Developing Ferroelectric Nanohybrid for Enhanced Photocatalyst

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Experimental Section:

Materials: Ferric chloride hexahydrate (FeCl₃·6H₂O), ethyleneglycol (EG), anhydrous ethanol, sodium acetate (NaAc), trisodium citrate (Na₃Ct), titanium(IV) fluoride (TiF₄), polyvinyl pyrrolidone (PVP, MW~55 K), potassium hydroxide (KOH) and barium hydroxide octahydrate (Ba(OH)₂·8H₂O) were purchased from Shanghai Chemical Crop. All chemicals were used as received without further purification. Deionized water was used for all experiments.

*Preparation of Fe*₃ O_4 *nanospheres:* The Fe₃ O_4 nanospheres were prepared by a solvothermal reaction. Typically, FeCl₃·6H₂O (2.6 g), NaAc (4.8 g) and Na₃Ct (1 g) were dissolved in EG (80 mL) under stir. After that, the mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave, and then the autoclave was heated at 200 °C for 10 h. Finally, the precipitates were washed with water and ethanol and dried at 60 °C in a vacuum.

Synthesis of Fe_3O_4 ($a)TiO_2$ nanospheres: As-prepared Fe₃O₄ nanospheres (0.08 g) and TiF₄ (0.02 g) were dispersed into the solution of deionized water and ethanol, followed by the addition of PVP (0.5 g). The mixture was then transferred to a Teflon-lined stainless steel autoclave and kept at 120 °C for 12 h. Finally, the products were harvested by centrifugation and washed with deionized water and ethanol before drying at 60 °C.

Synthesis of Fe_3O_4 (@TiO₂-BaTiO₃ nanospheres: Ba(OH)₂·8H₂O (40 mg), KOH (0.1 g) and the mixed solution containing 20 mg Fe₃O₄ (@TiO₂ nanospheres were added to a 50 mL autoclave under agitation. The system was sealed and treated at the 150 °C for 6 h. After the reaction had cooled to room temperature, the products were washed with plentiful acetic acid and deionized water to dissolve BaCO₃ and collected by centrifugation.

Materials Characterization: The size and morphology of the samples were examined by using transmission electron microscopy (TEM, JEOL 2100) at an acceleration voltage of 200 kV. The crystallographic information and phase purity of the products were investigated by powder X-ray diffractometry (XRD, Shimadzu 7000) with a Cu Ka (0.15418 nm) source. The magnetic hysteresis loop was measured by a vibrating sample magnetometer (VSM-7307, Lakeshore). The piezoelectric properties of products were investigated by using an atomic force microscope (AFM, Cypher, Asylum Research). The temperature dependent magnetization measurement was carried out by using the VSM module of a physics property measurement system (PPMS, Quantum Design) in the temperature range from 398 K to 300 K with a cooling rate of 1.5 K min⁻¹ under a constant magnetic field of 100 Oe.

Photocatalytic measurements: For photocatalytic degradation of Rhodamine B, 0.1g catalysts was added to the beaker containing 100 ml of 10 ppm dye solution (Rhodamine B). The mixture was continuously stirred in the dark for 1 h. Then, the photocatalytic test was conducted by irradiation with a 500 W xenon lamp. Samples collected at different reaction time were centrifuged for the absorbance measurements. Photoelectrochemical measurements were carried out at ambient temperature using a three-electrode configuration including the samples electrode, a 1 cm² Pt counter electrode, and a saturated calomel electrode (SCE) through a photoelectrochemical

system. The Photoluminescence spectra are collected by a PMT detector (spectral range of 300–400 nm) that ratios the emitted and incident light.



Figure S1. TEM images that $BaTiO_3$ NCs are exfoliated from the surface of Fe_3O_4 core.



Figure S2. TEM images of samples synthesized by the same ratio of barium hydroxide octahydrate and Titania. In this condition, $Fe_3O_4@TiO_2$ -BT core-shell structure could not be obtained.



Figure S3. Low-magnification TEM (a) and HRTEM (b, c) images of Fe₃O₄@BaTiO₃ core–shell nanoparticles formed in solution of 30ml water and 10ml ethanol.



Figure S4. UV-visible absorption spectra of Rh B over time with (a) Fe_3O_4 @TiO₂ NCs, (b) Fe_3O_4 @TiO₂-BT core-shell NCs and (c) Fe_3O_4 @BaTiO₃ core-shell NCs.



Figure S5. First-order plots for the photocatalytic of Rh B using Fe₃O₄@TiO₂ NPs, Fe₃O₄@TiO₂-BT NPs and Fe₃O₄@BaTiO₃ NPs. Meanwhile, apparent quantum efficiency (AQE, \emptyset_{app}) of the Fe₃O₄@TiO₂ NPs, Fe₃O₄@TiO₂-BT NPs and Fe₃O₄@BaTiO₃ NPs were 0.05427µmol/J, 0.14667µmol/J and 0.02138µmol/J, respectively. (\emptyset_{app} =(dc/dt)/(d[hv]_{abs}/dt), where c is reaction concentration and dc/dt is degradation rate; d[hv]_{abs}/dt Represents photon flux.)



Figure S6. (a) Chronoamperometry results of $Fe_3O_4@TiO_2$ -BT NPs, $Fe_3O_4@TiO_2$ NPs and $Fe_3O_4@BaTiO_3$ NPs. The potential used was 0.5 V versus the Ag/AgCl (3M KCl) electrode for chronoamperometry results. (b) Photoluminescence spectra of $Fe_3O_4@TiO_2$ -BT NPs and $Fe_3O_4@TiO_2$ NPs.



Figure S7. Efficiency of the Fe_3O_4 @TiO₂-BT NCs for the photocatalytic degradation of Rh B with six cycling under UV-vis. light after 180 min. The inset is a photograph after magnetic separation.