

## Capture of photogenerated electrons and holes at the B/Cl co-modified rutile TiO<sub>2</sub> nanorods during organic pollutant degradation

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### Electronic supplementary information (ESI):

#### SI-Experimental procedures

All substances used in this study were of analytical grade and used without further purification. Deionized water was used in all experiments.

**Preparation of TiO<sub>2</sub> Nanopowders.** Rutile TiO<sub>2</sub> was synthesized by a previous sol-hydrothermal method. Initially, 40 mL tetrabutyl titanate was dropwise added to 2 mol/L 250 mL hydrochloric acid (HCl) solution at the temperature below 10 °C. Then, the mixture was heated to 80 °C for 4 h so as to produce white suspension. Subsequently, the suspension was placed in Teflon-lined hydrothermal reactors and heated at 160 °C for 6 h. After that, a white precipitate was collected and washed repeatedly with isopropanol and distilled water to remove all the organics and dissociative chloride ions. Finally, the rutile TiO<sub>2</sub> sample referred to R was obtained by as drying the white precipitate at 100 °C for 12 h. The productivity was determined to be 90 % according to the mole ratio between as-received R sample and initial Ti(OBu)<sub>4</sub> precursor. To complete the modification with boric acid (H<sub>3</sub>BO<sub>3</sub>), 0.5 g of R powder was put into 40 mL of different concentration of H<sub>3</sub>BO<sub>3</sub> solution (the mass ratio of H<sub>3</sub>BO<sub>3</sub> and TiO<sub>2</sub> is 1, 2, 3 and 4, respectively). Then, this suspension was moved into Teflon-lined hydrothermal reactors and heated at 160 °C for 6 h again. After the sol-hydrothermal process, the product was washed with water for several times and then dried at 100 °C for 12 h. Thus, the H<sub>3</sub>BO<sub>3</sub>-modified TiO<sub>2</sub> powder was obtained. The modified sample is defined as XB-R, in which X is the mass ratio of H<sub>3</sub>BO<sub>3</sub> and TiO<sub>2</sub>.

In addition, the rutile  $\text{TiO}_2$  without chloride was prepared in order to probe the role of chloride to connect with B. Firstly, anatase  $\text{TiO}_2$  was synthesized by a similar above sol-hydrothermal process in which only hydrochloric acid was replaced by the same volume of deionized water. Then, the anatase  $\text{TiO}_2$  was calcined at  $800\text{ }^\circ\text{C}$  for 2 h and the pure rutile without chloride could be obtained. Finally,  $\text{H}_3\text{BO}_3$  with the mass ratio of  $\text{H}_3\text{BO}_3$  and  $\text{TiO}_2$  is two has also been modified on the pure rutile according to the above modification method.

**Characterizations of Materials.** The samples were tested using X-ray powder diffraction (XRD) with a Rigaku D/MAX-rA powder diffractometer, using  $\text{Cu K}\alpha$  radiation. Electron micrographs were taken on a JEOL JEM-2010 transmission electron microscope (TEM) operated at 200 kV. The surface composition and elemental chemical state of the samples were examined by X-ray Photoelectron Spectroscopy (XPS) using a Kratos-AXIS ULTRA DLD apparatus with an Al(Mono) X-ray source, and the binding energies were calibrated with respect to the signal for adventitious carbon. The UV-vis diffuse reflectance spectra (DRS) of the samples were measured with a Shimadzu UV-2550 spectrometer. The surface photovoltage (SPV) spectroscopy measurements of the samples were carried out with a home-built apparatus<sup>10</sup>. It was measured with a photovoltage cell, mainly consisting of two indium tin oxide (ITO) glass electrodes. During the SPS measurement, the powder sample was sandwiched between two ITO glass electrodes, which were arranged in an atmosphere-controlled sealed container. The schematic of the photovoltage cell for SPV measurement has been shown in figure 2. The SPS signals were the potential barrier change of the testing electrode surface between that in the presence of light and that in the dark.

Temperature-programmed desorption (TPD) of oxygen was conducted in a flow apparatus built by ourselves. 50 mg of powder sample was pretreated at  $100\text{ }^\circ\text{C}$  for 0.5 h in an ultrahigh-purity He flow, and then the sample was activated at  $100\text{ }^\circ\text{C}$  for 0.5 h in an ultrahigh-purity  $\text{O}_2$  flow. After that, the sample sequentially adsorbed  $\text{O}_2$  for 2 h at  $25\text{ }^\circ\text{C}$ . Finally, the desorbed  $\text{O}_2$  amount was monitored by a gas chromatograph (GC-2014, Shimadzu) with a TCD detector.

