



One-pot route to synthesize SnO₂-Reduced graphene oxide composites and their enhanced electrochemical performance as anodes in lithium-ion batteries



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HIGHLIGHTS

- One-pot, supercritical methanol route is used to synthesis SnO₂-RGO composites.
- Uniform deposition of SnO₂ nanoparticles with size of 3–11 nm on RGO.
- The composite exhibits highly porous structure.
- The SnO₂ loading of 58 wt% composite shows best performance of 776 mA g⁻¹.

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ABSTRACT

A simple, one-pot route was developed for the synthesis of SnO₂-reduced graphene oxide (RGO) composites. Simultaneous reduction of graphene oxide (GO) and heterogeneous nucleation and growth of SnO₂ on the surface of RGO under the supercritical methanol medium resulted in uniform deposition of well-dispersed SnO₂ nanoparticles on the RGO sheets. In comparison with the bare SnO₂ nanoparticles and bare RGO sheets, the as-synthesized SnO₂-RGO composites exhibited enhanced Li-ion storage and high rate performance. The SnO₂-RGO composite with a SnO₂ loading of 58 wt% delivered a reversible discharge capacity of 776 mAh g⁻¹ after 70 cycles at a current density of 0.1 A g⁻¹ and a rate performance of 147 mAh g⁻¹ at a high current density of 5 A g⁻¹. In addition, after 1000 continuous cycles at 1 A g⁻¹, the composite electrode exhibited a reversible discharge capacity as high as 531 mAh g⁻¹ with excellent capacity retention. The enhanced long-term cyclability and high-rate performance of the SnO₂-RGO composite can be attributed to the effective confinement of SnO₂ nanoparticles on the RGO sheets, and thus, the interparticle agglomeration and volume change associated with alloying–dealloying of SnO₂ during cycling can be prevented and cell integrity can be maintained.

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1. Introduction

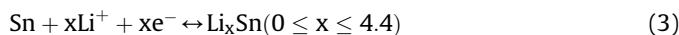
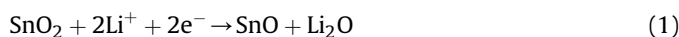
Currently, lithium-ion batteries (LIBs) are considered one of the most promising power sources in large-scale applications such as electric vehicles (EVs) and energy storage systems (ESS) because of

their high energy density, low self-discharge, long service life, and light weight [1,2]. Graphite, the current choice of anode active material in the market, may not be able to fulfill the increasing performance and safety demands of large-scale applications mainly because of its low theoretical capacity (372 mAh g⁻¹), low rate performance, and safety problems associated with metallic lithium formation during the low-voltage lithium-insertion process [1,3]. Much effort has been devoted to develop new electrode materials with high reversible capacity, long cycle life, and high safety standards [4–9]. SnO₂ is considered a potential alternative to graphite

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because of its high theoretical capacity (781 mAh g⁻¹), low discharge potential for Li alloying (<1.5 V), and low cost [10–14]. The electrochemical process for lithium-ion storage in SnO₂ is summarized by the following reactions:



The conversion of SnO₂ to SnO and Sn in Eqs. (1) and (2) is known to be irreversible in most cases, but could be reversible in the case of nanostructured SnO₂ [15,16]. Hence, the theoretical reversible capacity of SnO₂ is commonly estimated from the alloying–dealloying reaction in Eq. (3) [11,13]. Practical utilization of SnO₂-based electrodes has still not been achieved mainly because of the poor cycling performance of the electrodes, causing huge volume changes (up to 300%), and the severe interparticle aggregation of SnO₂ during the alloying–dealloying process [17–19]. This often leads to the pulverization of the composite electrode and loss of electrical contact between the active material and the copper collector, resulting in rapid capacity decay upon cycling. Various approaches have been developed to overcome the volume change and particle aggregation, including the design of porous or hollow SnO₂ particles [11–14,20], nanostructured or nanosized SnO₂ [21–23], and SnO₂/carbon composites [10,16,24–26].

Graphene has received tremendous attention in recent years as a support for metal-oxide nanoparticle-based composites owing to its high surface area, outstanding mechanically flexible 2D structure, excellent electronic conductivity, and chemical stability [27–29]. Uniform deposition of SnO₂ nanoparticles on the basal plane of graphene sheets can offer many benefits [15,30–36]: (1) the interparticle agglomeration and the electrode pulverization caused by the huge volume change associated with the alloying and dealloying of SnO₂ can largely be alleviated, (2) the electron transfer between SnO₂ and the copper collector can be facilitated via graphene sheets during the charge and discharge process, and (3) the large surface area of graphene sheets and its porous structure can allow easy access of Li-ions from the liquid electrolytes. Therefore, a properly designed SnO₂-graphene composite would possess excellent cycling stability and rate performance when tested as an anode in LIBs, which would meet the large-scale application requirements. Various solid- and liquid-state synthetic approaches have been proposed for uniform deposition of SnO₂ nanoparticles on graphene sheets [15,30–39]. Although previous studies have demonstrated that the reversible capacity and cycling stability of the composites can be improved, the synthetic methods for producing the composites typically involve multi-step and sophisticated experimental procedures, long reaction time, use of expensive chemicals, and generation of organic/aqueous waste, which would not be suitable for practical applications.

