



# Study on the separation mechanisms of photogenerated electrons and holes for composite photocatalysts g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub>



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## ABSTRACT

The separation mechanisms of photogenerated electrons and holes for composite photocatalysts have been a research focus. In this paper, the composite g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> photocatalysts with different main parts of C<sub>3</sub>N<sub>4</sub> or WO<sub>3</sub> were prepared by ball milling and heat treatment methods. The photocatalytic performance was evaluated by degradation of methylene blue (MB) and fuchsin (BF) under visible light illumination. The photocatalyst was characterized by X-ray powder diffraction (XRD), UV-vis diffuse reflection spectroscopy (DRS), transmission electron microscopy (TEM) and Brunauer-Emmett-Teller (BET) methods. The separation mechanisms of photogenerated electrons and holes of the g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> photocatalysts were investigated by electron spin resonance technology (ESR), photoluminescence technique (PL), and determination of reactive species in the photocatalytic reactions. When the main part of the g-C<sub>3</sub>N<sub>4</sub>-WO<sub>3</sub> photocatalyst is WO<sub>3</sub> (namely g-C<sub>3</sub>N<sub>4</sub>/WO<sub>3</sub>), the transport process of the photogenerated electrons and holes adopts the generic band-band transfer. Meanwhile, g-C<sub>3</sub>N<sub>4</sub> is covered by WO<sub>3</sub> powder, and the role of g-C<sub>3</sub>N<sub>4</sub> can not be played fully. The photocatalytic activity of the photocatalyst is not obviously increased. However, when the primary part of the WO<sub>3</sub>-g-C<sub>3</sub>N<sub>4</sub> photocatalyst is g-C<sub>3</sub>N<sub>4</sub> (namely WO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>), the migration of photogenerated electrons and holes exhibits a typical characteristic of Z-scheme photocatalyst, and the photocatalytic activity of the photocatalyst is increased greatly.

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## 1. Introduction

As photocatalysis can be applied to waste water treatment, environmental cleaning, and producing hydrogen from water splitting, it has been attracting much attention in recent years [1–3]. In order to achieve the above goals, two problems must be resolved, i.e., increasing the separation efficiency of photoexcited electron-hole pairs and extending the excitation wavelength range of photocatalysts [4,5]. To increase the absorption wavelength range, the semiconductor materials, such as oxides, sulfides, nitrides, and solid solutions etc., which can be excited by visible light, have been investigated extensively [6–9]. However, a single-phase photocatalyst exhibits significant limitations in the process of photocatalytic reactions due to the quick combination of photogenerated electrons and holes. To enhance the separation efficiency of photoexcited electron-hole pairs, the heterojunction composite photocatalysts have been fabricated extensively [10–13]. In general, when two semiconductors with the matching of band gap were

coupled into a heterojunction photocatalyst, the photoexcited carriers are transferred into valence band (VB) and conduction band (CB) of opposite semiconductor respectively due to their potential difference of VB and CB [14–16]. However, the oxidation and reduction ability of the transferred photoexcited carriers are lower than that of original photoexcited carriers because of the difference of band positions. So exploitation of semiconductor photocatalysts with simultaneous high photooxidation and photoreduction performance is always a hot topic. Recently, the Z-scheme principle of photocatalyst has become a focus of research because of its stronger oxidation and reduction capability and higher photocatalytic performance than the single component. For example, a plasmonic Z-scheme visible-light photocatalyst H<sub>2</sub>WO<sub>4</sub>·H<sub>2</sub>O/Ag/AgCl exhibits a much higher photocatalytic activity than the one-component or two-component photocatalysts [17]. ZnO/CdS Z-scheme photocatalyst prolongs the lifetime of photoexcited carriers [18], and increases the photocatalyst activity.

Recently, a polymer photocatalyst named graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has attracted intensive attention for hydrogen and oxygen evolution via water splitting, photocatalytic degradation of organic pollutants, and photosynthesis under visible light illumination [19–21]. It is known that the band gap of g-C<sub>3</sub>N<sub>4</sub> is about 2.7 eV, which can absorb visible light up to 460 nm. Furthermore, the CB

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minimum ( $-1.12$  eV vs. NHE) of  $g\text{-C}_3\text{N}_4$  is extremely negative, so photogenerated electrons should have high reduction ability. However, the photocatalytic efficiency of single  $g\text{-C}_3\text{N}_4$  is limited due to the high recombination probability of photoexcited electron-hole pairs. In order to improve photocatalytic activity, many strategies such as doping and coupling  $g\text{-C}_3\text{N}_4$  with other semiconductor materials or metal and nonmetal have been used to modify  $g\text{-C}_3\text{N}_4$  [22–26].

