Synthesis and Photocatalytic Properties of Metastable β-Bi2O3 Stabilized by Surface-Coordination Effects

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Metastable semiconductor, β-Bi₂O₃, was successfully synthesized with the precursor of Bi₂O₂CO₃ in this study, which showed much higher photocatalytic activity in the photooxidation of isopropyl alcohol (IPA) than thermal stable α-Bi₂O₃. The prepared samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM), and high-resolution transmission electron microscope (HRTEM). Based on the previous study, a surface CO₂ coordination effect was proposed to understand the formation mechanism of β-Bi₂O₃ at room temperature. This speculation was supported by the surface chemical states’ differences between α- and β-Bi₂O₃, which were studied by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric-differential thermal analysis (TG-DTA). Meanwhile, the energy band structures of α- and β-Bi₂O₃ were measured with ultraviolet-visible diffuse reflection spectroscope (UV-vis DRS) and valence band X-ray photoelectron spectroscopy (VB-XPS); the electronic structures were calculated using the plane-wave density functional theory (DFT) with the CASTEP program package. At last, the photo-induced charge separation efficiency and photocarriers’ lifetime of α-Bi₂O₃ and β-Bi₂O₃ were studied by steady state and dynamic photoluminescence (PL). Based on the results, the higher photocatalytic activity of β-Bi₂O₃ than that of α-Bi₂O₃ was attributed to its higher visible light harvest, the formation of O₂·⁻ with strong oxide ability, higher charge separation efficiency, and larger surface areas.

1. INTRODUCTION

In the past decades, semiconductor photocatalysis attracted increasing attentions as a potential green technology to solve environmental pollution and energy shortage. TiO₂, as the most known photocatalysts, has been extensively studied in the applications of the environmental cleaning and energy conversion due to its unique properties, such as chemical inertness, strong oxide ability, long-term stability against photo & chemical corrosion, cost effectiveness, and nontoxic. However, the relatively wide band gap (3.2 eV) limits its photoabsorption to the only UV-light, hindering its practical applications in our daily life. As a result, a series of narrow band-gap semiconductors (≤ 3.0 eV) have been developed to realize the efficient utilization of visible light, which accounts for about 40 % of the total sunlight. Bi₂O₃ crystals have been demonstrated to be a family of potential photocatalysts due to their appropriate band gaps.

Bi₂O₃ has six polymorphic forms, monoclinic α-phase, tetragonal β-phase, body-centered cubic γ-phase, face-centered cubic δ-phase, tetragonal ε-phase, and triclinic ω-phase. Among them, α-phase is the most stable phase at room temperature; δ-phase is the stable phase at high temperature (730 °C - 825 °C); the other four phases, i.e. β, γ, ε, and ω-phase, are metastable phase.

It was found that photocatalysts with different crystal structures show quite different photocatalytic performances. The previous study shows that α-Bi₂O₃, β-Bi₂O₃ and δ-Bi₂O₃ exhibit good photocatalytic activities in the degradation of pollutants. Up to now, α-Bi₂O₃ was mostly studied because of its thermal stability and easy preparation. However, the most active polymorph was proved to be β-Bi₂O₃. Since it is a metastable phase, much less research was reported. In the recent literatures, β-Bi₂O₃ was successfully prepared by using Bi₂O₂CO₃ as a precursor. Nevertheless, the formation mechanism is still unclear, and it’s difficult to controllably stabilize this metastable phase at room temperature. Therefore, it is important and meaningful to address this issue through a detailed research on the formation mechanism of β-Bi₂O₃ at room temperature.

