Enhanced photocatalytic performance of Z-scheme TiO₂/g-C₃N₄ heterojunction towards degradation of Rhodamine B

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Nanoflower-like rutile TiO₂ was synthesized by hydrothermal method and graphitic carbon nitride (g-C₃N₄) was prepared by thermal polycondensation of thiourea. Z-Scheme TiO₂/g-C₃N₄ photocatalysts with different mass ratios were prepared via a simple physical mixing method. The crystal structure, morphology, chemical states and optical properties of the samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) spectroscopy and UV–vis diffuse reflectance spectroscopy (DRS). The photocatalytic activity of catalysts was evaluated by the degradation of Rhodamine B (RhB) under simulated solar irradiation. Compared with pure g-C₃N₄ and TiO₂, all TiO₂/g-C₃N₄ composites exhibited higher photocatalytic activity, and the highest photocatalytic degradation efficiency of 95 % was achieved when the mass ratio of TiO₂ and g-C₃N₄ was 1:3. The enhanced photocatalytic activity of the TiO₂/g-C₃N₄ and TiO₂.

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1. Introduction

Water contamination has become more serious in recent decades due to the rapid growth of industry and the increasing discharge of wastewater [1-3]. So far, many strategies have been used to remove pollutant, such as adsorption, photocatalytic degradation, biological treatment and fluorescence precipitation [4–7]. Photocatalytic technology of semiconductor is considered to be a low-cost, sustainable and non-polluting method using solar energy.

As a new type of metal-free catalyst, graphitic carbon nitride (g-C₃N₄) is widely used in the field of photocatalysis because of its good thermochemical stability, unique electronic structure, medium bandgap (2.7 eV) and low cost [8–10]. However, the rapid recombination of photoexcited electron-hole pairs and low specific surface area suppress the photocatalytic performance of g-C₃N₄ [11,12]. Therefore, various strategies have been investigated to overcome these shortcomings, such as ions doping [13], morphology control [14] and heterojunction construction [15]. It is well known that the formation of heterojunction can effectively promote charge transfer and improve the photocatalytic performance of catalysts. It is reported that g-C₃N₄ could be coupled with TiO₂ [16], CeO₂ [17], WO₃ [18], BiVO₄ [19] and Bi₂WO₆ [20]. As a traditional photocatalytic semiconductor material, TiO₂ has attracted much attention for its nontoxicity, high stability and low cost [21–23]. Zhang et al. [24] prepared TiO₂/g-C₃N₄ binary

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photocatalysts with Z-scheme heterojunction by physical mixing, which exhibited higher photocatalytic activity than $g-C_3N_4$ and TiO_2 .

In this study, nanoflower-like rutile TiO_2 was synthesized by the hydrothermal method, and Z-scheme $TiO_2/g-C_3N_4$ composites with different mass ratios were prepared by physical mixing. The formation of Z-scheme heterojunction inhibited the recombination of electron-hole pairs, which resulted in excellent photocatalytic activity. In addition, a possible mechanism of photocatalytic degradation was proposed and discussed.

2. Experimental

2.1. Chemical and reagents

Thiourea, Hydrochloric acid (HCl), Tetrabutyl titanate (TBT) and Rhodamine B (RhB) were purchased from Kelong chemical company in Chengdu. All water used in the experiment was deionized water.

2.2. Synthesis of photocatalyst

The TiO₂ nanoflowers were synthesized by a hydrothermal method. In a typical procedure, 3 mL of HCl (37 wt%) and 3 mL of TBT were added into 27 mL distilled water and stirred for 15 min. The suspension was transferred to a 50 mL Teflon-lined autoclave and heated at 180 °C for 12 h. After the hydrothermal reaction, the white powder precipitate was washed several times with distilled water until the solution was neutral.

Bulk g-C₃N₄ was prepared by heating thiourea in a muffle furnace. 20 g of thiourea was calcined at 550 °C for 4 h with a heating rate of 5 °C/min. The TiO₂/g-C₃N₄ composites were fabricated by physical mixing. In brief, a certain amount of g-C₃N₄ and TiO₂ were added into ethanol with stirring, and then the suspension was dried in air at 80 °C. The samples were denoted as x-TCN (x=0.25, 0.5 and 0.75) when the mass ratios of TiO₂ and g-C₃N₄ in the composites were 1:3, 1:1 and 3:1, respectively.

2.3. Characterization

The crystal structure of the samples was characterized by the X-ray diffractometer (DX-2700B) with Cu K α radiation. The morphology and microstructure were observed by scanning electron microscopy (SEM, ZEISS Sigma 300). The surface composition and valence band of samples were carried out by X-ray photoelectron spectroscopy (XPS, Escalab Xi+). The UV-vis diffuse reflectance spectra (DRS) of catalysts were measured by a Persee TU-1901 UV-vis spectrometer using BaSO₄ as the reference. The photoluminescence spectra (PL) were detected by the fluorescence spectrometer (Edinburgh FLS1000) with an excitation wavelength of 350 nm. The Brunaure-Emmet-Teller (BET) surface area of the photocatalysts was carried out by nitrogen adsorption on a surface area analyzer (V-Sorb 2800P).

