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Thin bismuth oxide films prepared through the sol–gel method as photocatalyst

Wu Xiaohong *, Qin Wei, He Weidong

Harbin Institute of Technology, Box 408, Harbin 150001, PR China

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Abstract

In this paper, thin bismuth oxide films were prepared by the sol–gel method. The films were annealed at different temperatures, and then applied to degrade a kind of typical textile industry pollutant (Rhodamine B), respectively, in order to study the influence of bismuth oxide crystal phases on their photocatalytic properties. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) techniques and a surface profiler were applied to characterize the thin films annealed at different temperatures. The results show that different annealed temperatures cause the transformation between monoclinic phase and tetragonal phase of bismuth oxides and bismuth oxide films annealed at 550 °C contain a higher proportion of the tetragonal phase of bismuth oxides than those annealed at other temperatures, which leads to higher electronic binding energy and photocatalytic properties for these oxides in the films.
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Keywords: Sol–gel method; Bismuth oxide; Photocatalytic properties; Reaction constant

1. Introduction

Bismuth oxide Bi_2O_3 has a lot of merits, such as a wide energy gap change (from 2 to 3.96 eV) [1], high refractive index, dielectric permittivity, besides marked photoconductivity and photoluminescence [2]. It is known that bismuth oxides have polymorphism: five modifications, which are α, β, γ, δ and ω-Bi_2O_3. Among them, the low-temperature α and the high-temperature δ phases are stable and the others are high-temperature metastable [2]. Owing to their peculiar characteristics, bismuth oxides have been studied to be used various areas, such as sensor optical coatings [2], sensor technology [3], fine structure glasses [4] and electroreduction [5]. Recently, bismuth oxide particles have been produced in many kinds of methods, for example, co-precipitation, atomization [6] and low-temperature electrodeposition [7]. However, the use of bismuth oxide particles is often limited considering the difficulty of recycling them. Bismuth oxide films which can be recycled easily were produced through some methods in the past, for example, the rf sputtering or vacuum evaporation method [8], the pneumatic version of the spray pyrolysis process [9] or by CVD method under atmospheric pressure [10]. But the above methods are expensive and inconvenient. Proper sol–gel methods are proved to be good ways to get oxide films, for example, TiO_2 films can be obtained through sol–gel methods [11–14]. Taking into account that there are not so many reports about preparing the bismuth oxide films produced through sol–gel methods and the fact that the semiconductor of bismuth oxides with an appropriate energy gap can be applied to deal with pollutant, it is the goal of the present paper to produce bismuth oxide films through the sol–gel method and study the photocatalytic properties of the bismuth oxides films annealed at different temperatures.

2. Experimental

2.1. Film preparation

Thin bismuth oxide films were prepared with the following method: 5 g $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in a nitric solution (1:8 HNO_3:H_2O). PEG 200 ($HO(CH_2CH_2O)_{200}H$) and citric acid was added in the above solution, while OP (t-Oct-C_6H_4–$(OCH_2CH_2)_xOH$, $x = 9$–10) was added as surfactant. The above solution was beaten up for 3 h, and then sol solution was

* Corresponding author. Tel.: +86 451 86402522; fax: +86 451 86402522.
E-mail address: wxhqw@263.net (W. Xiaohong).

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produced. After that, pieces of simple glass were dipped into the sol solution where they were kept for 3 min, and then withdrawn at a rate of 5 cm min^{-1}. These pieces of glass were dried up at 100 °C in a baking oven. Then the sol solution was heated to 60 °C, where it was kept for 1 h to form a kind of yellow gel. Afterwards, the gel was subjected to differential thermal analysis and thermogravimetric analysis (DTA/TGA), using a comprehensive thermal analyzer (ZRY-2P from Shanghai Tianping) in order to establish the thermal treatment schedule for the films. Two exothermal peaks at 275 and 390 °C were noticed during this analysis. To match the DTA/TGA results, all the films were preliminarily treated with a heating rate of 1 °C min^{-1} to 390 °C, during the process of which two 30 min plateaus at 275 and 390 °C were maintained, respectively. At the same time, to get the films annealed at different temperatures, the films continued to be heated to 450, 500, 550 and 600 °C, respectively, at the same heating rate, where a 1 h plateau was maintained. The films treated following the above different routes were labeled as different samples.

