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Ionothermal synthesis of black Ti$^{3+}$-doped single-crystal TiO$_2$ as an active photocatalyst for pollutant degradation and H$_2$ generation

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Black Ti$^{3+}$/TiO$_2$ single-crystals synthesized via an ionothermal process exhibited high activity for photocatalytic degradation of pollutants and hydrogen evolution reaction.
Ionothermal synthesis of black Ti$^{3+}$-doped single-crystal TiO$_2$ as an active photocatalyst for pollutant degradation and H$_2$ generation

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Abstract

A black Ti$^{3+}$-doped single-crystal TiO$_2$ (Ti$^{3+}$/TiO$_2$) was one-pot synthesized by treating metal Ti in an ionic liquid containing LiAc and HAc under mild ionothermal conditions. The ionic liquid (1-methyl-imidazolium tetrafluoroborate) supplied an environment enriched with fluoride ions for dissolving titanium foil at ionothermal condition, followed by reducing protons in acetic acid to form Ti$^{3+}$ ions, leading to Ti$^{3+}$-doped single-crystal TiO$_2$ in black powder. EPR and XPS results indicated the high-concentrations of both Ti$^{3+}$-dopants and oxygen vacancies. The Ti$^{3+}$ incorporated into TiO$_2$ lattice could narrow the energy band gap of TiO$_2$ via forming intermediate energy levels, leading to the visible photocatalyst. Meanwhile, the oxygen vacancies could inhibit the photoelectron-hole recombination. As expected, such a black Ti$^{3+}$/TiO$_2$ exhibited high activity in photocatalytic degradation of organic pollutants and water splitting for H$_2$ production under irradiation with visible lights and/or simulated solar lights.

Keywords: Black Ti$^{3+}$-doped single-crystal TiO$_2$ (Ti$^{3+}$/TiO$_2$), ionothermal synthesis, visible photocatalyst, pollutant degradation and H$_2$ generation

Introduction:

TiO$_2$ photocatalyst has received more and more attentions in environmental cleaning and green energy production owing to its high activity, non-toxicity, easy availability, and strong stability for degradation of organic pollutants$^1$, H$_2$ production via water splitting$^2$ and direct photoelectric transformation.$^3$ Since the report of Fujishima and Honda in 1972$^4$, TiO$_2$-based
photocatalysts have been widely investigated in designing new photocatalysts, exploring fundamental theory and putting into practical applications. However, the application of pure TiO$_2$ photocatalyst is still quite limited since it can be activated by only UV lights due to the big energy band gap (anatase with a band-gap of 3.2 eV and rutile with a band-gap of 3.0 eV), taking into account that the sunlight contain large proportion of visible lights and very little fraction of UV lights. In the past two decades, cation-doping$^5, 6$, metal hybrid$^7$, semiconductor-doping$^8$, and nonmetal-doping etc.$^5, 6$ have been widely used to modify the electronic structure and consequently the light absorption range of TiO$_2$ for achieving visible photocatalysts in which there were using many methods to synthesis visible-light-driven-materials$^9, 10$, such as ionothermal method which could prepare TiO$_2$$^{11}$ and other materials$^{12, 13}$. In addition, Also changing the morphology$^{14}$, preparing TiO$_2$-based$^{15}$ or doped composite$^{16}$ and enhancing (001) facet exposure rate$^{17-20}$ of TiO$_2$ would be increasing the photocatalytic activity.

Recently, both the experimental results and theoretical prediction demonstrate that the Ti$^{3+}$-doped TiO$_2$ with great number of oxygen vacancies (Ti$^{3+}$/TiO$_2$) usually displays black color$^{21}$ and strong spectral response in visible area.$^{22}$ Up to now, a variety of methods have been developed for synthesizing black Ti$^{3+}$/TiO$_2$, such as hydrogen reduction of TiO$_2$ at high calcination temperature and pressure,$^{23, 24}$ high temperature induced molten aluminum reduction of TiO$_2$ etc.$^{25}$ Besides the harsh conditions and tedious experimental steps, these reported black Ti$^{3+}$/TiO$_2$ samples usually exhibited low photocatalytic activity under visible light irradiation due to the low-content of Ti$^{3+}$-dopants and the poor stability of Ti$^{3+}$-dopants against oxidation. Herein, a facile one-step approach was developed for synthesizing black Ti$^{3+}$-doped anatase TiO$_2$ single-crystal (Ti$^{3+}$/TiO$_2$) by treating Ti foil in 1-methyl-imidazolium tetrafluoroborate ionic liquid containing acetic acid (HAc), N,N dimethylformamide (DMF), and lithium acetate (LiAc) under 200 °C ionothermal conditions. The as-formed black Ti$^{3+}$/TiO$_2$ photocatalyst contained high-contents of Ti$^{3+}$-dopants and oxygen vacancies. The Ti$^{3+}$-dopants in the TiO$_2$ lattice could narrow energy band gap of TiO$_2$ semiconductor via forming intermediate energy levels, leading to the visible photocatalyst. Meanwhile, the oxygen vacancies could diminish the photoelectron-hole recombination and thus, could enhance the quantum efficiency of photocatalysis. As expected, this black Ti$^{3+}$/TiO$_2$ exhibited high activity in photocatalytic degradation of organic pollutants and water-splitting for H$_2$ generation under irradiation with visible lights and/or simulated solar lights.
Experiments

