**Supporting Information**

**Towards a Greener and Scalable Synthesis of Na2Ti6O13 Nanorods and Its Application as Anode in Batteries for Grid-Level Energy Storage**

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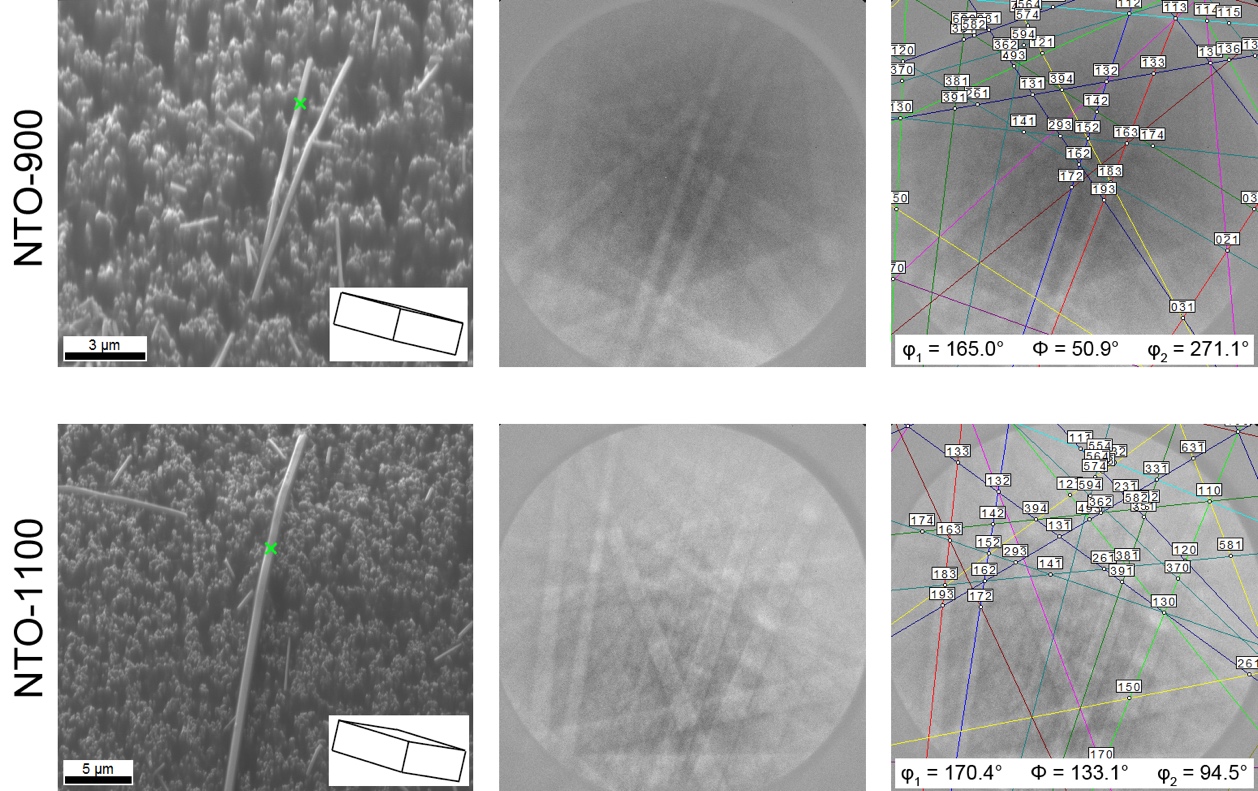
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**EBSD**