2.2. Film characterization

XRD with a Cu Kα source (D/max-r B from Ricoh) was applied to study the crystalline structure of the films with an accelerating voltage and an applied current of 40 kV and 30 mA, respectively. Also, XPS (Escalab-220IXL from VG Scientific Ltd.) was used to study the surface composition of the prepared samples. Besides the morphology of the produced films was examined by SEM (S-570 from Hitachi), and a profiler (Dektek 6 M from VECCO) was used to measure the thickness of the films.

2.3. Photo-degradation experiments

A cylindrical quartz cell with a size of 25 mm in diameter and 50 mm in height, a 20 W quartz UV lamp (from Tianjin Lvhuan Unique Lamp Company) with a maximum UV irradiation peak of 365 nm were used to compose the bench-scale photoreactor system. The schematic diagram of the photoreactor had been shown before [15]. The photocatalytic properties of the films produced through the sol–gel method were examined by measuring the removal of Rhodamine B dye solution (10 mg L^{-1}). To evaluate the experiments of degrading Rhodamine B using the bismuth oxide films, a blank test was done; the pollutant solution was photolyzed using a piece of simple glass to examine the photostability of Rhodamine B under the irradiation mentioned above. Square samples of 2.25 cm^2 were immersed into 10 mL aqueous Rhodamine B solution. The solution was stirred continuously and supplied with air during the reaction process. The UV light irradiated perpendicularly to the surface of the samples through the sidewall of the cylindrical quartz cell and the distance from the UV source to the films was 2 cm. The UV light irradiated for 2 h, in the process of which the change of Rhodamine B concentration with the irradiation time was measured by a UV spectrophotometer (722N from Shanghai Fine Instrument Company).

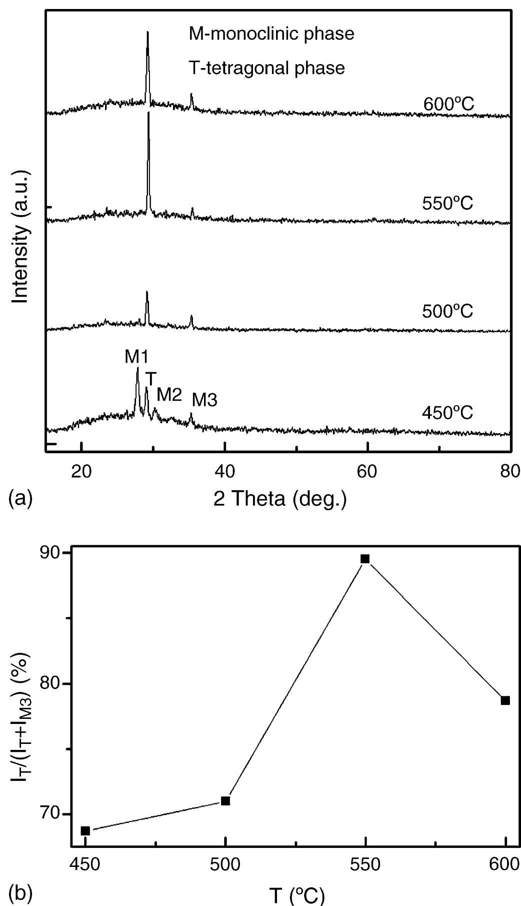


Fig. 1. (a) XRD spectra of the produced films annealed at different temperatures. (b) Proportion of intensity of T phase to the sum of those of T phase and M3 phase for bismuth oxide films annealed at different temperatures.

