



# Porous SnO<sub>2</sub>-CuO nanotubes for highly reversible lithium storage



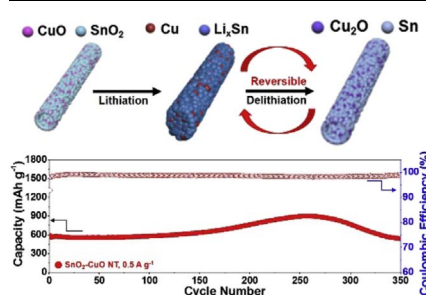
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## HIGHLIGHTS

- Porous SnO<sub>2</sub>-CuO nanotubes (SnO<sub>2</sub>-CuO p-NTs) by electrospinning & calcination.
- SnO<sub>2</sub>-CuO p-NTs exhibited superior ionic transport and penetration of electrolytes.
- The structure of SnO<sub>2</sub>-CuO p-NTs was maintained without pulverization.
- Introduction CuO into SnO<sub>2</sub> results in more reversible reaction with Li.
- SnO<sub>2</sub>-CuO p-NTs exhibited highly stable cycle retention up to 350 cycles.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

Facile synthesis of rationally designed structures is critical to realize a high performance electrode for lithium-ion batteries (LIBs). Among different candidates, tin(IV) oxide (SnO<sub>2</sub>) is one of the most actively researched electrode materials due to its high theoretical capacity (1493 mAh g<sup>-1</sup>), abundance, inexpensive costs, and environmental friendliness. However, severe capacity decay from the volume expansion and low conductivity of SnO<sub>2</sub> have hampered its use as a feasible electrode for LIBs. Rationally designed SnO<sub>2</sub>-based nanostructures with conductive materials can be an ideal solution to resolve such limitations. In this work, we have successfully fabricated porous SnO<sub>2</sub>-CuO composite nanotubes (SnO<sub>2</sub>-CuO p-NTs) by electrospinning and subsequent calcination step. The porous nanotubular structure is expected to mitigate the volume expansion of SnO<sub>2</sub>, while the as-formed Cu from CuO upon lithiation allows faster electron transport by improving the low conductivity of SnO<sub>2</sub>. With a synergistic effect of both Sn and Cu-based oxides, SnO<sub>2</sub>-CuO p-NTs deliver stable cycling performance (91.3% of capacity retention, ~538 mAh g<sup>-1</sup>) even after 350 cycles at a current density of 500 mA g<sup>-1</sup>, along with enhanced rate capabilities compared with SnO<sub>2</sub>.

## 1. Introduction

As one of the most promising energy storage devices up to the current date, lithium-ion batteries (LIBs) have been widely used in various applications, ranging from electric vehicles (EV) to laptops [1,2]. As energy demands continue to increase, LIBs with higher energy density are necessary. In response to the trend, a number of alternative anode materials with higher theoretical capacities are currently researched [3–6]. Among them, tin(IV) oxide (SnO<sub>2</sub>) has been one of the actively researched materials due to its higher theoretical capacity

(1493 mAh g<sup>-1</sup>) compared with graphite (372 mAh g<sup>-1</sup>), abundance, low cost, safety, and stability with electrolytes [7–9]. Nevertheless, two main issues hinder SnO<sub>2</sub> from its use as the viable anode materials for LIBs: unstable structural integrity that induces large volume expansion and hence rapid capacity decay and low intrinsic conductivity of SnO<sub>2</sub> that results in poor rate capabilities [10–12].

To overcome the above issues, a number of strategies have been implemented. To start with, both porous and hollow nanostructures have been employed to overcome the poor cycle retention characteristics of various metal oxides [13,14], where inner voids in the core

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could alleviate the overall volume changes. Although porous and hollow nanostructures may improve the overall structural integrity with enhanced cycle retention characteristics, the optimized morphology control of metal oxides alone cannot solve the low electronic conductivity of various metal oxides including SnO<sub>2</sub>. In order to improve the electric conductivity of SnO<sub>2</sub>, much attempt was made to combine SnO<sub>2</sub> with highly conductive elements, such as using carbon nanospheres [15], silver [16], and Cu foam [17]. Such combination of SnO<sub>2</sub> with conductive materials brings enhanced rate capabilities, but another issue arises: difficulty in one-pot synthesis of SnO<sub>2</sub> with highly conductive elements. As the synthesis of SnO<sub>2</sub> mostly requires calcination in air, most of highly conductive elements will undergo oxidation if they are combined together with Sn precursor for subsequent heat treatment. So far, most of conductive materials were coated on top of as-made SnO<sub>2</sub> or SnO<sub>2</sub> was synthesized on top of conductive materials, which bring additional steps in overall synthetic routes. Furthermore, simultaneous consideration in both careful morphology control of SnO<sub>2</sub> and facile synthesis of SnO<sub>2</sub> and conductive materials altogether appears very daunting task, as there should be a delicate balance between using facile synthesis while combining seemingly different materials in scalable manner.

