



Regular Article

In-situ synthesis of highly efficient visible light driven stannic oxide/graphitic carbon nitride heterostructured photocatalysts

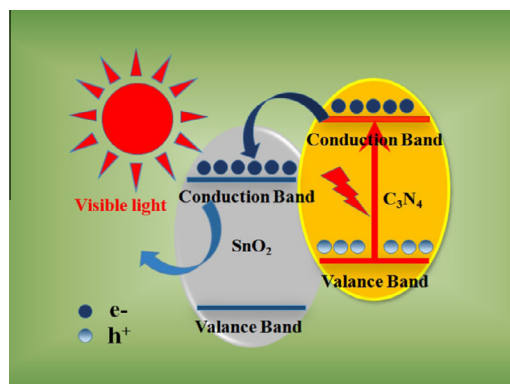


Binglin Tao, Zifeng Yan*

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, China University of Petroleum, Qingdao 266580, China

GRAPHICAL ABSTRACT

SnO_2 particles are highly dispersed on $\text{g-C}_3\text{N}_4$ sheets to form a new kind of heterojunctions. The as-fabricated $\text{SnO}_2/\text{g-C}_3\text{N}_4$ heterojunctions demonstrate extraordinary photocatalytic activity for degradation of rhodamine B. The large specific surface area, narrow band gap, strong interactions between two components, and high stability make them excellent candidate for water detoxification.



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ABSTRACT

Novel and efficient visible-light-driven stannic oxide/graphitic carbon nitride heterostructured photocatalysts are prepared via a simple in-situ solvothermal method. Characterization results demonstrate that there exist strong interactions between SnO_2 nanoparticles and $\text{g-C}_3\text{N}_4$ matrix, which indicates the formation of $\text{SnO}_2/\text{g-C}_3\text{N}_4$ heterojunction. The as-synthesized $\text{SnO}_2/\text{g-C}_3\text{N}_4$ composite exhibits improved efficiency for photodegradation of rhodamine B in aqueous solutions, with an apparent rate constant 6.5 times higher than that of commercial TiO_2 (Degussa P25). The enhanced photocatalytic activity is attributed to synergistic effect between SnO_2 and $\text{g-C}_3\text{N}_4$, resulting in effective interfacial charge transfer and prolonged charge-hole separation time. Moreover, $\text{SnO}_2/\text{g-C}_3\text{N}_4$ composite photocatalysts possess excellent durability and stability after 6 recycling runs, and a possible photocatalytic mechanism is also proposed. This research highlights the promising applications of two dimensional $\text{g-C}_3\text{N}_4$ based composite photocatalysts in the field of waste water disposal and environmental remediation.

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* Corresponding author.

E-mail address: zfyancat@upc.edu.cn (Z. Yan).

1. Introduction

Photocatalysis is of great interest because it provides a simple technique to solve selected environmental pollutions (e.g., gas and water purification [1]) and energy issues (e.g., water splitting [2] and carbon dioxide conversion [3]) facing the modern society. During the last 40 years, titanium oxide (TiO_2) has attracted much attention for its high efficiency, low cost and availability in the fields of water splitting for hydrogen production [4], water detoxification [5], air treatment [6], CO_2 reduction [7] and organic synthesis [8]. As the most widely used commercial photocatalyst, Degussa P25, composing of about 80% anatase and 20% rutile, is well-known to possess an insurmountable photocatalytic activity. Despite these remarkable advantages and considerable achievements, TiO_2 (P25) has also been much criticized for its two intrinsic shortcomings: the wide band gap and high recombination rate of photoinduced electron-hole pairs. Besides, the toxicity and safety for TiO_2 need to be further studied in detail [9]. Thus, numerous novel photocatalytic materials, for example, metal oxides [10,11], metal sulfides [12], metallates [13,14], metal halide [15], and even some metal-free semiconductors [16] have been proposed as substitutes for conventional TiO_2 photocatalysts.

Since the first report about hydrogen production by graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) in 2009 [17], this kind of metal-free polymer has attracted much attention in the field of photocatalysis due to its stability, low cost, and nontoxic properties. However, $\text{g-C}_3\text{N}_4$ possesses a high recombination rate, indicating its short lifetime and low separation efficiency of photogenerated electron-hole pairs, which leads to low quantum efficiency. Many approaches have been proposed to enhance the photocatalytic activity of $\text{g-C}_3\text{N}_4$, including exfoliation of bulk $\text{g-C}_3\text{N}_4$ into nanosheets [18], preparation of mesoporous $\text{g-C}_3\text{N}_4$ with large specific surface area [19], doping protogenous $\text{g-C}_3\text{N}_4$ with transition metals [20], and fabrication of $\text{g-C}_3\text{N}_4$ based semiconductor heterojunctions [21,22]. Among them, combining $\text{g-C}_3\text{N}_4$ with metal oxides to prepare heterostructured photocatalysts is supposed to be the most effective way to fully address the above mentioned issue. Consequently, a variety of $\text{g-C}_3\text{N}_4$ based composites, including $\text{Ag}_2\text{O/g-C}_3\text{N}_4$ [21], $\text{TiO}_2/\text{g-C}_3\text{N}_4$ [23], $\text{Bi}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ [24], $\text{AgVO}_4/\text{g-C}_3\text{N}_4$ [25] and $\text{In}_2\text{O}_3/\text{g-C}_3\text{N}_4$ [26] were prepared, which exhibited improved separation efficiency of photogenerated charge carriers and enhanced photocatalytic activities.

