RESEARCH PAPER

# $SnO_2$ Nanowires on Carbon Nanotube Film as a High Performance Anode Material for Flexible Li-ion Batteries

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**ARTICLE INFO**

*Article History:*
*Received 19 January 2018*
*Accepted 28 April 2018*
*Published 01 July 2018*

*Keywords:*
*Anode Material*
*CNT Thin Film*
*Flexible Lithium-Ion Battery*
*$SnO_2$ Nanowires*

**ABSTRACT**

Today, Li-ion batteries (LIBs) are the most common rechargeable batteries used in electronic devices. $SnO_2$ with theoretical specific capacity of 782 mAh/g is among the best anode materials for LIBs. In this report, Three-dimensional $SnO_2$ nanowires (NWs) on carbon nanotube (CNT) thin film ($SnO_2$ / CNT) is fabricated using a combination of vacuum filtration and thermal evaporation techniques. The resulting 3D heterostructure $SnO_2$/CNT was characterized by X-ray diffraction, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). This fabricated $SnO_2$/CNT electrode has been tested as a flexible and binder-free anode for LIB, which exhibits high initial discharge/charge capacity of 4.8/2.25 mAh/cm$^2$ at a current density of 0.25 A/g, much larger than discharge/charge capacity of bare CNT film (2.2/0.3 mAh/cm$^2$). Relatively high areal capacity of 1.23 mAh/cm$^2$ has been achieved for the fabricated LIB with $SnO_2$/CNT electrode after 20 cycles, proposing this material as a high performance flexible LIB anode material.

**How to cite this article**
*Abnavi A, Sadati Faramarzi M, Sanaee Z, Ghasemi S. $SnO_2$ Nanowires on Carbon Nanotube Film as a High Performance Anode Material for Flexible Li-ion Batteries. J Nanostruct, 2018; 8(3): 288-293.* DOI: 10.22052/JNS.2018.03.008

## INTRODUCTION

Flexible rechargeable lithium batteries are required for various applications such as wearable devices and hybrid electric vehicles. In recent years, the demand for such lightweight, thin and flexible LIBs has been steadily increasing [1-5]. In commercial LIBs, the copper foil is usually used as current collector. Practically, the weight of the copper foil is almost half of the total weight of the electrode. Apart that 50% of the overall capacity per volume is lost due to the weight of Cu foil itself in electrode level, the price of full battery is high due to the price of copper foil in the cells. weak adhesion between active materials and metallic foils is main drawback facing these current collectors, make it impossible to use them in highly flexible LIBs. Compared to metallic foils, carbon thin films exhibit higher surface roughness, superior chemical stability and lower weight [6]. The key role for variety of applications of LIB is played by electrode weight and thickness in flexible electronic devices [7,8]. Therefore, free-standing carbon-based electrodes have received great attention for flexible energy storage devices in the literture [9-14]. Despite their relatively lower capacity as an anode compared to recently important metal alloying anodes, they can be successfully used as current collector in LIBs, especially for $SnO_2$ NWs as anode materials for LIBs, which considerably improved their lithium storage properties [15-19].

The theoretical capacity of $SnO_2$ is 782 mAh/g, which is considerably higher than conventional graphite anodes in commercial LIBs (372 mAh/g)

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[20,21]. However, huge volume expansion during lithiation/de-lithiation in Sn-based anodes is a major concern, as it causes pulverization of structures. It has been proved that low-dimensional nanostructures could effectively solve this problem due to better electronic contact between current collector/active materials [21,22]. In previous reports, various $SnO_2$ nanostructures including NWs [23, 24], nanotubes [25], nanosheets [26] and nanoparticles [27] have been studied as LIB anode materials with improved performance. Combination of nanostructures with buffering matrix and conductive materials is the other way to reduce the induced mechanical stress.

Some effort has been performed on $SnO_2$ NWs as active material for developing LIBs anode. Ko *et al*. used thermal evaporation technique to obtain $SnO_2$ NWs on stainless steel with capacity of 510 mAh/g after 50 cycles at current density of 780 mA/g [24]. $SnO_2$ NWs grown on carbon cloth showed a areal capacity of 0.2 mAh/g after 50 cycles, as reported by Ren and co-workers [28].

