Studying Impact of Different Precipitating Agents on Crystal Structure, Morphology, and Photocatalytic Activity of Bismuth Oxide

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Abstract

Bismuth oxide (Bi$_2$O$_3$) is a well-studied photocatalyst for degradation of various environmental contaminants. In this research Bi$_2$O$_3$ has been synthesized by precipitation method using two different bases (NH$_4$OH and NaOH). The samples thus obtained were then analyzed using FTIR, XRD, and SEM for surface functionalization, crystal structures and morphological differences, respectively. The Bi$_2$O$_3$ precipitated using NH$_4$OH showed a flower like structure made up of individual plates having α-Bi$_2$O$_3$ crystal structure. The precipitate obtained using NaOH showed a honeycomb like flower structure with a mixture of both α-Bi$_2$O$_3$ and γ-Bi$_2$O$_3$ crystal structure. Degradation of methyl orange (MO) was used as a model system to test the photocatalytic activity of the bismuth oxide. The Bi$_2$O$_3$ synthesized using NH$_4$OH showed superior photocatalytic degradation of methyl orange than the one synthesized using NaOH.

Keywords: Bismuth oxide; Photocatalyst; Precipitation; Precipitating agents

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1. Introduction

Bismuth oxide (Bi$_2$O$_3$) is a yellow colored crystal with a melting point of 817 °C and the boiling point of 1890 °C and insoluble in water. This material has six crystallographic polymorphs, i.e. α-Bi$_2$O$_3$, β-Bi$_2$O$_3$, γ-Bi$_2$O$_3$, δ-Bi$_2$O$_3$, e-Bi$_2$O$_3$, and w-Bi$_2$O$_3$ [1,2]. The excellent optical and electrical properties like high refractive index, high dielectric permittivity and high oxygen conductivity make this material a suitable contender for various applications such as solid electrolyte fuel cells (SEFC) [3], lighting source [4], solid battery [5], photocatalyst [6], and gas sensor [7].

Chemical, structural and electrical properties of a material are dependent on its method of
synthesis [8,9]. In the case of supported oxide catalyst the deposition method also plays an important role in the performance of the catalyst. The deposition method determines whether the catalyst is uniformly distributed on the support or accumulation of the oxide takes place on the areas of the support [10,11,12]. Therefore, various methods have been reported for synthesis Bi$_2$O$_3$ that include hydrothermal [13], direct precipitation [14-19], microwave [6,20], solution combustion [21,22], and sol gel [1]. Of all these methods, described for the synthesis of Bi$_2$O$_3$ particles, the precipitation method is one of the least complex and energy efficient. Some of the most common substances used as the precipitating agents are hydroxide [14-16] and ammonia/ammonium salts [14,17,18].

Zhong et al. [17] studied the use of different ammonium salt precipitants on the formation of Bi$_2$O$_3$. They do not find any change in the structural properties of the Bi$_2$O$_3$ synthesized by changing the precipitant. Rather reported that the Bi$_2$O$_3$ synthesized using NH$_3$∙H$_2$O showed best photocatalytic activity due to high surface area, pore volume and pore size. Therefore, in the current study we test to see if the two most commonly used precipitants (i.e. NH$_4$OH and NaOH) have an effect structural and photocatalytic properties of Bi$_2$O$_3$. Additionally we used bismuth oxynitrate as a source of bismuth as compared to the commonly used bismuth nitrate [14-19]. The results suggested that the Bi$_2$O$_3$ synthesized using NH$_3$OH formed α-Bi$_2$O$_3$, whereas the one synthesized using NaOH formed a mixture of α-Bi$_2$O$_3$ and γ-Bi$_2$O$_3$. The photocatalytic properties of the Bi$_2$O$_3$ synthesized using NH$_3$OH showed better activity than the Bi$_2$O$_3$ synthesized using NaOH.

### 2. Materials and Methods

The materials used in this research were bismuth oxynitrate (Bi$_2$(O(OH))$_6$(NO$_3$)$_4$), nitric acid (65 %), NH$_3$OH, and NaOH which were purchased from Merck. The solutions were prepared in distilled water.

#### 2.1 Synthesis of bismuth oxide using precipitation method

Synthesis of bismuth oxide was undertaken by mixing 10 g Bi$_5$O(OH)$_9$(NO$_3$)$_4$ and 20 mL citric acid with stirring continuously (600 rpm). When the transparent solution was obtained, subsequently the weak base NH$_3$OH was added till the white turbid suspension with pH 9 was formed. The precipitate obtained was then filtered and washed using distilled water and dried in an oven at 110 °C for 24 hours. The white powder was then calcined in furnace at 600 °C for 1 hour. After calcination, a yellow powder was obtained and used for further characterization. This procedure was similar to the one followed in literature [14] with slight modifications. The above procedure was repeated for synthesis of bismuth oxide with different precipitating agent by replacing NH$_3$OH with NaOH. In addition, the equipment system for synthesis of bismuth oxide is presented in Figure 1.

#### 2.2 Characterization of the samples

The raw material bismuth subnitrate and the yellow powder were characterized using XRD (XRD Bruker with 2θ ranging from 10° to 80° and CuKα radiation (β = 0.15418 nm) at 40 kV and 30 mA), FT-IR (Prestige 21 (Shimadzu) with the wavenumber 400-4000 cm$^{-1}$), and SEM (JEOL-JSM-G510LV) in order to identify
the crystal structure, the changing of functional groups, morphology and particle size, respectively.

