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Three-dimensional porous graphene-encapsulated CNT@SnO_2 composite for high-performance lithium and sodium storage

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ABSTRACT

Tin oxide (SnO_2) is regarded as a promising anode material for both lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) due to its large theoretical capacity. However, poor electrical conductivity and the weak cyclability resulted from dramatic volume expansion upon cycling process still hinder its practical application. Herein, we report a facile two-step hydrothermal route to encapsulate core–shell structured carbon nanotube (CNT)@SnO_2 composite in a graphene coating with novel three-dimensional (3D) porous framework architecture (CNT@SnO_2@G) as anode for both LIBs and SIBs. The resultant CNT@SnO_2@G electrode suggests outstanding lithium and sodium storage performance with large specific capacity, remarkable cycling stability and excellent rate capability. For LIBs, it delivers a high initial discharge capacity of 1400 mAh g^{-1} at 100 mA g^{-1}, improved reversible capacity of 947 mAh g^{-1} after 100 cycles at 100 mA g^{-1}, and enhanced rate capability of 281 mAh g^{-1} at 3000 mA g^{-1}. In addition, sodium storage testing suggests that a high discharge capacity of 323 mAh g^{-1} after 100 cycles at 25 mA g^{-1} was achieved. The present unique structural design associated with the remarkable lithium and sodium storage performance ensures CNT@SnO_2@G as an advanced anode material for rechargeable LIBs and SIBs.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) and sodium-ion batteries (SIBs) have attracted tremendous attention with the urgent need of clean energy for the society [1,2]. Recently, LIBs have been widely used in portable electronic devices, electrical vehicles (EVs) and electrical energy storage (EES) owing to the high energy density [3–5]. Besides, benefiting from the abundant sodium resource and relatively low price, SIBs are considered as the promising alternatives to LIBs [6–8]. However, unlike the rapid development of LIBs, SIBs suffer from much lower energy density and lack of suitable electrode materials, specifically the appropriate anode materials for efficient Na-storage [9–11]. In the exploration of large energy density and long cycle life rechargeable batteries, study of suitable anode materials is still a critical concern for both LIBs and SIBs because of the unsatisfactory theoretical capacity of traditional graphite anode (372 mAh g^{-1}) for LIBs and inadequate Na^+ insertion hosts for SIBs [12–16].

Tin oxide (SnO_2) has been intensively investigated as one promising candidate anode material for both LIBs and SIBs due to the merits including high theoretical capacity (782 mAh g^{-1} for LIBs and 667 mAh g^{-1} for SIBs), chemical stability, low toxicity and low cost [17–19]. However, SnO_2 presents serious bottlenecks in dramatic volume expansion upon the alloying reaction with Li/Na, which results in rapid capacity loss and weak cycling stability [20–22]. Besides, the diffusion rate of Na^+ in SnO_2 is much lower than that of Li^+ according to a theoretical study by DFT calculation [23]. To achieve enhanced lithium and sodium storage performance, several strategies have been proposed such as designing nanostructured SnO_2 to efficiently reduce the absolute volume variation upon the charge/discharge process [24,25], constructing SnO_2–carbon composites with various architectures (especially for the porous structure) to accommodate the volume change and maintain the structural integrity, coupled with improvement in the electrical conductivity of SnO_2 [26–28], and preparing heteroatom doped SnO_2–carbon materials (e.g. nitrogen, fluorine) to offer increased electrical conductivity and added defect sites for efficient lithium and sodium storage [29,30].

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In particular, combing SnO_2 nanoparticles (NPs) with graphene or carbon nanotube (CNT) suggests great potential as high-performance LIBs/SIBs anode materials. Li et al. [31] synthesized SnO_2/graphene oxide composite via a fast supercritical methanol method and the composite demonstrated a reversible discharge capacity of 776 mAh g^{-1} after 70 cycles at a current density of 100 mA g^{-1} for LIBs. Li et al. [32] developed SnO_2 decorated graphene nanocomposites by a scalable wet-mechanochemical route and the composite delivered high discharge capacities of 270 mA h g^{-1} after 100 cycles at 100 mA g^{-1} for SIBs. Zhang et al. [33] constructed a SnO_2/carbon-nanotube hybrid by a microwave-assisted process and the hybrid achieved a reversible capacity of 710.4 mA h g^{-1} after 80 cycles at 200 mA g^{-1} for LIBs. Wang et al. [34] prepared SnO_2@CNTs nanocomposite by a solvothermal method, exhibiting capacity retention of 474 mAh g^{-1} over 50 cycles at 50 mA g^{-1} for SIBs. It is believed that the combination of SnO_2 with garphene or CNT could not only accommodate the volume expansion of SnO_2 upon the alloying reaction with Li/Na, but also provide fast electron and mass transport kinetics for the electrodes [35,36]. However, unstable solid electrolyte interphase (SEI) layer induced by the direct contact of SnO_2 with electrolytes and the aggregation of SnO_2 NPs on the surface of graphene and CNT substrates still remains great concerns.

Herein, we present the synthesis of core–shell structured CNT@SnO_2 composite encapsulated in a graphene coating with novel three-dimensional (3D) porous framework architecture (CNT@SnO_2@G) via a facile two-step hydrothermal method. Benefiting from the synergistic roles of CNT, graphene and SnO_2 NPs associated with an unique 3D porous framework architecture, the direct contact of SnO_2 with electrolytes can be well avoided, thus forming stable SEI layer on the surface of active materials. Additionally, great advantages could be achieved in the electrode, involving the promotion of ionic and electronic transport, supplement of sufficient active sites, reduction of ionic diffusion distance as well as accommodation of the aggregation and volume variation of SnO_2. As a consequence, the resultant CNT@SnO_2@G anode delivers remarkable lithium and sodium storage performances, with a high initial discharge/charge capacity of 1400/804 mAh g^{-1} at 100 mA g^{-1}, improved reversible capacity of 947 mAh g^{-1} after 100 cycles at 100 mA g^{-1}, and enhanced rate capability of 281 mAh g^{-1} at 3000 mA g^{-1} for lithium storage. Besides, it achieves a high discharge capacity of 323 mAh g^{-1} after 100 cycles at 25 mA g^{-1} as anode for sodium storage.

