Materials Research Bulletin 93 (2017) 91–101

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Fabrication of nanoplate-like g-C_3N_4/$Bi_{12}TiO_{20}$ heterojunction with enhanced visible-light photocatalytic activity

Yanhu Nan[a,d], Dong Yang[b,c], Zhenwei Tong[a,d], Yuanyuan Sun[b,d], Zhongyi Jiang[a,d,*]

[a] Key Laboratory for Green Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[b] Key Laboratory of Systems Bioengineering of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 30072, China
[c] School of Environmental Science and Engineering, Tianjin University, 300072 Tianjin, China
[d] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

ARTICLE INFO

Article history:
Received 9 January 2017
Received in revised form 11 April 2017
Accepted 19 April 2017
Available online 23 April 2017

Keywords:
A. Semiconductors
A. Nanostructure
B. Chemical synthesis
D. Catalytic properties

ABSTRACT

In recent years, the high-efficient visible-light-driven photocatalyst has become a research focus to realize the large-scale application of semiconductor photocatalysis. Herein, a novel nanoplate-like g-C_3N_4/$Bi_{12}TiO_{20}$ (CN/BTO) heterojunction was prepared by a facile hydrothermal-annealing method for visible-light photocatalysis, and its morphology, structure and optical property were characterized systematically. The characterization results verify that the C—O bond exists between g-C_3N_4 and BTO, thus confirming the formation of CN—BTO heterojunction. Furthermore, the CN/BTO heterojunctions display much higher photocatalytic performance for Rhodamine B (RhB) degradation than pure BTO and g-C_3N_4 under visible light irradiation. Among them, the CN/BTO-3 sample with 60 wt% of g-C_3N_4 exhibits the highest photocatalytic activity. The excellent photocatalytic activity can be primarily attributed to the energy band match and the heterojunction that can accelerate the migration and separation of photo-generated charge carriers. This kind of nanoplate-like CN/BTO heterojunction may find potential applications in numerous fields related to environment and energy.

1. Introduction

Heterogeneous semiconductor photocatalysis, as a promising green technology, has attracted considerable interest because of its potential applications in the field of energy and environment in the past decades [1–4]. Titanium dioxide (TiO_2) has been regarded as one of the most promising photocatalysts since the Fujishima-Honda effect was first found in 1972 [5]. However, the wide band gap (3.2 eV) that makes it only absorb the ultraviolet (UV) light in solar spectrum, restricts its extensive application. Therefore, it is urgent to develop the visible-light-driven photocatalyst, such as multi-metallic oxides [6,7] and graphitic carbon nitride (g-C_3N_4) [8,9].

G-C_3N_4 with a narrow band gap of about 2.7 eV has quickly emerged as a research focus in the photocatalysis field since it was first employed for hydrogen evolution by water splitting under visible light [8]. Its unique properties of high thermal and chemical stability, appropriate electronic band structure and facile synthesis have aroused great attention for the researchers [10–12]. However, the rapid recombination of photo-induced electron-hole pairs leads to the low quantum efficiency, and thus limiting the practical application of g-C_3N_4 [13]. In order to solve this problem, varieties of modified strategies have been developed to fabricate the high-efficient g-C_3N_4-based composites, such as coupling with other semiconductors, doping with metal or nonmetal elements and designing hierarchical structures [14]. Among these methods, coupling with other semiconductors can efficiently facilitate the transfer of photo-generated carriers and then inhibit their recombination, thereby improving the photocatalytic activity of g-C_3N_4 [15,16]. Until now, a large number of semiconductors have been coupled with g-C_3N_4 to form the heterojunction composites including metal oxides [17–22], multi-component oxides [23–33], metal oxynitrides [34], metal sulfides [35,36] and organic semiconductors [9,37]. For example, Tong et al. [17] synthesized the g-C_3N_4/TiO_2 nanosheet by a facile biomimetic method, which could almost degrade 100% Rhodamine B (RhB) molecules under simulated-sunlight irradiation within 50 min. The g-C_3N_4/TaON composite photocatalyst prepared by Yan et al. [34] displayed higher visible-light photocatalytic activity for the degradation of dye molecules than single-phase g-C_3N_4 or TaON. In spite of many g-C_3N_4-based composites, it remains to explore new

* Corresponding author at: Key Laboratory for Green Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.
E-mail address: zhyjiang@tju.edu.cn (Z. Jiang).

http://dx.doi.org/10.1016/j.materresbull.2017.04.024
0025-5408/

heterojunction composites for further elevating the photocatalytic activity of g-C_3N_4 still.

Recently, bismuth titanate with different phases (e.g. sillenite $Bi_{12}TiO_{20}$, Aurivillius-type $Bi_4Ti_3O_{12}$ and pyrochlore $Bi_2Ti_2O_7$), belonging to a family of layered perovskite compounds, has been highly concerned as a class of novel and promising photocatalysts due to their good photocatalytic activity in the degradation of organic pollutants under visible light [38]. They are usually synthesized by the solid state reaction [39], chemical solution decomposition [40], hydrothermal [7,41] or solvothermal method [42]. For example, Hou et al. [43] prepared $Bi_{12}TiO_{20}$ with complex architectures, such as nanospheres, nanowires and microflowers through a hydrothermal process, which exhibited higher photocatalytic activities than bulk $Bi_{12}TiO_{20}$ powders. Additionally, the composites of bismuth titanate materials with other semiconductors have also been reported to improve their photocatalytic activity [16,44–47]. For example, Guo et al. [16] prepared the g-C_3N_4/$Bi_4Ti_3O_{12}$ photocatalyst with the *p-n* heterojunction structure by ball milling, which exhibited a high photocatalytic behavior for the decomposition of acid orange-II (AO-7). More recently, Sun *et al.* [47] synthesized the microtetrahedronal $Bi_{12}TiO_{20}$/g-C_3N_4 composite with a facet coupling structure *via* a hydrothermal-ultrasonic assisted route. However, the microtetrahedronal morphology of $Bi_{12}TiO_{20}$ (BTO) hinders the tight binding with g-C_3N_4, thereby resulting in a moderate photocatalytic activity (degrading 75% HCHO within 7 h) for the degradation of gaseous formaldehyde under visible light irradiation.

