



# In-situ synthesis of direct solid-state Z-scheme $V_2O_5/g-C_3N_4$ heterojunctions with enhanced visible light efficiency in photocatalytic degradation of pollutants

Yuanzhi Hong<sup>a</sup>, Yinhua Jiang<sup>b</sup>, Changsheng Li<sup>a</sup>, Weiqiang Fan<sup>b</sup>, Xu Yan<sup>c</sup>, Ming Yan<sup>b</sup>, Weidong Shi<sup>b,\*</sup>

<sup>a</sup> School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, PR China

<sup>b</sup> School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China

<sup>c</sup> School of Energy and Power Engineering, Jiangsu University, Zhenjiang 212013, PR China

## ARTICLE INFO

### Article history:

Received 16 April 2015

Received in revised form 19 June 2015

Accepted 25 June 2015

Available online 16 July 2015

### Keywords:

Z-scheme heterojunction

$V_2O_5$

$g-C_3N_4$

Photocatalytic activity

Visible light

## ABSTRACT

The constructing of direct solid-state Z-scheme heterojunction photocatalytic system has received much attention in environmental purification and hydrogen generation from water. In this study, a novel direct solid-state Z-scheme  $V_2O_5/g-C_3N_4$  heterojunctions were synthesized via a facile *in-situ* growth strategy for the first time. The photocatalytic performance was evaluated by the degradation of rhodamine B (RhB) and tetracycline (TC) under visible light irradiation ( $\lambda > 420$  nm). Results show that the as-synthesized heterojunctions can significantly enhance photocatalytic activity in comparison with pure  $g-C_3N_4$  and  $V_2O_5$ . The optimum photocatalytic efficiency of VC1.0% sample for the degradation RhB was about 7.3 and 13.0 times higher than that of individual  $g-C_3N_4$  and  $V_2O_5$ , respectively. In addition, the VC1.0% sample as well as can efficiently degrade methyl orange (MO) and methylene blue (MB) under visible light. By further experimental study, the possible for the enhancing photocatalytic mechanism was found to be a direct solid-state Z-scheme heterojunction system based on the active species trapping and electron spin resonance (ESR) experiments, which not only can improve the photogenerated electron–hole pair's separation but also exhibit a strong oxidation and reduction ability for efficiency degradation of organic pollutants. This work will be useful for the design of other direct solid-state Z-scheme photocatalytic systems for application in energy conversion and environmental remediation.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Over the past years, semiconductor photocatalysis has been considered as a promising and green technology to resolve the increasing energy and environmental crisis by using of the solar light energy, such as for pollutants degradation and hydrogen generation from water [1–5]. As is known, the photogenerated electrons and holes of the single-component photocatalyst can easily recombine each other, which results in poor quantum efficiency and low photocatalytic performance [6]. In past years, the use of heterojunction-type photocatalytic system is an important strategy to overcome this drawback because it can efficiently improve the photoexcited electron–hole separation [7–9]. Unfortunately, the disadvantage of the typical heterojunction system is that the reducibility of photogenerated electrons and the oxidiz-

ability of photogenerated holes usually become weakened after charge transfer [10]. That is to say, the high charge-separation efficiency and strong redox ability are difficult to possess at the same time. Very recently, the construction of artificial Z-scheme photocatalytic system is an ideal and effective means because it not only can reduce the bulk electron–hole recombination, but also can preserve excellent redox ability [10,11]. However, the majority of the synthesized artificial Z-scheme photocatalytic systems usually had noble metal (Ag, Ru) [12–14] or redox pair ( $Fe^{3+}/Fe^{2+}$ ,  $IO_3^-/I^-$ ) [15,16], which will bring about great difficulties to their practical application. Thus, it is necessary to construct a novel Z-scheme system including only two visible-light-responsive solid-state photocatalysts. More recently, the synthesis of direct solid-state Z-scheme photocatalytic system has become a research hotspot for application in environmental purification and hydrogen generation from water [17–22]. The different charge carrier transfer path of typical heterojunction and novel direct solid-state Z-scheme heterojunction are depicted in Fig. 1.

