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Multilayer Zn-doped SnO_2 hollow nanospheres encapsulated in covalently interconnected three-dimensional graphene foams for high performance lithium-ion batteries

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HIGHLIGHTS

- Multilayer Zn-doped SnO_2 nanospheres are successfully synthesized by using Sn/Zn bimetallic organic nanoparticles.
- Large specific surface area, fast electron/ion transfer, and excellent structural stability.
- Cycle life extends to 1000 cycles with stable capacity.

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ABSTRACT

Multilayer Zn-doped SnO_2 nanospheres are successfully synthesized by using Sn/Zn bimetal-organic nanoparticles as precursor. These multilayer spheres are found to be very suitable for solving the critical volume expansion problem and mass transfer property due to its high surface area, small crystal size and hollow structure, which is critical for high capacity metal oxide electrodes for lithium-ion batteries. Moreover, the covalently interconnected three-dimensional graphene foams encapsulated these multilayer spheres are successfully obtained through self-assembly effect and chemical cross-linking of graphene oxide nanosheets. The graphene network could further greatly improve the cycling stability and rate capability of the Zn-doped SnO_2 spheres electrode due to its flexible buffering matrix and high electric conduction. As a result, the graphene encapsulating multilayer Zn-doped SnO_2 spheres anodes exhibit excellent rate capacity and a high reversible capacity of 446 mA h g^{-1} even after 1000 cycles at the current density of 1 A g^{-1}. These excellent electrochemical performances are ascribed to its large specific surface area, fast electron/ion transfer, and stable electrode structure. Furthermore, this strategy using covalently interconnected 3D graphene foams encapsulate the Zn-doped SnO_2 spheres not only develops a high performance anode material with long cycle life but also holds great promise for binder-free lithium ion batteries.

1. Introduction

Advance in high energy density, light weight, and durable energy storage devices are the keys to realization of high performance electric vehicles and intelligent electronic devices [1–3]. Owing to good sustainability, no memory effect, high energy density, and long cycle life, lithium-ion batteries (LIBs) have propelled them as one of the most ubiquitous power sources in recent years [4]. However, the limited storage capability and the sluggish energy output of traditional carbon materials are not able to fulfill the ever-growing demand for high capacity and power density applications [5]. As an innovative solution to address this challenging issue, anode electrodes are made up of a variety of transition metal oxides (TMOs) that have been found to exhibit theoretical capacities about two or three times larger than those based on commercial graphite [6,7]. In particular, SnO_2 has been part of extensive research activities, since it is expected to provide high capacity and excellent cycling performance. Unfortunately, the use of SnO_2 is still significantly hindered by large volume change that renders poor capacity retention upon cycling and poor electrical conductivity that results in low rate capability [8]. To tackle these pivotal issues, two useful approaches have been developed

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to enhance the structural stability and the electrical conductivity of SnO_2 based anodes. The first effective strategy is to design and synthesize hollow/porous nanostructured SnO_2 anodes. Hollow/-porous structure can not only significantly renders fast ion diffusion, but also provides additional free volume to alleviate the structural strain during the charge-discharge processes, resulting in better cyclic stability than bare solid SnO_2 anodes [9–11].

Recently, thin multilayer hollow microspheres have been considered as an ideal design due to their better performances over single-shelled counterparts for LIBs. The larger surface area of thin multilayer spheres provides better electrode-electrolyte contact area and thus offers shorter Li^+ diffusion length and more active sites for lithium redox chemistry. The shorter diffusion paths lead to a better rate capability, and the overall capacity is much higher as the result of the larger number lithium storage sites. In addition, the carefully crafted porous shell and hollow interior can provide additional free volume to alleviate the structural strain associated with repeated Li^+ insertion/extraction process and thus leads to improved cycling stability. As a result, Wang and co-workers have carried out some excellent work on this field and a variety of multi-shelled metal oxide anodes have been developed, including TiO_2, Fe_2O_3, Co_3O_4 and $CoFe_2O_4$ [12–15]. The universal and straightforward synthetic method of these reported multi-shelled spheres is always using carbon spheres as sacrificial templates. However, it is still a difficulty to simultaneously incorporate two kinds of metal ions to form binary metal oxide with controlling molar ratio by this approach [16]. Therefore, it is necessary to develop a new stratagem for the synthesis of multicomponent metal oxides hollow spheres. Recently, metal organic frameworks (MOFs) or metal-organic nanoparticles (MOPs) have been proposed as an effective way to fabricate porous materials for applications in LIBs. There also have been some reports on the synthesis of porous Sn based composites by direct carbonization of Sn-based MOFs, which exhibit excellent electrochemical performance [17,18]. Moreover, MOFs or MOPs are composed of metal ions and organic ligands. The removal of organic ligands during thermal treatment in air can synthesize numerous metal oxide-based products [19].