In this paper, a free-standing CNT thin film was prepared by a two-step fabrication process. Hierarchical $SnO_2$ NWs has been synthesized on prepared CNT film as an effective anode material for flexible LIBs by thermal evaporation method. CNT film as a flexible current collector provides good electrical contact for $SnO_2$ NWs and also serves as a mechanical support to prevent pulverization of the $SnO_2$/CNT electrode.

## MATERIALS AND METHODS

### *Preparation of CNT thin film*

Multi-walled CNTs with about 5-30 µm length and the outer diameter of 10-30nm were purchased from Merck. In the first step, CNTs were functionalized using the mixture of concentrated $HNO_3$ (65% w/v) and $H_2SO_4$ (98% w/v) acids with ratio of 3:1v/v at 80ºC with constant stirring for 2h. Functionalized CNTs were filtered and washed with DI water for several times, and dried in vacuum oven at 80ºC for 12h. In the second step, functionalized CNTs were dispersed in DI water and sonicated for 2h. The as-prepared suspension was vacuum filtered through a MCE membrane filter (0.22 µm pore size, 47 mm diameter) to make a uniform thin film. The final sample was dried in an oven at 60ºC for 3h. The as-produced CNT film was obtained by peeling it off from the filtration membrane. The fabrication process of the as-prepared CNT film is schematically illustrated in Fig. 1.

### *Synthesis of $SnO_2$ NWs on CNT film*

$SnO_2$ NWs were grown on CNT film substrate by thermal evaporation using Au as the catalyst layer and Sn powder as a source. Briefly, alumina boat filled with 50 mg of Sn powder (99.8%, 325 mesh, Sigma-Aldrich) was placed in a horizontal tube furnace (50mm diameter, 600mm length). CNT film coated with Au catalyst layer of about 20nm was placed on the top of the alumina boat, 5mm above the Sn powder. The furnace temperature was raised to 800 ºC at a rate of 20 ºC/min under argon gas flow. growth of $SnO_2$ nanowires was accomplished by setting the temperature on 800 ºC for 10 min. Schematic illustration of $SnO_2$ NWs synthesis on CNT film is demonstrated in Fig. 2.

### *Sample Characterization*

The morphology and structure of as-fabricated anode electrodes were characterized by scanning electron microscopy (SEM, Hitachi S4160) and transmission electron microscopy (TEM, Philips CM30). The X-ray diffraction (XRD) patterns of bare CNTs and SnO2/CNT film were obtained with

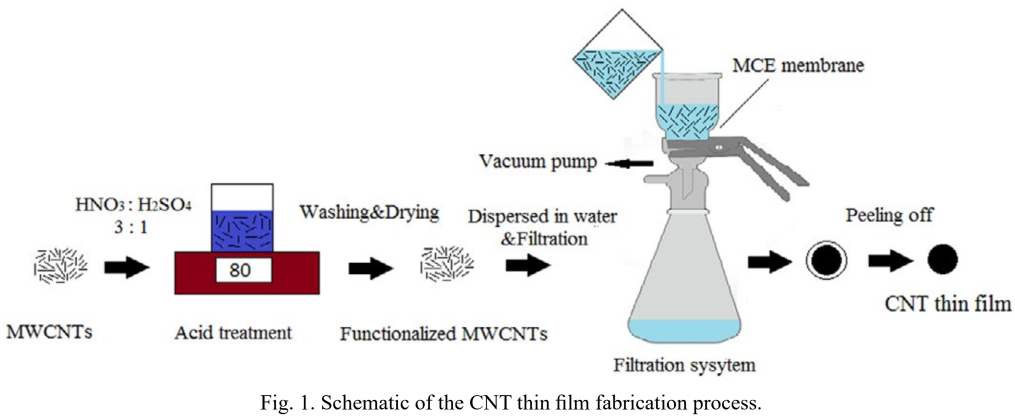


Fig. 1. Schematic of the CNT thin film fabrication process.

D4 X-ray diffractometer using Cu Kα radiation (λ = 0.15406 nm) as the X-ray source.

*Electrochemical Measurement*

The as-prepared bare CNT film and $SnO_2$ /CNT electrodes were vacuum dried for 24 h at 80°C, and then used as the LIB electrodes. The half-cells were assembled in an Ar-filled glove box using Celgard (no. 2032) as the separator, 1M $LiPF_6$ in EC/DMC (1:1) as the electrolyte, and Li metal foil as the counter and reference electrodes. The cells were charged and discharged at ambient temperature between 0.05V to 2 V at a current density of 0.25 A/g using a battery testing system (Kimiastat 126).