In this study, α-Bi₂O₃ and β-Bi₂O₃ were selectively synthesized with the same precursor of Bi₂O₂CO₃ under different calcination temperatures. The prepared samples were characterized by X-ray diffractometer (XRD), field-emission electron microscope (FE-SEM) and high-resolution transmission electron microscope (HRTEM). The energy band structures of the samples were studied by the UV-visible diffuse reflectance spectroscopy (UV-vis DRS), valence band X-ray photoelectron spectroscopy (VB-XPS), combined with the theoretical calculations. The photocatalytic properties were studied by the oxidation of IPA over α-Bi₂O₃ and...
α-Bi₂O₃ and β-Bi₂O₃ under visible light irradiations. The formation mechanism of β-Bi₂O₃ at room temperature was studied by the surface chemical states’ differences of α-Bi₂O₃ and β-Bi₂O₃, using Fourier transform infrared (FT-IR) spectrophotometer, X-ray photoelectron spectroscopy (XPS) and thermogravimetric-differential thermal analysis (TG-DTA). At last, the photo-induced charge separation efficiency and photocarriers’ lifetime of α-Bi₂O₃ and β-Bi₂O₃ were studied by steady state and dynamic photoluminescence (PL), which are important and meaningful for explaining the higher photocatalytic activity of β-Bi₂O₃ than α-Bi₂O₃ in the photooxidation of isopropyl alcohol (IPA).

2. EXPERIMENTAL SECTION

2.1 Material Preparation.

α-Bi₂O₃ and β-Bi₂O₃ were synthesized with Bi₂O₂CO₃ as the precursor. A typical preparation procedure of Bi₂O₂CO₃ was as follows: Firstly, 5.21g of Bi (NO₃)₃·5 H₂O was dissolved in 27 mL of dilute HNO₃ (1 M), while 6.78 g of Na₂CO₃ was dissolved in 107 mL of ultrapure water; Secondly, the Na₂CO₃ solution was added into the Bi (NO₃)₃ solution dropwise under constant stirring. At this step, large amounts of white precipitate was formed; Next, the suspension was stirred for 15 minutes, and then maintained at 60 °C for 12 hours without stirring; Finally, the product was collected and washed with ultrapure water and ethanol several times before being dried at 60 °C for 6 hours. Here, Bi₂O₂CO₃ was successfully prepared. In order to get α-Bi₂O₃ and β-Bi₂O₃, the prepared Bi₂O₂CO₃ was heated to 400 °C and 350 °C respectively with a rate of 10 °C·min⁻¹, and remained for 30 minutes.

2.2 Sample Charactetrizations.

The crystal structures of the precursor and Bi₂O₃ samples were determined with an X-ray diffractometer (X’pert Powder, PANalytical B. V., Netherlands) with Cu - Kα radiation. Field-emission electron microscope (FE-SEM) was performed to observe the morphologies on a JEOL 6701F microscope. High-resolution transmission electron microscope images were recorded with a high-resolution transmission electron microscope (HRTEM, Tecnai G2F30). The diffuse reflection spectra were measured with an integrating sphere equipped ultraviolet-visible (UV-vis) recording spectrophotometer (UV-2500PC, Shimadzu Co., Japan) using BaSO₄ as reference and the optical absorption spectra were converted from the diffuse reflection spectra according to the Kubelka-Munk equation. The specific surface areas were determined with a surface analyzer (BEL SorpMini II, BEL Japan Co., Japan) through nitrogen adsorption and desorption isotherms at 77K by the Brunauer-Emmett-Teller (BET) method. The FT-IR spectra were obtained with a Fourier transform-infrared (FT-IR) spectrophotometer (IRPrestige-21, Shimadzu Co., Japan). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi spectrometer equipped with 300W Al Kα radiation, while all binding energies were referenced to the C1s peak (284.6 eV) of the surface adventitious carbon. Thermogravimetric-differential thermal analysis (TG-DTA; Shimadzu, DTG-60H, Japan) was used to study the details in the calcination process of Bi₂O₂CO₃ at different temperatures. Steady state and dynamic PL of samples were measured using an excitation wavelength of 325 nm diode laser, respectively, on a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon). The experiments were carried out under ambient conditions.

2.3 Photocatalytic oxidations of IPA.

The photocatalytic oxidations of gaseous IPA were carried out to evaluate the photocatalytic activities of Bi₂O₃ samples. The experiments were carried out under visible light irradiation (420nm ≤ λ ≤ 800nm). The light source was a 300 W Xe-arc lamp (10 A impport current, focused through a 50 × 50 mm² shutter window) equipped with wavelength cut-off filters and a water filter. 100 mg of Bi₂O₃ powder was bespread uniformly on a glass dish with an area of 9 cm². A certain amount of gaseous IPA (~ 1400 ppm) was injected into the vessel and kept for 2 hour in the dark before irradiations. During the irradiation by visible light, 0.5 ml of the gas was sampled everyone 1 hour intervals. The products were analyzed with a gas chromatograph (GC-2014, Shimadzu, Japan) with a flame ionization detector (FID). Furthermore, the adsorption of IPA in dark over α-Bi₂O₃ and β-Bi₂O₃ were also carried out without light irradiation, as well as the self-degradation of IPA under visible light irradiation (420nm ≤ λ ≤ 800nm) without any catalyst.

