

Electronic supplementary information (ESI)

Lithium Niobate Particles with a Tunable Diameter and Porosity for Optical Second Harmonic Generation

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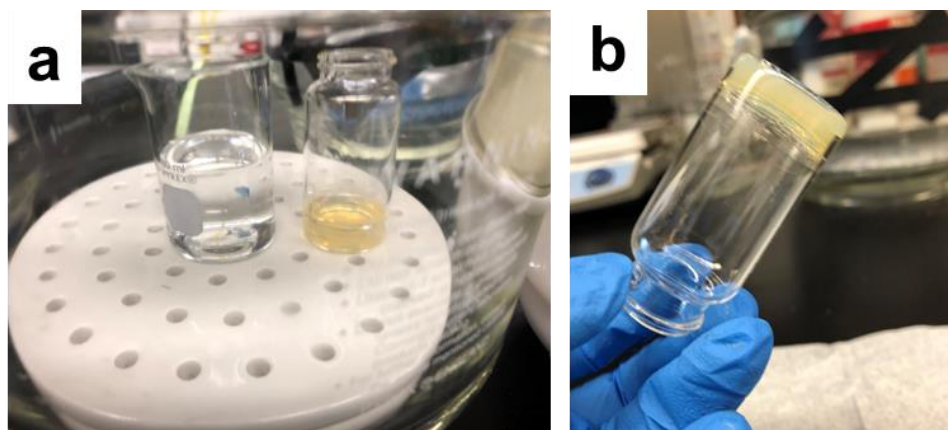


Fig. S1 Optical images depicting the process of gelation of the precursor under a humid atmosphere. The precursor solution was prepared by dissolving niobium-n-butoxide (Bu-Nb) in ethanol, and the resulting solution was aged for 72 h in a sealed desiccator containing an open source of water held in a beaker (clear solution in a). This process resulted in the formation of a gel-like precursor (yellow solution in a and b), which was subsequently mixed with an aqueous solution of 0.1 M lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$) to prepare a sol solution.

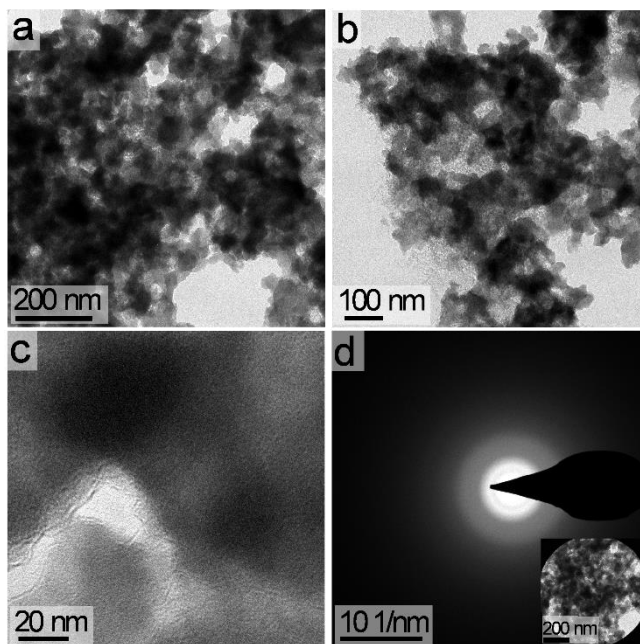


Fig. S2 Components of the sol solution prepared from the hydrolysis of the precursor as characterized by: (a, b) transmission electron microscopy (TEM); (c) high-resolution TEM (HRTEM); and (d) selected area electron diffraction (SAED). The inset TEM image in (d) depicts the region of the sample from which the SAED was collected for this analysis.

