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Short communication

Microwave hydrothermal synthesis of high performance tin–graphene nanocomposites for lithium ion batteries

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HIGHLIGHTS

► Sn–GNS were prepared by a microwave hydrothermal synthesis and a one-step H_2 reduction.
► Sn nanoparticles are homogenously sandwiched between highly conductive and flexible GNS.
► Altering the ratio between tin and graphene had critical influences on their morphologies.
► Sn–GNS exhibited a high lithium storage capacity of 1407 mAh g^{-1}.

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ABSTRACT

Tin–graphene nanocomposites are prepared by a combination of microwave hydrothermal synthesis and a one-step hydrogen gas reduction. Altering the weight ratio between tin and graphene nanosheets has critical influences on their morphologies and electrochemical performances. Field emission scanning electron microscope (FESEM) and transmission electron microscope (TEM) analysis confirm the homogeneous distribution of tin nanoparticles on the surface of graphene nanosheets. When applied as an anode material in lithium ion batteries, tin–graphene nanocomposite exhibits a high lithium storage capacity of 1407 mAh g^{-1}. The as-prepared tin–graphene nanocomposite also demonstrates an excellent high rate capacity and a stable cycle performance. The superior electrochemical performance could be attributed to the synergistic effect of the three-dimensional nanoarchitecture, in which tin nanoparticles are sandwiched between highly conductive and flexible graphene nanosheets.

1. Instruction

Lithium-ion batteries are widely used as the power sources for portable electronic devices, owing to their high energy density, high voltage and long cycle life than other rechargeable batteries. The electrochemical performances of lithium ion batteries are determined by both cathode materials and anode materials. For large-scale applications such as electric vehicles, new electrode materials must be developed to meet the increasing demand for high energy density and power density.

Carbon-based materials are the commercial anode materials for Li-ion batteries [1] with a limited theoretical capacity of 372 mAh g^{-1}, which cannot meet the demand for high specific capacities. Metal and metal oxides, such as silicon (Si) [2], tin (Sn) [3,4], cobalt oxide (Co_3O_4) [5–8], and nickel oxide (NiO) [6,8–10], have been considered as promising alternative anode materials for reversible lithium storage. In particular, metallic tin and tin based anode materials [11–15] are one of the attractive replacement materials for lithium ion batteries due to their high theoretical capacity $\geq$992 mAh g^{-1}. On the other hand, tin and tin based anode materials do not encounter solvent intercalation during discharge/charge cycling, leading to greatly reduced irreversible capacity loss, while large volume variation always occurs in tin based anode materials during lithiation and de-lithiation processes, which causes pulverization of the electrode [16–18]. In order to overcome this problem, many methods have been developed to buffer or prevent volume changes such as CNTs-encapsulation [17,19], formation of core–shell nanostructures [2,20–23], and decrease of particle size [24].

Graphene, discovered by Geim and Novoselov [25] in 2004, is an allotrope of carbon with a structure of one-atom-thick planar sheet

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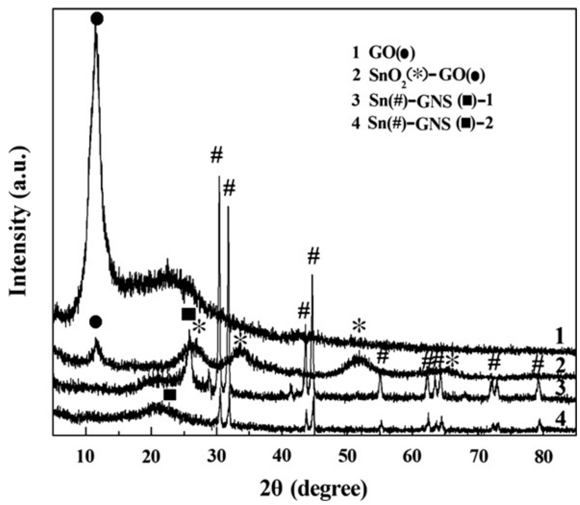

Fig. 1. Powder X-ray diffraction (XRD) patterns of graphite oxide (GO), SnO_2–graphene oxide (SnO_2–GO), Sn–GNS-1 and Sn–GNS-2.

of sp^2-bonded carbon. Many studies have demonstrated that graphene possesses outstanding physical, chemical and mechanical properties [26–30]. It has been proved that lithium ions could be absorbed on the two sides of graphene nanosheet, which increases the theoretical capacity to 744 mAh g^{-1} [31–35] according to the formation of Li_2C_6. Graphene nanosheet (GNS)-based materials have been investigated for lithium storage. Ji and co-worker [36] prepared a multilayer nanoassembly of Sn-nanopillar with graphene, which formed three-dimensional (3D) structure without polymer binder and carbon black. The initial reversible specific capacity reached 734 mAh g^{-1}. The specific capacity maintained 679 mAh g^{-1} after 30 cycles. Li and coworkers [37] reported that graphite oxide (GO) was simply reduced by Sn^{2+} ion, forming SnO_2/graphene anode materials with different weight ratios. It was found that different ratios between Sn^{2+} and GO led to different morphologies and specific capacities. In particular, the specific capacity reached 541.3 mAh g^{-1} at a current density of 200 mA g^{-1} in a voltage range of 1.5–0.01 V. Kim and co-workers [38] developed a SnO_2/graphene composite via loading Sn particles on GO, then reduced by NH_4OH and hydrazine at 80 °C for 8 h. The first reversible specific capacity was about 852 mAh g^{-1} and retained 634 mAh g^{-1} after 50 cycles at a current density of 100 mA g^{-1} between 0.001 and 3.0 V. When the current density was increased to 2000 mA g^{-1}, the reversible specific capacity was 389 mAh g^{-1}.

