Supporting Information

Ionothermal synthesis of black Ti^{3+}-doped single-crystal TiO_2 as an active photocatalyst for pollutant degradation and H_2 generation

Guisheng Li[1], Zichao Lian[1], Xin Li[1], Yuanyuan Xu[1], Wenchao Wang[1], Dieqing Zhang[1], Fenghui Tian[2], Hexing Li[3*]*

1. Key Laboratory of Resource Chemistry of Chinese Education Ministry, Shanghai Normal University, Shanghai 200234, China. Email: liguisheng@shnu.edu.cn. 2. Institute of Computational Science and Engineering, Qingdao University, Qingdao, 266071, China. 3. Department of Chemistry, Shanghai University of Electric Power, Shanghai 200090, China. Email: Hexing-Li@shnu.edu.cn.

Table S1. Ti^{3+}/Ti^{4+} molar ratio and oxygen vacancy content of the black Ti^{3+}/TiO_2 before and after being calcined at elevated temperatures.

Samples	Ti^{3+}/Ti^{4+} (atom ratio)	O vacancy (mol %)
As-prepared	0.162	6.25
300 °C	0.128	3.84
500 °C	0.101	3.10
700 °C	0	0

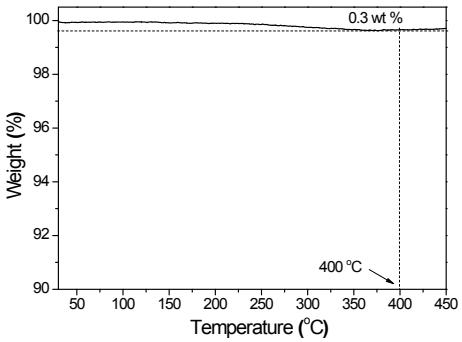

Figure S1. TGA curve of the black Ti^{3+}/TiO_2 obtained in an air atmosphere.

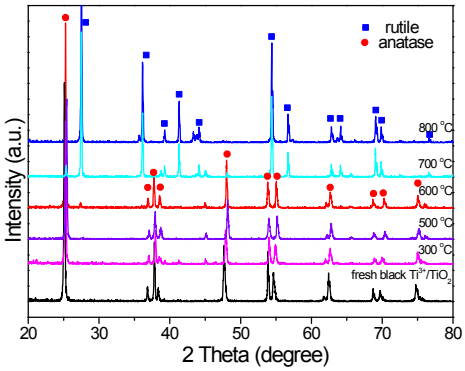

Figure S2. XRD patterns of the black Ti^{3+}/TiO_2 before and after being calcined at elevated temperatures.

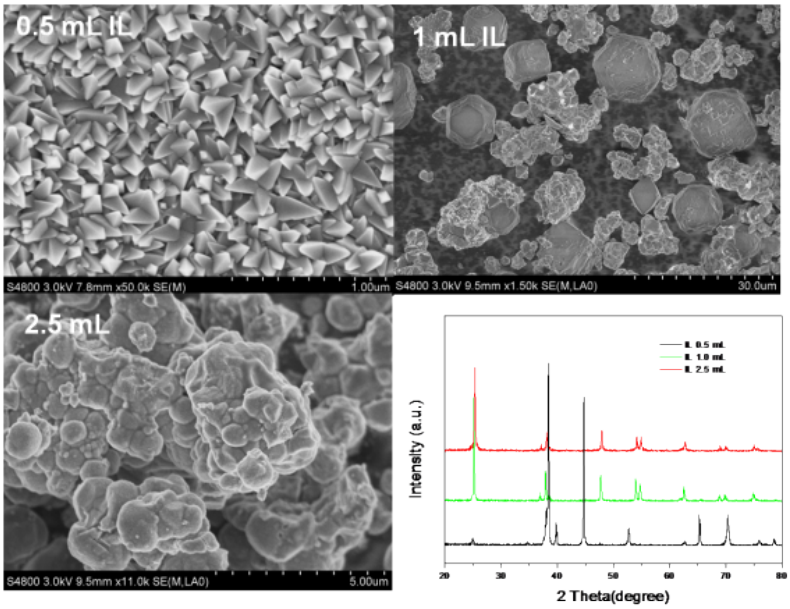

Figure S3. FESEM images and XRD patterns of the black Ti^{3+}/TiO_2 samples obtained at different volumes of ionic liquid.

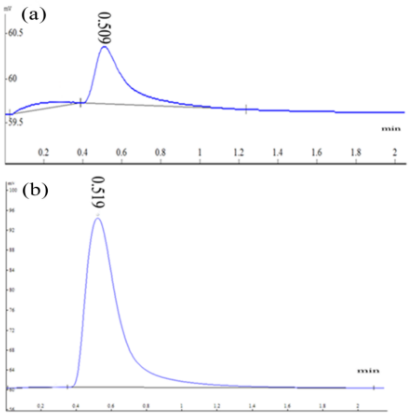

Figure S4. The GC patterns obtained from the gas in the autoclave after ionothermal process (a) and the gas in the autoclave before ionothermal process by introducing trace H_2 (b).

