Supporting Information

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Domain Wall Free Polar Structure Enhanced Photodegradation Activity in Nanoscale Ferroelectric Ba$_x$Sr$_{1-x}$TiO$_3$

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1. Supplementary Figures

Figure S1. Characterisation of the polar structure dependence of Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ powders on grain size and temperature. a, b, c, d, SEM images of Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ (possessed at 750 °C) post-annealed at 1350 °C, 1200 °C, 950 °C and 750 °C, respectively. e, DSC data for Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ samples processed with increasing temperatures.

To study the dependence of polar structure on grain size, Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ powders of different grain sizes were obtained by post-annealing the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ powders (possessed at 750 °C) at different temperatures. The Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ samples were post-annealed at 950 °C, 1200 °C and 1350 °C for 10 hours, respectively. Figure S1 a,b,c,d show SEM images of the as-obtained samples. It can be seen from the figures that the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ grain sizes increase dramatically with annealing temperature ranging from 750 °C to 1350 °C. Though large
grains with a sub-micro/micro size can be observed in all four samples, it is obvious that ultrafine grains with size smaller than 100 nm are dominating in the 750 °C sample and larger grains subsequently become the majority with increasing temperature, with micro-grains obtained in the 1350 °C sample. DSC measurement was conducted to check the dependence of phase transition thermal characteristics of the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ samples processed at different temperatures. Figure S1e gives DSC data for Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ samples. It can be seen that the endothermic feature near 60 °C which is attributed to the tetragonal-cubic transformation is only observed in the sample post-annealed at 1350 °C. With decreased post-annealing temperatures, the endothermic peak disappeared, which is analogous to the phenomenon observed by M. H. Frey et al.\cite{1} in the study of BaTiO$_3$ particles processed in different temperatures. This has been suggested to result from the single-domain feature by M. H. Frey et al. In their study, BaTiO$_3$ particles of different grain sizes exhibited multi-single domain transformation at the size of ~ 400 nm, demonstrated by the hot-stage TEM and DSC characterisations. Thus, it can be suggested that the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ sample annealed at 750 °C has a single-domain-single-grain structure. We show Raman spectra in Fig S2 indicating the transition to a non-polar material for the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ material as it passes through the Curie point. In order to determine the influence of the variation in the valance band position for the two different materials we have completed X-ray Photoelectron Spectroscopy (XPS) analysis for the two samples. The results are shown in Fig S3 and indicate that there is negligible change to the oxidation potential in the valence band for both materials. There are small changes to the fine detail of the band structure that are due to the defect states within the materials.
Figure S2. Raman spectra of Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ at different temperatures. Raman spectra of the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ sample (processed at 750 °C) collected over a range of temperatures between 25 °C and 200 °C have been obtained to reveal its phase transformation with temperature changing through the Curie point. With increasing temperature, the two peaks (at 302 cm$^{-1}$ and 722 cm$^{-1}$) exhibit larger linewidths, indicating that the tetragonality is accompanied by a decreased structural coherence$^{2}$. And the two peaks gradually vanish when the temperature increases from 25 °C to 90 °C, demonstrating a tetragonal to cubic phase transition.

Figure S3. X-Ray Photoelectron Spectroscopy (XPS) valence band spectra of Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ and Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ that indicates negligible change in the oxidation potential for a hole in both materials. There are some small changes to the fine detail of the band structure with the differences being associated with defect states.

