

Article

Ferroelectric Polarization-Enhanced Photocatalysis in BaTiO₃-TiO₂ Core-Shell Heterostructures

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Spontaneous polarization of ferroelectric BaTiO₃

The most extensively studied ferroelectrics are perovskite oxides (ABO₃). BaTiO₃ is the first identified ferroelectric material with perovskite structure. Figure S1 shows the crystal structure of BaTiO₃ at high temperature ($> T_c$, Curie point) and low temperature ($< T_c$). The crystal displays a cubic paraelectric phase at the temperature above T_c (120 °C). When the temperature is below T_c , Ti ions shift along the [001] axis to form a tetragonal ferroelectric phase, producing a spontaneous polarization ($P_s \sim 27 \mu\text{C}/\text{cm}^2$) [1].

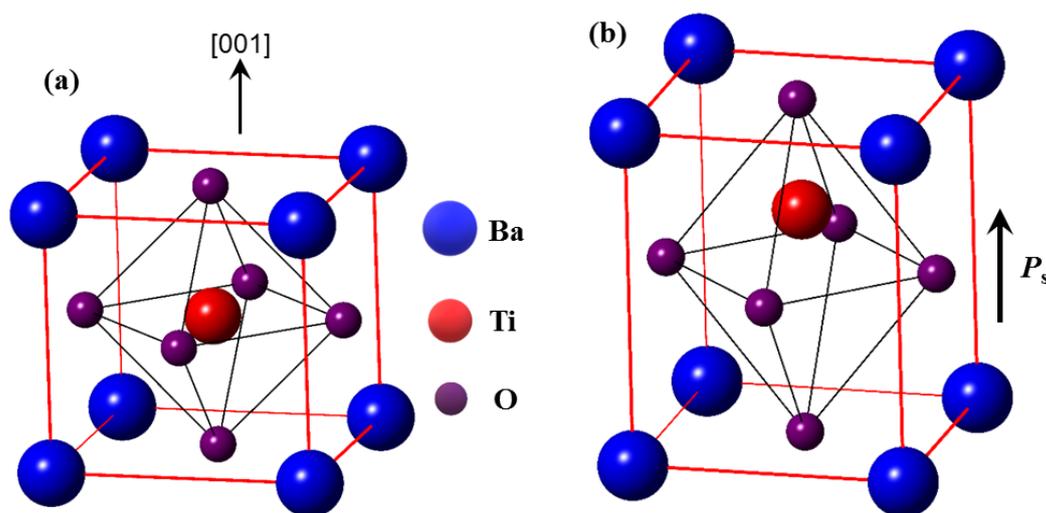


Figure S1. Crystal structure of (a) cubic (paraelectric) and (b) tetragonal (ferroelectric) BaTiO₃.

Characterization of ferroelectricity of BaTiO₃ crystallines

Commercial BaTiO₃ crystallines were subjected to the hydrothermal process at the absence of titanium isopropoxide (TIP) while keeping the other experimental conditions unchanged. Morphology of the BaTiO₃ crystallines were characterized by a field emission SEM (FESEM), showing their size range of 100 nm to 300 nm (Figure S2a). Reversible polarization and piezoelectric response of the BaTiO₃ were demonstrated by phase-voltage hysteresis and amplitude-voltage butterfly loops acquired from a switching spectroscopy piezoresponse force microscopy SSPFM (Figure S2b), indicating a good ferroelectric property of the BaTiO₃.