\* Corresponding author. Fax: +86 511 8879 1108.  
E-mail address: [swd1978@ujs.edu.cn](mailto:swd1978@ujs.edu.cn) (W. Shi).

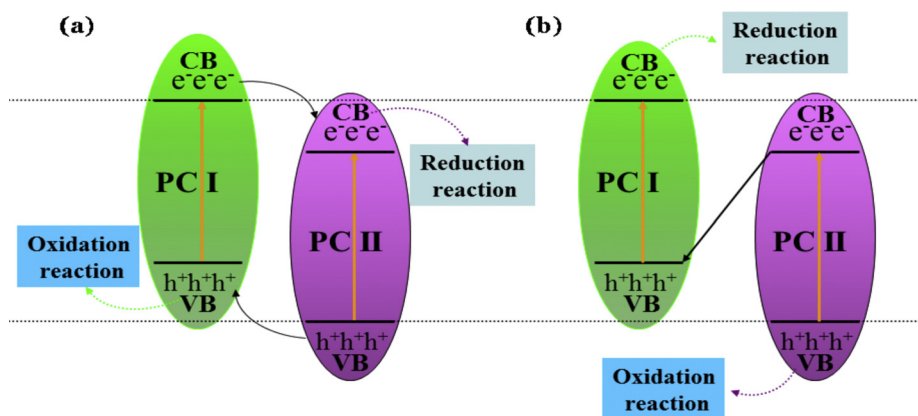


Fig. 1. Schematic illustration of the different charge carrier transfer path of (a) typical heterojunction and (b) novel direct solid-state Z-scheme heterojunction.

Graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ), a metal-free polymeric semiconductor, has attracted extensively attention due to its good thermal-chemical stability, electronic and optical characteristics [23]. In addition,  $g\text{-C}_3\text{N}_4$  as a novel visible-light-driven photocatalyst has been reported for hydrogen evolution and pollutant degradation under visible light irradiation [24–29]. Nevertheless, the photocatalytic application of individual  $g\text{-C}_3\text{N}_4$  is limited due to the rapid recombination of photogenerated electron–hole pairs, leading to the poor quantum efficiency and low photocatalytic activity. Up to now, only a few  $g\text{-C}_3\text{N}_4$ -based direct Z-scheme systems have been successfully prepared for enhancing photocatalytic activity, such as  $\text{TiO}_2/g\text{-C}_3\text{N}_4$  [30],  $\text{BiOCl}/g\text{-C}_3\text{N}_4$  [31],  $\text{Bi}_2\text{O}_3/g\text{-C}_3\text{N}_4$  [32],  $\text{WO}_3/g\text{-C}_3\text{N}_4$  [33] etc. However, the  $\text{TiO}_2$  and  $\text{BiOCl}$  can not excite in visible light because of their larger band gap ( $E_g > 3.0$  eV). On the other hand, although the  $\text{Bi}_2\text{O}_3$  and  $\text{WO}_3$  can respond to the visible light, they only can respond visible light with the wavelength shorter than 460 nm which limit their in solar energy conversion. Therefore, it is a great challenge to construct the  $g\text{-C}_3\text{N}_4$ -based direct solid-state Z-scheme system with a narrow band gap semiconductor photocatalyst for efficiently utilizing the solar light.

Vanadium pentoxide ( $\text{V}_2\text{O}_5$ ), an important transition metal-oxide semiconductor, has been widely used in lithium-ion batteries, gas sensors and optoelectronic devices [34–36]. Moreover,  $\text{V}_2\text{O}_5$  is a typical narrow band gap ( $\sim 2.3$  eV) semiconductor, which can be a good candidate for capable of capturing visible light [37,38]. What's more,  $\text{V}_2\text{O}_5$  has suitable band edges ( $ECB = 0.47$  eV,  $EVB = 2.73$  eV), which can match well with  $g\text{-C}_3\text{N}_4$  ( $ECB = -1.2$  eV,  $EVB = 1.5$  eV) to form a direct solid-state Z-scheme photocatalytic system [27,38]. If that can be accomplished, the photoexcited electron in conduction band (CB) of  $g\text{-C}_3\text{N}_4$  shows the strong reducibility and the photoexcited hole on valence band (VB) of  $\text{V}_2\text{O}_5$  exhibits the strong oxidizability, respectively.

