TiO_2$ (Fig. 1C and D) becomes coarser than that of Nano-$MnO_2$ (Fig. 1B), suggesting that $TiO_2$ has been successfully coated on Nano-$MnO_2$. Additionally, the SEM image in Fig. 1C suggests that nano sized $TiO_2$ particles are formed during the coating process of the Nano-$MnO_2$.

Nano-$MnO_2$ is formed from thermal decomposition of $MnCO_3$, accompanied with the evolution of carbon dioxide, which results usually in pores in the $MnO_2$ particles. To identify the pore structure in the products, Brunauer-Emmett-Teller (BET) measurements were performed. Fig. 1E presents the adsorption/desorption isotherm curve of Nano-$MnO_2$. It is characteristic of a type V adsorption/desorption behavior, suggesting that the Nano-$MnO_2$ has a mesoporous structure [42]. Apparently, the evolution of carbon dioxide leaves small pores in Nano-$MnO_2$. The pore size distribution curves (the insets of Fig. 1E) indicate that the pore sizes of Nano-$MnO_2$ are centered at 10 nm. The corresponding pore volume and Brunauer-Emmett-Teller surface area are 0.16 $cm^3\,g^{-1}$ and 52.4 $m^2\,g^{-1}$, respectively. As shown in Fig. 1F, the adsorption/desorption behavior of Nano-$MnO_2$@$TiO_2$ is similar to