

Supporting Information

PbTiO₃ Nanofibers with Edge-Shared TiO₆ Octahedra

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Materials and methods

Preparation: chemistry grade tetrabutyl titanate ($(C_4H_9O)_4Ti$) and lead nitrate $Pb(NO_3)_2$ were used as the starting materials, potassium hydroxide (KOH) was added as mineralizer, polyvinyl alcohol (PVA) and poly (acrylic acid) (PAA), and poly (ethylene glycol) (PEG) as additives. Deionized water was used to make all aqueous solutions in the preparation. Titanium was added in the form of precipitated hydroxide $TiO(OH)_2$ (abbr. TOH). $(C_4H_9O)_4Ti$ was dissolved in deionized ethanol to form 0.1 M Ti^{4+} solution, which was then introduced to a 0.15M ammonia solution under stirring condition to obtain precipitated TOH. For eliminating ammonium ions, the TOH precipitate was filtered and washed with deionized water six times. The as-prepared TOH precipitates were then dispersed in deionized water again under vigorous stirring. During stirring $Pb(NO_3)_2$, KOH pellets and polymer solution containing PVA, PEG and PAA were added. In the final suspension, the concentration of TOH and $Pb(NO_3)_2$ is the same of 0.1M, the KOH concentration 2M and PVA concentration $0.8g \cdot L^{-1}$, and the weight ratio of PAA to PVA (PEG) of 12.5:1 (10:1). The feedstock prepared above was charged into a 50 ml Teflon-lined stainless-steel autoclave. The hydrothermal treatment was performed by moving the autoclave into an oven and kept it at 200°C for 12 hrs, and then cooled to room temperature in air naturally. The products were filtered and washed several times with distilled water and absolute ethanol, and finally oven dried in air at 60°C for 24 hrs, resulting in the formation of white powders.

Characterization: X-ray powder diffraction patterns were collected at 300 K on Thermo ARL X'TRA powder diffractometer with Bragg-Brentano geometry by $Cu K_\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) under 0.82 \AA resolution. High sensitivity, low intrinsic noise and superior resolution were ensured by equipment of the Peltier cooled Si (Li) solid state detector. For structural analysis we used the XRD pattern recorded in the scanning-step mode with a step size 0.02 deg and 5s/step. To solve and refine crystal structure the MAUD programs was used. The neutron diffraction data of the sample was collected on the GEM diffractometer at the ISIS facility (U. K.) for $\frac{1}{2}$ h in

vanadium can with 6 mm inner diameter. The sample was not packed but only poured into the can. Rietveld refinement analyses of the neutron diffraction pattern was carried out using GSSA Program. Scanning electron microscope (SEM) images were collected by field emission Hitachi field emission SEM MODEL S-4800 equipped with an EDX detector. Transmission electron microscope images were collected by TEM (JEOL JEM-200CX, Japan, using an accelerating voltage of 160kV). HRTEM images and SEAD patterns were taken by JEOL 4000EX operated at 400kV (using a double-tilt holder) and JEOL-2010 using an accelerating voltage of 200kV (using a double-tilt holder). The sample was dispersed in absolute ethanol solution, and a drop of liquid was placed onto the Cu grid covered by carbon film and left under ambient conditions until all ethanol was evaporated. The cross-section TEM samples were made by embedding the nanofibers in epoxy resin and thereafter sliced by a microtome to a thickness of about 100nm. The thin slices were put on a Cu grid for TEM investigation.

Simulations: Electronic structure of pre-perovskite PbTiO_3 was calculated by a first-principles density-function method within the local density approximation. The extended norm-conserving pseudopotentials are used for all atoms, considering Pb(5d, 6s, 6p), Ti(3s, 3p, 3d, 4s) and O(2s, 2p) orbits expended using plane waves with a cutoff energy of 45 Hartree. A Monkhorst-Pack's mesh, considering a 21- k -point grid, is employed to perform the integration in the reciprocal space. The calculation was performed at computer SGI Onyx 3900 under *ABINIT* code a primitive cell containing 4 molecules.

Table S1 Fractional coordinates and refined bond lengths for the new structure of PbTiO₃ based on step-scanning X-ray diffraction data and neutron diffraction.