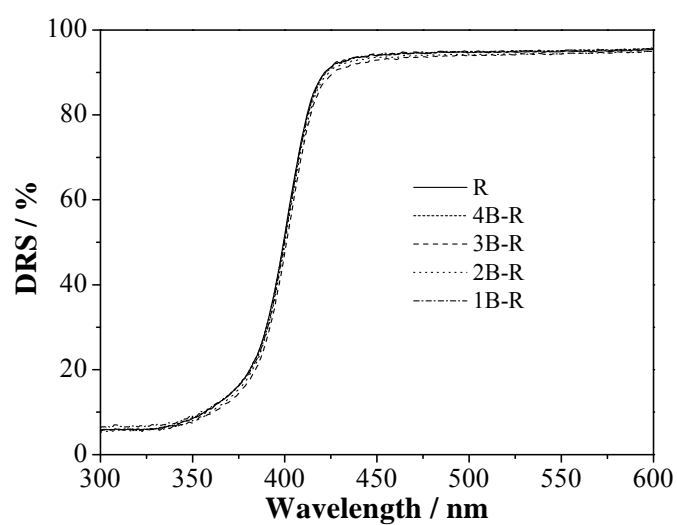
PEC experiments were performed in a glass cell with 0.5 M NaClO<sub>4</sub> solution as the electrolyte. The working electrode was the prepared TiO<sub>2</sub> film electrode. Platinum wire (99.9%) was used as the counter electrode, and a saturated KCl Ag/AgCl electrode was used as the reference electrode. High-purity O<sub>2</sub> was bubbled through the electrolyte before and during the experiments. Applied potentials were controlled by a commercial computer-controlled potentiostat (LK2006A made in China).

To analyze hydroxyl radical, 0.02 g of TiO<sub>2</sub> powder was dispersed in 50 mL of 1×10<sup>-3</sup> mol/L aqueous solution in a quartz reactor. At given irradiation time, a certain amount of the solution was transferred into a Pyrex glass cell for the fluorescence measurement of 7-hydroxycoumarin at around 456 nm under the light excitation of 332 nm with a spectrofluorometer (PerkinElmer LS 55).

***Photocatalytic Activity Evaluation.*** The activities of the samples were evaluated by photodegradation of the gas-phase acetaldehyde and liquid-phase phenol under a 150 W xenon lamp. A total of 0.1 g of TiO<sub>2</sub> sample was placed in a mixed gas system containing 810 ppm acetaldehyde, 20% O<sub>2</sub>, and 80% N<sub>2</sub> to carry out photodegradation reactions for 1 h. The determination of acetaldehyde concentration was performed with a gas chromatograph (GC-2014, Shimadzu) equipped with a flame ionization detector. For photodegradation of phenol, 0.05 g of the TiO<sub>2</sub> sample was dispersed in 30 mL of 5 mg/L phenol solution, and then the irradiation lasts for 1 h. The phenol concentration was measured according to the 4-aminoantipyrine spectrophotometric method at the characteristic optical absorption (510 nm) of phenol with a Shimadzu UV-2550 spectrophotometer after centrifugation.