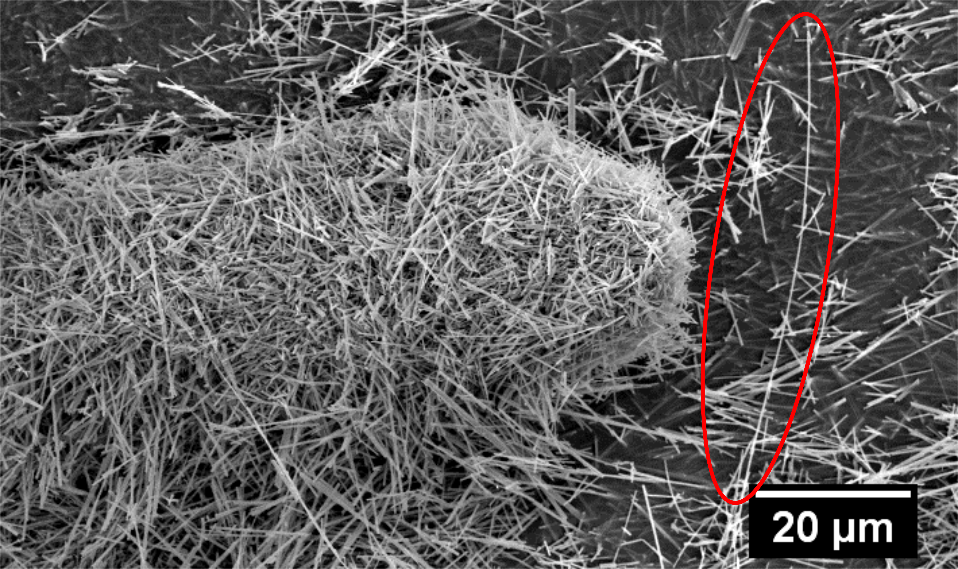
presents EBSD measurements of samples NTO-900 and NTO-1100. Note that the EBSD on NTO-1100 was performed on a different spot than that shown in Figure 2. As a result, all samples show the same growth direction, i.e. growth along <010>.



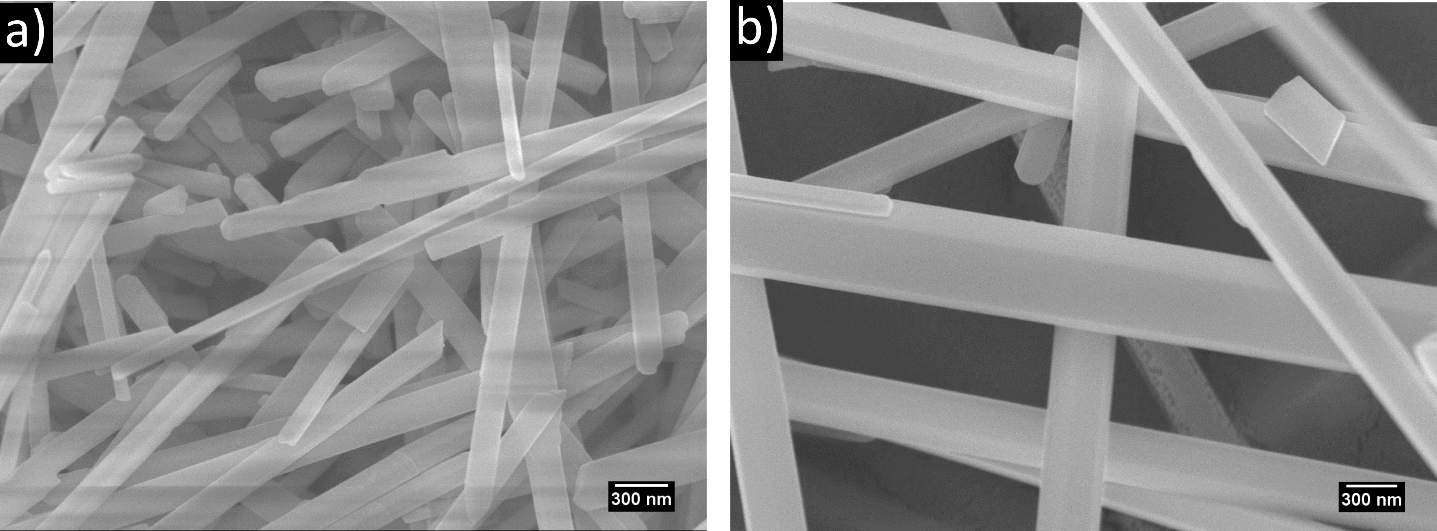
**Figure S 1.** EBSD data of sample NTO-900 (first line) and NTO-1100 (second line). The representation follows the pattern of the manuscript.

