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Synthesis, characterization and photocatalytic activity of new photocatalyst $CdBiYO_4$

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ABSTRACT

$CdBiYO_4$ was synthesized by a solid-state reaction method for the first time. The structural and photocatalytic properties of $CdBiYO_4$ had been characterized by X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and X-ray spectrometry. $CdBiYO_4$ crystallized with a tetragonal spinel structure by space group I41/amd. The lattice parameters for $CdBiYO_4$ were $a = b = 14.519$ Å and $c = 9.442$ Å. The band gap of $CdBiYO_4$ was estimated to be 2.41 eV. The photocatalytic degradation of methylene blue (MB) was realized under visible light irradiation with $CdBiYO_4$ as catalyst. The results showed that $CdBiYO_4$ owned higher photocatalytic activity compared with pure TiO_2 or N-doped TiO_2 for photocatalytic degradation of MB under visible light irradiation. The photocatalytic degradation of MB with $CdBiYO_4$ or N-doped TiO_2 as catalyst followed the first-order reaction kinetics, and the first-order rate constant was 0.0137 or 0.0033 min^{-1}. After visible light irradiation for 225 min with $CdBiYO_4$ as catalyst, complete removal and mineralization of MB were observed. The reduction of the total organic carbon, the formation of inorganic products, SO_4^{2-} and NO_3^-, and the evolution of CO_2 revealed the continuous mineralization of MB during the photocatalytic process. The possible photocatalytic degradation pathway of MB was obtained under visible light irradiation. $CdBiYO_4$/(visible light) photocatalysis system was found to be suitable for textile industry wastewater treatment and could be utilized to resolve other environmental chemical pollution problems.

1. Introduction

Dye effluents from textile industries and photographic industries were becoming a serious environmental problem because of their toxicity, unacceptable color, high chemical oxygen demand content, and biological degradation [1]. Many conventional methods had been proposed to treat industrial effluents, but each method had its shortcomings [1–7]. In the last decade, photocatalytic degradation processes had been widely applied as techniques for destruction of organic pollutants in wastewater and effluents, especially degradation of dyes [1,7–21]. Among various dyes, methylene blue (MB) dye was difficult to be degraded and was often utilized as a model dye contaminant to evaluate the activity of a photocatalyst both under ultraviolet light irradiation [18,19,22,23] and under visible light irradiation [20,21,24–32]. Up to now, there had been many reports of MB dye degradation under visible light irradiation such as the research from Jaroniec et al. with carbon-doped TiO_2 as catalyst [33], the research from Ye et al. with $CaIn_2O_4$ as catalyst [21] and the research from Lin et al. with $NiCo_2O_4$ and TiO_2 as photocatalysts [25]. Zhang [34] used N-doped TiO_2 as catalyst to photodegrade MB under visible light irradiation and found that the removal ratio of MB was only 35% after visible light irradiation for 180 min. It was known that ultraviolet light only occupied 4% of the solar energy. For this reason, substantive endeavors should be taken up with developing new photocatalysts which were capable of using more ample visible light, which occupied about 43% of the solar energy. Therefore, it was urgent to develop new visible light-driven photocatalysts.

Spinel-type oxide with a formula of AB_2O_4 was an important compound that had been found to possess many applications, for example, spinel-type oxide with a formula of AB_2O_4 could be utilized as chemical sensors [35–37], sorbents [1,38,39], or heterogeneous catalysts [40]. Recently, a series of semiconductor oxides with typical spinel structure, such as MIn_2O_4 (M = Ca, Sr, Ba) [21,25,36], $NiCo_2O_4$ [25] and $ZnFe_2O_4$/MWCNTs [24] were developed for MB degradation under visible light irradiation. The spinel oxide $CdFe_2O_4$ [41] was synthesized by wet chemical method and was also discovered to possess catalytic activity for thermal decomposition of ammonium perchlorate and hydroxyl terminated polybutadiene. $ZnFe_2O_4$ was also performed for methyl orange

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degradation under visible light irradiation [42]. A new photocatalyst $ZnBiGaO_4$ with spinel structure was utilized to decompose H_2S under visible light irradiation [43]. $ZnIn_2S_4$ was reported that it might be a good candidate for water disinfection under visible light irradiation owing to the fact that its narrow band gap corresponded well with the spectrum of sunlight [44].

