Novel strategy for the preparation of graphene-encapsulated mesoporous metal oxides with enhanced lithium storage

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ABSTRACT

As potential anode materials for lithium-ion batteries, mesoporous metal oxides show high reversible capacities but relatively poor cycle stability due to the structural collapse during cycles. Graphene-encapsulated mesoporous metal oxides may increase the electronic conductivity of the composite as well as stabilize the mesostructure of metal oxides, thereby enhancing the electrochemical performance of mesoporous metal oxides. Herein we describe a novel strategy for the preparation of graphene-encapsulated mesoporous metal oxides (SnO_2, Mn_3O_4), which exhibit superior electrochemical performance compared to pure mesoporous metal oxides. Moreover, some mesoporous metal oxides may be further reduced to low-valence metal oxides when calcined in presence of graphene. Mesoporous metal oxides with high isoelectric points are not essential for this synthesis method since metal oxides are connected with graphene through mesoporous silica template, thus expanding the types of graphene-encapsulated mesoporous metal oxides.

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1. Introduction

Lithium-ion batteries (LIBs) are one of the most popular types of batteries for portable electronics due to their outstanding advantages such as high energy density, long cycle life, no memory effect and environmental friendliness [1]. Among anode materials for LIBs, metal oxides are naturally abundant and possess much higher theoretical capacities (e.g., $\sim$782 mA h g^{-1} for SnO_2 and $\sim$937 mA h g^{-1} for Mn_3O_4) compared to the commercial graphite anode ($\sim$372 mA h g^{-1}) [2,3]. However, the poor electronic conductivity and the severe volume change of metal oxides during the charge and discharge process may result in the rapid capacity fading and even the end of the cycle life [4,5]. To overcome these drawbacks of metal oxides, some methods are developed such as fabrication of nanosized or hollow materials to alleviate the volume variation of metal oxides or introduction of carbon component to increase the electronic conductivity of the composite [6–9]. Mesoporous metal oxides have large surface areas and uniform mesopores, which may increase the contact area between metal oxides and the electrolyte, shorten the diffusion pathway of Li$^+$ ions and reduce the volume variation of metal oxides during cycles [10–12]. Thus mesoporous metal oxides usually exhibit better electrochemical properties than their bulk counterparts [13,14]. However, the mesopores of metal oxides may collapse during the lithiation and delithiation process owing to the reaction mechanism, leading to the decreased capacities after several cycles [15]. Up to now, the structural stability of mesoporous metal oxides during cycles is still one of the major factors that affect their electrochemical performance.

In our previous report, the electrochemical performance of mesoporous metal oxides can be highly improved by graphene encapsulation because the graphene shell can increase the structural stability and the electronic conductivity of the composite [16,17]. In a typical procedure for the synthesis of graphene-encapsulated mesoporous metal oxides, the surfaces of metal oxides and graphene oxide (GO) are oppositely charged over a broad range of pH values in order to wrap metal oxides in GO nanosheets. Accordingly, metal oxides with high isoelectric points (IEP > 6) are necessary in view of the low isoelectric point of GO (IEP = 3 $\sim$ 4) [16–18]. On the contrary, mesoporous SnO_2 (denoted as m-SnO_2) is hardly wrapped by GO nanosheets based on our previous study because its isoelectric point (IEP = $\sim$4) is very close to that of GO [19,20]. Although the surface modification of metal oxides with amino groups may increase the isoelectric point [21], the mesostructure of metal oxides is partially destroyed due to the harsh synthetic condition, which may reduce the electrochemical performance of mesoporous metal oxides. Therefore, a novel strategy for the coassembly of GO nanosheets and metal oxides

with low isoelectric points is desired for the further performance improvement of graphene-encapsulated mesoporous metal oxides (e.g., m-SnO$_2$).

