Supplementary Information for:

Rod-like $NaNbO_3$: mechanisms for stable solvothermal synthesis, temperature-mediated phase transitions and morphological evolutions

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The temperature-induced structural transitions of the sodium niobate could be further elucidated by Raman spectrum survey [Figure S1(a)]. The major Raman bands of $Na_7(H_3O)Nb_6O_{19}.14H_2O$ appeared in the regions of 100–300 cm^{-1}, 500–550 cm^{-1}, and 800–900 cm^{-1}. Among these regions, ν_5 (282 cm^{-1}) is assigned to an Nb-O stretching mode, ν_1 (212 cm^{-1} and 155 cm^{-1}) are two Nb-O-Nb bending modes, and 833 cm^{-1} stand for the short Nb = O terminal double bonds. In each Lindquist ion of $Na_7(H_3O)Nb_6O_{19}\cdot 14H_2O$, six NbO_6 octahedra create a larger octahedron by sharing edges, and Na atoms are scattered within the vacancies between the Lindquist octahedral sites [Figure S1(b)]. The edge-shared NbO_6 octahedra structures are also reflected by the bands at 524 and 904 cm^{-1}, which represent the edge-shared octahedral NbO_6 stretching mode and Nb = O surface sites, respectively. Considering the $NaNbO_3$ with an orthorhombic and monoclinic perovskite structure, the major

Raman band of the perovskite structures appears in the 600–615 cm^{-1} (ν_1) region and is accompanied by a shoulder at around 570 cm^{-1} (ν_2). These results are analogous to findings in a previous report.[1] Both orthorhombic and monoclinic forms are ideal perovskite structures with different degrees of distortion, which yields differences in their band distances and angles [Figure S1(c)]. A higher metal-oxygen bond order, which corresponds to a shorter bond distance, shifts the Raman bands to higher wavenumbers. As such, the Raman spectra of O-$NaNbO_3$ and M-$NaNbO_3$ are very similar except for some slight shifts. The sharpening of Raman bands from O-$NaNbO_3$ to M-$NaNbO_3$ as well as the additional small peak existing between 340 and 360cm^{-1} is likely induced by different distorted niobium oxide compounds. [2] The Raman spectra prove the strong dependence of the phase transformations of niobium oxide on the heat treatments.