2.4. Photocatalytic test

The photocatalytic performance of the prepared samples was evaluated by degradation of RhB under irradiation of a 500 W Xenon lamp (CEL-S500, AM 1.5, 100 mW/cm²). In a typical procedure, 100 mg of the photocatalyst was added into 100 mL RhB solution (10 mg/L), then the

solution was stirred for 30 min in the dark to establish adsorption-desorption equilibrium. During the irradiation, a certain amount of suspension was taken out from the mixture at certain time intervals and the absorbance of RhB was measured by the UV-vis spectrophotometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of $g-C_3N_4$, TiO₂ and 0.25-TCN samples. Two peaks of pristine $g-C_3N_4$ can be found at 13.0° and 27.5°, belonging to the minor crystal plane (100) and main crystal plane (002), respectively. The strong diffraction peak at 27.5° is caused by the interplanar stacking peak of the aromatic system, while the weak diffraction peak at 13.0° is formed by the stacking of the interlayer structure [25]. The peaks at $2\theta = 27.5^\circ$, 36.1° , 41.2° , 54.3° and 56.6° in the XRD pattern of TiO₂ are indexed to the (110), (101), (111), (211) and (220) planes of rutile TiO₂ (JCPDS# 21-1276), respectively. Both diffraction peaks of $g-C_3N_4$ and rutile TiO₂ can be detected in the XRD pattern of 0.25-TCN sample, which indicates that the TiO₂/g-C₃N₄ composites are successfully synthesized by physical mixing method.



Fig. 1. XRD patterns of g- C_3N_4 , TiO₂ and 0.25-TCN samples.



Fig. 2. The SEM images of (a, b) g-C₃N₄, (c) TiO₂ and (d) 0.25-TCN.

Fig. 2 exhibits the morphology of g-C₃N₄, TiO₂, and 0.25-TCN. The g-C₃N₄ displays an irregular layer structure with nanopores (Fig. 2b). As shown in Fig. 2c, TiO₂ nanoflowers are aggregated by many rods with a diameter of 25 nm. It can be seen clearly from Fig. 2d that the lamellar g-C₃N₄ is surrounded by a number of TiO₂ nanoflowers. Meanwhile, the specific surface area of g-C₃N₄, TiO₂, and 0.25-TCN is measured as 10.2, 33.9, and 16.0 m²/g, respectively. Compared with g-C₃N₄, the specific surface area of TiO₂/g-C₃N₄ composites becomes larger due to the introduction of TiO₂. The larger surface area may provide more active sites for photocatalytic degradation of RhB.



Fig. 3. XPS spectra of 0.25-TCN: (a) the survey spectrum, (b) C 1s, (c) N 1s, (d) Ti 2p, and (e) O 1s.

Fig. 3a shows the XPS survey spectrum of 0.25-TCN, revealing the existence of C, N, Ti, and O elements. As shown in Fig. 3b, the C 1s peak is deconvoluted into three peaks at binding energies of 284.9, 286.4 and 288.5 eV, which can be assigned to the C-C bond, C-N group and sp² C in C=N heterocycle, respectively [26]. In the N 1s spectrum (Fig. 3c), three peaks at the binding energies of 399.0, 400.7 and 404.7 eV correspond to the sp²-hybridized nitrogen in triazine rings (C=N–C), the tertiary nitrogen of N–(C)₃ groups and the effect of charging reaction, respectively [27]. For the Ti 2p high-resolution spectrum in Fig. 3d, two peaks at the binding energies of 458.8 and 464.7 eV are attributed to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively, suggesting the presence of Ti⁴⁺ in the rutile TiO₂ [28]. The O 1s spectrum (Fig. 3e) shows two peaks of binding energies at 530.1 and 531.7 eV, which are related to the lattice oxygen (Ti-O) and O-H bond, respectively [29].



Fig. 4. (a) UV-vis diffuse reflectance spectra of g- C_3N_4 , TiO₂, and 0.25-TCN; (b) the bandgap of g- C_3N_4 and TiO₂.

The optical absorption properties of catalysts were measured by UV-vis diffuse reflectance spectroscopy. As shown in Fig. 4a, the absorption edges of $g-C_3N_4$, TiO₂, and 0.25-TCN are approximately 469, 410, and 421 nm, respectively. Compared with pure TiO₂, TiO₂/g-C₃N₄ composites demonstrate stronger absorption capacity in the visible region, which is attributed to the coupling with g-C₃N₄. According to Kubelka-Munk equation [30], the bandgap (Eg) of g-C₃N₄ and TiO₂ can be determined as 2.39 eV and 2.85 eV, respectively.