In this work, metal oxides (SnO$_2$ and MnO$_2$) are formed inside the pores of mesoporous silica template, and then the surface of silica is positively charged by grafting of amino groups. After wrapped by GO nanosheets, the silica template is removed, resulting in the formation of mesoporous metal oxides within the graphene shell. This novel synthesis method avoids the structural destruction of mesoporous metal oxides, and can be extended to the preparation of other graphene-encapsulated mesoporous materials. In addition, some mesoporous metal oxides (e.g., m-MnO$_2$) can be reduced when calcination in presence of graphene, providing an alternative approach to the synthesis of low valence mesoporous metal oxides (e.g., m-Mn$_3$O$_4$) [22]. Compared to m-SnO$_2$ and m-Mn$_3$O$_4$, graphene-encapsulated M-SnO$_2$ and M-Mn$_3$O$_4$ (denoted as GE-m-SnO$_2$ and GE-m-Mn$_3$O$_4$) exhibit higher reversible capacity and superior cycle/rate performance. Furthermore, the electrochemical behavior of G-m-SnO$_2$ is also better than that of graphene-encapsulated mesoporous SnO$_2$ reported in our previous work due to the high-quality graphene encapsulation [19].

2. Experimental

2.1. Sample preparation

GO and mesoporous silicas (SBA-15 and SBA-16) were synthesized according to literature methods (see the Supporting Information) [23–25]. M-SnO$_2$ was prepared using SnCl$_2$ as the precursor and SBA-15 as the template. In a typical synthesis, 1.5 g of SnCl$_2$·2H$_2$O and 1.0 g of SBA-15 (or SBA-16) were mixed and grinded for 1 h to obtain the homogeneous powder. Subsequently, the powder was calcined at 700 °C for 3 h in a muffle furnace with a temperature heating rate of 1.5 °C min^{-1}. After cooling down to the room temperature, SBA-15 containing SnO$_2$ (denoted as SBA-15-SnO$_2$) was obtained. After removal of the silica template in a 2 M NaOH solution at 80 °C for 2 h, m-SnO$_2$ was collected by centrifugation, washed with distilled water several times and dried at 60 °C in an oven. Mesoporous SnO$_2$ prepared using SBA-16 as the template was denoted as m-SnO$_2$-x.

GE-m-SnO$_2$ (or GE-m-SnO$_2$-x) was synthesized by a modified stepwise heterocoagulation method. In a typical synthesis, 0.1 g of SBA-15-SnO$_2$ was first dispersed into 20 mL of n-hexane via sonication. After 30 min, 0.2 mL of APTES (3-Triethoxysilylpropylamine) was poured into the above solution and refluxed for 12 h at 70 °C to obtain APTES-modified SBA-15-SnO$_2$ (denoted as SBA-15-SnO$_2$-NH$_2$). Subsequently, 0.04 g of SBA-15-SnO$_2$-NH$_2$ was dispersed in 80 mL of distilled water, and 0.01 g of GO was dispersed in another 80 mL of distilled water by ultrasonication for 1 h. The pH of GO solution was adjusted to ~8 with aqueous ammonia, and the pH of SBA-15-SnO$_2$-NH$_2$ suspension was adjusted to ~5 with dilute hydrochloric acid. The SBA-15-SnO$_2$-NH$_2$ suspension was then added dropwise into the GO solution under mild magnetic stirring. After 1 h, the precipitate was collected and calcined at 400 °C for 10 min in a tubular furnace under a N$_2$ flow in order to reduce GO to graphene. After removal of the silica template in a 2 M NaOH solution at 80 °C for 2 h, GE-m-SnO$_2$ was collected by centrifugation, washed with distilled water several times and dried at 60 °C in an oven.

