Supporting information

Metastable cubic phase of sodium niobate nanoparticles stabilized by chemically bonded solvent molecules

Qilin Gu[abc], Kongjun Zhu[a], Qiaomei Sun[ab], Jinsong Liu[b], Jing Wang[a], Jinhao Qiu[a], John Wang[c]

[a] *State Key Laboratory of Mechanics and Control of Mechanical Structures, College of Aerospace Engineering, Nanjing University of Aeronautics and Astronautics, 29 Yudao Street, Nanjing, 210016, China.*

[b] *College of Materials Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China.*

[c] *Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore.*

Corresponding Author, E-mail: kjzhu@nuaa.edu.cn (Kongjun Zhu), Fax: +86 25 84895759, Tel: +86 25 84895982

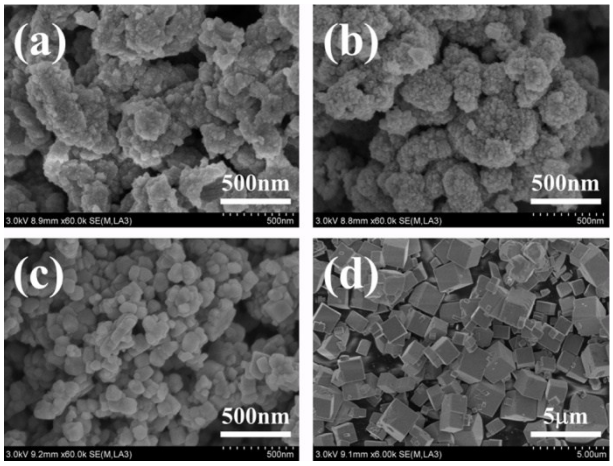

Figure S1. FE-SEM images of the samples synthesized at 220 °C for 4 h with different EG/water ratios: (a) 40/0, (b) 35/5, (c) 30/10, (d) 0/40.

The texture of the $NaNbO_3$ powders prepared with different EG/water ratios observed by FE-SEM, are shown in Figure S1. The cubic $NaNbO_3$ presents a severe degree of aggregation composed of nanoparticles with an average size of ~ 50 nm [Figure S1(a)]. With increasing water content [Figure S1(b-d)], the dispersity of these nanopowders is slightly improved, and their edges could be clearly identified. As the EG/water ratio further increased to 35/5, the average particle size increases to ~100 nm, and some cubic-shaped particles emerge [Figure S1(b)]. In pure water, orthorhombic $NaNbO_3$ presents the cubic morphology with an average size of 2.0 μm [Figure S1(d)].