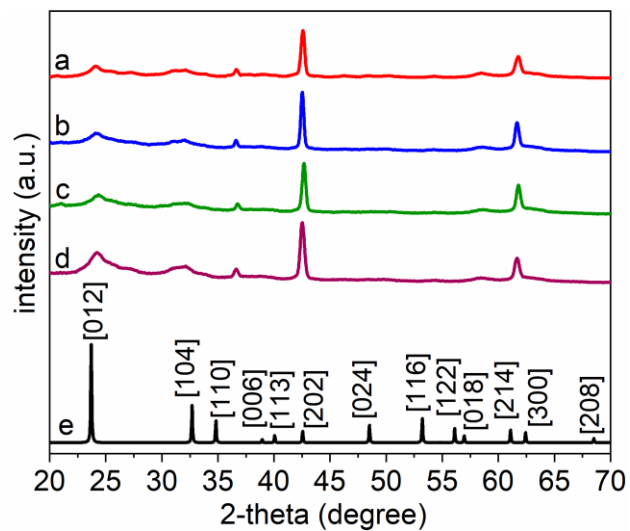


Fig. S3 Powder X-ray diffraction (XRD) patterns of pristine lithium niobate (LiNbO_3) particles obtained after a hydrothermal reaction time of: (a) 24 h; (b) 48 h; (c) 72 h; and (d) 96 h. Also included are XRD patterns for (e) a reported LiNbO_3 reference (ICSD No. 28294).

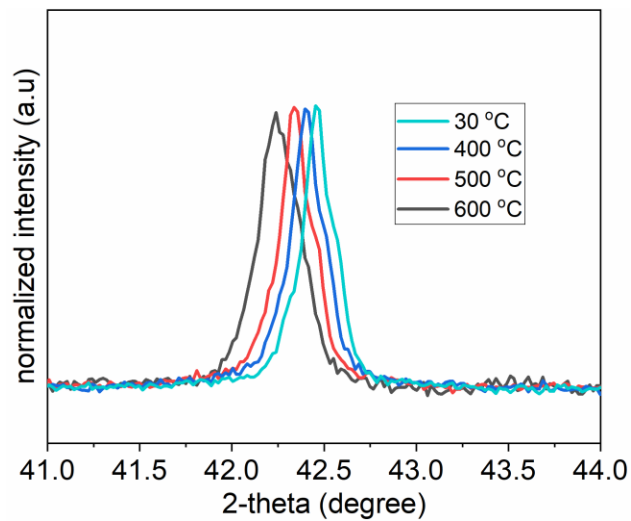


Fig. S4 Temperature-dependent XRD patterns of LiNbO₃ particles at 2-theta values from 41° to 44°, indicating a shift toward lower 2-theta values with an increase in temperature. This shift represents a change in the crystallinity of the sample and an evolution of the (202) peak of LiNbO₃.

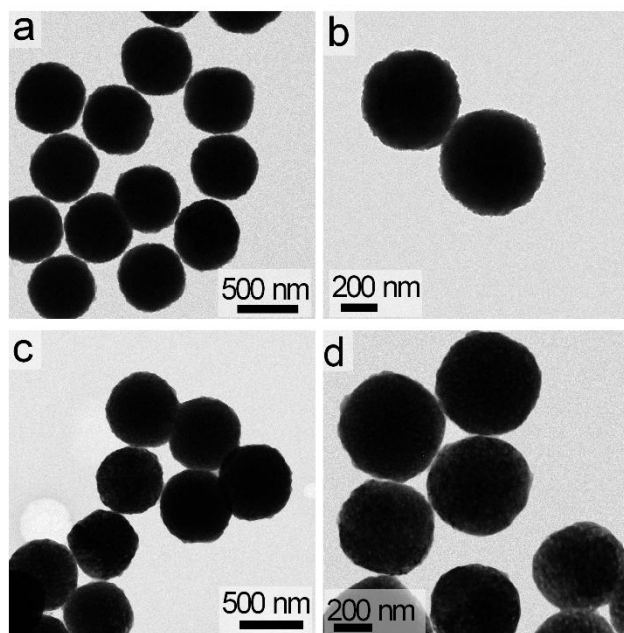


Fig. S5 The TEM analyses of LiNbO_3 particles obtained after 24 h of hydrothermal treatment: (a, b) before calcination; and (c, d) after calcination at 600 °C.