Tungsten oxide ( $\text{WO}_3$ ) is regarded as a promising material because of its special photocatalytic and electrochromic properties [27–30]. Compared with  $\text{TiO}_2$ ,  $\text{WO}_3$  has a smaller optical band gap (2.7 eV), and the VB position of  $\text{WO}_3$  is extremely close to that of  $\text{TiO}_2$ . Therefore, the hole generated on the VB of  $\text{WO}_3$  has a similar oxidative capability to that of  $\text{TiO}_2$ . However, the CB level of  $\text{WO}_3$  is more positive than that of  $\text{TiO}_2$ , which results in the electron generated on the CB of  $\text{WO}_3$  with a limited reductive ability than of  $\text{TiO}_2$ .

When  $\text{WO}_3$  is combined with  $g\text{-C}_3\text{N}_4$ , a  $g\text{-C}_3\text{N}_4/\text{WO}_3$  heterojunction photocatalyst may be formed between  $\text{WO}_3$  and  $g\text{-C}_3\text{N}_4$ . The transfer of the photoexcited carriers of  $g\text{-C}_3\text{N}_4$  and  $\text{WO}_3$  will happen because of the position differences of VB and CB. There are two ways for the transfer of the photoexcited carriers. One is band–band transfer, and the other is Z-scheme principle transfer. It is known that the VB position of  $g\text{-C}_3\text{N}_4$  is about 1.57 eV, and the CB position of  $\text{WO}_3$  is about 0.74 eV [21,29]. Because of the short distance between the VB of  $g\text{-C}_3\text{N}_4$  and the CB of  $\text{WO}_3$ , a Z-scheme system photocatalyst may be formed. If so, the holes generated on the VB of  $g\text{-C}_3\text{N}_4$  are easily combined with the electrons generated on the CB of  $\text{WO}_3$ . Consequently, the photogenerated electrons on the CB of  $g\text{-C}_3\text{N}_4$  exhibit strong reduction ability, and the photogenerated holes on the VB of  $\text{WO}_3$  show excellent oxidation ability. However, to the best of our knowledge, there has been no report on the investigation of  $g\text{-C}_3\text{N}_4\text{-WO}_3$  photocatalyst. Especially, the separation mechanisms of photoexcited carriers for the heterojunction photocatalysts have not been investigated extensively.

In this paper, different ratios of  $g\text{-C}_3\text{N}_4\text{-WO}_3$  photocatalysts were prepared with ball milling and heat treatment methods. The photocatalytic activity was evaluated by degradation of methylene blue and fuchsin under visible light illumination. The  $g\text{-C}_3\text{N}_4\text{-WO}_3$  photocatalysts were characterized in detail. The separation mechanisms of photogenerated electrons and holes of the  $g\text{-C}_3\text{N}_4\text{-WO}_3$  photocatalysts were investigated by electron spin resonance technology, photoluminescence technique, and determination of reactive species in the photocatalytic reactions. Some interesting results were obtained. The separation mechanisms of photoexcited carriers for the composite photocatalysts were proposed.

## 2. Experimental

### 2.1. Materials

Melamine powder (Pur. >99.0%) used in the experiments was supplied by Aladdin Chemistry Co. Ltd. Ammonium tungstate hydrate was supplied by Sinopharm Chemical Reagent Co. Ltd. MB, BF, and other chemicals used in the experiments were purchased from Shanghai and other China chemical reagent Ltd. They are of analytically pure grade and used without further purification. Deionized water was used throughout this study.

### 2.2. Preparation of samples

$g\text{-C}_3\text{N}_4$  powder was prepared via heating melamine in a tube furnace. A certain amount of melamine was put into an alumina crucible which was first heated at  $500^\circ\text{C}$  for 2 h and was further heated at  $520^\circ\text{C}$  for 2 h with a temperature rise rate of  $10^\circ\text{C}/\text{min}$ . After the

reaction, the alumina crucible was cooled naturally to room temperature. The as-prepared  $g\text{-C}_3\text{N}_4$  was collected and ground into powder. Pure  $\text{WO}_3$  powder was prepared by the same heat treatment method using ammonium tungstate hydrate as a precursor.

