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Novel Synthesis Method of Sheet-like Agglomerates β-Bi_2O_3 with High Photocatalytic Activity

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Abstract: Sheet-like agglomerates β-Bi_2O_3 were synthesized *via* an extraction-precipitation stripping-decomposition method using a leaching solution of bismuthinite as raw materials in acidic chloride media. Phase form of as-prepared Bi_2O_3 was confirmed by X-ray diffraction (XRD) and its morphology was observed by scanning electron microscope (SEM) and transmission electron microscope (TEM). Moreover, photocatalytic activity of the β-Bi_2O_3 was evaluated by measuring the degradation of Rhodamine B (RhB) under visible light irradiation. The results showed that the powders consisted of nanoflakes. The β-Bi_2O_3 exhibited a smaller band gap energy and larger absorbance edge than α-Bi_2O_3 and reported β-Bi_2O_3. In addition, 99.23% of the RhB was degraded under 4 h visible light irradiation and β-Bi_2O_3 was a fairly stable photocatalyst under the experimental conditions.

Key words: β-Bi_2O_3; leaching solution from bismuthinite; extraction; stripping precipitation; degradation

Environmental pollution has been a global issue, and photocatalytic oxidation is a promising technology to degrade pollutants. Semiconductor photocatalysts, as versatile materials that can efficiently use solar energy to degrade organic pollutant or eliminate heavy metal pollution of water have received considerable attention[1-2]. Among various oxide semiconductors, Bi_2O_3, which can be excited by visible light, has been widely investigated as a photocatalyst[3]. There are four polymorphs for Bi_2O_3, of which β-Bi_2O_3 shows a better photocatalytic activity than the others, with a narrower band gap and higher optical absorption in the visible light region[4-5]. In addition, Bi_2O_3 can be easily converted into $(BiO)_2CO_3$ during the photocatalytic degradation process, which limits its further applications[4]. Therefore, more attention should be paid to the synthesis of high photocatalytic activity β-Bi_2O_3 with strong resistance to photocorrosion. At present, there are many methods available for the preparation of β-Bi_2O_3 photocatalysts, such as precipitation methods[6], solvothermal methods[7], Sol-Gel methods[8], solid-state chemical methods[9], *etc*[3]. Unexceptionally, analytic reagents such as bismuth salts or high purity bismuth ingots have been used as a bismuth source for the preparation of β-Bi_2O_3 photocatalysts in these methods.

Precipitation stripping-decomposition is a novel method for preparing oxide materials. The benefits of this method are economization of materials and time by combining the stripping and precipitation processes into a single process[10]. During the process, metal ions of a solution are extracted into an organic phase, followed by stripping precipitation with an oxalate or carbonate as the precursor of the required oxides. Usually, the precipitation stripping process is widely employed for recovering rare earth metals. For example, Chen, *et al*[11] prepared Y_2O_3 *via* the extraction-precipitation stripping method. Valentina, *et al*[12] prepared yttrium oxalate *via* extraction-precipitation stripping method from a leaching solution of fluorescent lamp phosphors. However, to the best of our knowledge, there have been no reports on the preparation of β-Bi_2O_3 photocatalysts by the extraction-precipitation stripping-decomposition method. In the present study, this approach was proposed to prepare β-Bi_2O_3 sheet-like agglomerate photocatalysts using the leaching solution from bismuthinite as the raw materials. Simultaneously, photocatalytic activity of β-Bi_2O_3 photocatalysts was investigated using Rhodamine B (RhB) as the model pollutant.