Therefore, we have sought to take an unusual approach to simultaneously control the overall morphology of SnO<sub>2</sub>-based nanostructures while improving the low conductivity of SnO<sub>2</sub> by using facile synthetic procedure to fabricate porous SnO<sub>2</sub>-metal oxide composite nanotubes, where the combined metal oxide is transformed into highly conductive metal upon Li insertion to allow faster electron transport. Here in this work, we have successfully fabricated porous SnO<sub>2</sub>-CuO composite nanotubes (hereafter, SnO<sub>2</sub>-CuO p-NTs) by simple electrospinning and subsequent calcination step, which can deliver not only stable cycle retention but also enhanced rate capabilities. Instead of simple metal oxide composites [18] or coating of SnO<sub>2</sub> on buffer metal oxide [19], the adopted approach can be modulated to fabricate rationally designed nanoarchitectures. Electrospinning is a feasible tool for fabricating one-dimensional (1D) nanostructures [20,21], where the SnO<sub>2</sub>-CuO p-NTs were synthesized by employing electrospinning process and subsequent calcination. Numerous mesopores can be formed on the wall of NTs due to the thermal decomposition of matrix polymer. Porous nanotubes (p-NTs) synthesized by electrospinning have several merits in i) short Li ion diffusion length, ii) mesopores that allow less volume expansion and iii) better electrolyte penetration arising from the macropores between the p-NTs. Upon the introduction of CuO, SnO<sub>2</sub>-CuO p-NTs exhibited less volume expansion where CuO also acted as a buffer agent. Moreover, the reduction of CuO in the first discharge process resulted in highly conductive Cu nanograins embedded between the SnO<sub>2</sub> nanograins, which can significantly improve the overall rate capabilities. In particular, because SnO<sub>2</sub> and CuO react with Li at different voltage, more reversible and uniform reaction with Li can simultaneously take place by combining SnO<sub>2</sub> with CuO in 1D architecture. The SnO<sub>2</sub>-CuO p-NTs delivered excellent cycle retention (91.3% of capacity retention after 350 cycles) and superior rate capabilities (~260 mAh g<sup>-1</sup> at a current density of 5.0 A g<sup>-1</sup>), compared with not only CuO but also SnO<sub>2</sub>.

## 2. Experimental section

### 2.1. Synthesis of SnO<sub>2</sub>-CuO p-NTs and SnO<sub>2</sub> NTs

Pristine SnO<sub>2</sub> NTs and SnO<sub>2</sub>-CuO p-NTs with relative ratios of 10:1, 5:1, and 5:2 were fabricated by electrospinning and subsequent calcination in air. An electrospinning solution consisting of metal precursor and polymer were dissolved in the solvent. For the SnO<sub>2</sub>-CuO (5:1) p-NTs, 0.25 g of tin (II) chloride dihydrate (SnCl<sub>2</sub>·2H<sub>2</sub>O, Sigma Aldrich, USA), 0.051 g of copper chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O, Sigma Aldrich, USA), and 1.25 g of ethanol (C<sub>2</sub>H<sub>6</sub>O, Merck, Germany) were mixed first and stirred for 4 h. Then, the 0.35 g of polyvinylpyrrolidone

