Preparation and photocatalytic application of terbium and sulfur co-doped titanium nanomaterials

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Abstract
Titanium-based nanomaterials co-doped with terbium (Tb) and sulfur (S) were synthesized by sol–gel method via a facile step. Physicochemical properties of the resulting composites were characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM), X-ray photo-electron spectroscopy (XPS) and UV–Vis diffused reflectance spectroscopy (DRS). Methylene blue (MB) was used as a degradation target for evaluating the photocatalytic performance. The factors which influence the photocatalytic activity were investigated, including calcined temperatures and S doping amount. Tb, S (2 wt%) co-doped TiO₂ composite calcined at 500 °C exhibited the highest photocatalytic activity with a degradation rate of 72.4% in 3 h. The reaction constant was 0.11529, 0.26025, 0.35038 and 0.41462 h⁻¹ for undoped TiO₂, Tb-doped TiO₂, S-doped TiO₂ and Tb, S co-doped TiO₂, respectively. Importantly, the synergistic effect of terbium and sulfur dopants was profoundly discussed. Furthermore, recycling tests and acute toxicity experiments were carried out to confirm the reusability and biosafety of Tb, S co-doped TiO₂.

Keywords Dye wastewater · Photocatalytic application · Synergistic effect · Tb, S co-doped TiO₂

Introduction
Heterogeneous photocatalysis is considered to be one of the most promising technologies in wastewater treatment, particularly for dye contaminants (Chiu et al. 2019). Most of these contaminants are carcinogenic, harmful and cannot be degraded by biological methods due to their complex structure and excellent stability, which destroys the aquatic ecosystem and threatens human health (Nguyen et al. 2018; Zhao and Cai 2020). In general, catalysts are of significant importance in a photocatalytic process. Among various oxide semiconductor photocatalysts, TiO₂ has attracted much attention as an ideal photocatalytic material due to its strong oxidation ability, cost effectiveness, environmental friendliness, long-term stability against photo and chemical corrosion (Kumaravel et al. 2019; Yan et al. 2019; Ananpattarachai et al. 2016). However, its practical applications are restricted by some shortcomings, among which the most serious one is the wide band gap (3.2 eV), resulting in low utilization of sunlight (Karthikeyan et al. 2020). In addition, TiO₂ exhibits relatively high electron–hole recombination rate which is unfavorable for improving the photocatalytic performance (Tbessi et al. 2019). Therefore, modified materials are in demand for development to overcome the inherent weaknesses of TiO₂.

Generally, the photocatalytic activity of TiO₂ depends on multiple factors that affect the separation efficiency of electron–hole pairs, such as crystal size, phase and surface area (Rahmanian et al. 2018). Considerable attempts have been made to the modification of traditional TiO₂, consisting of ion doping, dye sensitization, precious metal deposition and semiconductor coupling (Zhou et al. 2016; Wang et al. 2018a, b, c; Gao et al. 2017; Nzaba et al. 2018). Notably, ion doping, including metal and non-metallic ions, has been regarded as a facile and effective modification method (Wang et al. 2018a, b, c; Malathi et al. 2018; Ren et al. 2017). However, the recombination centers of the impurity band partially occupied which caused by mono-doping may inhibit the transfer of charge carriers to the surface of TiO₂.
leading to a reduction of photo-generated current; thus, the titanium dioxide could not be fully utilized (Yao et al. 2017). Accordingly, double-doped and multi-doped photocatalysts have aroused general interest.

In particular, TiO\textsubscript{2} co-doped with rare earth ions and non-metallic elements has greatly attracted people’s attention. Rare earth ions have a special 4f\times 5d\times y electronic configuration, which could react with various Lewis bases including acids, alcohols, amines, aldehydes and thiols to form the complexes (Nasir et al. 2016). It is favorable for the transfer of interfacial charges to the contaminants and leads to the formation of new energy levels between valence band, conduction band and oxygen vacancies. Moreover, rare earth ions could substitute for Ti\textsuperscript{4+} and significantly reduce the recombination rate of electron–hole pairs (Zhou et al. 2017).

