

Tin dioxide dodecahedral nanocrystals anchored on graphene sheets with enhanced electrochemical performance for lithium-ion batteries



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ABSTRACT

Combination of transition metal oxides and graphene sheets (GS) is an effective strategy to improve the electrochemical performance of transition metal oxides. In the present work, we report a facile and simple hydrothermal method to synthesize the nanocomposite of SnO₂ dodecahedral nanocrystals (DNCs) anchored on GS as an advanced anode material for high-performance lithium-ion batteries (LIBs). Benefiting from the unique properties of graphene, the SnO₂ DNCs-GS nanocomposite exhibits significant enhanced Li-battery performance compared with the pure SnO₂ DNCs. The initial discharge and charge capacities of the SnO₂ DNC-GS electrode are 1653.2 and 1085.6 mA h g⁻¹, respectively. After 50 cycles, it still exhibits a high discharge capacity of 783.9 mA h g⁻¹ at the current density of 200 mA g⁻¹. Remarkably, the discharge capacity of the SnO₂ DNCs-GS can still retain as high as 730.3 mA h g⁻¹ at a high rate of 5 A g⁻¹, indicating good rate capability. The electrochemical results suggest the SnO₂ DNCs-GS nanocomposite would be a promising candidate as anode material in energy storage applications for high-performance LIBs. Our study also highlights the importance of rational design and synthesis of graphene-based materials for high-performance LIBs.

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1. Introduction

As one of the most important topics in the 21st century, energy storage has received worldwide attention and research interest with the rapid depletion of fossil fuels and increasing environmental concerns [1,2]. Among various energy storage systems, lithium-ion batteries (LIBs) have attracted extensive attention because of their advantages such as high energy density, long cycle life, light weight, safety, low-cost, and environmentally friendly [3–5]. It's known that the theoretical capacity of the commercial graphite anode is only 372 mA h g⁻¹, which cannot fulfill the increasing demands of consumers [6,7]. Since the electrochemical performance of LIBs mainly depends on the electrode materials used, therefore great efforts have been devoted to developing new high-performance electrode materials to replace the conventional graphite anode.

Transition metal oxides with high capacities have been considered as promising anode materials for high-performance LIBs [1,3,8,9]. During the last decade, various metal oxides (e.g., Mn₃O₄, SnO₂, NiO, Fe₂O₃, Co₃O₄, TiO₂, et al.) have been extensively studied [10–18]. Among them, tin dioxide (SnO₂) has received particular attention due to its high theoretical Li storage capacity of 790 mA h g⁻¹, which is more than two times larger than that of commercial graphite anode. So far, a variety of SnO₂ nanostructures (such as small nanoparticles, nanorods, nanosheets, nanoboxes, and hollow structures) have been successfully synthesized and displayed enhanced electrochemical performance for LIBs [12,19–22]. However, similar to other transition metal oxides, a large volume changes (>300%) and huge internal stress can occur during the lithium insertion/extraction processes, resulting in pulverization of the electrodes and aggregation of electrode materials, leading to poor cycling stability. Furthermore, the rate capability of SnO₂ at high current density is unsatisfactory owing to its low electrical conductivity [3,12,22]. These two major shortcomings of SnO₂ anode seriously restrict its practical use for high-performance LIBs.

An effective strategy to resolve the problem above mentioned is to make composites by combining conductive materials and

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transition metal oxides [23,24]. Graphene, a new two-dimensional carbon material, has received great research interest due to its high conductivity, large surface area, strong mechanical strength, and chemical/thermal stability [25,26]. Benefiting from these unique characteristics, graphene has been chosen as an ideal conductive material to make composites with metal oxides for high-performance electrode materials. Recently, great successes have been achieved for synthesis of metal oxides and graphene sheets (GS) composites, which exhibited high reversible capacity, long cycle life and good rate performance for high-performance LIBs [27–37]. For example, Dai and coworkers reported the hybrid materials of Mn_3O_4 nanoparticles and GS for LIBs, which showed a high specific capacity of 900 mAh g^{-1} , near their theoretical capacity, as well as good rate capability and cycling stability [27]. Recently, scientists have proved that the crystal plane structure of the nanomaterials also has a significant effect on the Li^+ transport and the electrochemical performance [10,15,16,18]. For examples, Li et al. reported that the Co_3O_4 octahedron with the (111) plane had the highest reversible capacity and the best rate capability [16]. Lou et al. reported the anatase TiO_2 nanosheets exposed with (001) facets for fast and efficient lithium insertion/extraction [18]. In this work, we successfully synthesize the nanocomposite of SnO_2 dodecahedral nanocrystals (DNCs) exposed with {221} and {110} facets anchored on GS through a facile and simple hydrothermal method for the first time. The as-prepared SnO_2 DNCs-GS nanocomposite and pure SnO_2 DNCs are then investigated as anode materials for LIBs. Impressively, the SnO_2 DNCs-GS nanocomposite exhibits significant enhanced Li-battery performance with high reversible capacity, long cycle life and good rate performance, which would hold great promise for applications in high-performance LIBs.