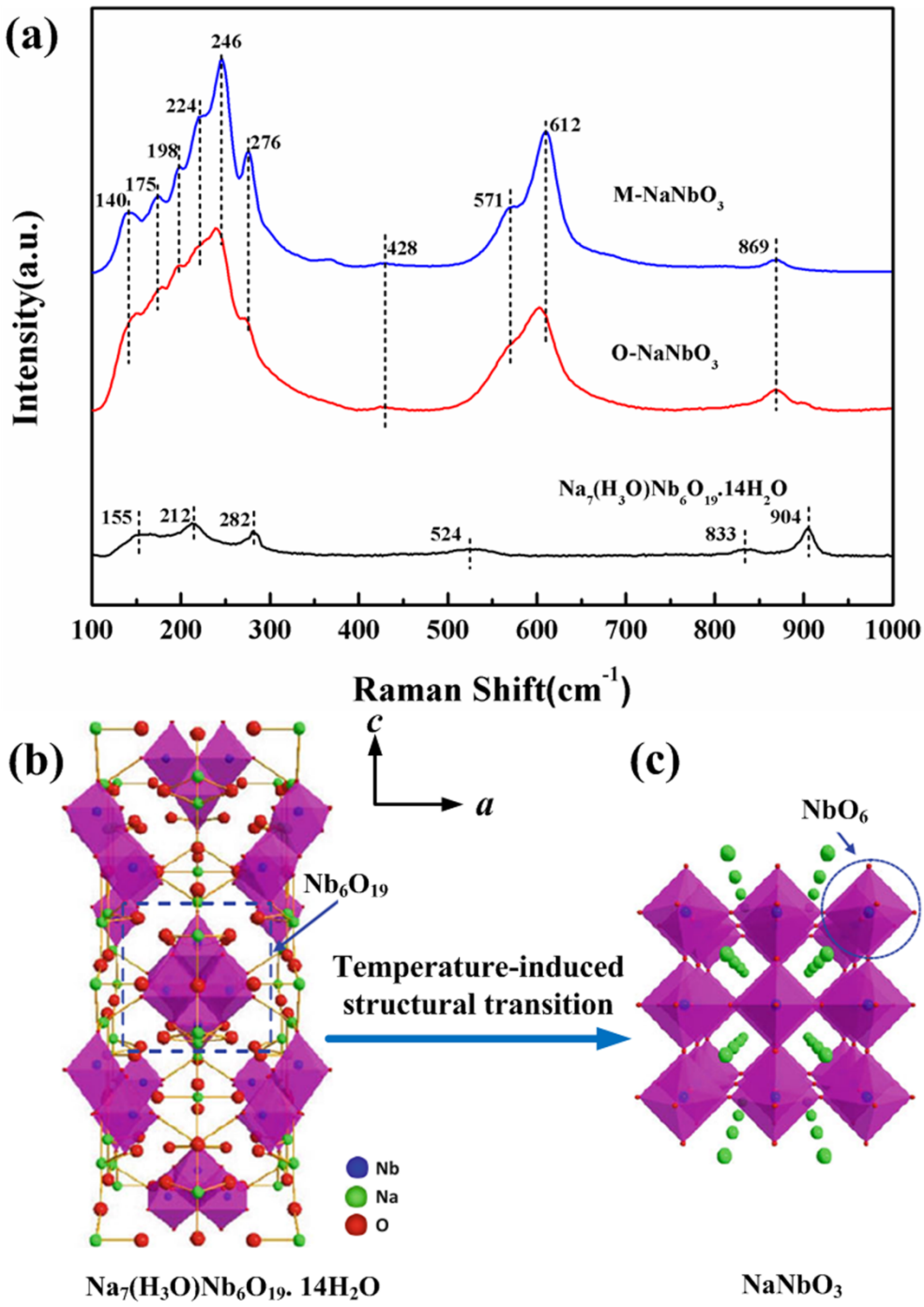

Figure S1. Raman spectra of $Na_7(H_3O)Nb_6O_{19}\cdot 14H_2O$ and the products treated at 400°C (O-$NaNbO_3$) and 800°C (M-$NaNbO_3$), respectively.

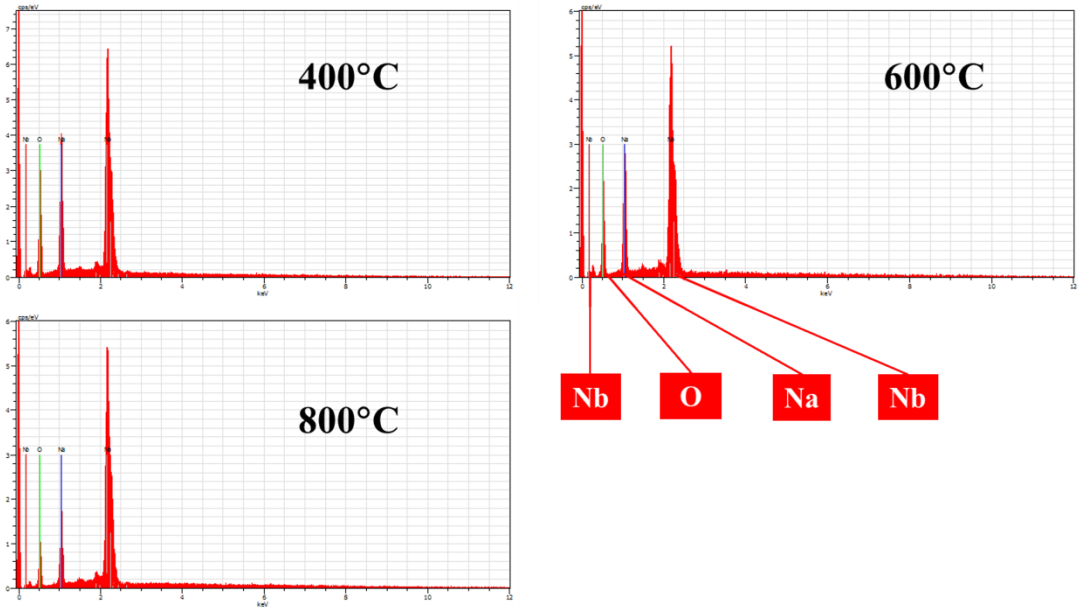

Figure S2. Compositional analysis of solvothermal synthesized powders treated at 400°C, 600°C, 800°C by Energy-dispersive X-ray spectroscopy (EDS), respectively.