2.4 Theoretical Calculation.

The band structures of α- and β-Bi₂O₃ were calculated using the plane-wave density functional theory (DFT) with the CASTEP program package. The core electrons were replaced by ultrasoft pseudopotentials with a plane-wave basis cutoff energy of 380.0 eV, and the interactions of exchange and correlation were treated within the framework of the local density approximation (LDA). The FFT grids of basis in all the models were 40 × 54 × 48 and 54 × 54 × 40 for α-Bi₂O₃ and β-Bi₂O₃, respectively. The k-point sets of 3 × 2 × 2 for α - Bi₂O₃ and 2 × 2 × 2 for β-Bi₂O₃ were used.

3. RESULTS AND DISCUSSIONS

3.1 Crystal structures.

The crystallographic phases of the prepared Bi₂O₃ and precursor samples were characterized by X-ray diffraction (XRD). As described in Fig. 1, the precursor shows a good single orthorhombic crystal phase of Bi₂O₂CO₃, and all the peaks are accordance with the standard database (ICSD No. 70-8631)⁹. When the precursor was calcined for 30 minutes at 350 °C, the crystal changed to β-Bi₂O₃ in tetragonal crystal corresponding to the ICSD file of No. 27-0050⁹. With an increase of the calcination temperature to 400 °C, the crystal gradually changed to α-Bi₂O₃.

![Fig. 1 XRD patterns of Bi₂O₂CO₃, α-Bi₂O₃ and β-Bi₂O₃](image)
after 30 minutes. All the diffraction peaks could approximately be indexed to a monoclinic α-Bi$_2$O$_3$ (ICSD No. 41-1449)\textsuperscript{19}. The schematic crystal structures of Bi$_2$O$_2$CO$_3$, β-Bi$_2$O$_3$ and α-Bi$_2$O$_3$\textsuperscript{18, 19} were displayed in Fig. 2. Therefore, α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ can be selectively prepared by Bi$_2$O$_2$CO$_3$ at different calcination temperatures.

The crystal structures of the precursor and Bi$_2$O$_3$ samples were further confirmed by field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HRTEM) and high-resolution transmission electron microscopy.

From Fig. 3, we can see that Bi$_2$O$_2$CO$_3$ precursor is constituted by large amounts of nanosheets [Fig. 3 (A)]; β-Bi$_2$O$_3$ sample is composed of the nanosheets and smaller nanoparticles [Fig. 3 (B)]; α-Bi$_2$O$_3$ sample mainly consists of the nanoparticles with the size of about 300 nm [Fig. 3 (C)]. The morphology changes of the samples probably results from the decomposition of Bi$_2$O$_2$CO$_3$ precursor\textsuperscript{19}. As exhibited in Fig. 3 (D), two sets of orthorhombic fringes with the lattice spacing of 0.293 nm and 0.278 nm could be indexed to the (103) and (110) planes of orthorhombic Bi$_2$O$_2$CO$_3$. Fig. 3 (E) shows that the lattice space is measured to be 0.295 nm, matching with the space of the (211) crystal plane of tetragonal Bi$_2$O$_3$. From Fig. 3 (F), the lattice with a space of 0.332 nm is observed, which is corresponded to the (111) planes of monoclinic α-Bi$_2$O$_3$. In addition, the BET surface areas of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ were measured to be 3.6 and 4.5 m$^2$/g, respectively.

