

Carbon coated SnO₂ particles stabilized in the elastic network of carbon nanofibers and its improved electrochemical properties

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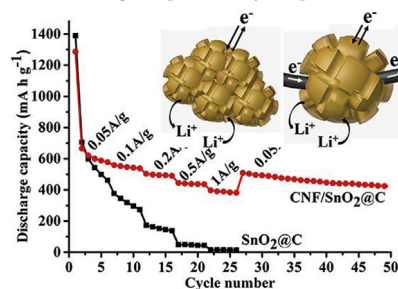


HIGHLIGHTS

- Carbon coated SnO₂ grown in CNFs network by hydrothermal and post-annealing.
- SnO₂ reaches to 50 wt% meanwhile the composite film remains the flexibility.
- CNF/SnO₂@C demonstrates improved rate performance and cyclic stability.
- Buffering effect of CNFs is studied by using ex-situ SEM in the cycled electrodes.
- CNFs provide conductive channel and buffering network.

GRAPHICAL ABSTRACT

CNFs as substrate provide excellent conductive channel improving rate capability and effective matrix buffering volume change to promote cyclic performance.



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ABSTRACT

Three dimensional networks, herein carbon coated SnO₂ micron-sized particles are fixed in carbon nanofibers (CNF/SnO₂@C), is fabricated and synthesized by using hydrothermal method and carbonization. The weight ratio of SnO₂ reaches to 50% of CNF/SnO₂@C, meanwhile, CNF/SnO₂@C remains its flexibility. CNF/SnO₂@C film is directly used as a binder-free anode for lithium ion batteries without conductive additive and polymer binder. The discharge capacities of CNF/SnO₂@C are 1286 mAh g⁻¹ at 0.05 A g⁻¹ and 397 mAh g⁻¹ at 1 A g⁻¹, respectively. The buffering effect of CNFs is studied by using ex-situ SEM in the cycled electrodes operated at various lithiation states. The particles size of SnO₂@C sample increase to 4 μm after 20 charge/discharge cycles, and a serious aggregation of particles occurs in the cycled SnO₂@C electrode which is in coincidence with its rapidly faded capacity. The particles of CNF/SnO₂@C sample also present the increased size from the original size of 2 μm to the lithiated size of 4 μm but they are still fixed in CNFs network without any aggregation. The improved specific capacity, cyclic stability and rate performance of CNF/SnO₂@C are attributed to the structural synergy of CNFs and SnO₂ particles, because CNFs as flexible substrate provides excellent conductive channel improving the rate capability and effective network buffering the volume change to promote the cyclic performance.

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1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been widely used as power sources for electronic portable devices and electric vehicles (EVs) [1–3]. The current LIBs cannot meet the increasing demands in high-performance energy storage devices. For example, graphite being the anode material of the current commercial LIBs has a low theoretical capacity (372 mAh g^{-1}), which seriously restricts its further development in high-performance LIBs. Developing novel anode materials with higher specific capacity becomes one of the important research topics in the field of high-performance LIBs [4–6].

SnO_2 -based materials with high theoretical capacity, environmental friendliness, and abundant resources are considered as promising candidates to replace graphite as anode materials for high-performance LIBs [6–16]. However, SnO_2 display particles aggregation and large volume changes ($> 300\%$) during lithiation/delithiation. These defects lead to the pulverization of active materials, breakage of solid electrolyte interphase (SEI), and finally rapid capacity fading. Besides, bare SnO_2 leads to poor rate capability because it is semiconductor with low conductivity [17,18].

In order to solve the above problems, researchers have designed varied nanostructure of SnO_2 to alleviate the volume expansion, such as nanotubes [12,19], nanorods [14,20], nanosheets [21,22], nanoparticles [11,15,16], nanowires [23,24] and hollow structures [12,25,26]. Reducing the size to SnO_2 can alleviate the volume change, but nanoscaled SnO_2 particles seriously aggregate each other after several charge/discharge cycles. Another method is being composite contained SnO_2 and other materials such as metallic oxide and carbonaceous materials [5–16,23–29]. Among them, SnO_2 /carbonaceous materials have been extensively studied. Tian and coworkers have synthesized SnO_2 /Sn/carbon nanowires that the composite presents excellent lithium storage properties [28].

In the previous work, the composite SnO_x @carbon nanofiber (SnO_x @CNF) was synthesized by using an in-situ preparation route in which the precursor of tin salt and polyacrylonitrile (PAN) were together electrospun before carbonization [30,31]. SnO_2 nanoparticles embedded inside of CNFs instead of outside of CNFs, provides much improved capacity and presents excellent cycling performance, because the flexible and elastic CNFs effectively buffer the volumetric change of SnO_2 and hinder the aggregation of SnO_2 nanoparticles. Moreover, the composite film of SnO_x @CNF can be directly used as binder-free anode for LIBs without slurry making, which not only simplify the process but also reduce the development cost. The question is the low weight ratio of SnO_2 in the above mentioned SnO_2 @CNF sample, because excess amount of metal oxide enwrapped inside of CNF causes fiber breakage and losing its flexibility [32]. To increase the weight ratio of SnO_2 , ex-situ loading will be an effective strategy which metal oxide particles are fixed outside of CNFs instead of inside of CNFs. Li et al. reported 3D networks consisted of C/ SnO_x /C hybrid nanofibers that were prepared by a simple dip-coating process and subsequent CVD growth. The improved electrochemical performance can be ascribed to the morphological stability and the low resistance of the nanofibers with the CVD carbon skin. Furthermore, the embedded and de-aggregated SnO_x nanoparticles in the carbon matrix provide large numbers of reaction sites for lithium ions [33].

