Electronic Supplementary Information

Porous SnO_2/layered titanate nanohybrid with enhanced electrochemical performance for reversible lithium storage

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Theoretical capacity of STN. (Supporting information)

Lithium insertion reaction for the lepidocrocite-type layered titanate is as follows:

$Ti_{1.83}O_4 + xLi + xe^- \rightarrow Li_xTi_{1.83}O_4$, where the maximum insertion coefficient, *x*, is determined to be about 0.7.[1]

Thus, the theoretical capacity of the layered titanate could be calculated to 171 mAh/g.

The theoretical capacity of SnO_2 can be also calculated in the same way as the layered titanate. The reaction of SnO_2 with lithium is as follows:

$SnO_2 + 4Li \rightarrow Sn + 2Li_2O$ and $Sn + xLi \leftrightarrow Li_xSn$. The maximum theoretical capacity of the SnO_2 anode is determined to be 781 mAh/g by this mechanism.[2]

Finally, the theoretical capacity of the hypothetical mixture between the layered titanate and the SnO_2 nanoparticle ($C_{theoretical}$ for STN) was calculated by considering the $C_{layered\ titanate}$ (171 mAh/g), $C_{rutile\ SnO2}$ nanoparticle (781 mAh/g), and the elemental ratio of both components in STNs (layered titanate : SnO_2 = 40% : 60%).

$C_{theoretical}$ for STN is 537 mAh/g.

Supporting table

Table 1. Parameters obtained from N_2 adsorption-desorption measurements.

Compound	S_{BET}[a)] (m^2/g)	V_t[b)] (mL/g)	Pore size[c)] (nm)	BDDT classification
STN-I	132	0.075	0.75	Type I
STN-II	177	0.104	2.4	Type I + IV

[a)] BET specific surface area calculated from the linear part of the BET plot.
[b)] Total pore volume (taken from the volume of N_2 adsorbed at about P/P0 = 0.950).
[c)] The average pore diameter was estimated from the t-plot and the Barrett-Joyner-Halenda (BJH) formula for STN-I and STN-II, respectively.

Supporting figures

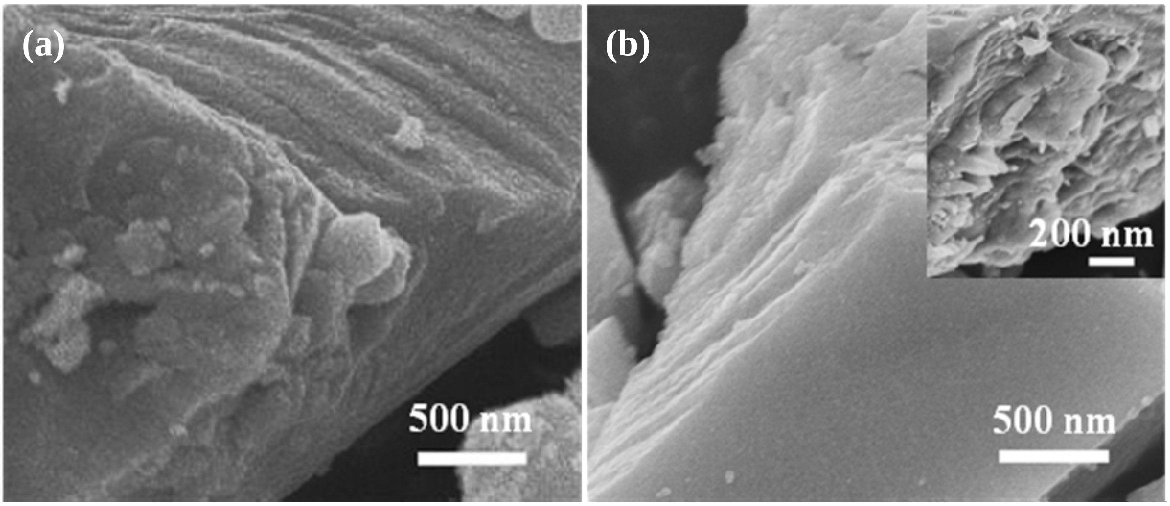

Figure S1. SEM images for (a) STN-I and (b) STN-II.

