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FACILE SYNTHESIS OF BISMUTH OXIDE NANOPARTICLES BY A HYDROLYSIS SOLVOTHERMAL ROUTE AND THEIR VISIBLE LIGHT PHOTOCATALYTIC ACTIVITY

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Abstract

The bismuth oxide (Bi_2O_3) nanoparticles are easily synthesized from a solution of bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) in ethylene glycol by a hydrolysis solvothermal route at temperatures of 120-150°C. X-ray diffraction, scanning electron microscopy and UV-visible diffuse reflectance spectroscopy are used to characterize the products. The results show that the reaction temperature, the reaction duration and the initial solution concentration play important roles in the formation of the Bi_2O_3 nanoparticles, and all the as-synthesized Bi_2O_3 samples have the cubic phase structure. In addition, studies of the photocatalytic properties by exposure to visible light irradiation demonstrate that the as-obtained Bi_2O_3 nanoparticles show potential photocatalytic application.

Key words: bismuth oxide, nanocrystalline materials, photocatalyst, semiconductors

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1. Introduction

Bi_2O_3 is an advanced functional material with potential applications such as functional electronic material, burning rate catalyst, photocatalytic decomposition material, optical material, medical composite material and anti-radiative material. Among various applications, Bi_2O_3 arouses increasing attentions as a photocatalyst over the last few years, and bismuth oxide in different forms such as nanoparticles, nanostructures and thin films have been developed for studying their photocatalytic properties (Chen et al., 2011; Duan et al., 2010; Hao et al., 2014; He et al., 2007a; Iyyapushpam et al., 2012; Sood et al., 2015; Wu et al., 2007; Xiao et al., 2013; Zhang et al., 2010). At present, various methods are introduced for the synthesis of the nanoscale Bi_2O_3 particles including sol-gel method (Anilkumar et al., 2005; He et al., 2007a, 2007b; Pan et al., 2008; Wu et al., 2007), magnetron sputtering deposition (Sirota et al., 2012), precipitation process (Iyyapushpam et al., 2012; Jha et al., 2005; Li, 2006; Wu et al., 2013; Yang et al., 2014), gel to crystal conversion route (Patil et al., 2005), chemical-bath method (Hajra et al., 2014), low-temperature oxidation method (Xia et al., 2012), oxidative metal vapor transport deposition technique (Qiu et al., 2006), flame spray pyrolysis (Mädler and Pratsinis, 2002), polyol method (Jungk and Feldmann, 2001), hydrolysis route (Schlesinger et al., 2013a, 2013b), microwave-assisted method (Huang et al., 2011), solvothermal method (Qin et al., 2012) etc.

Although the previous methods have been proven to be successful in the synthesis of Bi_2O_3, they normally requires high temperature heating, long synthesis period, post treatment and so on. At the same time, the common chemical synthesis method based on the polyol medium has been well developed for the synthesis of bismuth oxide. However, the previous polyol method required the

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alkali as precipitation reagent during the synthesis process. Hence, it is expected that a more simple synthesis method, which is precipitant-free, additive-free and low costing, is proposed for the synthesis of Bi_2O_3 nanoparticles.

In the present work, we have developed a facile hydrolysis solvothermal method to synthesize Bi_2O_3 nanoparticles, including a rapid self-hydrolysis of bismuth nitrate pentahydrate in ethylene glycol and subsequent solvothermal dehydration and crystallization processes, and no catalysts and additives are added to the reaction system during the synthesis process. In addition, the obtained sample is tested for its performance as a photocatalyst.

2. Experimental section

2.1. Materials and apparatus

All chemicals (bismuth nitrate pentahydrate, ethylene glycol etc.) used in the study were of analytical grade quality. A powder diffractometer (Bruker D8 Advance, Germany) with Cu Kα radiation (λ= 0.15418 nm), the accelerating voltage of 40 kV and the emission current of 40 mA was used to determine the crystal phase composition and the crystallite size of the synthesized samples. A scanning electron microscope (LEO1530VP, Germany) was employed to observe the shape and size of the synthesized samples.

The UV-Vis diffuse reflectance spectroscopy was obtained using a UV-visible spectrophotometer (TU-1901, Beijing Purkinje General Instrumental Co., China).

