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Template-free preparation of macro/mesoporous g-C_3N_4/TiO_2 heterojunction photocatalysts with enhanced visible light photocatalytic activity

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ABSTRACT

Mesoporous photocatalytic materials with macroporous structures have attracted more and more attention because of their textural mesopores and intrinsic interconnected pore networks, which are able to efficiently transport guest species to framework binding sites. In this work, macro/mesoporous g-C_3N_4/TiO_2 heterojunction photocatalysts were fabricated without templates or additives by a facile calcination method using tetrabutyl titanate and melamine as the feedstocks. Photocatalytic experiments of the as-prepared samples were measured by the photocatalytic oxidation degradation of RhB solution at room temperature under visible light irradiation. The results indicated that the melamine content in the precursors had an important influence on photocatalytic activity of the as-prepared samples. At the optimal loading content, the apparent reaction rate constant (k) was 47.8×10^{-3} min^{-1} for RhB degradation, exceeding that of pure TiO_2 (6.6×10^{-3} min^{-1}) and g-C_3N_4 (15.2×10^{-3} min^{-1}) by factor of 7.2 and 3.1 respectively. The improved photocatalytic activity was attributed to high surface area and heterostructure formation of g-C_3N_4/TiO_2 composites. The trapping experiment results showed that $^{\bullet}O_2^-$ and h^+ were main active species in the decomposition of RhB. A possible enhanced photocatalytic mechanism of g-C_3N_4/TiO_2 heterojunction photocatalysts was proposed.

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1. Introduction

The utilization of semiconductor photocatalysts for the decomposition of organic pollutions has been regarded as an efficient method to solve environmental pollution problems [1–4]. Among various oxide semiconductor photocatalysts, TiO_2 was regarded as a promising material for widespread environmental applications due to their particular performance such as strong oxidizing power, chemical stability, low cost and non-toxic [5–7]. Nevertheless, the photocatalytic performance of titania must be further enhanced owing to the fast recombination rate of the photogenerated electron-hole pairs within the TiO_2 particles and the restricted UV-light response (only about 4% of total sunlight) [8,9]. To date, numerous effective strategies were developed to extend the response range from UV to visible light and improve the visible light photocatalytic activity of TiO_2, such as noble metal depositing [10,11], metal and non-metal ion doping [12–14], semiconductor coupling [15–17], surface sensitization [18], and so on. Among them, semiconductor coupling has been an efficient method to improve visible light photocatalytic activity of TiO_2 and attracted widespread interest owing to the formation of a close interface between two semiconductor materials [19–23]. This special structure can promote the separation of the photoinduced hole-electron pairs, hence resulting in improved visible light photocatalytic activity [24,25].

g-C_3N_4 has been proved to be a non-toxic, stable and facile organic semiconductor photocatalysts [26–28]. The band gap of g-C_3N_4 is approximately 2.7 eV, which exhibits a strong response for the visible-light region [29–31]. In addition, g-C_3N_4 was easily obtained by mild thermolysis routes from inexpensive nitrogen-rich precursors such as urea, melamine, thiourea, cyanamide and dicyandiamide [32–34]. Recent results show that the hybridization of TiO_2 with g-C_3N_4 displays an enhanced photocatalytic

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activity because of the unique heterojunction structure [35–38]. Therefore, the preparation of g-C_3N_4/TiO_2 heterojunction photocatalyst is a promising strategy to improve charge separation and enhance photocatalytic performance of TiO_2 [39,40]. For example, Zhang et al. [41] confirmed that heterojunctions in g-C_3N_4/TiO_2 (B) nanofibres with exposed (0 0 1) plane showed superior photocatalytic performance in decomposition of RhB solution under visible light illumination. The enhanced activities of the g-C_3N_4/TiO_2 heterojunction photocatalysts relied on stable interfacial structure between g-C_3N_4 and the plane (110) of TiO_2 (B). Wang et al. [42] demonstrated that g-C_3N_4/P25 heterojunction photocatalysts showed higher photocatalytic performance toward degradation phenol and RhB. Huang et al. [43] reported that the photocatalytic activity of g-C_3N_4/TiO_2-HNB heterojunction photocatalysts was greatly improved via (1 0 1) facets because of efficient removal of photoinduced electrons accumulate on (1 0 1) facets of TiO_2.

Mesoporous photocatalytic materials with macroporous structures have attracted more and more attention because of their textural mesopores and intrinsic interconnected pore networks, which are able to efficiently transport guest species to framework binding sites. The macro/mesoporous structures are beneficial for the increase in the specific surface area, thereby offering more active sites for photocatalytic reaction. In our work, the g-C_3N_4/TiO_2 heterojunction photocatalysts were prepared by a facile calcination method using tetrabutyl titanate and melamine as the feedstocks. The as-prepared g-C_3N_4/TiO_2 heterojunction photocatalysts have large specific surface area than pure TiO_2 (34.8 m^2/g) and pure g-C_3N_4 (14.3 m^2/g). Moreover, the close interface contact between TiO_2 and g-C_3N_4 inhibited the fast recombination of electron-hole pairs, resulting in an enhanced visible light photocatalytic activity for the degradation of RhB. To the best of our knowledge, this work is the first report about macro/mesoporous g-C_3N_4/TiO_2 heterojunction photocatalysts for decomposition of RhB at room temperature under visible light irradiation. The present work may provide a new insight for the smart design and synthesis of various highly efficient photocatalysts for environmental and energy applications.