1 Experimental

1.1 Materials and synthesis

Tributyl phosphate (TBP) was used as extractant without further purification and sulfonated kerosene was used as diluent. As a source of Bi(Ⅲ), stock solutions of $BiCl_3$ were prepared with 19.06 g/L Bi^{3+}, 4.40 g/L Fe^{3+}, 0.09 g/L Cu^{2+},

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0.90 g/L Mn^{2+} and 0.61 g/L Pb^{2+} according to a previous study[13]. 20 mL of the organic phase with 575 g/L TBP and a 20 mL solution containing Bi(Ⅲ) were added to a separatory funnel and then equilibrated mechanically in an orbital shaker at 25℃ for 10 min. The volume ratio of the organic phase to the aqueous phase (O:A) was 1∶1. Afterwards, the organic phase and aqueous phase were separated. Thus, the as-obtained Bi(Ⅲ)-loaded organic phase was mixed with an equal volume of 20% oxalic acid solution at 25℃ for 30 min. The precipitates (namely, the precursor of β-Bi_2O_3) were washed with ethanol and dried at 80℃ for 12 h. Finally, β-Bi_2O_3 powders were prepared by decomposition of the precursor at 300℃ for 2 h in air.

1.2 Characterizations

The crystalline phase of the sample was determined by powder X-ray diffraction (XRD) analysis on an XD-3 unit using Cu Kα radiation. The morphology of the sample was investigated using a transmission electron microscope (TEM) (Model H-7650, Hitachi Corp., Japan). Ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy (DRS) spectra was recorded on a spectrophotometer (Model UV-2550, Shimadzu Corp., Japan). Photocatalytic activity was evaluated by the degradation of RhB solution (100 mL, 20 mg/L) with a 500 W Xe lamp used for visible light irradiation.

1.3 Photocatalytic experiments

The reaction was carried out by dispersing each 0.2 g of catalyst in 100 mL of 20 mg/L RhB solution. The suspensions were kept in dark for 30 min in flowing water before visible light irradiation from the Xe lamp. At a given time interval, 5 mL of solution was collected and centrifuged until all of the solution had been processed. The residual concentration of RhB was measured at 554 nm using a UV-Vis spectrophotometer (Model Lambda 25, Perkin Elmer Co., USA). The degradation of RhB was then calculated.

2 Results and discussion

TBP served as a kind of neutral extractant. In acidic chloride media, the species $BiCl_5^{2-}$ and $BiCl_6^{3-}$ maintain at a stable level in the solution when $[Cl^-]$>36.5 g/L. Therefore, the extraction of bismuth with TBP can be expressed by the following reactions[14]:

$$BiCl_6^{3-}+x\overline{TBP}=\overline{BiCl_3\cdot xTBP}+3Cl^- \quad (x=2 \text{ or } 3) \qquad (1)$$

$$BiCl_5^{2-}+x\overline{TBP}=\overline{BiCl_3\cdot xTBP}+2Cl^- \quad (x=2 \text{ or } 3) \qquad (2)$$

The extraction yield of bismuth from the leaching solution reached up to 98.5% after four count-current extractions at O:A of 1:1, TBP concentration of 575 g/L, time of 10 min, $[Cl^-]$ concentration of 36.5 g/L, and temperature of 25℃.

The resultant Bi(Ⅲ)-loaded organic phase was stripped by oxalic acid. The precipitation stripping reaction between the $\overline{BiCl_3\cdot xTBP}$ (x=2 or 3) and oxalic acid may be written as follows[14]:

$$2\overline{BiCl_3\cdot xTBP}+3H_2C_2O_4+7H_2O=$$
$$Bi_2(C_2O_4)_3\cdot 7H_2O_{(s)}+2x\overline{TBP}+6HCl \quad (x=2 \text{ or } 3) \qquad (3)$$

Under the conditions of 20% oxalic acid with O:A of 1:1 and a contact time of 30 min, 99.20% bismuth in organic phase was stripped in the form of white precipitates. The comprehensive recovery rate of Bi^{3+} reached up to 97.7% from a leaching solution of bismuthinite. XRD pattern of the precursor is shown in Fig. 1. All the diffraction peaks in Fig. 1 can be indexed as $Bi_2(C_2O_4)_3\cdot 7H_2O$ (JCPDS 38–0548). Figure 2 shows that the precursor presents a hierarchical flower-like morphology consisting of microflakes (inset of Fig. 2).