### 3.2 Energy band structures.

The UV-vis absorption spectra of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ samples are displayed in Fig. 4, and both of the samples show high visible light responses. The absorption edges of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ are about 430 nm and 520 nm, respectively. The band gaps ($E_g$) of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ are determined by the following equation\textsuperscript{21} (Tauc equation):

\[
(\alpha v)^n = A (hv - E_g)^n
\]

In this equation, $\alpha$, $v$, $A$ and $E_g$ are the absorption coefficient, light frequency, proportionality constant, and band gap. The value of the index $n$ depends on the property of the materials: for the direct band-gap semiconductors, $n = 2$; for the indirect band-gap semiconductors, $n = 1/2$\textsuperscript{22}. According to the electronic structures calculation of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$, α-Bi$_2$O$_3$ is an indirect semiconductor [Fig. 5 (A)], and β-Bi$_2$O$_3$ is a direct semiconductor [Fig. 5 (B)]. Therefore, the value of $n$ is determined to be 1/2 for α-Bi$_2$O$_3$, while it is 2 for β-Bi$_2$O$_3$. Based on the results, we can get the Tauc plots of $(\alpha v)^n$ vs. photo energy, as shown in the inset of Fig. 4. The band gaps of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ are estimated from the tangent lines to be 2.82 eV and 2.55 eV, respectively. The calculated band gaps of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ in Fig. 5 are 2.08 eV and 1.76 eV, which are smaller than the experimental value. This difference may be caused by the limitation of the LDA functional that underestimates the band gaps in semiconductor simulation. Both the experimental and theoretical results show that β-Bi$_2$O$_3$ possesses a narrower band gap than α-Bi$_2$O$_3$, and the narrower band gap indicates a higher visible light absorption.

Furthermore, VB-XPS were also carried out to study the energy band structures of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$. As shown in Fig. 6, the energy differences between the Fermi levels and the valence bands of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ are almost the same, and the value is +1.35 eV. According to the earlier literatures, the Fermi levels of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ are +1.73 eV\textsuperscript{23} and +0.54 eV\textsuperscript{24}, respectively.

Combining the energy differences between the Fermi levels and the valence bands, the value of the Fermi levels, and the band gaps of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$, we can get their detailed energy band
3.3 Effect of CO$_3$\(^{2-}\) on the stability of β-Bi$_2$O$_3$.

To understand the formation mechanism of β-Bi$_2$O$_3$, FT-IR and XPS measurements were used to study the surface conditions of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$.

For the FT-IR spectra [Fig. 7 (A)] of β-Bi$_2$O$_3$, the intensive peaks at about 850 cm\(^{-1}\) and 1395 cm\(^{-1}\) can be attributed to the v$_3$ and v$_1$ mode of CO$_3$\(^{2-}\). These vibration peaks of CO$_3$\(^{2-}\) are possibly generated from the residual carbonate on the surface of β-Bi$_2$O$_3$ [350°C, Fig. 7 (B)]. All the peaks derived from CO$_3$\(^{2-}\) have sharply decreases in the IR spectra with the increase of the calcination temperatures, and the XRD pattern in Fig. 7 (B) shows that the prepared samples calcined at 400 °C, 450 °C, and 500 °C, are monoclinic α-Bi$_2$O$_3$. In addition, the intensity decrease of the peaks derived from CO$_3$\(^{2-}\) means that CO$_3$\(^{2-}\) contents on the surface of Bi$_2$O$_3$ decreases as the calcination temperature increases.

To get more detailed information of the surface chemical states and compositions of the elements in the prepared α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$, XPS analysis were carried out. From Fig. 8 (A), the presence of Bi, O and C were revealed in the survey spectra of α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$. Then firstly, two types of carbon were found in Fig. 8 (B), and they are attributed to the surface adventitious carbon and the carbon in CO$_3$\(^{2-}\) group. The percentage of carbon for CO$_3$\(^{2-}\) in β-Bi$_2$O$_3$ is determined to be 29 %, while it is a little less in α-Bi$_2$O$_3$ (26 %). Next, from Fig. 8 (C), the two characteristic peaks of Bi$^{3+}$ in both α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ were observed and ascribed as Bi$^{3+}$O$_2$ and Bi$^{3+}$O$_2$\(^{+}\). We can also see that the two peaks of β-Bi$_2$O$_3$ with slightly higher energy than those of α-Bi$_2$O$_3$. This is probably because of more CO$_3$\(^{2-}\) exists on the surface of β-Bi$_2$O$_3$. At last, the XPS peaks of O1s were displayed in Fig. 8 (D). According to the earlier literatures, the three peaks were attributed to the oxygen in H - O - H\(^+\), CO$_3$\(^{2-}\) and Bi - O - Bi\(^{+}\). Similarly to Fig. 8 (B), the oxygen for CO$_3$\(^{2-}\) in β-Bi$_2$O$_3$ (52 %) is also more than that in α-Bi$_2$O$_3$ (44 %).