2. Supplementary Tables
Table S1. Particle Size and Surface Area of Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ and Ba$_{0.2}$Sr$_{0.8}$TiO$_3$

| Sample             | Average particle size (nm, SEM) | BET surface area (m$^2$/g) |
|--------------------|---------------------------------|-----------------------------|
| Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ | 70.8                            | 7.3904                      |
| Ba$_{0.2}$Sr$_{0.8}$TiO$_3$  | 65.2                            | 7.9646                      |

3. Supplementary Methods

Sample preparation

Barium strontium titanite nanocrystals were prepared by molten-salt synthesis (MSS) method. Barium oxalate (99.999%), Strontium oxalate (95%), Sodium chloride (99.0%) and Potassium chloride (99%) were obtained from Alfa Aesar and used as received. Titanium dioxide (nanopowder, 21 nm primary particle size, ≥99.5%) were obtained from Sigma-Aldrich and used as received. In a typical synthesis procedure of Ba$_{0.8}$Sr$_{0.2}$TiO$_3$, 0.08 mol of BaC$_2$O$_4$ and 0.02 mol SrC$_2$O$_4$ along with 2 mol NaCl and 2 mol KCl were added to a PTFE pot and mixed thoroughly by ball milling for 4 h using ethanol and zirconia balls. The obtained slurry was dried out at 100 °C overnight. The processed mixture was placed in a ceramic crucible, heated at a ramp rate of 5 °C /min to an annealing temperature at 750 °C for 1 h, and cooled thereafter to room temperature within the furnace. Samples were subsequently washed several times with hot distilled water and filtered by vacuum suction. The as-prepared powders were collected and dried at 80 °C in an oven overnight. Preparation of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ powders was employed using different molar ratios of the initial precursors. Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ samples prepared at 750 °C were post-annealed at 950 °C, 1200 °C and 1350 °C to investigate the effect of grain size on the domain structure. The post-annealing treatments were conducted by heating the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ samples up to the desired temperatures by a rate of 10 °C/min and held for 10 hours, followed by cooling down in a rate of 5 °C/min. If not noticed specifically,
the Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ samples mentioned in the paper refer to the original samples processed at 750 °C.

**Characterisation**

X-ray diffraction (XRD) patterns of the powders were obtained with a Panalytical Xpert Pro diffractometer using Cu Ka radiation. The morphology of the powders was observed using a scanning electron microscope (SEM, FEI Inspect F) and a transmission electron microscope (TEM, FEI Titan Themis (200 kV)). Optical absorption of the obtained BST powders was measured using a PerkinElmer Lambda 950 UV-vis spectrophotometer. X-Ray Photoelectron Spectroscopy (XPS) was performed to determine the valence band maximum of the two BST samples. The XPS is a bespoke system with Specs GmbH Phoibos 150 mm 9-channeltron analyser. The valence band spectra were acquired with 20 eV pass energy and 0.1 eV energy steps using a VG Microtech twin-anode Al K-alpha source. Temperature dependent Raman spectra were acquired by Raman scattering spectrometer (Horiba Jobin-Yvon HR800, France) with a 532 nm wavelength laser and was equipped with a Linkam THMSE 600 heating stage. Thermal properties of the materials were analyzed using a differential scanning calorimeter (DSC) (DSC822e, Mettler-Toledo, OH, USA) under a N$_2$ atmosphere.

Photocatalytic activity of the catalysts was evaluated through decolorization of Rhodamine B (Rh B, Sigma, 99.99%) dye solution. In a typical procedure, 0.15 g catalyst powder was mixed with 50 ml of 10 ppm dye solution in a Petri dish. After kept in dark for 30 min under constant stirring, the mixture was placed under a solar simulator (Newport). Irradiation intensity of the simulator was fixed at 1 sun (100 mW/cm$^2$) using a silicon reference cell. A 2 ml solution sample was taken at fixed intervals of 30 min, followed by centrifugation at 10000 rpm for 15 min to remove the catalyst powder. Optical absorption of the obtained dye solution was measured by UV-vis spectrophotometer.

[1] M. H. Frey, D. A. Payne, *Phys. Rev. B* **1996**, *54*, 3158.
[2] M. B. Smith, K. Page, T. Siegrist, P. L. Redmond, E. C. Walter, R. Seshadri, L. E. Brus, M. L. Steigerwald, *J. Am. Chem. Soc.* **2008**, *130*, 6955.