In this work, flexible CNFs network is first synthesized by electrospinning and carbonization, then SnO_2 micron-sized particles are grown on and confined in CNFs network under hydrothermal condition, finally SnO_2 particles are coated by carbon to improve the electrochemical performance. The as-produced CNF/SnO_2 @C sample is flexible film and is directly used as binder-free anode, in which the energy density of the composite electrode is much higher than that of bare SnO_2 sample. The crystal structure and electrochemical properties of CNF/SnO_2 @C are studied in detail.

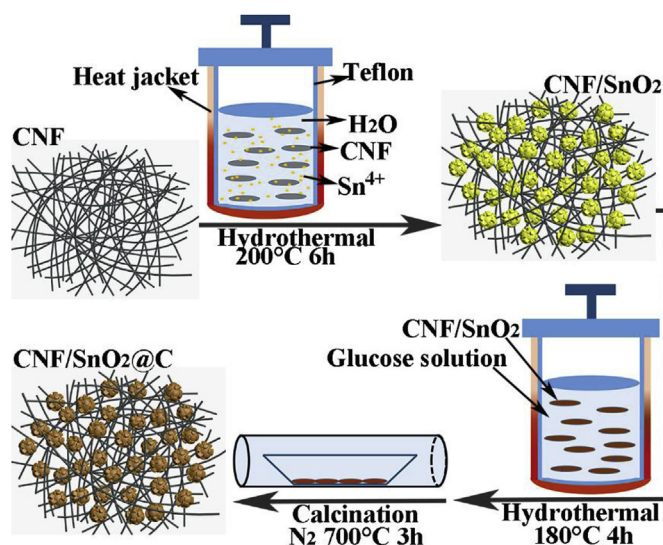


Fig. 1. Schematic representations of the route for preparing CNF/SnO_2 @C.

2. Experimental

Materials Preparation: According to the previous publications, the preparing process of CNF network includes electrospinning and carbonization of PAN. The mass of CNF film is about 1 mg cm^{-2} . $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.42 g), NaOH (0.48 g) and sodium dodecyl sulfate (0.028 g) were mixed in 40 mL of distilled water under ultrasonic process for 10 min to obtain a clear solution. Then, CNF film and the solution were together transferred into a Teflon-lined autoclave, followed by a hydrothermal treatment at 200°C for 6 h. After the autoclave cool down to room temperature naturally, the as-produced CNF/SnO_2 sample was washed for several times using distilled water.

Glucose as carbon source was converted to carbon coated on CNF/SnO_2 . The procedure of preparing CNF/SnO_2 @C was schematically shown in Fig. 1. 2 g of glucose was dissolved in 50 mL of distilled water and stirred for 10 min. The solution of glucose and CNF/SnO_2 film were transferred into a Teflon-lined autoclave and maintained at 180°C for 4 h. Finally, the as-produced carbon-coated CNF/SnO_2 was heated at 700°C for 3 h in N_2 atmosphere to improve the crystallization of SnO_2 and the carbonization degree of the surface carbon layer. As a comparison sample, SnO_2 @C were prepared through the above procedure without CNF film in hydrothermal condition.

Structure and Morphology Characterization: The crystal structures of the products were identified by X-ray powder diffraction (XRD, Rigaku Cu- K_α radiation) in the 2θ from 10 to 80° . The morphological characterization was carried out using scanning electron microscope (FE-SEM, SIGMA, ZEISS 20 kV) and X-ray energy dispersive spectroscopy (EDS, Oxford Instruments Analytical), transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-200CX, 200 kV). Thermal gravimetric analyzer (TGA/DTA851E) was performed under oxygen atmosphere with a heating rate of 5°C min^{-1} from 25°C to 900°C . X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab250Xi, Al- K_α as X-ray source) were performed to evaluate the valence state of the C, O and Sn elements on the surface of sample. The binding energies obtained in the XPS analysis were calibrated against the C 1s peak that was locked at 284.6 eV .

Electrochemical measurement: The flexible CNF/SnO_2 @C film was directly used as working electrode. The comparison sample of SnO_2 @C powder (75 wt%), acetylene black (10 wt%), and poly(vinylidene fluoride) (PVDF) (15 wt%) were dispersed in the solvent of N-methyl-2-pyrrolidone (NMP) being stirred overnight to form a slurry. The slurry of SnO_2 @C was pasted onto copper foil and dried in vacuum at 110°C for 12 h.

Electrochemical tests were evaluated by CR 2016 coin-type cell. The

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