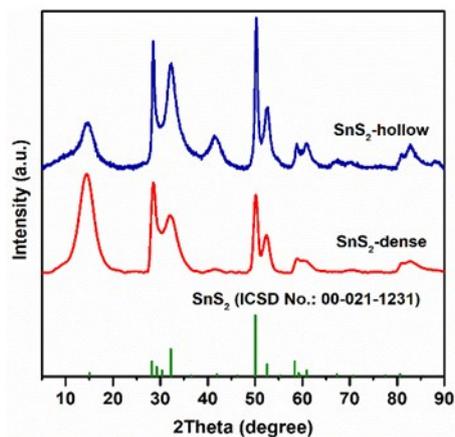


Electronic Supplementary Information (ESI)

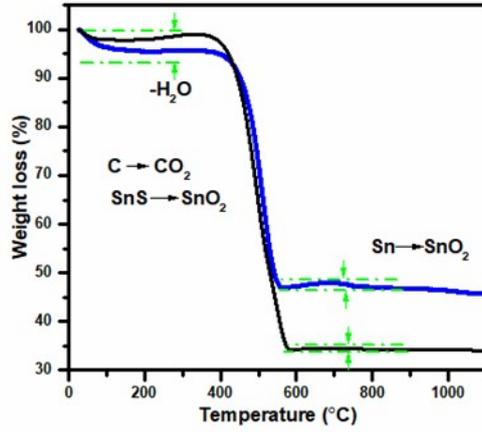
# SnS/N-doped carbon composites with enhanced Li<sup>+</sup> storage and lifetime by controlled hierarchical submicron- and nanostructuring

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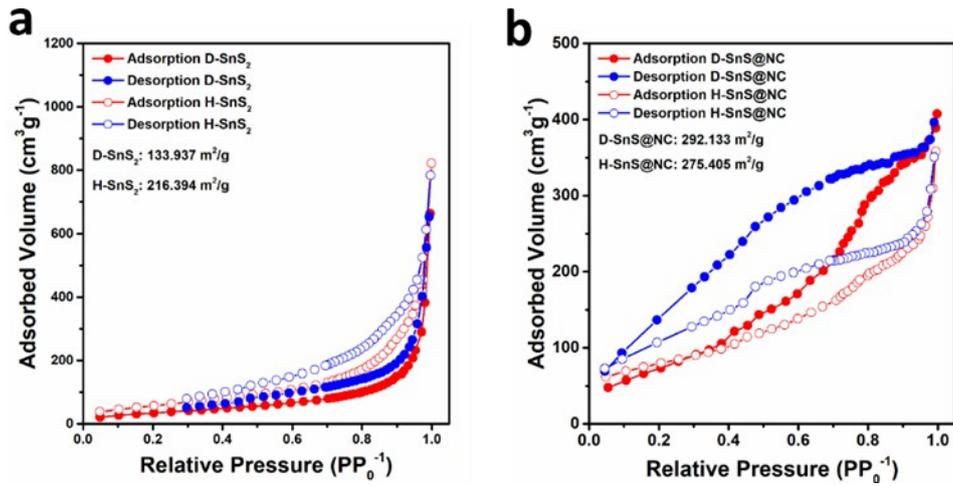
Laboratory for Multifunctional Materials, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, 8093 Zurich, Switzerland.



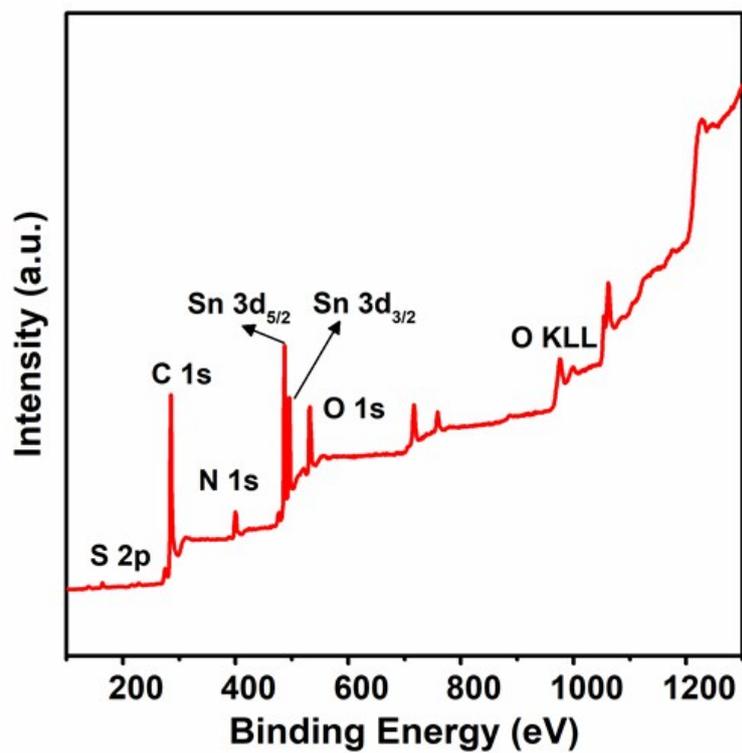
**Figure S1.** XRD patterns of as-prepared H- and D-SnS<sub>2</sub>.



