Enhanced active oxidative species generation over Fe-doping defective TiO$_2$ nanosheets for boosted photodegradation

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Materials

Tetrabutyl titanate (Ti(OBu)$_4$), tetracycline hydrochloride (TC-HCl), ethylenediaminetetraacetic acid (EDTA) and bulk anatase TiO$_2$ were purchased from Aladdin Co., Ltd. Iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) and tertiary butyl alcohol (TBA) were obtained from Tianjin Fuchen Chemical Reaction Factory. The Ti(OBu)$_4$ and Fe(NO$_3$)$_3$·9H$_2$O were of analytical grade. Anhydrous ethanol, hydrofluoric acid (HF, 40 wt.%), and hydrogen peroxide (H$_2$O$_2$, 30wt.%) were purchased from Beijing Chemical Corporation. Rhodamine B (RhB) and p-benzoquinone (PBQ) were obtained from Sinopharm Chemical Reagent Co., Ltd. Ultra-pure water was used in all experiments.

Synthesis of X%-TiO$_2$ nanosheets (where X% is the mole percent of Fe, expressed as $100\% \times \frac{\text{mol Fe}}{\text{mol Ti}}$)

In a typical synthesis, 0.1685 g, 0.2808 g, 0.3931 g, 0.5054 g of Fe(NO$_3$)$_3$·9H$_2$O were added into anhydrous ethanol (40 mL) containing Ti(OBu)$_4$ (10 mL) and HF (1.2 mL), respectively. After stirring for 30 min, the solution was transferred into a stainless steel autoclave (100 mL) and then heated at 180°C for 2 h. The products were collected by centrifugation and washed repeatedly with ultra-pure water. Finally, the products were dried at 60°C under vacuum for 24 h.

Photocatalysts characterization

XRD patterns for photocatalysts were recorded by X-ray diffractometer (XRD, Bruker D8 Advance). The morphology of photocatalysts was characterized using a high-resolution transmission electron microscopy (HRTEM, JEOL-2100). Elemental analyses were obtained on inductively coupled plasma atomic emission spectroscopy (ICP-AES-7500, SHIMADZU). Chemical composition analyses were performed using a scanning transmission electron microscope (STEM, FEI Tecnai G2 F30) equipped with energy dispersive X-ray (EDX). Raman spectra were collected on Renishaw in Via spectrometer system. X-ray photoelectron spectroscopy (XPS) was performed on a KRATOS AXIS SUPRA system equipped with an Al Kα X-ray source. Brunauer-Emmett-Teller (BET) surface areas and N$_2$ physisorption isotherms were measured with a surface area and porosity analyzer (ASAP 2460t, Micromeritics), using liquid
nitrogen adsorbent at 77 K. Ultraviolet-Visible diffuse reflectance spectra (UV-DRS) were measured on a spectrophotometer (UV-3600, Shimadzu) using BaSO$_4$ as the reflectance standard. Photoluminescence spectra (PL) were obtained at room temperature using a fluorescence spectrophotometer (FLS700, Hitachi) (EM Start WL: 260.0 nm). Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker EPR-E500 spectrometer. The thickness of the 3.5%-TiO$_2$ nanosheets was determined by atomic force microscopy (AFM) (Bruker FastScan).