Catalyst preparation

All chemicals were analytical grade and used as received without any further purification. In a typical run of synthesis, 12 mL DMF (as solvent), 0.6 g LiAc·2H₂O and 18 mL glacial HAc (as buffer solution) were mixed in a 100-mL pyrex beaker and magnetically stirred for 15 min to get a clear solution. The mixture was then transferred to an autoclave (50 mL). Meanwhile, a piece of Ti foil (99.5 %, 20 mm*33 mm*0.3 mm) was ultrasonically cleaned in a mixed solution of deionized water, acetone, and ethanol with volume ratios of 1:1:1, followed by adding into the autoclave together with 2 mL ionic liquid (1-methyl-imidazolium tetrafluoroborate). The mixture was kept at 200°C for 24 h and then, the black product was washed with water and ethanol for three times, followed by drying at 80 °C for 12 h.

Characterizations

X-ray diffraction (XRD) patterns were collected on a Rigaku Dmax-3C with Cu Ka radiation. Selected area electron diffraction (SAED) images and transmission electronic microscopy (TEM) morphologies were recorded on a JEM-2010. Field emission scanning electron microscopy (FESEM) images were performed on a JEOL JSM-6380LV. Raman spectra and UV-vis diffuse reflectance spectra (UV-vis DRS) were conducted on Dilor Super LabRam II and MC-2530 instruments, respectively. For expelling the local heating effect, same laser source (wavelength = 633 nm) was utilized in the Raman characterization for all samples. The photoluminescence spectroscopy (PLS) was collected on Varian Cary-Eclipse 500 excited with 280 nm lights. The photocurrent responses in the light on-off process were determined in a homemade three electrode quartz cell containing 0.5 mol/L Na₂SO₄ aqueous solution under visible lights (> 420 nm) irradiation at an applied potential of 0.5 V vs. SCE with electrochemical workstation (CHI 660D, Chen Hua Instrument Co., Ltd.). X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin-Elmer PHI 5000C ESCA system. All binding energies were calibrated by using the contaminant carbon (C₁s = 284.6 eV) as a reference. Thermogravimetric analysis (TG) were carried out on a DTG-60H thermogravimetric analyzer with a heating speed of 10 °C/min under air atmosphere. The electron paramagnetic resonance (EPR) spectra were recorded at 100 K using a
Bruker EMX-8/2.7 EPR spectrometer. Solid state $^1$HNMR was recorded on a Bruker Avance400. Photoelectrochemical measurements were carried out in a conventional three-electrode, single-compartment quartz cell on an electrochemical station (CHI 660D). The $\text{Ti}^{3+}/\text{TiO}_2$ electrodes with an active area of ca. 1 cm$^2$ were served as working electrode. For the working electrodes, 20 mg of the photocatalyst was ground with 0.01 g polyethylene glycol (PEG, molecular weight 20000) and 0.5 mL ethanol to make a slurry. Afterward, the slurry was coated onto a 3 cm*1 cm F-doped SnO$_2$-coated glass (FTO glass) electrode by the doctor blade method, with an active area of ca.1 cm$^2$. The electrodes were calcined at 200 °C for 3 h in a ceramic plate heater. All the electrodes used had a similar thickness (1.0-1.5 mm). The counter electrode and the reference electrode were platinum sheet and saturated calomel electrode (SCE), respectively. A bias voltage of 0.5 V was utilized for driven the photo-generated electrons transfer from working electrode to platinum electrode. A 300 W Xe lamp with an ultraviolet filter ($\lambda > 420$ nm) was used as visible light source and positioned 10 cm away from the photo-electrochemical cell. A 0.5 mol/L Na$_2$SO$_4$ aqueous solution was used as the electrolyte. The transient photocurrent curves were measured under an applied bias of 0.5 V.

