# Tube-in-tube Tin Dioxide Superstructures with Enhanced Lithium Storage Performances

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## Experimental

*Materials:* All reagents used in the experiments are of analytical grade purity and used as received without further purification. Iron (Ⅲ) chloride hexahydrate (99%), tin (II) chloride dehydrate (98%), absolute ethanol and ammonia solution (25%) were bought from Sinopharm Chemical Reagent Co. Ltd. Potassium thiocyanate (98.5%) was gotten from Nanjing Chemical Reagent Co. Ltd. Deionized water was utilized in all experiments.

*Synthesis of α-$Fe_2O_3$ hollow prisms:* Typically, 0.12 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 10 mL of deionized water and then 0.05 g of potassium thiocyanate was added into the solution. When the solution was mixed uniformly, 10 mL absolute ethanol was added. The whole solution was

transferred into a stainless-steel autoclave lined with poly (tetrafluoroethylene) and maintained at 160 °C for 12 h and then naturally cooled to room temperature. The product at the bottom of the autoclave was collected, washed with absolute ethanol and deionized water for 3 times, respectively, then dried in the air.

*Synthesis of $SnO_2$ TTS and $SnO_2$@C TTS:* For the synthesis of $SnO_2$ TTS, 0.03 g of α-$Fe_2O_3$ was dispersed in 30 ml of deionized water through ultrasonic processing. Then, 0.06 g of tin (Ⅱ) chloride dehydrate (98%) and 0.5 ml of hydrochloric acid (36%) were put into the above suspension. After 3 hours of ultrasonic treatment, the rusty red suspension was transferred into a Teflon-lined stainless steel autoclave (40 ml) and maintained at 180 ℃ for 20 h. The precipitate was collected and washed with deionized water and ethanol. The washed sample was dried at 80 ℃ overnight. To obtain carbon-coated $SnO_2$ TTS ($SnO_2$@C TTS), the procedure was the same as the synthesis of $SnO_2$ TTS except that in the ultrasonic step of synthesis route, glucose was added into the suspension along with $SnCl_2$ and hydrochloric acid. After hydrothermal reaction, the black product was collected and calcined in $N_2$ at 450°C for 2 h .

*Characterizations:* X-ray diffraction (XRD) patterns were obtained from a Shimadzu XRD-6000 powder X-ray diffractometer with Cu $K_\alpha$ radiation (λ=1.5418Å). Scanning electron microscopy (SEM) images were collected on a Hitachi S-4800 field-emission microscope operated at 10 KV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were taken on a JEOL JEM-2100 microscope operated at 200 KV. $N_2$ adsorption-desorption isotherms were obtained at 77 K on a Micrometrics ASAP 2020 surface area and porosity analyzer after the sample had been degassed in vacuum at 120 °C.

*Electrochemical tests:* The anode was prepared by mixing sample powder (70 wt%) with acetylene blank (20 wt%) and ploy (vinylidene difluoride) (10 wt%) dissolved in N-methyl-2-pyrrolidinone. The slurry mixture was painted on a copper foil and dried at 60 ℃ overnight in vacuum furnace. Then, the copper foil with the active material was cut into round disks with a diameter of 2 mm with the mass of the active material in each cell of about 0.70-0.80 mg. The cells consisted of the as-prepared working electrode, lithium metal used as the counter and reference electrode, and an electrolyte of 1.0 M $LiPF_6$ dissolved in a mixture of EC (ethylene carbonate), DMC (dimethyl carbonate) and DEC (diethyl carbonate) with the volume ration of 1:1:1. The cell assembly was carried out in a glove box filled with highly pure argon (oxygen and water concentrations below 5 ppm). The electrochemical measurements were performed on LAND CT-2001A instrument (Wuhan, China). The specific capacity and current density were calculated based on the mass of the active material in the working electrode. All the electrochemical measurements were carried out using a three-electrode system at ambient temperature.

**Table S1** The comparison between $SnO_2$ TTS and the reported $SnO_2$ as anode material for LIBs.

| Anode material | Synthesis method | Discharge capacity ($mAh \cdot g^{-1}$) after several cycles | Current density ($mA \cdot g^{-1}$) | Reference |
|---|---|---|---|---|
| 3D $SnO_2$ TTS | Hard Template | 630, 370 cycles | 100 | Present work |
| | | 410, 420 cycles | 800 | |
| Multi-shelled $SnO_2$ hollow spheres | Hydrothermal | 214, 100 cycles | 100 | [1] |
| $SnO_2$ nanosheets | Microwave-Hydrothermal | 257.8, 50 cycles | 100 | [2] |
| $SnO_2$ nanowires | Thermal evaporation | 240, 50 cycles | 100 | [3] |
| $SnO_2$ nanotubes | Solution method | 280, 100 cycles | 500 | [4] |
| $SnO_2$ nanoparticles | Solution method | 100, 20 cycles | 50 | [33] |

**References**


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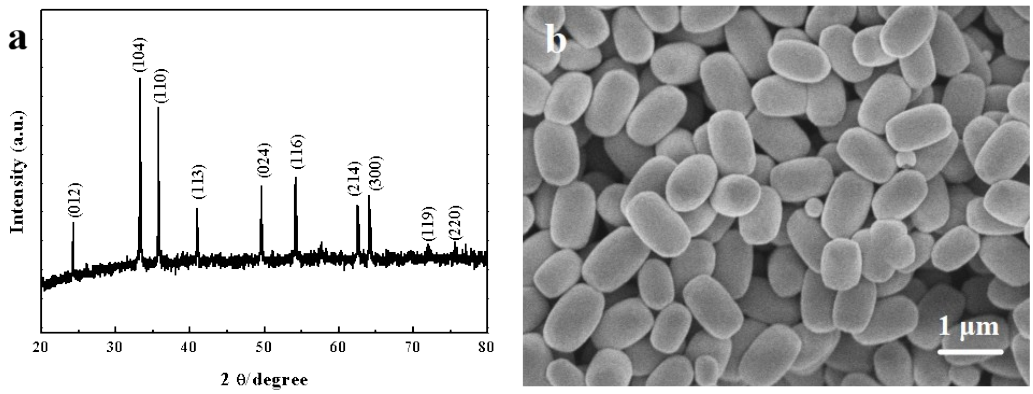