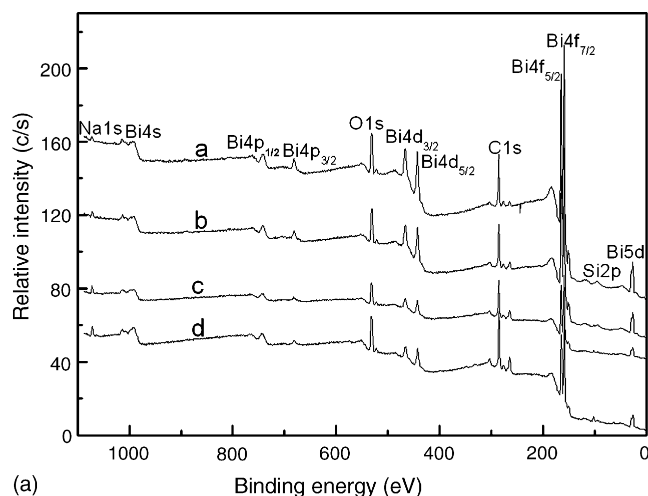
3. Results

3.1. Analysis of XRD results

Fig. 1a displays XRD spectra of the films. It can be seen from the spectra that the bismuth oxide films annealed at different temperatures are mainly composed of monoclinic and tetragonal bismuth oxides, which are labeled as M and T, respectively. To match the XRD spectra, a curve with the proportion of intensity of T phase to the sum of those of T phase and M3 phase as vertical ordinate and annealed temperature as abscissa, is established, as shown in Fig. 1b. It can be seen from Fig. 1b that the proportion increases with the annealed temperature before 550 °C, and reaches the biggest at 550 °C, which is 89.5%, 20.8% higher than that at 450 °C. However, the proportion decreases when the annealed temperature above 550 °C continues to increase.

3.2. Results of XPS measurements

Fig. 2A displays the spectra of XPS, from which it can be seen that the prepared bismuth oxide films mainly consist of Bi, O and other elements such as C, Si, Na from the simple glass substrates. The $Bi4f_{7/2}$ XP spectra of bismuth oxide films annealed at different temperatures are displayed in Fig. 2B, the



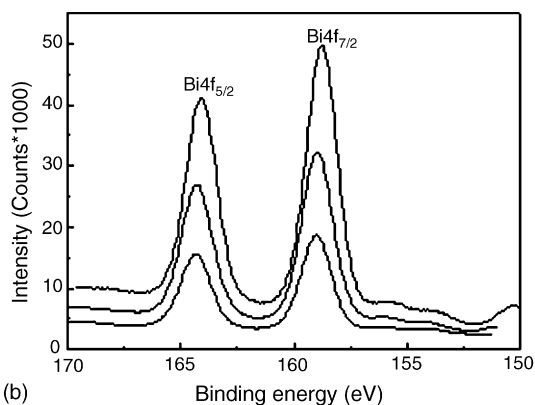


Fig. 2. (A) XPS survey spectra for the surface of bismuth oxide films annealed at different temperatures: (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 600 °C. (B) Bi4f XP spectra of bismuth oxide films annealed at different temperatures (from top to bottom): 450, 500 and 550 °C.

binding energies are 158.77, 159.01, 159.07 and 159.01 eV for 450, 500, 550 and 600 °C, respectively. It can be observed from Fig. 2B that binding energy shifts to a higher value for $Bi4f_{7/2}$ as the annealed temperature increases from 450 to 550 °C.

3.3. Analysis of SEM results

The SEM microphotograph of the film annealed at 550 °C magnified by 30k times is displayed in Fig. 3. It can be noticed from the SEM microphotograph that the film is uniform and the particles in the film are almost of the same size and shape.

3.4. Results of the surface profiler measurement

The thickness of the films is 120 ± 10 nm for the four kinds of samples according to the measured results of the surface profiler measurement.