**Activity test**

1. **Photocatalytic degradation.** Briefly, 50 mg photocatalyst was dispersed in 50 mL Rhodamine B (RhB) aqueous solution (10 mg/L) and stirred in dark for 1 h for reaching the adsorption/desorption equilibrium. During photocatalysis, a 300 W Xenon lamp (PLS-SXE300CUV, UV percent = 5.2 %) was used to simulate solar lights. For achieving visible lights induced photocatalysis, all the lights with wavelength shorter than 420 nm were cut-off by a filter to get visible-lights. After reaction for 4 h under 1000 r/min stirring, 2.0 mL suspension was sampled into plastic tube and centrifuged to remove the photocatalyst particles. The concentration of remained RhB was determined by UV-visible spectrophotometer analysis at its characteristic wavelength of 554 nm, from which the photocatalytic degradation yield was obtained by comparing with the initial RhB concentration. For comparison, the photocatalytic degradation of RhB was also conducted by using a 300 W Xenon lamp without removing UV lights with wavelength shorter than 420 nm. Meanwhile, 8 LED lamps (light intensity = 3.5 mW/cm$^2$, UVEC-4 II devices purchased from Shenzhen Lamplpic Science Co., Ltd) with single wavelength of 420 nm were used instead of a 300 W Xenon lamp for driving photocatalytic degradation of
RhB. In addition, photocatalytic degradation of aniline in aqueous solution (10 mg/L) was also carried out by using visible lights with wavelength longer than 420 nm from a 300 W Xenon lamp. The concentration of remained aniline was determined by UV-visible spectrophotometer analysis at its characteristic wavelength of 230 nm, from which the photocatalytic degradation yield was obtained by comparing with the initial aniline concentration.

2. Photocatalytic H\textsubscript{2} generation. Hydrogen production by photocatalytic water-splitting was carried out at room temperature in a three flat-bottomed flask reaction cell. Typically, 50 mg photocatalyst doped with 1 wt% Pt through \textit{in situ} photo-reduction of H\textsubscript{2}PtCl\textsubscript{6} was dispersed in 80 mL aqueous solution containing 20 mL methanol as the sacrificial reagent under ultrasonication. A 300 W Xenon lamp was used as simulated solar lights, positioned 1 cm away from the reactor. The evolved H\textsubscript{2} amount was determined using a gas chromatograph (Shanghai Ke Chuang, GC-9800, TCD, N\textsubscript{2} carrier and 5 A molecular sieve columns).

**Results and discussion:**

As shown in Fig. 1a, the as-received Ti\textsuperscript{3+}/TiO\textsubscript{2} sample was present in black powders. TGA analysis (Fig. S1) displayed no significant weight loss until 450 \degree C, indicating the absence of organic species. The XRD pattern in Fig. 1b demonstrated the single-crystal anatase TiO\textsubscript{2} (JCDPS 21-1272) in about 20-30 µm regular particles (see the SEM image in Fig. 1c). HRTEM (Fig. 1d) shows that the as-prepared TiO\textsubscript{2} nanocrystals were covered with disordered layers. Both HRTEM and the SAED images (Fig. 1d) further confirmed the single-crystal anatase phase. Based on the SAED, it can be defined that the as-prepared samples had the exposed facets which were \{001\} and \{101\} combined with Fig 1c. In addition, the SAED in Fig. 1(d) shows the (002) and (011) atomic planes with a lattice spacing of 0.189 nm and 0.352 nm respectively. The XRD patterns (Fig. S2) further confirmed that the as-prepared black Ti\textsuperscript{3+}/TiO\textsubscript{2} remained anatase phase until the calcination temperature reaching 600 \degree C and then totally transferred into rutile phase at 700 \degree C, showing excellent thermal stability against phase change.
As shown in Fig. 2, the $^1$H NMR spectra revealed that, besides a weaker signal at 4.7 ppm indicative of the H at bridging sites observed in pure white TiO$_2$, the black Ti$^{3+}$/TiO$_2$ displayed three additional strong signals at -0.18 ppm, 0.97 ppm and 1.90 ppm, corresponding to the terminal and internal hydroxyl groups of anatase TiO$_2$. These groups were associated with the H located in the disordered surface layer of the black Ti$^{3+}$/TiO$_2$, which could be completely removed after being calcined in air at 700 °C.

Figure 1. (a) Digital picture, (b) XRD pattern, (c) SEM image, and (d) HRTEM image of the as-prepared black Ti$^{3+}$/TiO$_2$. The inset is the SAED image. Scale bar in (a): 10 mm.

Figure 2. $^1$H NMR spectra of black Ti$^{3+}$/TiO$_2$ (a) and white TiO$_2$ obtained by calcining Ti$^{3+}$/TiO$_2$ at 700 °C (b).

