Electronic Supplementary Information

Enhanced photodegradation of dyes on titania-based photocatalysts by adding commercial GeO_2 in aqueous suspension

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Synthesis.

(1) Preparation of TiO_2 (DDA)

TiO_2 (DDA) was synthesized by a modified process as follows[1]： 2 g dodecylamine (DDA) was added in 40 mL ethanol and stirred until all the DDA had dissolved, followed by the addition of 9 mL titanium tetraisopropoxide (TTIP). After stirred for 1 h, 120 mL H_2O was introduced dropwise. The final mixture was stirred for 24 h and then transferred into a Teflon bottle and treated under autogenous pressure without stirring at 363 K for 7 days. The slurry was filtered, washed, dried, and then calcined at 673 K in air for 6 h.

(2) Preparation of Pt/TiO_2

1 g Hydrogen Hexachloroplatinate Hexahydrate ($H_2PtCI\cdot 6H_2O$) was dissolved in 50 mL ethanol. 3 g P25 was added in 20 mL ethanol and exposed to ultrasonication for 20 min, followed by the addition of 3 mL $H_2PtCI\cdot 6H_2O$ solution and exposed to ultrasonication for another 5 min. Subsequently, 0.03 g Hydrazine hydrate ($N_2H_4\cdot H_2O$) was added into the reaction solution. After stirred for 1 h, the sample was dried at 368 K for 72 h in an air atmosphere.

(3) Preparation of IM-TiO_2

IM-TiO_2 was prepared by wet impregnation method[2]. 0.2 g of pure TiO_2 powder was impregnated with 1 L aqueous solution containing 0.06 g GeO_2. After stirring at room temperature for 24 h, catalyst was filtered, then heated at 373 K for 24 h. Subsequently, the dried solids were calcined in air at 673 K for 6 h. The final powders were denoted as IM-TiO_2.

(4) Preparation of IM-TiO_2 (DDA)

In a typical wet impregnation procedure, 0.2 g of as-synthesized pure TiO_2 (DDA) was impregnated with 1 L aqueous solution containing 0.06 g GeO_2. After stirring at room temperature for 24 h, catalyst was filtered, then heated at 373 K for 24 h. Subsequently, the dried solids were calcined in air at 673 K for 6 h. The final powders were denoted as IM-TiO_2 (DDA).

(5) Preparation of IM-P25

0.2 g of pure P25 powder was impregnated with 1 L aqueous solution containing 0.06 g/L GeO_2. After stirring at room temperature for 24 h, catalyst was filtered, then heated at 373 K for 24 h. Subsequently, the dried solids were calcined in air at 673 K for 6h. The final powders were denoted as IM-P25.

Characterizations.

X-ray photoelectron spectroscopy (XPS) measurement was performed on a PHI5500ESCA analyzer. The main parameters were as follows: Mg Ka, 200 W, vacuum ~10-7 Pa.

UV–vis spectra were measured at room temperature in air on a SHIMADZU UV-2401PC photometer over the range from 200 to 800 nm. 10 mg titania photocatalysts was dispersed in 50 mL water without dye but with or without adding GeO_2 (with concentration of 0.06 g/L) and then magnetically stirred in the dark for 24 h. Finally, the spetrum was taken over the range from 200 to 800 nm without further treatment.

Measurement of photocatalytic activity

The reactions of the photocatalytic degradation of dyes in solution were carried out in a glass batch photoreactor containing 50 mL of a model solution with concentration of 10 mg/L and 10 mg of photocatalyst. GeO_2 was added in the reaction suspension together with the photocatalysts. The suspensions were magnetically stirred in the dark for 24 h to attain adsorption–desorption equilibrium between dye and the catalyst. After 24 h in the dark. The photodegradation experiments of dyes over TiO_2-based photocatalysts under artificial solar light irradiation were performed using homemade photochemical system. A 500 W Xe lamp ($290 < \lambda < 800$ nm) was used as artificial solar light resource. The photodegradation experiment of dyes over TiO_2-based photocatalysts under visible-light or UV light irradiation were performed using XPA-7 Photochemical System (Xujiang Electromechanical Plant, Nanjing, China). A 800 W Xe lamp ($290 < \lambda < 800$ nm) with optical filter to filtering out the UV emission below 400 nm was used as visible light resource while a 500 W Hg lamp ($320 < \lambda < 380$ nm) was used as UV light resource. Laboratory film was used to seal the photoreactor so that the volume of the suspension decreased little after the experiment. The initial concentration of each dye solution was equal to 10 mg/L. Samples were measured by Shimadzu UV-2401PC photometer over the range from 200 to 800 nm after centrifugation (1500 rpm for 10 min) and filtered with microporous filter (with pore size of 0.45 μm).