The  $g\text{-C}_3\text{N}_4\text{-WO}_3$  composite photocatalyst was fabricated as follows: The mixtures of melamine and ammonium tungstate hydrate with a certain ratio were added into a zirconia tank. Two different sizes of zirconia balls were mixed in the zirconia tank, and water was used as a dispersant. The mixed samples were ball milled for 1 h at the speed of 400 rpm, and then the wet powder was dried at  $60^\circ\text{C}$  in air. The obtained powders were heated at the temperatures of  $500^\circ\text{C}$  and  $520^\circ\text{C}$  for 2 h, respectively. In this way, different  $\text{WO}_3(\text{wt.}\%)/g\text{-C}_3\text{N}_4$  photocatalysts (wt. = 0, 1.0, 3.0, 5.0, 7.0, 10, 30, 50, 70, 90, 93, 95, 97, 99, 100) were obtained, respectively. For convenience, when wt. < 10, i.e., the main part of the photocatalyst is  $g\text{-C}_3\text{N}_4$ , it is written as  $\text{WO}_3/g\text{-C}_3\text{N}_4$ ; when wt. > 90, i.e., the main part is  $\text{WO}_3$ , it is written as  $g\text{-C}_3\text{N}_4/\text{WO}_3$ .

### 2.3. Photoreaction apparatus and procedure

Experiments were carried out in a photoreaction apparatus. The photoreaction apparatus consists of two parts [31,32]. The first part is an annular quartz tube. A 500 W Xenon lamp (Institute of Electric Light Source, Beijing) with a maximum emission at about 470 nm was used as visible light source. The wavelength of the visible light was controlled through a 400 nm cutoff filter ( $\lambda > 400$  nm, Instrument Company of Nantong, China). The lamp is laid in the empty chamber of the annular tube, and running water passes through an inner thimble of the annular tube. Owing to continuous cooling, the temperature of the reaction solution is maintained at approximately  $30^\circ\text{C}$ . The second part is an unsealed beaker with a diameter of 12 cm. At the start of the experiment, the reaction solution (volume, 300 ml) containing reactants and photocatalyst was put in the unsealed beakers, and a magnetic stirring device was used to stir the reaction solution. The distance between the light source and the surface of the reaction solution is 11 cm. In the experiments, the initial pH of the reaction solution is 5.0. The illumination time is 60 min, and the amount of the photocatalyst used is 2.0 g/l. The initial concentrations of MB and BF are  $0.9 \times 10^{-5}$  mol/l and  $1.0 \times 10^{-5}$  mol/l, respectively. In order to disperse the photocatalyst powder, the suspensions were ultrasonically vibrated for 20 min prior to irradiation. After the illumination, the samples (volume of each was 5 ml) taken from the reaction suspension were centrifuged at 7000 rpm for 20 min and filtered through a  $0.2 \mu\text{m}$  millipore filter to remove the particles. The filtrate was then analyzed. In order to determine the reproducibility of the results, at least duplicated runs were carried out for each condition for averaging the results, and the experimental error was found to be within  $\pm 4\%$ .

### 2.4. Characterization

In order to determine the crystal phase composition and the crystallite size of the photocatalysts, XRD measurement was carried out at room temperature using a Bruker D8 advance X-ray powder diffractometer with  $\text{Cu K}\alpha$  radiation and a scanning speed of  $3^\circ/\text{min}$ . The accelerating voltage and emission current were 40 kV and 30 mA, respectively. The crystallite size was calculated by X-ray line broadening analysis using the Scherrer equation. TEM and high-resolution transmission electron microscopy (HR-TEM) images were performed with a JEOL-2010 transmission electron microscope, using an accelerating voltage of 200 kV. DRS measurements were carried out using a Hitachi UV-365 spectrophotometer equipped with an integrating sphere attachment. The analysis range was from 300 to 700 nm, and  $\text{BaSO}_4$  was used as a reflectance standard. PL emission spectra were recorded on a JASCO FP-6500

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