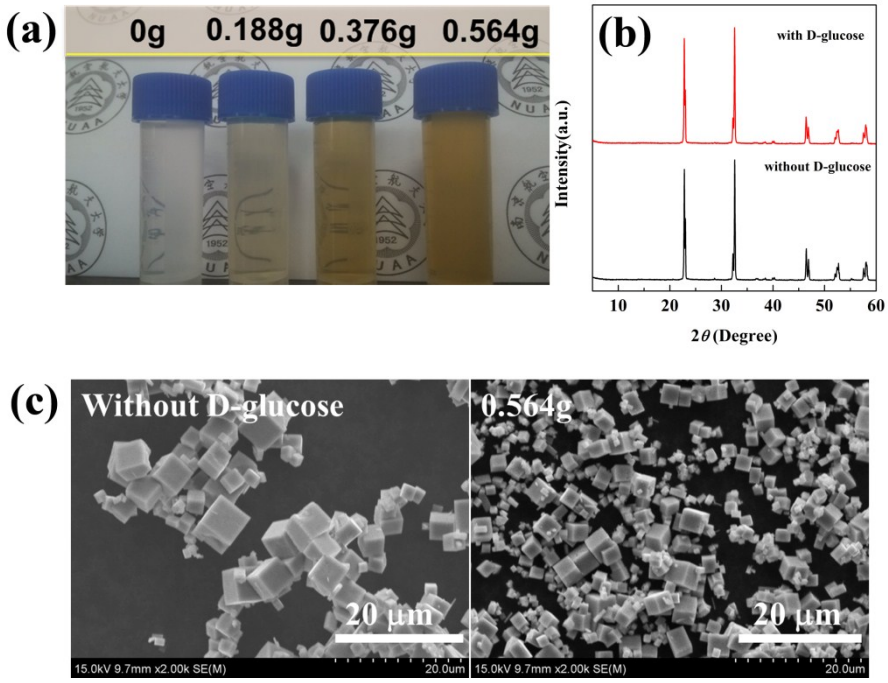

Figure S2. Hydrothermal synthesis of $NaNbO_3$ with the addition of D-glucose: (a) photographs of the residual solution after reaction with different amount of D-glucose, (b) XRD patterns of the samples synthesized with and without D-glucose, (c) FE-SEM images of the samples synthesized with and without D-glucose.

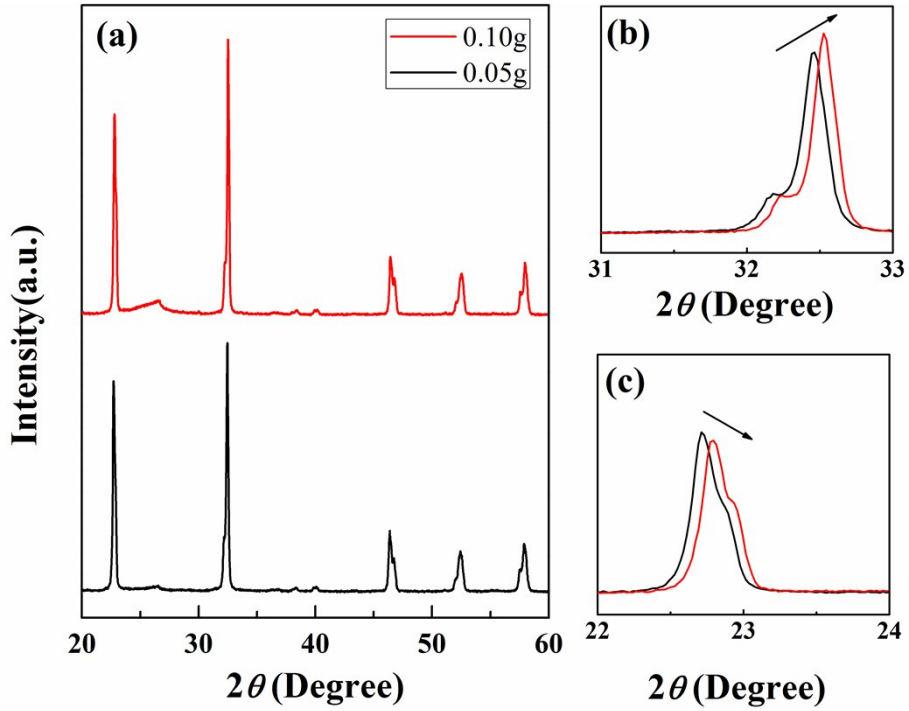

Figure S3. (a) XRD patterns of hydrothermally synthesized $NaNbO_3$ powders with different amount of carbon powders in the precursors, local enlarged view of XRD patterns: (b) $2\theta = 31 \sim 33°$, (c) $2\theta = 22 \sim 24°$.

When different amounts of D-glucose (0 ~ 0.564 g) are introduced into the hydrothermal precursors, there is a change in the appearance of solution after hydrothermal reaction, from transparent to brown [Figure S2(a)]. XRD patterns and FE-SEM images in Figure S2(b) and Figure S2(c) show that the products are orthorhombic $NaNbO_3$ cubes, and the presence of D-glucose has only decreased the particle size. The XRD patterns of $NaNbO_3$ derived from hydrothermal process with the presence of carbon nanoparticles are shown in Figure S3. It remains an orthorhombic structure [Figure S3(a)], and there is only a slight change in the intensity and position of diffraction peaks [Figure S3(b-c)]. This indicates that carbon particles may have changed the relative growth rate of (100) and (110) planes.