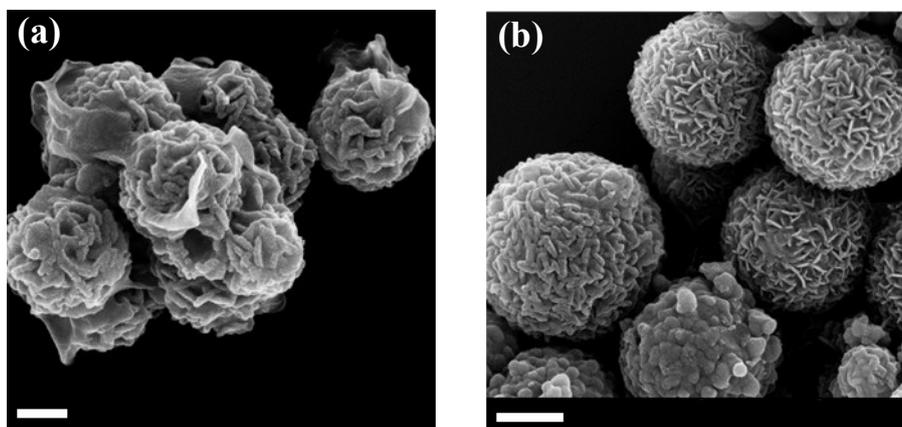
**Figure S2.** TGA curves of the as-prepared H- (blue) and D-SnS@NC (black).



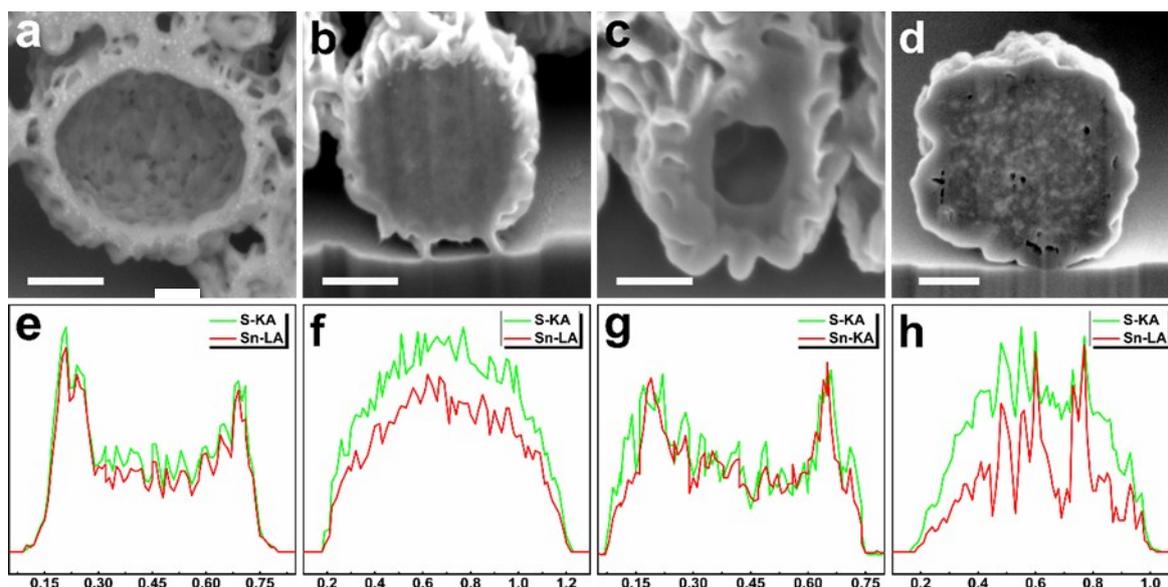
**Figure S3.** Nitrogen adsorption and desorption isotherms of a) H- and D-SnS<sub>2</sub> and (b) H- and D-SnS@NC.



