## **Supporting Materials:**

**Experimental:** In a typical synthesis procedure, 0.5 g of metallic Nb powder was dispersed in a 40 mL aqueous solution of 1~15 M NaOH, the obtained mixture was poured into a Teflon-lined stainless-steel autoclave with a capacity of 80 mL and autoclaved at 423 K (hydrothermal reaction) for a period between 6 h and 10 h to yield white floccules. Thereafter, the autoclaves were cooled down to room temperature in air spontaneously. Then the as-prepared floccules were washed with deionized water several times till to neutral and air dried prior to characterization. The morphology of the samples was observed on a scanning electron microscopy (SEM, FEI Quanta-200) and high-resolution transmission electron microscopy (HRTEM, JEM-2010 UHR) operating at 200 kV. The crystal structure of the products were determined by powder X-ray diffraction (XRD) analyses which were performed on a Bruker-D8Advance X-ray diffractometer, with graphite monochromatized high-intensity Cu K $\alpha$  radiation ( $\lambda$ = 1.5418 Å) at 40 KV and 30 mA, the XRD patterns were recorded from 10 to  $80^{\circ}$  (2 $\theta$ ) with a scanning step of 0.05° at a counting time of 0.2 s per step. IR spectra were recorded on an FTIR spectrometer (Nicolet AVATAR-360 America) in the mid-IR range of 370-4000 wavenumbers operated in the transmittance mode at a spectral resolution of 4  $\text{cm}^{-1}$ , the KBr pellet technique with about 1~3 wt% of sample was used for sample preparation. Thermal analysis (TG, STA 409PC, Netzsch, Germany) was performed at a heating rate of 10 K/min under a nitrogen atmosphere, about 3 mg of dried solid sample was heated from 313 K to 1273 K in nitrogen flow of 15 mL/min.



*Figure 1.* TEM micrographs of (a) the Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O precursor and (b) NaNbO<sub>3</sub> nanowires.

Fig.1. shows the  $Na_2Nb_2O_6$ ·H<sub>2</sub>O precursor was conveniently converted into the corresponding NaNbO<sub>3</sub> nanowires without distortion in morphology, while the diameter of nanowire decrease from ~80 nm to ~60 nm due to the dehydration of  $Na_2Nb_2O_6$ ·H<sub>2</sub>O.



*Figure 2.* XRD patterns of (a) the  $Na_2Nb_2O_6$ ·H<sub>2</sub>O precursor and (b) NaNbO<sub>3</sub> nanowires.

Fig. 2. shows the XRD patterns of the precursor and NaNbO<sub>3</sub> nanowires. the XRD pattern of the precursor (Fig. 1a) corresponds with that of the microporous molecular sieves, SOMS, with a formula of Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O, XRD pattern suggests that there is only one crystal phase of a monoclinic lattice with a unit cell of a=17.0511 Å; b=5.0293 Å; c = 16.4921 Å;  $\beta$ =113.942°.<sup>1</sup> Fig. 1b is the XRD patterns of the NaNbO<sub>3</sub> obtained from the thermal decomposition of Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O. The NaNbO<sub>3</sub> phase is indeed well crystallized. All of the peaks can be indexed to Orthorhombic NaNbO<sub>3</sub> (Pbma, JCPDS Card No. 33-1270, *a* = 5.5687 Å, *b* = 15.523 Å, *c* = 5.5047 Å). No other diffraction peaks were detected.



*Figure3.* Typical FTIR spectra of (a) the  $Na_2Nb_2O_6$ ·H<sub>2</sub>O precursor and (b) NaNbO<sub>3</sub> nanowires obtained by calcinations of the precursor.

