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Nanoscale Kirkendall Effect Synthesis of Echinus-like SnO_2@SnS_2 Nanospheres as High Performance Anode Material for Lithium Ion Batteries

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ABSTRACT

Crystalline echinus-like SnO_2@SnS_2 shell-shell-structured nanospheres (SSN) are fabricated by a hydrothermal method based on nanoscale Kirkendall Effect. Single crystal SnS_2 nanorods with length of approximately 50 nm and width of approximately 8-15 nm are arranged regularly on the surface of the nanospheres. When the echinus-like SnO_2@SnS_2 SSN are used as anode materials for Li-ion batteries, the initial capacity is 1558 mA h g^{-1}, and the reversible capacity after 100 cycles of the products is 548 mA h g^{-1}. The SnO_2@SnS_2 nanocomposites also display excellent rate capability with a reversible capacity of 443.4 mA h g^{-1} even at the current rate of 5 C. The high electrochemical performance is attributed to the synergistic effect of the hierarchical hollow nanostructure: (1) fast ion diffusion and electron transport at electrode/electrolyte interface, (2) sufficient space to minimize the damage to the electrode caused by the volume expansion of tin-based materials during charge-discharge process. The encouraging experimental results suggest that the novel echinus-like hollow shell-shell structured nanospheres have great potential for practical applications of Li-ion batteries.

1. Introduction

One of the most important tasks for scientists and engineers worldwide is to develop sufficient and reliable storage of energy. [1–5] In order to buffer the power grids of wind/solar power plants due to their intrinsic properties of intermittent in time and localized in space, the desire for advanced high-performance energy storage devices is extremely high. [6,7] Li-ion batteries (LIBs) are one kind of most promising energy storage devices. Currently, most researches on the device has been focused on searching optimal electrode materials in terms of large specific energy, high power density and superior cycle stability. Numerous efforts have been devoted to the development of new electrode materials to meet the demand for LIBs with high energy density and excellent cycle performance. Metal oxides, such as Co_3O_4, [8] Fe_3O_4, [9] NiO, [10] MnO_2 [11] and SnO_2, [12,13] have high theoretical capacity and great natural abundance. They become the most promising candidates for the anode materials in the next generation LIBs.

In particular, the use of SnO_x nanomaterials in LIBs have been intensively studied for the last few decades. [14–19] Despite their considerable advantages, SnO_x nanomaterials in LIBs applications were impeded with problems that hindered their practical applications. For example, the capacities decay rapidly with increasing number of cycles because of large polarization at high charge/discharge rates (caused by the slow diffusion of lithium ions in active materials), increment of the resistance of the electrolyte, high reaction potential with Li ions make it a serious problem to fabricate high energy density full cell just as most metal oxides, and severe volume expansion/contraction (up to about 300%) during charging/discharging processes. [20,21]

It is known that the electrochemical performance of SnO_x strongly relies on the morphology of their nanostructure. [22] Therefore, many types of SnO_x nanostructures, such as nanoparticles, [23] nanowires and nanorods, [24,25] and core/shell [26] and hollow structures [27], have been reported to exhibit enhanced electrochemical activities. Especially, hollow shell-shell structured electrode can provide sufficient space to overcome the damage caused by the volume expansion of SnO_x, which may exhibit excellent cycling performance. According to the previous reports by many groups, hybridization of SnO_x with carbon or graphene is another effective resolution to this intrinsic drawback of volume

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expansion, which manifests obvious advantages as the following: 1) carbon and graphene can improve the electrical conductivity of electrodes; and 2) the volume changes associated with lithiation and delithiation can be cushioned by the implementation of carbon and graphene. [27–29] However, the introduction of carbon and graphene would sacrifice the capacity of SnO_x. Meanwhile, the reliable fabrication of well-designed SnO_x@carbon (SnO_x@graphene) nanocomposites remains a major challenge. Therefore, it is necessary to develop a simple and facile method to prepare SnO_x nanocomposites with both hollow shell-shell structure and excellent electrical conductivity.

Nanoscale Kirkendall Effect is a one-step template-free and facile method for generating hollow inorganic micro- and nanostructures. The nanoscale Kirkendall Effect was first proposed by Yin et al. [30] to explain the formation of hollow nanoparticles of cobalt oxide and chalcogenides through the reaction of colloidal Co with oxygen, sulfur, and selenium. Following similar strategies, inorganic hollow nanoparticles and nanotubes such as CoSe, [31] ZnO [32] and $ZnAl_2O_4$ [33] have been synthesized. However, to the best of our knowledge, there are no reports on the synthesis of hollow nanospheres with shell-shell structure via nanoscale Kirkendall Effect. Hollow nanospheres with shell-shell structure prepared via Kirkendall Effect can not only extend the manufacture method based on Kirkendall Effect but also play an important role in LIBs industrial production because the hollow structure can afford adequate room for the volume change during cycling and provide a great number of electrochemical active sites for storing Li^+ due to its high specific surface area.