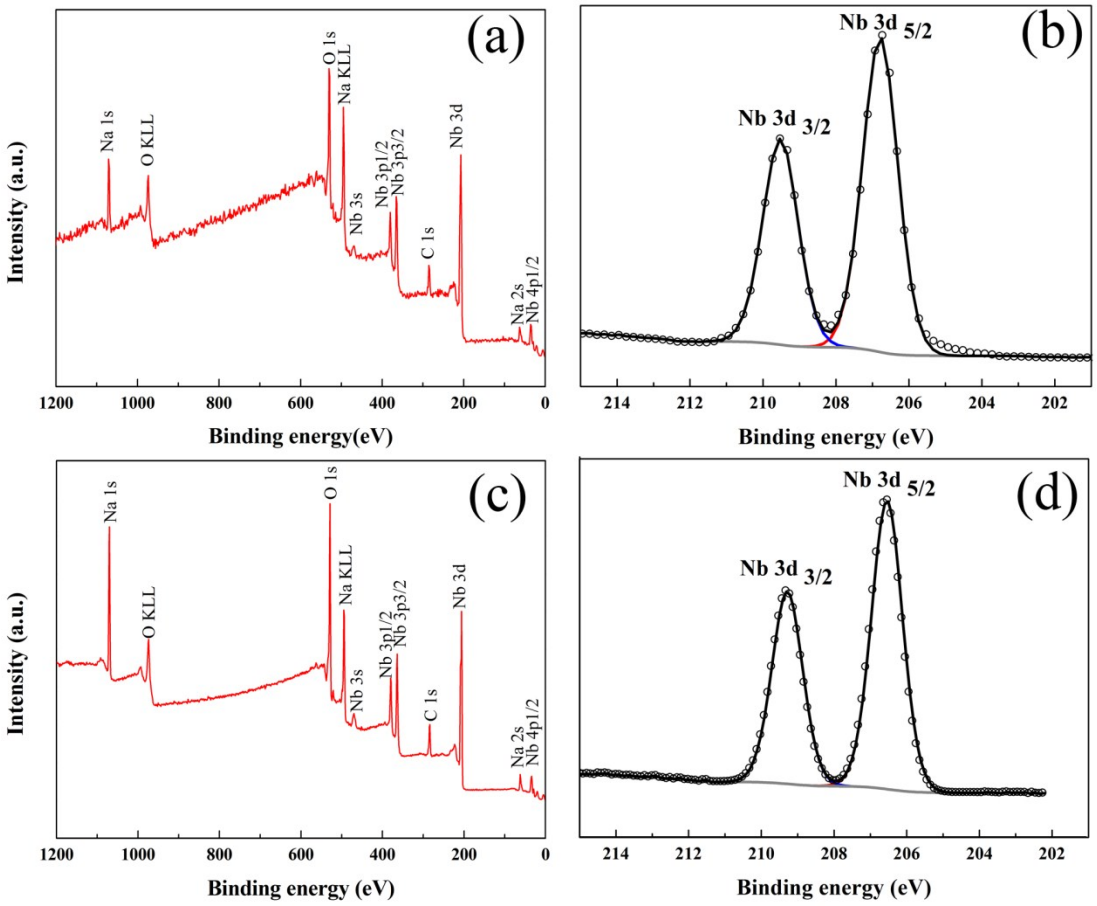

Figure S4. (a) XPS survey spectra and (b) high-resolution XPS of Nb *3d* core levels detected in orthorhombic $NaNbO_3$ crystals; (c) XPS survey spectra and (d) high-resolution XPS of Nb *3d* core levels detected in orthorhombic $NaNbO_3$ crystals. Scattering circles, dark line, gray line and other color lines represent experimental data, fitting data, background and resolved peak, respectively.

