Supporting Information:

Novel lead-free ferroelectric film by ultra-small $Ba_{0.8}Sr_{0.2}TiO_3$ nanocubes assembly for large electrocaloric effect

Ran Su,[1] Dawei Zhang,[1] Yang Liu, [2] Jiangbo Lu,[3] Zhipeng Wang,[1] Linglong Li,[1] Jihong Bian,[1] Ming Wu,[1] Xiaojie Lou,[1] Yaodong Yang[*,1 a)]*

[1]Frontier Institute of Science and Technology, State Key Laboratory for Mechanical behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China

[2]Laboratoire Structures, Propriétés et Modélisation des Solides, CentraleSupélec, CNRS-UMR8580, Université Paris-Saclay, Grande Voie des Vignes, Châtenay-Malabry Cedex 92295, France

[3]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China

yaodongy@mail.xjtu.edu.cn

Experimental section

Materials. $Ba(NO_3)_2$, $Sr(NO_3)_2$, tetrabuty titanate ($Ti(Bu)_4$), NaOH, 1-butanol solution, oleylamine, oleic acid, toluene, ethanol, ethyl acetate and acetonitrile were purchased from Shanghai Chemical Crop. All chemicals were used as received without further purification. Deionized water was used for all experiments.

Methods.

Synthesis of $Ba_{0.8}Sr_{0.2}TiO_3$ nanoparticles. $Ba_{0.8}Ti_{0.2}O_3$ nanocubes were synthesized using a hydrothemal reaction. 10 ml of aqueous solution containing 1.6 mmol $Ba(NO_3)_2$, 0.4 mmol $Sr(NO_3)_2$ and 10 mmol NaOH, 3.6 ml oleic acid, 1.8 ml oleylamine and 20 ml of 1-butanol solution containing 2 mmol $Ti(Bu)_4$ were added to a 50ml autoclave tube under agitation. The system was sealed and treated at the 120 ^oC for 18 h. After the reaction was cooled to room temperature, the products were collected by centrifugation with ethanol and were dispersed in toluene yielding a stable milky colloidal solution.

Assembly of $Ba_{0.8}Sr_{0.2}TiO_3$ films. The substrates ($Si/SiO_2/Ti/Pt$) were first cleaned twice in acetone via sonication for 15 min. Then the substrates treated with UV light for 15 min. The BST nanocubes (20mg/ml) dispersion in toluene was spin-coated onto the substrate at 3,000 rpm for 30 s. To increase the film thickness, the films were prepared in 3 steps, and each layer was 300^oC-treated after deposition. Finally, BST films were annealed at 1000 ^oC for 30min in rapid annealing furnace and then slow annealed at 800^oC for 1h in a tube furnace.

Characterization. The crystal phase of the as-prepared $Ba_{0.8}Sr_{0.2}TiO_3$ and the assembled $Ba_{0.8}Sr_{0.2}TiO_3$ film were determined by powder X-ray diffractometry (XRD, Shimadzu 7000) with a Cu Ka (0.15418nm) source. The morphology of the as-prepared $Ba_{0.8}Sr_{0.2}TiO_3$ and the assembled $Ba_{0.8}Sr_{0.2}TiO_3$ film were examined using transmission electron microscopy (TEM, JEOL 2100) at an acceleration voltage of 200 kV. The piezoelectric properties of the assembled $Ba_{0.8}Sr_{0.2}TiO_3$ film were investigated by an atomic force microscope (AFM, Cypher, Asylum Research). The surface morphology of the assembled $Ba_{0.8}Sr_{0.2}TiO_3$ film was examined using transmission electron microscopy (SEM, JEOL 2100)

Ferroelectric measurements. Temperature-dependent dielectric permittivity constant and loss were measured using an Agilent4980A LCR meter with a frequency range from 100 Hz to 1 MHz at 1 V_{rms} with a parallel equivalent circuit. The *D-E* loops of the assembled $Ba_{0.8}Sr_{0.2}TiO_3$ film were measured by a Sawyer-Tower circuit (Radiant Workstation).