Furthermore, the crystalline phase of the as-prepared samples was characterized. In Fig. 3, all the peaks correspond to JCPDS 78–1793, indicating that pure tetragonal Bi_2O_3 was obtained after the precursor was decomposed at 300℃ for 2 h. The purity of as-prepared β-Bi_2O_3 was 99.923% with 99×10^{-6} for Fe, 21×10^{-6} for Cu, 13×10^{-6} for Zn and 56×10^{-6} for Cl. Typical SEM

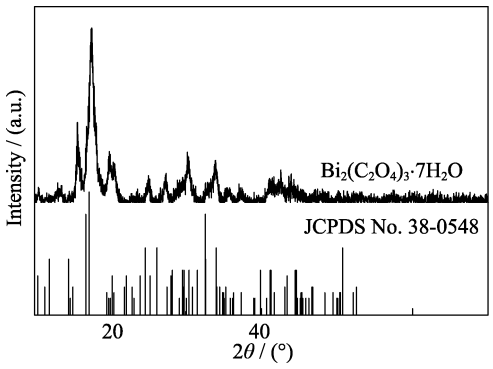

Fig. 1 XRD pattern of the precursor

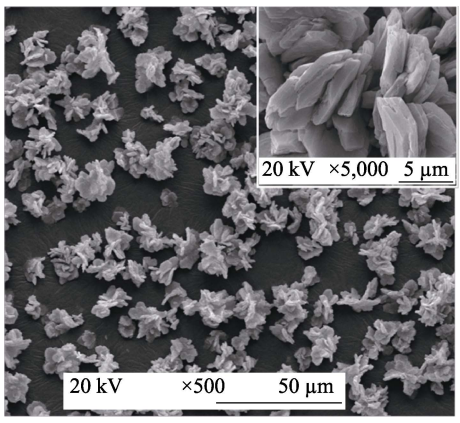

Fig. 2 SEM images of the precursor

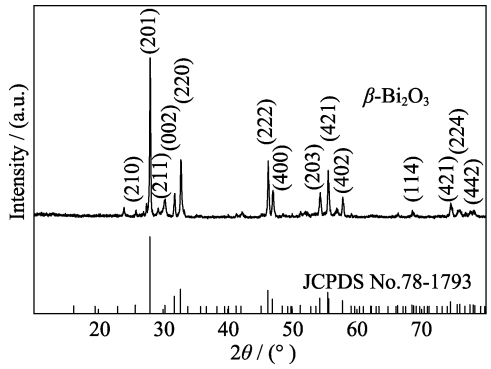

Fig. 3　XRD patterns of β-Bi_2O_3

and HRTEM images of β-Bi_2O_3 indicate that sheet-like agglomerates consist of nanoflakes (Fig. 4(a) and 4(b)). The measured lattice distance with *d*-spacing of 0.319 nm correspond to the (201) plane of β-Bi_2O_3 (Fig. 4(c)).

The UV-Vis DRS of β-Bi_2O_3 are shown in Fig. S1. The band gap absorption edge of β-Bi_2O_3 was determined to be at 525 nm (Fig. S1), corresponding to a band gap energy of 2.36 eV (inset of Fig. S1), which was lower than that of α-Bi_2O_3[15] (2.83 eV) and the reported β-Bi_2O_3[2,16-17], indicating higher visible light photocatalytic activity. Figure 5(a) represents the photodegradation of RhB in the presence of β-Bi_2O_3, P25, as well as no photocatalyst for comparison. The results demonstrate that almost no change in the concentration of RhB is observed in the absence of photocatalyst, indicating that the self-photolysis of RhB can be ignored. After 4 h irradiation, 42% and 99.23% of RhB is photocatalytically degraded by P25 and β-Bi_2O_3, which was higher than that of β-Bi_2O_3 prepared by the hydrothermal method[18] (degradation rate 45%). To test the stability of the as-prepared β-Bi_2O_3, it was reused four times. As shown in Fig. 5(b), there was no significant decrease for RhB degradation rate after irradiation for 4 cycles (99.23% for the first cycle, 98.98% for the second cycle, 97.70% for the third cycle, and 95.40% for the fourth cycle). In addition, the Bi_2O_3, after being used four times, was characterized again by XRD (Fig. S2). The results showed that all peaks can be indexed as tetragonal Bi_2O_3 with much lower crystallinity, revealing that the as-prepared β-Bi_2O_3 was stable without photocorroded. The high photocatalytic activity of β-Bi_2O_3 probably related to the synthetic method and its raw materials, leading to a narrower band gap. The reason for this merit needs further study. The possible reaction mechanism of degradation RhB of β-Bi_2O_3 is shown in Fig. 6.