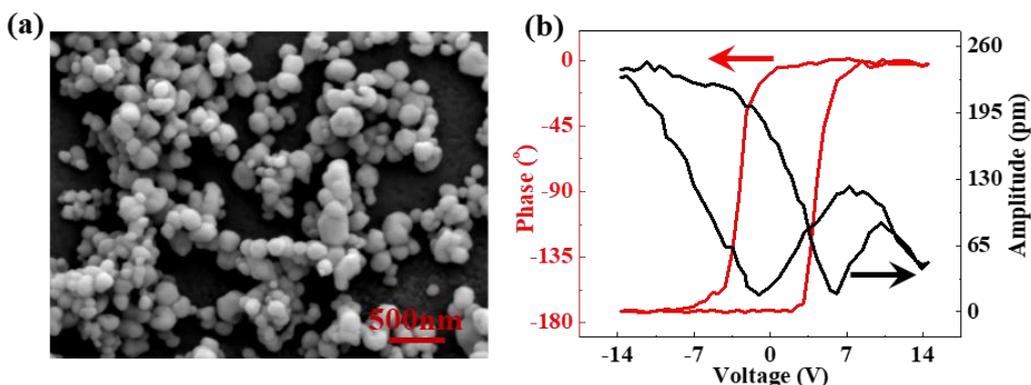


Figure S2. FESEM image (a) and (b) representative phase-voltage hysteresis loop (red) and amplitude-voltage butterfly loop (black) of BaTiO₃ after subjected to the hydrothermal process.

Hydrolysis reaction for forming mesoporous TiO₂ nanoshells on BaTiO₃

NH₃·H₂O is used as a catalyst for promotion of the hydrolysis reaction of TIP, the precursor of TiO₂ [2]. The amount of TIP and NH₃·H₂O, and the stirring rate during the hydrolysis reaction were varied in order to coat mesoporous TiO₂ nanoshells on BaTiO₃. Based on the photodegradation of RhB in the presence of catalysts synthesized at the different amount of TIP and NH₃·H₂O, and the varied stirring rate (Figure S3), the optimal condition of the hydrolysis reaction was concluded as 0.16 ml of TIP with 0.1 ml of NH₃·H₂O at the stirring rate of 200 rpm during the hydrolysis reaction.

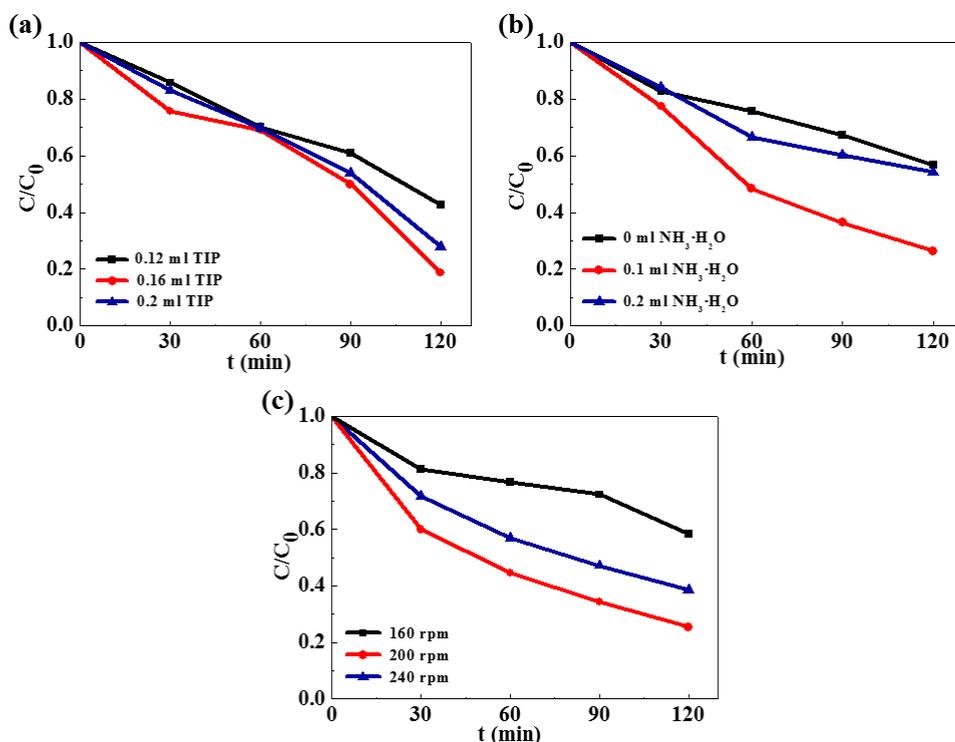


Figure S3. Photodegradation of RhB in the presence of catalysts synthesized at the different amount of TIP and NH₃·H₂O, and the varied stirring rate during the hydrolysis reaction.