2. Experimental

2.1. Materials

All raw materials used in this experiment were analytical reagents and used without further purification. Deionized water was used in all synthesis and treatment processes. Tetrabutyl titanate (TBOT, $C_{16}H_{36}O_4Ti$), melamine ($C_3H_6N_6$), anhydrous ethanol (C_2H_6O) and tertiary butyl alcohol (TBA, $C_4H_{10}O$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylenediamine tetraacetic Acid (Na_2-EDTA, $C_{10}H_{18}N_2Na_2O_{10}$) and *p*-benzoquinone (*p*-BQ, $C_6H_4O_2$) were purchased from Aladdin Industrial Corporation.

2.2. Sample preparation

Macro/mesoporous g-C_3N_4/TiO_2 heterojunction photocatalysts were fabricated by calcining the mixtures of the melamine and amorphous macro/mesoporous TiO_2 powders. First, the amorphous macro/mesoporous TiO_2 powders were prepared according to the literature procedure [44]. In brief, 20 mL of TBOT was added dropwise dissolved in 200 mL of distilled water without vigorous stirring. The mixture of the reagents was aged at room temperature for 36 h. Subsequently, the white precipitates were collected by filtration rinsed four times with distilled water and anhydrous ethanol alternately. After the washed samples were dried in an oven 60 °C for 12 h, the amorphous macro/mesoporous TiO_2 powders were obtained. Second, 3 g of melamine was dispersed in 100 mL hot distilled water, and then 0.5 g of amorphous macro/mesoporous TiO_2 was added. The suspension solution were transferred to a 250 mL beaker and then dried in an oven at 100 °C for 12 h. Subsequently, this dried mixture was placed in an alumina crucible with a cover and then calcined in a muffle furnace for 2 h at 550 °C with a ramping rate of 5 °C min^{-1} in air atmosphere. After cooling down to room temperature, the final light yellow macro/mesoporous g-C_3N_4/TiO_2 products were obtained. In order to discuss the role of g-C_3N_4 content on the photocatalytic activity of g-C_3N_4/TiO_2 heterojunction photocatalysts, samples with different amount of melamine in the precursors were prepared under the same conditions. The products were named as CNT*x*, where the *x* referred to the mass weight of melamine used (Table 1). For example, CNT3 represented the sample prepared from 3 g of melamine and 0.5 g of amorphous macro/mesoporous TiO_2. For comparison, pure g-C_3N_4 and TiO_2 (CNT0) were directly annealed at the above condition by using melamine and amorphous macro/mesoporous TiO_2 as feedstocks, respectively.

2.3. Sample characterization

The powder X-ray diffraction (XRD) patterns were acquired on Bruker D8 Advance X-ray diffractometer (Bruker AXS, German) with Cu Kα1 radiation (λ = 1.5418 Å) at a scanning speed of 0.02° s^{-1}. The accelerating voltage and applied current were 40 KV and 20 mA, respectively. The morphology of the g-C_3N_4/TiO_2 powders was observed on a field emission scanning electron microscope (FESEM) (JSM-7000F, Japan) with an acceleration voltage of 15 kV and a transmission electron microscope (TEM) (Tecnai G20, USA) using an acceleration voltage of 200 kV, respectively. Fourier transform infrared (FT-IR) spectra were conducted on Niconet 5700 FT-IR spectrometer with the samples dispersed in KBr desiccative in the range of 400–4000 cm^{-1}. TGA-7 analyzer (PE, USA) was used to characterize the thermal chemical and physical properties of the samples. Nitrogen adsorption-desorption isotherms were analyzed by a Micromeritics ASAP 2020HD 88 nitrogen adsorption apparatus (USA). The samples were degassed at 180 °C for 4 h prior to nitrogen adsorption measurements. The S_{BET} of the samples were measured by adsorption segments in the relative pressure P/P_0 range of 0.05-0.20. The data of desorption were used for determining the pore size using the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was measured on a K-Alpha (1486.68 eV) X-ray sources (USA). The RhB concentration in aqueous solution was determined at 552 nm by a UV–vis spectrophotometer (UV-2550, Shimadzu, Japan). The UV–vis absorption spectras of as-prepared photocatalytsts were measured by a Shimadzu UV–vis spectrophotometer (Japan) with $BaSO_4$ used as a reflectance standard. PL spectra of the samples were measured by a Perkinelmer LS55 fluorescence spectrophotometer (Germany, slit 10 nm, scanning speed 1200 nm min^{-1}, excitation wavelength 320 nm). The total organic carbon (TOC) tests were performed by the Apollo9000 TOC analyzer before and after photocatalytic reaction for 80 min.

2.4. Measurement of photocatalytic activity

The photocatalytic activity of the photocatalysts was estimated by photocatalytic decomposition of RhB aqueous solution at room temperature under visible light irradiation. Detail experiments were examined as follows: 0.04 g of the sample was dispersed in 20 mL of deionized water. The resulting suspensions were sonicated for 40 min and then poured into a dish with diameter of about 9 cm, which was dried in an oven at 60 °C for 3 h to evaporate the water. Secondly, 30 mL of RhB (1×10^{-5} M) solution was transferred into the above dish with the sample. Prior to visible-

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