



# Facile Fabrication of Binder-free Metallic Tin Nanoparticle/Carbon Nanofiber Hybrid Electrodes for Lithium-ion Batteries



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## ABSTRACT

In this work, a Sn nanoparticle (NP)/carbon nanofiber (CNF) hybrid with unique structure has been designed and fabricated via electrospinning and subsequent heat treatment. The cell assembled by the binder-free Sn NP/CNF hybrid demonstrates an effective capacity ( $46 \text{ mAh g}^{-1}$  at  $200 \text{ mA g}^{-1}$  after 200 cycles) with high coulombic efficiency (up to 99.8%), suggesting a facile strategy for the scalable fabrication of electrochemically stable electrodes for LIBs. For understanding the electrochemical behaviors of the metallic Sn and carbon nanofibers in the lithiation/delithiation process, *in situ* transmission electron microscopy was applied to study the single hybrid structure. In the first charge/discharge process, real-time size variation of the Sn NP and CNFs was mainly focused, suggesting a two-step lithiation process in the metallic Sn NP. Structural characterization also indicates an irreversible delithiation in a single Sn NP/CNF hybrid structure. The electrochemical performance based on influence of carbonization temperature has also been discussed. The results and fundamental understanding of the lithiation/delithiation in the Sn-based hybrid anodes enables the communities to design flexible high-performance electrodes based on metallic active materials in a rational way.

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## 1. Introduction

Lithium ion batteries (LIBs) with long cycle life and high energy density have been widely applied to various portable electronic devices, electric vehicles and plug in hybrid electric vehicles [1–4]. In the last few years, urgent requirement for LIBs of higher performance has been raised, and one of the most emerging challenges for further development of LIBs relies on the novel electrode materials of much more rational design [5–7]. As one of the most promising anode materials, metallic Sn and its oxides (e.g.  $\text{SnO}_2$ ) have drawn considerable attention for much higher theoretical capacity ( $\sim 992 \text{ mAh g}^{-1}$  in Sn and  $\sim 790 \text{ mAh g}^{-1}$  in  $\text{SnO}_2$ ) [8] compared to traditionally commercial graphite of limited capacity ( $\sim 372 \text{ mAh g}^{-1}$ ). Upon repeated insertion and extraction of Li ions, Sn suffers from severe volume change (up to 270%), leading to pulverization of active materials and unstable solid electrolyte interphase (SEI) growth. Consequently, the resulting dramatic capacity fading has largely prevented commercial implementation [9–11].

Apart from the achievement in the anode materials developed upon Sn-based alloys [12–15], a variety of strategies towards such issues have been recently widely pursued, including fabrication of Sn-based nanostructures with various morphologies and design of Sn-based/carbon hybrid nanostructures [16–23]. The former suggests much improved electrochemical performance owing to the shortened diffusion length and largely alleviated mechanical stress during lithiation/delithiation processes [24]; In the latter, the conductive carbon matrices could effectively prevent Sn-based active materials from aggregation to alleviate mechanical stress and meanwhile enable them to form stable SEI films. Among the design of Sn-based/carbon composite nanomaterials, Sn-based/carbon nanofiber hybrids with unique conductive networks are highly attractive in the scalable production of binder-free and free-standing anode materials [25]. However, the understanding of the lithiation/delithiation behaviors in such Sn-based/carbon nanofiber hybrids has been rarely documented, typically for the lithium ion transport behavior across the conductive network and the accommodation of volume expansion/extraction of Sn-based materials.

More recently, the concept and practice of *in situ* transmission electron microscopy (TEM) technique has particularly demonstrated a tremendous approach for a deep-insight exploration on the lithiation/delithiation mechanism of active materials. Upon

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this powerful technique, investigations have been carried out in the typical anode materials of bare nanostructures, such as SnO<sub>2</sub> nanowires [26,27], Si nanowires [28], Ge nanowires [29], Si nanorods [30], ZnO nanoparticles [31], Si spheres [32,33] and Sn particles [34,35]. However, the application of bare anode materials is severely hampered by the problems like low conductivity, aggregation, pulverization and etc. For further understanding the lithiation/delithiation behaviors of the active materials with the presence of carbon matrices, typical carbon-based hybrid structures, such as Si/C nanofibers [36], yolk-shell Si/C nanoparticles [37], Fe<sub>2</sub>O<sub>3</sub>/graphene anodes [38] and Co<sub>9</sub>S<sub>8</sub>/Co carbon nanotubes [39] have been also designed and studied. According to the *in situ* TEM observation, the implication of using Si/C hybrid structures has demonstrated more advantageous features, including the enhancement in kinetics, suppression of particle aggregation and alleviation of volume expansion, which is consistent with the electrochemical performance achieved in the assembled cell systems [37]. Therefore, fundamental understanding of the lithiation/delithiation mechanism in Sn-based/carbon hybrid structures could offer significant guidance in the rational design of high-performance Sn-based anode materials.

