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Electronic Supplementary Information

In situ reduction and coating of SnS_2 nanobelts for free-standing SnS@polypyrrole-nanobelt/carbon-nanotube paper electrodes with superior Li-ion storage

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Experimental Sections

Fabrication of uniform SnS_2 nanobelts

SnS_2 nanobelts were synthesized through a template-free dodecanethiol-modified solvothermal route. In a typical synthesis process, 12 mL CS_2 and 12 mL dodecanethiol were firstly added to the mixture of 100 distilled water and 30 mL $NH_3{\cdot}H_2O$; subsequently, 20 mmol tin (IV) chloride was dissolved in this mixed solution to form a primrose solution, which was then transferred to Teflon-lined stainless steel autoclave at 180 °C for 48 h. After the solution was cooled down to room temperature, the obtained yellow precursors were collected by centrifuging the mixture, which were then washed with ethanol and distilled water several times and dried in vacuum at 60 °C.

During the solvothermal crystallization of SnS_2 nanobelts, the formation mechanism of the SnS_2 phase is based on the reaction among tin (IV) chloride, CS_2, $NH_3{\cdot}H_2O$ and dodecanethiol, which can be described as below:[1]

$$4NH_3 + CS_2 \rightarrow NH_4SCN + (NH_4)_2S \tag{1}$$

$$SnCl_4 + 2(NH_4)_2S \rightarrow SnS_2 + 4NH_4Cl \tag{2}$$

$$SnS_2 + kC_{12}H_{25}SH + kSn^{4+} \leftrightarrow (SnS_2)_m(kC_{12}H_{25}SH)_k^{3+} + kH^+ \tag{3}$$

$$(SnS_2)_m(kC_{12}H_{25}SH)_k^{3+} \leftrightarrow (SnS_2)_m(Sn)_k^{4+} + kSC_{12}H_{25}^- \tag{4}$$

$$(SnS_2)_m(Sn)_k^{4+} + 2LS^{2-} \leftrightarrow (SnS_2)_n \tag{5}$$

In the above, via equation (1) and (2), SnS_2 began to form. However, in the absence of dodecanethiol, SnS_2 would be dissolved by S^{2-}. Dodecanethiol was absorbed tightly on SnS_2 surface, which prevented S^{2-} from attacking. According to previous research work,[2] dodecanethiol could coordinated with Sn^{4+} via equation (3), forming $(SnS_2)_m(kC_{12}H_{25}SH)_k^{3+}$ complexed clusters in the solution. Equation (4) indicated the dissolution of $SC_{12}H_{25}^{-}$ from the complexed SnS_2 clusters. Finally, stable SnS_2 was formed through equation (5).

Fabrication of free-standing SnS@PPy-NB /CNT paper electrode

Firstly, SnS@PPy nanobelts were synthesized via pyrrole-induce reductive transformation reaction in hydrothermal environment. In a typical chemical transformation procedure, SnS_2 samples (0.1 g) were added to deionized water to form a dispersion solution under constant strong stirring. Then, pyrrole (0.4 mL) was added to the dispersion solution and kept stirring for 30 min. The dispersion was transferred into a Teflon-lined autoclave. The sealed vessel was then maintained at 160 °C for 40 h, and cooled naturally. The samples were collected and washed six times with ethanol and water, respectively, and dried under vacuum at 50 °C. Finally, 90 mg SnS@PPy nanobelts and 15.9 mg multi-walled CNTs (Figure S2,4 in Electronic Supplementary Information) were dispersed in 120 mL H_2O then sonicated for 1 h and filter through a mixed cellulose ester membrane (1.2 μm pore size, milipore). Then obtained filter film was then vacuum dried for 24 h to get free-standing film.

Materials characterization

The collected products were characterized by an X-ray diffractometry (XRD) on a

Rigaku-DMax 2400 diffractometer equipped with the graphite monochromatized Cu Kα radiation flux at a scanning rate of 0.02°s^{-1}. Scanning electron microscopy (SEM) analysis was carried using a Zeiss Gemini DSM 982 scanning electron microscope. The structure of these SnS_2 nanobelts and SnS@PPy porous nanobelts was investigated by means of transmission electron microscopy (TEM, JEOL 4000FX). Nitrogen adsorption and desorption isotherms were measured at 77 K with a Quadrachrome Adsorption Instrument.