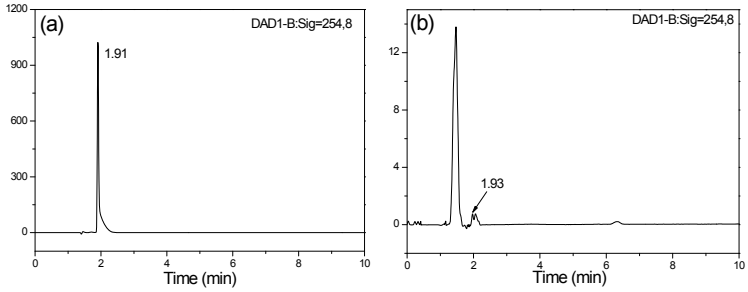

Figure S5. LC-MS patterns (HPLC-MS, Agilent 6410 series Triple Quad, equipped with Agilent C18 column at the characteristic adsorption wavelength of 254 nm) of pure acetic anhydride (a) and the ionic liquid containing HAc and LiAc after treating Ti for 24 h under ionothermal conditions (b).

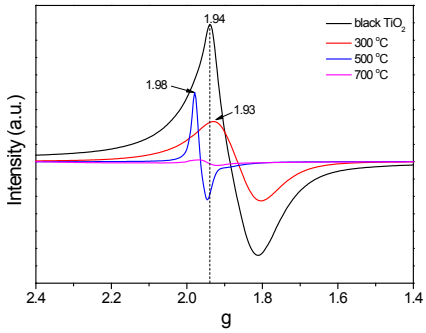

Figure S6. EPR spectra of the black Ti^{3+}/TiO_2 before and after being calcined at elevated temperatures.

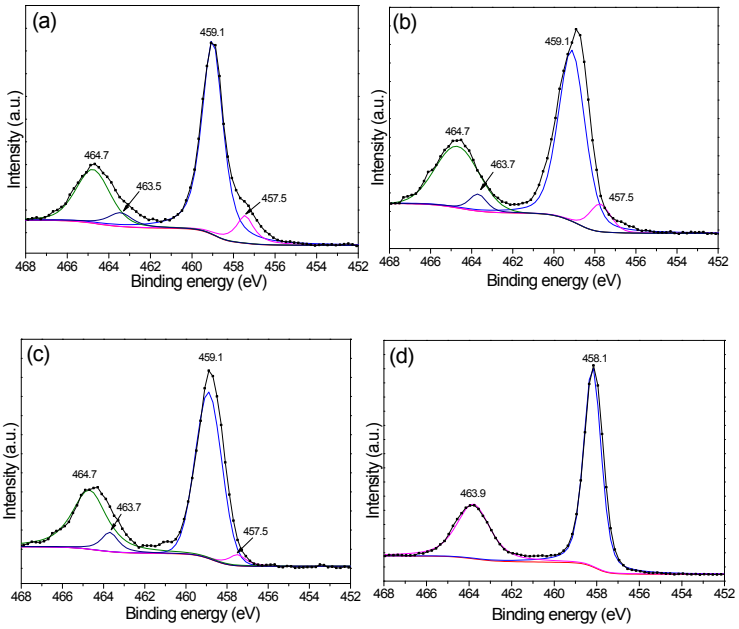

Figure S7. XPS spectra in Ti 2p level of the black Ti^{3+}/TiO_2 before (a) and after being calcined at 300 ^oC (b), 500 ^oC (c) and 700 ^oC (d), respectively.

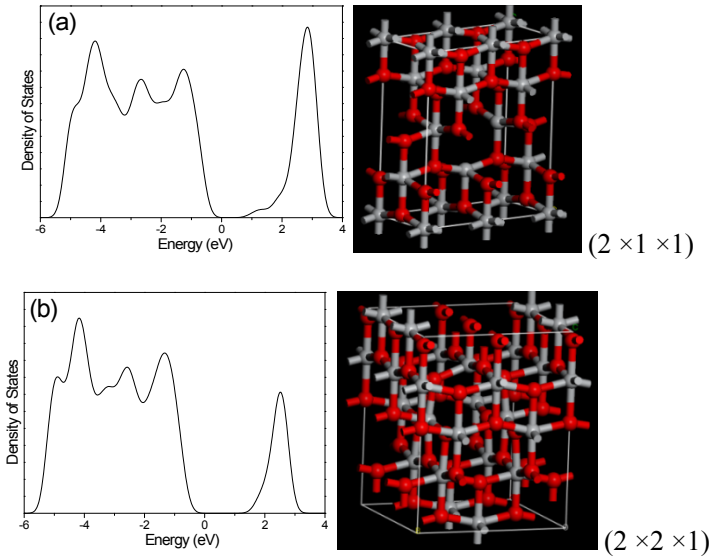

Figure S8. Calculated density of electronic states for anatase TiO_2. The zero of the energy is taken at the top valence band of the defect-free anatase crystal. Details of the density of states around the Fermi level for the oxygen vacancy for different concentrations of vacancies: (a) one per 16 and (b) one per 32 O atoms, respectively. Red ball (O atoms), Grey ball (Ti atoms).