	Crystal system: Tetragonal			Space group: I/4m(No.87)		
	X-ray diffraction			Neutron diffraction		
	a=b= 12.3584(8) Å	c= 3.8117(5) Å		a=b=12.3668(5)Å	c=3.8084(1) Å	
	x	y	z	x	y	z
Pb(8h)	0.1645(96)	0.15024(12)	0.5	0.16504(24)	0.1517(33)	0.5
Ti(8h)	0.47163(55)	0.14315(19)	0.5	0.47112(76)	0.14273(59)	0.5
O1(8h)	0.60125(87)	0.02934(19)	0.5	0.60590(43)	0.02820(38)	0.5
O2(8h)	0.16483(17)	0.2913(76)	0	0.16977(39)	0.28997(46)	0
O3(8h)	0.54901(73)	0.25132(68)	0.5	0.54341(3)	0.26036(40)	0.5
Bond distance(Å)	Average			Average		
Ti-O	1.6437,1.8709,1.950(×2),2.1317,2.3141		1.9851	1.644, 1.871, 1.973(×2), 2.132, 2.316		2.01
Pb-O	2.2295, 2.5060(×2), 2.5829(×2)		2.4815	2.166, 2.504(×2), 2.560(×2)		2.4732

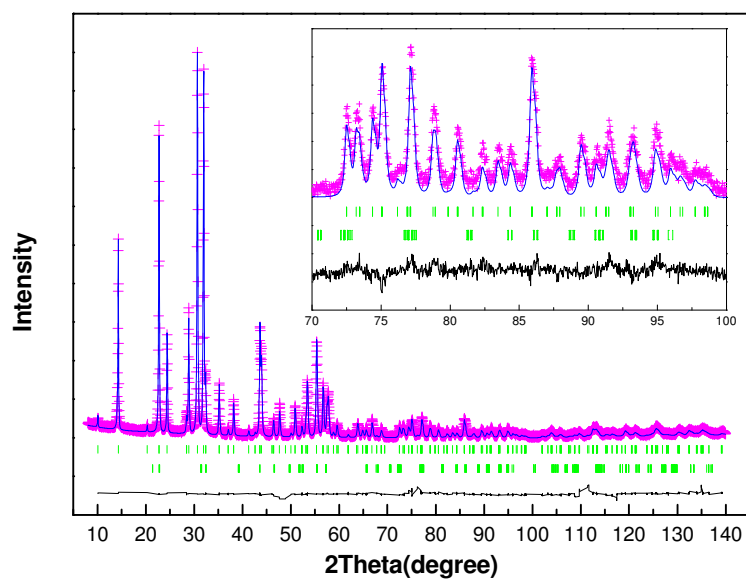


Fig. S1 Observed (blue solid line), calculated (red crosses) X-ray diffraction intensities of the new structured PbTiO₃ using I4/m space group at room temperature. The structure was refined by rietveld method. In the final refinement, R_{wp} = 0.058, R_p = 0.0119. The lower plot represents the difference between observed and calculated intensities. Short vertical lines show the Bragg peak positions of the pre-perovskite phase (upper) and normal perovskite phase of PbTiO₃ (lower). Inset shows enlarged part of the pattern between 70°-100°.

