Supplementary for:

Electric polarization modulation through continuous phases regulation of $KNbO_3$ nanocrystal at room temperature

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Sample preparation. Niobium pentoxide (Nb_2O_5, ⩾99% purity) and potassium hydroxide (KOH, superior grade) were chosen as starting materials. First, 0.351 g (0.033 mol) of Nb_2O_5 was weighed and fixed as the constant reactant. Aqueous KOH solutions with concentrations of 7.6 – 13.3 mol/L were prepared, corresponding to KOH:Nb_2O_5 molar ratios of 13.30:0.033, 12.33:0.033, 11.44:0.033, 10.48:0.033, 9.50:0.033, 8.58:0.033, and 7.60:0.033. The pre-weighed Nb_2O_5 was added to each KOH solution to form suspensions, which were thoroughly stirred. The suspensions were then transferred into 50 mL Teflon-lined autoclaves, heated at 180℃ for 12 hours, and naturally cooled to room temperature. The resulting $KNbO_3$ powders were collected via centrifugation and purified by ultrasonic cleaning with anhydrous ethanol.

Characterization. XRD measurements were performed using an Ultima IV diffractometer (Rigaku) with Cu Kα radiation (λ=1.5406 Å), covering a 2θ range of 10° - 80° at a step size of 0.02°, for phase composition analysis. Scanning electron microscopy (SEM) observations were conducted on a Thermo Apreo 2C microscope operated at 5 kV to examine sample morphology. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) analyses were carried out using a JEOL JEM-2100F microscope at 200 kV, with SAED patterns indexed via the ICDD PDF-2 database, to resolve atomic-scale structures and crystallographic orientations. Raman spectra were recorded on a LabRAM HR Evolution Micro-Raman spectrometer (HORIBA) in scattering configuration, excited by a laser with λ=473 nm. Second-harmonic generation (SHG) spectra were acquired

in a back-reflection geometry using a homemade femtosecond spectroscopy setup with a 1033 nm excitation laser (pulse width ≈ 80 fs). A 100× Olympus objective was used to focus the beam, and the average incident power was maintained below 0.5 mW. For angle-resolved SHG, both parallel and perpendicular polarization configurations were employed. A polarization analyzer before the detector selected the SHG component parallel or perpendicular to the excitation, while a half-wave plate in the common optical path allowed fine control of the polarization state.

Theoretical calculation. All first-principles calculations were performed using the Vienna Ab initio Simulation Package (VASP)[1]. The electron-ion interactions were described by the projector augmented-wave (PAW) pseudopotential method[2], and the exchange-correlation functional were treated by the Perdew-Burke-Ernzerhof (PBE) under the framework of generalized gradient approximation (GGA)[3]. The energy cutoff was set as 520 eV, and the k-points mesh is generated by specifying the grid density of 8000 per atom using pymatgen[4]. The theoretical models are built based on the structural information of three different crystalline configurations of orthorhombic, monoclinic and tetragonal phase, as shown in Tab. S1. the initial structure for M, O, and T phases are obtained from XRD characterizations, and then those structures are optimized using first principles method as described in the main text. The experimental and theoretical lattice parameters are listed as the following table. The calculated parameters are slightly different with experiments (GGA usually overestimate lattice parameters), the difference is quite small.

Table S1 Lattice parameters for KNbO3

	T	O	M
Experiments	a = 4.007 Å, c = 4.033 Å	a = 5.704(2) Å, b = 3.991(1) Å, c = 5.703(2) Å	a = 4.045(2) Å, b = 3.997(1) Å, c = 4.020(3) Å, β = 90.15(2)°
Calculations	a = 3.995 Å, c = 4.201 Å	a = 5.823 Å, b = 3.984 Å, c = 5.786 Å	a = 4.105 Å, b = 3.983 Å, c = 4.104 Å, β = 90.36°
Relative error	a = -0.29%, c = 4.16%	a = 2.09%, b = -0.18%, c = 1.46%	a = 1.48%, b = -0.35%, c = 2.09%, β = 0.23%

The self-consistent electronic iterations tolerance was set to 1×10^{-7} eV, and the lattice was fully relaxed until the force on each atom was smaller than 0.01 eV/Å. The Berry phase method was applied to calculate the polarization[5]. In this method (taking T phase as an example, as Fig.S1), the ferroelectric and paraelectric phases are required, and nine structures

are then generated by interpolation between the ferroelectric and paraelectric phases. For each phase, the energy and polarization are evaluated using first principles method. Finally, the polarization-energy curve for each phase is obtained.