Scheme 1 briefly illustrates the formation of black Ti$^{3+}$/TiO$_2$ by the reaction between the Ti
foil and the ionic liquids (ILs) under ionothermal conditions. During the reaction, the fluoride enriched ionic liquid (IL) could dissolve Ti foil gradually. The SEM images and XRD patterns (Fig. S3) revealed that very little ionic liquid (0.5 mL) could dissolve only the outer surface of Ti foil, leading to a thin anatase TiO$_2$ film on the Ti foil. The Ti foil could be severely dissolved into bumps in the presence of 1.0 mL IL, corresponding to the formation of black Ti$^{3+}$/TiO$_2$ either in the solution or on the surface of Ti bumps. Further increase of IL to 2.0 mL resulted in complete dissolve of Ti foil, leading to the pure black Ti$^{3+}$/TiO$_2$ in regular particles with an average size about 20–30 µm in Fig. 1c. During the dissolving process of Ti foil under ionothermal conditions, H$_2$ gas could be produced via the reduction of H$^+$ from acetic acid by metal Ti, which could be confirmed by the following controlled experiment. After ionothermal treatment of Ti foil for 24 h, the autoclave was opened in a self-made glove box (volume = 60 L) filled with high purity N$_2$. 0.5 mL gas was sampled and analyzed by GC (GC9800, Shanghai Ke Chuang Chromatograph Instruments Co. Ltd, China, TCD, with nitrogen as a carrier gas and 5 A molecular sieve columns), which clearly displayed a typical H$_2$ peak as observed by introducing H$_2$ into autoclave before ionothermal process (see Fig. S4), indicating the H$_2$ generation during Ti foil dissolving under ionothermal conditions.

![Scheme 1. The formation process of the black Ti$^{3+}$/TiO$_2$ under ionothermal conditions.](image)

Based on the above results, it is reasonable that the black Ti$^{3+}$/TiO$_2$ formation process may include the following 4 steps. 1) Ti foil reacted with the H$^+$ ions resulted from ionization of HAc to form Ti$^{4+}$/Ti$^{3+}$ ions and hydrogen gas in which the concentration of Ti$^{4+}$ ions could be much
higher than that of Ti$^{3+}$ ions. 2) Some of the formed Ti$^{4+}$ ions will be further reduced to Ti$^{3+}$ ions by the metal Ti$^{2+}$. 3) The Ti$^{4+}$ and Ti$^{3+}$ ions underwent ionothermal hydrolysis owing to the presence of trace H$_2$O resulted from the dehydration of acetic acid. The LC-MS patterns (Fig. S5) clearly displayed the presence of acetic anhydride in the ionic liquid obtained after ionothermal treatment of Ti foil for 24 h. During ionothermal hydrolysis process, Ti$^{4+}$ transformed into anatase TiO$_2$ and Ti$^{3+}$ ions may corporate into TiO$_2$ lattice. 4) The in-situ generated H$_2$ could be strongly adsorbed onto the TiO$_2$ surface and dissociated into H atom to form H-TiO$_2$-x disordered layer.

Some important reactions involved the whole process are listed as follows.

\[
\begin{align*}
H_3C\overset{\text{OH}}{\longrightarrow}O\overset{\text{OH}}{\longrightarrow}H_3C + H^+ \quad (1) \\
H^+ + Ti & \rightarrow Ti^{3+}/Ti^{4+} + H_2 \\
Ti^{4+} + Ti & \rightarrow Ti^{3+} \\
Ti^{4+} + H_2O & \rightarrow TiO_2 \\
TiO_2 + H_2 & \overset{\text{diffusion}}{\rightarrow} H-TiO_2 \quad (5) \\
\end{align*}
\]