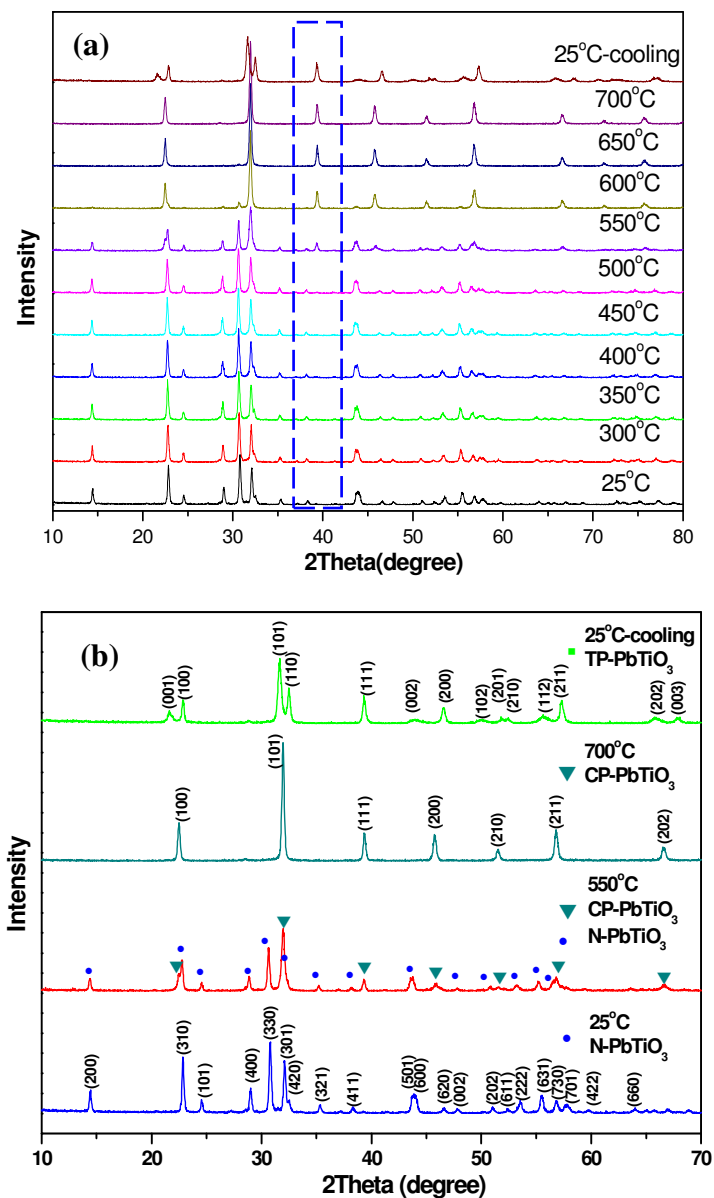


Fig. S2 (a) *in-situ* XRD patterns of pre-perovskite PbTiO_3 nanofibers at different temperatures. (b) indexed XRD patterns at several temperatures deriving from Fig. S2a. New structured PbTiO_3 : N- PbTiO_3 ; Cubic perovskite PbTiO_3 : CP- PbTiO_3 ; Tetragonal perovskite PbTiO_3 : TP- PbTiO_3 .

The heating treatments are as follows: 25°C-550°C (5°C/min); 550°C-650°C (2°C/min); and 650°C-700°C (10°C/min). At each temperature, XRD data were recorded. In-situ XRD patterns of new structured PbTiO_3 nanofibers are shown in Fig. S2a. Below 500°C, no phase transition was observed for new structured PbTiO_3 nanofibers in Fig. S2a. At 550°C, obvious and new diffraction peaks grow in the XRD pattern, compared to that at 500°C, which is emphasized by a rectangular frame (dot line) in Fig. S2a. At 700°C (Fig. S2b), another phase was obtained, which can be indexed into a normal perovskite PbTiO_3 with cubic structure ($a=3.97\text{\AA}$, space group: Pm-3m, Ref. 9 in the text). When temperature decreasing to 25°C again (Fig. S2b), this cubic PbTiO_3 transforms into a typical tetragonal perovskite PbTiO_3 ($a=3.90\text{\AA}$, $c=4.15\text{\AA}$, space group: P4mm, Ref. 9 in the text).

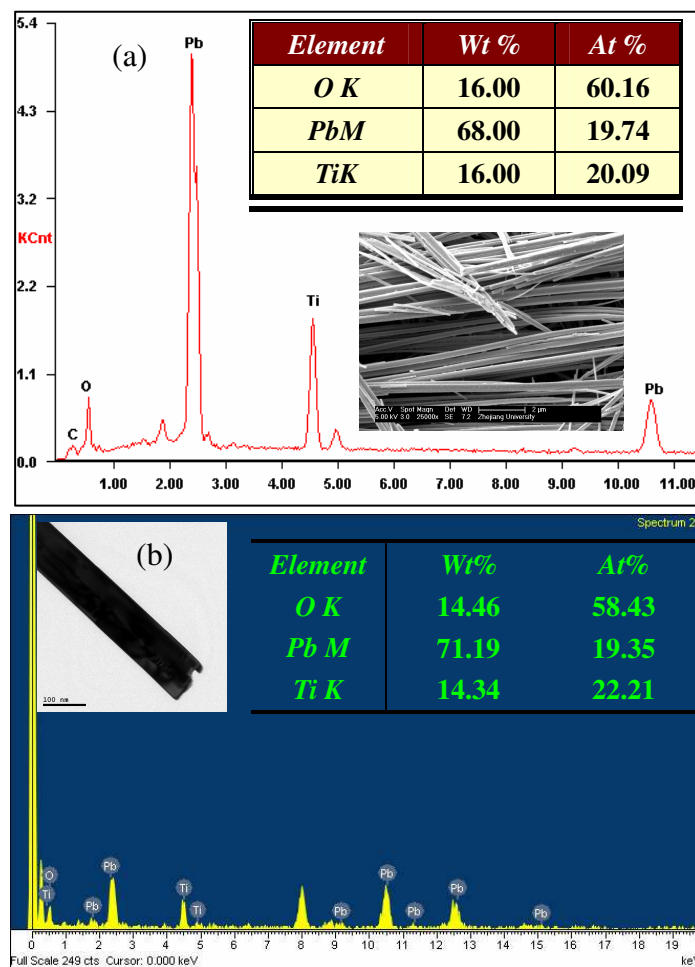


Fig.S3 (a) Energy dispersive spectroscopy of x-rays (EDX) collection of the new structure PbTiO_3 nanofibers using SEM. Insets show a SEM image of the nanofibers and corresponding element analysis. (b) EDX spectroscopy of the new structure PbTiO_3 nanofibers using TEM. Insets show a single nanofiber and corresponding element analysis.