Electrochemical testing

The electrochemical performances of the as-prepared products were measured by using two-electrode Swagelok-type cells. The free-standing SnS@PPy-NB/CNT paper was cut and directly investigated as an anode for Li-ion batteries. For assembling Li-ion batteries, a Li foil was used as the counter electrode and a solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume) was used as electrolyte. The charge/discharge curves and cycling capacity were evaluated by an Arbin MSTAT battery test system in the cut-off voltages of 0.01 and 3.0 V. Cyclic voltammetry (CV) was performed using a VoltaLab 80 electrochemical workstation.

References

1. D. Ma, W. Zhang, Q. Tang, R. Zhang, W. Yu, Y. Qian, *J. Nanosci. Nanotech.* **2005**, *5*, 806.

2. H. Zhang, Y. J. Ji, X. Y. Ma, J. Xu, D. Yang, *Nanotechnology* **2003**, *14*, 974.

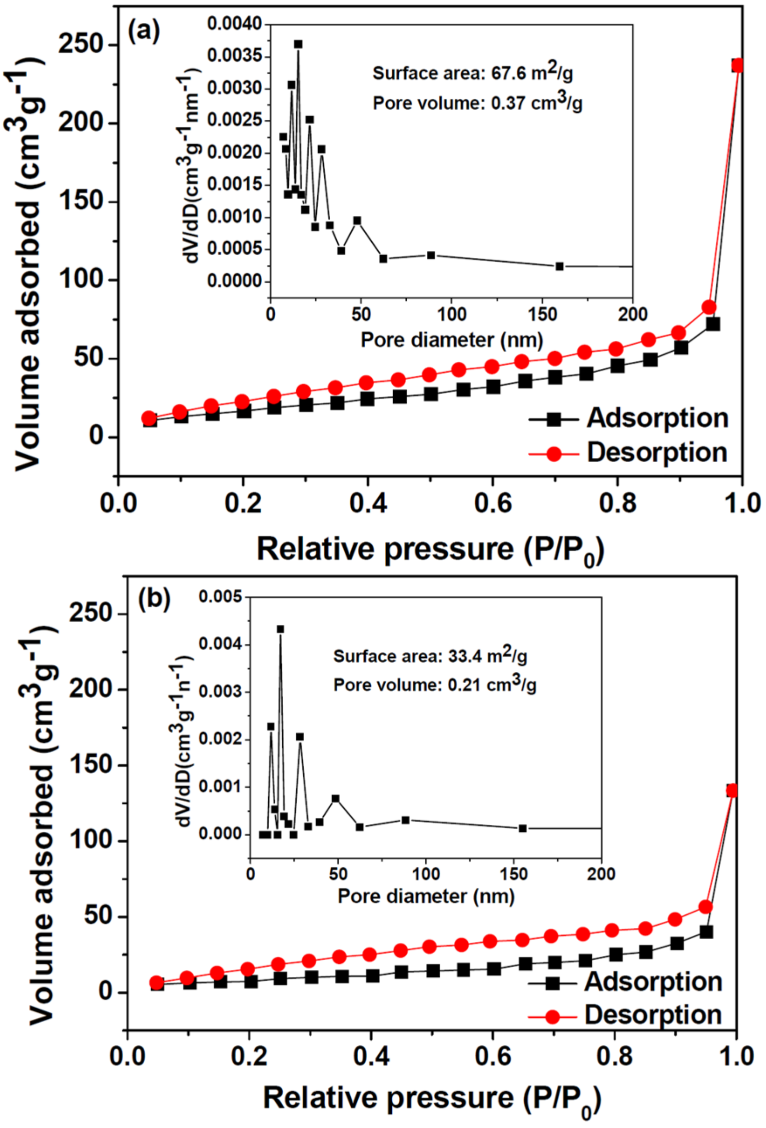

Figure S1. N_2 adsorption/desorption isotherms and the corresponding pore size distribution (the inset) of SnS@PPy porous nanobelts (a) and SnS_2 nanobelts (b). As shown in the inset of Figure S1a and S1b, the SnS_2 nanobelt precursor has a surface area of 33.4 m^2/g and pore volume of 0.21 cm^3/g. While after the reduction, the surface area and pore volume of SnS@PPy-NBs sample has increased into 67.6 m^2/g and 0.37 cm^3/g, respectively. The generated pores during the reduction of SnS_2 are mesopores, and mainly distributed in the range of 17 nm to 26 nm.

