# Formation of SnS nanoflowers for lithium ion batteries

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## Experimental Details

### Materials:

Tin (II) Iodide ($SnI_2$, >99%), Tin (IV) Bromide ($SnBr_4$, 99%), Tin (IV) Iodide ($SnI_4$, 95%), and sulfur powder (99.5%) were purchased from Alfa Aesar. Oleylamine (>40%) was purchased from TCI America. Hexamethyldisilazane (HMDS, >99%) was purchased from Aldrich. All chemicals were used as received. Synthesis was carried out under Ar using standard Schlenk techniques. All work-up procedures were performed in air.

### Characterization:

Powder X-ray diffraction (XRD) data were collected using a Bruker D8 Advance X-ray diffractometer equipped with CuK$\alpha$ radiation. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained using a JEOL 1200 EX II operating at 80 kV. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) data were performed on a FEI Nova NanoSEM 630 field-emission SEM.

Battery measurements were performed by first making a slurry in N-Methyl-2-pyrrolidone (NMP) consisting of an 80:10:10 weight ratio of annealed SnS nanoflowers, Super P carbon black, and PVDF, respectively, was spread on a Cu foil using a doctor-blade coating method, and then dried at 100 °C under vacuum overnight. The as-prepared electrode, counter electrode (lithium metal) and separate membrane (Celgard 2400) were incorporated into a CR2016 coin-type cell in a glove box filled with Ar gas. The electrolyte was a 1 M $LiPF_6$ solution in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) with a volume ratio of 1:1:1. The coin-type cells were galvanostatically cycled on a battery testing system (BTS-5V1mA, Neware) under 50 mA $g^{-1}$ at room temperature. The cutoff potentials for charge and discharge were set at 1.1 V and 0.01 V vs. $Li^+/Li$, respectively.

### Synthesis:

A 1 M oleylamine-sulfide (OAM-S) stock solution was first prepared by dissolving 320 mg (10 mmol) of sulfur powder in 10 mL of oleylamine and sonicating until a dark red solution was obtained. In a typical synthesis of SnS nanoflowers, 40 mg (~0.1 mmol) of

$SnI_2$ and 20 mL (~60 mmol) of oleylamine were added to a 20 mL scintillation vial and sonicated until a clear colorless solution was obtained. This solution was then added to a 3-neck round-bottom flask fitted with a condenser, thermometer adapter, thermometer, and rubber septum. Next, 0.25 mL of the 1 M OAM-S stock solution (~0.25 mmol) and 1 mL (4.71 mmol) of hexamethyldisilazane (HMDS) were also added and stirred for 15 min. Finally, the solution was slowly heated to 200 °C at ~10 °C/min, resulting in the formation of a black-colored solution. This solution was allowed to age for 30 min and then was rapidly cooled by removing the reaction flask from the heating mantle. The samples prepared using $SnBr_4$ and $SnI_4$ were prepared using an identical procedure to the one above except that 90 mg and 60 mg of the starting Sn-precursor (~0.1 mmol) were used, respectively. The SnS nanoflowers were precipitated by adding 30 mL of a 3:1:1 acetone/hexane/toluene mixture and then centrifuged at 12,000 rpm for 10 min. The obtained powder was washed three times with a 1:1 toluene/ethanol mixture with centrifugation in between each wash. The product could then be suspended in toluene, hexane, ethanol, or methanol for further characterization, with dispersibility lasting on the order of a few minutes.