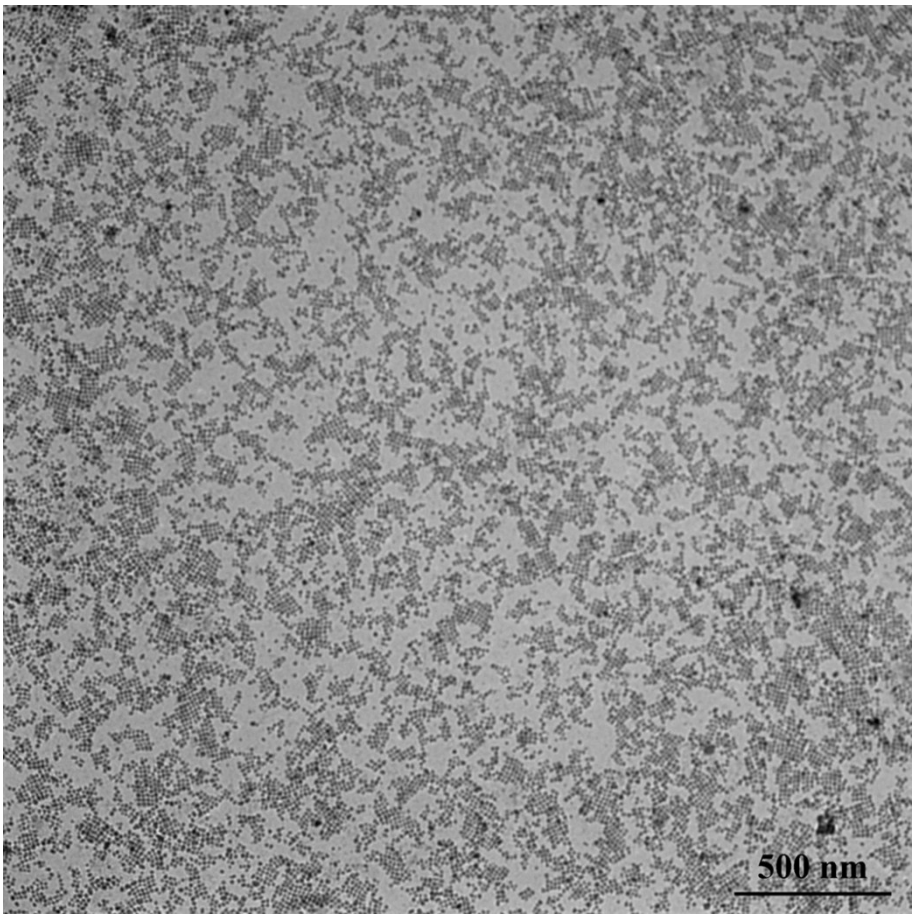

Figure S1. Low-magnification TEM image of $Ba_{0.8}Sr_{0.2}TiO_3$ nanocubes.