**SEM**

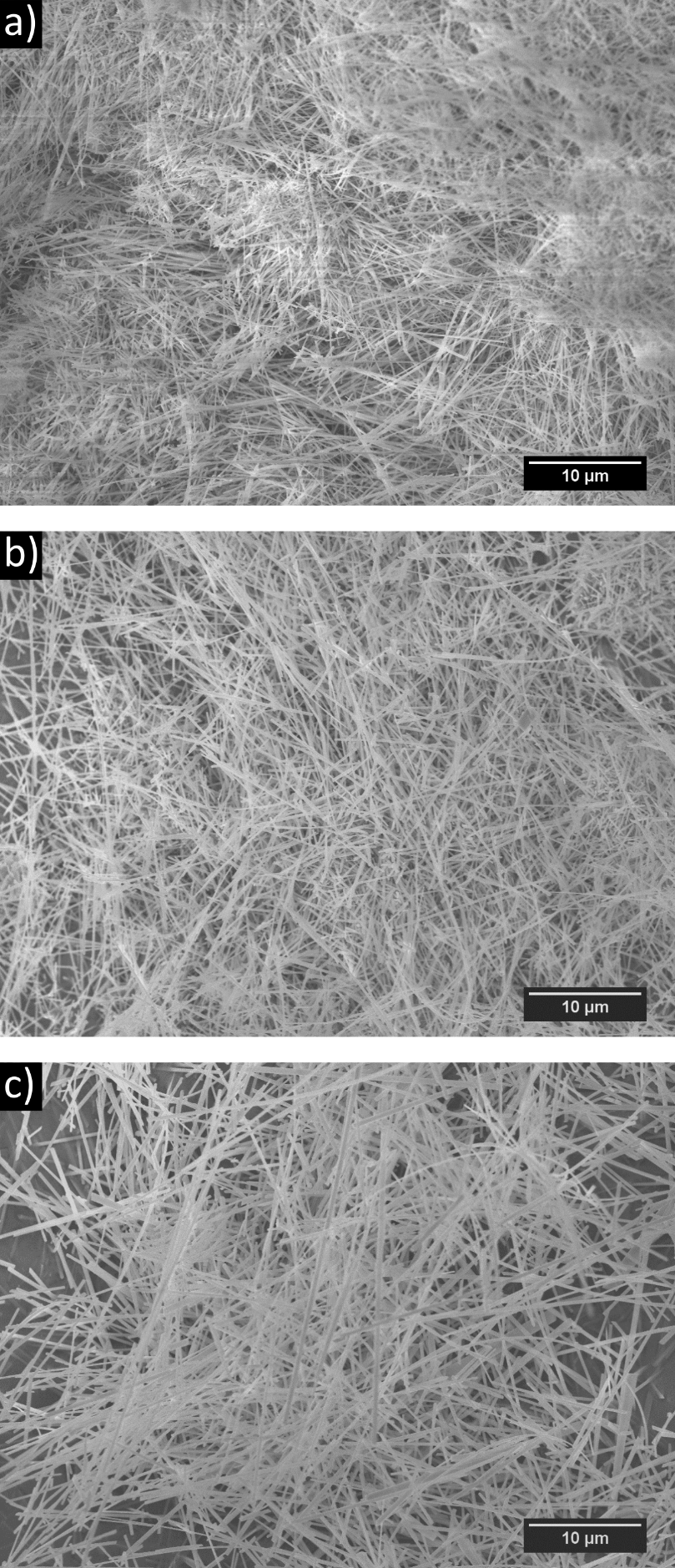
and present SEM micrographs of NTO-900 and NTO-1100 at lower and at higher magnification. It is clear from the first glance that the nanorods average thicknessin NTO-1100 is about 50% larger than that in NTO-900. gives a better overview of the samples providing low magnification micrographs.