## Additional Figures

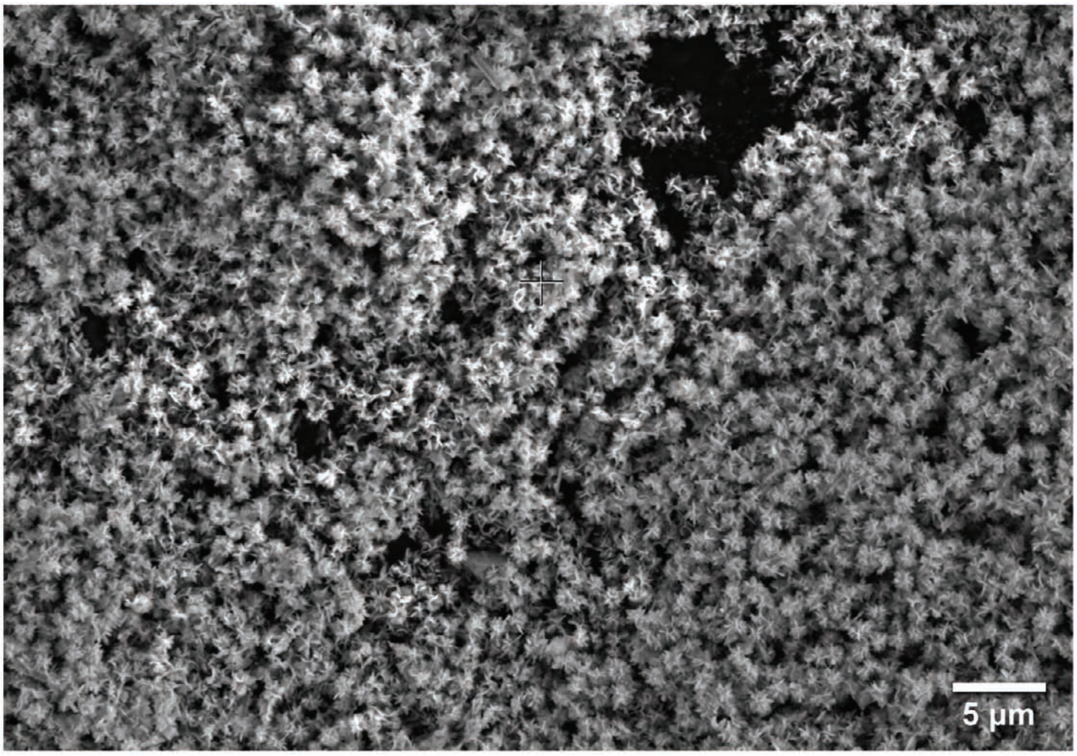

***Figure S1.*** Large-area FESEM image showing that the nanoflowers comprise the bulk of the sample.

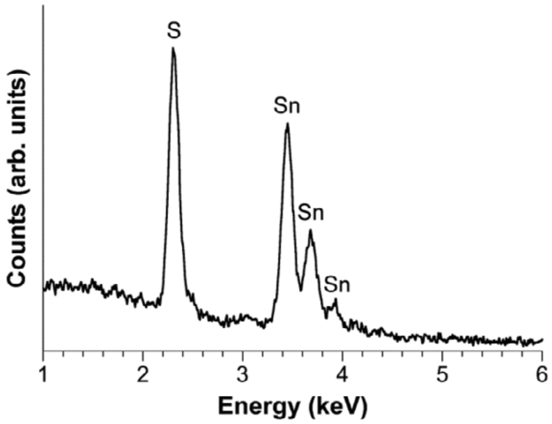

***Figure S2.*** EDX spectrum confirming the presence of Sn and S in a ~1:1 ratio.

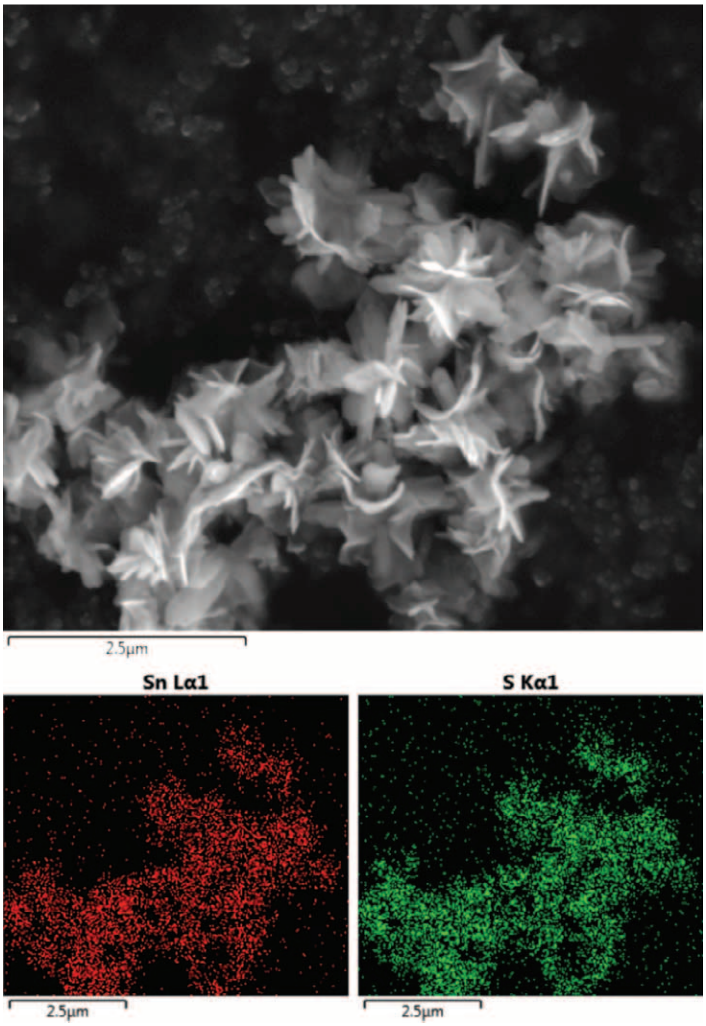

***Figure S3.*** EDX mapping data, showing the co-localization of Sn and S.

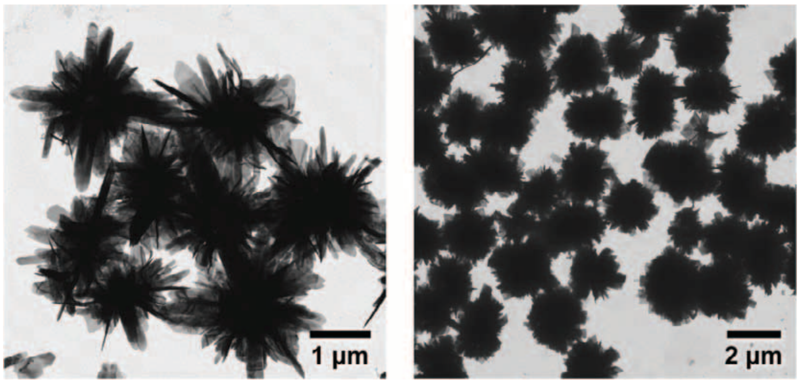

***Figure S4.*** SnS nanoflowers formed using $SnI_4$ (left) and $SnBr_4$ (right) as the Sn reagent.

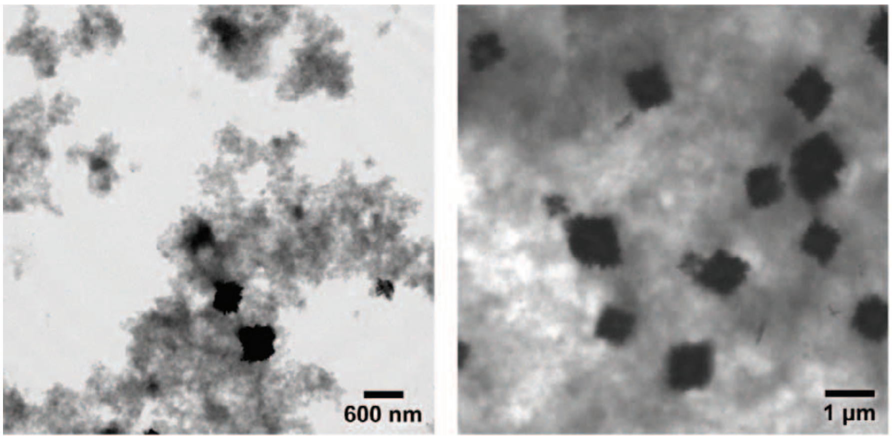