Fig. 5. PL spectra of g- C_3N_4 , TiO₂ and 0.25-TCN.

Photoluminescence (PL) spectroscopy is used to analyze the photoinduced electron-hole recombination rate. Typically, lower PL signal suggests higher separation efficiency of photoinduced electron-hole pairs. Fig. 5 demonstrates the PL spectra of $g-C_3N_4$ and 0.25-TCN. Obviously, the PL intensity of 0.25-TCN sample is lower than that of $g-C_3N_4$, which indicates that the heterojunction between $g-C_3N_4$ and TiO₂ facilitates the separation of photogenerated charge carriers.



Fig. 6. (a) UV–vis absorption curves of RhB dye over 0.25-TCN; (b) Photocatalytic degradation efficiency and (c)pseudo-first-order kinetic curves over all samples.

Fig. 6a displays the absorbance change in RhB solution during the degradation process. As the illumination time increases, the absorbance of the RhB decreases gradually, indicating the degradation of RhB. As shown in Fig. 6b, the photocatalytic degradation efficiency of x-TCN is significantly higher than that of pure g-C₃N₄ (39.7 %) and TiO₂ (43.6 %) within 30 min. The removal efficiency of RhB over 0.75-TCN catalyst is 76.1 %, and the photocatalytic activity improves gradually with increasing g-C₃N₄ content. The 0.25-TCN sample demonstrates the highest photocatalytic activity with degradation efficiency of 95 % within 30 min. It can be explained by the formation of heterojunction between g-C₃N₄ and TiO₂, which inhibits the recombination rate of electron-hole pairs. The kinetic constants (k) of different samples were fitted according to the pseudo-first-order kinetic model (Fig. 6c). The kinetic constant of RhB degradation on 0.25-TCN is 0.099 min⁻¹, which is 5.2 and 4.5 times higher than that of g-C₃N₄ (0.016 min⁻¹) and TiO₂ (0.018 min⁻¹), respectively.



Fig. 7. XPS valence band (VB) spectra of (a) $g-C_3N_4$ and (b) TiO₂.

Fig. 7 shows the XPS VB spectra of $g-C_3N_4$ and TiO₂ and the estimated VB values are 2.54 eV and 2.35 eV, respectively. To obtain the final VB positions relative to the normal hydrogen electrode (NHE), a correction is required by the equation $E_{NHE} = \Phi + E_{VL}$ - 4.44 [31], where E_{NHE} , Φ , and E_{VL} are the potential of normal hydrogen electrode, the electron work function of the instrument (4.6 eV) and potential of vacuum level, respectively. The actual VB values of $g-C_3N_4$ and TiO₂ are calculated to be 2.70 eV and 2.51 eV, respectively. Based on the bandgap and VB results above, the conduction band (CB) values for $g-C_3N_4$ and TiO₂ are 0.31 eV and -0.34 eV, respectively.



Fig. 8. Possible mechanism of Z-scheme $TiO_2/g-C_3N_4$ heterojunction under irradiation.

On the basis of the results and discussion above, the possible photocatalytic reaction mechanism is proposed in Fig. 8. $g-C_3N_4$ and TiO₂ are excited by simulated solar light to generate

electrons and holes. The photogenerated electrons (e⁻) in the CB of g-C₃N₄ rapidly combine with the photogenerated holes (h⁺) in the VB of TiO₂. Meanwhile, the CB potential of TiO₂ (-0.34 eV) is more negative than the O₂/•O₂⁻ potential (-0.33 eV). Therefore, the e⁻ remained in the CB of TiO₂ can reduce O₂ to form superoxide radicals (•O₂⁻). At the same time, the VB position of g-C₃N₄ (2.70 eV) is more positive than OH⁻/•OH potential (2.4 eV) and the h⁺ in the VB of g-C₃N₄ can oxidize H₂O to generate hydroxyl radicals (•OH). Herein, h⁺, •O₂⁻ and •OH are beneficial for the degradation of RhB dye. The result reveals that the formation of Z-scheme heterojunction is conducive to charge transfer, which makes more active species in the reaction system and then improves the photocatalytic performance.

4. Conclusion

In summary, TiO₂ nanoflowers were synthesized via hydrothermal method, and Z-scheme heterojunction TiO₂/g-C₃N₄ composites with different mass ratios were prepared by physical mixing. The photocatalytic activity of catalysts was evaluated by the degradation of RhB under simulated solar irradiation. When the mass ratio of TiO₂ to g-C₃N₄ was 1:3, the composites displayed the highest degradation efficiency of 95 % within 30 min. The formation of the Z-scheme heterojunction structure greatly promoted the separation of photogenerated charge carriers, resulting in more reactive species in the reaction system. This work provides a simple and efficient approach to prepare Z-scheme photocatalysts for photocatalytic degradation of organic pollutant under solar light irradiation.

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