**Photocatalytic activity evaluation**

The photocatalytic performance of all the as-prepared samples was investigated by measuring the degradation rate of RhB aqueous solution (10 mg L$^{-1}$) and TC-HCl aqueous solution (20 mg L$^{-1}$) under simulated sunlight irradiation (300 W xenon lamp, CEL-HXF300, Beijing Zhongjiao Jinyuan Technology Co., Ltd.). In each photocatalytic reaction, 80 mg photocatalysts and 1.5 mmol H$_2$O$_2$ were added into an aqueous RhB solution of 80 mL, and then the suspensions were stirred in the dark for 40 min to reach the adsorption-desorption equilibrium between photocatalysts and RhB solutions. Under light irradiation, 4 mL of RhB solution was sampled at 5 min interval and filtered to remove the photocatalysts for optical absorbance measurements. To analogous, 10 mg sample and 1.5 mmol H$_2$O$_2$ were added into an aqueous TC-HCl solution of 80 mL, and then the suspension was stirred in the dark for 40 min to reach the adsorption-desorption equilibrium between photocatalysts and TC-HCl solutions. During irradiation, 4 mL of TC-HCl solution was sampled at 10 min interval and filtered to remove the photocatalysts for optical absorbance measurements. The absorbance of reaction solution was measured with a UV-vis spectrophotometer (UVmini-1240, Shimadzu), and the concentration of pollutants was determined by the RhB and TC-HCl standard curve. According to Beer’s law, the absorbance at 553 nm (the characteristic absorption wavelength of RhB) and 357 nm (the characteristic absorption wavelength of TC-HCl) were proportional to the concentration of RhB and TC-HCl in the reaction solution, respectively. Furthermore, the kinetic behaviors of photocatalysts were investigated through a pseudo-first-order model, $\ln[C/C_0] = -kt + \alpha$. Here, $C_0$ and $C$ present the initial concentration before irradiation and the residual
concentration of RhB and TC-HCl solution after irradiation for $t$ min, respectively, and $k$ is the apparent rate constant.

In the cycle test experiments, photocatalytic performance of 3.5%-TiO$_2$ was evaluated by performing 20 min of RhB photodegradation and 60 min of TC-HCl photodegradation experiments. Then the photocatalysts were recovered from the reaction solution, repeatedly washed with ethanol/ultrapure water and dried, and reused in photodegradation tests (ethanol was completely removed from the photocatalysts before the photocatalytic testing). A total of 4 such reaction cycles were performed (with approximately the same amount of photocatalyst used in each reaction cycle).

**Active oxidative species (AOS) trapping**

Generally, holes ($h^+$), superoxide radical ($\cdot O_2^-$), and hydroxyl radicals ($\cdot OH$) are considered as predominant AOS for dyes and antibiotics photodegradation.$^{1,2}$ To investigate the predominant AOS involved, radicals trapping experiments were performed, which is similar to former photocatalytic activity measurement. In this process, TBA (10 mmol L$^{-1}$), PBQ (10 mmol L$^{-1}$), and EDTA (10 mmol L$^{-1}$) were used as the scavengers for $\cdot OH$, $\cdot O_2^-$, and $h^+$, respectively.

**EPR tests**

EPR tests were performed by using a Bruker EPR-E500 spectrometer operating at room temperature. The $\cdot O_2^-$ radicals can be captured by 5,5-dimethyl-l-pyrroline N-oxide (DMPO). For the detection of DMPO-$\cdot O_2^-$ adducts, 20 mg of 3.5%-TiO$_2$ photocatalyst and a small amount of H$_2$O$_2$ were added into 50 μL of 5 wt.% DMPO/DMSO solution.

**Electrochemical measurements**

The electrochemical measurements were performed on a CHI 660E electrochemical workstation equipped with a three-electrode cell. The working electrode was a glassy carbon electrode coated with catalysts, the counter electrode was a platinum foil, and the reference electrode was a saturated Ag/AgCl electrode with saturated K$_2$SO$_4$ (1 mol L$^{-1}$) as the electrolyte. The electrochemical impedance spectroscopy (EIS) measurements were conducted over a frequency range 0.01-10$^5$ Hz without light. Photocurrent measurements and Mott-Schottky experiments were conducted with voltage range from -1.5 V-0 V, in accordance with procedures previous work.$^3$
Poisson’s equation can be solved to give the Mott–Schottky equation:\textsuperscript{4}

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 e A^2 N_D} \left(V - V_{fb} - \frac{k_B T}{e}\right)
\]

Where $C$ and $A$ are the interfacial capacitance and area, respectively, $N_D$ the number of donors, $V$ the applied voltage, $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $e$ is the electronic charge. Therefore, a plot of $C^{-2}$ against voltage should yield a straight line from which $V_{fb}$ can be determined from the intercept on the voltage axis.