3　Conclusion

Sheet-like agglomerates β-Bi_2O_3 were easily synthesized for RhB degradation. In particlular, the precursor of β-Bi_2O_3 was prepared by solvent extraction-precipitation stripping from leaching solution of bismuthinite. Pure tetragonal Bi_2O_3 was obtained by decomposition of the precursor.

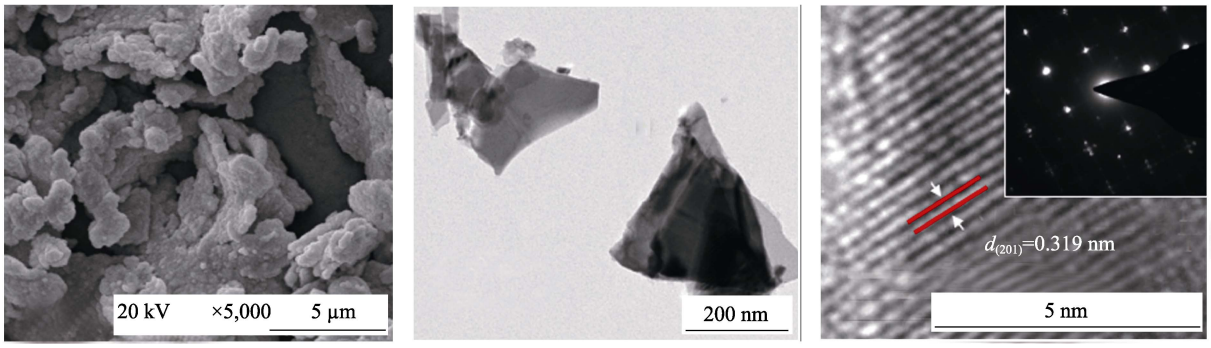

Fig. 4　(a) SEM, (b) TEM and (c) HRTEM images of β-Bi_2O_3

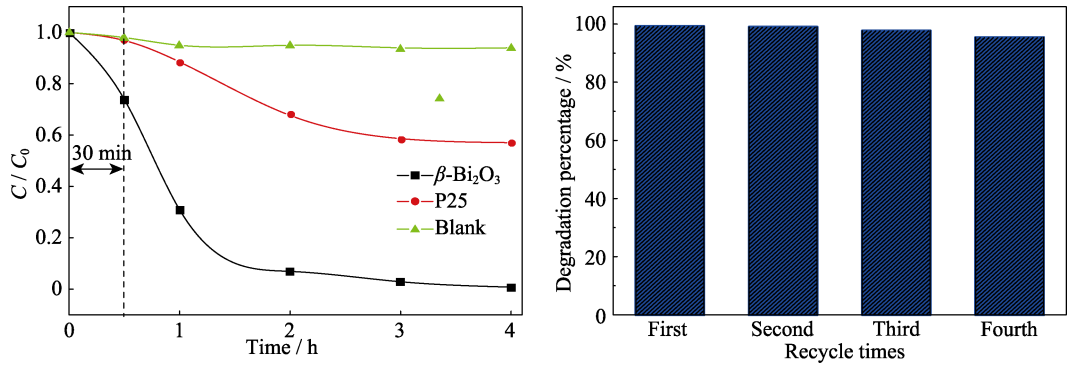

Fig. 5　(a) RhB concentration changes with irradiation and (b) RhB degradation in the first four cycle runs for β-Bi_2O_3

