# Supplementary information

Insights into mechanism of the symmetry dependent SHG properties in low dimensional KNbO<sub>3</sub> structures

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### Methods.

The calculation Methods for body contribution and surface contribution. For a lowdimensional NLO nanomaterial, SHG intensity is primarily dependent on structural symmetry and high-density surface defects, e.g., body contribution (B) and surface contribution (S). Body contribution is based on the non-centrosymmetric (NCS) nature of crystal structure, while surface contribution originates from high-density defects on particle surfaces. For a centrosymmetric (CS) nanomaterial, SHG signals are all derived from surface contributions (SHG = S), while in a NCS nanomaterial, the SHG signal is equal to the sum of the surface contribution and body contribution (SHG = S + B). Here, perovskite-type KNbO<sub>3</sub>, one of the most significant bulk NLO materials with very strong NLO coefficient ( $d_{32}$ =20.5 pm/V, using KH<sub>2</sub>PO<sub>4</sub> (KDP) with  $d_{36} = 0.39$  pm/V for a reference), possessing various polymorphism-the ability of a compound to self-assemble into multiple crystalline structures, was used as model structure for quantitative analysis of the body contribution and surface contribution on SHG response. We demonstrate a simple synthetic strategy for controllable synthesis of three kinds of different structural-symmetry KNbO3 nanomaterials (CS cubic KNbO3 with space group Pm3m, NCS orthorhombic KNbO3 with space group Amm2, and NCS monoclinic KNbO3 with space group Pm), which exhibit smooth exposed surface and similar micron scale (NCS orthorhombic KNbO<sub>3</sub> nanomaterial with a length of ~2.0 µm, CS cubic KNbO<sub>3</sub> nanomaterial with an average width about  $3.5 \,\mu\text{m}$ , NCS monoclinic KNbO<sub>3</sub> nanomaterial with length up to 1.6 µm). Notably, when the size is reduced to tens of nanometers scale, a very strong collective oscillation can be observed, due to the fact that electrons in the conduction band can move more easily from one surface of the particle to the other; thus, size variation of nanomaterials at a nanometer-scale level will have a significant impact on the surface contribution.<sup>S1-S2</sup> Different from the nanometer-scale structure, three kinds of different structure-symmetry KNbO3 nanomaterials with smooth exposed surface possess similar micron scale (NCS orthorhombic KNbO<sub>3</sub> with a length of ~2.0 µm, CS cubic KNbO<sub>3</sub> with an

average width about 3.5 µm and NCS monoclinic KNbO<sub>3</sub> with length up to 1.6 µm), which would show weak collective oscillations from inert electron migration.<sup>S3</sup> Thus, the very small size variations at the micron-scale level have little effect on surface contribution, and we consider that there are the same surface contribution roughly in three KNbO<sub>3</sub> nanomaterial. Therefore, the SHG signal of CS cubic KNbO<sub>3</sub>, NCS orthorhombic KNbO<sub>3</sub> and NCS monoclinic KNbO<sub>3</sub>, can be expressed as follows:  $SHG_{(cubic)} = S_0$ ,  $SHG_{(orthorhombic)} = S_0 + B_1$ ,  $SHG_{(monoclinic)} = S_0 + B_2$ . Subsequently, the three kinds of KNbO<sub>3</sub> samples was illuminated with a commercial *fs*-pulsed Ti:sapphire laser, and SHG intensity of the samples were recorded by a spectrometer at 1064 nm. The results exhibit that NCS monoclinic KNbO<sub>3</sub> possess the strongest SHG efficiency, about twice that of NCS orthorhombic KNbO<sub>3</sub>, while SHG intensity of CS cubic KNbO<sub>3</sub> is the lowest among the three kinds of samples. Due to SHG efficiency of CS cubic KNbO<sub>3</sub> only derived from surface contribution (SHG<sub>(cubic)</sub> =  $S_0$ ), the magnitude of body contribution for NCS orthorhombic KNbO<sub>3</sub> and NCS monoclinic KNbO<sub>3</sub> can be calculate as, SHG<sub>(orthorhombic)</sub>-SHG<sub>(cubic)</sub>, SHG<sub>(monoclinic)</sub>-SHG<sub>(cubic)</sub>, respectively, thus achieving the separable relative contribution of 2.6% and 97.4% in orthorhombic KNbO<sub>3</sub> (corresponding value to the of SHG<sub>(cubic)</sub>/SHG<sub>(orthorhombic)</sub>, [SHG<sub>(orthorhombic)</sub>-SHG<sub>(cubic)</sub>]/SHG<sub>(orthorhombic)</sub>), 1.4% and 98.6% in monoclinic KNbO<sub>3</sub> (corresponding to the value of SHG<sub>(cubic)</sub>/SHG<sub>(monoclinic)</sub>, [SHG<sub>(monoclinic)</sub>-SHG<sub>(cubic)</sub>]/SHG<sub>(monoclinic)</sub>) for surface contribution and body contribution, respectively. The ratio of body contribution and surface contribution in NCS orthorhombic KNbO3 and NCS monoclinic KNbO3, can slao be calculated by [SHG<sub>(orthorhombic)</sub>-SHG<sub>(cubic)</sub>]/SHG<sub>(cubic)</sub>, [SHG<sub>(monoclinic)</sub>-SHG<sub>(cubic)</sub>]/SHG<sub>(cubic)</sub>, respectively, with the numbers of 37.5 and 70.4, respectively.