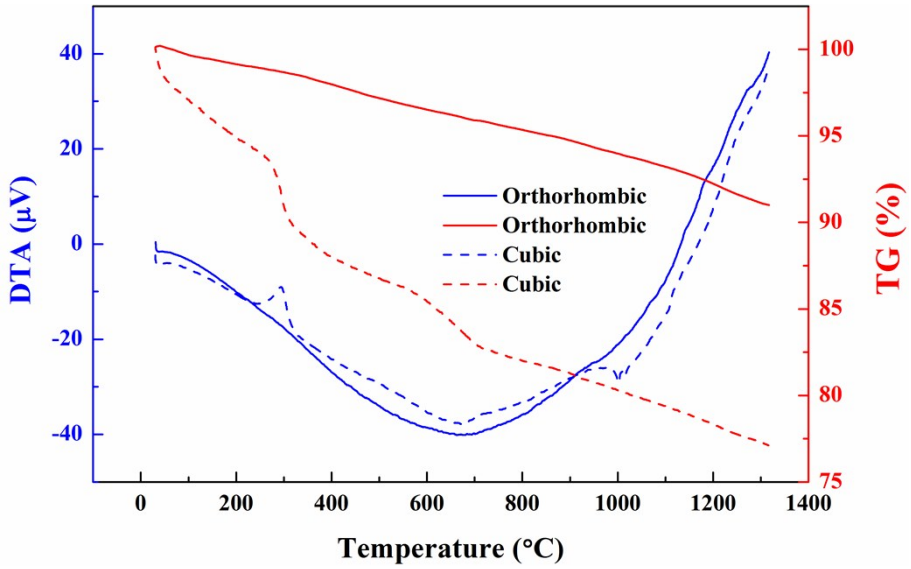

Figure S5. Thermal behavior of as-synthesized cubic (dashed line) and orthorhombic (solid line) $NaNbO_3$ powders reflected by DTA (blue line) and TG (red line) as a function of temperature (25 ~1300 °C)

Figure S5 depicts the DTA-TG curves of cubic and orthorhombic $NaNbO_3$ crystals. With the temperature increasing from room temperature to 1300 °C, three distinct weigh losses, at about 100°C, 300 °C and 650 °C are observed in cubic $NaNbO_3$, while for orthorhombic $NaNbO_3$, there is a gent weight loss emerged over the whole temperature range.

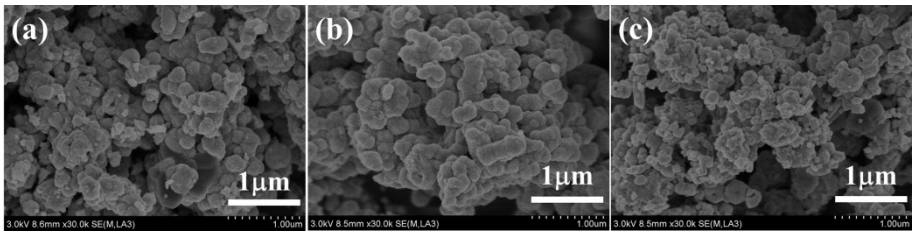

Figure S6. FE-SEM images of as-synthesized cubic $NaNbO_3$ powders followed by calcination treatment at (a) 200 °C, (b) 400 °C and (c) 600 °C for 5 h in air.

