Electronic Supplementary Material

Impact of ferroelectricity on photodegradation of charged dye species: significance of polarity match

Yiqing He,[a] Muwei Ji,[a,b,c] Yao Hu,[a] Qinghua Yang,[a] Changxu Yan,[a] Yuxiong Chen,[a] Shengding Chang,[a] Bo Li,[a] and Jin Wang [a,]*

[a] *Graduate school at Shenzhen, Tsinghua University, Shenzhen, 518055, P. R. China.*

[b] *College of Chemistry and Environment Engineering, Shenzhen University, Shenzhen, 518060, P. R. China.*

[c] *Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China.*

**Corresponding author: wang.jin@sz.tsinghua.edu.cn*

Experimental

Chemical and reagents

Barium nitrate ($Ba(NO_3)_2$) , Barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) , titanium isopropoxide, oleic acid (OA) , NaOH, KOH, Rhodamine B (Rh B) and Methyl Orange (MO) were purchased from Alfa Aesar Co., Ltd.. Ethylenediaminetetraacetic acid disodium salt (EDTA) were purchased from Beijing InnoChem Science & Technology Co., Ltd. Oleylamine(OM) and Titanium(III) chloride ($TiCl_3$) were purchased from Acros. All the chemical reagents are analytical grade and used without further purification in the experiments of this study.

2 Surfactant-assisted synthesis of $BaTiO_3$ nanoparticles (BTO-1)

BTO-1 was synthesized via a hydrothermal reaction. [S1,S2] 8.75 mmol NaOH, 1 mmol $Ba(NO_3)_2$ and 1 mmol $TiCl_3$ was dissolved in a mixture of 6mL ethanol and 0.5mL water under ultrasonication, and then added drop by drop into a mixture of 1 mL oleylamine(OM) and 2 mL oleic acid(OA) under vigorous stirring with the temperature kept at 80 °C to avoid solidification. After the slurry was further stirred for 30 min, it was sealed in a 10 mL capacity Teflon-lined autoclave. The autoclave was heated at 200 °C for 10 h, and then cooled to 80 °C. The obtained white product was dispersed in cyclohexane under ultrasonication until no apparent residue could be seen. The product was then precipitated with ethanol (6:1 in volume ratio) and centrifuged at 8000 rpm for 15 min to remove excess OA and OM. After four cycles of washing, the final precipitate was dispersed in water and then was dried in an oven at 60 °C to obtain BTO nanoparticles. The same procedure except that 1 mmol $Ba(NO_3)_2$ was replaced by 1 mmol $Sr(NO_3)_2$ was used to prepare $SrTiO_3$ nanoparticles (STO-1).

3 Surfactant-free synthesis of $BaTiO_3$ nanoparticles (BTO-2)

The fabrication consisted of two-step treatment: surfactant-free hydrothermal synthesis of $BaTiO_3$ nanopowder precursors and subsequent thermal annealing of the precursors. The method for preparation of $BaTiO_3$ nanopowder precursors is the same as that proposed by Wu *et al*. [S3] Typically, 1.5 mmol $BaCl_2 \cdot 2H_2O$ and 3 g KOH were dissolved in 10ml deionized water to form a homogeneous solution. Then, the solution was quickly added into a mixture of 10 ml ethanol and 1.5 mmol titanium isopropoxide under vigorous stirring. A white gelatinous suspension was immediately produced and then aged at room temperature for about 6h. The product was washed by deionized water and ethanol respectively for 3 cycles and dried. Finally, the powder was heated at 800 °C for 4 h in air in a muffle furnace, followed by natural cooling.

Structural analysis

Structural analysis. The X-ray diffraction (XRD) pattern of the product was conducted on a X-ray diffractometer (MiniFlex, Rigaku, Japan) with Cu/Kα radiation (λ=1.5406 Å). The morphology of the powders was characterized with scanning electron microscope (SEM, SUPRA@55, ZEISS, Germany) and transmission electron microscope (TEM, Tecnai G^2 F30, FEI, America).The specific surface area of samples was measured by BET (BelSorp Max, BEL, Japan).