In the present study, we have firstly prepared the direct solid-state Z-scheme  $\text{V}_2\text{O}_5/g\text{-C}_3\text{N}_4$  heterojunction photocatalysts by a facile *in-situ* growth strategy. The photocatalytic performance was evaluated by the degradation of RhB and TC under visible light irradiation ( $\lambda > 420$  nm). The as-synthesized Z-scheme  $\text{V}_2\text{O}_5/g\text{-C}_3\text{N}_4$  photocatalysts could significantly enhance photocatalytic activity in comparison with pure  $g\text{-C}_3\text{N}_4$  and  $\text{V}_2\text{O}_5$ . In addition, the VC1.0% sample exhibited the optimum photocatalytic activity as well as possessed excellent photostability after five times cycling photocatalytic reactions. Moreover, the VC1.0% sample also can efficiently decompose other pollutant organic dyes such as methyl orange (MO) and methylene blue (MB) under visible light. Furthermore, a novel direct solid-state Z-scheme photocatalytic mechanism for the enhancing photocatalytic activity was also

proposed based on the active species trapping experiments and electron spin resonance (ESR) analysis.

## 2. Experimental

### 2.1. Materials

Melamine,  $\text{NH}_4\text{VO}_3$ , triethanolamine (TEOA), 1,4-benzoquinone (BQ), isopropanol (IPA), and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were analytical grade agents and purchased from Aladdin (China). Rhodamine B (RhB), tetracycline (TC), methyl orange (MO) and methylene blue (MB) were analytically pure and used without further purification.

### 2.2. Photocatalysts preparation

The metal-free bulk  $g\text{-C}_3\text{N}_4$  powders were synthesized by the thermal treatment of melamine according to the previous paper [39]. Typically, 10 g melamine was put into a 50 mL alumina crucible with a cover, then heated in a muffle furnace at a rate of  $2.3^\circ\text{C}/\text{min}$  and kept for 4 h at  $550^\circ\text{C}$ . After being cooled to room temperature, the resulting products were collected and milled into powder in an agate mortar for further use.

The direct solid-state Z-scheme  $\text{V}_2\text{O}_5/g\text{-C}_3\text{N}_4$  heterojunction photocatalysts were prepared by a facile *in-situ* growth strategy as illustrated in Fig. 2. Specifically, a certain amount of bulk  $g\text{-C}_3\text{N}_4$  and different amount of  $\text{NH}_4\text{VO}_3$  were added into an agate mortar, and grounded together. The resultant powders were transferred to a covered alumina crucible, then calcined at  $500^\circ\text{C}$  for 1 h with a heating rate of  $5^\circ\text{C}/\text{min}$ . To make clarity, the  $\text{V}_2\text{O}_5/g\text{-C}_3\text{N}_4$  composites with expected  $\text{V}_2\text{O}_5$  contents of 0, 0.5, 1.0, 1.5, 2.5 and 5.0 wt% are referred to as pure  $g\text{-C}_3\text{N}_4$ , VC0.5%, VC1.0%, VC1.5%, VC2.5% and VC5.0%, respectively. For comparison, bare  $\text{V}_2\text{O}_5$  was prepared similarly but without the addition of  $g\text{-C}_3\text{N}_4$ .

### 2.3. Characterization

All of the phase compositions and crystal structures of the prepared samples were determined by powder X-ray diffraction (XRD) method using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ), (D/MAX-2500 diffractometer, Rigaku, Japan) with  $\text{Cu-K}\alpha$  radiation source ( $k = 1.54056$ ) over the  $2\theta$  range of  $5.0\text{--}80^\circ$  at a scanning rate of  $7.0^\circ \text{ min}^{-1}$ . The morphology of as-prepared samples was observed by scanning electronic microscopy (SEM) on an S-4800 field emission SEM (SEM, Hitachi, Japan). The transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and High angle angular dark field-scanning transmission electron microscopy (HAADF-STEM)

Download English Version:

<https://daneshyari.com/en/article/45286>

Download Persian Version:

<https://daneshyari.com/article/45286>

[Daneshyari.com](https://daneshyari.com)