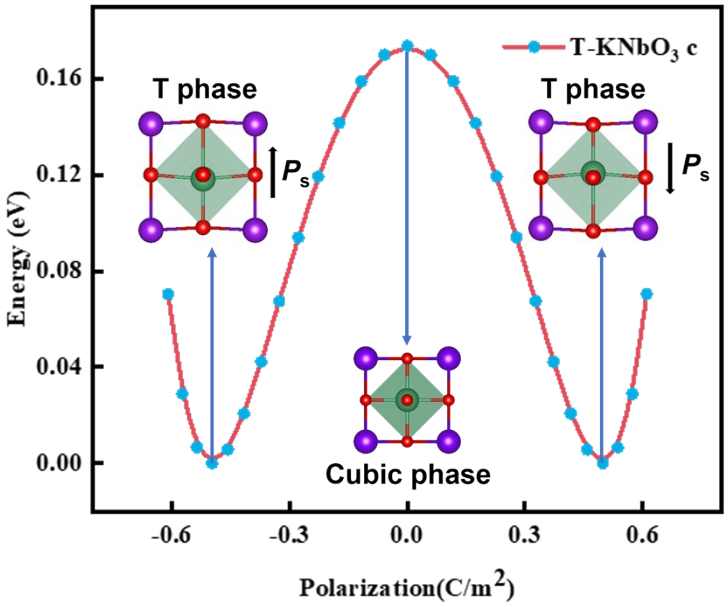

Fig. S1 The Berry phase method of T-$KNbO_3$

SEM images of $KNbO_3$ crystals with varied phases. At the highest KOH: Nb_2O_5 molar ratio (13.30 mol:0.033 mol), the sample exhibits a mixed morphology consisting of 1-3 μm bulk particles and 200 nm short nanowires (Fig. S2a). This phenomenon stems from sharply elevated local solution supersaturation due to excessively high OH^- concentration: high supersaturation triggers instantaneous nucleation, facilitating the formation of bulk particles (thermodynamically favored for the high-symmetry tetragonal phase). Meanwhile, ion depletion in surrounding regions causes delayed nucleation and growth, yielding short nanowires. With the KOH: Nb_2O_5 molar ratio reduced to 11.44 mol:0.033 mol (Fig. S2b) and 10.48 mol:0.033 mol (Fig. S2c), the sample transforms into high-aspect-ratio nanowires. Moderately high OH- concentration preserves adequate ion mobility, favoring [001]-directional growth while preventing excessive supersaturation and suppressing bulk particle formation. Upon further reducing the KOH: Nb_2O_5 molar ratio to 9.50 mol:0.033 mol (Fig. S2d) and 8.58 mol:0.033 mol (Fig. S2e), the sample evolves into short nanowire assemblies. At the low molar ratio (7.60 mol:0.033 mol), the sample displays irregular agglomerated particles with a size distribution centered at ~500 nm (Fig. S2f).

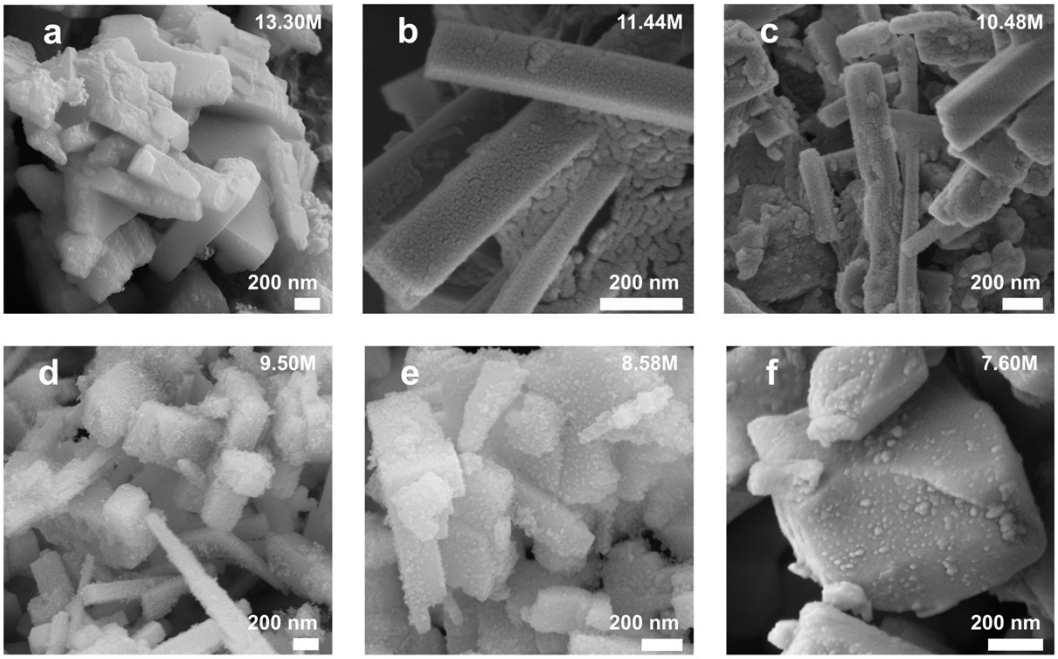

Fig. S2 SEM images of as-grown $KNbO_3$. (a) - (f) The morphology of samples preparing at KOH concentrations of 13.30 M, 11.44 M, 10.48 M, 9.50 M, 8.58 M, and 7.60 M, respectively.

References

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