Metallic Sn is not required to consume lithium resource for being reduced from oxides (e.g. SnO<sub>2</sub>) in the lithiation [25,40], thus delivering higher theoretical capacity than its oxides (SnO<sub>2</sub>). In this work, free-standing Sn NP/CNF hybrid was fabricated and used as the binder-free electrode directly, and thus the electrochemically inactive binders could be fully avoided. The resulting cell demonstrated effective capacity (460 mAh g<sup>-1</sup> at 200 mA g<sup>-1</sup> after 200 cycles, with coulombic efficiency up to 99.8%). Furthermore, an in-depth observation on the lithiation/delithiation behaviors of an individual Sn NP/CNF was performed using *in situ* TEM. The volume expansion and shrinkage based on real-time observation was mainly studied in the first life cycle. Along with the structural evolution, these results indicate a two-step lithiation mechanism and an irreversible delithiation process. The related fundamental mechanism for the lithiation/delithiation in the metallic Sn and corresponding promising strategy for designing a high-performance electrode were also discussed.

## 2. Experimental Section

### 2.1. Materials

Poly acrylonitrile (PAN, Mw = 150,000) was provided by Aldrich. N-N dimethylformamide (DMF) and SnCl<sub>4</sub>·5H<sub>2</sub>O were purchased from Beijing Chemicals Co. Ltd. All the as-received chemicals were used without further purification.

### 2.2. Fabrication of SnO<sub>2</sub> NPs

The precursor SnO<sub>2</sub> NPs were synthesized by the hydrothermal method [41]. In a typical preparation, SnCl<sub>4</sub>·5H<sub>2</sub>O (2.0 g) was firstly dissolved in 100 ml deionized water. The clear solution was then transferred into a 200 ml Teflon-lined stainless steel autoclave, followed by heating in an oven at 120 °C for 28 h. The white precipitations were obtained by centrifugation at 5000 g, and were subsequently vacuum freeze dried for 3 days to achieve the SnO<sub>2</sub> NPs.

### 2.3. Fabrication of Sn NP/CNF hybrids

The Sn NP/CNF hybrids were fabricated by the electrospinning process. In the typical preparation, SnO<sub>2</sub> NPs (0.35 g) were firstly dispersed in DMF (4.5 g) solution, followed by stirring and sonication for 3 h to obtain a homogeneous suspension.

Subsequently, PAN (0.5 g) was added to the suspension and was vigorously stirred at 40 °C for 8 h. The resulting SnO<sub>2</sub> NP/PAN suspension was then transferred into a 5 ml syringe equipped with a stainless steel nozzle (outer diameter = 0.8 mm). The electrospinning was carried out with a flow rate of 0.015 ml/min at ambient temperature. The distance between the nozzle tip and collector was stabilized at 15 cm with an applied voltage of 15 kV. The as-spun fiber networks were peeled off and stabilized at 280 °C (heating rate of 3 °C min<sup>-1</sup>) for 1 h in the air, followed by carbonization at 700 °C for 3 h (5 °C min<sup>-1</sup>) under the nitrogen atmosphere. Two reference samples were fabricated with the same conditions except for carbonization at 600 °C and 800 °C.

### 2.4. Material Characterizations

Field emission scanning electron microscopy (FE-SEM) were performed on a ZEISS supra 55 system. Transmission electron microscopy (TEM) was carried out on a TECHAI G220 Scanning-TEM system and *in situ* TEM was performed on a JEOL, JEM-2010 system. X-ray diffraction (XRD) patterns were acquired on a Rigaku D/max-RB system. X-ray photoelectron spectra (XPS) were recorded using a K-alpha (Thermo Fisher Scientific, ESCALAB 250xi). Raman spectra were investigated using a LabRAM Aramis Ar-Ion laser source for 514.5 nm excitation. Thermogravimetric Analysis (TGA) data was obtained using a TGA/DSC1 system (Mettler-Toledo).

### 2.5. Electrochemical Properties

Electrochemical experiments were performed using two-electrode CR2032 coin-type cells. The Sn NP/CNF hybrids were cut into appropriate size (around 1 mg in mass for each piece) and directly used as the working electrode without any binder and conductive agent. The electrolyte was 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate (1: 1: 1). Polypropylene micro-porous film (Celgard 2400) was utilized as separators and neat lithium metal sheet was used as the counter electrode. The CR2032 coin-type cells were assembled in an argon-filled glovebox. The discharge (lithiation) and charge (de-lithiation) measurements of the batteries were performed on the battery test system (LAND CT2001A, Wuhan Jinnuo Electronics, Ltd.) in the fixed voltage window between 0.01 and 3.0 V at room temperature. Cyclic voltammetry (CV) was carried out on an electrochemical workstation (CHI660C, Shanghai Chenhua).

### 2.6. In Situ TEM setup

In the typical preparation of the TEM sample, a piece of Sn NP/CNF hybrid network was firstly grinded into fined fractions, followed by dispersing in an ethanol solution under sonication. Subsequently, a small amount of the dried fractions were attached to a gold probe of a specific dual-probe biasing TEM holder using conductive resins. On the other hand, the tungsten probe (counter electrode) was softly scratched on a metal lithium sheet for attaching lithium and then kept in air for a few seconds, allowing its surface to be oxidized to Li<sub>2</sub>O. In this configuration, the attached Sn NP/CNF, metal lithium and Li<sub>2</sub>O worked as the working electrode, counter electrode and solid electrolyte, respectively. The as-prepared probes were transferred into the TEM testing chamber, followed by connecting counter electrode with an individual Sn NP/CNF to form a half cell. The schematic of the half-cell for *in situ* TEM is shown in Fig. 2d. In the lithiation process, a -3 V bias was applied to the working electrode, and the applied voltage was tuned to 0 V in the delithiation.

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