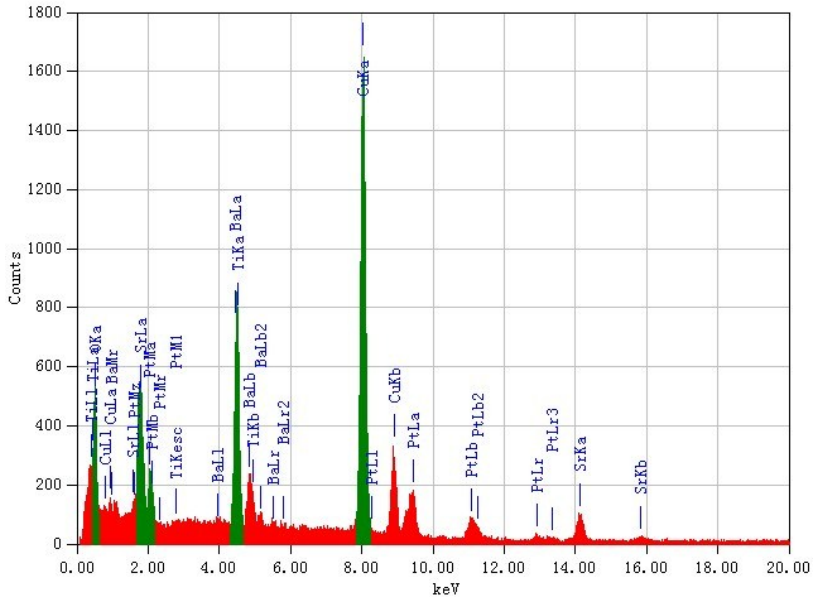

Figure S2. EDS examinations of $Ba_{0.8}Sr_{0.2}TiO_3$ nanocubes (Ba:Sr≈4.464:1.106).

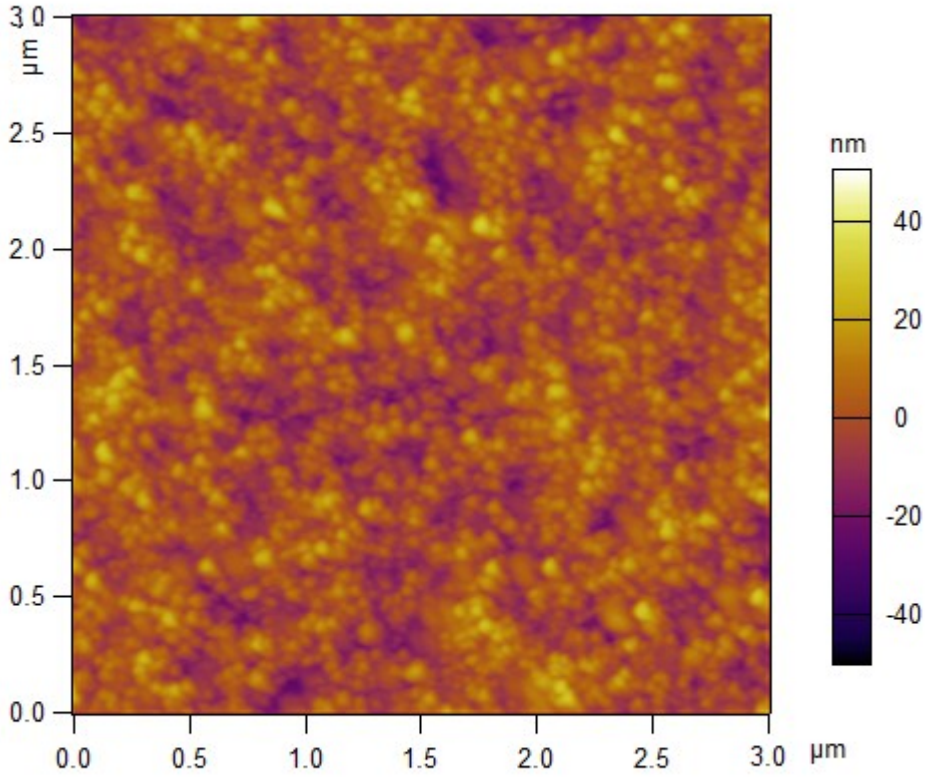

Figure S3. Low-magnification AFM image of the assembled $Ba_{0.8}Sr_{0.2}TiO_3$ film.