Calculation of photodegradation yield:

$$\text{photodegradation yield} = \frac{\left(C_o - \mathrm{C_a} - \mathrm{C_b}\right)}{C_o} \times 100$$

C_o is the initial concentration of dye, C_a is the concentration after photodegradation of dye and C_b is the decrease concentration because of the direct photolysis.

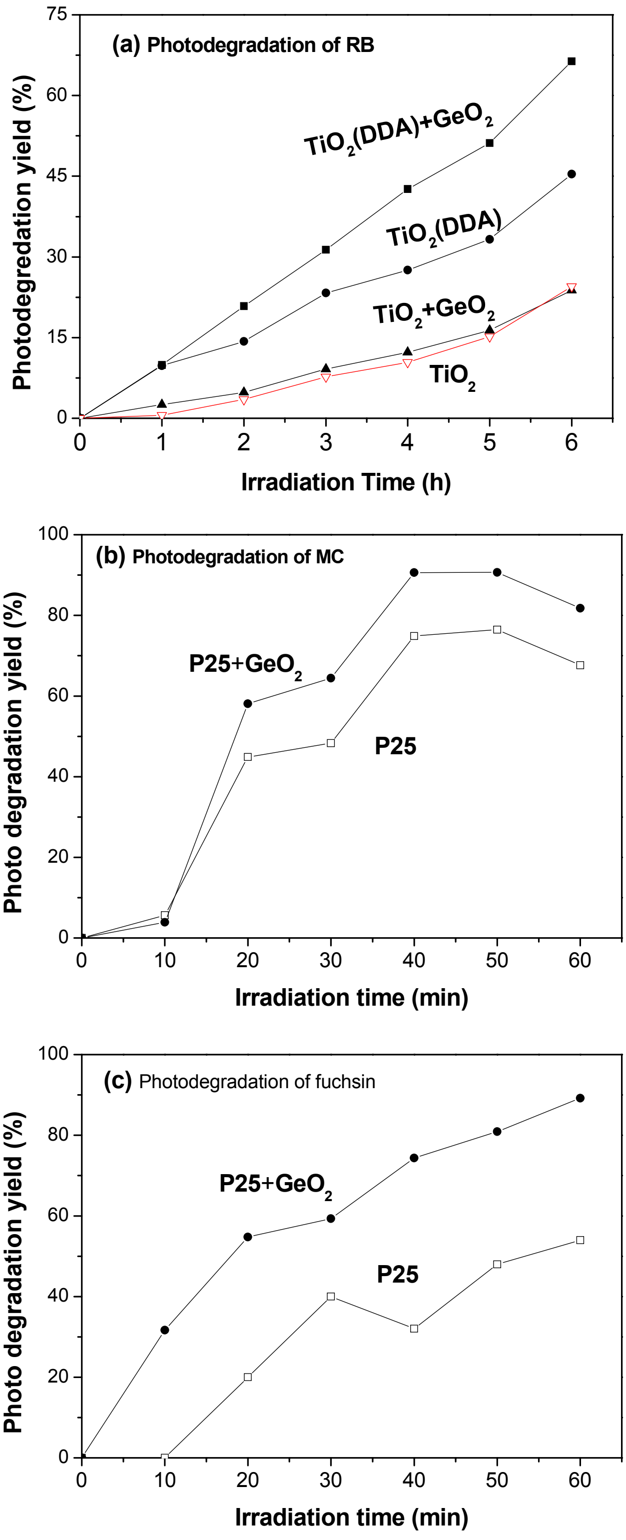

Figure SI-1 Effect of adding GeO_2 (with concentration of 0.06 g/L) in the reaction suspension on the photodegradation yield of TiO_2 and TiO_2(DDA) for degradation of (a) Rhodamine B, (b) methylthionine chloride and (c) fuchsin under artificial solar light.