2. Experimental Section

2.1. Materials preparation

All chemical reactants are of analytical grade and used without further purification. Graphene oxide (GO) was prepared from the graphite powder by a modified Hummers' method, as reported elsewhere [38]. The composite of SnO_2 DNCs anchored on GS was synthesized by a facile hydrothermal method. In a typical synthesis, 10 mg of GO, 0.315 g of polyvinylpyrrolidone (PVP) and 0.15 g of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$ were dispersed in ethanol/distilled water (6.00 mL, 1/1 v/v), followed by 30 min intense ultrasonication and stirring to make a homogeneous suspension. After that, 0.4 mL of concentrated hydrochloric acid was added dropwise into the above solution under vigorous stirring. The resulting solution was then transferred to a 25 mL Teflon-lined stainless steel autoclave and kept at 200°C for 12 h. The black products were collected by centrifugation at 8000 rpm, and washed several times with distilled water and ethanol. The pure SnO_2 DNCs were prepared via the same process without the addition of GO.

2.2. Materials characterization

The composition and phase of the as-prepared products were recorded on an X-ray diffractometer (XRD, Rigaku Ultima IV) with $\text{Cu K}\alpha$ irradiation. The morphology and crystal structure of the as-prepared products were observed by using a scanning electron microscopy (SEM, Hitachi S4800) and a transmission electron microscopy (TEM, JEOL JEM2100) with an acceleration voltage of 200 kV. All TEM samples were prepared by depositing a drop of diluted suspension in ethanol on a copper grid coated with carbon film. Thermogravimetric analysis (TGA) was performed in air to detect the weight percentage of graphene in the SnO_2 -GS nanocomposite.

2.3. Electrochemical measurements

The electrochemical characterizations were carried out by using CR2016-type coin cells, which were assembled in an argon-filled glovebox with water and oxygen contents less than 1 ppm. Pure lithium sheets were used as both counter and reference electrodes. The working electrodes were fabricated by dispersing 80 wt% of active material (SnO_2 DNCs-GS nanocomposite or pure SnO_2 DNCs), 10 wt% of conductivity agents (acetylene black), and 10 wt% of carboxyl methyl cellulose into a distilled water-absolute alcohol mixture to form a homogeneous slurry. The slurry was then pasted onto a copper foil and dried at 80°C in a vacuum oven for 12 h. The electrolyte solution was 1 M LiPF₆ in ethylene carbonate–dimethyl carbonate–diethyl carbonate (1 : 1 : 1, in wt%). A Celgard 2400 microporous polypropylene membrane was used as separator. Cyclic voltammetry (CV) measurements were performed on a CHI660C electrochemical workstation. The cells were discharged and charged galvanostatically in the voltage window from 0.01 to 3.0 V using a Land battery tester (China) at room temperature.

3. Results and Discussion

The as-prepared nanocomposite was first characterized by XRD. The XRD patterns of the GO, GS, SnO_2 DNCs-GS and pure SnO_2 DNCs are shown in Fig. 1 and Fig. S1. A single diffraction peak at around 10° is observed in the pattern of GO, indicating that GO has been successfully obtained through the chemical oxidation of graphite powder [33]. The diffraction peak of GO is not detected in the SnO_2 -GS nanocomposite, indicating the successful reduction of GO to GS after the hydrothermal treatment. The GS was synthesized via the same process without the addition of $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$. A broad peak at 25° is observed, further indicating the reduction of GO. The XRD patterns of the SnO_2 DNCs-GS nanocomposite and pure SnO_2 DNCs agree well with the tetragonal rutile phase of SnO_2 (JCPDS no. 41-1445) [19,21]. The intensive diffraction peaks reveal the well crystallization of these SnO_2 nanocrystals anchored on the GS.

The morphology and structure of the SnO_2 DNCs-GS nanocomposites and pure SnO_2 sample were then characterized by SEM. The low-magnification images show that the SnO_2 nanocrystals are uniformly and firmly anchored on or between the GS matrix (Fig. 2a and b). Even after the ultrasonication, the SnO_2 nanocrystals still don't fall off from the GS. The high-magnification images reveal that these SnO_2 nanocrystals are of well-defined dodecahedral shape with smooth surfaces (Fig. 2c and d). High-magnification SEM images also directly show that the SnO_2 nanocrystals are linked to graphene (Fig. S2). Without the addition of GO, the pure SnO_2 DNCs are also synthesized, as shown in Fig. 2e and f. The weight percentage of graphene in the SnO_2 -GS

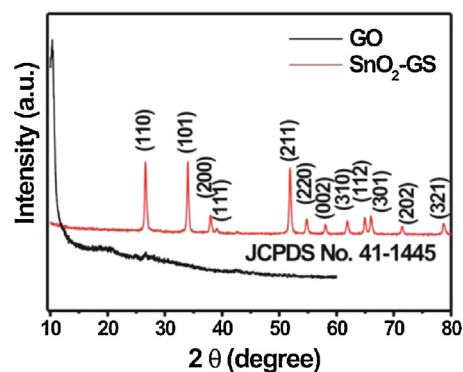


Fig. 1. XRD patterns of the GO and the SnO_2 DNCs-GS nanocomposite.

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