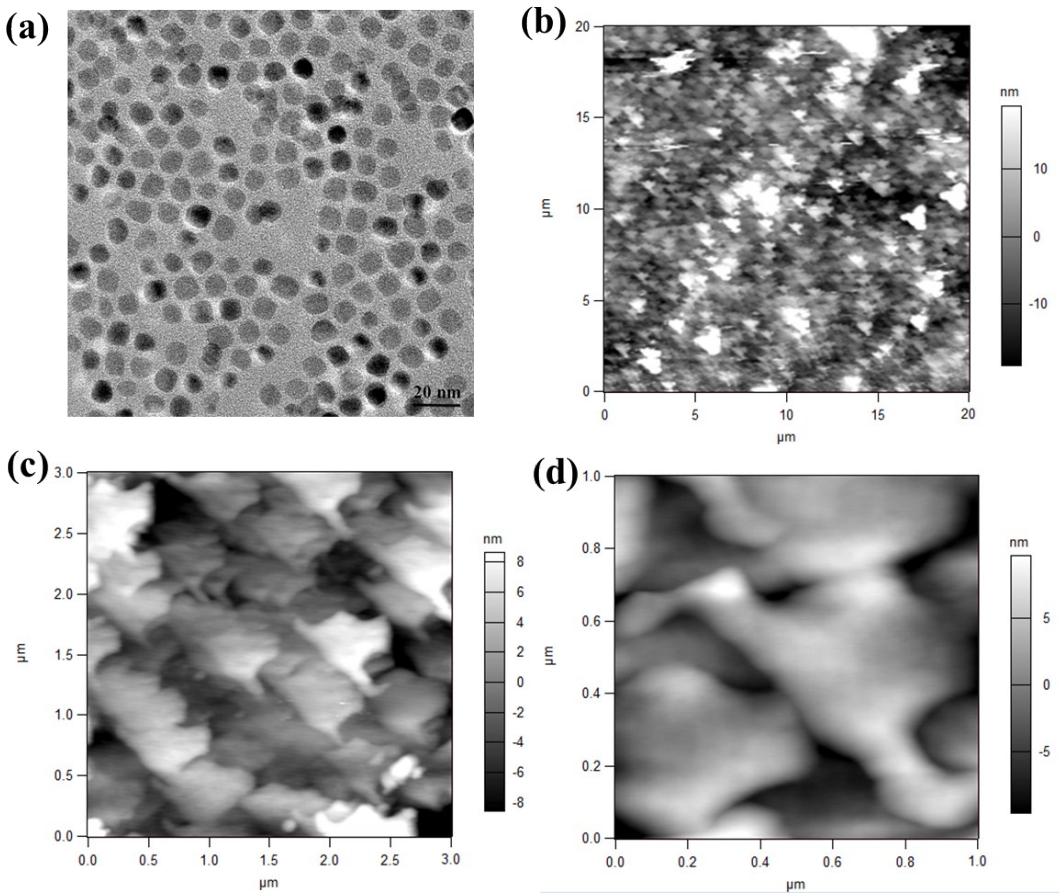

Figure S4. AFM images of the assembled film by $Ba_{0.8}Sr_{0.2}TiO_3$ nanospheres.

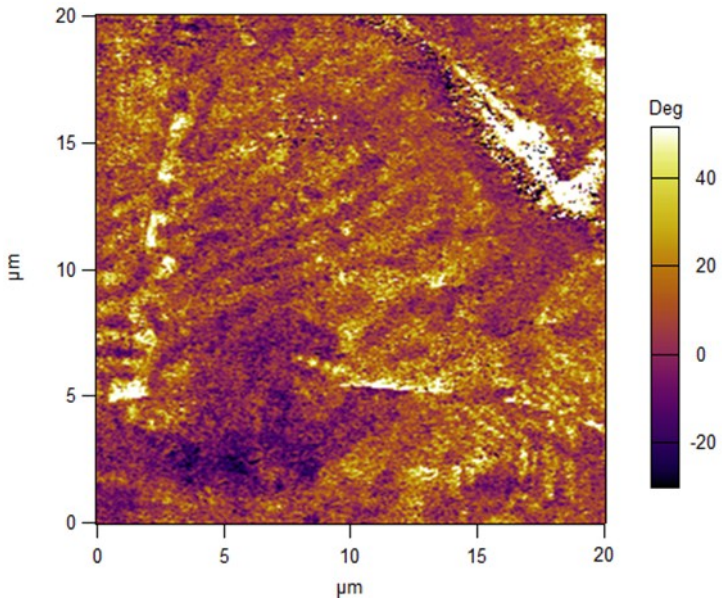

Figure S5. PFM phase images of $Ba_{0.8}Sr_{0.2}TiO_3$ ceramic exhibiting ferroelectric domains.