**Figure S 2.** SEM image reporting nanorods with a length of 40 µm contained in NTO-1100.



**Figure S 3.** comparison of the thicknesses of the nanorods synthesized respectively at a) 900 °C (NTO-900) and b) 1100 °C (NTO-900). These two pictures are magnifications of the samples reported in Fig 4a) and 4e).

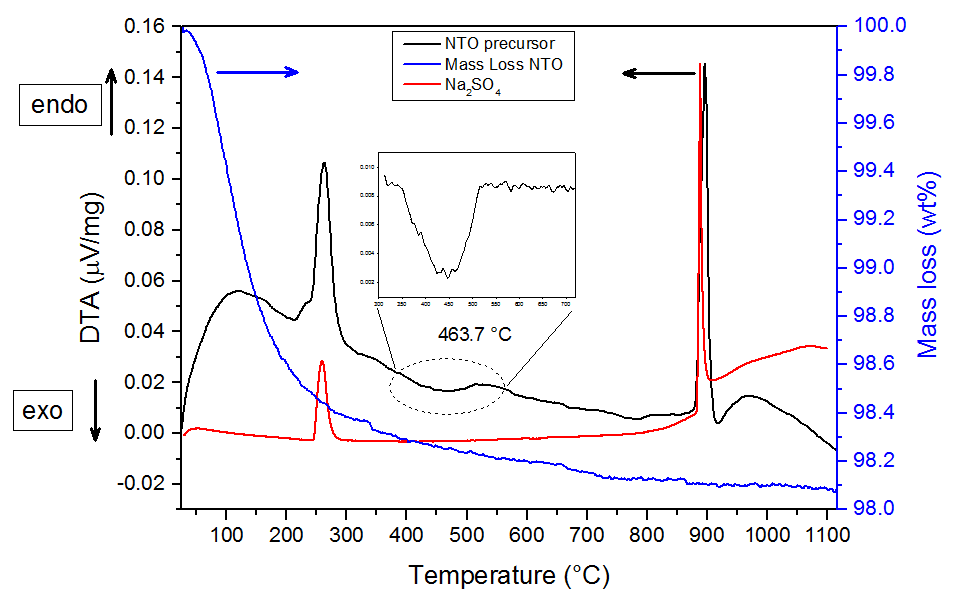


**Figure S 4.**Low magnification SEM images of a) NTO-900, b) NTO-1000 and c) NTO-1100.

**DTA-TGA**

Thermogravimetric analysis of the precursor mixture was performed with a STA 429 (TGA/DTA-Sensor), (NetzschGerätebau GmbH, Selb (Bavaria), Germany) in a continuous flow of synthetic air (75 mL/min).