**Figure S4.** XPS survey spectrum of H-SnS@NC.



**Figure S5.** Low-magnification SEM images of the as-prepared (a) H-SnS@NC and (b) D-SnS@NC, scale bar=200 nm.

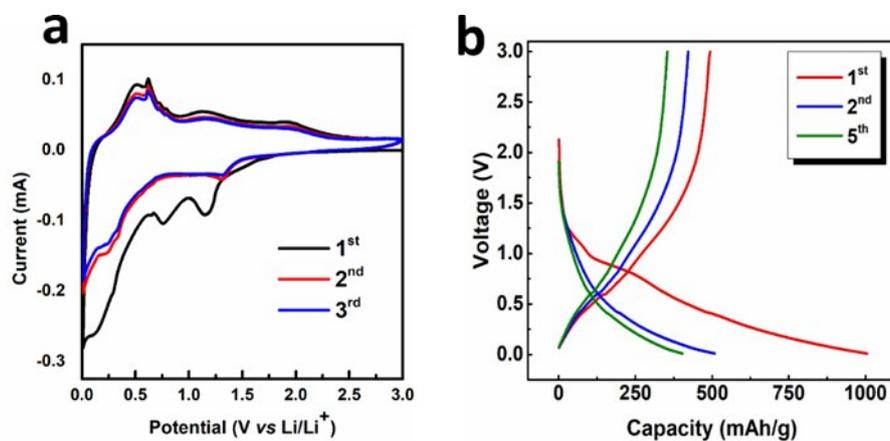


**Figure S6.** SEM images of focused-ion beam (FIB) cut cross-sections and the EDX element profile line scan of (a, e) H-SnS<sub>2</sub>, (b, f) D-SnS<sub>2</sub>, (c, g) H-SnS@NC and (d, h) D-SnS@NC, scale bar=200 nm.

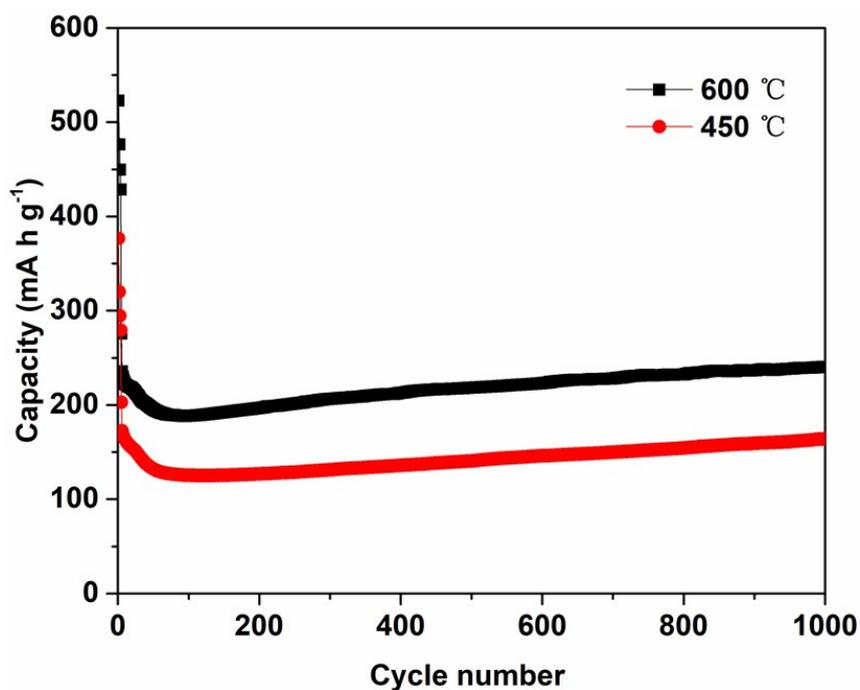
To obtain the SEM images of the particle cross-sections, the samples were prepared by first adhering particles onto silicon chips, which were mounted via conductive silver paint onto SEM-stubs and sputter coated with 2 nm Pt/Pd, while rotating. The samples were analysed in a FEI Helios 600i FIB/SEM at a stage tilt of 52°. Cross sections were milled perpendicular to the chip-plane with gallium ions at 30kV and 24pA. SEM images shown in Fig. S5a-c were taken in secondary electron mode and backscatter electron mode at 2kV. Shown particle cross sections were tilt-corrected, overview images show the tilted situation without perspective correction. From one situation a stereo pair was acquired (52° and 46°) for presenting a 3D-impression. During the polishing process some redeposition of the milled material occurred, resulting in some rounding of the surface structures.

