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Preparation and photocatalytic properties of sillenite $Bi_{12}TiO_{20}$ films

Haiping Zhang [a,b], Mengkai Lü [a,*], Suwen Liu [b], Zhiliang Xiu [b], Guangjun Zhou [a], Yuanyuan Zhou [a], Zifeng Qiu [a], Aiyu Zhang [a], Qian Ma [a]

[a] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China
[b] Shandong Institute of Light Industry, Jinan 250100, PR China

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ABSTRACT

Sillenite $Bi_{12}TiO_{20}$ thin films with high photocatalytic activity have been successfully fabricated by means of chemical solution decomposition, and characterized by X-ray diffraction, energy-dispersive spectroscopy, atomic force microscopy, scanning electron microscopy and UV–Vis spectrophotometry. The photocatalytic activity of $Bi_{12}TiO_{20}$ thin films has been evaluated by photodegrading methyl orange solution and the effect of processing conditions on the photocatalytic activity has been studied in detail.

1. Introduction

$Bi_{12}TiO_{20}$ belongs to a family of sillenite compounds. Sillenites with the structure of metastable cubic γ-Bi_2O_3 (space group I23) are a well known group of non-centrosymmetric crystals [1,2]. Sillenites are formed during reaction of Bi_2O_3 with many metallic and non-metallic oxides of Ge, Si, Ti, Pb, Ga, B, etc, mainly in 6:1 molar ratio [1]. The family of sillenite compounds has the general formula of $Bi_{12}MO_{20}$ where M represents a tetravalent ion or a combination of ions, which gives an average charge of 4^+. The overall structure of the $Bi_{12}TiO_{20}$ crystal may be described in terms of the seven-oxygen coordinated Bi polyhedra, which share corners with other identical Bi polyhedra and with TiO_4 tetrahedra [3].

Sillenites have very good photorefractive, electrooptic, piezoelectric, and photochromic properties. They can be used in signal processing and optical memories for data storage [2]. In comparison with other sillenites, bismuth titanate $Bi_{12}TiO_{20}$ receives more attention for its relatively higher photoconductivity, electro-optical coefficients, holographic sensitivity in the red spectral region, and its relatively lower optical activity [2,4,5]. Recently, Yao et al. have prepared $Bi_{12}TiO_{20}$ powders and have found that $Bi_{12}TiO_{20}$ is a new photocatalyst with high photocatalytic activity [3,6–8]. However, there are two practical problems in using powders for photocatalytic processing: (1) it is difficult to separate the catalysts from the suspension after the reaction, and (2) since powder catalysts aren't immobilized, particulate suspensions are not easily applicable to continuous photocatalytic processes [9]. Thus, photocatalyst prepared in film form can be an appropriate solution to deal with these difficulties.

Several phases in Bi–Ti–O system are known, including $Bi_4Ti_3O_{12}$, $Bi_2Ti_2O_7$, $Bi_2Ti_{14}O_{11}$, $Bi_{12}TiO_{20}$, $Bi_{20}TiO_{32}$, etc. $Bi_{12}TiO_{20}$ films have been fabricated with atomic layer deposition (ALD) [10]. $Bi_4Ti_3O_{12}$ and $Bi_2Ti_2O_7$ thin films have been prepared using the technique of chemical solution decomposition (CSD) [11–13]. The CSD method can provide better control over the texture of the resulting materials and ensures an increased uniformity of the product [14], and it does not need expensive apparatus required in ALD.

In our paper, $Bi_{12}TiO_{20}$ thin films with high photocatalytic activity were successfully prepared by means of CSD for the first time to the best of our knowledge. Moreover, its photocatalytic activity was studied in detail. After illumination under UV light for 2 h, the methyl orange solution was degraded by 94% on the $Bi_{12}TiO_{20}$ thin films prepared by annealing at 500 °C for 15 min. Under the same conditions, the photodegradation rate was only 68% for anatase TiO_2 thin films prepared by us.

