



Preparation and enhanced visible-light photocatalytic activity of graphitic carbon nitride/bismuth niobate heterojunctions



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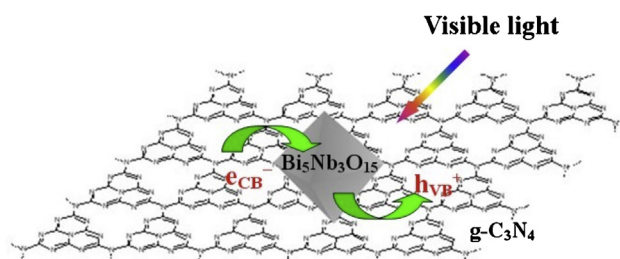
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HIGHLIGHTS

- Graphitic $C_3N_4/Bi_5Nb_3O_{15}$ heterojunctions were demonstrated for the first time.
- Graphitic $C_3N_4/Bi_5Nb_3O_{15}$ exhibited enhanced visible-light photocatalytic activity.
- Graphitic $C_3N_4/Bi_5Nb_3O_{15}$ possessed excellent photocatalytic stability.
- The excellent photocatalytic activity of graphitic $C_3N_4/Bi_5Nb_3O_{15}$ was explained.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of graphitic carbon nitride/bismuth niobate ($g-C_3N_4/Bi_5Nb_3O_{15}$) heterojunctions with $g-C_3N_4$ doping level of 10–90 wt% were prepared by a facile milling-heat treatment method. The phase and chemical structures, surface compositions, electronic and optical properties as well as morphologies of the prepared $g-C_3N_4/Bi_5Nb_3O_{15}$ were well-characterized. Subsequently, the photocatalytic activity and stability of $g-C_3N_4/Bi_5Nb_3O_{15}$ were evaluated by the degradation of aqueous methyl orange (MO) and 4-chlorophenol (4-CP) under the visible-light irradiation. At suitable $g-C_3N_4$ doping levels, $g-C_3N_4/Bi_5Nb_3O_{15}$ exhibited enhanced visible-light photocatalytic activity compared with pure $g-C_3N_4$ or $Bi_5Nb_3O_{15}$. This excellent photocatalytic activity was revealed in terms of the extension of visible-light response and efficient separation and transportation of the photogenerated electrons and holes due to coupling of $g-C_3N_4$ and $Bi_5Nb_3O_{15}$. Additionally, the active species yielded in the pure $g-C_3N_4$ - and $g-C_3N_4/Bi_5Nb_3O_{15}$ -catalyzed 4-CP photodegradation systems were investigated by the free radical and hole scavenging experiments.

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1. Introduction

Photocatalytic oxidation of aqueous organic pollutants into CO_2 , water and other nonhazardous compounds is one of the few effective approaches to remove the organic pollutants in water

completely in an environmentally friendly manner [1–6]. One of the primary challenges in practical application of this technique is to engineer a robust, cheap and stable photocatalyst that exhibits obvious visible-light absorption as well as efficient separation and transportation of the photogenerated holes (h_{VB}^+) and electrons (e_{CB}^-). Although it is very effective under near-UV light irradiation, conventionally applied TiO_2 photocatalyst is not ideal for this purpose because TiO_2 performs rather poorly in the processes associated with solar photocatalysis [7]. TiO_2 can utilize no more than 5% of the total solar energy impinging on the surface of

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the earth due to its wide bandgap (3–3.2 eV). Therefore, much effort has been devoted to developing more efficient and stable photocatalysts. On the one hand, new TiO₂-based photocatalytic materials were designed including metal or non-metal doping and heterostructuring design of integrated multi-semiconductor systems. Purposes of these designs are to promote the separation of $h\nu_{VB}^+ - e_{CB}^-$ pairs and/or to improve the sunlight harvesting ability of the photocatalysts [8]. On the other hand, the alternative photocatalysts to TiO₂ for solar or visible-light photocatalysis applications has emerged during the last decade. Among these, metal oxides with d^{10} main group elements (e.g. Bi₂O₃, In₂O₃ or Ga₂O₃) as well as complex metal oxides containing the cations of d^0 and/or d^{10} electronic configurations (e.g. niobates, vanadates, tungstates, titanates, tantalates and germanates) are the most successful alternative photocatalysts [7,9]. These metal oxides or complex metal oxides possess steep absorption edges in the visible-light region, being different from the more structured spectrum of the doped TiO₂ materials.