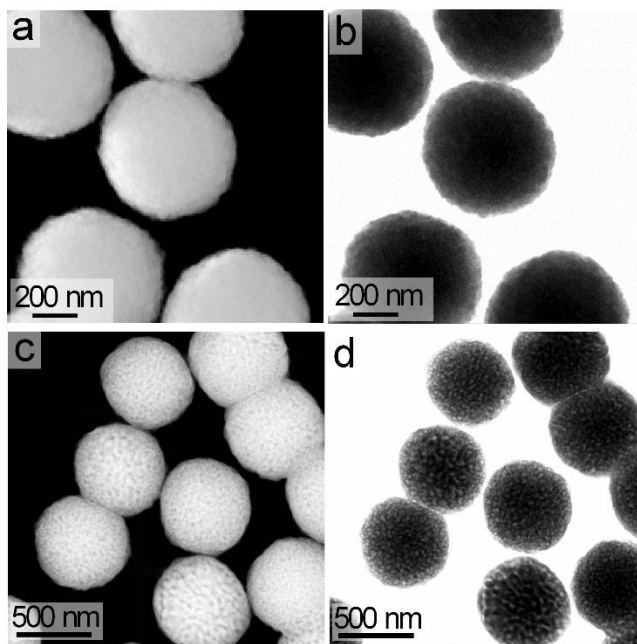


Fig. S6 Scanning transmission electron microscopy (STEM) analyses of LiNbO_3 particles obtained after 24 h for hydrothermal treatment: (a, b) before calcination; and (c, d) after calcination at 600 °C. The Fig. contains high-angle annular dark-field (HAADF) STEM images (a, c), and bright-field STEM images (b, d).

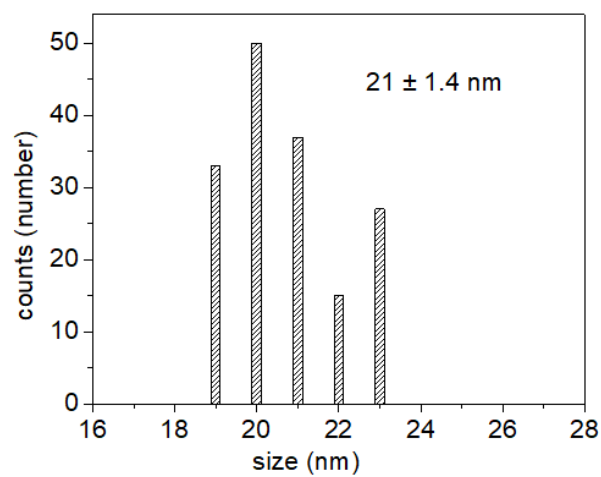


Fig. S7 Histogram of the diameter of the pores measured within calcined LiNbO_3 particles. The mean size of these pores was 21 nm as determined from 162 independent pores within the particles. The variance of 1.4 nm is reported as one standard deviation from the calculated mean value.

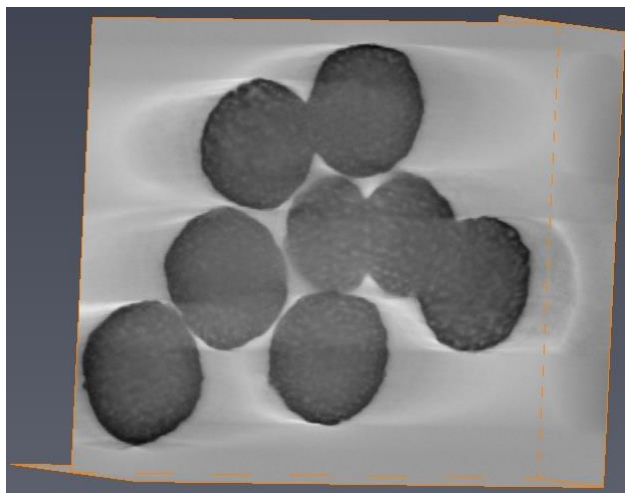


Fig. S8 Reconstructed and rendered STEM tomogram of LiNbO_3 particles obtained after their calcination at $600\text{ }^\circ\text{C}$, which indicated a mesoporous structure throughout these particles. Data were acquired using the FEI Tecnai Osiris using the FEI Xplore3D and Inspect3D acquisition, post-alignment, and reconstruction software packages.