The value of $N_D$ is determined from the slope with knowledge of $\varepsilon$ and $A$.\textsuperscript{5,6}
Fig. S1 TEM images of (a) 0%-TiO$_2$ nanosheets and (b) Bulk-TiO$_2$. 
Fig. S2 (a) AFM image and (b) corresponding height profiles of 3.5%-TiO$_2$ nanosheets (the numbers 1, 2 and 3 correspond to the line scan number in (a).
Table S1 ICP-AES data for the actual contents of Fe doping in X%-TiO$_2$ nanosheets (X = 1.5, 2.5, 3.5, 4.5).

| sample       | cFe (ppm) | cTi (ppm) | X (%)     |
|--------------|-----------|-----------|-----------|
| 1.5%-TiO$_2$ | 4.716     | 233.2     | 1.70%     |
| 2.5%-TiO$_2$ | 7.833     | 239.1     | 2.75%     |
| 3.5%-TiO$_2$ | 10.93     | 236.4     | 3.89%     |
| 4.5%-TiO$_2$ | 12.37     | 216.3     | 4.80%     |

cFe and cTi represent the concentration of metal ions in the catalysts solution.
Fig. S3 (a) Raman spectra for X%-TiO$_2$ nanosheets (X=0, 1.5, 2.5, 3.5, 4.5) and Bulk-TiO$_2$. 
Fig. S4 XPS spectra of O 1s in the (a) Bulk-TiO$_2$ and (b) 0%-TiO$_2$ nanosheets.
Table S2 Comparison of RhB photodegradation of various photocatalysts reported.

| Catalyst                  | Light source                             | The amount of catalyst (mg) | RhB concentration (ppm) | Photocatalytic degradation rate (min⁻¹) | Reference |
|---------------------------|------------------------------------------|----------------------------|-------------------------|----------------------------------------|-----------|
| 3.5%-TiO₂                 | 300 W xenon lamp                         | 80                         | 10                      | 0.3073                                 | This work |
| Ce-doped TiO₂             | 300 W xenon lamp                         | 400                        | 10                      | 0.00348                                | [7]       |
| B-doped BiOCl             | 350W xenon lamp                          | 10                         | 10                      | 0.01704                                | [8]       |
| N-doped ZnWO₄             | sunlight                                 | 10                         | 10                      | 0.1708                                 | [9]       |
| B-doped Bi₂MoO₆           | 250 W halogen Lamp                       | 20                         | 5                       | 0.016                                  | [10]      |
| Pt-doped TiO₂             | 220W mercury lamp                        | 3                          | 10                      | 0.0053                                 | [11]      |
| I/C-doped TiO₂            | 300 W Xe arc lamp                        | 50                         | 20                      | 0.1600                                 | [12]      |
| C-N-S-doped TiO₂          | 8 W UV lamp                              | 20                         | 10                      | 0.01234                                | [13]      |
| Fe–N–S-tri-doped TiO₂     | 500 W Xenon lamp                         | 200                        | 20                      | 0.0291                                 | [14]      |
| C/N-doped Au/TiO₂         | 500 W xenon lamp                         | 5                          | 4.79                    | 0.0071                                 | [15]      |
Fig. S5 Cycling runs of 3.5%-TiO$_2$ nanosheets for photocatalytic degradation of (a) RhB and (b) TC-HCl solution.
According to the International Union of Pure and Applied Chemistry (IUPAC) classification,\textsuperscript{16} the isotherm curves of Bulk-TiO\textsubscript{2} can be classified as Type-II isotherms, which manifested the nature of micropores.\textsuperscript{17} The X%-TiO\textsubscript{2} nanosheets showed Type-IV isotherms with H2-type hysteresis in the relative pressure of 0.4-0.8, which confirmed the presence of mesopores in the ultrathin X%-TiO\textsubscript{2} nanosheets.

**Fig. S6** (a) N\textsubscript{2} adsorption-desorption isotherms of X%-TiO\textsubscript{2} nanosheets and Bulk-TiO\textsubscript{2}. (b) Pore size distribution of X%-TiO\textsubscript{2} nanosheets and Bulk-TiO\textsubscript{2}.
Fig. S7 (a) UV-DRS data and (b) Tauc plots for X%-TiO$_2$ nanosheets and Bulk-TiO$_2$. 
Fig. S8 XPS valence band spectra of 3.5%-TiO$_2$.