Bismuth niobate (Bi₅Nb₃O₁₅) is one of the alternative photocatalysts to TiO₂, and it possesses mixed layered Aurivillius phase structure expressed as [Bi₂O₂] + [NbO₄] + [Bi₂O₂] + [BiNb₂O₄]. Bi₅Nb₃O₁₅ is composed of both main group Bi element of $d^{10}s^2$ electronic configurations and transition metal Nb element of d^0 configurations, which can introduce s -states into the valence band (VB). Hybridization of these s -states with O $2p$ states contributes to an up-shift of the top of the VB and thereby to a narrowing of the bandgap. Bi₅Nb₃O₁₅ has been conventionally prepared by a high temperature solid-state route, which results in the compound with large agglomerated particles and irregular morphology [10]. In our recent work, a mild hydrothermal treatment method was applied for the first time to obtain single-crystalline orthorhombic Bi₅Nb₃O₁₅ with octahedron-like morphology, and the aggregation of Bi₅Nb₃O₁₅ particles was effectively inhibited. Bandgap of the prepared Bi₅Nb₃O₁₅ is 2.9 eV that allows a light absorption edge extend to 450 nm, and the photocatalytic tests show Bi₅Nb₃O₁₅ exhibits visible-light photocatalytic activity toward the degradation of a light insensitive compound, tetrabromobisphenol A [11,12]. However, it should be admitted that the photocatalytic activity of pure Bi₅Nb₃O₁₅ is usually unsatisfactory due to the narrowed visible-light response range.

In addition to the classic semiconductor photocatalysts, a fascinating metal-free sustainable photocatalyst, graphite-like carbon nitride ($g\text{-C}_3\text{N}_4$), has recently attracted worldwide attention due to its polymeric π -conjugated structure, leading to its remarkable physical and chemical properties [13,14]. For example, $g\text{-C}_3\text{N}_4$ exhibits an appealing electronic structure with bandgap of 2.7 eV that allows a maximal light absorption in the visible-light region (400–460 nm). Additionally, $g\text{-C}_3\text{N}_4$ can be feasibly synthesized via thermal polycondensation of cheap nitrogen rich precursors such as cyanamide, dicyandiamide, melamine, urea, ammonium thiocyanate, thiourea and triazine [15–30]. Nonetheless, metal-free $g\text{-C}_3\text{N}_4$ suffers from disadvantages such as rapid recombination of e_{CB}^- and $h\nu_{VB}^+$ as well as low visible-light utilization efficiency [15,28,31–37]. Accordingly, the development of reliable and facile strategies to fabricate the modified $g\text{-C}_3\text{N}_4$ -based photocatalysts with unique photocatalytic performances is of growing interests. For this purpose, $g\text{-C}_3\text{N}_4$ -based heterostructured photocatalysts such as $g\text{-C}_3\text{N}_4/\text{TiO}_2$, $g\text{-C}_3\text{N}_4/\text{TaON}$, $g\text{-C}_3\text{N}_4/\text{ZnO}$ and $g\text{-C}_3\text{N}_4/\text{Bi}_2\text{WO}_6$ have been constructed, and the enhanced photocatalytic activity of $g\text{-C}_3\text{N}_4$ /semiconductor heterojunctions with respect to $g\text{-C}_3\text{N}_4$ is revealed by the fast separation and transportation of $h\nu_{VB}^+$ and e_{CB}^- carriers [38–41].