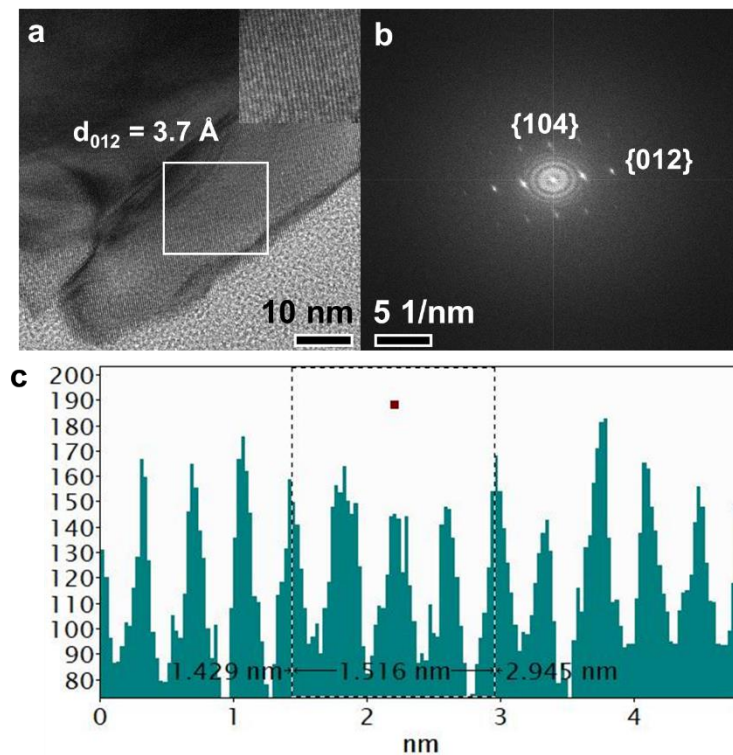


Fig. S9 Mesoporous LiNbO_3 particles as characterized by (a) HRTEM showing the crystalline nature of the particles. (b) Analysis of the inset HRTEM image by a fast Fourier transformation (FFT) indicated the presence of $\{012\}$ and $\{104\}$ facets. (c) A detailed analysis of the d -spacings observed within the HRTEM image. These analyses further confirmed the crystallinity of the particles.

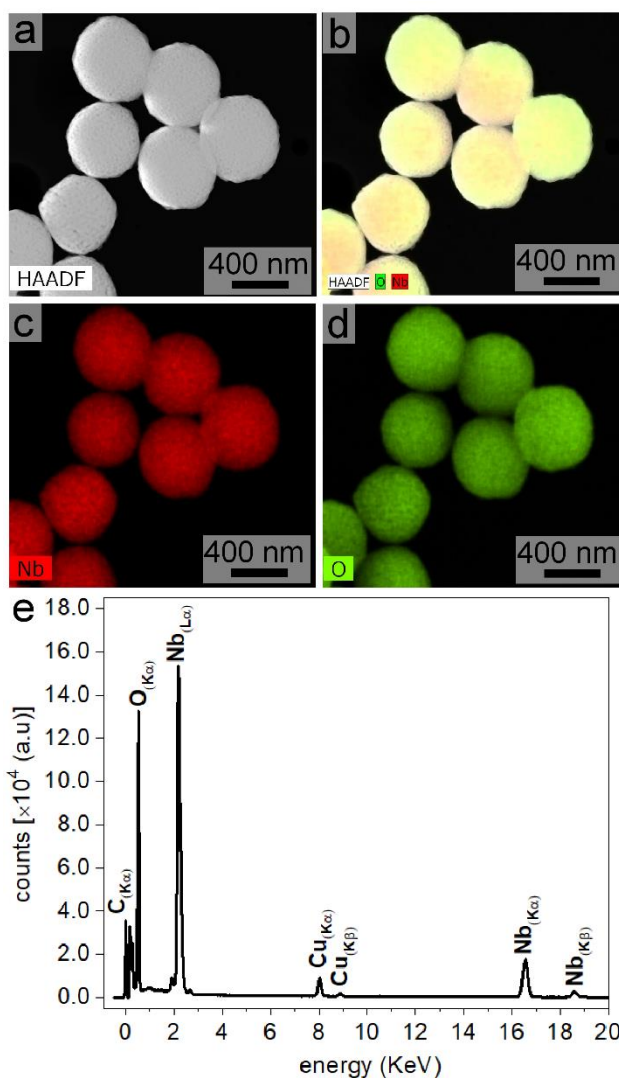


Fig. S10 (a) A representative HAADF-STEM image of the products from a 24 h hydrothermal treatment of the precursors and calcination of the resulting particles at 600 °C. (b-d) Elemental maps of these particles obtained by energy-dispersive X-ray spectroscopy (EDS). (b) The distribution of Nb and O within each particle, overlaid upon the HAADF image. The dispersion of (c) Nb and (d) O species within the sample indicate a uniform distribution of these species in the particles. (e) A typical EDS spectrum corresponding to the particles, which indicated the presence of Nb and O in the product. The C and Cu contributions were from the TEM grids supporting the sample.