Stannic oxide (SnO_2), as an n-type semiconductor with a band gap of ~ 3.60 eV, was shown to be a less active photocatalyst for water detoxification [27]. However, SnO_2 has been more widely employed as an additive to improve catalytic behaviors of the main photocatalysts. For example, ZnO-SnO_2 nanofibers prepared via sol-gel method and electrospinning technology possessed a much higher photocatalytic activity than the pure ZnO and SnO_2 nanofibers for the degradation of rhodamine B under ultraviolet irradiation, possibly owing to the formation of ZnO-SnO_2 heterojunctions which could facilitate the separation of electron-hole pairs [28]. Theoretically, the combination of SnO_2 and $\text{g-C}_3\text{N}_4$ could lead to the formation of a new kind of semiconductor heterojunction ($\text{SnO}_2/\text{g-C}_3\text{N}_4$), which possesses a well matched band structure and reduces the electron-hole recombination rate.

There are few publications focused on the preparation of $\text{SnO}_2/\text{g-C}_3\text{N}_4$ heterostructured photocatalysts. Most recently, $\text{SnO}_2/\text{g-C}_3\text{N}_4$ composite was synthesized by a traditional solvent evaporation method [29]. The combination of SnO_2 and $\text{g-C}_3\text{N}_4$ was beneficial for effective interfacial charge transfer thus prolonged electron-hole pairs' lifetime. However, the large crystal size (20 nm), small specific surface area ($38.5 \text{ m}^2/\text{g}^{-1}$), and bulk $\text{g-C}_3\text{N}_4$ sheets render $\text{SnO}_2/\text{g-C}_3\text{N}_4$ composite possesses a limited photocatalytic activity. Besides, the synthesis procedure was still tedious.

A novel in-situ method for the fabrication of $\text{SnO}_2/\text{g-C}_3\text{N}_4$ heterostructured photocatalysts is described here. These new composites were prepared via a solvothermal method in which urea-derived $\text{g-C}_3\text{N}_4$ acted as matrix and stannic acetate served as SnO_2 precursor. They exhibited considerable activity for rhodamine B degradation in aqueous solutions, which was directly related to their unique structures.

2. Experiment section

2.1. Materials

Urea and dimethylsulfoxide were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Stannic acetate was purchased from Alfa Aesar. TiO_2 (Degussa P25, 20% rutile and 80% anatase) was provided by Degussa (China) Co., Ltd. All the reagents were analytical pure and used as received without further purification. Ultrapure water (resistivity $\geq 18 \text{ M}\Omega \text{ cm}$) was produced by a Millipore system.

2.2. Synthesis of $\text{g-C}_3\text{N}_4$

The metal-free semiconductor $\text{g-C}_3\text{N}_4$ powders were synthesized by simply heating urea in a muffle furnace. Typically, 20.0 g of urea was placed in a 100 mL semi-closed crucible with a cover. Then temperature was raised to 550 °C at an accelerating rate of $15 \text{ }^\circ\text{C min}^{-1}$ and the condensation process was maintained at 550 °C for 4 h [30]. After the crucible was cooled down to room temperature naturally, the yellow product was collected and ground into fine powders. For 20.0 g of urea, the $\text{g-C}_3\text{N}_4$ yield was 0.87–0.89 g.

2.3. Fabrication of $\text{SnO}_2/\text{g-C}_3\text{N}_4$ composite photocatalysts

$\text{SnO}_2/\text{g-C}_3\text{N}_4$ composite photocatalysts were synthesized via an ordinary solvothermal method. In a typical synthesis, 0.4 g of $\text{g-C}_3\text{N}_4$ and 0.1571 g of stannic acetate were sequentially added into 70 mL of dimethylsulfoxide contained in a 250 mL beaker. After sonication for 60 min, the above solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, and then heated at 180 °C for 20 h. Subsequently, the precipitate was collected by filtration, washed with water and ethanol for several times, and dried at ambient conditions. Finally the composite photocatalysts were annealed at 400 °C for 3 h. According to this method, a series of $\text{SnO}_2/\text{g-C}_3\text{N}_4$ composites with selected mass ratios of SnO_2 and $\text{g-C}_3\text{N}_4$ (1:20, 1:10, 1:4, 1:1, and 2:1) were prepared by changing the dosages of stannic acetate. Pure SnO_2 particles were prepared by decomposing stannic acetate in dimethylsulfoxide directly.

2.4. Characterization

Crystal structure of the as-prepared products were characterized by a PANalytical PRO X-ray Diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ nm}$). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer using KBr disc technique. Nitrogen adsorption-desorption isotherms were obtained on a Micromeritics Tristar 3000 equipment at $-196 \text{ }^\circ\text{C}$. Prior to measurement, all the samples were degassed at 300 °C for 3 h. Surface property analysis was performed on an Escalab 250 X-ray photoelectron spectrometer. The C1s binding energy of 284.6 eV of adventitious carbon was used as the reference. Morphologies of the as-prepared composites were obtained from a Hitachi S-4800 scanning electron microscope at an accelerating voltage of 5 kV. The lattice structure and selected area electron diffraction were observed on a JEM-2100UHR transmission electron microscope. Diffuse reflectance spectra were recorded by a

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