In the search for novel alternative photocatalyst to TiO₂ and further improving the visible-light photocatalytic activity of $g\text{-C}_3\text{N}_4$ or Bi₅Nb₃O₁₅, herein, a series of $g\text{-C}_3\text{N}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15}$ heterojunctions with different $g\text{-C}_3\text{N}_4$ doping levels (10–90 wt%) are developed by

a simple milling-heat treatment method. The visible-light response range of Bi₅Nb₃O₁₅ is extended by the introduction of $g\text{-C}_3\text{N}_4$, while a more efficient photogenerated carrier separation of $g\text{-C}_3\text{N}_4$ can be realized by coupling with Bi₅Nb₃O₁₅. The phase and chemical structures, surface compositions, electronic and optical properties as well as morphologies of the $g\text{-C}_3\text{N}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15}$ heterojunctions were well characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectra (XPS), UV–vis diffuse reflectance (UV–vis/DRS), photoluminescence (PL) spectroscopy and transmission electron microscope (TEM). Subsequently, the visible-light photocatalytic activity of the $g\text{-C}_3\text{N}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15}$ was evaluated by the degradation of two typical organic pollutants, dye methyl orange (MO) and light insensitive compound 4-chlorophenol (4-CP). Catalytic tests show that as-prepared $g\text{-C}_3\text{N}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15}$ exhibit excellent visible-light photocatalytic activity to decompose of MO or 4-CP, and at suitable $g\text{-C}_3\text{N}_4$ doping levels the visible-light photocatalytic activity of the heterojunctions outperforms the sating $g\text{-C}_3\text{N}_4$ or Bi₅Nb₃O₁₅. This enhanced photocatalytic activity is explained by the combination of the extended light absorption and more efficient separation and transportation of the $h\nu_{VB}^+$ and e_{CB}^- carriers. Special attention is paid to provide direct evidence of the enhanced separation and transportation ability of the photogenerated carriers in the heterojunction system by PL and photoelectrochemistry measurements. Simultaneously, the active species yielded in the pure $g\text{-C}_3\text{N}_4$ - and $g\text{-C}_3\text{N}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15}$ -catalyzed 4-CP photodegradation systems were investigated by free radical and hole scavenging experiments. Finally, the catalytic stability of as-prepared $g\text{-C}_3\text{N}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15}$ was evaluated through five consecutive cycles.

2. Experimental

2.1. Preparation of $g\text{-C}_3\text{N}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15}$

Bi₅Nb₃O₁₅ was prepared by our previous reported hydrothermal treatment method [11,12]. Bi(NO₃)₃·5H₂O (2 mmol) and NbCl₅ (1.4 mmol) were dissolved in ethanol (10 mL), respectively, under vigorous stirring at room temperature for 0.5 h. The obtained NbCl₅ solution was added dropwise into the above Bi(NO₃)₃ solution. After stirring for 0.5 h, NH₃·H₂O (13 mol L⁻¹) was added into the mixture to adjust the acidity of the system to pH 9. Subsequently, the solution was stirred for 0.5 h to obtain a white suspension at room temperature. The white suspension was transferred into an autoclave and then heated to 200 °C for 24 h with a heating rate of 2 °C min⁻¹. After cooling down to room temperature, the product was filtered and washed with distilled water and ethanol for three times, and then it was dried at 80 °C.

Graphitic C₃N₄ powder was prepared by heating urea in a muffle furnace. In a typical run, 10 g of urea powder was put into a semi-closed alumina crucible with a cover. The crucible was heated to 250 °C for 1 h, 350 and 550 °C for 2 h, successively, at a heating rate of 2 °C min⁻¹. The resultant yellow powder was washed with distilled water and ethanol for two times, successively, and then it was dried at 80 °C.

The $g\text{-C}_3\text{N}_4$ and Bi₅Nb₃O₁₅ powders were thoroughly ground together to achieve a homogeneous mixture. The resultant mixture was collected and calcined at 400 °C for 1 h in a muffle furnace. After cooling down to room temperature, the product was obtained and denoted as $g\text{-C}_3\text{N}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15-x}$, where x refers to $g\text{-C}_3\text{N}_4$ loading (wt%) in the composite.

2.2. Characterization of $g\text{-C}_3\text{N}_4/\text{Bi}_5\text{Nb}_3\text{O}_{15}$

Powder XRD patterns were obtained on a D/max-2200 VPC diffractometer using CuK α radiation. FT-IR spectra were recorded

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