## SI-figures

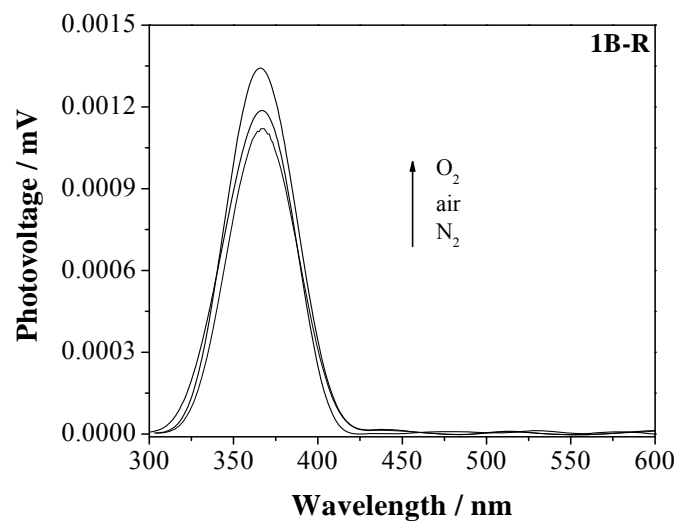
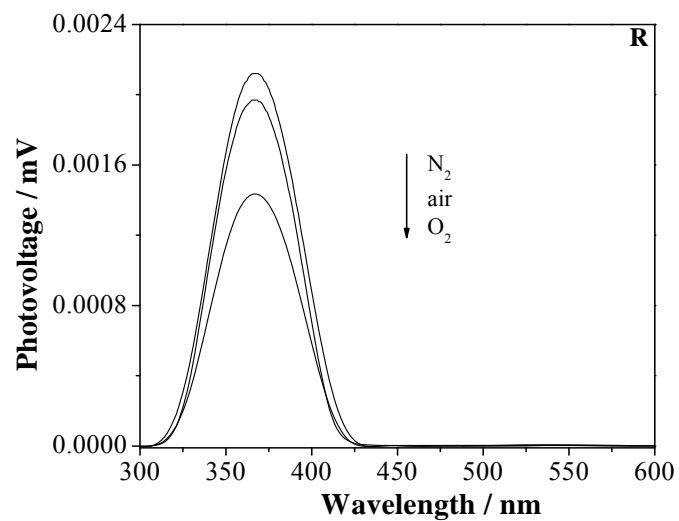
**Figure S1.** DRS spectra of un-modified and H<sub>3</sub>BO<sub>3</sub>-modified TiO<sub>2</sub>

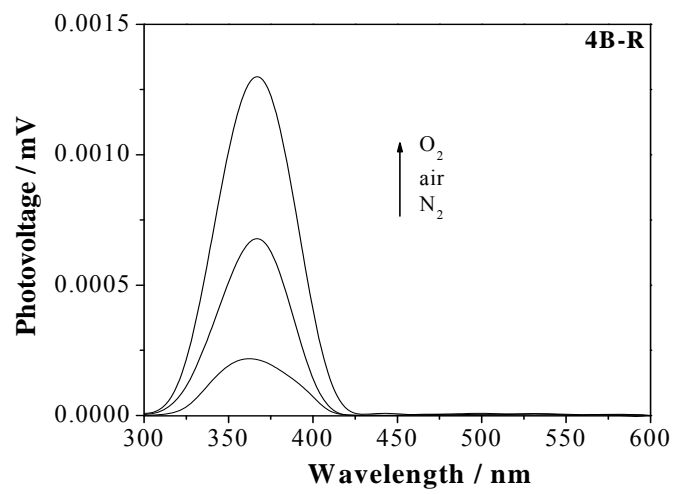
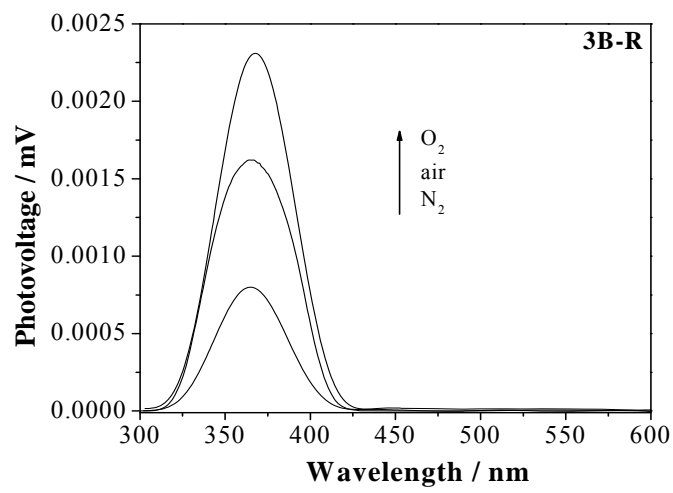
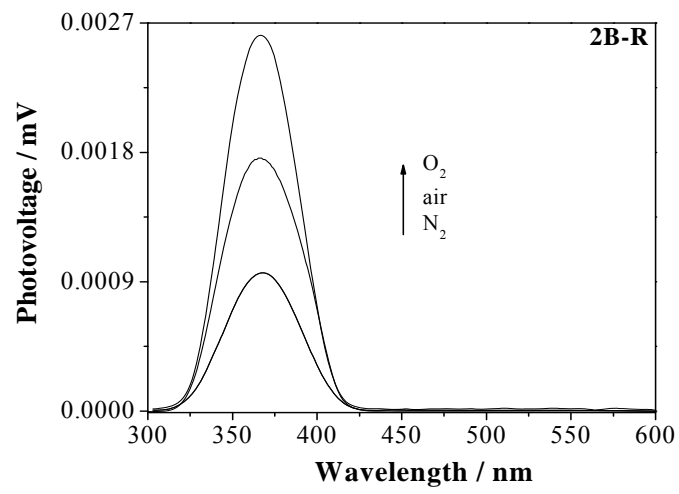