Microwave-assisted hydrothermal synthesis (MAHS) method has many advantages such as fast heating, high yield rate, and good homogeneity. Both cathode and anode materials for lithium ion batteries with novel structures and special morphologies have been prepared by the MAHS method and demonstrated improved properties [39–41]. Most of the previous reports involved in the preparation of SnO_2–graphene nanocomposites. Zhong et al. synthesized SnO_2–graphene composites and achieved a stable capacity of 590 mA g^{-1} at a current density of 100 mAh g^{-1} [41]. Zhu and coworkers developed SnO_2–graphene composites, in which tin oxide particles (100–200 nm) uniformly anchored on the surface of graphene [42]. Herein, we report a simple and novel synthetic route to prepare Sn–graphene nanocomposites using a combination of microwave hydrothermal reaction and H_2 reduction. The homogeneous dispersion of Sn nanoparticles on graphene nanosheets was achieved by the MAHS method. The as-prepared Sn–graphene nanocomposites exhibited a better electrochemical performance for lithium storage in lithium ion batteries than that of the previously reported results.

2. Experimental

Graphene oxide (GO) was prepared according to the previously published procedure [43]. Two batches of Sn–graphene nanosheets (Sn–GNS) composites were synthesized with weight ratios of 1:1

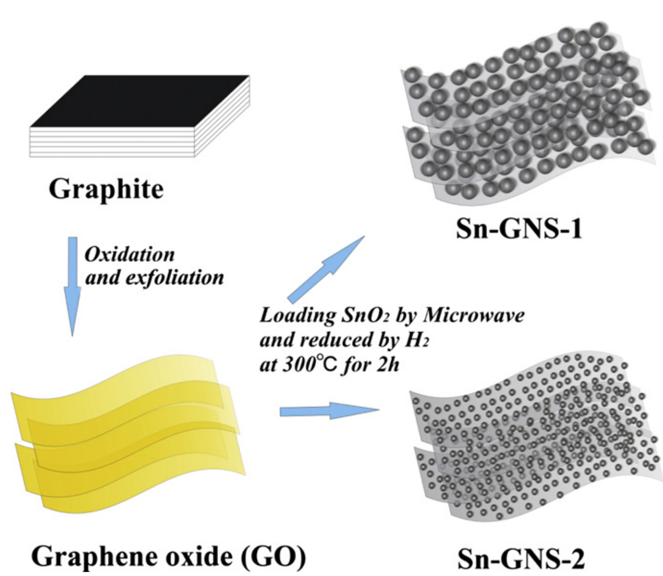

Fig. 2. A schematic illustration for the preparation process of Sn–graphene (Sn–GNS) nanocomposites.

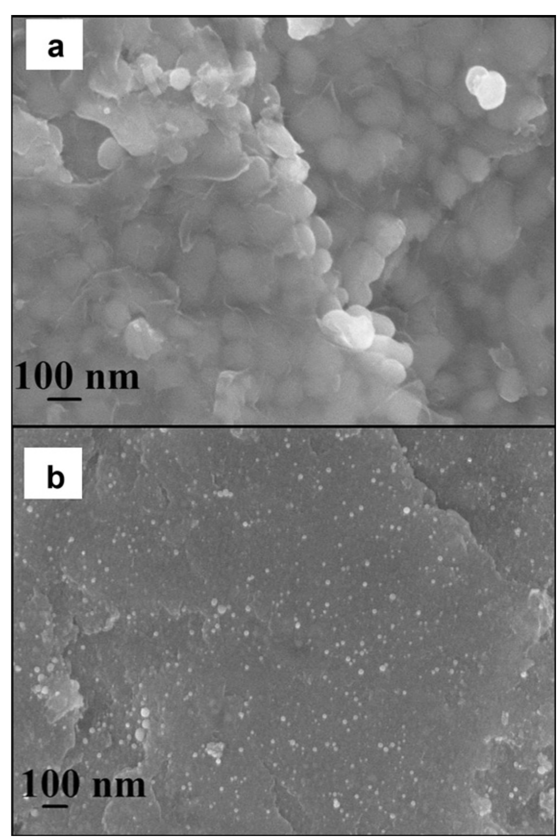

Fig. 3. SEM images of Sn–graphene nanocomposites: (a) Sn–GNS-1, (b) Sn–GNS-2.