Therefore, the XPS results also prove that the CO$_3$\(^{2-}\) on the surface of β-Bi$_2$O$_3$ is more than that of α-Bi$_2$O$_3$, which is the same with the FT-IR results.

It is known that, β-Bi$_2$O$_3$ is only stable at about 650 °C, and it will transform to α-Bi$_2$O$_3$ when it is cooled down to room temperature. However, as mentioned previously, β-Bi$_2$O$_3$ can often be successfully prepared by heating Bi$_2$O$_3$CO$_3$ at low temperature and stable at room temperature. We can’t help to ask, what factors make it stable at room temperature. In the earlier literatures, the surface-coordinated organic ligands were proved to be effective to lower the surface energy of NaNbO$_2$ and induce the formation of cubic NaNbO$_2$, which is also a metastable phase. Based on this explanation, the similar speculation is proposed in this paper. Bi$_2$O$_3$CO$_3$ crystal can be gradually decomposed when it is heated to the temperature of that higher than 308 °C. In this process, the carbonate ions in its crystal structures will move out from the interior to the surface, and then leave the body of the Bi$_2$O$_3$CO$_3$ crystals, releasing CO$_2$. When the temperature is not high enough (350 °C), there will be some CO$_3$\(^{2-}\) left on the surface of Bi$_2$O$_3$ crystals, inducing the formation of the metastable β-Bi$_2$O$_3$; however, when the calcination temperature was increased to higher temperature (400 °C or above), less CO$_3$\(^{2-}\) will be left on the surface of β-Bi$_2$O$_3$ crystals after 30 minutes. In this case, the left surface-coordinated CO$_3$\(^{2-}\) is not enough to keep the crystal structure of β-Bi$_2$O$_3$, inducing the crystal structure transformation to thermal stable α-Bi$_2$O$_3$ (As shown in Scheme 1). In other words, the surface-coordinated CO$_3$\(^{2-}\) can lower the surface energy of β-Bi$_2$O$_3$, and make it stable at room temperature. In addition, the speculation was further studied by TG-DTA to confirm this decomposition detail of the Bi$_2$O$_3$CO$_3$ precursor in the calcination process. From the TGA spectra in Fig. 9, about 8 % weight losses are both observed in the two different calcination processes.
The results show that the acetone production was negligible under these conditions. The difference in the photocatalytic activity between α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ is probably attributed to their different band gaps. Since β-Bi$_2$O$_3$ has a narrower band gap than α-Bi$_2$O$_3$, it can absorb more visible light in a wider region, implying higher photocatalytic activity under visible light irradiation.

It was reported that, IPA can be photocatalytic oxidized through two typical reaction processes as below: 

1) h$^+$ oxidation:
$$\text{CH}_3\text{CHOHCH}_3 + h^+ \rightarrow \text{CH}_2\text{COCH}_3 + 2\text{H}^+ + e^-$$

2) O$_2$ oxidation:
$$\text{CH}_3\text{CHOHCH}_3 + e^- + \text{O}_2 + \text{H}^+ \rightarrow \text{CH}_2\text{COCH}_3 + \text{HO}^- + \text{H}_2\text{O}$$

Between them, since O$_2^-$ will be produced in the O$_2$ oxidation process$^{31,32}$, α-Bi$_2$O$_3$ can only oxide the IPA molecular to acetone through h$^+$ oxidation process, due to its low conduction band (+0.26 V vs. NHE). Meanwhile, β-Bi$_2$O$_3$ can realize the IPA oxidation to acetone through both the two processes because of its higher conduction band potential (-0.66 V vs. NHE) than the oxide reaction of O$_2$ to O$_2^-$ (-0.33 V vs. NHE). This is another important reason of that β-Bi$_2$O$_3$ shows much higher photocatalytic activity than α-Bi$_2$O$_3$. The differences of the photocatalytic oxidation mechanism of the IPA to acetone by α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ are described detailedly in Scheme 2.