2.2. Synthesis procedure

All chemicals used in the study were commercial available without further treatment. In a typical synthesis, a given amount of $Bi(NO_3)_3 \cdot 5H_2O$ was firstly dissolved in 80ml ethylene glycol under vigorously stirring, and the resulting solution was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 100 mL. Subsequently, the sealed autoclave was heated at a given temperature for a certain time, and naturally cooled to room temperature. Finally, the as-synthesized products were separated from the solid-liquid mixture by the high-speed centrifugation, washed with ethanol for several times, dried in vacuum at 80°C for 2h, and the Bi_2O_3 nanoparticles were obtained. In the synthesis process, uniform hydrolysis of $Bi(NO_3)_3 \bullet 5H_2O$ was accomplished to form an amorphous or nano-grain sized hydrated oxide precursor via its own crystallization water in ethylene glycol acting as solvent and esterification agent, followed by solvothermal dehydration and crystallization processes. The chemical reactions for synthesis of Bi_2O_3 can be formulated as Eqs. (1-3):

$$2Bi(NO_3)_3 + (x+3)H_2O \xrightarrow{Hydrolysis} 2BiONO_3 \rightarrow Bi_2O_3 \bullet xH_2O + 6HNO_3 \quad (1)$$

$$Bi_2O_3 \bullet xH_2O \xrightarrow{Dehydration\ and\ Crystallization} Bi_2O_3 + xH_2O \quad (2)$$

$$HNO_3 + CH_2OH - CH_2OH \xrightarrow{Esterification} CH_2OH - CH_2ONO_2 + H_2O \quad (3)$$

2.3. Photocatalytic activity measurement

The photocatalytic degradation experiments were carried out in a photochemical reactor using a 500 W Xe lamp with a 420-nm UV cutoff filter, and the photocatalytic performance of the prepared Bi_2O_3 was evaluated by the photodegradation of methyl orange (MO). The reaction temperature was kept at room temperature by cooling water to prevent any thermal catalytic effect. The reaction suspension was prepared by adding 0.25 g of the Bi_2O_3 powder into 100 ml MO aqueous solutions with the concentration of 20 mg/L. Prior to irradiation, the suspension was stirred in a dark to establish adsorption–desorption equilibrium between photocatalyst and MO.

Once the concentration of methyl orange got stabilized, the reaction mixture was irradiated, signaling the start of photocatalysis. At given time intervals, the sample was collected, centrifuged, and filtered through a 0.2 μm millipore filter. Then the filtrate was analyzed on a spectrophotometer at 464 nm, which is the maximum absorption wavelength of MO, to determine the concentration of MO.

3. Results and discussion

3.1. Influence of reaction temperature on phase composition and crystallite size

To determine the crystal phase composition and crystallite size of the synthesized samples, the powder X-ray diffraction (XRD) measurements are carried out at room temperature in the diffraction angle (2θ) range from 20° to 80°. Fig. 1 shows the XRD patterns of samples synthesized with the bismuth nitrate initial concentration of 0.1 mol/L at 120, 130, 140, 150 °C for 2 h, respectively.

In Fig. 1, the spectra are indexed to the crystal planes of the cubic phase bismuth oxide (JCPDS Card No. 27-0052), when the solvothermal temperature is below 140°C, and there are a continuous sharpening and intensifying of the diffraction peaks for Bi_2O_3 with increasing solvothermal temperature, indicating that the crystallite size of Bi_2O_3 increases with the reaction temperature going up. The crystallite size of Bi_2O_3 synthesized at different reaction temperatures can be calculated according to the Scherrer equation.

The results show that the mean sizes of Bi_2O_3 are 8.3, 13.7 and 26.1 nm at 120, 130 and 140°C, respectively. In addition, the characteristic diffraction peaks of Bi (JCPDS Card No. 44-1246) are observed from Fig. 1 at 150°C. While below 140°C, only the diffraction peaks of Bi_2O_3 appear in patterns. It indicates that Bi_2O_3 will be partly reduced to form

the metal bismuth when the solvothermal temperature is 150 °C and above.