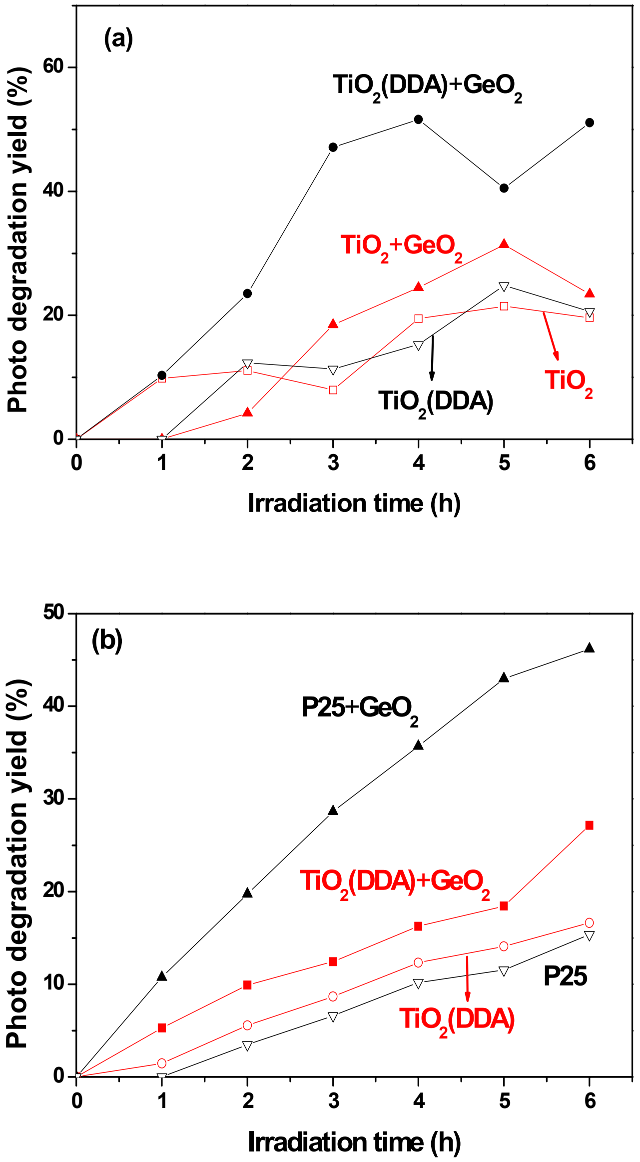

Figure SI-2 Effect of adding GeO$_2$ (with concentration of 0.06 g/L) in the reaction suspension on the photodegradation yield of (a) TiO$_2$ and TiO$_2$(DDA) for degradation of gentian violet and (b) P25 and TiO$_2$(DDA) for degradation of rhodamine B under visible light

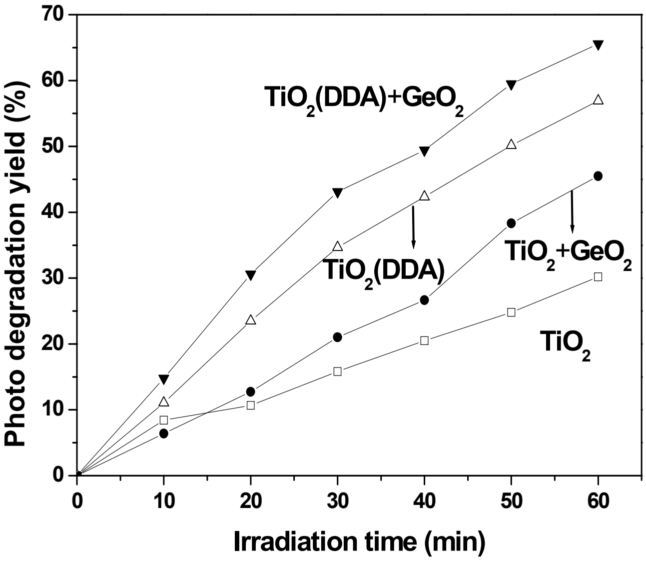

Figure SI-3 Effect of adding GeO_2 (with concentration of 0.06 g/L) in the reaction suspension on the photodegradation yield of TiO_2 and TiO_2(DDA) for degradation of rhodamine B under UV light.