Energy-dispersive X-ray spectroscopy (EDX) was performed on X-FEG Talos in line scan mode for S and Sn as shown in Fig. S5e-h. The down-/up-bent curves nicely match with the

cross-section morphology, confirming the hollow and dense internal structure in H-SnS<sub>2</sub>, D-SnS<sub>2</sub>, H-SnS and D-SnS, respectively.

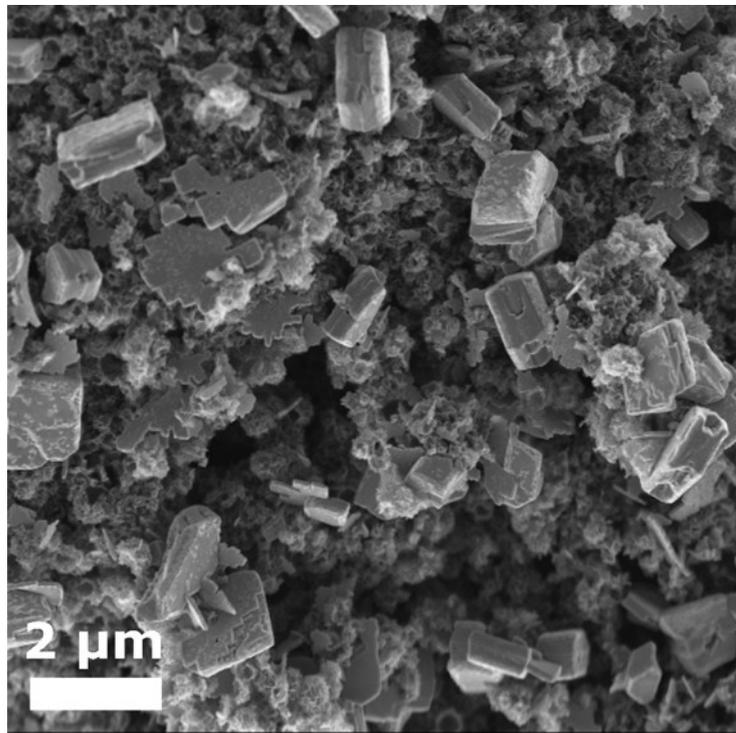


**Figure S7.** (a) CV curves of the D-SnS@NC at a scan rate of 0.05 mV s<sup>-1</sup>. (b) Galvanostatic discharge-charge curves of the D-SnS@NC for the 1<sup>st</sup>, 2<sup>nd</sup> and 5<sup>th</sup> cycle at a current density of 100 mA h<sup>-1</sup> g<sup>-1</sup>.



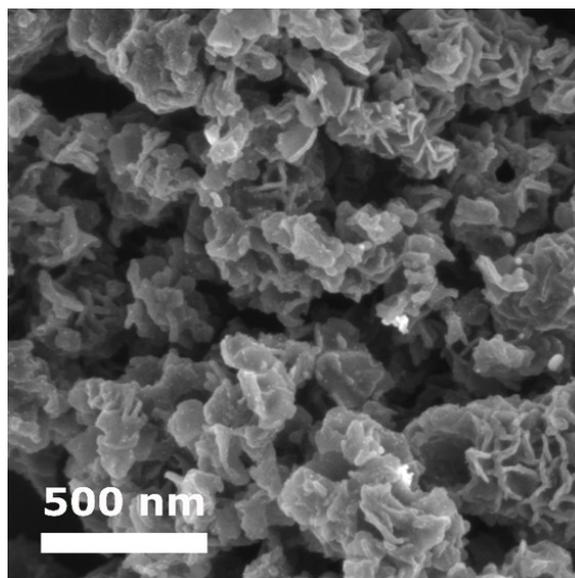
**Figure S8.** Cycling performance of H-SnS@NC annealed at 450 °C and 600 °C, respectively, at a current density of 1 A·g<sup>-1</sup>.

The cycling performance of H-SnS@NC annealed at 600 °C shows a higher specific capacity (about 240 mAh/g) after 100 cycles compared to the sample annealed at 450 °C (164 mAh/g). Both values are lower than the one obtained for the sample annealed at 700 °C (420 mAh/g). This observation supports the influence of the annealing temperature on the formation of the conductive graphitic carbon layer, improving the electrochemical performance of the particles.