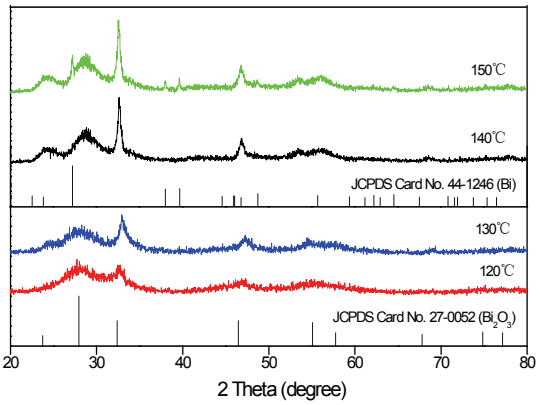

Fig. 1. XRD patterns of samples synthesized at different solvothermal temperatures

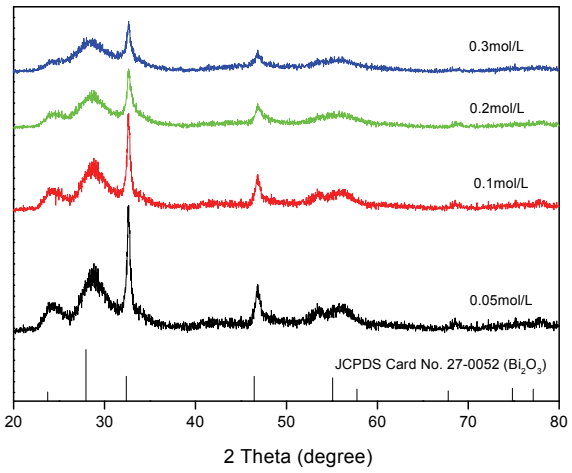

Fig. 2. XRD patterns of samples synthesized under the condition of the different initial bismuth nitrate concentrations

3.2. Influence of bismuth nitrate initial concentration on crystallite size

Fig. 2 shows the XRD patterns of the products synthesized at 140 °C for 2 h with the different initial bismuth nitrate concentrations. The average crystallite sizes of the as-prepared products are calculated by the Scherrer equation and are ca. 30.7, 26.1, 17.2 and 13.4 nm corresponding to the initial concentrations of 0.05, 0.1, 0.2 and 0.3 mol/L, respectively. The results indicate that the initial bismuth nitrate concentration has significant influence on the crystallite sizes of products, and the crystallite sizes of the Bi_2O_3 decrease gradually with the increasing of the initial bismuth nitrate concentrations.

It can be explained that the nucleation rate of the predecessor $Bi(OH)_3$ is greater than the its growth rate under the condition of the higher initial bismuth nitrate concentrations, and the small predecessor results in the formation of small Bi_2O_3.

3.3. Morphology and size distribution of the sample

In order to study the morphology and size distribution of the synthesized samples, scanning electron microscopy (SEM) is used.

Fig. 3 shows the SEM image of the Bi_2O_3 sample synthesized at the solvothermal temperature of 140 °C for 2 h with the initial bismuth nitrate concentration of 0.1 mol/L. SEM micrograph reveals that the obtained sample is the approximate spherical particles with a little agglomeration, and the particle sizes of them are in the range of 50−90 nm, which are larger compared with the results obtained from XRD analysis. The result declares that the synthesized product is a polycrystalline state.

3.4. UV-Vis diffuse reflectance spectra

The absorption spectra of commercial Degussa P25 TiO_2 and Bi_2O_3 synthesized at the solvothermal temperature of 140 °C for 2 h with the initial bismuth nitrate concentration of 0.1 mol/L are shown in Fig. 4. It can be seen that both the samples have a strong absorption at the wavelength range from 230 to 400 nm.

In addition, it can be observed from Fig. 4 that the absorption band of the Bi_2O_3 sample is red-shifted compare with that of TiO_2, which is a well known largely studied material for photo-degradation, and the Bi_2O_3 sample has obvious absorption in the visible region (>400 nm).