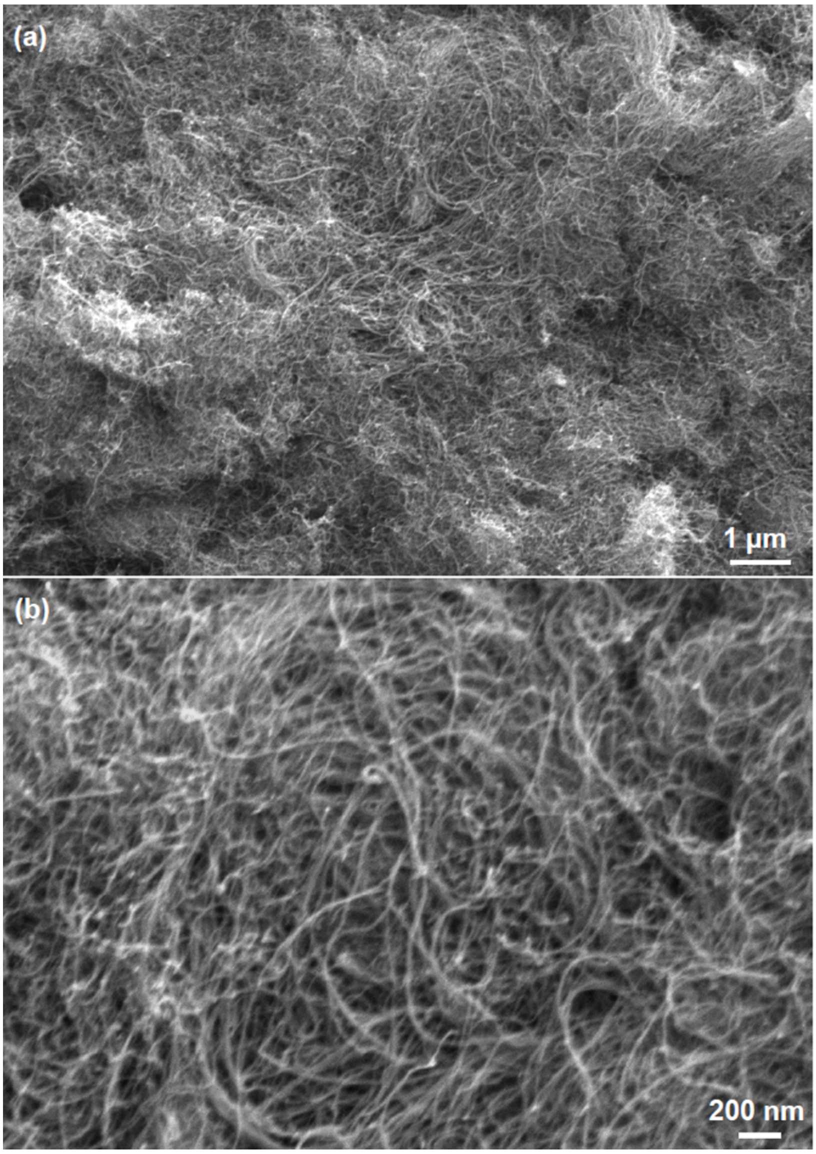

Figure S2. Low and high-magnification SEM images of commercial multi-walled CNTs with diameter of 6-9 nm produced by Sigma-Aldrich Co. LLC.

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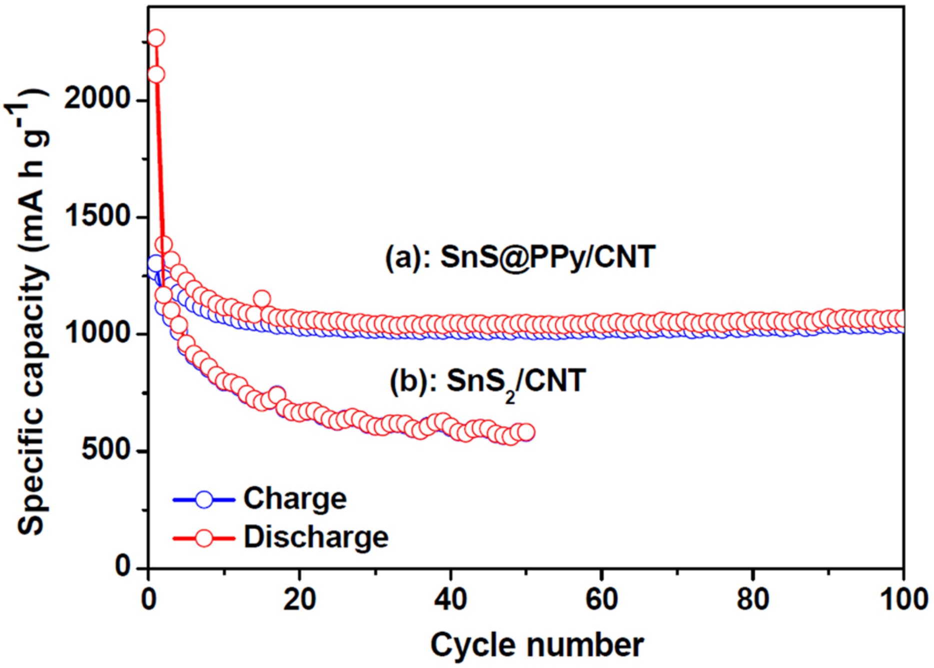