In the SEM images, the layered platelets morphology with several micrometer widths was observed for both STNs when viewed from the top. However, the SEM image from the edge side of STN-II, the layers are not well ordered, but rather randomly stacked, which is suggestive to the formation of house-of-card type porous structure. As the calcination temperature increased the external surface became smooth without forming any bulk deposition of SnO_2 nanoparticles, implying that the remarkable capacity fading arising from the volume expansion of SnO_2 nanoparticles may not occur during the first few Li insertion/extraction cycles in LIB application.

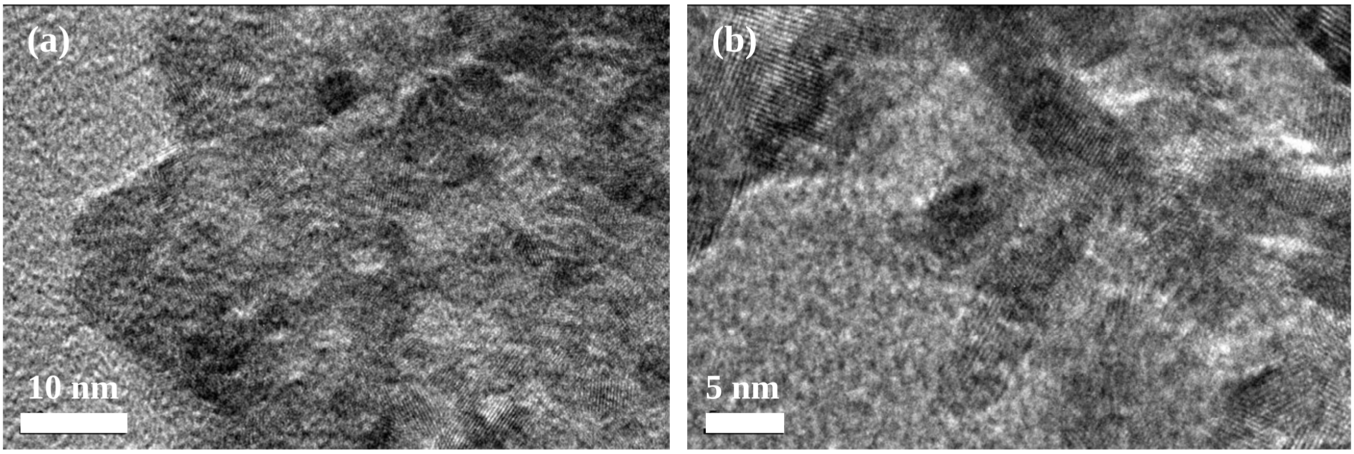

Figure S2. HR TEM images for (a) SnO_2 nanoparticles calcined at 250 °C and (b) SnO_2 nanoparticles calcined at 400 °C.

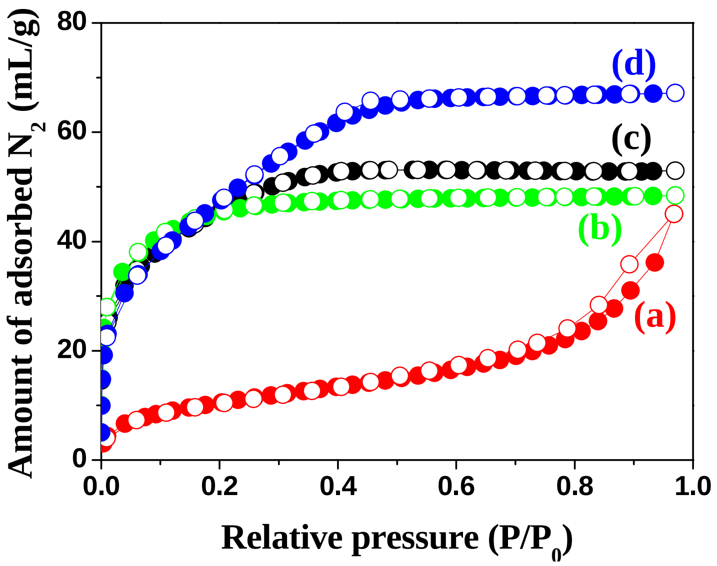

Figure S3. N_2 adsorption desorption isotherms for (a) restacked titanate, (b) STN-I, (c) SnO_2 nanoparticles, and (d) STN-II. The filled and open symbols represent adsorption and desorption data, respectively.