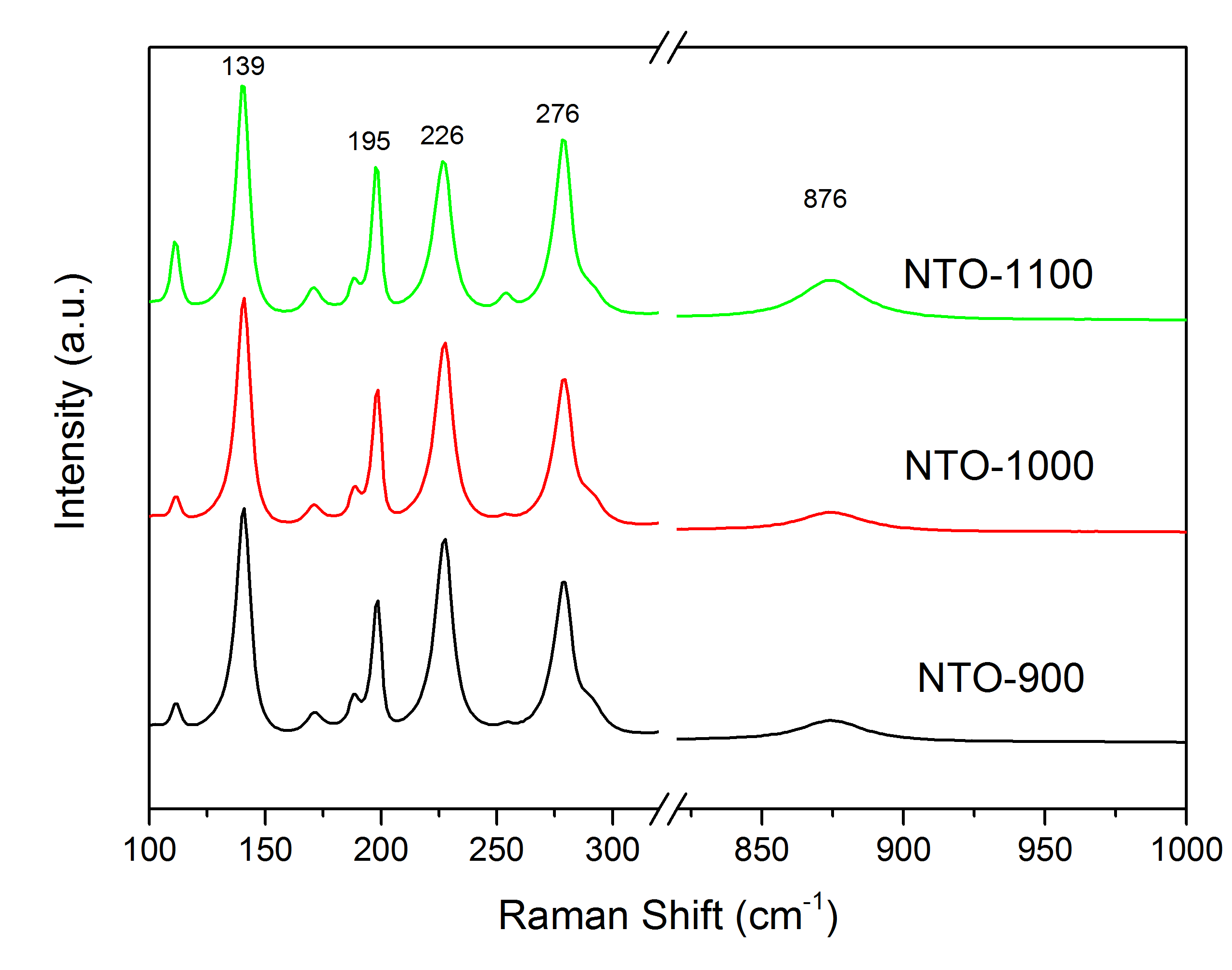
DTA has beenperformed on the dried powder obtained after the first synthesis step. The DTA analysis reveals two strong endothermic peaks at 243.9 °C and 882.1 °C (see ). They are attributed to the structural change of Na2SO4[1](phase transition V-I) and to the melting of the salt matrix. These findings are confirmed by the measurement performed on pure Na2SO4 (see red curve in ). Other endothermic peaks with lower intensity are recorded at 119.8 °C and 974.8 °C. The first is explained by the evaporation of water as confirmed by the TG measurement (mass loss of about 1.2 % of total 1.86wt%). The second peak at 974.8 °C is ascribed to the evaporation of gaseous species like SOx. According to Sauvet et al.[2] Na2Ti6O13 crystallization process is exothermic, taking place at a lower temperature (463.7 °C). However this feature could also be attributed to the crystallization of amorphous anatase.[3] No crystalline anatase is formed in our MSS. Otherwise the characteristic exothermic peak of the transition anatase into rutile would be visible in the temperature range from 700-1100 °C. Therefore, theexothermic peak at 463.7 °C (see inset in ) can be addressed to thecrystallization of Na2Ti6O13.The rather low intensity might be ascribed to the composition of the measured powder, consisting of more than 90% of Na2SO4.