Figure S3. Li-ion storage performances of the PPy-coated SnS@PPy/CNT (a) and without PPy-coated SnS_2/CNT (b) electrodes at a current density of 0.1C. The enhanced electrochemical performance of PPy-coated samples should be ascribed to that the polymerized conductive PPy thin layers not only improve the electrode's conductivity, but also protect the inner SnS nanobelts from mechanical damage during charging/discharging.

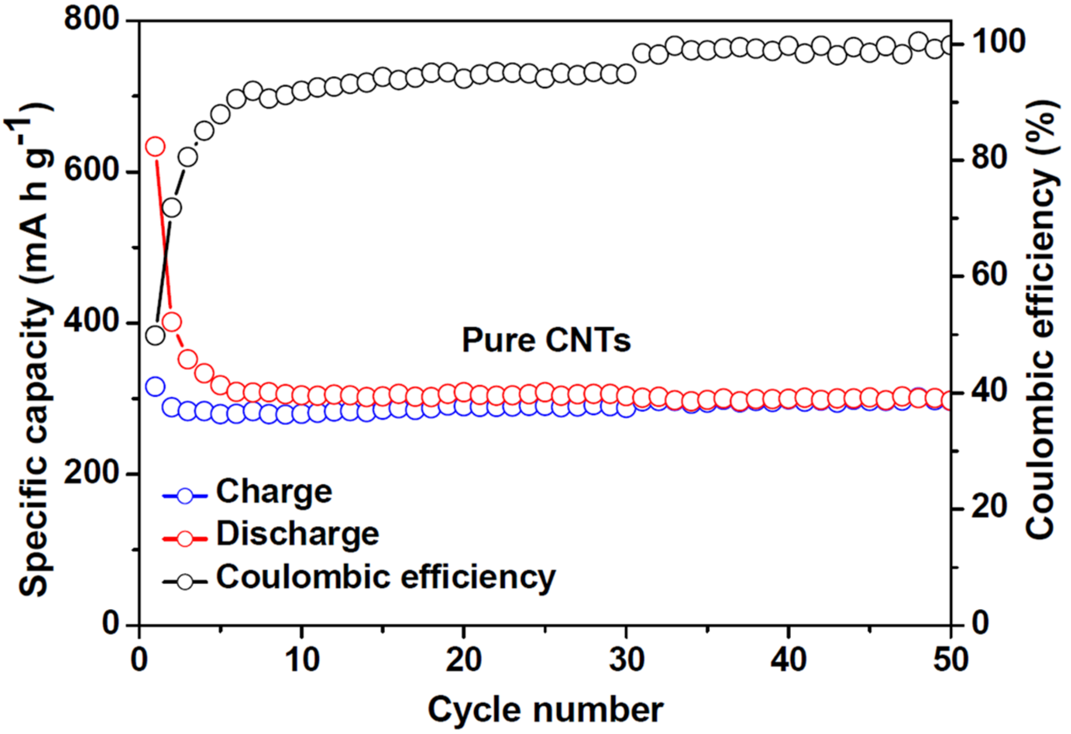

Figure S4. Cycling capacity for the 50 galvanostatic cycles of pure CNTs and its according Coulombic efficiencies. The pure CNT anode was cycled between 3.0 and 0.01 V versus Li/Li^{+} at a current density of 100 mA g^{-1}. Electrochemical measurements have revealed that pure CNTs exhibited a highly stable cycling performance, retained about 290 mA h g^{-1} after the 50th cycle as shown in Figure S4. However, in our fabricated SnS@PPy-NB/CNT paper anode, only 15% (wt) multi-walled CNTs were used, so the contribution of CNT in specific capacity is relatively very small (43.5 mA h g^{-1} for CNTs *vs.* 1129.5 mA h g^{-1} for SnS@PPy-NBs).

