Supplementary Information for:

Superstructure ZrV_2O_7 nanofibres: thermal expansion, electronic and lithium storage properties

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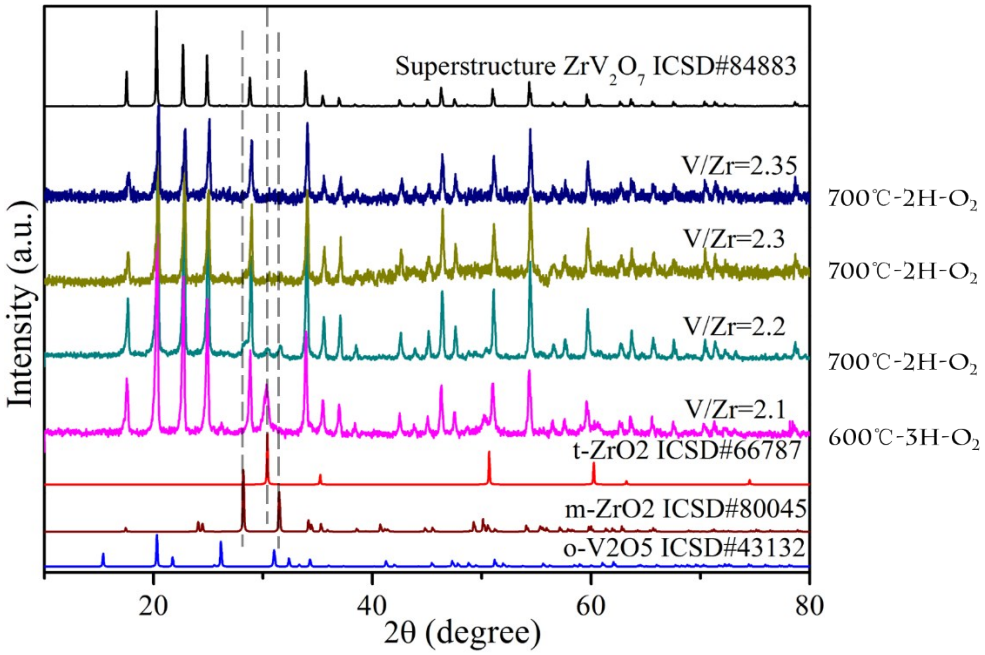

Fig. S1 XRD patterns of synthesized samples with different V/Zr ratio and annealing temperature.

When the V/Zr ratio was set to be 2.1 with subsequent annealing at 600°C in oxygen

atmosphere, a relatively strong peak of tetragonal ZrO_2 can be seen from the XRD pattern of the obtained sample. The small peak of orthorhombic V_2O_5 at about 26° was also presented in the pattern, indicating the incomplete reaction. After increasing the calcination temprature to 700°C and V/Zr ratio gradually to 2.2, 2.3 and finally 2.35, the peaks of impurities weaken slowly to disappeared. A completely pure phase can be obtained when temperature was added to 800°C.

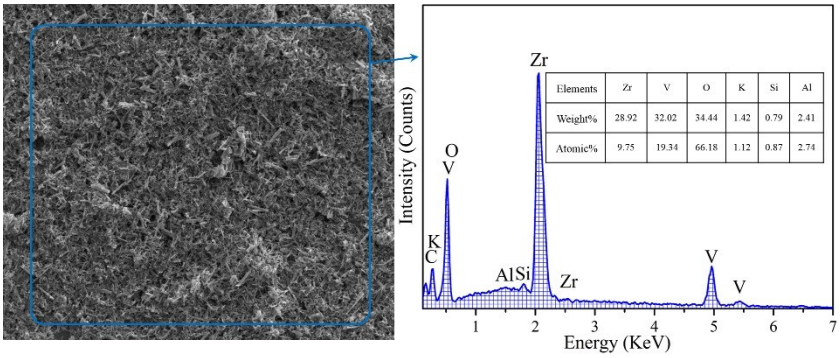

Fig. S2 EDS results of a large selected area of the fibrous region.