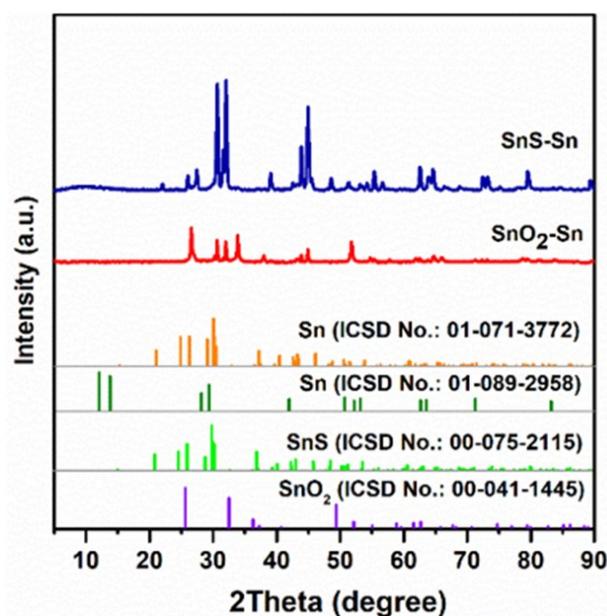
**Figure S9.** SEM image of H-SnS@NC annealed at 850 °C.

The SEM image in Fig. S9 shows that after annealing at 850 °C the hierarchical microstructure of the hollow spheres was damaged and bulky particles formed.



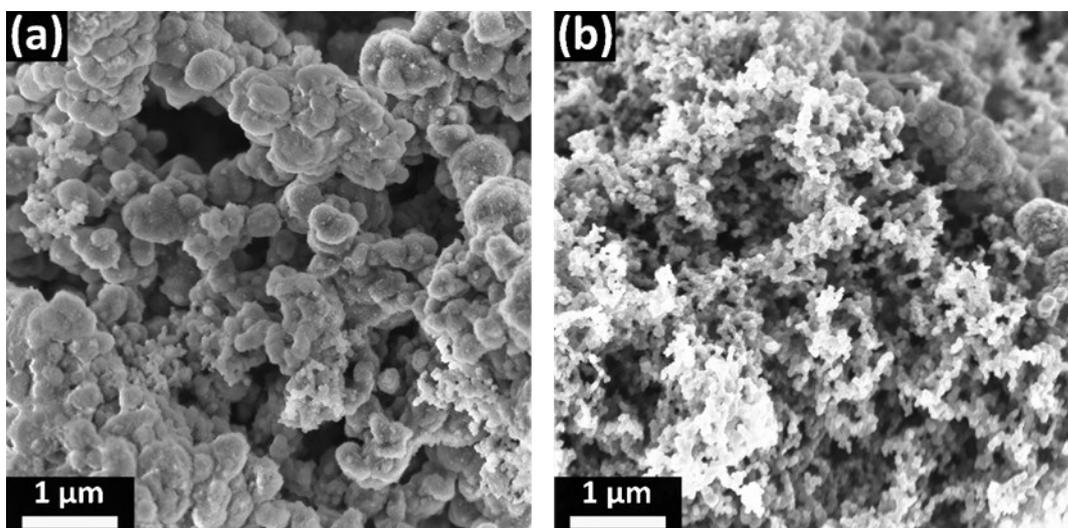
**Figure S10.** SEM image of H-SnS@NC annealed with a heating rate of 5 °C/min.

A SEM image of H-SnS@NC annealed with a heating rate of 5 °C/min (Fig. S10) shows that most of the hollow structures cannot be preserved under these conditions.



**Figure S11.** Comparison of the XRD patterns of H-SnS@NC annealed in argon (blue) and in N<sub>2</sub> (red) as protecting gases.

As shown in Fig. S11, when N<sub>2</sub> was used as the protecting gas instead of argon, SnO<sub>2</sub> as an impurity phase was observed in the corresponding XRD pattern.



**Figure S12.** SEM images of the (a) H-SnS@NC and (b) D-SnS@NC electrodes after 5 cycles.

To verify the stress buffering effect of the hollow structures upon cycling, we performed *ex-situ* SEM on the electrode particles after 5 cycles at 0.1 A/g. H-SnS@NC, as shown in Fig. S12a, is composed of spherical particles, indicating that the morphology is preserved during lithiation and delithiation, because the stress can be relaxed towards both inside or outside direction in a hollow particle. In the SEM image displaying D-SnS@NC (Fig S12b), much finer particles were observed instead of large spheres, indicating that the highly accumulated stress, especially in the interior center of the particles, leads to pulverization that results in the poorer electrochemical performance.