$CdBiYO_4$ had never been produced and the data about its structural and photophysical properties such as space group and lattice constants had not been found previously. In addition, the photocatalytic properties of $CdBiYO_4$ had not been studied by other investigators. $CdBiYO_4$ seemed to possess potential for improvement of photocatalytic activity by modification of its structure because it had been proved that a slight modification of a semiconductor structure would lead to a remarkable change in photocatalytic properties [21]. Based on above analysis, we could assume that the replacement of Fe^{3+} by Bi^{3+} and Y^{3+} in $CdFe_2O_4$, or the replacement of Zn^{2+} by Cd^{2+}, the replacement of Fe^{3+} by Bi^{3+} and Y^{3+} in $ZnFe_2O_4$ might increase carriers concentration. As a result, a change and improvement of the electrical transportation and photophysical properties could be found in the novel $CdBiYO_4$ compound. By analogy, we thought that $CdBiYO_4$ should have some photocatalytic activities under visible light irradiation. In this paper, $CdBiYO_4$ was prepared for the first time by the solid-state reaction method and the structural and photocatalytic properties of $CdBiYO_4$ were studied in detail. The photocatalytic MB degradation under visible light irradiation was also performed to evaluate the photocatalytic activity of $CdBiYO_4$. A comparison between the photocatalytic properties of $CdBiYO_4$ and N-doped TiO_2 was achieved in order to elucidate the structure–photocatalytic activity relationship in $CdBiYO_4$.

2. Experimental

2.1. Synthesis of $CdBiYO_4$ and N-doped TiO_2

$CdBiYO_4$ powder was first synthesized by the solid-state reaction method. CdO, Bi_2O_3 and Y_2O_3 with the purity of 99.99% were utilized as raw materials which were purchased from Sinopharm Group Chemical Reagent Co. (Shanghai, China) and utilized without further purification. All powders were dried at 200 °C for 4 h before synthesis. In order to synthesize $CdBiYO_4$, the precursors were stoichiometrically mixed in a quartz mortar, subsequently pressed into small columns and put into an alumina crucible (Shenyang Crucible Co., LTD, China). Finally, calcination was carried out at 900 °C for 36 h in an electric furnace (KSL 1700X, Hefei Kejing Materials Technology Co., Ltd., China). After sintering and grinding within a quartz mortar, ultrafine $CdBiYO_4$ powder was fabricated. Nitrogen-doped titania (N-doped TiO_2) catalyst with tetrabutyl titanate as a titanium precursor was prepared by using the sol–gel method at room temperature. The following procedure was that 17 mL tetrabutyl titanate and 40 mL absolute ethyl alcohol were mixed as solution A, subsequently solution A was added dropwise under vigorous stirring into the solution B that contained 40 mL absolute ethyl alcohol, 10 mL glacial acetic acid and 5 mL double distilled water to form transparent colloidal suspension C. Subsequently aqua ammonia with N/Ti proportion of 8 mol% was added into the resulting transparent colloidal suspension under vigorous stirring condition and stirred for 1 h. Finally, the xerogel was formed after being aged for 2 days. The xerogel was ground into powder which was calcined at 500 °C for 2 h, subsequently above powder was ground in an agate mortar and screened by shaker to obtain N-doped TiO_2 powders.