GE-m-Mn$_3$O$_4$ was synthesized using a similar procedure. In a typical synthesis, 1.5 g of Mn(NO$_3$)$_2$·9H$_2$O was dissolved in 20 mL ethanol and then 1.0 g of SBA-15 was added into this solution. After the solvent was evaporated out at room temperature, the powder was collected and annealed at 300 °C for 5 h in a muffle furnace with a temperature heating rate of 1 °C min^{-1}. After cooling down to the room temperature, SBA-15 containing MnO$_2$ (denoted as SBA-15-MnO$_2$) was obtained. After modified the surface of SBA-15-MnO$_2$ with APTES, SBA-15-MnO$_2$-NH$_2$ was wrapped by GO nanosheets. The powder was then calcined at 400 °C for 10 min in a tubular furnace under a N$_2$ flow, and MnO$_2$ was reduced to Mn$_3$O$_4$ in presence of graphene. Finally, GE-m-Mn$_3$O$_4$ was collected after removal of the silica template in NaOH solution. For comparison, m-Mn$_3$O$_4$ was prepared by heating GE-m-Mn$_3$O$_4$ at 400 °C for 5 h in a muffle furnace to remove graphene.

2.2. Sample characterization

Specimens were initially characterized using X-ray diffraction (XRD) on a Phillips X'pert Pro MPD diffractometer with Cu Kα radiation. A Quantachrome NOVA 2000e sorption analyzer was used to examine the N$_2$ adsorption and desorption properties of specimens at liquid nitrogen temperature. The Zeta-potencials of GO, m-SnO$_2$ and SBA-15-SnO$_2$-NH$_2$ suspension were measured by ZetaPlus zetapotencial analyzer (Brookhaven Instruments Corporation). The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet-380 Fourier-transform infrared spectrometer in the range of 400–4000 cm^{-1}. X-ray photoelectron (XPS) spectra were recorded on a Shimadzu Axis Ultra spectrometer with an Mg Kα = 1253.6 eV excitation source. Further characterization was performed by using transmission electron microscopy (TEM), high-resolution TEM (HRTEM) on a JEOL JEM-2011 electron microscope operated at 200 kV, and scanning electron microscope (SEM) on a JEOL JSM-6700F electron microscope at an accelerating voltage of 1 kV. Energy-dispersive X-ray microanalysis (EDX) attached in an electron microscope was used to qualitatively determine the present elements.

2.3. Electrochemical measurements

For electrochemical characterization, the composite electrodes were fabricated by mixing the active materials, acetylene black and polyvinylidene difluoride (PVDF) dissolved in N-methyl-2-pyrrolidine (NMP) in a weight ratio of 80:10:10. The mixed slurry was pressed onto a copper foil and dried at 110 °C in vacuum for 24 h. Cell assembly was carried out in an Ar-filled glove box. The electrolyte was 1 M solution of LiPF$_6$ dissolved in a EC:DEC:DMC solution with a 1:1:1 volume ratio. The area of the electrode was 2.0 cm^2 and the mass loading of active materials was about 1.8 mg cm^{-2}. Electrochemical performance was measured using a CR2032-type coin cell with lithium metal as the negative electrode. The galvanostatic charge–discharge performance was measured with a LAND test system at room temperature, and the voltage range was from 0.01 to 3.0 V (versus Li/Li$^+$), with a constant current of 0.1–2C (1C equals to 782 mA h g^{-1} for SnO$_2$-containing samples, and 937 mA h g^{-1} for Mn$_3$O$_4$-containing samples). Cyclic voltammetry tests were performed between 0.01 and 3.0 V with a scan rate of 0.5 mV s^{-1}, and the electrochemical impedance spectroscopy (EIS) was carried out in the frequency range from 100 kHz to 10 mHz on a Gamry Interface 1000 electrochemical station.

3. Results and discussion

3.1. m-SnO$_2$ and GE-m-SnO$_2$

The porosities of m-SnO$_2$ and m-SnO$_2$-x were examined using the N$_2$ adsorption/desorption technique (see the Supporting Information). The N$_2$ adsorption/desorption isotherms and pore size distributions of m-SnO$_2$ and m-SnO$_2$-x (Fig. S1) indicate that these SnO$_2$ particles are mesoporous materials with uniform pores [26,27]. The overall synthesis procedure of m-SnO$_2$ and GE-m-SnO$_2$ is shown Fig. 1A. The Sn-containing precursor is first injected