The EPR spectra (Fig. S6) of the as-prepared black Ti$^{3+}$/TiO$_2$ displayed strong signals in the g range from 1.99 to 1.94 which could be remained after being calcined at the temperature up to 500 °C, confirming the presence of Ti$^{3+}$ species.\textsuperscript{30} After being calcined at 700 °C, nearly all the Ti$^{3+}$ species were oxidized into pure TiO$_2$. The XPS spectra in Ti 2p level (Fig. S7) also demonstrated the co-existence Ti$^{3+}$ (457.5 eV 2P$_{3/2}$ and 463.7 eV 2P$_{1/2}$) and Ti$^{4+}$ (459.1 eV 2P$_{3/2}$ and 464.7 eV 2P$_{1/2}$)\textsuperscript{31} in the black Ti$^{3+}$/TiO$_2$ when it was calcined below 500 °C and completely transformed into pure TiO$_2$ after being calcined at 700 °C. A semi-quantitative analysis of Ti$^{3+}$/Ti$^{4+}$ molar ratio could be calculated based on the XPS spectra (Table S1). The fresh black Ti$^{3+}$/TiO$_2$ displayed a Ti$^{3+}$/Ti$^{4+}$ molar ratio of 0.162, which quickly decreased after calcinations at elevated temperatures due to the oxidation of Ti$^{3+}$. From 300 °C to 500 °C, the Ti$^{3+}$/Ti$^{4+}$ molar ratio decreased from 0.128 to 0.101. After being calcined at 700 °C, the Ti$^{3+}$/Ti$^{4+}$ ratio decreased to about 0, indicating all of the Ti$^{3+}$ ions were transferred to Ti$^{4+}$ ions owing to the oxidation effect of O$_2$. In addition, the Raman spectra also confirmed the presence of oxygen vacancies. As well known, the pure anatase TiO$_2$ displays 6 typical peaks around 144, 197, 639, 399, 519, and 513
cm$^{-1}$, corresponding to the $E_g(1)$, $E_g(2)$, $E_g(3)$, $B_1g(1)$, $B_1g(2)$ and $A_1g$ modes$^{32,33}$. As shown in Fig. 3, the fresh black Ti$^{3+}$/TiO$_2$ exhibited a principal peak around 157.0 cm$^{-1}$ characteristic of oxygen vacancies. Calcining at 300 °C had no significant influence on the Raman spectra. Increase the calcination temperature to 500 °C resulted in a negative shift of the principal peak from 157.0 cm$^{-1}$ to 151.3 cm$^{-1}$. Further increasing the calcining temperature to 700 °C led to the formation of anatase TiO$_2$ to rutile TiO$_2$ as indicated in both Fig. 3a and aforementioned XRD pattern (Fig. S2), together with the continued negative shift to about 147.1 cm$^{-1}$, implying a great decrease in oxygen vacancies$^{34}$. These results clearly demonstrated that the oxygen vacancies produced due to the replacement of Ti$^{4+}$ ions with Ti$^{3+}$ ions in TiO$_2$ lattice (see the following equation)$^{35}$ and the number of oxygen vacancies decreased gradually during calcinations at elevated temperatures due to the oxidation of Ti$^{3+}$ into TiO$_2$.

$$4\text{Ti}^{4+} + \text{O}_2 \rightarrow 4\text{Ti}^{4+} + 2e^-/\square + 0.5 \text{O}_2 \rightarrow 2\text{Ti}^{4+} + 2\text{Ti}^{3+} + \square + 0.5 \text{O}_2$$

![Figure 3](image_url)

**Figure 3.** Raman spectra (a) and the corresponding enlarged Raman spectra from 100 to 200 cm$^{-1}$ (b) of the as-prepared black Ti$^{3+}$/TiO$_2$ before (A) and after being calcined at elevated temperatures 300 °C (B), 500 °C (C), 700 °C (D).

The UV-Vis DRS spectra in Fig. 4 revealed that the black Ti$^{3+}$/TiO$_2$ displayed an extended absorption band up to ca. 800 nm. And the calcined samples had the broad peak at ca. 680 nm which is consistent with the color change of the samples. The broad peak at 680 nm might be due to forming oxygen vacancy energy level in the bandgap. In the illumination, the photo-generated electron was graded transition. Calcining the black Ti$^{3+}$/TiO$_2$ samples at elevated temperatures resulted in the gradual blue-shift of the light absorbance$^{21}$. The black Ti$^{3+}$/TiO$_2$ and calcining at
different temperature samples all had the decreasing optical bandgap with the color-dependence. Thus, the visible light absorbance of the black Ti$^{3+}$/TiO$_2$ could be mainly ascribed to the existence of defect states in TiO$_2$ band gap owing to the presence of Ti$^{3+}$-dopants and oxygen vacancies in accordance with the XPS analysis.

![UV-vis diffuse reflectance spectra (DRS) and digital photos of the as-prepared Ti$^{3+}$/TiO$_2$ before and after being calcined at elevated temperatures.](image)

**Figure 4.** The UV-vis diffuse reflectance spectra (DRS) and digital photos of the as-prepared Ti$^{3+}$/TiO$_2$ before and after being calcined at elevated temperatures.