**Fig. S1** (a) XRD pattern of the hollow prisms; (b) SEM image of solid α-$Fe_2O_3$ prisms formed at the beginning of the reaction.

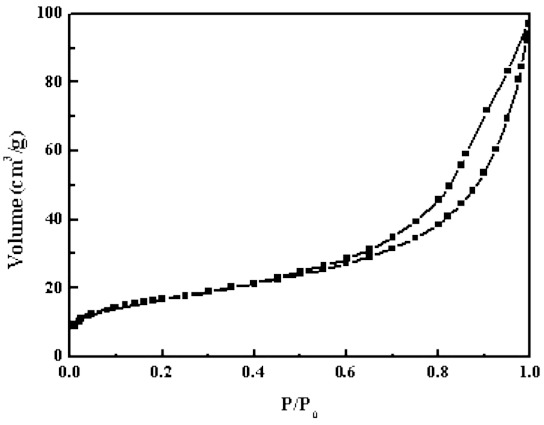


**Fig. S2** Nitrogen adsorption/desorption isotherms of $SnO_2$ TTSs.

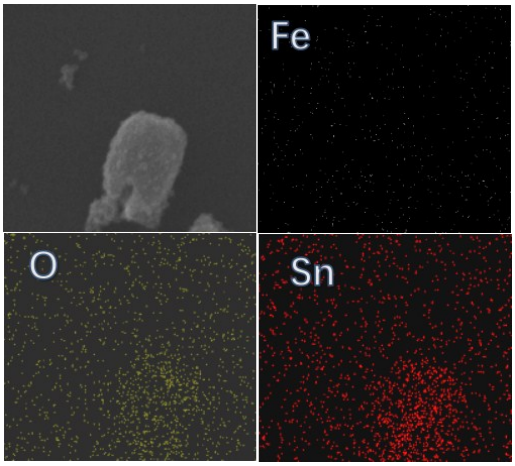


**Fig. S3** Elemental mapping images of $SnO_2$ TTS.

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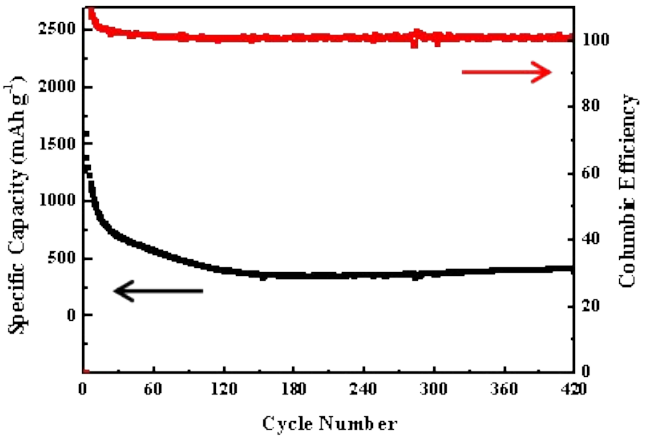



**Fig. S4** Cycle performance of $SnO_2$ TTSs at 800 $mA \cdot g^{-1}$.

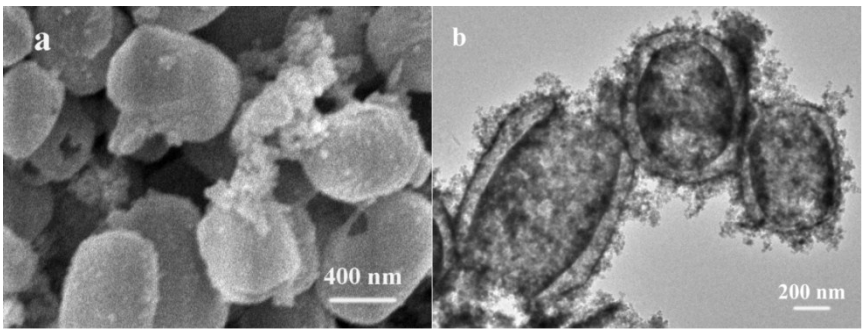
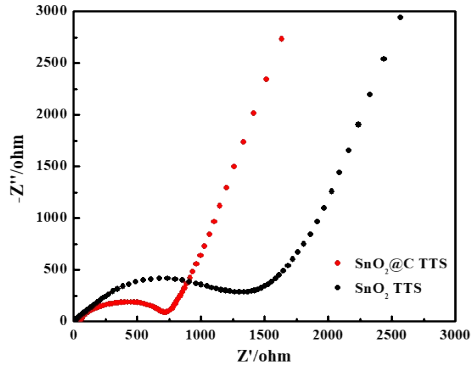



**Fig. S5** (a) SEM and (b) TEM images of $SnO_2$ TTS after circulation as LIB anode materials.


3000
2500
2000
1500
1000
500
0
-Z''/ohm
0
500
1000
1500
2000
2500
3000
Z'/ohm
SnO2@C TTS
SnO2 TTS