Fig. 3 a shows the FT-IR spectra of the obtained Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O precursor at room temperature, the hydroxyl groups and water molecules are confirmed by the broad bands detected at high frequency at around 3362 cm<sup>-1</sup> and 3209 cm<sup>-1</sup>, the broaden of this band is associated with the O-H stretch, the small adsorption peaks at 3209 cm<sup>-1</sup> and 1637 cm<sup>-1</sup> is belonged to the H-O-H bend of the molecular water bonded to the Na sites,<sup>2</sup> the sharp peaks at 870 cm<sup>-1</sup>, 769 cm<sup>-1</sup>, 645 cm<sup>-1</sup>, 527 cm<sup>-1</sup> and 450 cm<sup>-1</sup> are correspond to the vibrations of the Na-niobate framework including Nb-O stretching, Nb-O-Nb bending and lattice vibrations<sup>1</sup>. It becomes remarkable after calcination as shown in Fig.2b, IR spectra of NaNbO<sub>3</sub> nanowires shows that hydroxyl groups absorption peaks are greatly weakened, even vanish in the range 3209 cm<sup>-1</sup>, The Nb-O bands in the region of 608 cm<sup>-1</sup> broaden clearly after heating the precursors.



*Figure 4.* TG and DSC profiles of Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O precursor.

To measure the water content of our synthesized  $Na_2Nb_2O_6$ ·H<sub>2</sub>O precursor, TG/DSC (Thermogravimetric/differential scanning calorimetric analyzer) is conducted, as show in Fig. 3, the largest weight loss appears in a widen temperature range from 473 to 673 K, the relative weight loss is about 4.9%, which is very close to the expected theoretical value 5.2 %, based on the stoichiometry of  $Na_2Nb_2O_6$ ·H<sub>2</sub>O. This value is lower than the ideal 5.2%, we attribute it to its dehydrated  $Na_2Nb_2O_6$  (microporous) and  $NaNbO_3$  (perovskite) phases at room temperature.<sup>3</sup> the DSC curve shows the exothermic transition at 828 K is associated with conversion to a  $NaNbO_3$  form.



**Figure 5.** Temperature-induced crystalline phase evolution of  $Na_2Nb_2O_6H_2O$  precursor, the heat treatment time is 0.5 h. XRD spectra show the crystalline  $Na_2Nb_2O_6H_2O$  turn into amorphous structure at 623 K, while orthorhombic NaNbO3 phase appear at 673 K, and the orthorhombic NaNbO3 crystalline phase peak increased with the increasing temperature.

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*Figure 6.* HRTEM image of the Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O nanowires precursor.



**Figure 7.** HRTEM image of the initial state of he  $Na_2Nb_2O_6$ ·H<sub>2</sub>O nanowires precursor heat treated at 623 K for 30 min, inset is the magnified TEM micrographs of the amorphous structure , showing the crystalline  $Na_2Nb_2O_6$ ·H<sub>2</sub>O turn into amorphous structure with the increasing temperature..



**Figure 8.** HRTEM image of the oriented rearrangement intergradation's process (at 673 K for 0.5 h). There are many quasi-oriented rearranged NaNbO<sub>3</sub> nanoparticles (marked by the white circle) attached on the outside of the nanowire.

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**Figure 9.** HRTEM image of the oriented rearrangement process of NaNbO<sub>3</sub> nanowires (at 873 K for 0.5 h). HRTEM study indict that the orderly and layered lattice fringes of Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·H<sub>2</sub>O, paralleled to the long-axis direction (see Fig.6.) turn into the mussily arranged amorphous nanoparticles (see Fig.7.), then form quasi-oriented rearranged NaNbO<sub>3</sub> nanoparticles on the outside of the nanowire (see Fig.8.), which provide the direct evidence of oriented rearrangement. The finally formation of the ordered crystalline structures of NaNbO<sub>3</sub> through the solid-phase oriented rearrangement with the increasing temperature were clearly shown in Fig.9., The existing oriented rearranged nanoparticles (marked by the blue circle in Fig.9.) attached on the outside of the nanowire further confirm the oriented rearrangement mechanism.



*Figure 10.* HRTEM image of crystallized NaNbO<sub>3</sub> nanowires (at 873 K for 6 h). It shows that dehydration of sandia octahedral molecular sieves (SOMS)  $Na_2Nb_2O_6$ ·H<sub>2</sub>O and temperature-induced nanoscale solid-phase oriented rearrangement finally form single crystalline NaNbO<sub>3</sub> nanowires.