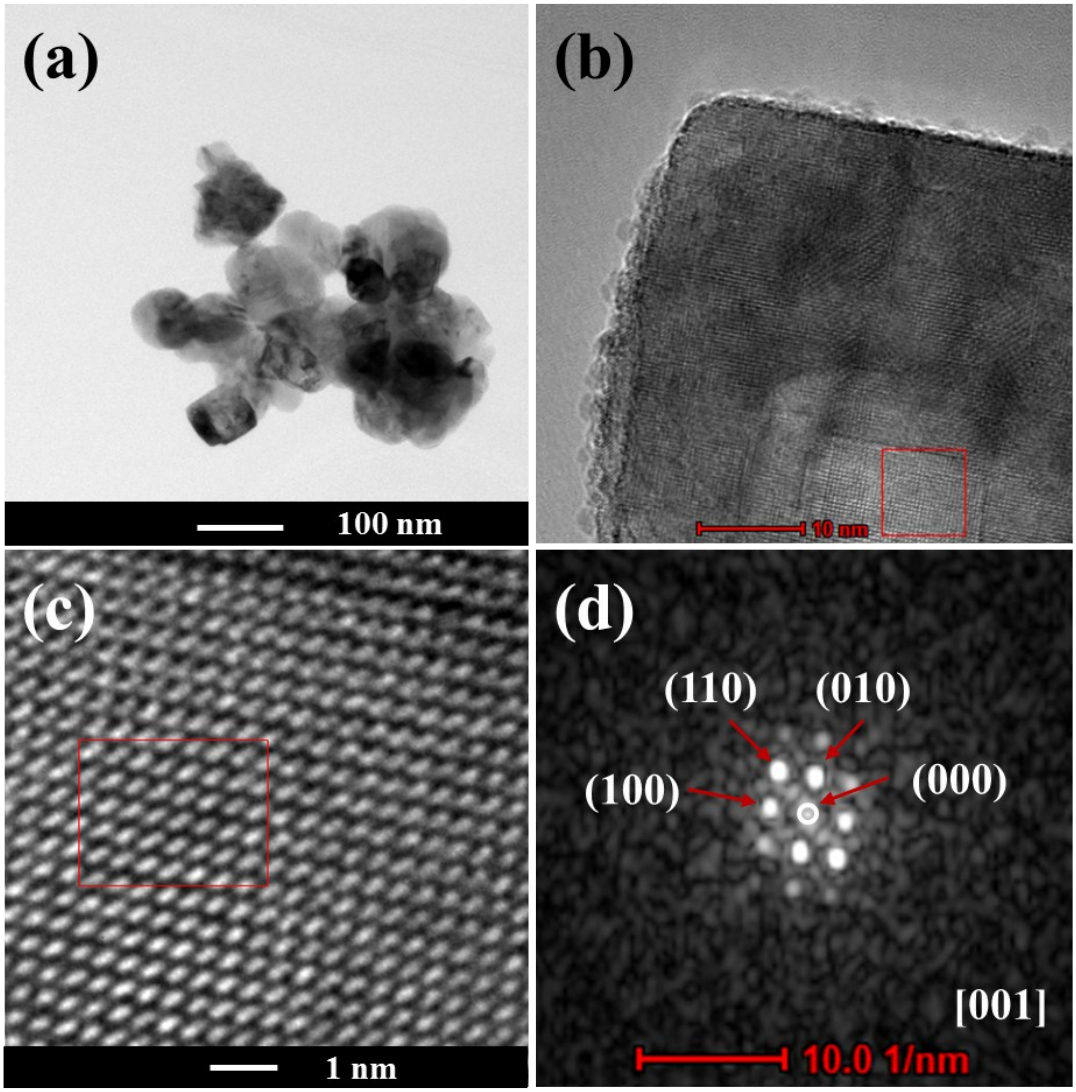

Figure S7. (a) TEM image of samples calcined at 500 °C for 5 h in air, (b, c) HR-TEM image and (d) FFT patterns of orthorhombic $NaNbO_3$.

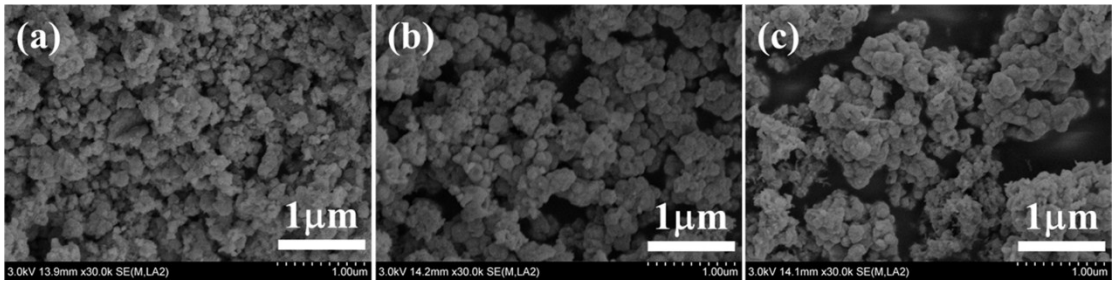

Figure S8. FE-SEM images of as-synthesized cubic $NaNbO_3$ powders followed by calcination treatment at (a) 400 °C, (b) 600 °C and (c) 700 °C for 5 h in argon.