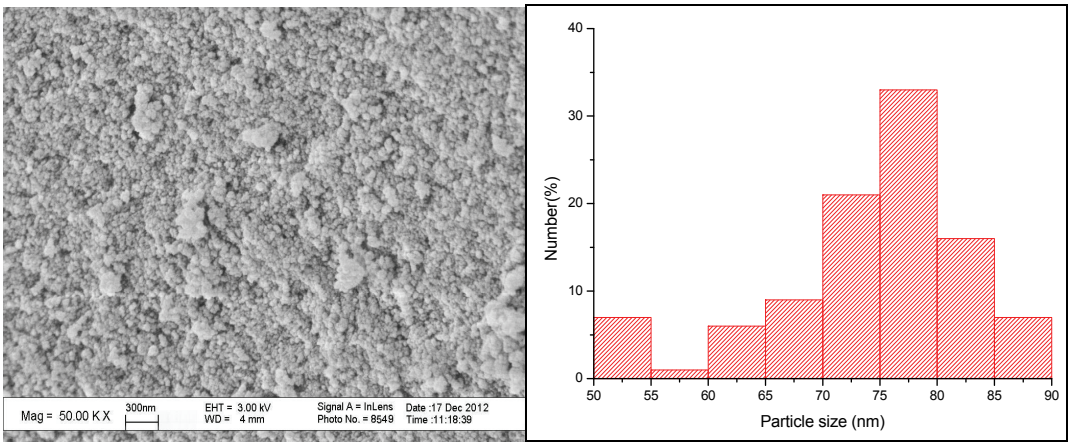

Fig. 3. SEM image and particle size distribution of the synthesized sample

The absorption band of the Bi_2O_3 is extended to a visible region due to its low-energy band-gap of ca. 2.8 eV, responding to visible irradiation.

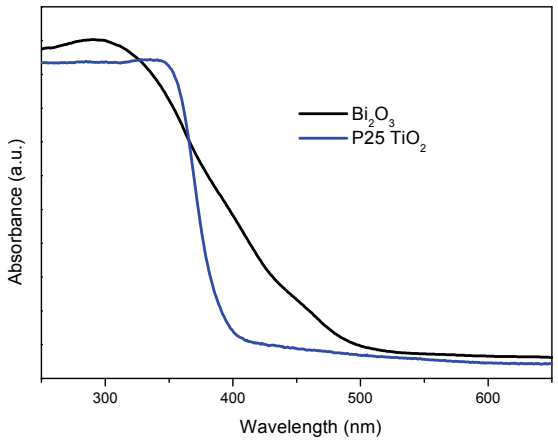

Fig. 4. UV-Vis diffuse reflection spectra

3.5. Photocatalytic activity

The photocatalytic activity of the Bi_2O_3 synthesized at the solvothermal temperature of 140 °C for 2 h with the initial bismuth nitrate concentration of 0.1 mol/L is evaluated through the photodegradation of MO under the visible light irradiation. The experimental results are illustrated in Fig. 5.

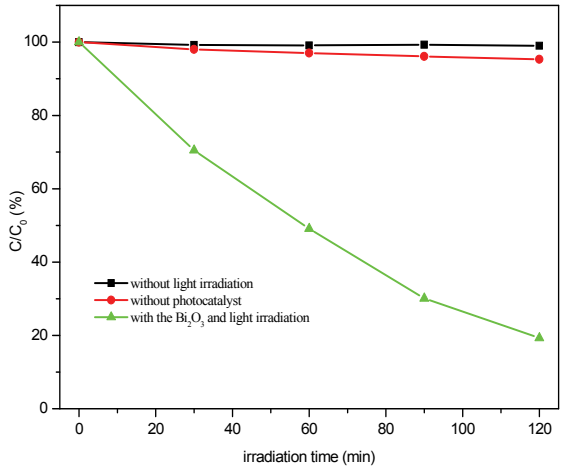

Fig. 5. Photocatalytic activity of the synthesized Bi_2O_3

It shows that the synthesized Bi_2O_3 sample exhibits a high photocatalytic activity for decomposition of MO under the visible light irradiation, and the photocatalytic degradation ratio of MO reaches to 81.3% after irradiation for 2 h. For the purpose of comparison, both blank experiments are also carried out.

The result shows that the MO is not decomposed in the absence of irradiation and has only less than 5% of degradation for 2 h irradiation without the Bi_2O_3. It suggests that the as-synthesized Bi_2O_3 is an effective photocatalyst for the degradation of MO under irradiation of visible light.

4. Conclusions

The Bi_2O_3 has been successfully synthesized by a simple and cost-effective hydrothermal method. The hydrothermal reaction temperature and the initial bismuth nitrate concentrations obviously influence the phase composition and crystallite size of synthesized powders, and the crystallite sizes of Bi_2O_3 nanoparticles are controlled in the range of 13.4 – 30.7 nm with the initial bismuth nitrate concentrations of 0.05 – 0.3 mol/L at 140 °C for 2 h.

The synthesized Bi_2O_3 shows red shift compared with TiO_2, and exhibits a higher photocatalytic activity in degradation of MO under visible light irradiation.

Acknowledgments

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