3.4 Photocatalytic oxidation of IPA.

The photocatalytic activities of both α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ were evaluated by the oxidation of gaseous IPA under visible light irradiation. In the IPA oxidation, the production of acetone, the unique observed product, was as the main index to judge the reaction activities. After 8 hours’ irradiation by visible light (420nm ≤ λ ≤ 800nm), the acetone productions over α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ samples were determined to be 1045 ppm and 485 ppm, respectively, while the negligible acetone was produced from IPA under visible light irradiation in the absence of any catalyst [Fig. 10]. Obviously, β-Bi$_2$O$_3$ shows higher photocatalytic activity in the oxidation of IPA than α-Bi$_2$O$_3$. Meanwhile, the adsorption of IPA by α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ samples in the dark was also carried out.

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**Scheme 1** Schematic diagram of the decomposition process to form β-Bi$_2$O$_3$ and α-Bi$_2$O$_3$.

(350 °C and 400 °C for 30 min), corresponding to the theoretical weight loss (8.6 %) due to the removal of CO$_2$. We also observe that the weight loss at 400 °C for 30 min is slightly more than that at 350 °C for 30 min, which indicates that more CO$_2$ was removed for forming α-Bi$_2$O$_3$. As the DTA curves, accompanied with the weight loss processes of the TGA curves, there are a thermonegative peak and a thermopositive peak during the formation process of α-Bi$_2$O$_3$, while there are only one thermonegative peak during the formation process of β-Bi$_2$O$_3$. The common thermonegative peak (peak 1) of the two processes is attributed to the decomposition of Bi$_2$O$_2$CO$_3$ and the formation of β-Bi$_2$O$_3$, and the thermopositive peak (peak 2) in the formation process of α-Bi$_2$O$_3$ is due to the transformation from β-Bi$_2$O$_3$ to α-Bi$_2$O$_3$. Therefore, the TG-DTA results well explain the detailed decomposition process of Bi$_2$O$_2$CO$_3$ to β-Bi$_2$O$_3$ and α-Bi$_2$O$_3$ at different calcination temperatures.

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**Fig. 8** XPS spectra of (A) survey; (B) C1s; (C) Bi4f; (D) O1s for α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$.

**Fig. 9** TG-DTA of the Bi$_2$O$_2$CO$_3$ calcined at 350 °C and 400 °C for 30 min.

**Fig. 10** Photocatalytic oxidation of gaseous IPA over α-Bi$_2$O$_3$ and β-Bi$_2$O$_3$ under different conditions.
photocatalytic activity of β-Bi₂O₃ is attributed to the following four reasons: (1) the narrower band gap of β-Bi₂O₃ than that of α-Bi₂O₃ indicates higher visible light harvest; (2) higher conduction band potential of β-Bi₂O₃ than that of α-Bi₂O₃ results in the formation of O₂·⁻ with strong oxide ability; (3) higher charge separation efficiency; (4) larger surface area of β-Bi₂O₃ than that of α-Bi₂O₃. These four factors collectively explain the higher photocatalytic activity of β-Bi₂O₃ in the IPA oxide reaction.

4. CONCLUSIONS

In conclusion, α-Bi₂O₃ and β-Bi₂O₃ were selectively synthesized with the same precursors of Bi₂O₂CO₃ under different calcination temperatures. The formation mechanism of β-Bi₂O₃ was studied by analyzing the surface chemical states of α-Bi₂O₃ and β-Bi₂O₃ through FT-IR and XPS spectra. The results indicate that the surface-coordinated CO₃²⁻ can lower the surface energy of β-Bi₂O₃ and make it stable at room temperature. The photocatalytic performances of α-Bi₂O₃ and β-Bi₂O₃ for the oxidation of IPA were also studied in this work; β-Bi₂O₃ shows much higher photocatalytic activity than α-Bi₂O₃, which is attributed to its higher visible light harvest, the formation of O₂·⁻ with strong oxide ability, higher charge separation efficiency and larger surface areas. The study on the formation mechanism of β-Bi₂O₃ provides the important guidance for its preparations. This work also proves that the surface chemical states of the materials have significant effects on their crystal structures’ stabilities, further affecting their photocatalytic activities.

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Notes and references

6. Notes and references

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