In addition, SnS_2, when used as electrode material, is another tin-based material with excellent cycling stability. [34–36] To realize high-performance LIBs for practical application, we design and rationally synthesize echinus-like SnO_2@SnS_2 shell-shell-structured nanospheres (SSN) based on nanoscale Kirkendall Effect. In our approach, we not only focus on designing shell-shell-structured electrode material by a simple and facile method but also utilize the synergistic effect of the good electric conductivity of SnS_2 (SnO_2 has a wide band gap of 3.8 eV, while SnS_2's indirect band gap is 2.21 eV, so SnO_2 tends to inject electrons into the SnS_2, and the junction is expected to be ohmic) [37] and the high capacity of SnO_2. Hence, this design of nanospheres electrode enhances the ion diffusion as well as electron transportation at the electrode/electrolyte interface. As results, the echinus-like SnO_2@SnS_2 SSN exhibit excellent capability and long lifespan, in comparison with each individual component.

In this paper, we used a facile hydrothermal method to prepare echinus-like SnO_2@SnS_2 SSN based on nanoscale Kirkendall Effect, and investigated their electrochemical properties as anode materials for LIBs. The electrodes exhibited the first discharge and charge capacities of 1558 and 962 mA h g^{-1}, respectively. Besides, the composite electrodes had discharge capacities of 842, 741, 596 and 548 mA h g^{-1} in the 10^{th}, 20^{th}, 50^{th} and 100^{th} cycles, respectively. The hollow SSN composites displayed an excellent rate capability and delivered a reversible capacity of 870.5, 733.7, 626.4, 577.7 and 551.8 mA h g^{-1} at the high rate of 0.1, 0.2, 0.5, 1 and 2 C, respectively. Even when the rate increased to 5 C, the reversible capacity of the composites also could achieve 443.4 mA h g^{-1}. Moreover, after the current rate returned to 0.1 C, the electrode delivered a specific discharge capacity of about 779.1 mA h g^{-1}, showing a high capacity retention of 89.5%. Such superior electrochemical results were ascribed to the hollow structures with sufficient space which could overcome the damage caused by the volume expansion of tin-based materials. Our results demonstrated that this simple method based on Kirkendall Effect could be extended for the synthesis of other nanocomposites with shell-shell nanostructure and interesting applications in other fields. The superior performance indicates that the hollow SnO_2@SnS_2 SSN may be a good candidate in Li-ion battery industrialization.

2. Experimental

2.1. Materials synthesis

All chemical reagents utilized in the study were of analytical grade and used without further purification.

2.1.1. Synthesis of SnO_2 Nanospheres

SnO_2 echinus-like nanospheres were fabricated by a simple hydrothermal method. 1 mmol $Na_2SnO_3{\cdot}2H_2O$ was dissolved in a mixed solution of 15 mL deionized water and 25 mL anhydrous ethanol at room temperature under constant stirring. After 15 min, the obtained white suspension solution was transferred into a 50-mL Teflon-lined stainless-steel autoclave and then maintained at 200 °C for 24 h. The precipitates were centrifuged, washed several times with ethanol and water, and then dried at 60 °C for 12 h.

2.1.2. Synthesis of SnO_2@SnS_2 Shell-Shell Structured Hollow Spheres

Then 0.1 mmol of the as-synthesized SnO_2 nanospheres were dispersed in 40 ml solution containing 0.5 mmol thiacetamide (TAA), with constant stirring. Next, the white suspension solution was transferred into a 50-mL Teflon-lined stainless-steel autoclave and then maintained at 180 °C for 6 h. After cooling to room temperature, the canary precipitates were washed with deionized water and anhydrous ethanol repeatedly to remove the possible impurities and then dried at 60 °C for 12 h. Then the product was calcined at 773 K for 2 h in argon atmosphere.

2.2. Characterization

The as-prepared products were characterized by a powder X-ray diffraction (XRD, Siemens D-5000) with Cu Kα (λ = 0.15418 nm). The morphology of the synthesized samples was examined using field-emission scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL-2010) operated at an accelerating voltage of 200 kV.

2.3. Electrochemical Measurement

The as-prepared products were used as the anodes with 1 M $LiPF_6$ in ethylene carbonate and diethyl carbonate (1:1 v/v) as the electrolyte. The anode electrode consisted of 80 wt % active material, 10 wt % conductivity agents, and 10 wt% binder polymer binder on a copper foil and dried at 80 °C under vacuum overnight before assembly. The counter electrode was Li metal, polypropylene (PP) film (Celgard 2400) was used as separator and CR2025 coin cells were assembled in an argon-filled glove box. The cells were tested on a computer controlled battery tester system (Arbin BT-2000). The profiles of charging and discharging curves were obtained at a potential range of 0.01 to 3 V (vs Li^+/Li) at a current density of 100 mA g^{-1}. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation over the potential range of 0.01 – 3.0 V (vs Li^+/Li) at a scanning rate of 0.5 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were conducted by applying an AC potential of 5 mV amplitude in the frequency range from 0.01 to 100 kHz.

3. Results and Discussion

The SEM images of as-grown echinus-like SnO_2 nanospheres and SnO_2@SnS_2 SSN are shown in Figure S1 (Supporting Information (SI)). Figure S1A shows the typical SEM image of the