Photocatalytic experiment

The photocatalytic activity of the BTO powders was evaluated by the decolorization of Rh B solution and MO solution. 25mg of catalyst powder was mixed with 50 mL of dye solution in a quatz flask after mixing. The mixture was stirred in the dark for 30min before exposure to a solar simulator (CEL-HXF300, Beijing China Education Au-light Co., China) at a distance of 16 cm from the light source. The irradiation intensity was fixed at 300W. A 4 mL aliquot of solution was taken for sampling at fixed intervals, followed by centrifugation at 10000 rpm for 20min to remove any catalyst powder. The optical absorption spectrum of the sampled dye solution was measured with a UV-vis spectrophotometer (UV-2600, Shimadzu Co., Japan)

Figure S1- S5:

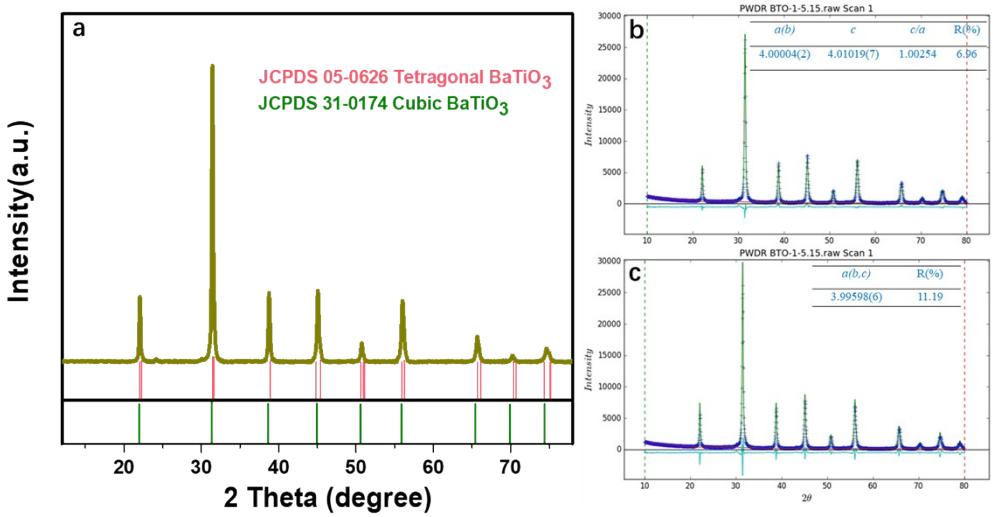

Figure S1. a) XRD pattern of as-prepared BTO-1 nanoparticles; b) The XRD refinement of BTO-1 with tetragonal cell (JCPDS No.05-0626); c) The XRD refinement of BTO-1 with cubic cell (JCPDS No.31-0174).

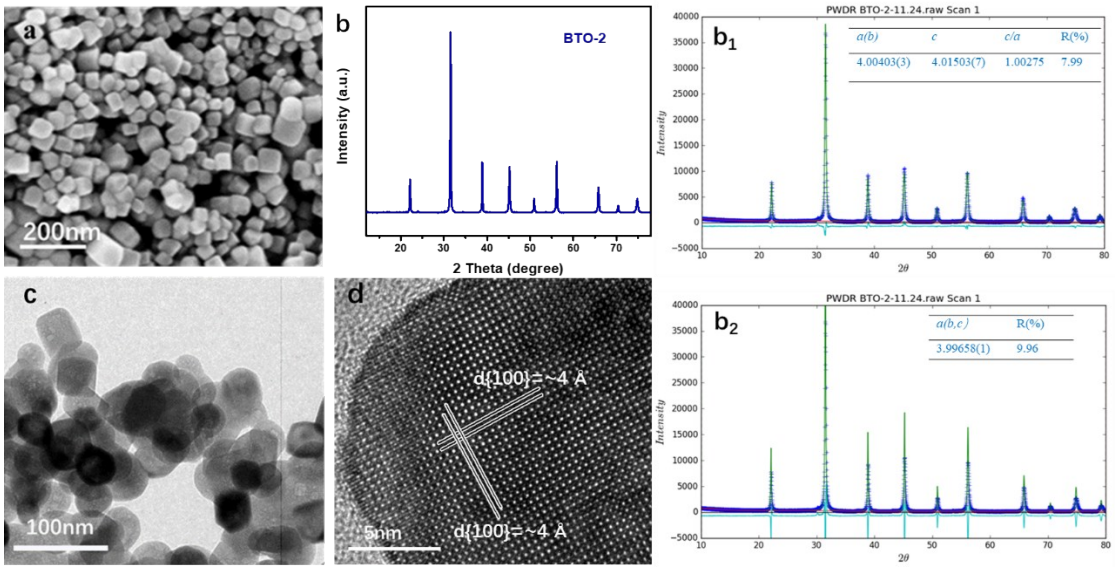

Figure S2. a) SEM image; b) XRD pattern; b1) The XRD refinement of BTO-2 with tetragonal cell (JCPDS No.05-0626); b2) The XRD refinement of BTO-2 with cubic cell (JCPDS No.31-0174); c) LRTEM image; and d) HRTEM pattern of BTO-2 nanoparticles.