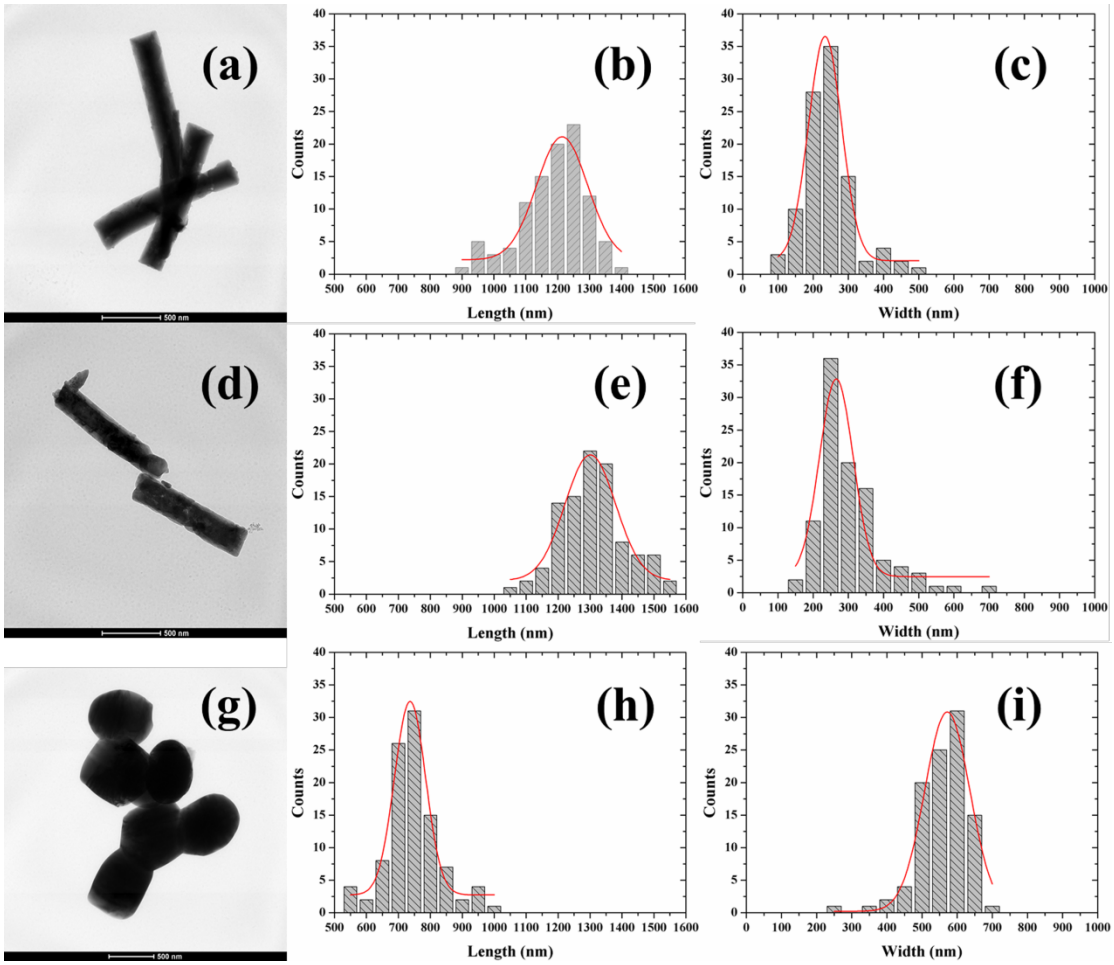

Figure S3. (a) (d) (g) Representative TEM images and size distributions in (b) (e) (h) length and (c) (f) (i) width of powders (a) (b) (c) synthesized solvothermally and treated at (d) (e) (f) 400°C and (g) (h) (i) 600°C for 4h, respectively.

Reference

(1) R. J. C. Lima,; P. T. C. Freire, J. M. Sasaki, A. P. Ayala, F. E. A. Melo, J. M. Filho, K. C. Serra, S. Lanfredi, M. H. Lente, J. A. Eiras, *J. Raman Spectrosc.,* 2002, 33, 669–674.

(2) J. M. Jehng, I. E. Wachs, *Chem. Mater.,* 1991, 3, 100–107.