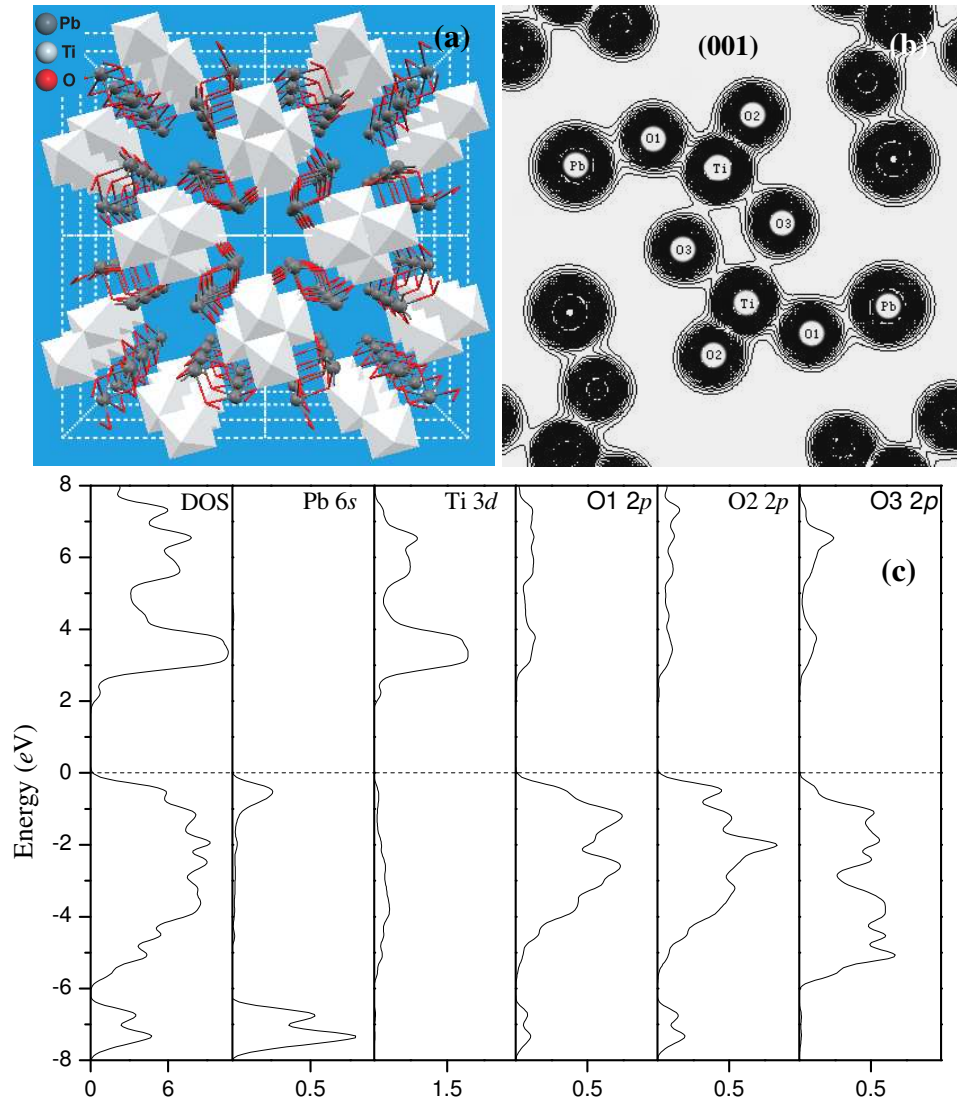


Fig. S4. (a) crystal structure of the new structured PbTiO₃ viewed along c axis. (b) the electron density distributions on the (001) plane of pre-perovskite PbTiO₃. (c) the partial density of states (PDOS) of the pre-perovskite PbTiO₃. Lowest contour is 0.04e/Bohr³ and interval is 0.02e/Bohr³.