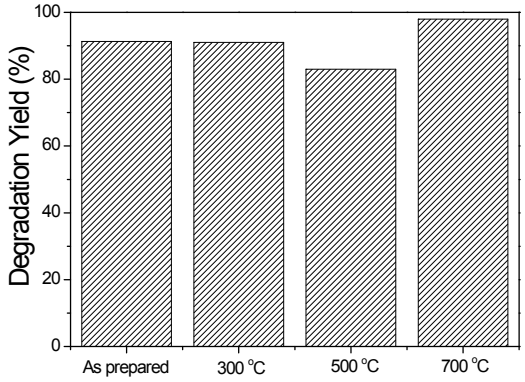

Figure S9. Efficiencies of photocatalytic RhB degradation on the black Ti^{3+}/TiO_2 before and after being calcined at elevated temperatures illuminated with simulated solar lights by using a 300 W Xe lamp without removing UV lights. Reaction time = 3 h and other conditions are given in Fig. 7(a).

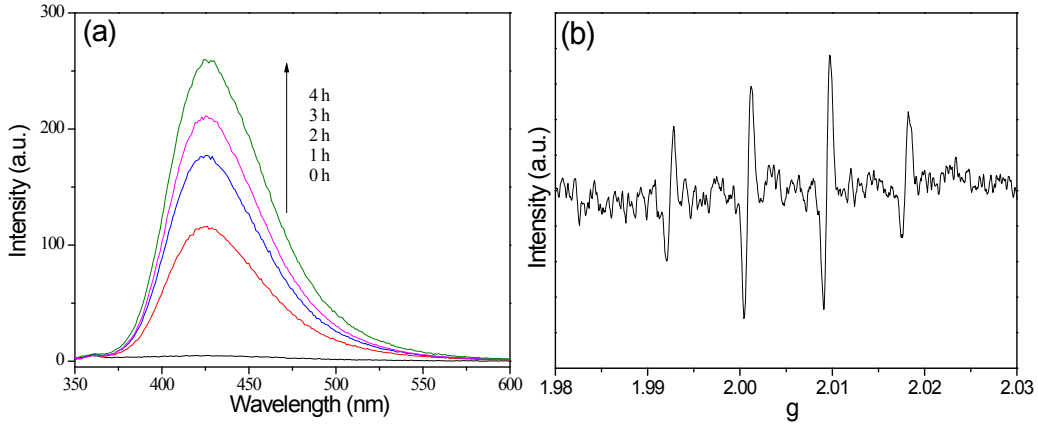

Figure S10. (a) ·OH-trapping photoluminescence spectra of black Ti^{3+}/TiO_2 in 0.05 M terephthalic acid and 0.1 M NaOH solution at different irradiation time (ex, 312 nm; em, 426 nm); (b) ESR signals of the DMPO-•OH adducts formed in the suspensions of black Ti^{3+}/TiO_2 (20 mg) after visible light irradiation (a 300 W Xe lamp and a cut-off filter ($\lambda > 420$ nm)). Other conditions: 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as a spin trap (7.4 mM); The settings for the ESR spectrometer were center field=3520 G; sweep width=100.0 G; microwave frequency=9.874 GHz; and power = 6.368 mW.

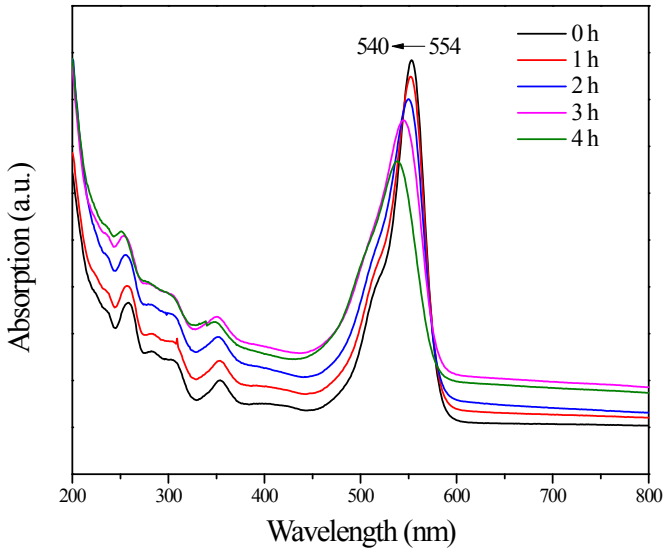

Figure S11. The absorption spectrum in the RhB degradation process of the black Ti^{3+}/TiO_2.