In our previous work, it has been proved that terbium doping is an effective means to improve photocatalytic activity, based on its special electronic configuration, variable valence and the ability to generate more energy levels (Wang et al. 2019). For non-metallic ion doping, sulfur has been confirmed that could provide obvious beneficial effects for photocatalytic reactions. It is conducive to reduce the band gap and increase the quantum yield through mixing p states of S with O2p states in titanium dioxide. Besides, surface modification is of great significance in raising adsorption of contaminants and facilitating desorption of oxidation products (Qian et al. 2019). Although the contribution of terbium and sulfur for improving the photocatalytic performance of traditional titanium dioxide is well known, to our best knowledge, Tb, S co-doping in titanium dioxide has not been reported, especially the synergistic effect of dopants and its specific photocatalytic mechanism (Spanu et al. 2018). Therefore, combining the advantages of these both dopants and conducting in-depth research on their related theories would be a very meaningful attempt.

In this work, we fabricated Tb, S co-doped TiO\textsubscript{2} nanocomposites by a facile and feasible route. Methylene blue (MB) was applied to evaluate the photocatalytic performance. The factors which influence the photocatalytic activity were investigated in detail. Besides, recycling tests and acute toxicity experiments were conducted to confirm the reusability and biosafety of Tb, S co-doped TiO\textsubscript{2} composites, respectively. Importantly, the synergistic effect of Tb and S co-dopants was further discussed.

### Experimental

#### Materials

Methylene blue (≥ 99.7% purity) was supplied by the company of Shanghai Macklin Biochemical Technology. Tetrabuty titanate is of analytical grade and can be used without further purification. Tetrabuty titanate, terbium(III) nitrate hexahydrate and thioureal were purchased from Sigma-Aldrich Chemical Company. Zebrafish (2.60 ± 0.45 cm in length) used in experiments were obtained from aquarium. The fish was placed under natural light and domesticated at room temperature (25 ± 1 °C) for 7 days before the acute toxicity experiments. Dissolved oxygen of water was in the range of 7.21–8.14 mg L\textsuperscript{-1}. Note that the aeration was performed continuously.

#### Characterization

The crystal structure of the photocatalysts was measured by a D8 Advance X-ray diffractometry (Bruker, Germany). The test was operated from 10° to 80° (2θ), and Cu K\textsubscript{α} was used as the radiation source. Crystalline sizes \((D)\) of the resulting photocatalysts were calculated by Scherrer’s equation \(D = K\lambda /B\cos \theta\). The BET surface area of the samples was obtained from N\textsubscript{2} adsorption–desorption isotherms measured at 77 K (Micromeritics ASAP2460, USA). XPS spectra were recorded on an AXIS SUPRA spectroscopy (Shimadzu, Japan) to analyze the surface elements and chemical valence. UV–Vis diffused reflectance spectra were performed by a Lambda 750 s spectrophotometer (PerkinElmer, USA), using white barium sulfate as the reference. Morphology image was obtained from a S-4800 scanning electron microscope (Hitachi, Japan). PL spectra were measured by a F-4600 spectrophotometer with an excitation wavelength of 315 nm (Hitachi, Japan). U-2910 UV–Vis spectrophotometer (Hitachi, Japan) was used to measure the absorbance of MB. An S-7500 inductive coupled plasma emission spectrometer (ICP) was utilized to measure the S doping amount (Shimadzu, Japan).

