Optimization of Boron Doped TiO$_2$ as an Efficient Visible Light-Driven Photocatalyst for Organic Dye Degradation With High Reusability

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No visible light activity is the bottle neck for wide application of TiO$_2$, and Boron doping is one of the effective way to broaden the adsorption edge of TiO$_2$. In this study, several Boron doped TiO$_2$ materials were prepared via a facile co-precipitation and calcination process. The B doping amounts were optimized by the degradation of rhodamine B (Rh B) under visible light irradiation, which indicated that when the mass fraction of boron is 6% (denoted as 6B-TiO$_2$), the boron doped TiO$_2$ materials exhibited the highest activity. In order to investigate the enhanced mechanism, the difference between B-doped TiO$_2$ and bare TiO$_2$ including visible light harvesting abilities, separation efficiencies of photo-generated electron-hole pairs, photo-induced electrons generation abilities, photo-induced charges transferring speed were studied and compared in details. $h^+$ and $\cdot O_2^-$ were determined to be the two main responsible active species in the photocatalytic oxidation process. Besides the high degradation efficiency, 6B-TiO$_2$ also exhibited high reusability in the photocatalysis, which could be reused at least 5 cycles with almost no active reduction. The results indicate that 6B-TiO$_2$ has high photocatalytic degradation ability toward organic dye of rhodamine B under visible light irradiation, which is a highly potential photocatalyst to cope with organic pollution.

Keywords: TiO$_2$, doping, boron, dye pollution, photocatalytic degradation

INTRODUCTION

Environmental problems are global issues and effect all of human kind. These issues and pressures increase in severity as society continues to develop at a very fast pace (Samanta et al., 2002; Shao et al., 2017; Chen et al., 2018; Chowdhary et al., 2018; Tian et al., 2018; Hong et al., 2020). Water pollution is one of the most serious environmental problems and attracts much attention (Wang and Yang, 2016; Jiang et al., 2019b; Kapelewskas et al., 2019; Quesad et al., 2019; Wu et al., 2019; Zhao et al., 2019b). Organic dyes have been synthesized on a large scale and are widely applied in our daily lives, resulting in tons of dyes being discharged into the aqueous environment every year, causing many serious environmental problems (Sohni et al., 2019; Tu et al., 2019; Zhan et al., 2019; Zhou X. et al., 2019). Rhodamine B is a toxic alkaline cationic dye, which was used as a food additive, but has been forbidden due to its high carcinogenic potential (Wu et al., 2018; Lops et al., 2019; Tian et al., 2019; Guo et al., 2020). Furthermore, it can also cause other serious diseases such as visceral disease and red skin staining (Alcocer et al., 2018; Liu et al., 2019; Maria Magdalane et al., 2019). It is very difficult to degrade rhodamine B under natural conditions. Methods for the effective removal of rhodamine B are therefore of great importance.
In recent decades, photocatalysis has exhibited its high potential in waste water treatment, due to its inherent merits including low costs, renewability, being environment-friendly, and its high efficiency. TiO$_2$ is a widely used photocatalyst because of its chemical stability, high redox reactivity, easy preparation, and low cost. However, it can not adsorb and use visible light because of its wide energy band gap. So only $\sim 4\%$ solar energy of ultraviolet light can be used by TiO$_2$, and 45% solar energy of visible light can not be used (Jiang et al., 2018a, 2019a; Yin et al., 2018; Ahadi et al., 2019; Zhou F. et al., 2019; Komtchoua et al., 2020). In order to broaden the light adsorption of TiO$_2$ to visible light, many efforts have been conducted (Zhao et al., 2019a; Zhang et al., 2020). Doing has attracted increasing interest in recent years (Jiang et al., 2018a; Kamaludin et al., 2019; Lu et al., 2019; Xiu et al., 2019; Yan et al., 2019).

In this study, boron was used to dope into TiO$_2$ to prepare the photocatalyst of B-TiO$_2$. B-TiO$_2$ shows high photocatalytic degradation ability toward rhodamine B under visible light. The preparation conditions were optimized, and the structure and photocatalytic performance of B-TiO$_2$ were carefully investigated. Based on the experimental results, the photocatalytic degradation mechanism was discussed. This study indicates that B-TiO$_2$ has the potential to treat dye pollution through visible light irradiation.

**EXPERIMENT**

**Materials**

All the chemicals used in this study were of analytical pure grade. Boric acid and aqueous ammonia were purchased from Xilong Science Co., Ltd, China. Rhodamine B and tetrabutyl titanate were bought from the Aladdin reagent company, China. Other chemicals are all commercial. Deionized water (DI water) was used throughout the study. The materials were directly used without any treatment.

