



# Monodisperse SnO<sub>2</sub> anchored reduced graphene oxide nanocomposites as negative electrode with high rate capability and long cyclability for lithium-ion batteries



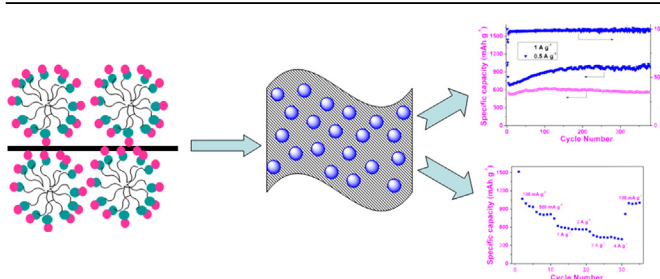
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## HIGHLIGHTS

- Monodisperse SnO<sub>2</sub> anchored rGO composite is synthesized as anode materials.
- Aided with SDS, SnO<sub>2</sub> nanocrystal is dispersed on rGO sheets uniformly and tightly.
- Urea is used to control the precipitation of SnO<sub>2</sub> and reduce GO into rGO.
- The sample shows high capacity, excellent rate capability and cyclic performance.
- TEM images in different charge–discharge cycles reveal the electrode evolution.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this manuscript, we present a facile and friendly wet chemical method to prepare monodisperse SnO<sub>2</sub> nanocrystals assembled on reduced graphene oxide (RGO). Aided with sodium dodecyl sulfonate, small SnO<sub>2</sub> nanoparticles (~5 nm) are deposited onto the flexible support evenly and tightly. A cheap compound, urea, is used for the controlled precipitation of SnO<sub>2</sub> and the reduction of graphene oxide. When tested as the anode material, the hybrid composite electrode delivers excellent cyclability at high current density, such as high reversible capacity over 1000 mAh g<sup>-1</sup> after 400 cycles at 0.5 A g<sup>-1</sup> and ~560 mAh g<sup>-1</sup> after 400 cycles at 1 A g<sup>-1</sup>. The composites also exhibit superior rate capability varying from 0.1 to 4 A g<sup>-1</sup>, and possess capacity of 423 mAh g<sup>-1</sup> at 4 A g<sup>-1</sup>. This synthesis strategy seems to be suitable for industrial production and can also be extended to produce a variety of metal oxide/RGO composites.

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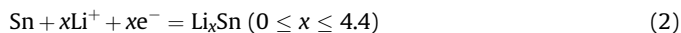
## 1. Introduction

Since their first commercialization about 20 years ago, rechargeable lithium-ion batteries (LIBs) have become the

dominant power sources for portable electronic devices, due to their high energy density, fast charge/discharge rate, light weight, and long cycle life. However, the conventional graphite anode, which is limited by its low theoretical capacity of 372 mAh g<sup>-1</sup>, poor rate capability, and security issue originated from lithium dendrite, cannot fulfill the growing demands for high performance LIBs, especially for the applications in electric vehicles and hybrid electric vehicles [1,2]. Therefore, exploration of the next-generation

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anode materials with high capacity, excellent rate capability, and high safety has been put on the schedule. For instance, tin oxide ( $\text{SnO}_2$ ) has received special attention, since it is expected to deliver a high theoretical capacity. It is believed that, two principal electrochemical processes including conversion and alloy mechanisms are involved in the  $\text{SnO}_2$ -based anode:



Normally, the conversion process of Eq. (1) is thought to be electrochemically irreversible and has no contribution to the reversible capacity, so the theoretical capacity of  $\text{SnO}_2$  is calculated to be  $790 \text{ mAh g}^{-1}$  based on the highly reversible alloy reaction of Eq. (2) [3–6]. Recently, the fully/partially reversible conversion reaction of Eq. (1) has been observed in some nanosized  $\text{SnO}_2$ -based anodes [7–10] and the theoretical capacity of  $\text{SnO}_2$  can be extended to  $1490 \text{ mAh g}^{-1}$  accordingly. Unfortunately, the commercialization of  $\text{SnO}_2$  anodes for LIBs is still largely hampered by their serious capacity fading upon cycling and/or poor rate capability, mainly ascribing to the large volume changes ( $\sim 300\%$ ) upon  $\text{Li}^+$  insertion/extraction [11–14].

To circumvent these issues, various  $\text{SnO}_2$  nanostructures have been designed and constructed to improve their electrochemical performance, such as hollow nanostructures [5,15–17], hybrid  $\text{Fe}_2\text{O}_3/\text{SnO}_2$  nanorattles [18], nanosheets [4,19], nanoboxes [20], nanotubes [21,22], nanowires [23,24], and nanospheres [25].  $\text{SnO}_2$  has also been incorporated with carbon to prepare  $\text{SnO}_2$ -C hybrid electrode materials [26–41], because carbon can not only alleviate the volume change but also result in good electrical contact and enhanced pathways for electronic transport kinetics. Among them, graphene oxide (GO), especially reduced graphene oxide (rGO), has been investigated extensively due to its high surface area, superior electronic conductivity, and excellent mechanical flexibility [5,7,27,32–41]. However, these synthesis processes are commonly time and energy consuming, and associated with complicated and rigorous conditions.