## RESULTS AND DISCUSSION

Fig. 3a,b show the SEM image of the fabricated CNT film as well as its porous surface. As-grown

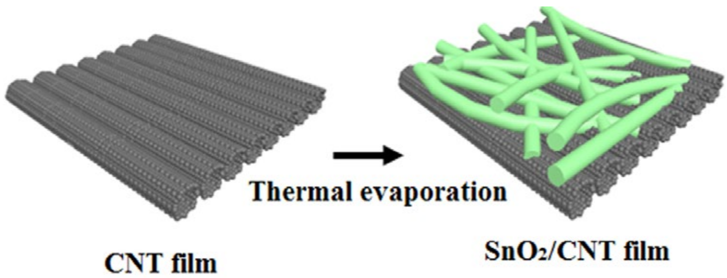


Fig. 2. Schematic diagram of $SnO_2$ NWs fabrication process on CNT film.

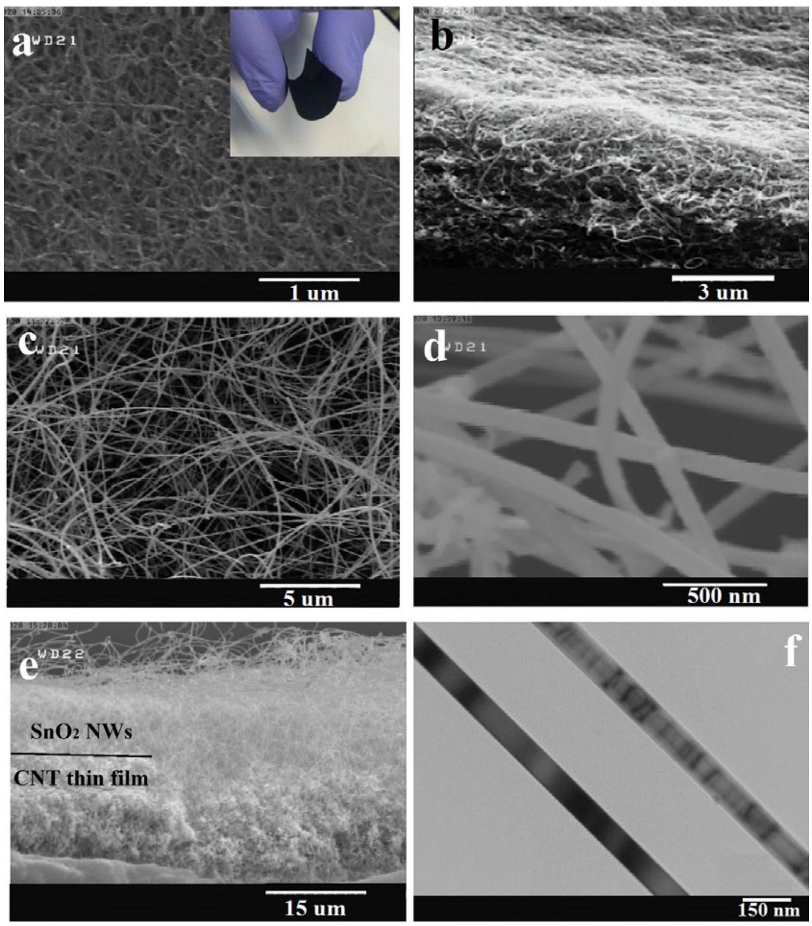


Fig. 3. SEM images of (a,b) CNT film, (c,d) $SnO_2$ on CNT film. (e) Cross-sectional SEM of $SnO_2$/CNT film. (f) TEM image of $SnO_2$ nanowire.

$SnO_2$ NWs on CNT film (Fig. 3c,d) have diameters ranging from 40nm to 120nm with typical lengths of several hundred micrometers. $SnO_2$ NWs have been densely grown on the CNT film with a mass loading of about 3.3 mg/cm$^2$. In addition, the flexibility of fabricated CNT film can be seen in the inset of Fig. 3a. The cross-sectional SEM image of $SnO_2$/CNT film in Fig. 3e demonstrates that CNT and $SnO_2$ NWs form a 3D network consists of entangled nanotubes and dense nanowires with total thickness of only 30 µm. In Fig. 3f the straight shape with smooth surface of $SnO_2$ nanowires is revealed from the TEM image.