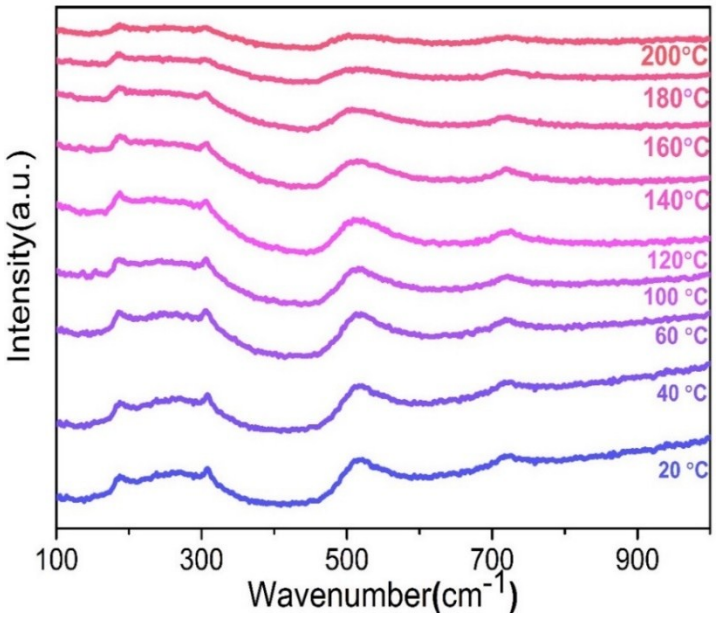

Figure S3. Raman spectra of BTO-2 nanoparticles at different temperature: the polarity of BTO-2 reduced as the temperature increasing resulted in the Raman peaks at 313 cm^{-1} weaken and vanished.

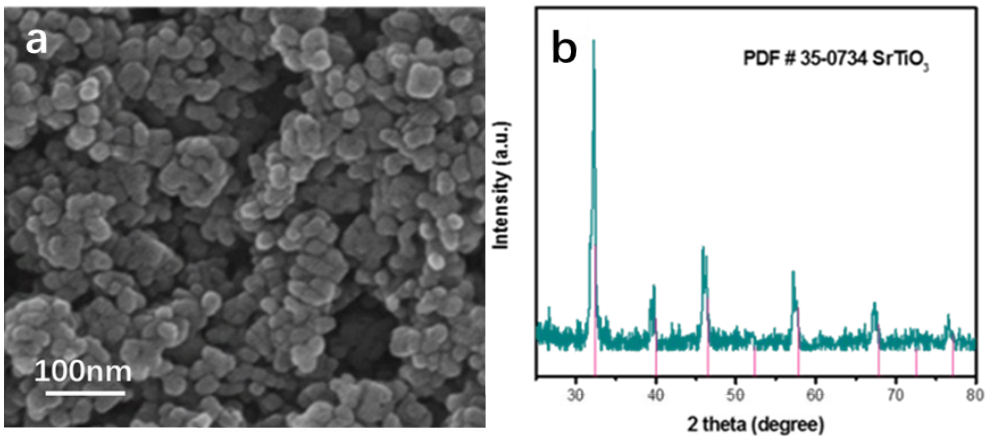

Figure S4. a) SEM image and b) XRD pattern of BTO-2 nanoparticles .

references

S1 X. Wang, J. Zhuang, Q. Peng and Y. Li, A General Strategy for Nanocrystal Synthesis. *Nature* **2005**, 437, 121-124.

S2 S. Hu, H. Liu, P. Wang and X. Wang, Inorganic Nanostructures with Sizes down to 1 nm: A Macromolecule Analogue. *J. Am. Chem. Soc.* **2013**, 135, 11115-11124.

S3 Q. Wu, J. Liu, G. Wang, S. Chen and S. Yu, A surfactant-free route to synthesize $Ba_xSr_{1-x}TiO_3$ nanoparticles at room temperature, their dielectric and microwave absorption properties. *Sci China Mater*. **2016**, 59(8), 609-617.