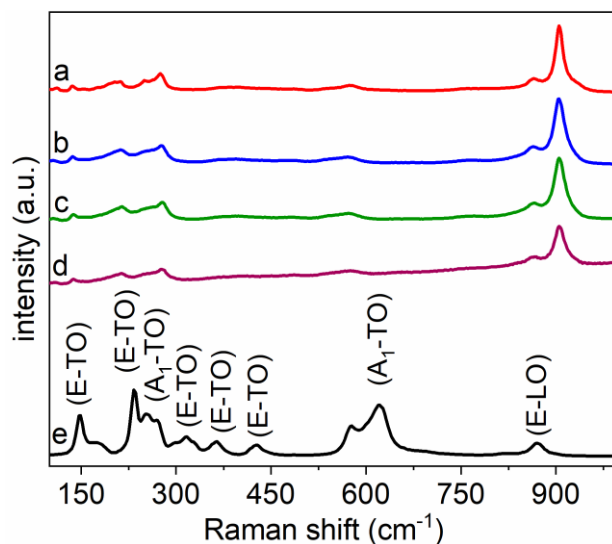


Fig. S11 Analyses by Raman spectroscopy of pristine LiNbO_3 particles obtained after a reaction time of: (a) 24 h; (b) 48 h; (c) 72 h; and (d) 96 h. (e) Data are also included for a commercial LiNbO_3 powder for comparison with the as-prepared products. The maximum peak intensity within each spectrum was used to normalize the data for ease of comparison.

Table S1. Bond vibrations associated with the Raman spectral bands of LiNbO₃.

wavenumber (cm ⁻¹)	vibrations
~150	Nb-O vibrations
~260	δ (Li-O + LiO ₆)
~225 and ~334	NbO ₆ deformations
~375 and ~430	δ (Nb-O-Nb)
~620	ν_s (NbO ₆)
~870	ν_{as} (Nb-O-Nb)
~900	ν (Nb=O)

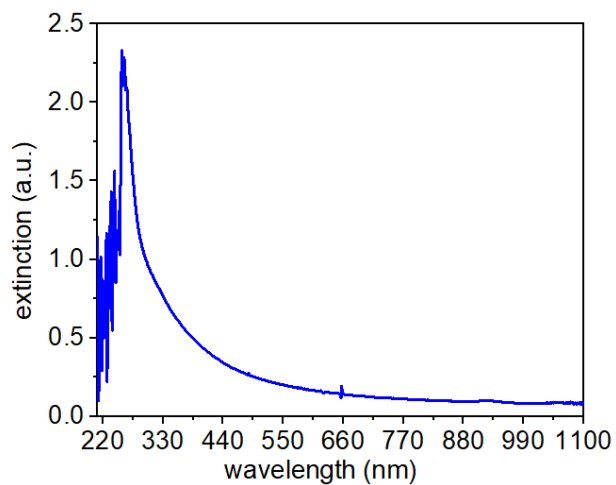


Fig. S12 An extinction spectrum across ultraviolet (UV)-visible wavelengths for an aqueous suspension of mesoporous LiNbO₃ particles. These porous particles were obtained by calcination of the products prepared after hydrothermal treatment of the precursors for 24 h. This spectrum indicates the optical transparency of the suspension of particles from > 300 to 1,100 nm. The peak observed at ~260 nm is attributed to light scattered from the suspended particles.¹

References

- 1 Y. Furukawa, K. Kitamura, A. Alexandrovski, R. K. Route, M. M. Fejer and G. Foulon, *Appl. Phys. Lett.*, 2001, **78**, 1970–1972.