Despite the above-mentioned structural advances, the intrinsic poor conductivity drawback of SnO_2 still limits its rate capability. To increase the electronic conductivity, doping alien cations and coating electronically conductive materials have been proved to be effective methods [20]. The impurity ionization and defect can increase the electron density and improve the electronic conductivity of acceptor. For example, the primary mechanism of Zn doping on electrochemical performance of $LiFePO_4$ has been shown that the doping Zn atom can increase the lattice spacing to accommodate more lithium ions [21]. In the meantime, the charge transfer resistance is reduced and the electrochemical performances are well improved. Ali et al. synthesized Zn doped mesoporous TiO_2 microspheres and Shen et al. prepared hollow $Co_xFe_{3-x}O_4$, both of which showed higher electrical conductivity, cycle life, and specific discharge capacity than their undoped materials [22,23]. A great number of studies have also shown that the intrinsic electronic conductivity of SnO_2 can be significantly enhanced via Zn doping, which is attributed to an increase in donor density [24–26]. Although the Zn doped SnO_2 has been studied for using as photoanodes and gas sensitive materials, the electrochemical evaluations of Zn-doped SnO_2 as anodes for LIBs are still rarely reported at present. To further improve electronic conductivity and structural stability, constructing nanostructured SnO_2 with a carbonaceous matrix (especially graphene) is another very promising method. Graphene is an ideal matrix candidate due to its good mechanical properties, high conductivity, and large surface area. Its large surface area can provide excellent electrical contact with the active materials with only a small amount of graphene. Therefore, graphene/SnO_2 nanoparticles have exhibited an enhanced cyclic performance in previous studies [27]. However, the powder-liker or physically connected graphene/SnO_2 composites are hard to meet the self-standing and binder-free requirements of LIBs. Recently, three-dimensional (3D) electrode architecture has been shown to substantially enhance the electrochemical performance of LIBs because the 3D porous structure provides enough void space and large surface area in the electrode, which can facilitate electrolyte diffusion while maintaining good electron transport and accommodating large volume changes [3,28–30].

Herein, to take advantage of structure merits and synergetic effects, a novel multilayer Zn-doped SnO_2 nanospheres were synthesized using metal-organic nanoparticles (MOPs) as precursor and an original way to make cross-linked 3D networked rGO foam anchored with them as advanced LIB anode. This MOP-derived strategy to fabricate multilayer spheres is simple and versatile. Benefiting from the multilayer structure, the doping-related effects and carbonaceous coating, the as-obtained Zn-doped SnO_2/rGO foams can prevent the negative effect of pulverization, and be directly used as binder-free anode. The covalently interconnected rGO sheets can serve as a strain cushion to alleviate large volume change of the Zn-doped SnO_2 and prevent the hierarchical structure from collapsing, while also as a conductive network to remarkably enhance the electrical conductivity and structural integrity of the overall electrode. The synergetic combination of multilayer spheres and flexible rGO are expected to lead to large reversible capacity, long cycling life and excellent rate capability.

2. Experimental

2.1. Synthesis of multilayer Zn-doped SnO_2 hollow spheres

Multilayer Zn-doped SnO_2 hollow spheres were prepared by using MOPs as precursor. The MOPs were synthesized through condensation-driven cooperative polymerization of a bisimido boronic acid (Im-BA) molecule and a bisimido catechol (Im-Ca) molecule in methanol, and then coordination reaction with metal ions. Briefly, 1 mL 3 mg/mL methanol solution of Im-Ca was added into 1 mL 3 mg/mL solution of Im-BA to form deep orange suspension. Then 10 mL 0.028 mol/mL Sn^{4+} and 0.0028 mol/mL Zn^{2+} solution was added to the orange suspension. After reaction for 6 h, the resultant MOPs were washed with methanol and dried in oven at 80 °C for 12 h. Finally, the resultant MOPs were heated to 500 °C in air at the rate of 2 °C min^{-1}, and with holding of the temperature at 500 °C for 2 h. The triple-shelled Zn-doped SnO_2 hollow spheres were collected as white powders. Similarly, the pure multilayer SnO_2 spheres were made by the same method.

2.2. Preparation of covalently interconnected graphene oxide

The graphene oxide (GO) was synthesized via an improved hummers' method [31,32]. The covalently interconnected GO was synthesized via the crosslinking reaction of glutaraldehyde (GDA) and individual GO sheets [33]. In a typical procedure, 4 mL of a GO suspension (5 mg/mL) mixed with 8.8 mg glutaraldehyde and 4.8 mg resorcinol. Then, the resulting viscous GO solution was sonicated for 1 h, and the suspension was then freeze dried to obtain the macroporous GO foam.

2.3. Fabrication of Zn-doped SnO_2/rGO composite foam

To produce the Zn-doped SnO_2/rGO composite foam, we rationally designed the synthetic reaction steps as follows. The GO (5 mg/mL) and the Zn-doped SnO_2 hollow spheres dispersion (20 mg/mL) were homogeneously mixed under stirring and sonication for 15 min. The weight percent of Zn-doped SnO_2 was typically kept