EDS mapping of BaTiO₃-TiO₂ core-shell heterostructures

An energy-dispersive X-ray spectroscopy (EDS) line-scan profile across the representative individual BaTiO₃-TiO₂ core-shell heterostructure shows the distribution of Ba localized in the core, while the distribution of Ti and O is throughout the structure. In combination with the FESEM image (Figure S4a), the line-scan EDS profile (Figure S4b) indicates that the heterostructure consists of BaTiO₃ core surrounded by TiO₂ shell.

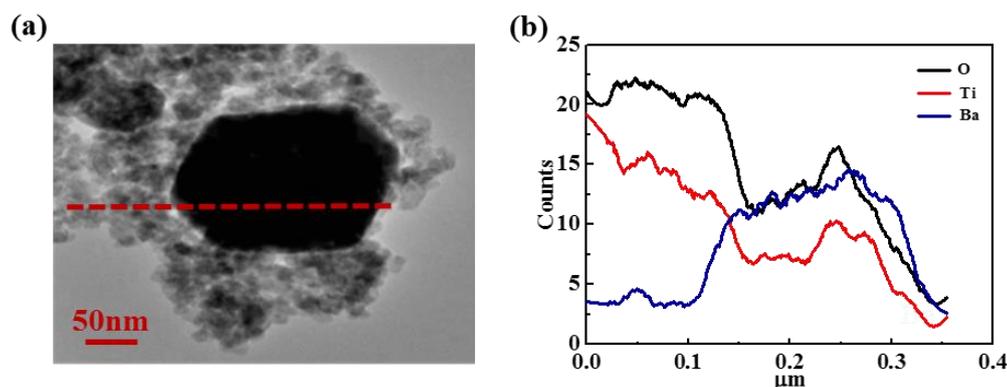


Figure S4. Line-scan EDS profile (b) along the red dot dash line crossing the BaTiO₃-TiO₂ core-shell heterostructure (a).

Absorption spectra of RhB solution after photodegradation

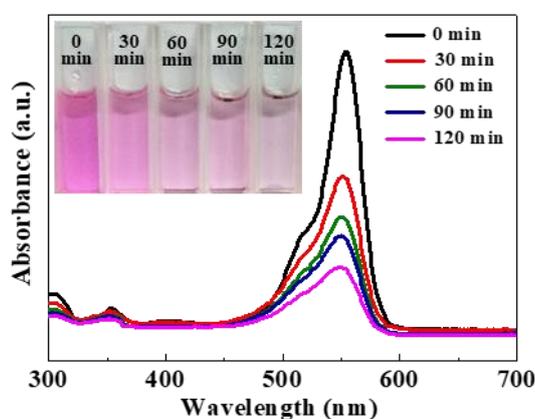


Figure S5. Absorption spectra of RhB solution in the presence of BaTiO₃-TiO₂ core-shell heterostructures (1.2:1) under UV light irradiation. Inset shows color changes of the RhB solution.

Photodegradation of RhB based on BaTiO₃-TiO₂ core-shell heterostructures

Electron-hole pairs were photogenerated mostly from the TiO₂ shell under the UV light irradiation. An internal electric field originated from spontaneous polarization of the BaTiO₃ core can penetrate through the TiO₂ shell with a thickness less than 100 nm and work as a driving force for separating photogenerated electron-hole pairs and promoting carrier transport to the surface of TiO₂ [3].

During the photocatalytic process, photogenerated electrons (e⁻) on the surface of TiO₂

attract oxygen molecules in RhB solution and produce superoxide radicals of $\bullet\text{O}_2^-$ as shown in the following equation



On the other hand, photogenerated holes (h^+) react with OH^- in the solution to form hydroxyl radicals of $\text{OH}\bullet$



The degradation of RhB is caused by the superoxide radicals ($\bullet\text{O}_2^-$) and hydroxyl radicals ($\text{OH}\bullet$) through electrochemical redox reaction in RhB solution governed by the following relation



The reactions described above repeat over the time during the photocatalytic process.

Supplementary References

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