**Figure S 5.** DTA (black line) and TG (blue line) measurement performed on the NTO precursor. The DTA of Na2SO4 is reported for comparison (red line). The inset shows a magnification of the exothermic peak at 463.7 °C with baseline correction.

**Raman spectroscopy**

presents an enlarged view of the Raman data shown in Fig. 5 in the manuscript. The Raman lines of NTO-900 and NTO-1100 have been integrated in order to compare the intensity change with synthesis temperature. While the area of all the lines except 226 cm-1 and 876 cm-1 stay almost constant, the 226 cm-1 linedecreases of about 20% whereas the 876 cm-1 line increasesby about 80% (see ).



**Figure S 6.**Enlarged view of Fig. 5, obtained with a brakein the Raman shift. This allows a detailed view on the intensity variations in the Raman measurements depending on the temperature.

**Table S 1.** integrated peak areas of the Raman lines of sample NTO-900, NTO-1000 and NTO-1100. The area difference is calculated between NTO-900 and NTO-1100.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Integrated peak area of different Raman lines | | | | | |
| Sample | 139 cm-1 | 195 cm-1 | 226 cm-1 | 276 cm-1 | 876 cm-1 |
| NTO-900 | 9.21 | 2.71 | 8.56 | 6.34 | 2.34 |
| NTO-1000 | 9.09 | 2.73 | 8.06 | 6.01 | 2.15 |
| NTO-1100 | 8.70 | 3.01 | 6.84 | 6.77 | 4.20 |
| Area change from 900 °C to 1100 °C | -5.59% | 11.23% | -20.11% | 6.75% | 79.49% |

**FFT patterns from HRTEM**

shows that the acquired FFT pattern of NTO-900 and NTO-1100 agree well with JEMS[4] calculations with the structural data input taken from Perez-Flores[5]. No large discrepancy between experiment and model is being found.



**Figure S 7.** Comparison of FFT’s calculated from HRTEM images with calculated NTO spot patterns for samples NTO-900 a) and b) and NTO-1100 c) and d), respectively.

**EDX**

shows the EDX spectra of NTO-900 and NTO-1100 single nanorods, respectively. The additional C and Si peak are due to the surrounding araldite embedding material. The quantification of both spectra is presented in below.



**Figure S 8.** EDX spectra of sample NTO-900 and NTO-1100, respectively. Si and C originate from surrounding araldite.

**Table S2.** Relative quantification of EDX spectra acquired from a single Na2Ti6O13 nanorod using the Cliff-Lorimer k-factor method for both samples.

|  |  |  |  |
| --- | --- | --- | --- |
| Sample | Na [at%] | Ti [at%] | O [at%] |
| k-factor | 0.9432 | 1.0291 | 1.0000 |
| NTO-900 | 8.46 ± 1.93 | 29.16 ± 5.06 | 62.38 ± 6.98 |
| NTO-1100 | 7.10 ± 1.65 | 33.19 ± 5.95 | 59.70 ± 7.20 |
| Nominal | 9.52 | 28.57 | 61.90 |

shows the results of a quantitative EDX analysis via Cliff-Lorimer method. The results agree within experimental error with the nominal composition presented in the last row ofTable S2.

# References E.S.I.

[1] S. E. Rasmussen, J. E. Jørgensen, B. Lundtoft, *J. Appl. Crystallogr.***1996**, *29*, 42–47.

[2] A.-L. Sauvet, S. Baliteau, C. Lopez, P. Fabry, *J. Solid State Chem.***2004**, *177*, 4508–4515.

[3] A. Baszczuk, M. Jasiorski, M. Winnicki, *J. Therm. Spray Technol.***2018**, *27*, 1551–1562.

[4] “https://www.jems-swiss.ch/,” **n.d.**

[5] J. C. Pérez-Flores, F. García-Alvarado, M. Hoelzel, I. Sobrados, J. Sanz, A. Kuhn, *Dalt. Trans.***2012**, *41*, 14633–42.