Based on 1*1*2 and 2*2*1 anatase TiO$_2$ super cells, the electronic structure of the black Ti$^{3+}$/TiO$_2$ could be calculated by using CASTEP model. To calculate the concentration of oxygen vacancy, one O atom is removed from each super cell. During the calculation, a suitable plane-wave basis set with an energy cutoff of 408 eV was selected for the ultra-soft pseudopotential with Perdew-Burke-Ernzerhof exchange correlations. Brillouin-zone integration is computed with k points in a Monkhorst-Pack (10, 10, 5) grid. As known, the H disorder-adsorbed on the surface of black Ti$^{3+}$/TiO$_2$ could form a mid-gap state. It can form a continuum extending to or overlapping with the conduction band edge, named band tail states. It is found that the Fermi level is much closer to the conduction band tail states at high oxygen vacancy concentration (see Fig. S8). Thus, it is reasonable that the high concentration of oxygen vacancy may break the selection rule for indirect transitions, leading to an enhanced absorption for photon energy below the direct band gap, in good accordance with the UV-vis DRS spectra (see Fig. 4). Based on above calculation, a scheme of the structure and density of states (DOS) is illustrated in Fig. 5. The gap states form a mini-band below the conduction band edge. It could be seen that the conduction band edge will turn broad at enhanced oxygen vacancy concentration. Meanwhile, the band of defect-states resulted from oxygen vacancy is very close to the conduction band edge,
allowing photo-generated electrons to easily exchange between two bands. Under visible-light irradiation, the electron from the valence band (VB) can easily transfer to the oxygen vacancy level existing in the band gap. Therefore, the electronic transfer from both valence band and oxygen vacancy level localized states to tailed conduction band (CB).

**Figure 5.** The scheme of the structure and density of states (DOS) for pure TiO$_2$ (left) and black Ti$^{3+}$/TiO$_2$ (right), together with conduction and valence levels of bulk semiconductor (Ec and Ev).

As shown in Fig. 6a, all the Ti$^{3+}$/TiO$_2$ samples display PLS peaks at around 560 nm regardless of the calcination temperature. The intensity increased with the enhanced calcination temperature, indicating the increased photoelectron-hole recombination rate,$^{40}$ since the reduced concentration of Ti$^{3+}$-dopants caused the decrease in oxygen vacancies, which could capture photoelectrons and thus inhibit the photoelectron-hole recombination. Meanwhile, as shown in Fig. 6b, the black Ti$^{3+}$/TiO$_2$ exhibited strong photocurrent response. Calcinations of the black Ti$^{3+}$/TiO$_2$ at elevated temperatures in air resulted in significant decrease in photocurrent response, which could be attributed to both the decrease in absorbance for visible lights (see Fig. 4) and the increase of photoelectron-hole recombination rate (see Fig. 6a)$^{41}$ due to the reduced concentration of Ti$^{3+}$-dopants and oxygen vacancies.
As shown in Fig. 7a, the as-prepared black Ti$^{3+}$/TiO$_2$ exhibited relatively high activity during visible light driven photocatalytic degradation of RhB. The photocatalytic activity decreased gradually after being calcined at elevated temperature from 300 °C to 700 °C, which could mainly be attributed to the decrease in both the Ti$^{3+}$ content and the oxygen vacancy number due to the oxidation in air at high temperature. The white TiO$_2$ obtained at 700 °C displays no significant activity, obviously due to the complete transformation of Ti$^{3+}$ into TiO$_2$ and the total disappearance of oxygen vacancies, taking into account that either the pure anatase or the pure rutile TiO$_2$ could not be activated by visible-light due to their big energy band gaps$^{39}$. As shown in Fig. 7b, the as-prepared black Ti$^{3+}$/TiO$_2$ also exhibited strong durability and could be used for 4 times without any deactivation. For excluding the self-sensitization effect of RhB at 554 nm, the 8 LED lamps with wavelength of 420 nm and light intensity of 3.5 mW/cm$^2$ were employed as a single-wavelength light source for driving the photocatalytic reaction. As shown in Fig. 7c, 40 % RhB removal rate was obtained after reaction for 4 h over the fresh black Ti$^{3+}$/TiO$_2$, which was similar to that obtained under Xenon light irradiation with wavelength longer than 420 nm. Meanwhile, Fig. 7d also demonstrated the efficient degradation of colorless aniline under visible light irradiation ($\lambda > 420$ nm, Xenon lamp). It was also noted that only a about 19 % removal rate was obtained via choosing phenol as another colorless organic pollutants. For better comparison, commercial P25 was also utilized as standard. P25 exhibited an 79.7 % removal rate of RhB under under Xenon light irradiation with wavelength longer than 420 nm, however its activity was greatly decreased to very low (about 5 % removal rate) under 420 nm LED irradiation while
keeping other conditions unchanged. 79.7 % removal rate of RhB for P25 is attributed to its strong RhB-sensitization effect, which was evidenced by our earlier reported work.\textsuperscript{42} To the case of 420 nm LED irradiation, the RhB-sensitization effect was avoided with the formation of a negative activity for P25. All these results indicated that the present visible-light induced photocatalytic degradation was attributed to the intrinsic properties of the black Ti\textsuperscript{3+}/TiO\textsubscript{2} rather than the photosensitizing effect.