**Synthesis of B-TiO$_2$**

0.1 mol tetrabutyl titanate was dissolved into 100 ml absolute alcohol to form a clean solution. Boric acid was dissolved into a solution containing 2 ml nitric acid, 50 ml absolute alcohol and 50 ml DI water. After that, the tetrabutyl titanate solution described above was dripped into the boric acid solution and vigorously stirred. At the same time, aqueous ammonia was dripped into the mixture described above to adjust the pH value to 7. The formation of precipitation was found in the process. After being aged for 5 days, the precipitation was separated and dried at 110$^\circ$C. Finally, it was calcinated at 500$^\circ$C to obtain the B doped TiO$_2$ denoted as B-TiO$_2$. The feeding amounts of boric acid were changed to obtain B-TiO$_2$ with a B mass ratio of 0, 3, 6, 9, 12, and 15%, and are denoted as TiO$_2$, 3B-TiO$_2$, 6B-TiO$_2$, 9B-TiO$_2$, 12B-TiO$_2$, and 15 B-TiO$_2$, respectively. The methodology is shown in Scheme 1.

**Photocatalytic Degradation**

Ten milligrams of photocatalyst was added into 25 ml rhodamine B solution at a concentration of 5 mg/L. The mixture was stirred in the dark for 30 min to obtain adsorption equilibrium. After that, the mixture was irradiated under visible light by a 500 W
Xe lamp (Perfectlight, Beijing, China) with $\lambda \leq 400$ nm cutoff, and sampled at determined intervals to examine the rhodamine B concentration in the suspension, which was determined by the adsorption at 552 nm.

**Characterization**

The morphology of the sample was investigated by scanning electron microscopy (SEM) (Hitachi-4800, Japan) and a transmission electron microscope (TEM) (JEM-2100, Japan). An X-ray powder diffractometer (XRD, Rigaku III/B max, Cu Ka) was used to analyze the samples. The pH values of solutions were determined by a JENCO 6175 pH meter (Renshi electronics Co. Ltd. USA). Electrochemical impedance spectroscopy (EIS) and photocurrent response analysis were performed by CH1660C electrochemical workstation (Shanghai Chenhua, China). Photoluminescence (PL) spectra were recorded on a F-7000 fluorescence spectrophotometer (Hitachi, Japan). UV-vis diffuse-reflectance spectra (DRS) of samples were obtained on a UV-vis-NIR spectrometer (Lambda 900).

**RESULTS AND DISCUSSION**

**Optimization of B Doping Amount**

The bare TiO$_2$ and B doping TiO$_2$ were investigated by XRD analysis, and the results are shown in Figure 1. It can be seen that the samples show similar XRD characteristics. However, it is notable that there is a new peak at $\sim 25.5^\circ$, which is attributable to rutile TiO$_2$ (Wang et al., 2015; Warkhade et al., 2017), appears in the spectra of B doping TiO$_2$, but is not the case in the spectrum of bare TiO$_2$. This phenomenon indicates that under the experimental conditions of this study, the doping of B, no
matter how much the doping amount is, can induce the pure anatase TiO$_2$ to transform to mixed crystal phases of anatase and rutile (Cui et al., 2017). These results indicate that B has been successfully doped into the crystal lattice of TiO$_2$.

All the samples, including the bare TiO$_2$ and the B doping TiO$_2$, were used to degrade rhodamine B under visible light irradiation. As shown in Figure 2, the degradation ability first increases with the B doping amount, and when the B doping amount reaches 6%, the degradation ability decreases with the rise of B doping amount. This phenomenon indicates that 6% of the B mass ratio is the optimal value. Thereafter, 6B-TiO$_2$ was determined as the optimal sample, and 6% was determined as the optimal feeding amount of B in the preparation.
Characterization of B Doping TiO₂ Samples

In order to investigate the mechanism of the enhanced photocatalytic performance of 6B-TiO₂, the samples of bare TiO₂ and B doping TiO₂ were investigated by photocurrent response, EIS and PL spectrum, and the results are shown in Figure 3. It can be seen in Figure 3A that 6B-TiO₂ shows highest photocurrent response, indicating that more electrons can be generated in 6B-TiO₂ by visible light irradiation (Hu et al., 2019; Murali et al., 2019; Wang et al., 2019). In the EIS analysis (Figure 3B), 6B-TiO₂ exhibits a semicircle of the EIS Nyquist plot with the smallest radius, indicating the smallest interfacial charge transference impedance as compared to those of bare TiO₂ and other B doping TiO₂ (Dai et al., 2015; Zou et al., 2016; Manwar et al., 2019). As shown in Figure 3C, 6B-TiO₂ indicates the lowest photoluminescence intensity, which suggests that 6B-TiO₂ has the lowest recombination rate of electron-hole pairs (Cai et al., 2019; Huang et al., 2019; Yuan et al., 2019). It can be found from the above analysis, that the most electrons can be generated by visible light in 6B-TiO₂, and the charge carriers can transfer in 6B-TiO₂ with the lowest impedance and recombination rate. All of these characteristic can favor the subsequent photocatalytic reaction, so there is no doubt that 6B-TiO₂ exhibits the best photocatalytic performance as compared to bare TiO₂ and other B doping TiO₂.