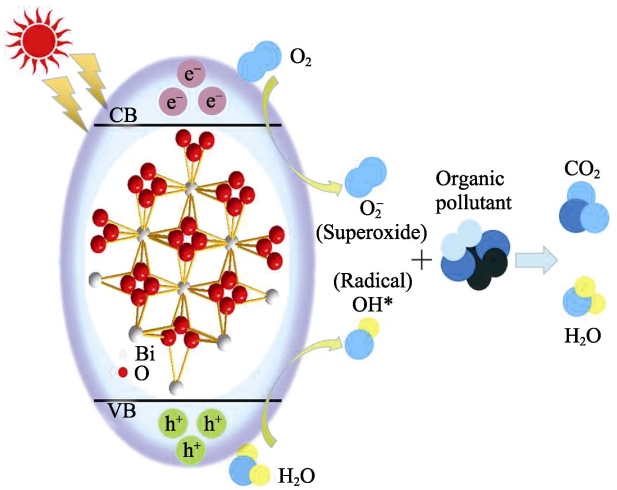

Fig. 6 Possible reaction mechanism of β-Bi_2O_3 photocatalysts for RhB photodegradation

Photodegradation results confirmed that the as-prepared β-Bi_2O_3 exhibited enhanced photocatalytic activity with lower band gap energy and higher photocorrosion resistance. It was also found that the preparation method and the raw materials favored the improvement of its photocatalytic activity. The proposed approach for preparing efficient β-Bi_2O_3 photocatalysts has great potential in large-scale industrial applications.

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合成具有高效光催化活性的片状 β-Bi_2O_3 的一种新方法

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摘 要: 采用萃取–反萃–热分解法以辉铋矿的盐酸浸出液为原料制备了层片状的 β-Bi_2O_3。所制备的样品分别用 X 衍射仪及透射电镜对其物相及形貌进行表征, 以罗丹明 B 为污染物研究了其光催化活性。结果表明: 所制备的 β-Bi_2O_3 是一种层状的纳米片, 具有较低的禁带宽度。在实验条件下, 对罗丹明 B 进行 4 h 的降解, 降解率达到 99.23%, 样品的重复降解实验还表现出良好的循环稳定性。

关 键 词: β-Bi_2O_3; 辉铋矿浸出液; 萃取; 反萃; 降解

中图分类号: TF125 **文献标识码:** A

Supporting information:

Novel Synthesis Method of Sheet-like Agglomerates β-Bi_2O_3 with High Photocatalytic Activity

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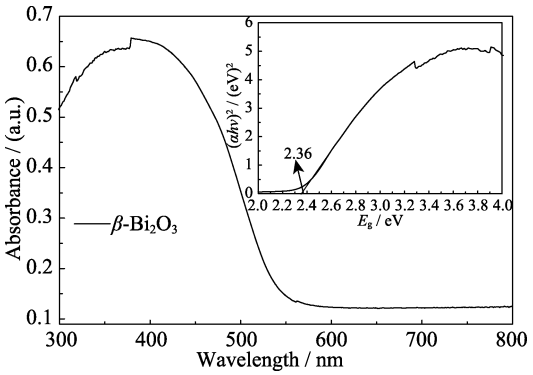

Fig. S1　UV-Vis diffuse reflectance spectra of as-prepared β-Bi_2O_3 (inset: plots of $(\alpha hv)^2$ *vs*. photon energy)

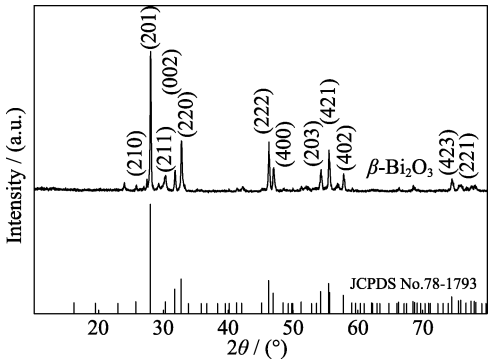

Fig. S2　XRD patterns of as-prepared β-Bi_2O_3 after degradation of RhB