It was also found that the RhB degradation yield greatly enhanced up to 91% even after reaction for 3 h by using a 300 W Xenon lamp irradiation without removing UV lights (see Fig. S9), implying that the UV lights in the Xenon lamp could more effectively activate the black Ti\textsuperscript{3+}/TiO\textsubscript{2}, which could also be observed for the black Ti\textsuperscript{3+}/TiO\textsubscript{2} after being calcined at elevated temperatures. Moreover, it was found that the concentrations of both the Ti\textsuperscript{3+}-dopants and oxygen vacancies had very little influence on the photocatalytic activity induced by UV lights since no much change in RhB degradation yield was observed even after calcination of the black Ti\textsuperscript{3+}/TiO\textsubscript{2} up to 500 °C. From those results, we could guess that the Ti\textsuperscript{3+}-dopants and oxygen vacancies promoted photocatalytic activity mainly via generating intermediate energy levels to narrow the energy band gap rather than via capturing photoelectrons to reduce photoelectron-hole recombination. To our surprise, the black Ti\textsuperscript{3+}/TiO\textsubscript{2} after being calcined at 700 °C exhibited slightly higher activity than the fresh sample, which could be ascribed to the formation rutile/anatase TiO\textsubscript{2} heterojunctions, allowing a fast photo-generated electron transfer rate.\textsuperscript{43}
Figure 7. (a) Photocatalytic activities of the black Ti$^{3+}$/TiO$_2$ before and after being calcined at elevated temperature and (b) Recycling test of the fresh black Ti$^{3+}$/TiO$_2$ for RhB degradation in aqueous solution under visible-light ($\lambda > 420$ nm) irradiation. Reaction conditions: 50 mg photocatalyst, 50 mL RhB aqueous solution (10 mg/L), room temperature, 4 h. (c) The photocatalytic degradation of RhB with the fresh black Ti$^{3+}$/TiO$_2$ under 8 LED lamps (each light intensity = 3.5 mW/cm$^2$) illumination. Other reactions are the same as those in Figure 7(a). (d) The photocatalytic degradation of aniline (10 mg/L) with the fresh black Ti$^{3+}$/TiO$_2$ under visible-light illumination ($\lambda > 420$ nm). Other reactions are the same as those in Figure 7(a).

To clarify the mechanism of the photocatalytic degradation of aqueous RhB in the presence of the as-prepared black Ti$^{3+}$/TiO$_2$, we introduced various reactive species scavengers, including sodium oxalate (10 mg), isopropanol (1.0 mL), AgNO$_3$ (10 mg), and nitrogen gas, to the photocatalytic reaction system for investigating the effect of holes (h$_{vb}^+$), hydroxyl radicals (·OH), photo-generated electrons (e$^-$) and oxygen anion molecules (·O$_2^-$) on the removal efficiency of RhB under visible-light irradiation. As shown in Figure 8, it was found that the addition of AgNO$_3$, as the electron scavenger, had only a weak influence on the photocatalytic degradation of RhB. This indicates that the photogenerated electrons are not the key for degrading RhB. As known, the formation of superoxide anions (·O$_2^-$), an important active radical for photocatalytic reactions, resulted from the reaction between the dissolved oxygen in the reaction system and photogenerated electrons. Upon purging with nitrogen gas, oxygen molecules could be expelled from the reaction system, inhibiting the formation of superoxide anions. The removal rate of RhB was also decreased slightly. This indicates that ·O$_2^-$ is not the key factor affecting the photocatalytic performance of the black Ti$^{3+}$/TiO$_2$. In addition, when adding isopropanol (IPA) to minimize the formation of OH radicals, it was found that the addition of isopropanol greatly reduced the photodegradation rate of RhB from 43% to about 15% in the black Ti$^{3+}$/TiO$_2$. The ·OH radicals were further detected by a terephthalic acid photoluminescence probing. The
fluorescence intensity was found to increase steadily with irradiation time (Fig. S10a), indicating that hydroxyl radicals can be generated in the black Ti$^{3+}$/TiO$_2$ system under visible light ($\lambda > 420$ nm) irradiation. The ESR spin-trap technique (with DMPO) was also further chosen to probe the hydroxyl radicals generated on the surface of the black Ti$^{3+}$/TiO$_2$. As shown in Fig. S10b, four characteristic peaks of DMPO-•OH were obviously observed in the suspension of black Ti$^{3+}$/TiO$_2$. This is consisted with the description of by using the terephthalic acid to probe hydroxyl radicals in PL experiment.

