Supplementary Information: Crystal-crystal phase transformation via surface-induced virtual pre-melting

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Movie S1. Large change in shape of the sample from rod to cube during heating at 600°C. This video was recorded about 1 min.

In-situ XRD investigation. In-situ XRD patterns of pre-perovskite PbTiO\textsubscript{3} nanofibers are shown in Fig. S1. Below 500°C, no phase transition has been observed for pre-perovskite PbTiO\textsubscript{3} nanofibers from Fig. S1a. 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. S1a. At 700°C (Fig. S1b), another phase has been obtained, which can be indexed into a conventional perovskite PbTiO\textsubscript{3} with cubic structure (a=3.97Å, space group: Pm-3m) (Glazer A.M., Mabud S.A. Powder profile refinement of lead zirconate titanate at several temperatures. II. Pure PbTiO\textsubscript{3}. *Acta Cryst.* B 1978, 34, 1065-1070). When temperature decreasing to 25°C again (Fig. S1b), this cubic PbTiO\textsubscript{3} transforms into a typical tetragonal perovskite PbTiO\textsubscript{3} (a=3.90Å, c=4.15 Å, space group: P4mm).
Fig. S1  (a) In-situ XRD patterns of pre-perovskite PbTiO₃ nanofibers at different temperature. (b) Indexed XRD patterns at several temperature points deriving from Fig. S1a. Pre-perovskite PbTiO₃: PP-PbTiO₃; Cubic perovskite PbTiO₃: CP-PbTiO₃; Tetragonal perovskite PbTiO₃: TP-PbTiO₃.
Fig. S2 *In-situ* TEM investigation of perovskite PbTiO$_3$ nanocrystals after phase transformation of pre-perovskite PbTiO$_3$ nanofibers at 600°C: (a) TEM image of perovskite PbTiO$_3$ nanocrystals; (b) and (c) Selected area electron diffraction pattern and HRTEM image of a PbTiO$_3$ nanocrystal as arrow points in Fig. S2a. These results confirm that the nanocrystals are single-crystal in nature, which can indexed into a conventional cubic structure (a=3.97Å, space group: Pm-3m) (3).
Fig. S3 XRD patterns of the pre-perovskite PbTiO\textsubscript{3} nanofibers after annealing in air for different time at 650°C. Note that the annealed sample for 10min at 650°C was quickly quenched to room temperature. The sample consists of PP and perovskite PbTiO\textsubscript{3} phase after 10min annealing and quick cooling to room temperature, while PbTiO\textsubscript{3} nanofibers adopt single tetragonal perovksite structure when the heating time is up to 30min and above.
Fig. S4 XRD patterns of the pre-perovskite PbTiO$_3$ nanofibers after annealing in air for different time at 800°C. The annealed sample after 5min annealing at 800°C was quickly quenched to room temperature. After heated in air for 5min at 800°C, the PP nanofibers almost transform into perovskite ones, and in particular, the regular morphology of the nanofibers basically keep.
**Fig. S5** SEM images of the samples prepared at different conditions: (a) as-prepared by hydrothermal method; (b) annealed in air for 10 min at 650°C, and then quickly quenched to room temperature; (c) annealed in air for 60 min at 650°C and (d) annealed in air for 5 min at 800°C, and then quickly quenched to room temperature.