The XRD patterns of bare CNT film and $SnO_2$ NWs grown on film are shown in Fig. 4. The peaks observed at 2θ = 26° and 43° are attributed to the (002), (101) planes of CNT film (JCPDS 26-1079). In comparison, the peaks of $SnO_2$ NWs grown on CNT film are consistent with the rutile phase of pure crystalline $SnO_2$ (JCPDS 41-1445).

The electrochemical reactions of $SnO_2$ and CNT in $SnO_2$/CNT during lithiation/de-lithiation are proposed by the following equations [24, 28]:

$$SnO_2 + 4Li \rightarrow 2Li_2O + Sn \quad (1)$$

$$C(carbon\,nanotube) + xLi \leftrightarrow Li_xC \quad (2)$$

Equation (1) illustrates irreversible reduction of $SnO_2$ to Sn and $Li_2O$ and formation of solid electrolyte interface (SEI) layer, responsible for the large initial capacity loss in the Sn-based electrodes. The other equation represent the reversible lithiation/de-lithiation of CNT during charge and discharge of electrode.

Fig. 5 shows the galvanostatic charge-discharge curves and the cycling performance of fabricated electrodes at current density of 0.25 A/g in the potential range of 0.05-2 V. Fig. 5a,b display galvanostatic charge-discharge curves of the CNT film and $SnO_2$/CNT electrodes for the first five cycles, respectively. The first discharge and charge capacities of 4.8 and 2.25 mAh/cm$^2$ are obtained for $SnO_2$/CNT electrode, respectively, which is much larger than bare CNT film (2.2, 0.3 mAh/cm$^2$). A large capacity loss observed at first cycle in both profiles, is related to the formation of SEI layer on the surface of nanostructures and reactions that consumes Li ions. Cycling stability of $SnO_2$/CNT anode at current density of 0.25 A/g in the potential range of 0.05-2 V is shown in Fig. 5c.

Due to the high mass loading of the active materials (3.3 mg/cm$^2$), the initial areal charge capacity of the $SnO_2$/CNT is 2.25 mAh/cm$^2$, and it maintains 1.23 mAh/cm$^2$ after 20 cycles (Fig. 5c), while the capacity of CNT film decreased below 0.2 mAh/cm$^2$ in 5th cycle. To the best of our knowledge, this areal capacity obtained from $SnO_2$/CNT electrode is much higher than previous reports on $SnO_2$ NWs, as summarized in Table 1. Coulombic efficiency of $SnO_2$/CNT (Fig. 5c) also increases to 95% in the 20th cycle, showing good cyclic stability and reversibility.

The thickness and areal density of the metallic copper foil in commercial LIBs is around 20 um and 16 mg/cm$^2$, respectively, while prepared CNT film exhibits a thickness of less than 15 um with areal density of about 1.35 mg/cm$^2$. Furthermore, the total thickness of most commercial LIBs anodes are more than 100 um, while our $SnO_2$/CNT electrode has a total thickness of less than 30 um [6, 28]. CNT film substrate ensures high electric conductivity through $SnO_2$ NW cores, and enables the flexibility of the electrode. $SnO_2$ NWs as suitable electron transport network provide high contact area between the electrode and electrolyte.

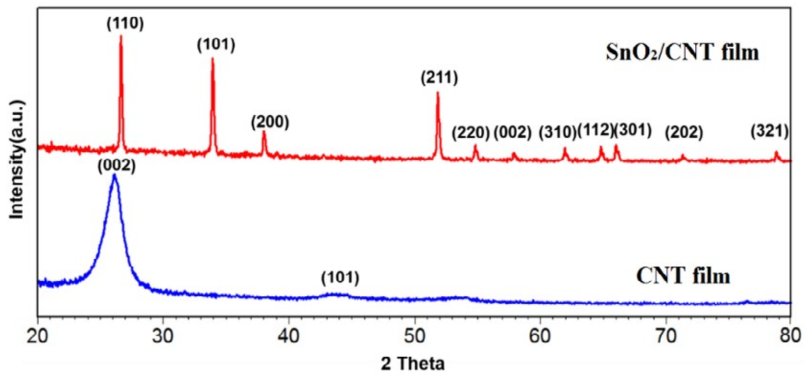

Fig. 4. XRD patterns of CNT film and $SnO_2$/CNT film.