#### Photocatalysts preparation

Tb, S co-doped TiO\textsubscript{2} nanocomposites were synthesized by sol–gel method via a facile step. In a typical preparation, 20 mL of tetrabutyl titanate (TBT) and 25 mL of absolute ethanol were mixed under vigorous stirring at room temperature, which namely solution A. Meanwhile, 0.1335 g of terbium(III) nitrate hexahydrate, 20 mL of deionized water, 10 mL of glacial acetic acid, 25 mL of absolute ethanol and an appropriate amount of thiourea (1.0940 g, 0.1880 g, 0.2820 g and 0.3760 g, respectively) were added to a beaker; the stirring was continued for 0.5 h to form solution B. Thereafter, solution B was slowly added to solution A, and the reaction temperature was adjusted to 70 °C. The uniform TiO\textsubscript{2} sol was obtained after 2 h and subsequently subjected to aging and drying procedure. Finally, the resulting photocatalysts were obtained after the mixture calcined in a muffle furnace for 4 h under different temperatures (300 °C, 400 °C, 500 °C, 600 °C). It is worth mentioning that the Tb amount
was kept constant, and S-doping ratio was set to 1%, 2%, 3% and 4%, respectively, corresponding to the above mentioned thiourea mass. The exact S doping ratios of the sample were examined by ICP, and the specific values were 1.0102%, 2.0059%, 2.9863% and 4.0077%, respectively, which were basically in agreement with the theoretical ones. For comparison, pure TiO₂, Tb- and S- mono-doped TiO₂ nanomaterials were also synthesized via similar step (Wang et al. 2019).

**Photocatalytic evaluation**

The photocatalytic activity of the catalysts was evaluated by degradation of 10 mg L⁻¹ MB in aqueous solution with 0.1 g of the catalysts. Prior to photocatalytic reaction, dark experiments (0.5 h) were carried out for the sufficient adsorption of dye molecules on the catalysts. In a typical photocatalytic process, continuous magnetically stirring was kept under light irradiation. At specific time intervals, 5 mL of the suspension was taken and centrifuged. Changes in MB concentration were measured via the absorbance values at 662 nm.

**Acute toxicity experiments**

Acute toxicity experiments were conducted with a static method. In other words, keeping the zebrafishes without eating and the test solutions were not replaced during the experiments. Firstly, 5 L of water and 15 zebrafishes were put into each aquarium. After that, an appropriate amount of Tb, S co-doped TiO₂ composites was added to control solution concentrations to be 0, 12.5 mg L⁻¹, 25 mg L⁻¹ and 50 mg L⁻¹, respectively. The survival of zebrafishes was recorded at a specific time, and dead zebrafishes were promptly removed. Finally, the mortality was calculated at 24, 48, 72 and 96 h, respectively, and the half lethal concentration (LC₅₀) was further determined.

**Results and discussion**

**Photocatalyst characterization**

Generally, the anatase has more oxygen vacancies than rutile. It is easier to capture electrons and effectively suppress the recombination of electron–hole pairs; thus, the photocatalytic activity of anatase is higher than that of rutile (Spanu et al. 2018). Therefore, the calcined temperatures were controlled in the range of 300–600 °C to obtain the samples with good photocatalytic performance. XRD patterns of Tb, S co-doped TiO₂ composites under different calcined temperatures are presented in Fig. 1a. Peaks at 20 of 25.38°, 37.88°, 48.10°, 54.10°, 55.28°, 63.15° and 76.21 would be the characteristics for (101), (004), (200), (105), (211) and (204) of anatase, respectively (PDF NO. 894921), indicating that no rutile phase diffraction was detected for all of the composites under different calcined temperatures. On the basis of XRD patterns, the crystallite size of different samples was calculated by Scherrer’s equation, as listed in Table 1. The increasing of calcined temperatures resulted in an enhancement of the crystallite size. Tb, S co-doped TiO₂ composite calcined at 500 °C was with a crystallite size of 11.5 nm, less than that of undoped TiO₂ calcined at 500 °C (12.7 nm). It suggested that Tb and S co-doping

![Fig. 1](image-url) (a) XRD patterns of Tb, S (2 wt%) co-doped TiO₂ composites under different calcined temperatures; (b) SEM image of Tb, S co-doped TiO₂ composites calcined at 500 °C

| Samples                | Crystallinity (%) | Crystallite size (nm) | BET (m²/g) |
|------------------------|------------------|-----------------------|------------|
| Tb, S co-doped TiO₂-300 °C | 93.44            | 9.9                   | 94         |
| Tb, S co-doped TiO₂-400 °C | 95.07            | 10.8                  | 89         |
| Tb, S co-doped TiO₂-500 °C | 98.97            | 11.5                  | 82         |
| Tb, S co-doped TiO₂-600 °C | 99.56            | 13.9                  | 73         |
| Undoped TiO₂-500 °C     | 99.68            | 12.7                  | 76         |