2. Experimental

2.1. Preparation of $Bi_{12}TiO_{20}$ thin films

The following sections presents steps involved in preparation of $Bi_{12}TiO_{20}$ thin films using CSD method. Bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) and tetrabutyl titanium ($Ti(OC_4H_9)_4$) were chosen as starting materials. Glacial acetic acid (CH_3COOH) was selected as a solvent. At first, bismuth nitrate was dissolved in the glacial acetic acid. In the second step, the solution was diluted with 2-methoxyethanol (CH_3OCH_2OH) to adjust the viscosity and surface tension of the solution. Thirdly, a certain amount of acetylacetone ($C_5H_8O_2$), used as stabilizing and chelating agent, was added to the solution to keep the solution stable. Then, the

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* Corresponding author. Tel.: +86 531 8364591; fax: +86 531 8565403.
E-mail address: mklu@icm.sdu.edu.cn (M. Lü).

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above mixed solution was slowly added to the stoichiometric amount of tetrabutyl titanium liquid under constant stirring. After stirring for 1 h, the impurities were filtered through a 0.2 μm syringe filters and a clear yellowish precursor solution was obtained.

The silicate glasses were used as substrates. Each substrate was pretreated in acid solution ultrasonically for 15 min and then washed with distilled water and anhydrous ethanol. The cleaned substrates were spin-coated with the prepared precursor solution at a speed of 3000 rpm for 30 s, then the wet film was dried on a hot-plate at 100 °C for 10 min. The coating and drying processes were repeated several times to obtain a film with an appropriate thickness. These films were finally annealed at various temperatures ranging from 450–600 °C for 15 min or annealed at 500 °C for different time intervals from 5 min to 30 min with a heating rate of 5 °C/min. Unless stated otherwise, the coating cycle was repeated four times.

2.2. Characterization of $Bi_{12}TiO_{20}$ thin films

The thermal gravimetric analysis-different scanning calorimetry (TG-DSC) measurement of the powders derived from drying the precursor solution was performed on Perkin Elmer Pyris Diamond thermal analyzer, with a temperature rate of 10 °C/min in air. The crystallization of the thin films was studied by X-ray diffraction (XRD) using a Rigaku D/MAX-gA X-ray diffractometer, with graphite monochromatized Cu Kα irradiation (λ=1.5418 Å). The thickness of the thin films and the surface element composition were gained by JSM-6700F scanning electron microscopy (SEM) equipped with energy-dispersive spectroscopy (EDS). The surface image of the films was characterized by a NanoScope IIIa (Digital Instruments) atomic force microscopy (AFM), using contact mode amplitude modulation. UV–Vis absorption spectrum was monitored using a UV757CRT ultraviolet–visible spectrophotometer.

2.3. Evaluation of photocatalytic activity of $Bi_{12}TiO_{20}$ thin films

The photocatalytic experiment was carried out for degradating of the methyl orange aqueous solution under irradiation of a 20 W low-pressure mercury lamp (the main wavelength is 253.7 nm). The illumination distance was 6 cm. Four pieces of 25×25 mm glass substrates coated with $Bi_{12}TiO_{20}$ films were placed at the bottom of a beaker (Φ=90 mm) in which 40 ml methyl orange solution with a concentration of 20 mg/L was introduced. Then the beaker was put on a magnetic stirrer and the solution was stirred for 30 min under dark to establish adsorption/desorption equilibrium prior to irradiation. After irradiation for 2 h, 0.5 ml solution sample was taken out and analyzed. The extent of photocatalytic degradation was evaluated by measuring the absorbance A of the solution samples with a UV–Vis spectrophotometer (UV757CRT) at λ_{max}=463 nm. According to Lambert/Beer formula ($A=kCb$), where k and b are constants, the solution concentration C was a linear function to the absorbance A. The degradation ratio η (%) of methyl orange was estimated using the expression of [15]:

$$\text{degradation ratio}\ \eta(\%) = [(C_0 - C)]/C_0 \times 100 = [(A_0 - A)]/A_0 \times 100$$

where C_0 and C are the initial and residual methyl orange concentration in solution, respectively, A_0 and A are the pre- and post-irradiation absorbances of the methyl orange solution, respectively. All the photocatalytic experiments were conducted at a room temperature.