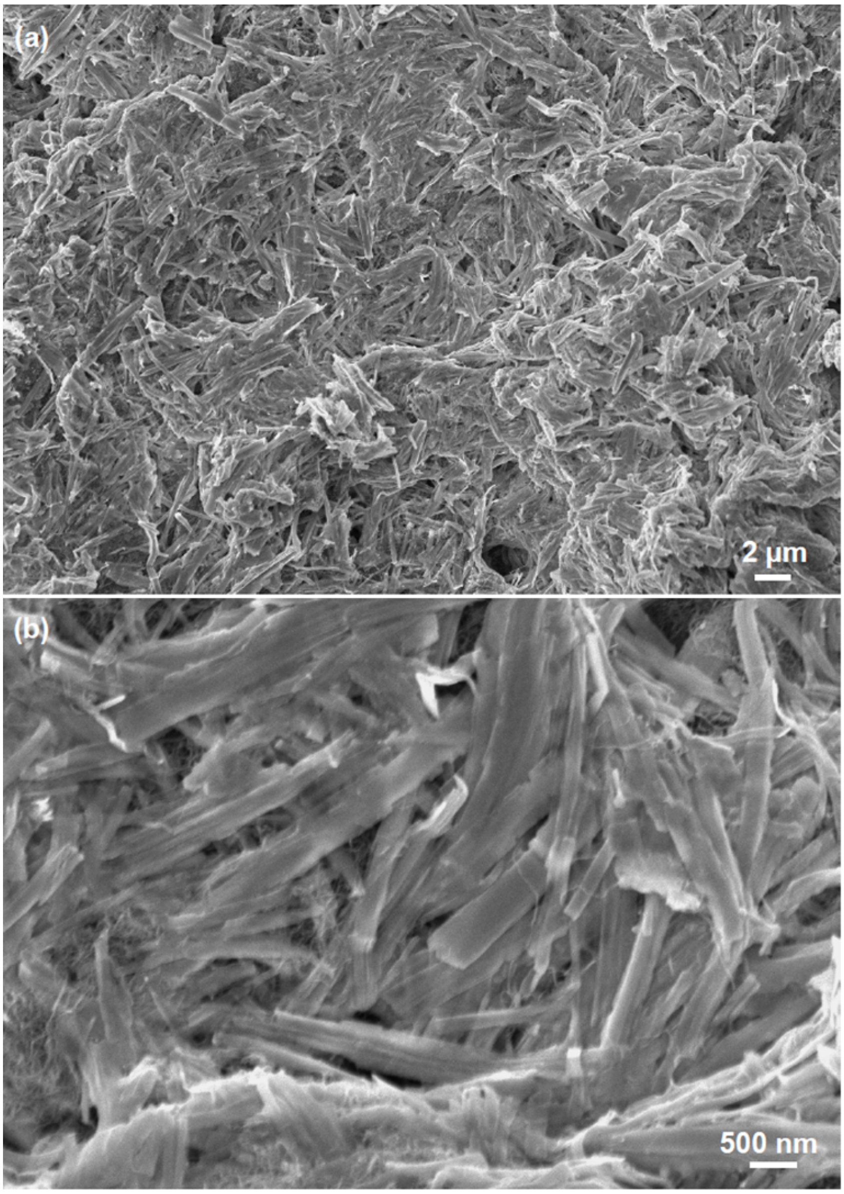

Figure S5. SEM images of SnS@PPy-NB/CNT paper electrode after 100 charging/discharging cycles at 0.1C rate, showing that conductive PPy coated SnS nanobelt unit has superior structure stability.

Table S1. Stable specific capacity of lithium storage for the SnS@PPy-NB and for the whole electrode (SnS@PPy-NB/CNT)

Current density (C)	SnS@PPy-NB (mA h g^{-1})	Whole electrode (mA h g^{-1})
0.1	1173	997
0.2	1032	877
0.5	870	739
1	891	757
2	609	518
5	349	297