*Evaluated by Jade 5.0 software
BCalculated by Scherrer’s equation
could inhibit grain growth of TiO₂, owing to the deformation of lattice and oxygen vacancies left by the substitution of O atoms for Tb or S atoms. Correspondingly, specific surface area of Tb, S co-doped TiO₂ composite calcined at 500 °C was larger than that of undoped TiO₂. Figure 1b shows the SEM images of Tb, S co-doped TiO₂ composites calcined at 500 °C. Regularly shaped agglomerate spherical particles with diameters of about 17 nm were clearly observed.

XPS analysis was performed to analyze the surface elements and chemical valence. Figure 2 presents the O 1 s, Ti 2p, Tb 3d and S 2p spectra of the Tb, S co-doped TiO₂ composite. Two peaks located at 528.63 and 530.3 eV could be observed in O 1 s spectra (Fig. 2a), which were ascribed to Ti–O and superficial oxygen of chemically adsorbed hydroxyl species (Liu and Yang 2019). The results of the XPS spectra for Ti 2p are displayed in Fig. 2b. It could be fitted into four peaks, which were assigned to the characteristic peaks of Ti³⁺ and Ti⁴⁺ state (Wang et al. 2018a, b, c). Note that the presence of Ti³⁺ might be caused by the reduction of Ti⁴⁺ in the preparation process. This interesting phenomenon could induce defects in the TiO₂ lattice and further resulted in the formation of oxygen vacancies. As seen from Fig. 2c, two broad spin–orbit doublet peaks at 1226.84 and 1242.7 eV belong to Tb³⁺ 2P₃/₂ and Tb³⁺ 2P₅/₂, respectively, which was indicative of the formation of Tb₂O₃ and shallow traps on the surface of photocatalysts (Wang et al. 2019). Accordingly, the carriers could be quickly captured, facilitating the separation of photogenerated electrons and holes. For S 2p spectra (Fig. 2d), the peaks at 168.0 eV and 167.3 eV were ascribed to S⁶⁺ 2P₃/₂ and S⁶⁺ 2P₁/₂. Generally, the substitution of Ti³⁺ by cationic S is energetically more favorable than replacing O²⁻ with S²⁻ (Vorontsov and Valdes 2019). It could result in a charge imbalance in the lattice, and the excess positive charge might be neutralized by hydroxide ions; thus, the recombination of electrons and holes was effectively suppressed. Besides, the binding energy related to S⁶⁺ 2P₃/₂ and S⁶⁺ 2P₁/₂ levels has confirmed the formation of SO₄²⁻ on the surface of TiO₂, which could effectively capture the photo-generated electrons and holes. All of these results demonstrated that Tb, S co-doping was favorable for the improvement of photocatalytic performance.

Factors influencing the photocatalytic efficiency

Calcined temperature and doping amount of the elements are two important factors affecting the photocatalytic performance. It has been reported that calcined temperature profoundly influenced the structural characteristics, including crystallinity, crystallite size and specific surface. Owing to the change in structural characteristics, the surface defects and active sites of the photocatalyst were further changed (Liu et al. 2018). Figure 3 reveals the result of photocatalytic
experiments. As illustrated in Fig. 3a, S doping amount of the composites was fixed at 2%; Tb, S co-doped TiO₂ composites calcined at 500 °C exhibited the highest photocatalytic performance with a degradation rate of 72.4% in 3 h. The reduced performance of photocatalyst with high calcined temperature should be due to the destruction of the structured morphology and decrease of the specific surface area (Table 1). On the contrary, low-temperature calcined catalysts with weak purification, more defects and low active sites also led to poor photocatalytic performance. Therefore, 500 °C was chosen as the optimal calcined temperature for further studies. In addition to calcined temperature, the effect of S doping amount on the photocatalytic performance was also investigated. As shown in Fig. 3b, the increment of S doping amount from 1 to 2% resulted in an enhancement of the photocatalytic activity. However, a decrease of the degradation rate was obviously observed in the range of 2–4%. The decrease in photocatalytic activity was attributed to the presence of excess sulfur ions, which acted as recombination centers for electrons and holes pairs (Gyorgy et al. 2018). Moreover, it could absorb incident photons and reduce the light exposed to the catalyst; subsequently, the photocatalytic activity decreased. Therefore, 2% was chosen as the optimal doping amount for further studies.