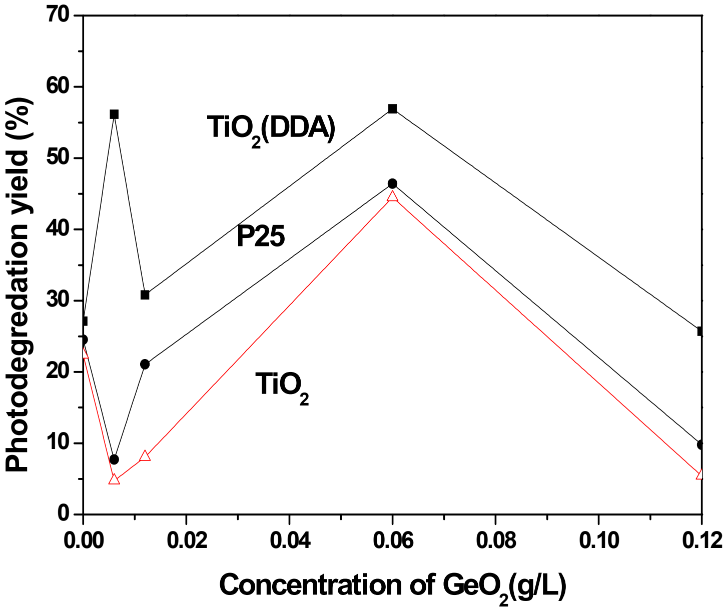

Figure SI-4 Effect of the amount of GeO_2 on the photodegradation yield of TiO_2 and TiO_2(DDA) at 2h and P25 at 1 h for degradation of gentian violet under artificial solar light.

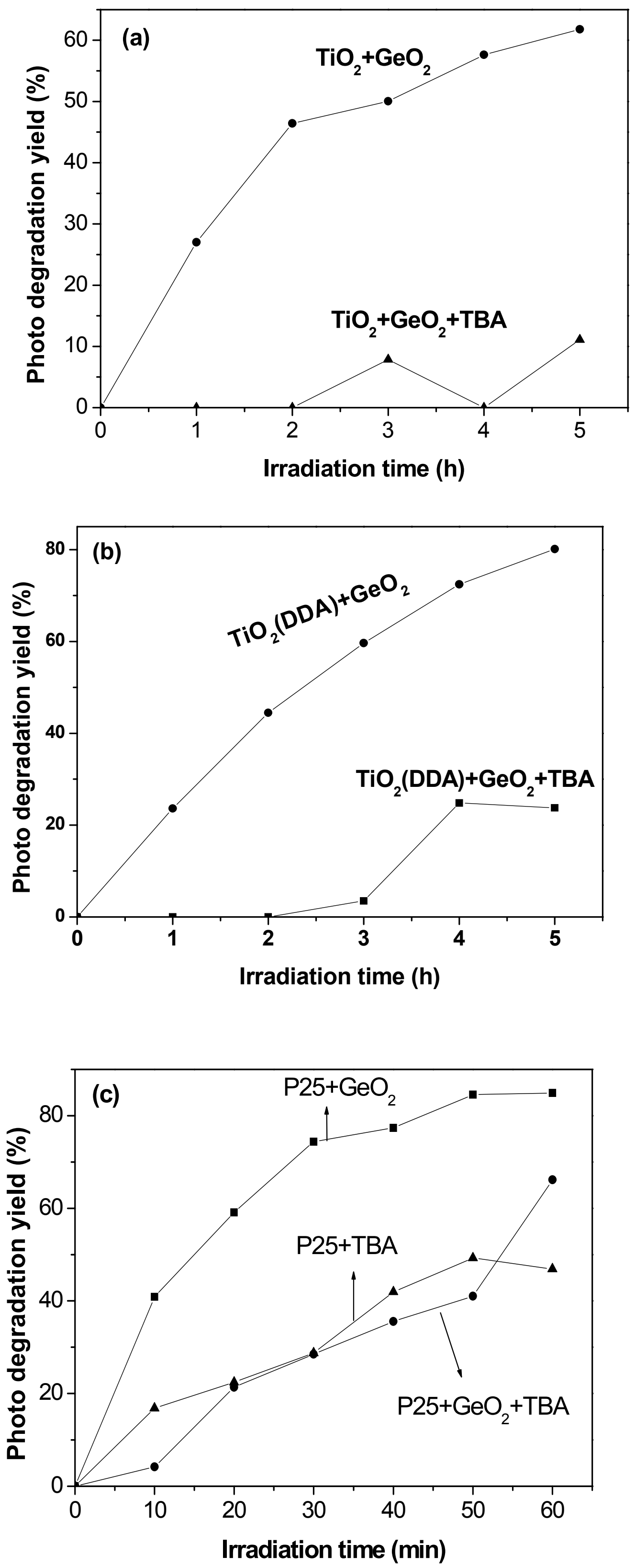

Figure SI-5 Decrease of photocatalytic photodegatation yield of (a) TiO_2, (b) TiO_2(DDA) and (c) P25 in the presence of *tert*-butanol under artificial solar light.

References

1. W. Yao, H. Fang, E. Ou, J. Wang and Z. Yan, *Catal. Commun*, 2006, **7**, 387.
2. A. D. Paola, G. Marcı, L. Palmisano, M. Schiavello, K. Uosaki, S. Ikeda and B. Ohtani, *J. Phys. Chem. B,* 2002**, 106**, 637.