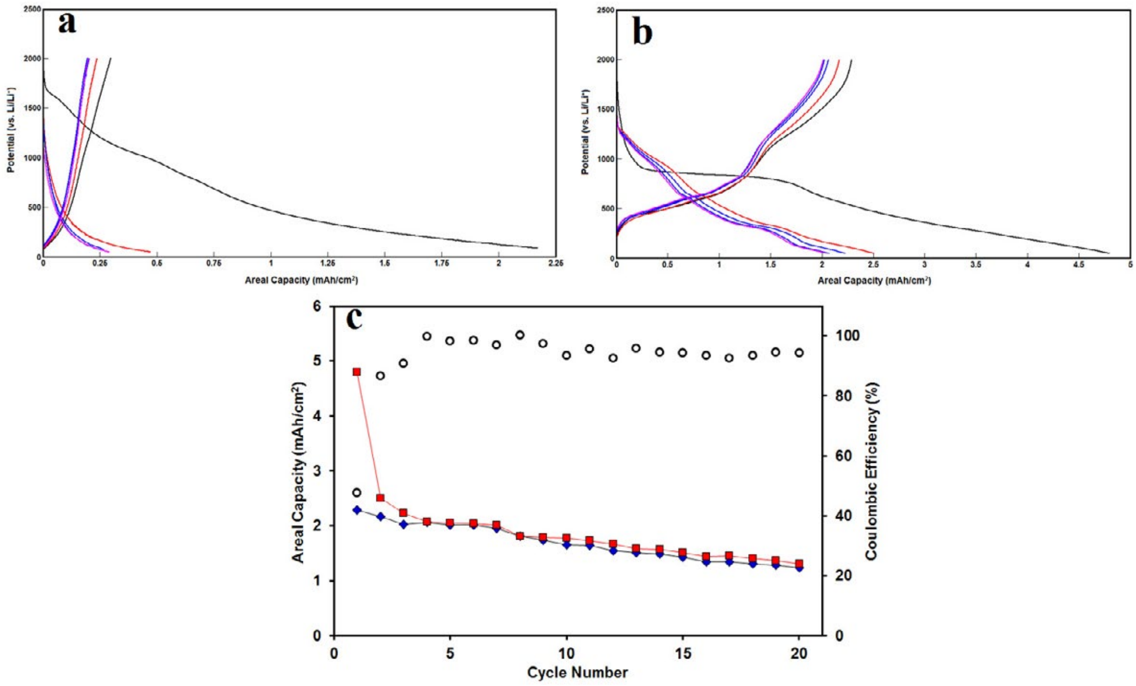


Fig. 5. Galvanostatic charge-discharge profiles of (a) CNT film, (b) $SnO_2$/CNT film for first five cycles. (c) Cycling performance of $SnO_2$/CNT electrode with coulombic efficiency for 20 cycles.

Table 1. Comparison and summary of the mass load, substrate and, capacity performance of different $SnO_2$ NW, compared to what is achieved in this work

| Structure | Mass load ($mg/cm^2$) | Substrate | Current density | Cycles | Capacity after cycles (mAh/g) | Areal capacity after cycles ($mAh/cm^2$) | References |
|---|---|---|---|---|---|---|---|
| $SnO_2$ NW array | --- | Stainless steel | 780 mA/g | 50 | 510 | --- | [24] |
| $SnO_2$ NW array | 0.5 | Carbon cloth | 0.38 $mA/cm^2$ | 50 | --- | 0.2 | [28] |
| $SnO_2$ NW array | --- | Cu foil | 100 mA/g | 50 | 300 | --- | [30] |
| $SnO_2$ NW array | 3.3 | CNT thin film | 250 mA/g | 20 | --- | 1.23 | This work |

## CONCLUSION

The $SnO_2$/CNT film electrode was synthesized as an effective binder-free anode for flexible LIBs. Free-standing CNT film was prepared by a vacuum filtration method. Then, $SnO_2$ NWs were grown on CNT film by thermal evaporation approach. The electrochemical tests show a high areal capacity of 1.23 $mAh/cm^2$ after 20 cycles. The high areal capacity, good cycling stability, excellent flexibility and light weight obtained from this anode structure show its potential as an excellent anode for high performance flexible LIBs.

## ACKNOWLEDGEMENT

Authors would like to thank Prof. Shams Mohajerzadeh, Mr. Ala Mohajerzadeh, Mr. Ali Abdollahi and Mrs. Mehrnoosh Sadeghi for their technical assistance. The authors also would like to thank Dr. Irina Gocheva for her helpful discussion and useful comments.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publicaton of this manuscript.

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