**Table S1.** Cl2p and B1s binding energy (BE) and atomic number ratio of Ti, adsorbed Cl and B.

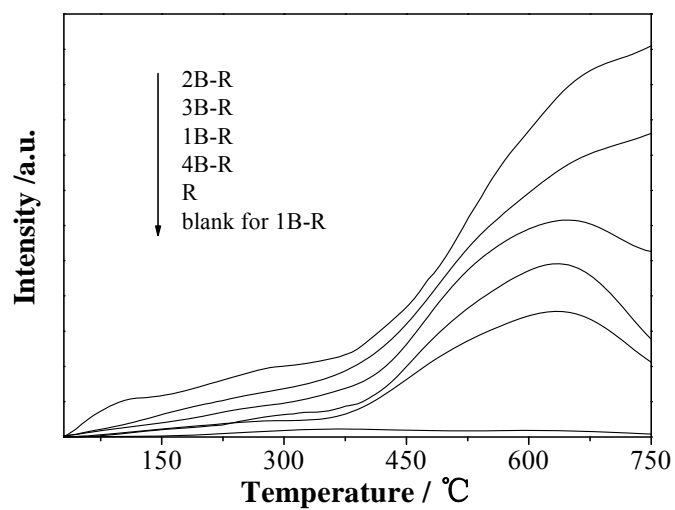
Samples	Binding Energy (eV)			Atomic number ratio of Ti, adsorbed Cl and B
	Adsorbed Cl2p	Doped Cl2p	B1s	
R	197.4	199.3	----	100: 1.3: 0
1B-R	197.1	199.3	191.4	100: 1.0: 9.8
2B-R	196.9	199.3	191.6	100: 0.6: 10.8
3B-R	196.8	199.3	191.8	100: 0.4: 14.5
4B-R	196.7	199.3	191.8	100: 0.3: 19.4

**Figure S2.** SPV responses of un-modified and  $\text{H}_3\text{BO}_3$ -modified  $\text{TiO}_2$  in different  $\text{O}_2$ -concentration atmospheres