3.5. Results of photo-degradation of Rhodamine B

The removals of Rhodamine B using and not using the produced films are shown in Fig. 4a. It can be noticed that the removal speed of Rhodamine B is very low in the absence of

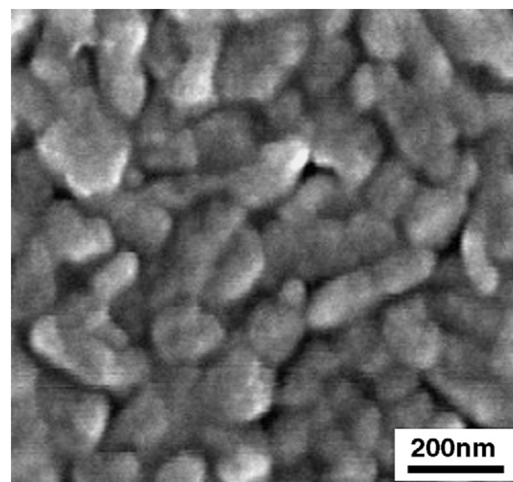
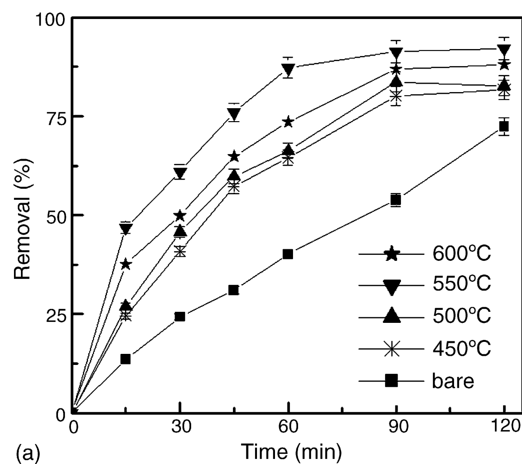


Fig. 3. SEM image of the produced film annealed at 550 °C.

the Bi_2O_3 films under the UV-illumination, while the removals of Rhodamine B using different bismuth oxide films are bigger than that using simple glass. It has been found that the removal of Rhodamine B increases with the annealed temperature before 550 °C and the removal for 2 h reaches 92% when the temperature reaches 550 °C. However, as the temper-



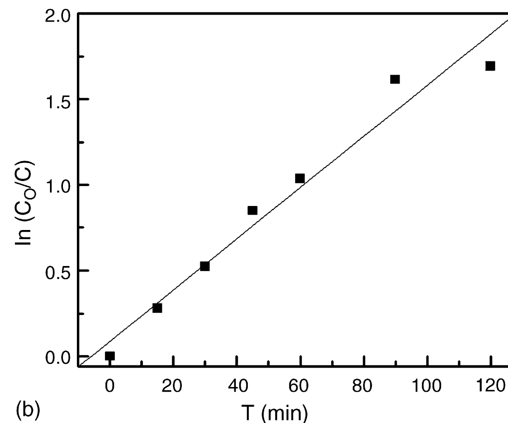


Fig. 4. (a) Removals of Rhodamine B with bismuth oxide films annealed at different temperatures. (b) Kinetic linear simulation curve of Rhodamine B photocatalytic degradation with bismuth oxide films annealed at 450 °C.

ature above 550 °C continues to increase, the removal decreases instead.

4. Discussion

4.1. The reaction kinetics of photo-degradation of Rhodamine B with the films

It has been well established [16,17] that photocatalysis experiments follow the Langmuir–Hinshelwood model, where the reaction rate R is proportional to the surface coverage θ (Eq. (1)):

$$R = -\frac{dC}{dt} = k_r\theta = \frac{k_r KC}{1+KC} \quad (1)$$

where k_r is the reaction rate constant, K the adsorption coefficient of the reactant at the surface of the film and C its concentration. When C is very small, the product KC is negligible with respect to unity so that Eq. (1) describes first-order kinetics. The integration of Eq. (1) with the limit condition that at the start of irradiation, $t=0$, the concentration is the initial one, $C=C_0$, gives:

$$-\ln\frac{C}{C_0} = k_{app}t = k_r Kt \quad (2)$$

where k_{app} is the apparent first-order reaction constant. Furthermore, a kinetic linear simulation curve of Rhodamine B photocatalytic degradation using bismuth oxide flims annealed at 450 °C is shown in Fig. 4b. It is clear that the curve with time (t) as abscissa and $\ln(C_0/C)$ as vertical ordinate, is close to a linear curve. It can be concluded that the photocatalytic degradation of Rhodamine B using bismuth oxide films as catalyst fits well with the first-order exponential decay curve, which follows the first-order reaction kinetics. So a linear equation can be set up, as Eq. (2) shows. In Eq. (2), k_{app} is the first-order reaction constant, which signifies the efficiency of photo-degradation of Rhodamine B. The values of k_{app} for the bismuth oxide films annealed at 500, 550 and 600 °C are 0.015, 0.016, 0.022 and 0.018 min^{-1}, respectively. As a consequence, the bismuth oxide films annealed at 550 °C have the best efficiency of all to degrade Rhodamine B, while the films annealed at 500 °C precede those annealed 450 °C to degrade Rhodamine B.

4.2. The photocatalytic mechanism

It has been well known that semiconductors with a proper energy gap can probably be used as catalysts, and bismuth oxides are among them. Bismuth oxides can induce the forming of conduction band electrons and valence band holes when absorbing radiation with energy equal to or bigger than their energy gap. Then these electrons and holes have redox activities, and the photogenerated holes can react with -OH around the catalyst to produce •OH with high redox activities. The above description can be illustrated by the following expressions [(1) and (2)]:

$$Bi_2O_3 + h\nu \rightleftharpoons h^+ + e^- \quad (1)$$

$$OH^- + h^+ \rightarrow {}^{\bullet}OH \quad (2)$$

The photogenerated hydroxyl radicals have high redox activities, which are able to decompose the pollutant. Apparently it is more difficult for the bismuth oxides of a phase with a higher energy gap than those with a lower band gap to be excited by the irradiation of light with a long wavelength to produce conduction band electrons and valence band holes, which can incite the birth of high reactive radicals, such as •OH, so as to facilitate the degradation of Rhodamine B. Nonetheless, as irradiated by the same light with energy big enough to activate two phases of bismuth oxides, the bismuth oxides of a phase with a bigger value of energy gap are superior to those with a smaller value, because of the higher redox activities.

4.3. The relationship of temperature, structure and properties

High electronic binding energy indicates a high band gap for bismuth oxides which leads to high redox activities of photogenerated holes and electrons of these oxides. The electronic binding energy of the bismuth oxides in the films annealed at 550 °C is the biggest of all for the four kinds of the films as showed in Fig. 2, so these oxides are supposed to be the most photocatalyticly active. Furthermore it can be observed from Fig. 1 that the T phase is more dominant for the bismuth oxide films annealed 550 °C than that for those annealed at other temperatures, while it is adverse for the M phase. So it can be induced that the biggest electronic binding energy for these oxides is due to the increase of bismuth oxides of T phase. Therefore, the bismuth oxides of the T phase have higher photocatalytic activities than those of M phase.

The above analysis can be supported well by the results of photo-degradation of Rhodamine B. It can be noticed in Fig. 4 that the removal for 2 h of Rhodamine B using the bismuth oxide films annealed at 550 °C is as high as 92% and the value of k_{app} is as big as 0.022 min^{-1} while the removal is only 81% and the k_{app} value is only 0.015 min^{-1} for those annealed at 450 °C which contain the smallest proportion of the T phase of bismuth oxides and the biggest proportion of the M phase of bismuth oxides.

5. Conclusion

In conclusion, relatively uniform bismuth oxide films mainly composed of T phase and M phase can be prepared through the sol–gel method annealed at different temperatures. Different temperatures result in the change of the proportion of T phase intensity to M phase intensity, which leads to the difference of the kinetics of photocatalytic degradation of Rhodamine B using bismuth oxide films annealed different temperatures. It has been found that 550 °C is prior to the other annealed temperatures in the research to get high proportion of the T phase bismuth oxides with high electronic binding energy. The bismuth oxide films prepared by being annealed at 550 °C show high photocatalytic properties, using which the first-order reaction constant is 0.022 min^{-1}and the removal of Rhodamine B photocatalyzed for 2 h using these films is as big as 92% while the removal is 81% and the first-

order reaction constant is $0.015\,\text{min}^{-1}$ using those annealed at $450\,^{\circ}\text{C}$.

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