**Synergistic effect discussion**

In order to investigate the synergistic effect of co-dopants in a photocatalytic process, TiO₂, S-, Tb- and Tb, S co-doped TiO₂ were used as catalysts for comparative experiments. The photocatalytic performance of MB degraded by different catalysts is displayed in Fig. 4a. It is worth emphasizing that the photocatalytic performance of doped catalysts was better than undoped catalysts. Notably, Tb, S co-doped TiO₂ composite presented a remarkable increment in the photocatalytic performance with a degradation rate of 72.4%. As revealed in Fig. 4b, good linear relationship between − ln(C/C₀) and irradiation time were observed in all cases, indicating that MB degradation followed a pseudo-first-order pattern. Reaction rate constant (k) was determined by the slope of graph plotted between − ln(C/C₀) and irradiation time. The value of k was 0.11529, 0.26025, 0.35038 and 0.41462 h⁻¹ for TiO₂, Tb-, S- and Tb, S co-doped TiO₂, respectively. The reaction rate of Tb, S co-doped TiO₂ composites was approximately 3.6 times compared with pure TiO₂, which might be attributed to the synergistic effect of terbium and sulfur dopants. The UV–Vis diffused reflectance spectra of photocatalysts are illustrated in Fig. 4c. It is clearly observed that doping of mono- or double ions would enhance light absorption capacity in ultraviolet region compared to pure TiO₂. The intensity of the absorption peaks can be arranged in the following order, Tb-S-TiO₂ > S-TiO₂ > Tb-TiO₂ > TiO₂, suggesting that Tb and S dopants have an obvious synergistic effect on improving the photocatalytic efficiency. Furthermore, the corresponding Tauc plots is shown in Fig. 4d. Band gap values of TiO₂, Tb-, S- and Tb, S co-doped TiO₂ were estimated to be 3.18, 3.20, 2.93 and 2.90 eV, respectively. S-doped and Tb, S co-doped TiO₂ exhibited a slight red-shift, whereas Tb-doped TiO₂ showed no obvious change into the visible region compared to pure TiO₂. These results demonstrated S doping could result in narrowing the bandgap and increasing quantum efficiency of visible light utilization. Figure 4e presents the UV–Vis spectra of MB in a degradation process. The absorbance decreases with the enhancement of irradiation time, which was indicative of the gradual degradation of MB by Tb, S co-doped TiO₂ composites. Taking advantage of the synergistic effect of terbium and sulfur dopants, Tb, S co-doped TiO₂ composites exhibited obvious enhancement in the photocatalytic activity. Tb, S co-doping could strengthen the response to light irradiation and facilitate the separation of electron holes. On the other hand, Tb, S co-doped TiO₂ composites with smaller average crystallite size could provide larger specific surface area and more active centers, which was favorable for the adsorption between dye molecules and catalysts. Besides, the smaller crystallite size was beneficial for the rapid transfer of photogenerated electrons and holes to the surface of the TiO₂ (Gyorgy et al. 2018).
Formation process of •OH was confirmed by a PL spectroscopy. Terephthalic acid was applied as a scavenger, and the experimental details were the same as previously reported (Wang et al. 2019; Amer et al. 2019). Fluorescence spectra of •OH tracking process is illustrated in Fig. 4f. A positive relationship between the photocatalytic degradation and the amount of •OH radicals was observed, which demonstrated that •OH radicals have been one of the primary reactive species responsible for the degradation of dye contaminants. Electrons (e\(^-\)) and holes (h\(^+\)) were generated by photons under light irradiation, and electrons transferred from the valence band (VB) to the conduction band (CB). However, these charge carriers were easily recombined, resulting in low photocatalytic performance (Santacruz et al. 2020; Cheng et al. 2016). After doping of terbium ion, it could be served as trapping centers for the photogenerated electrons to reduce the recombination rate, which allowed the catalyst to produce more active species and improve the photoactivity.