***Figure S5.*** Nanoparticle agglomerates formed in the earliest stages of SnS nanoflower growth (comparable to Figures 3a and 3h).

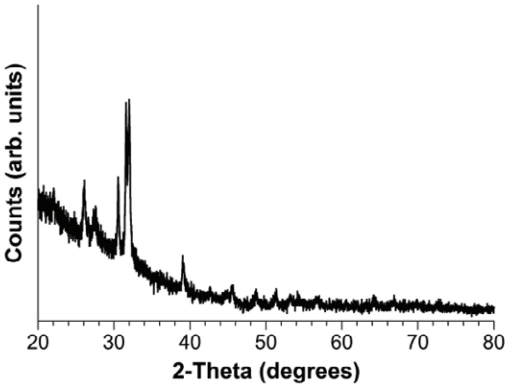

***Figure S6.*** Powder XRD pattern for SnS nanoflowers annealed at 600 °C for 1 h under $N_2$ (g).

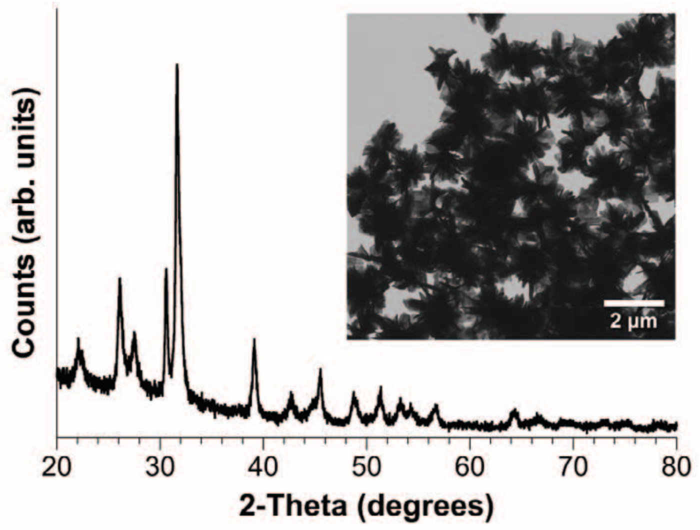

***Figure S7.*** Powder XRD pattern showing SnS nanoflowers after ~6 months of aging under ambient conditions in powder form. A TEM image showing the particle morphology after ~6 months of ambient storage is included in the inset.