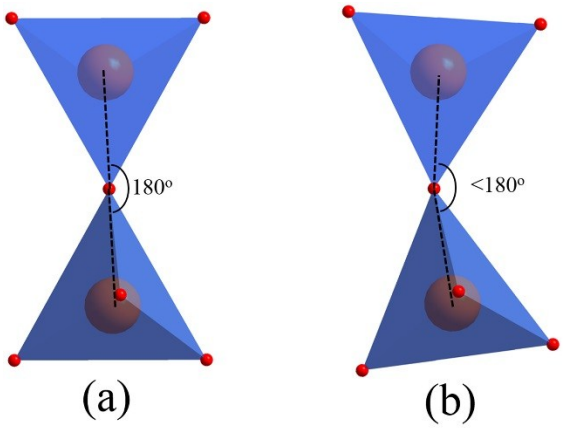

Fig. S3 The schematic V-O-V bond angle in ZrV_2O_7 normal structure (a) and superstructure (b).

In normal ZrV_2O_7 structure cell, the six V_2O_7 groups are constrained to be 180°.

While of the six unique V_2O_7 groups in ZrV_2O_7 superstructure cell, two of which are constrained by symmetry to contain linear V-O-V linkages, the remaining four are free to bend away from 180°.

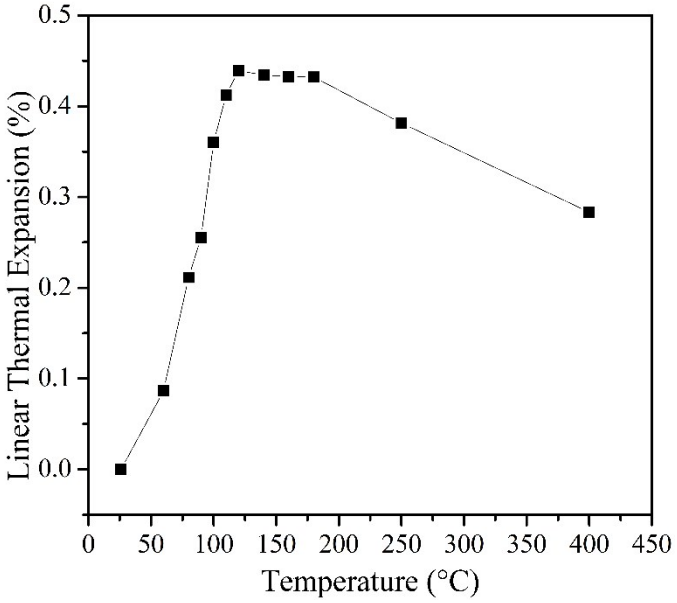

Fig. S4 Linear thermal expansion of superstructure ZrV_2O_7 nanofibres in the temperature range of RT~400°C

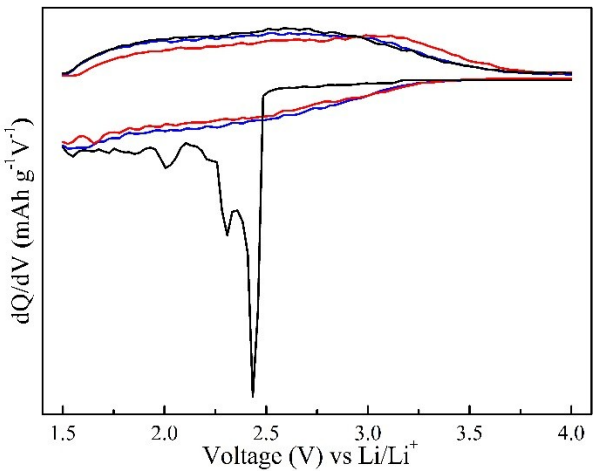

Fig. S5 CV curves of ZrV_2O_7 nanofibres electrode at a voltage window of 1.5~4 V vs. Li/Li^+.

Table S1 The detailed values obtained by data fitting of the EIS spectra to equivalent circuit model.

State	$R_s\,(\Omega)$	$R_{ct}\,(\Omega)$
Open circuit	1.553	502.5
After 1st cycle	1.542	235.3
After 2nd cycle	1.85	166.8
After 10th cycle	8.151	140.53
After 20th cycle	4.7	87.39