According to the UV-DRS (Fig. S7a-b) and Mott-Schottky diagram (Fig. 5d), the band gap and conduction band (CB) position of 3.5%-TiO$_2$ nanosheets were estimated to be 2.04 eV and -0.54 eV, respectively. The valence band (VB) position of 3.5%-TiO$_2$ nanosheets was thus calculated to be about 1.50 eV. The VB maximum of 3.5%-TiO$_2$ was also measured by XPS valance spectra, a VB edge was 2.06 eV and a band tailing was 1.51 eV (Fig. S8). In addition, the band edge energy ($E_{CB}$, $E_{VB}$) of 3.5%-TiO$_2$ nanosheets was further calculated according to the empirical equation as follow:

$$E_{VB} = \chi - E_C + \frac{1}{2}E_g$$

where $\chi$ represents the electronegativity of the semiconductors (here, the value of $\chi$ is 5.18 eV for 3.5%-TiO$_2$), $E_C$ is the standard hydrogen electrode scale (NHE) ($E_C = 4.5$ eV$^{21}$ and $E_g$ is the bandgap for 3.5%-TiO$_2$ ($E_g = 2.04$ eV). The calculated $E_{VB}$ for 3.5%-TiO$_2$ is found to be about 1.70 eV. Considering the above calculation results, experimental data and inevitable experimental errors, the VB position of 3.5%-TiO$_2$ is inferred between 1.50-2.06 eV. According to the previous reports, some typical semiconductor photocatalysts with VB position between 1.50-2.06 eV can also generate holes with sufficient oxidation potential for the photodegradation of RhB and TC-HCl in water.$^{23-24}$ Moreover, both superoxide radical ($\bullet$O$_2^-$) and photo-generated holes contributed to the photodegradation of RhB and TC-HCl, as proved by radicals trapping experiments and EPR tests (Fig. 6a-c). Considering that both $\bullet$O$_2^-$ and the photo-
generated holes of 3.5%-TiO$_2$ possess sufficient oxidation ability to oxidize RhB and TC-HCl, so it would be safe to deduce that the 3.5%-TiO$_2$ nanosheets has sufficient oxidation for oxidizing the pollutants.
To explore the role of H$_2$O$_2$ in the photocatalytic reaction, we carried out a series of control experiments. As shown in Fig. S9, when there is no catalyst and only H$_2$O$_2$ in the reaction system, the concentration of RhB remained basically unchanged after 20 min light irradiation, which means that H$_2$O$_2$ itself cannot achieve the RhB photodegradation without the aid of photocatalysts. For Bulk-TiO$_2$, regardless of whether H$_2$O$_2$ is added to the reaction solution, the removal efficiency of RhB was almost unchanged after 20 min light irradiation, while the 0%-TiO$_2$ nanosheets displayed improved degradation performance in the presence of H$_2$O$_2$, with the RhB removal efficiency of 19.2%, which is higher than that for 0%-TiO$_2$ in the absence of H$_2$O$_2$. Since ultrathin 0%-TiO$_2$ nanosheets possessed higher concentration of Vo than Bulk-TiO$_2$, it is assumed that H$_2$O$_2$ can play a role in boosting the photocatalytic degradation only in the presence of photocatalysts rich in Vo. This inference may also be valid for 3.5%-TiO$_2$ nanosheets.

In the photocatalysis process, H$_2$O$_2$ can be reduced to •OH by photo-generated electrons,\textsuperscript{25-26} while it can also be oxidized to •O$_2$$^-\textsuperscript{−}$ by photo-generated holes.\textsuperscript{25, 27-28} Through radical capture experiments, the main oxidative species for RhB/TC-HCl degradation by 3.5%-TiO$_2$ were identified to be holes and •O$_2$$^-\textsuperscript{−}$, rather than •OH (Fig. 6a-b). Thence, it is possible that Vo-rich TiO$_2$ nanosheets converted H$_2$O$_2$ into more •O$_2$$^-\textsuperscript{−}$ which contribute to the pollutants degradation. The above experimental results

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**Fig. S9** Time profiles of RhB degradation for 0%-TiO$_2$ nanosheets and Bulk-TiO$_2$ with or without H$_2$O$_2$. 

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manifested that H$_2$O$_2$ could not only participate in the Fenton reaction, but also be oxidized to •O$_2^-$ by photo-generated holes in the assistance of Vo-rich TiO$_2$ photocatalysts, thereby further promoting the degradation of RhB or TC-HCl.
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