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Sonochemical synthesis of SnO_2/carbon nanotubes encapsulated in graphene sheets composites for lithium ion batteries with superior electrochemical performance

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ABSTRACT

The SnO_2/carbon nanotubes encapsulated in graphene sheets (CSGN) composites are synthesized via a sonochemical method which is straightforward, low-cost and operable under ambient conditions. The open spaces formed by carbon nanotubes and graphene offering the accommodation of volume change and the access of an easy electrolyte-wetting, and the improved electrical conductivity by the presence of graphene and carbon nanotubes, lead to the superior cycling performance. As a result, the CSGN with SnO_2 content of 61.4 wt% exhibits a reversible specific capacity of 842.9 mAh g^{-1} at the first cycle and retains 793.8 mAh g^{-1} after 50 cycles at a current density of 125 mA g^{-1}, indicating a high capacity retention rate of 94%. The cycling performance is attributed to the unique structure of CSGN and enhanced electrical conductivity, which may make much sense to the structure designing of other electrode materials for lithium ion batteries.

1. Introduction

With the expansion of consumer electronics, electric vehicles and energy storage devices, rechargeable Lithium-ion batteries (LIBs) with high energy density, high safety, low cost and long life have attracted great research interest worldwide [1–6]. SnO_2, a candidate anode material of LIBs, has received much attention because of its much higher specific capacity (1494 mAh g^{-1}) than that of commercially used graphite (372 mAh g^{-1}) [1,2]. However, the practical uses of SnO_2 are restricted by the severe capacity fading upon repeated charge-discharge cycles stemming from huge volume changes (around 300%) during Li^+ insertion and extraction [3]. To overcome these problems, many approaches have been developed. Among them, two of the leading ideas are nanostructuring of electrodes, which could decrease the size of particles and improve the structure stability [4], and hybridization of active materials and carbonaceous ones, which will enhance electronic conductivity, mechanical strength, and buffer huge volume changes [5–8]. So far, a variety of SnO_2/carbon-based nanocomposites with different morphologies have been intensively studied, such as nanoparticles, hollow spheres, nanowires, nanotubes and nanosheets [6,9–12].

Carbon nanotubes (CNTs) have recently attracted a good deal of attention for lithium storage [6,9,10]. Metal-oxide-coated CNTs display a better electrochemical performance than that of pure metal oxide particles because of the advantageous effects of CNTs, such as a one-dimensional tubular structure and high electrical conductivity. A variety of routes for synthesizing SnO_2/CNTs nanocomposites have been reported, such as sol-gel reaction, wet-chemical method, hydrothermal route and so on [9,13,14]. However, the methods mentioned above need more or less additive or high temperature, which mean high cost. Thus it remains a challenge to find a straightforward method with low-cost to synthesize SnO_2/CNTs-based nanocomposites with improved electrochemical performance for lithium ion batteries.

Another typical carbon materials, graphene (GN) has also been investigated as the functional additive for SnO_2-based nanostructures due to its extremely large specific surface area and excellent electronic conductivity, which can not only buffer the substantial volume change of SnO_2, but also facilitate the transfer of electrons during cycling [15,16]. SnO_2/graphene-based composites have been reported by some earlier researchers, in which SnO_2 is fully encapsulated by graphene [17–19]. With the addition of graphene, the composites' electrochemical performances are improved obviously. Although a fully encapsulated nanostructure is favorable for electrical conductivity, electrolyte-wetting and lithium transport might not be easy [20]. Thus the approach of

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synthesizing SnO_2-base composite without fully covered of graphene is worth to discover.

As mentioned above, CNTs and GN, served as the highly conductive representative of one-dimensional and two-dimensional carbon materials, could improve electrochemical performance observably when applied to SnO_2 modification. But it also exists some problems on preparation process and properties. Combining the advantages of CNTs and GN is likely to be an effective approach to solve these problems. Recently, Zhang et al. incorporated CNTs into SnO_2-graphene to prepare a SnO_2-graphene-CNT composite based on an in situ chemical method with a remarkably capacity of 635 mAh g^{-1} at 250 mA g^{-1} [21]. Chen et al. synthesized SnO_2-reduced graphene oxide-carbon nanotube composites through a microwave-assisted method with a capacity of 502 mAh g^{-1} after 50 cycles at 100 mA g^{-1} [22]. Herein, we employ CNTs as a framework to support SnO_2 nanoparticles, and graphene nanosheets as the open spaces to permit an easy electrolyte-wetting. The SnO_2/carbon nanotubes encapsulated in graphene sheets (CSGN) composites were synthesized via a sonochemical method which is straightforward, low-cost and operable under ambient conditions, as compared with conventional methods [21]. As anode material for lithium ion batteries, the CSGN composite exhibit outstanding electrochemical performance.

2. Experimental

2.1. Sample preparation

The SnO_2/carbon nanotubes encapsulated in graphene sheets (CSGN) composites were synthesized via a sonochemical method. All chemicals were of analytical grade. The graphene oxide (GO) employed here was synthesized from natural graphite by the method reported in our previous work [23].