Moreover, a significant 72 % decrease in the photocatalytic activity was attributed to the addition of sodium oxalate (Na$_2$C$_2$O$_4$) for trapping photogenerated holes (h$_{vb}^+$). These results imply that the degradation of RhB by the black Ti$^{3+}$/TiO$_2$ photocatalyst seemed to be ascribed to a dual mechanism involving both surface h$_{vb}^+$ and OH radicals. To the case of the sample, the black Ti$^{3+}$/TiO$_2$, the absorptive intensity of RhB at a wavelength of 554 nm gradually decreases and the absorption band shifts to shorter wavelengths at 540 nm as shown in Figure S11. Furthermore, no new absorption bands appear in either the visible or the UV region. This suggests the complete photocatalytic decomposition of RhB during the reaction on black Ti$^{3+}$/TiO$_2$ sample.

Therefore, it can be concluded that the photo-oxidation mechanism occurring on the surface of the black Ti$^{3+}$/TiO$_2$ may involve the direct reaction of the organic chemical (dye) with surface h$_{vb}^+$ and indirect reaction with OH radicals, or a dual mechanism involving both surface h$_{vb}^+$ and OH radicals (equation 7).

$$h_{vb}^+/OH + \text{dye (RhB)} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (7)$$
Figure 8. Effect of sodium oxalate (Na$_2$C$_2$O$_4$), AgNO$_3$, N$_2$ and isopropanol on the photocatalytic performance of black Ti$^{3+}$/TiO$_2$ for degrading RhB (10 mg/L) in 4 hours under visible light.

Besides the high activity in photocatalytic degradation of organic pollutants, such a black Ti$^{3+}$/TiO$_2$ could also be employed in photocatalytic water-splitting for H$_2$ evolution under simulated solar lights irradiation (a 300 W Xenon lamp without removing UV lights) via choosing methanol as the sacrificial reagent. As shown in Table 1, the as-prepared black Ti$^{3+}$/TiO$_2$ displayed similar activity to both the S-doped TiO$_2^{25}$ and the I-doped TiO$_2^{45}$, which were widely recognized as highly active visible photocatalysts for H$_2$ evolution via water splitting. Meanwhile, its H$_2$ evolution activity (0.26 mmol/h·m$^2$) was about two times of that of P25, suggesting the as-prepared black Ti$^{3+}$/TiO$_2$ had excellent intrinsic activity.

Table 1. H$_2$ evolution rates over different photocatalysts irradiated with simulated solar lights$^a$

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>H$_2$ evolution rate (mmol/h·m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Ti$^{3+}$/TiO$_2$</td>
<td>0.26</td>
</tr>
<tr>
<td>S-doped TiO$_2$</td>
<td>0.29</td>
</tr>
<tr>
<td>I-doped TiO$_2$</td>
<td>0.25</td>
</tr>
<tr>
<td>P25</td>
<td>0.13</td>
</tr>
</tbody>
</table>

$^a$Reaction conditions: 50 mg photocatalyst doped with 1 wt% Pt, 80 mL aqueous solution containing 20 mL methanol, a 300 W Xenon lamp located at 10 cm away from the reaction system, room temperature.
Conclusions

This work developed a facile strategy to prepare black Ti$^{3+}$-doped single-crystal anatase TiO$_2$ (Ti$^{3+}$/TiO$_2$) in one-pot by treating Ti in an ionic liquid containing LiAc and HAc under mild ionothermal conditions. This Ti$^{3+}$/TiO$_2$ contained high-contents of Ti$^{3+}$-dopants incorporated into TiO$_2$ lattice and oxygen vacancies, which facilitated the activation by visible lights and also reduced the photoelectron-hole recombination. It exhibited high activity in both photocatalytic degradation of organic pollutants and H$_2$ generation under irradiation with visible lights and/or simulated solar lights.

Supporting Information

Ti$^{3+}$/Ti$^{4+}$ and oxygen vacancy molar percentages, O2s XPS spectra of black TiO$_2$, FESEM images of the as-prepared samples via choosing various amount of ionic liquids (1-methylimidazolium tetrafluoroborate), TGA curve of the black TiO$_2$ sample under an air flow, the detection of hydrogen produced in the ionothermal treatment process of Ti foil by the gas chromatograph measurement, XRD patterns for as-prepared samples with different calcining temperature, EPR spectra, Ti 2p XPS spectra of various samples, calculated density of electronic states for anatase TiO$_2$, the photocatalytic degradation of RhB with the samples calcined at various temperature in air under Xenon lamp illumination. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCE


38 M. S. C. Accelrys, Inc. Accelry, San Diego, 2011.