In this study, BTO is chosen as the coupled semiconductor to improve the photocatalytic activity of g-C_3N_4 owing to its good visible-light activity, facile synthesis and high physical/chemical stability *etc.* G-C_3N_4 and BTO were first synthesized *via* the calcination and hydrothermal method, respectively, and then annealed together to fabricate the g-C_3N_4/$Bi_{12}TiO_{20}$ (CN/BTO) heterojunction. The morphology, structure and optical property of as-prepared CN/BTO heterojunction were characterized and discussed. Besides, their visible-light photocatalytic activities were evaluated by the RhB degradation, and a tentative photocatalytic mechanism was also proposed based on the energy band theory and experimental results.

2. Materials and methods

2.1. Materials

Melamine ($C_3H_6N_6$) was purchased from Tianjin Guangfu Technology Development Co. Ltd. Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) was supplied by Sun Chemical Technology Co. Ltd. (Shanghai, China). Tetrabutyl titanate ($Ti(OC_4H_9)_4$) was purchased from Tianjin Damao Chemical Reagent Company. Potassium hydroxide (KOH) was purchased from Tianjin Jiangtian Chemical Technology Co. Ltd. All chemicals were analytically pure grade and used without further purification. Deionized water was used throughout all experiments.

2.2. Synthesis of CN/BTO heterojunctions

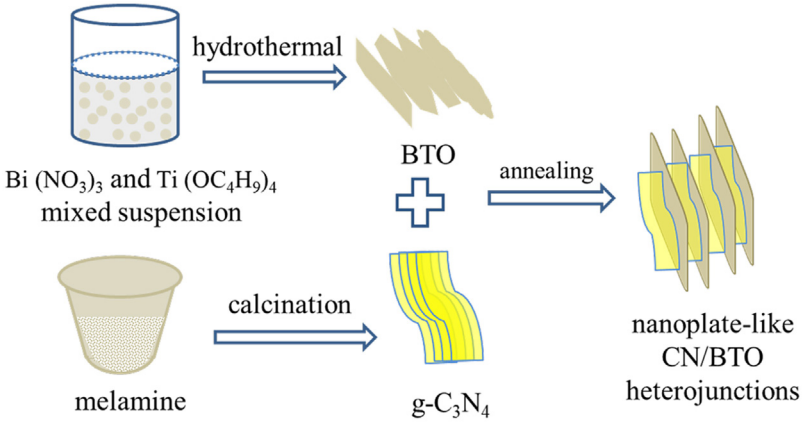
The whole synthetic procedure of CN/BTO heterojunctions is illustrated in Scheme 1. At first, the g-C_3N_4 powders were prepared by calcining melamine in a semi-closed system according to the literature [17]. A certain quantity of melamine was placed in an alumina crucible with a cover in a muffle furnace. The crucible was heated to 550 °C at a heating rate of 5 °C min^{-1} in air atmosphere, kept at 550 °C for 4 h and cooled down to room temperature. The obtained yellow product was collected and ground into powder for further use.

Secondly, the BTO was synthesized by a hydrothermal method as follows: 1.75 g of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 20 mL of 1 mol L^{-1} HNO_3 aqueous solution under vigorous stirring for 30 min, and then 0.102 g of $Ti(OC_4H_9)_4$ was added to this solution. Next, 10 mol L^{-1} KOH aqueous solution was added dropwise to adjust the solution pH to 8.0, and the transparent solution changed to the white suspension during this process. The suspension was transferred to a 100 mL Teflon-lined autoclave up to about 80% capacity after stirring for 30 min and ultrasonication for another 30 min. The hydrothermal synthesis was conducted at 180 °C for 24 h and then cooled to ambient temperature. The precipitation was collected by centrifugation, washed with deionized water for three times, dried at 80 °C for 4 h and ground into powder.

At last, the CN/BTO heterojunctions were obtained by an annealing method. A certain amount of BTO powder was mixed and ground with bulk g-C_3N_4 together. The mixture powders were transferred to a crucible and calcined at 400 °C for 2 h. A series of CN/BTO heterojunctions were prepared with different weight fraction of g-C_3N_4 and labeled as CN/BTO-X, in which X = 1, 2, 3, 4 represent that the weight fractions of g-C_3N_4 are 20, 40, 60 and 80, respectively. The pure BTO calcined under the same conditions and the mechanical mixture of g-C_3N_4 and BTO (M-CN/BTO-3) without annealing treatment were also prepared as control samples.

2.3. Characterization

The crystal structure of the samples was studied by the X-ray diffraction (XRD) with a Rigaku D/max 2500 V/PC X-ray diffractometer (Cu Kα, λ=0.154 nm, 40 kV, 200 mA) in the range of 10−70°



Scheme 1. Schematic illustration for the synthetic procedure of CN/BTO heterojunctions.