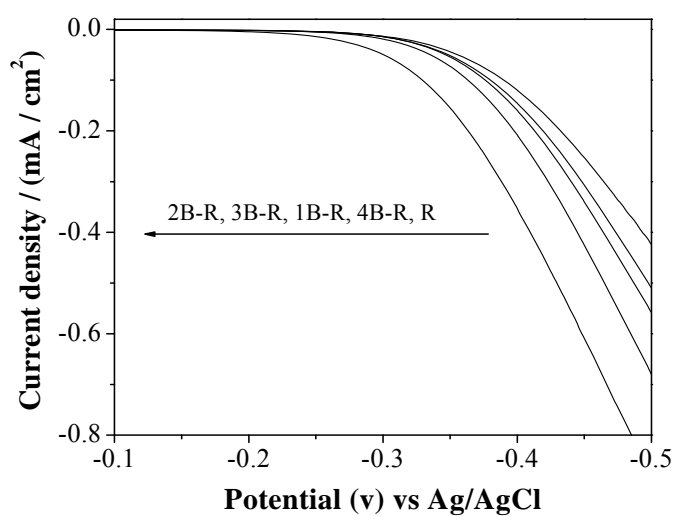




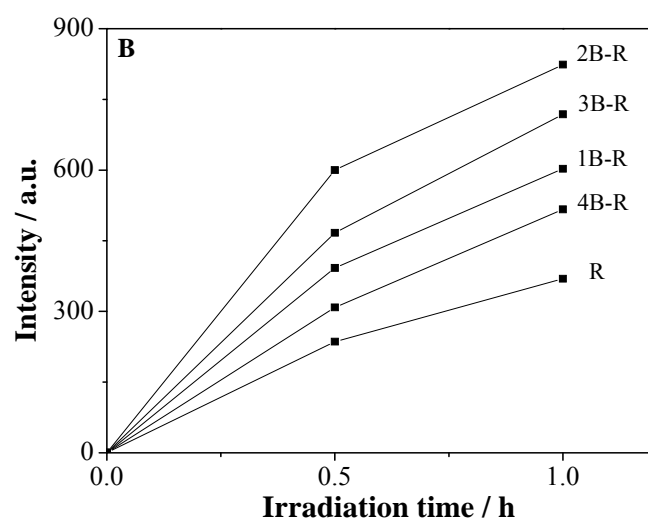
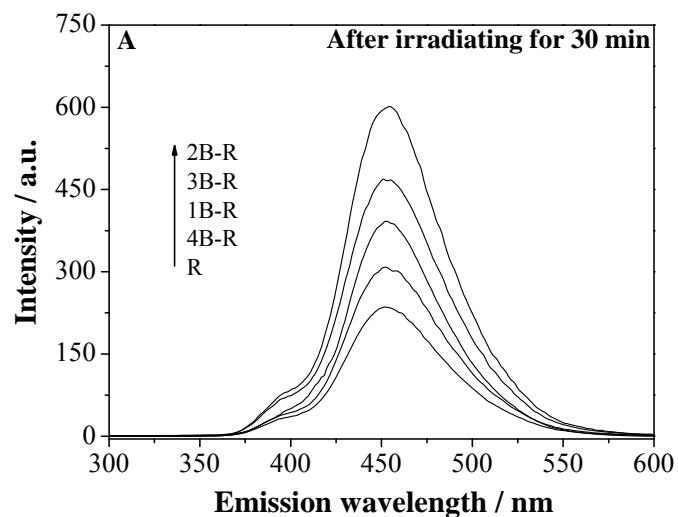
**Figure S3:** Curves of O<sub>2</sub> temperature-programmed desorption of un-modified and H<sub>3</sub>BO<sub>3</sub>-modified TiO<sub>2</sub>



**Figure S4:** Electrochemical reduction of O<sub>2</sub> on un-modified and H<sub>3</sub>BO<sub>3</sub>-modified TiO<sub>2</sub>

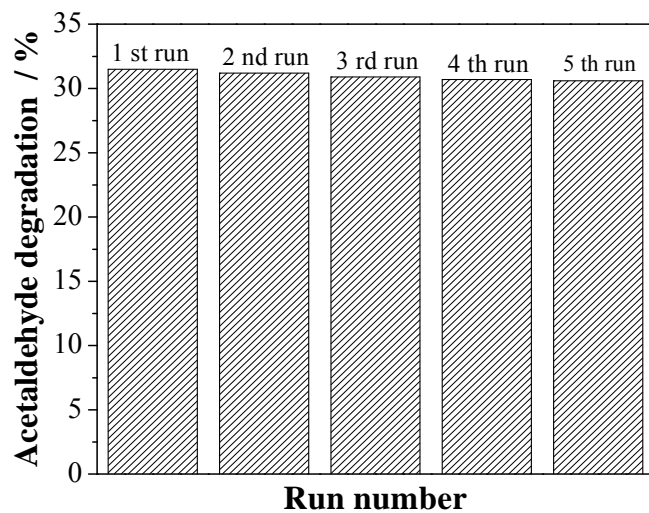


**Figure S5:** Temporal profiles of hydroxyl radicals on un-modified and H<sub>3</sub>BO<sub>3</sub>-modified TiO<sub>2</sub> (A) and the fluorescence spectra related to the formed hydroxyl radical amount after irradiation for 1 h (B)





**Figure S6:** the cycling runs of photocatalytic degradation of gas-phase acetaldehyde on the 2B-R sample



**Figure S7:** XRD patterns (A), SPV responses in different atmosphere (B), SPV responses in air (C) and photocatalytic activity for phenol degradation (D) of pure and  $H_3BO_3$ -modified rutile  $TiO_2$  without chloride

