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Synthesis of nanometer-size Bi_3TaO_7 and its visible-light photocatalytic activity for the degradation of a 4BS dye

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ABSTRACT

Most of tantalate photocatalysts are mainly synthesized by solid-state (SS) reaction methods and only show photocatalytic activity under UV light irradiation. Ta_2O_5 as a raw material shows an extremely high chemical stability, limiting its application to a few systems. A novel nanometer Bi_3TaO_7 photocatalyst was synthesized by a facile and low-cost sol–gel method using Ta_2O_5 and $Bi(NO_3)_3{\cdot}5H_2O$ as the Ta and Bi sources, respectively. The as-obtained samples were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), UV–vis diffuse reflection spectroscopy (DRS) and Fourier transform infrared spectroscopy (FT-IR). The band gap energy of the as-obtained nanometer Bi_3TaO_7 photocatalyst was determined to be about 2.75–2.86 eV. The Bi_3TaO_7 nanopowders show a strong adsorbability and a high visible-light photocatalytic activity for the degradation of 4BS, which can be ascribed to the surface physicochemical properties and structure of the Bi_3TaO_7 nanometer catalyst. The degradation of 4BS is attributed to the photocatalysis but not to the adsorption of 4BS on the as-prepared catalyst.

1. Introduction

It is well known, that the presence of dyes in effluent, even at very low concentrations, is highly visible and undesirable [1,2]. Due to the chemical stability and low biodegradability of these dyes, conventional biological wastewater treatment systems, including physical- and chemical-treatment processes, cannot effectively treat the wide range of dye wastewater [1,3]. Thus, many approaches have been used to investigate the decomposition of dye wastewater. Amongst them, the photocatalytic decomposition of dye wastewater using TiO_2 as a catalyst [4–6] is thought to be one of the most important methods. Although the TiO_2 photocatalyst shows a high photocatalytic activity, it has a wide band gap and can only utilize UV light. Therefore, the development of new photocatalysts with visible-light responsiveness is now a high priority [7–9].

Recently, much interest has been paid to Bi-containing compounds, including Bi_2WO_6 [10–12], $Bi_{12}GeO_{20}$ [13], $BiVO_4$ [14], *etc.*, because of their high visible-light photocatalytic activities.

Tantalates possess conduction bands consisting of a tantalum (Ta) 5d orbital located at a more negative potential than titanates (Ti3d) and niobates (Nb4d), which have conduction bands at a higher potential [15]. Therefore, in recent years, Ta based compounds have attracted great attention because of their high photocatalytic properties. Zhu et al. [16,17] synthesized monomolecular-layer perovskite $Ba_5Ta_4O_{15}$ nanosheets with hexagonal structures and $BaTa_2O_6$ nanorods with uniform cylindrical structures, using a hydrothermal method, which both show high photocatalytic activity in the degradation of Rhodamine B. Zou et al. [18,19] synthesized new pyrochlore-type structure compounds Bi_2GaTaO_7 and Ga_2BiTaO_7 by solid-state (SS) reaction methods and evaluated their photocatalytic properties for the degradation of methylene blue (MB) dye under ultraviolet and visible-light irradiation. Other tantalate photocatalysts including $BiTaO_4$ [20], $NaTaO_3$ [21,22] and NiM_2O_6 (M = Nb, Ta) [23] have also been studied because of their excellent photocatalytic activities.

However, most of the tantalate photocatalysts are mainly synthesized by the SS method and only have photocatalytic activity under UV light irradiation. Ta_2O_5 as a raw material shows an extremely high chemical stability, limiting its application to only a few systems. It is very difficult to prepare nanosized and single phase stoichiometric tantalates by the SS reaction method. The photocatalysts obtained by the SS reaction method have small specific surface areas and low adsorbabilities which result in low photocatalytic efficiency, in very dilute solutions. This is because the pollutants in wastewater are usually thought to be harmful, even if they are present in extremely low concentrations in the environment. Wet chemical routes are a promising alternative, since they fully control the whole process from the molecular precursor to the final

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material to give highly pure and homogeneous materials. In addition, wet routes allow low reaction temperatures, so that the size and morphology of the synthesized particles may be fully controlled, and the desired phase can be prepared [24,25]. Several chemical routes have been developed for synthesizing some of the nanosized tantalum-based compounds, but current studies have concentrated on the use of only a few tantalum precursors that show several problems. For instance, tantalum alkoxides are expensive, they need special care such as the use of dry solvents and inert atmospheres, and can produce polluting side products; the use of tantalum chloride produces toxic HCl gas during the synthesis process. Therefore, it is important to synthesize new nanosized tantalate photocatalysts with high visible-light photocatalytic activity via a facile and low-cost sol–gel method [26].

In this work, we successfully synthesized a novel nanosized Bi_3TaO_7 photocatalyst by a facile and low-cost sol–gel method using Ta_2O_5 and $Bi(NO_3)_3{\cdot}5H_2O$ as the Ta and Bi sources. This new photocatalyst shows a strong optical absorption in the visible-light region ($\lambda > 400$ nm) and a high adsorption ability for the 4BS dye. The photocatalytic properties of the Bi_3TaO_7 nanopowders were evaluated by the degradation of 4BS aqueous solution under visible-light irradiation.