In a typical synthesis, 0.8 g $SnCl_2{\cdot}2H_2O$ was dissolved in 20 mL of ethanol solution after stirring for 3 h. Then 10 mL of distilled water was added into the above solution under vigorous stirring with 15 min. At the same time, 0.1 g multi-walled CNTs (supplied by Nanjing XFNano Material Tech Co., Ltd, purity >95%, out diameter: 10-20 nm, length: 10-30 μm) was added into another 20 mL of ethanol solution and pretreated under ultrasound for 30 min to get finely dispersed solution. Then the $SnCl_2$ solution and CNTs solution were mixed together under ultrasound for 3 h at room temperature to form SnO_2/CNTs solution. In addition, 55 mL of GO (1.84 mg mL^{-1}) was pretreated under ultrasound for 1 h, followed by mixing the GO solution and SnO_2/CNTs solution under ultrasound for another 1 h. After this, 1 mL of hydrazine hydrate was added to reduce GO [24] with magnetic stirring at room temperature overnight. Finally, the precipitate was washed thoroughly with distilled water, and then dried at 120°C for 12 h in a vacuum oven.

In this work, CSGN derived from 0.8 g $SnCl_2{\cdot}2H_2O$ and 0.5 g $SnCl_2{\cdot}2H_2O$ were labeled as CSGN-1 and CSGN-2 respectively. In addition, SnO_2/GN (SGN-1) and SnO_2/CNTs (CS-1) composites were prepared according to the formula of CSGN-1.

2.2. Sample characterization

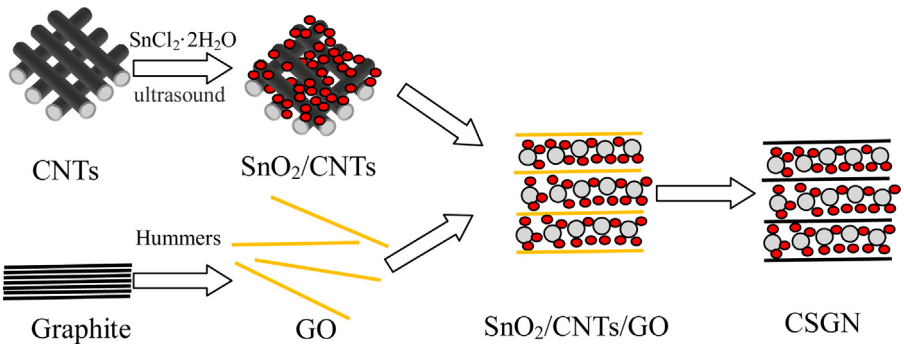
The morphologies and structures of the as synthesized composites were characterized by X-ray diffraction (XRD, Rigaku- TTRIII, Japan), scanning electron microscope (SEM, Nova NanoSEM 230) and transmission electron microsopy (TEM, JEM-2100F, Japan). X-ray photoelectron spectra (XPS) were recorded using an X-ray photoelectron spectrometer (K-Alpha 1063) with a monochromatic Al Ka X-ray source. Thermal gravimetric analysis (TGA, SNTQ600) was done using a heating rate of 10°C min^{-1} under air flow.

2.3. Electrochemical measurements

The electrodes were prepared by mixing 80 wt% as-prepared composites, 10 wt% polyvinylidene fluoride (PVDF), 10 wt% acetylene carbon black in N-methyl-2-pyrrolidone (NMP) to prepare a slurry which was then coated onto a copper foil and dried overnight at 120°C in a vacuum oven. The SGN-1 electrode was prepared by mixing 60 wt% SGN-1, 20 wt% PVDF and 20 wt% acetylene carbon black. Half-battery (2025 coin type) was manufactured in an argon-filled glove box with Li foil as the counter electrode, polyethylene film as separator, and 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1:1) as the electrolyte. Charge-discharge measurements were performed on LAND CT-2001A in the potential range 0.005-3.0 V (vs. Li/Li^+) at a current density of 125 mA g^{-1}. Cyclic voltammograms (CV) experiment was performed in the potential window of 0.005-3.0 V at a scanning rate of 0.5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were performed with an impedance analyzer in the 100 kHz to 0.01 Hz frequency range in automatic sweep mode from high to low frequency. The specific capacities were calculated based on the mass of the synthesized composites. A typical active mass loading on the electrode was 1.0-1.3 mg cm^{-2}.

3. Results and discussion

The SnO_2/carbon nanotubes encapsulated in graphene sheets (CSGN) composites were fabricated by a sonochemical method as shown in Scheme 1. First, carbon nanotubes nets were obtained through ultrasonic treatment of CNTs. Then, $SnCl_2{\cdot}2H_2O$ solution was added into the CNTs net with ultrasonication for getting SnO_2/CNTs solution. Meanwhile, GO solution was prepared by oxidizing nature graphite via the Hummers method. Lastly, CSGN composites were obtained after adding GO into SnO_2/CNTs solution under ultrasound, which was then reduced by hydrazine hydrate.



Scheme 1. Illustration of the formation of CSGN composite via a sonochemical method.