In this work, a facile wet chemical method is employed to synthesize monodisperse  $\text{SnO}_2/\text{rGO}$  composites (M-SGCs) as schematically illustrated in Fig. 1. Here, urea is used to control the release rate of  $\text{NH}_3$ , which promotes the reduction of GO into rGO and precipitates  $\text{SnO}_2$  nanoparticles mildly [42]. Sodium dodecyl sulfonate (SDS) plays the key role to anchor  $\text{SnO}_2$  nanocrystals on the rGO sheets tightly and insures their even distribution. The resultant M-SGCs that benefit from the highly active monodisperse  $\text{SnO}_2$  nanoparticles ( $\sim 5 \text{ nm}$ ), the flexible mechanical support of

rGO sheets, and unhindered electron flow between  $\text{SnO}_2$  and rGO, exhibit excellent cyclability at high current density and superior rate capability when tested as anode materials for LIBs.

## 2. Experimental

### 2.1. Sample preparation

All reactants are of analytical grade and used as purchased without further purification. GO sheets are first synthesized following a modified Hummers method described elsewhere [43]. In the typical synthesis route of M-SGCs,  $0.25 \text{ g}$  SDS is dissolved in  $7 \text{ mL}$  GO dispersion ( $10 \text{ mg mL}^{-1}$ ) under magnetic stirring. The mixture is diluted to  $30 \text{ mL}$  and sonicated for  $15 \text{ min}$  and then is added into a  $10 \text{ mL}$  portion of  $0.12 \text{ M}$   $\text{SnCl}_4$  in  $3.8 \text{ wt}\%$  HCl solution. After  $4.8 \text{ mL}$  of  $1 \text{ M}$  urea is added dropwise, the mixture is diluted to  $100 \text{ mL}$  and is further refluxed at  $90 \text{ }^\circ\text{C}$  in a sealed round bottom flask for  $16 \text{ h}$ . The obtained precipitate is washed with water thoroughly to remove the residual SDS and then dried at  $40 \text{ }^\circ\text{C}$  in vacuum. Finally, the sample is sintered at  $450 \text{ }^\circ\text{C}$  under an argon atmosphere for  $3 \text{ h}$  with a heating rate of  $2 \text{ }^\circ\text{C min}^{-1}$  to obtain the M-SGCs.

### 2.2. Materials characterization

The samples are characterized with X-ray powder diffraction (XRD) by a Philips X'-pert X-ray diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154056 \text{ nm}$ ). Raman spectroscopy is obtained in the confocal microprobe Raman system (LabRam-010,  $632 \text{ nm}$  as excitation source). Fourier transform infrared (FTIR) spectra are recorded with FTIR analyzer (Nicolet Magna-IR750). The thermogravimetric (TG) analysis is measured with TG2091F from room temperature to  $800 \text{ }^\circ\text{C}$  with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in air. Scanning electron microscope (SEM) is obtained with a JEOL JSM-7500F scanning electron microscope. Transmission electron micrographs (TEM) analysis is performed with FEI TECNAI F30.

The electrochemical tests are carried out with the CR2016-type coin cell. Metallic lithium sheet is used as negative electrodes. The working electrode is fabricated by compressing a mixture of M-SGCs, conductive material (acetylene black) and binder polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 onto a copper foil. The electrode is dried at  $120 \text{ }^\circ\text{C}$  for  $24 \text{ h}$  in vacuum oven and the cell assembly is operated in a glove box filled with pure argon. The Clegard 2300 microporous film is used as the separator. The electrolyte solution is  $1 \text{ M}$   $\text{LiPF}_6$  dissolved in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 in volume) (Zhangjiagang, China). Charge–discharge experiments are performed between  $3$  and  $0.01 \text{ V}$  with the LAND CT2001A Battery Cycler (Wuhan China). Cyclic voltammetry (CV) measurements are characterized using a three-electrode cell and metallic lithium is used as the counter and reference electrode. The experiments are performed on CHI660A (CH Instruments, China) over the potential range from  $0.01$  to  $2.0 \text{ V}$  vs.  $\text{Li}^+/\text{Li}$  at a scan rate of  $0.1 \text{ mV s}^{-1}$ .

## 3. Results and discussion

The overall synthetic solution of M-SGCs is illustrated in Fig. 1. Firstly, a certain concentration of SDS molecules in aqueous solution tends to form micelle with the hydrophilic ends outside [44]. After the addition of  $\text{Sn}^{4+}$ , SDS<sup>−</sup> absorbs  $\text{Sn}^{4+}$  cations using its naked anion. Then the micelles with highly positively charged  $\text{Sn}^{4+}$  anchor tightly onto the surface of GO sheets through the strong electrostatic interaction, which are negatively charged under aqueous solution. On the other hand, the repulsive force between

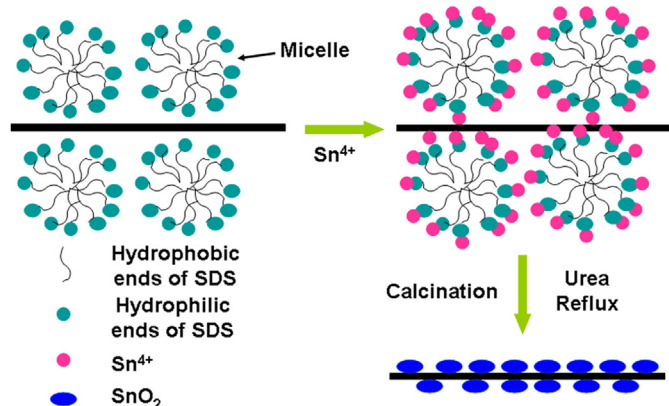


Fig. 1. Schematic diagram for the synthesis route of M-SGCs.

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