2.2. Characterization of $CdBiYO_4$

The crystalline phase of $CdBiYO_4$ was analyzed by X-ray diffractometer (D/MAX-RB, Rigaku Corporation, Japan) with CuKα radiation ($\lambda = 1.54056$ Å). The patterns were collected at 295 K with a step-scan procedure in the range of $2\theta = 20–90°$. The step interval was 0.05° and the time per step was 1 s. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. The chemical composition of the compound was determined by scanning electron microscope–X-ray energy dispersion spectrum (SEM–EDS, LEO 1530VP, LEO Corporation, Germany), X-ray fluorescence spectrometer (XFS, ARL-9800, ARL Corporation, Switzerland) and X-ray photoelectron spectroscopy (ESCALABMK-2, VG Scientific Ltd., U.K.). The Cd^{2+} content, Bi^{3+} content, Y^{3+} content and O^{2-} content of $CdBiYO_4$ and the valence state of elements were also analyzed by X-ray photoelectron spectroscopy (XPS). The chemical composition within the depth profile of $CdBiYO_4$ was examined by the argon ion denudation method when X-ray photoelectron spectroscopy was utilized. UV–visible diffuse reflectance spectrum of $CdBiYO_4$ was measured with a Shimadzu UV-2550 UV–visible spectrometer, and $BaSO_4$ was utilized as the reference material. The surface areas of $CdBiYO_4$ and N-doped TiO_2 were measured by the Brunauer–Emmett–Teller (BET) method (MS-21, Quantachrome Instruments Corporation, USA) with N_2 adsorption at liquid nitrogen temperature. The particle sizes of the photocatalysts were measured by Malvern's mastersize-2000 particle size analyzer (Malvern Instruments Ltd, United Kingdom).

2.3. Photocatalytic activity tests

The photocatalytic activity of $CdBiYO_4$ was evaluated with methylene blue ($C_{16}H_{18}ClN_3S$) (Tianjin Bodi Chemical Co., Ltd., China) as model material. The photoreaction was carried out in a photochemical reaction apparatus (Nanjing Xujiang Machine Plant, China). The internal structure of the reaction apparatus was as following: the lamp was put into a quartz hydrazine which was a hollow structure and located in the middle of the reactor. The recycling water through the reactor maintained a near constant reaction temperature (20 °C) and the solution was continuously stirred and aerated. Twelve holes which were utilized to put quartz tubes evenly distribute around the lamp and the distance between the lamp and each hole was equal. Under the condition of magnetic stirring, the photocatalyst within the MB solution was in the state of suspension. In this paper, the photocatalytic degradation of MB was performed with 0.3 g $CdBiYO_4$ in 300 mL 0.025 mM MB aqueous solution in quartz tubes with 500 W Xenon lamp (400 nm $< \lambda <$ 800 nm) as visible-light source. Prior to visible light irradiation, the suspensions which contained the catalyst and MB dye were magnetically stirred in the darkness for 45 min to ensure establishment of an adsorption/desorption equilibrium among $CdBiYO_4$, the MB dye and atmospheric oxygen. During visible light illumination, the suspension was stirred at 500 rpm and the initial pH value of the MB solution was 7.0 without pH adjustment in the reaction process. Above experiments were performed under oxygen-saturation conditions ($[O_2]_{sat} = 1.02 \times 10^{-3}$ M). One of the quartz tubes was taken out from the photochemical reaction apparatus at various time intervals. The suspension was filtered through 0.22 μm membrane filters. The filtrate was subsequently analyzed by a Shimadzu UV-2450 UV–visible spectrometer with the detecting wavelength at 665 nm. The experimental error was found to be within ±2.2%. In order to check the stability of the photocatalyst $CdBiYO_4$, 0.3 g $CdBiYO_4$ was reused for six times within different 300 mL 0.025 mM MB aqueous solution. At the same time, the turnover number which represented the ratio between the total amount of evolved gas and dissipative catalyst was calculated after 0.3 g $CdBiYO_4$ being reused for six times within different 300 mL 0.025 mM MB aqueous solution.

pH adjustment was not carried out and the initial pH value was 7.0. The inorganic products which were obtained from MB