**Photocatalysts re-usability**

Reusability is one of the major concerns for the practical applications of photocatalysts\(^{[28]}\). Therefore, four successive recycling tests for the degradation of MB were conducted to investigate the photocatalyst reusability. In a typical experiment, the catalysts were collected by a centrifugal process after each run. The separated photocatalysts were washed thoroughly with deionized water and ethanol, and dried at 105 °C for 3 h before the beginning of the next cycle. Note that the photocatalysts should be calcined at 500 °C before use of the fourth cycle. It can be observed from Fig. 5 that...
the degradation rate was 72.4%, 68.2% and 63.7% for the first to the third runs, respectively. A slight decrease in the degradation rate was mainly due to the absorbed intermediates on the surface or interface of the catalyst as well as to the loss of a small amount of photocatalyst during the recovery process. It is worth emphasizing that the degradation rate of the fourth cycle was only 2.2% less than that of the fresh cycle, demonstrating that a calcined process was favorable for the regeneration of the photocatalysts. In conclusion, re-usability tests have confirmed that the resulting Tb, S co-doped TiO₂ composites owned good stability and could be potentially employable for continuous photocatalytic processes.

**Acute toxicity of photocatalysts**

Biological safety of photocatalysts is of great significance for their potential applications in wastewater treatment. Herein, we evaluated the effects of Tb, S co-doped TiO₂ on the aquatic ecosystem via acute toxicity experiments. As presented in Fig. 6, mortality of zebrafish was increased with the increasing of catalyst concentrations. Tb, S co-doped TiO₂ showed low toxicity on zebrafishes with a half lethal concentration of 20.3 mg L⁻¹ (96 h-LC₅₀ > 10 mg L⁻¹).

**Conclusions**

Terbium and sulfur co-doped TiO₂ composites were successfully synthesized by sol–gel method via a facile step. All the samples existed in the pattern of only anatase structure. The crystallite size of Tb, S co-doped TiO₂ calcined at 500 °C (11.5 nm) was less than undoped TiO₂. According to the XPS results, sulfur was doped in the forms of $S^{4+}$ and $S^{6+}$ cations and oxidation state of terbium was Tb³+. The resulting Tb-S (2 wt%) co-doped TiO₂ composite calcined at 500 °C exhibited the highest photocatalytic performance with a reaction constant of 0.41462 h⁻¹. Owing to the synergistic effect, Tb and S dopants in the structure of TiO₂ resulted in a remarkable strengthening response to light irradiation and caused significant separation of the electron–hole pairs. Moreover, smaller crystallite of the Tb, S co-doped TiO₂ composite could provide more active centers, facilitating the interaction between organic molecules and photocatalysts, thereby effectively improving the photocatalytic activity. The photocatalysts have been proved to be used repeatedly at least four cycles, and only a slight decline in photocatalytic activity was observed. Acute toxicity experiments demonstrated that the photocatalysts presented low toxicity on zebrafishes with a half lethal concentration of 20.3 mg L⁻¹. All these results reveal that the promising prospects of Tb, S co-doped TiO₂ composite in the practical application of water treatment.

**Author contribution** ZW participated in the experimental operation and drafted the manuscript; YW collected and analyzed the data. TT conceived, designed and coordinated the study and helped draft the manuscript.

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**Availability of data and materials** Not applicable.

**Declarations**

**Ethics approval** The experimental protocols were approved by the Animal Care and Protection Committee of Hainan Medical University.
Competing interests The authors declare no competing interests.

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