Little hysteresis loops indicative of the reversible N_2 adsorption/desorption process were observed for both STNs, implying that Li ion migration through the channels could be also reversible in electrochemical performance giving rise to the high cycling stability.[3] This phenomenon would be attributed to the pores in STNs, which was controlled precisely by thermal treatment under Ar atmosphere.

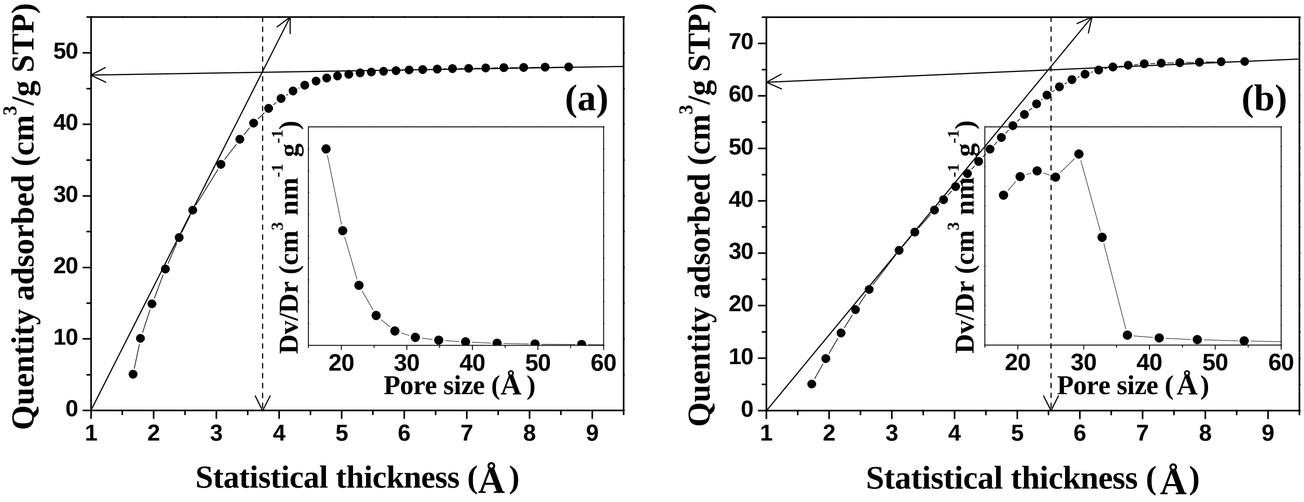

Figure S4. Pore size distribution curve for (a) STN-I and (b) STN-II estimated from the t-plot and Barrett-Joyner-Halenda (BJH) formula (inset).

As plotted in the Figures for STN-I, no mesopores could be observed, but an average pore diameter of about 0.75 nm was obtained from t-plot extrapolation. However, STN-II contains mesopores with an average pore size of about 2.4 nm, which should be attributed to thermal decomposition of pore-blocking organic species after the heat treatment at 400 °C. In addition, it was observed that the mean size of micropores (about 1.1 nm) in STN-II was bigger than that in STN-I. As a consequence, STN-II could allow the access of Li ions and electrolyte molecules more easily than STN-I, which could result in a higher specific capacity.

Supporting references

1 M. Ohashi, *Mol. Cryst. Liq. Cryst.* 2000, **341**, 265; M. Ohashi, *Mol. Cryst. Liq. Cryst.* 1998, **311**, 51

2 I. A. Coutney, and J. R. Dahn, *Electrochem. Soc.*, 1997, **144**, 2045.

3 K. Kosuge, and P. S. Singh, *Chem. Mater.*, 2000, **12**, 421.