The morphology of 6B-TiO₂ was investigated by SEM and TEM. As shown in Figures 4a,b, 6B-TiO₂ exhibits nano spherical morphology with a litter aggregation. Elemental mapping indicates that elements of B, O, and Ti homogeneously distribute on the surface of 6B-TiO₂, confirming the successful doping of B (Figures 4c–f).

The bare TiO₂ and 6B-TiO₂ were investigated by DRS, and the results are shown in Figure 5A. It can be seen that the light adsorption edge of bare TiO₂ is about 383 nm, indicating no visible light adsorption activity. As B was doped to form 6B-TiO₂, the light adsorption edge significantly red shift to about 411 nm, which indicates that 6B-TiO₂ can adsorb visible light. The band gap energies of the two samples were calculated by Tauc plot according to the DRS results by Jiang et al. (2018b), Kato et al. (2019), Khan et al. (2019), and are shown in Figure 5B. As one can see, bare TiO₂ has a wide band gap of 3.35 eV, which is too high to be excited by visible light. However, after B doping, the band gap was narrowed to 2.85 eV, and can be excited to produce electrons by visible light. The results clearly show that B doping significantly narrows the band gap of TiO₂, and broadens the light adsorption edge to a visible light range.

Investigation of the Active Species in the Photocatalytic Degradation

In order to study the photocatalytic mechanism, the potential active species in the photocatalytic degradation course were investigated. There are usually four active species involved in the photocatalytic degradation course. They are \( \cdot \text{O}_2^\cdot \), \( \cdot \text{OH} \), e\(^{-} \), and h\(^+\). 0.05 mmol different scavengers were added, respectively, in the photocatalytic degradation system, and other conditions were the same as described in “2.3 Photocatalytic degradation.” The scavengers are i-propanol (OH scavenger), triethanolamine (h\(^+\)
scavenger), 1, 4-Benzooquinone (‘O₂’) and AgNO₃ (e⁻ scavenger) (Asmus et al., 1967; Zhang et al., 2013; Huyen et al., 2018). It can be seen in Figure 6 that h⁺ and ‘O₂’ play the most important roles in the degradation of rhodamine B, because the addition of the scavengers for these two active species can dramatically decrease the degradation capacity. One can also find that ‘OH takes part in the degradation, because the addition of i-propanol can impress the degradation too. h⁺, ‘O₂’ and ‘OH are three highly oxidative species. The results indicate that their high oxidative activities may be used to degrade rhodamine B in this photocatalysis course. It is notable that the addition of AgNO₃ can promote the degradation. The reason is that AgNO₃ can consume e⁻ as an e⁻ scavenger, which depress the recombination of e⁻-h⁺ pairs, and enhance the photocatalytic ability.

Investigation of Reusability

In order to evaluate the reusability of 6B-TiO₂, the used 6B-TiO₂ was collected and washed with DI water. After being dried, it was used in the photocatalytic degradation of rhodamine B again, and the experimental conditions are the same as described in “2.3 Photocatalytic degradation” with little modification of sampling time. As one can see in Figure 7, 6B-TiO₂ can be continuously used to effectively degrade rhodamine B at least in five cycles.

CONCLUSION

B doping TiO₂ were successfully prepared in this study, and 6B-TiO₂ was determined as the optimal B doping amount. 6B-TiO₂ shows the best photocurrent response ability, fastest charge transference speed and lowest recombination rate of e⁻-h⁺ pairs, which significantly enhances its photocatalytic performance. B doping significantly narrows the band gap of TiO₂, and therefore broaden the light adsorption edge to visible light range. h⁺ and ‘O₂’ are the most important active species in the photocatalytic degradation, and ‘OH is also involved in the degradation. 6B-TiO₂ shows high reusability, which can be effectively used in at least five degradation cycles. 6B-TiO₂ is a potential photocatalyst with visible light responsible ability, which can be used to effectively treat dye pollution.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/supplementary material.

AUTHOR CONTRIBUTIONS

PN did the experiments. PC and HJ designed the experiments. GW, HZ, and QC were devoted to the discussion and analysis.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.