2. Experimental Section

2.1. Materials

Graphene oxide (GO) solution was prepared using graphite powders (4000 meshes, Aladdin) as raw materials by our previous method [37]. Multi-wall carbon nanotubes (CNTs: 10–20 nm in diameter, 5–15 μm in length, and 40–300 m^2 g^{-1} in surface area) was obtained from Shenzhen Nanotech Port Co. Ltd, China. Ethyl alcohol (AR), Concentrated sulfuric acid (H_2SO_4, AR), Concentrated nitric acid (HNO_3, AR), Cetyltriethylammoniumbromide (CTAB, AR), Sodium hydroxide (NaOH, AR), and Ethylenediamine (EDA, AR) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. Tin (IV) Chloride Pentahydrate ($SnCl_4 \cdot 5H_2O$, 99%) was purchased from Tianjin Fuchen Chemical Regents Factory, China.

2.2. Synthesis of CNT@SnO_2 composite

CNT@SnO_2 composite was synthesized by a typical hydrothermal reaction. Firstly, activated CNTs were obtained by treating the CNTs in a mixed HNO_3/H_2SO_4 (1: 3 by volume) solution at 80 °C for 10 h. Then, 0.3 g of activated CNTs was dispersed into a mixture of distilled water/ethyl alcohol (40 mL/60 mL) under constant stirring. Next, 1.2 g CTAB, 1.8 g NaOH and 3.6 g $SnCl_4 \cdot 5H_2O$ were added into the above dispersion successively. Afterward, the formed mixture was thermally treated in a Teflon-lined autoclave at 160 °C for 24 h. At last, the naturally cooled reaction solution was treated by vacuum filtration, washing with distilled water and drying at 80 °C for 24 h. The obtained black powders were so called CNT@SnO_2 composite.

2.3. Preparation of CNT@SnO_2@G composite

To prepare CNT@SnO_2@G, 0.15 g of the CNT@SnO_2 was firstly added into 50 mL GO dispersion (2 mg mL^{-1}) and then treated by intense ultrasonication for 1 h. Afterward, 1.5 mL EDA (served as assistant reducing agent) was added into the above solution and the mixture was stirred under an ice bath for another 1 h. Next, 3 ml of the mixture was placed in a 5 ml bottle and then sealed in a 25 mL Teflon-lined autoclave followed by a heat treatment at 120 °C for 2 h. After the autoclave was cooled to ambient temperature, the as-formed hydrogel was taken out and soaked within 1 L distilled water/ethyl alcohol mixed solvent (4: 1 by volume) for 48 h. Finally, CNT@SnO_2@G was obtained by freeze drying the sample with a subsequent annealing process at 500 °C in N_2 atmosphere for 2 h. Neat graphene framework without CNT@SnO_2 loading was prepared by the same method to evaluate the morphology evolution of CNT@SnO_2@G, and pure SnO_2 NPs (see the synthesis in our previous work [26]), CNT@SnO_2 and SnO_2@G (graphene framework loaded with SnO_2 NPs, synthesized by the same process with CNT@SnO_2@G) as the control samples.

2.4. Characterizations

The morphology of the as-prepared samples was investigated using field emission scanning electron microscope (FE-SEM, JSM-6330, JEOL) and transmission electron microscope (TEM, JEM-2011, JEOL). The observation of the phase structure was performed using X-ray diffraction (XRD, D/max-Rb, Rigaku) with Cu Kα radiation. The chemical composition was examined using X-ray photoelectron spectroscopy (XPS, EscaLab 250Xi, Thermo Scientific) with Al Kα irradiation. The SnO_2 loading in CNTs@SnO_2@G and CNTs@SnO_2 was conducted by thermal gravimetic analysis (TGA, STA449F3, NETZSCH) at a heating rate of 10 °C min^{-1} under air atmosphere. N_2 adsorption/desorption curve was determined by a Micromeritics Analyzer (ASAP 2460, MicroActive).

2.5. Electrochemical measurements

CR2032 coin half-cells were assembled in an argon-filled glove box to evaluate the electrochemical performance of the resultant anode materials. Typically, the electrode slurry containing 80 wt% active materials (CNT@SnO_2@G, SnO_2@G, CNT@SnO_2 and pure SnO_2), 10 wt% super P, and 10 wt% polyvinylidene fluoride was cast on a fresh copper foil current collector. The as-cast copper foil was treated at 80 °C overnight and then 110 °C for 10 h under vacuum condition. Afterward, the dried electrode along with copper foil was punched into disks with a diameter of 14 mm. Li foil and Na bulk were employed as the counter/reference electrodes and Celgard 2400 polypropylene film as the separator. The electrolyte of LIBs was 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) (1: 1: 1 by volume). In addition, a solution of 1 M of $NaClO_4$ in an EC/DEC (1: 1 by volume) mixture with 5 vol % fluoroethylene carbonate (FEC) was used as the electrolyte of SIBs. Galvanostatic discharge and charge tests of the cells were conducted on a LAND CT2001A instrument, within a cutoff potential range of 0.01–3.0 V. Cyclic voltammetry curves were collected on an electrochemical