2. Materials and methods

2.1. Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, SCRC, China), potassium hydroxide (KOH, SCRC, China), citric acid (CA, SCRC, China), nitric acid (HNO_3, SCRC, China), oxalic acid (OA, SCRC, China), Ta_2O_5, ammonia ($NH_3{\cdot}H_2O$, SCRC, China) and ethylene diamine tetraacetic acid (EDTA, SCRC, China) which were purchased from Sinopharm Chemical Reagent Co., Ltd. China, and were used as starting chemical reagents. All the chemical reagents employed were of analytical grade. 4BS dye (Direct Red 23, C.I. 29160, Fig. 1) is a commercial product. Deionized water was used in all experiments.

2.2. Preparation

The nanosized Bi_3TaO_7 powders were prepared by a sol–gel method. The synthesis procedure for the sample is shown in Fig. 2. First, 2 g of Ta_2O_5 was mixed with potassium hydroxide in a molar ratio of 1:10, and was then placed in a corundum crucible. The mixture was sintered at 500 °C for 3 h, and then the sintered substances were leached with hot deionized water and after filtration, a clear solution was obtained. The tantalum acid precipitate was obtained after adjusting the pH of the solution to 1–2 using nitric acid, and was then washed successively until the potassium ions were completely removed. 1 g of the as-prepared tantalum acid was dissolved in an oxalic acid solution, a tantalum–oxalic acid solution (Ta–OA) was obtained and the mass ratio of tantalum acid to oxalic acid was about 1:8. The concentration of tantalum in the solution was determined by inductively coupled plasma (ICP) spectrometry. $Bi(NO_3)_3{\cdot}5H_2O$ was added into a citric acid (CA) solution, and then EDTA–ammonia solution was added slowly into the solution, under continuous stirring, until $Bi(NO_3)_3{\cdot}5H_2O$ was completely dissolved, and the Bi–CA solution was obtained.

In order to obtain the Bi–Ta precursor solution, the Ta–OA complex and the Bi–CA solution were mixed together in a molar ratio of [Bi]:[Ta] = 3:1 and the pH of the mixed solution was adjusted to 7–8 with ammonia, and then citric acid was added to the solution in the molar ratio of CA/metal cations = 3:1. The as-obtained precursor solution was stirred at 80 °C until it became a transparent colloid, and was then further heated until the formation of amorphous polymeric precursors occurred. It was then subjected to calcination at 350 °C for 2 h and the precursors were then ground and sintered at varying temperatures. Subsequently, the nanosized Bi_3TaO_7 powders were obtained.

The conventional SS reaction [18,19] was used to synthesize the Bi_3TaO_7 powders at 900 °C for 4 h using Ta_2O_5 and Bi_2O_3 as the raw materials.

2.3. Characterization

The structure and crystallinity of the as-prepared samples were determined using a D/MAX-RB powder X-ray diffractometer with CuKα radiation ($\lambda = 1.54184$ Å) under the operating conditions of 40 kV and 50 mA. The samples were scanned in the 2θ range of 5–70°. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses were conducted with a JEM-2100F electron microscope (JEOL, Japan), using a 200 kV accelerating voltage. Scanning electron microscopy (SEM) was performed on a JSM-5610LV scanning electron microscope. The absorption edge of the Bi_3TaO_7 samples was measured using a UV–vis spectrophotometer (UV2550, Shimadzu, Japan). $BaSO_4$ was used as a reflectance standard in the UV–vis diffuse reflectance experiment. The Brookhaven Zeta-Plus system was used to determine the zeta potentials. The chemical bonds on the surface of the catalyst were detected by Fourier transform infrared spectroscopy (FT-IR) (Nexus, Thermo Nicolet). BET (Brunauer–Emmett–Teller) specific surface area was determined by nitrogen adsorption (BelSorp-Mini system). The photoluminescence (PL) spectra of the samples were recorded with a Perkin Elmer (LS 55) fluorescence spectrometer, at room temperature, using an excitation wavelength of 240 nm.

2.4. Photocatalytic activity

Photocatalytic activities of the as-prepared photocatalysts were evaluated by the degradation of azo dye 4BS aqueous solution under visible-light irradiation ($\lambda > 400$ nm). A 300 W Dy lamp was used as a light source with a 400 nm cutoff filter to provide visible-light irradiation. 0.10 g of the as-prepared catalyst was added to 100 mL of 4BS aqueous solution (30 mg/L). The pH values in all experiments were about 6.8. Before illumination, the suspension was stirred for 10 min in darkness to disperse the catalyst. The concentration of 4BS aqueous solution was determined by its absorbance at 500 nm using a UV–vis spectrophotometer (UV751GD, China) [27].

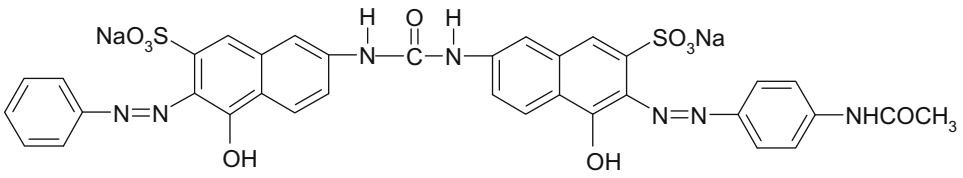

Fig. 1. The structure of 4BS dye (C.I. 29160).