3. Results and discussion

3.1. The phase formation of $Bi_{12}TiO_{20}$

The precursor solution was dried at 100 °C for 5 h to remove the solvents and some organic matter, and powders were obtained. The TG-DSC curves of the obtained powders are shown in Fig. 1. The DSC curve shows two exothermic peaks maximum at 167 °C and 275 °C, which are accompanied by two stages of weight loss in the TG curve, respectively. The first DTA peak is attributed to the combustion of organic compounds, such as solvent, ligand, etc. The second peak may be due to the transformation of $Bi_{12}TiO_{20}$ from amorphous to crystalline phase and the further combustion of organic compounds residues. There is no further weight loss above 450 °C.

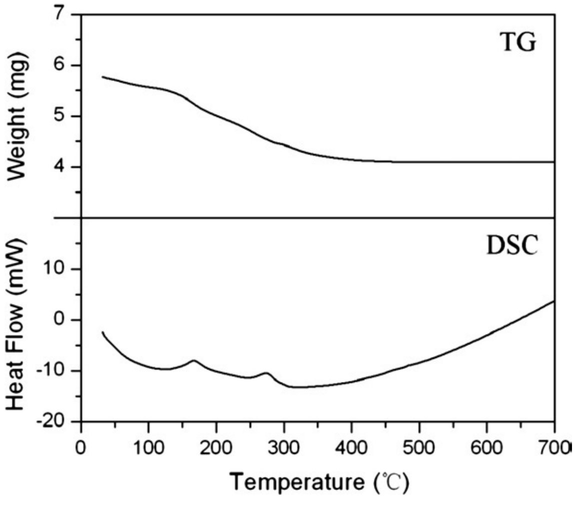

Fig. 1. TG-DSC curves of as-synthesized powders.

3.2. Characterization of the prepared $Bi_{12}TiO_{20}$ thin films

3.2.1. XRD analysis

X-ray diffraction (XRD) is used to identify the structure of the prepared films. Fig. 2(a) and (b) shows the XRD patterns of the films calcined at various temperatures for 15 min and calcined at a fixed temperature of 500 °C for different times, respectively. All the peaks except a small one marked by ▲ are indexed based on the sillenite $Bi_{12}TiO_{20}$ (JCPDS 34–97), of which the space group is I23. The small peak marked by ▲, which disappears gradually with the increasing annealing temperature, may come from a metastable phase during the formation process of $Bi_{12}TiO_{20}$ crystallite. As the annealing temperature or time is increased, the peak intensities of sillenite phase increase and the full widths at half maximum (FWHM) decrease, indicating better crystallinity and an increase in grain size [16].

3.2.2. EDS analysis

Fig. 3 shows the energy-dispersive spectrum (EDS) of the surface of $Bi_{12}TiO_{20}$ $Bi_{12}TiO_2$/glass. Except for the peaks of Bi, Ti and O elements, there also exists a peak of C element. Since $Bi_{12}TiO_{20}$ films are insulators, carbon must be sputtered onto the surface of $Bi_{12}TiO_{20}$ films before the EDS testing process. The peak of C element might be caused by the introduced carbon and the residue of organic compounds precursor. No elements of silicate glass substrate, such as Na, Si and Al, are detected in the test.

3.2.3. AFM and TEM analysis

Fig. 4 depicts 2- and 3-D AFM images of the surface of $Bi_{12}TiO_{20}$ thin films annealed at 500 °C for 15 min by four coating cycles. The surface appears to be uniform and free from cracks. It can be observed that the films consist of small crystalline particles of about 100–120 nm in average diameter and have a porous polycrystalline structure. The root-mean-square roughness (RMS) derived from the AFM measurement for the surface of $Bi_{12}TiO_{20}$ thin films is 5.224 nm. The randomly distributed micropores, together with the big roughness, can increase the specific