**Figure S1.** The final three-dimensional structure of (a) cubic phase KNbO<sub>3</sub> (JCPDS No. 32-0822), (b) orthorhombic phase KNbO<sub>3</sub> and (c) monoclinic phase KNbO<sub>3</sub>.

All three kinds of  $KNbO_3$  feature 3D  $[NbO_3]^-$  anionic framework composed of a crystallographically independent  $[NbO_6]$  octahedron containing  $[Nb_4O_4]$  eight-membered squares in the  $[NbO_2]_{\infty}$ -layer-containing bc plane, and with Cs<sup>+</sup> cations serving as the counter cations for charge balance.



**Figure S2.** (a) The corresponding XRD patterns in the JCPDS database card for orthorhombic phase KNbO<sub>3</sub> (JCPDS No. 32-0822), cubic phase KNbO<sub>3</sub> (JCPDS No. 08-0212) and the XRD patterns of monoclinic phase KNbO<sub>3</sub> from the ref. 29. (b) Expanded view of the XRD patterns at  $2\theta = 44-46^{\circ}$  for O-KNbO<sub>3</sub>, C-KNbO<sub>3</sub>, and M-KNbO<sub>3</sub>.

The notable difference between monoclinic, cubic and orthorhombic KNbO<sub>3</sub> is  $2\theta$ -values located at 44-46. For M-KNbO<sub>3</sub>, there are three peaks that are well resolved (200), (002) and (020), respectively. In the case of O-KNbO<sub>3</sub>, two diffraction peaks located at 45.0 and 45.5 are indexed to (220) and (002), and only one peak is well resolved and indexed to (200) in C-KNbO<sub>3</sub>.



Figure S3. O-KNbO<sub>3</sub> NRs and M-KNbO<sub>3</sub> NWs powder in 1.5 mL vial.

The addition of KCl not only promotes the conversion of O-KNbO<sub>3</sub> NRs to M-KNbO<sub>3</sub> NWs, but also greatly increases the yield of M-KNbO<sub>3</sub> NWs (about twice) because KCl power make the reaction more complete.



Figure S4. Synthesis conditions of various KNbO<sub>3</sub> samples.

When  $C_{OH}$  is greater than  $C_{K+}$ , no nanocrystals are obtained irrespective of temperature and reaction time. When  $C_{OH}$  was equal to  $C_{K+}$ , the KNbO<sub>3</sub> was formed with an orthorhombic phase at 150°C for 24 h. Along with the reaction temperature increased to 180°C, cubic phase was formed with the reaction time shortened to 12 h. Notably, the monoclinic phase cannot be obtained under this condition. However, when  $C_{K+}$  is greater than  $C_{OH}$ , the monoclinic phase was obtained at 150°C for 12 h, indicating that an proper concentration of K<sup>+</sup> is essential for the M-KNbO<sub>3</sub> NWs growth.



Figure S5. SEM images of the O-KNbO<sub>3</sub> NRs. Scale bars are 3.5  $\mu$ m (a) and 1.6  $\mu$ m (b), respectively.

The SEM images of O-KNbO<sub>3</sub> NRs clearly show that some micro-sized irregular shaped block-like morphologies have been arranged in a stacking pattern to form rod-like structures, in which the width of the block gradually decreases from the bottom to the top, creating a stair-like effect.



Figure S6. SEM images of the C-KNbO<sub>3</sub> MCs. Scale bars are 5  $\mu$ m (a) and 2.5  $\mu$ m (b), respectively.

At higher temperatures, the O-KNbO<sub>3</sub> NRs can be transformed into another thermodynamic product, i.e., C-KNbO<sub>3</sub> MCs, by supplying sufficient thermal energy, which can be described as the stacking of cubic particles with different sizes. However, a small number of defects were still observed round the corner in the final sample, which also confirmed our supposition about joining of the blocks.



**Figure S7.** TEM images of the M-KNbO<sub>3</sub> NWs prepared at five different concentration ratios of K<sup>+</sup> and OH<sup>-</sup>: (a) 1:1, (b) 1.015:1, (c) 1.03:1, (d) 1.045:1 and (e) 1.06:1. Scale bars are 2  $\mu$ m (a), 2  $\mu$ m (b), 1  $\mu$ m (c), 0.5  $\mu$ m (d), 0.5  $\mu$ m (e), respectively.

The KNbO<sub>3</sub> sample in this work exhibited a tendency to become shorter and thinner with the increase of  $K^+$  concentration, in which with the continued increase in the concentration of  $K^+$ , the length of the sample gradually increases to form the final M-KNbO<sub>3</sub> NWs.



**Figure S8.** a) Schematic diagram of the test device. b) Photograph of the self-made nonlinear optical performance test device.



Figure S9. Schematic of the experimental setup for SHG measurements.

## References

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