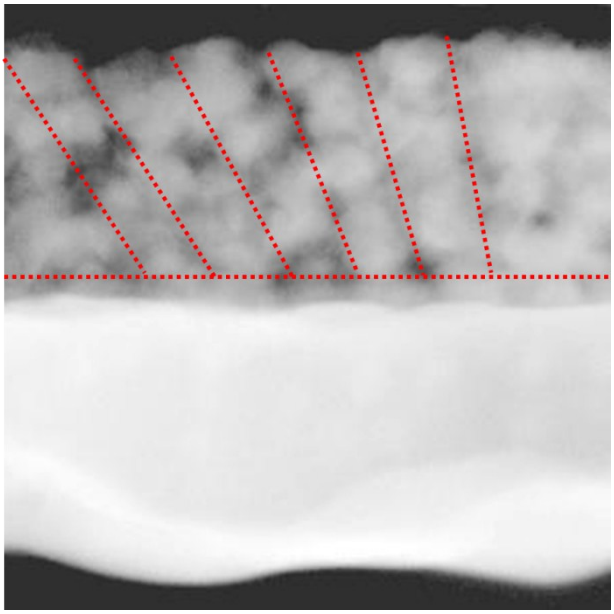

Figure S6. Low-magnification TEM image of the $Ba_{0.8}Sr_{0.2}TiO_3$ assembled film.

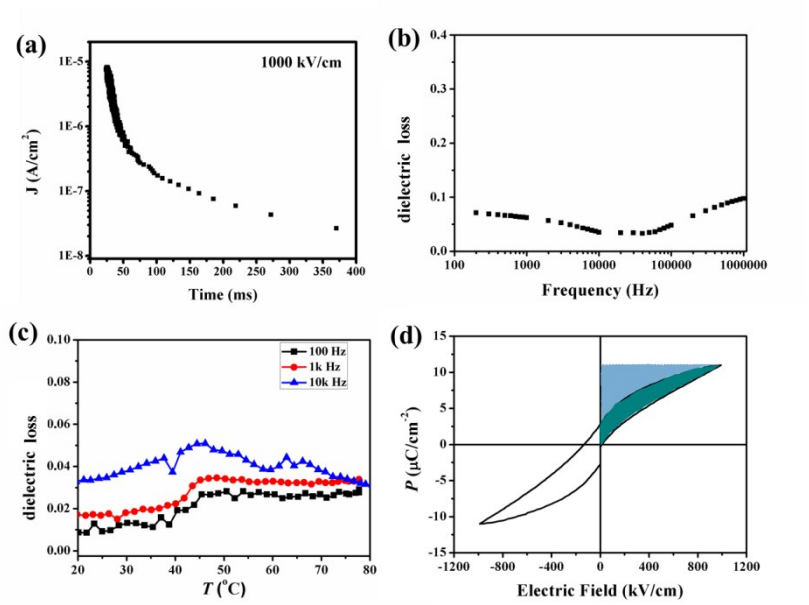

Figure S7. (a) Dielectric relaxation current of the assembled $Ba_{0.8}Sr_{0.2}TiO_3$ film. (b) Room temperature frequency-dependent dielectric loss of the $Ba_{0.8}Sr_{0.2}TiO_3$ assembled film. (c) The temperature-dependent dielectric loss of the $Ba_{0.8}Sr_{0.2}TiO_3$ assembled film. (d) The energy storage efficiency is evaluated by polarization-electric field loop (*P*-*E* loop) of the assembled $Ba_{0.8}Sr_{0.2}TiO_3$ film.