(PVP, M<sub>w</sub> = 1,300,000, Sigma Aldrich, USA) and 1.25 g of N-dimethylformamide (DMF, Sigma Aldrich, USA) were added into the pre-existing electrospinning solution and stirred for 4 h. Similarly, for SnO<sub>2</sub>-CuO (10:1) p-NTs and SnO<sub>2</sub>-CuO (5:2) p-NTs, identical amount of all ingredients was used except Cu precursor (CuCl<sub>2</sub>·2H<sub>2</sub>O) (0.026 g of CuCl<sub>2</sub>·2H<sub>2</sub>O for SnO<sub>2</sub>-CuO (10:1) p-NTs and 0.102 g of CuCl<sub>2</sub>·2H<sub>2</sub>O for SnO<sub>2</sub>-CuO (5:2) p-NTs). For the synthesis of SnO<sub>2</sub> NTs, 0.25 g of SnCl<sub>2</sub>·2H<sub>2</sub>O was first mixed with 1.25 g of ethanol and stirred for 4 h. Then, the 0.35 g of PVP and 1.25 g of DMF were added into the pre-existing electrospinning solution and stirred for another 4 h. After the subsequent stirring, the electrospinning solution became transparent and it was transferred into the syringe and the 25 gauge needle was used to proceed with electrospinning. The following electrospinning condition was used: an applied voltage of 16 kV, a distance of 15 cm between the tip of the needle and the syringe, and a flow rate of 20 μl min<sup>-1</sup>. All the as-spun NFs for both SnO<sub>2</sub> NTs and SnO<sub>2</sub>-CuO p-NTs underwent calcination at 600 °C for 1 h with a heating rate of 10 °C min<sup>-1</sup>.

### 2.2. Characterizations

The surface morphology of as-spun Sn precursor/PVP composite NFs, Sn precursor/Cu precursor/PVP composite NFs, SnO<sub>2</sub> NTs, and SnO<sub>2</sub>-CuO p-NTs with different weight ratio of SnO<sub>2</sub> and CuO was characterized by field emission scanning electron microscopy (FE-SEM, SU5000, Hitachi) operating at 10 kV. The crystal structures and surface morphology of SnO<sub>2</sub> NTs and SnO<sub>2</sub>-CuO p-NTs were characterized by high resolution TEM (HR-TEM, JEM-2100F, JEOL) operating at 200 kV and field emission transmission electron microscopy (FE-TEM, Tecnai TF30 ST, FEI) operating at 300 kV. To calculate the surface area of SnO<sub>2</sub>-CuO p-NTs, Brunauer-Emmett-Teller (BET) analysis was conducted (Tristar II 3020, Micromeritics). The crystal structures of all specimens were analyzed using high resolution powder x-ray diffractometer (XRD) (SmartLab, Rigaku) with Cu Kα radiation (λ = 1.54 Å) between 10° and 90° at a scan rate of 0.166° s<sup>-1</sup>. To confirm the surface chemical states of Sn and Cu for SnO<sub>2</sub>-CuO p-NTs, surface analysis was conducted using the X-ray photoelectron spectroscopy (XPS, K-α, Thermo VG Scientific). The thermophysical properties of SnO<sub>2</sub>-CuO p-NTs were further confirmed by thermogravimetry analysis (TGA, TG 209 F3, NETZSCH). The amount of carbon was confirmed by elemental analyzer (EA, FLASH 2000 series, Thermo Scientific).

### 2.3. Cell assembly and electrochemical testing

In order to examine the electrochemical properties of respective electrode materials, 2032 coin-type half cells were assembled. The anodes were composed of 80 wt% of active materials (SnO<sub>2</sub> NTs, SnO<sub>2</sub>-CuO (10:1) p-NTs, SnO<sub>2</sub>-CuO (5:1) p-NTs, and SnO<sub>2</sub>-CuO (5:2) p-NTs), 10 wt% of binder consisting of poly(acrylic acid)/sodium carboxymethyl cellulose (wt%/wt% = 50/50), and 10 wt% of super P carbon black. The electrode materials were first mixed together and then slurry-casted on Cu foil and dried under vacuum at 150 °C for 2 h. The mass loading of active materials was about 1.2 mg cm<sup>-2</sup> for all the electrodes. For the general cell assembly process, the 2032 coin-type half cells were composed of Li metal as a counter electrode, a Celgard 2325 as a separator, and an electrolyte consisting of 1.3 M lithium hexafluorophosphate (LiPF<sub>6</sub>) in ethylene carbonate/diethylene carbonate (EC/DEC, v/v = 3/7) with 10 wt% of fluoroethylene carbonate (FEC) (PANAX ETEC.). Coin-type half cells were all assembled under Ar-filled glove box and cycled at a 50 mA g<sup>-1</sup> for the formation cycle between 0.005 and 3 V and later at a current density of 100–5000 mA g<sup>-1</sup> between 0.01 and 3 V using battery testing device (Maccor Series 4000, KOREA THERMO-TECH). Cyclic voltammetry (CV) was conducted at 0.1 mV s<sup>-1</sup> within a range of 0.01–3.0 V using battery testing device (Maccor Series 4000, KOREA THERMO-TECH).

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