In this work, a simple and fast supercritical methanol (scMeOH) route was developed for one-pot, simultaneous deposition of SnO₂ nanoparticles on RGOs and reduction of graphene oxide (GO). Owing to their unique properties, including low viscosity and zero surface tension, fast diffusion, high nucleation rates, and tunable physical properties depending on process parameters (temperature, pressure, etc.), supercritical fluids are excellent media for the synthesis of various types of materials for LIBs, such as LiMPO₄ (M = Fe, Mn, Co) [40–45], Li₂MSiO₄ (M = Co, Mn, Fe) [46–50], Li₄Ti₅O₁₂ [51–55], and TiO₂ [56]. More recently, the unique reduction ability associated with supercritical alcohols has been utilized

to develop an environmentally benign deoxygenation process for producing supercritical alcohol-reduced graphene oxide (SRGO) [57–59]. In a scMeOH medium, GO is deoxygenated to form RGO, and at the same time, SnO₂ nanoparticles are nucleated and grow on the surface of the RGO sheets, resulting in uniform deposition of SnO₂ on RGO. When tested as an anode in LIBs, the SnO₂-SRGO composite exhibits excellent reversible capacity (776 mAh g⁻¹ at 0.1 A g⁻¹ after 70 cycles) and high-rate performance (147 mAh g⁻¹ at 5 A g⁻¹). In particular, at a continuous high charge–discharge rate of 1 A g⁻¹, the SnO₂-RGO composite electrode can deliver a stable capacity of 531 mAh g⁻¹ even after 1000 cycles with almost 100% Coulombic efficiency. A comparison of the electrochemical and physicochemical properties of the SnO₂-SRGO composite electrodes with those of bare SnO₂ and SRGO is also presented.

2. Experimental section

2.1. Materials

Tin(II) acetate (purity of 99.0%) and graphite (powder, purity of 99.99%) were purchased from Sigma–Aldrich, Co. (St. Louis, MO, USA). Methanol (HPLC grade) was obtained from J. T. Baker (Phillipsburg, NJ, USA). Distilled and deionized (DDI) water was prepared using a Milli-Q[®] ultrapure water purification system equipped with a 0.22 μm filter (Billerica, MA, USA). Poly(vinylidene difluoride) (PVDF, Kureha Chemical Industry Co., Tokyo, Japan), acetylene black (DENKA Co. Ltd., Tokyo, Japan), and 1-methyl-2-pyrrolidinone (NMP, purity of 98%, Alfa Aesar, MA, USA) were used as received.

2.2. Preparation of SnO₂-SRGO composites

Fig. 1 shows a schematic of the synthesis the SnO₂-SRGO composites. GO was prepared by the oxidative treatment of natural graphite using the modified Hummers' method [60,61]. The detailed preparation procedure of GO is reported in previous papers [57,58]. In a typical experiment for the synthesis of the SnO₂-SRGO composites, a known amount of tin(II) acetate was dissolved in methanol (24 mL) with sonication for 5 min, and then a known amount of GO was added to the solution with vigorous stirring at room temperature. Then, the mixed suspension (4 mL) was introduced into a SUS 316 reactor with an inner volume of 11 mL. After being tightly sealed, the reactor was immersed into a molten salt bath (salt weight ratio of KNO₃:NaNO₃:Ca(NO₃)₂ = 46:24:30) and reacted at 400 °C for 30 min. After the reaction, the reactor was taken out from the salt bath and quenched in a cold water bath. The produced SnO₂-SRGO composites were purified by three cycles of decantation and centrifugation to remove residual organic species using ethanol and filtered through an FP-Vericel[®] PVDF membrane filter. Wet SnO₂-SRGO composites were dried in a vacuum oven at 60 °C overnight and sieved using a 75 μm sieve. The ratio of GO and tin(II) acetate was changed to control the SnO₂ loading in the composite (see Table 1).

2.3. Characterization

The functional groups on the surface of the samples were characterized using a NICOLET iS10 Fourier-transform infrared (FT-IR) spectrometer (Thermo Electron Co. NJ, USA). The phase structure of the samples was analyzed using a D/Max-2500V/PC Rigaku X-ray diffractometer (Tokyo, Japan) with Cu Kα radiation at 40 kV and 50 mA. X-ray Photoelectron spectroscopy (XPS) of the samples was performed using a PHI 5000 Versa Probe (ULVAC-PHI Inc., Kanagawa, Japan) spectrometer. The morphology of the samples was observed using a Hitachi S-4100 field-emission scanning

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