2.3 Photocatalytic activity test

Photocatalytic activity of both Bi₂O₃ was tested using procedure reported previously [22]. 0.2 g bismuth oxide was added into 100 mL of 5 ppm methyl orange (MO). The mixture was irradiated using a solar simulator (PEC-L01, Peccell Technologies, Inc., Japan) as demonstrated in Figure 2 to simulate sunlight conditions with the powered density incident 1000 Wm⁻². In order for the dye to be completely adsorbed on the surface of catalyst prior to photocatalysis, the dye and catalyst solution was stirred in dark for 30 min. The photocatalysis experiment was carried out for 120 min under artificial solar irradiation and a sample was retrieved after every 20 min. The retrieved reaction mixture was then centrifuged at 6000 rpm for 5 min to separate the photocatalyst. The concentration of the supernatant was then measured using UV-Vis spectrophotometer at 463 nm.

3. Results and Discussion

The synthesis of Bi₂O₃ by precipitation method using NH₄OH and NaOH produced a white powder (Bi(OH)₃) after drying in the oven at 110 °C for 24 hours as seen in Figure 3a and 3b, respectively. After calcination at 600 °C for 1 h, the white powder changed its color to light yellow as seen in Figure 3c and 3d. The change in color indicated the formation of Bi₂O₃. As bismuth oxynitrate was used as a bismuth precursor as compared to previous reports that used bismuth nitrate [14-19], the reaction chemistry (with NH₄OH) is presented as follows:

\[
\begin{align*}
\text{Bi}_2\text{O}(\text{OH})_9(\text{NO}_3)_4 (s) + \text{HNO}_3 (aq) & \rightarrow 5 \text{Bi(NO}_3)_3 (aq) + \text{HNO}_3 (aq) + 10\text{H}_2\text{O} (l) \\
\text{Bi(NO}_3)_3 (aq) + 3\text{NH}_4\text{OH} (aq) & \rightarrow \text{Bi(OH)}_3 (s) + 3\text{NH}_4\text{NO}_3 (aq) \\
4 \text{Bi(OH)}_3 (s) & \rightarrow 2 \text{Bi}_2\text{O}_3 (s) + 6 \text{H}_2\text{O}
\end{align*}
\]

The XRD data for the synthesized Bi₂O₃ precipitate, using NH₄OH and NaOH, can be seen in Figure 4. When the Bi₂O₃ particles are synthesized using NH₄OH (Figure 4a), they seem to be in α-Bi₂O₃ phase. Iyyapushpam et al. [14] reported similar results, unfortunately no pH values were reported in their study. Later, Iyyapushpam et al. [15] reported the presence of γ-Bi₂O₃ using NH₄OH at pH 9.6.

![Figure 3. White product synthesized after heating the precipitate for 24 hours at 110 °C (a) using NH₄OH, and (b) using NaOH respectively. Pale yellow precipitate formed after calcination (c) of white powder formed using NH₄OH, and (d) of white powder formed using NaOH, respectively.](image-url)
and their study suggests that Bi$_2$O$_3$ synthesized at pH below 9.6 should be in γ-Bi$_2$O$_3$ phase. However, in this study the resultant reaction mixture pH was 9 and the phase of Bi$_2$O$_3$ obtained is α-Bi$_2$O$_3$. The calcination temperature used during the synthesis of Bi$_2$O$_3$ in the current study and by Iyyapushpam et al. [14] is higher than that used by Iyyapushpam et al. [15] which could be the reason for the formation of α-Bi$_2$O$_3$. It is known that α-Bi$_2$O$_3$ is a stable phase of bismuth oxide and other phases of Bi$_2$O$_3$ transform to the α-Bi$_2$O$_3$ phase under high temperature [19,23]. This indicates that both the resultant pH and the calcination temperature determine the phase of Bi$_2$O$_3$.

The XRD pattern for the Bi$_2$O$_3$ synthesized using NaOH is presented in Figure 4b. The phase of the Bi$_2$O$_3$ obtained using NaOH has a mixture of two phases. The most intensive peak 27.2° is close to the most intensive peak of both α-Bi$_2$O$_3$ and γ-Bi$_2$O$_3$[19]. On comparing the diffraction patterns (a) and (b) in Figure 4, it can be seen that there are two additional peaks in pattern (b) (marked with asterisk) that correspond to γ-Bi$_2$O$_3$[19]. This suggests that the material synthesized using NaOH is a mixture of both α-Bi$_2$O$_3$ and γ-Bi$_2$O$_3$, where α-Bi$_2$O$_3$ is the most dominant phase as seen from Figure 4b. Combining the results of this study with the previous study of Iyyapushpam et al. [14] suggests that during calcification the Bi$_2$O$_3$ first γ-Bi$_2$O$_3$ phase is formed and then it transforms into α-Bi$_2$O$_3$ phase. Therefore, the desired phase of Bi$_2$O$_3$ synthesized using precipitation method can be synthesized by regulating the calcification temperature alone.

FTIR spectra of Bi$_2$O$_3$ synthesized by precipitation method using NH$_4$OH and NaOH can be seen in Figure 5. The FTIR of the starting material (see Ref. [22]) shows sharp and intense vibration band at 1200-1700 cm$^{-1}$ indicating the presence of nitrate (NO$_3$) and has been discussed previously [22]. Peaks observed between 3200-3600 cm$^{-1}$ indicate the presence of OH groups [24,25]. The absence of dominant peaks between 1200-1700 cm$^{-1}$ and 3200-3600 cm$^{-1}$ in Figure 5 indicate the absence of both nitrate and hydroxide groups on the Bi$_2$O$_3$ surface. Moreover, the observed vibrational band between wavenumber 700-600 cm$^{-1}$ and at ~830 cm$^{-1}$ can be assigned to Bi–O–Bi vibration [24-27].

The SEM images of the Bi$_2$O$_3$ synthesized using NH$_4$OH show small plate like structures arranged in the flower like manner as seen in Figure 6a. It can be seen the flower like structure is made up of individual plate like structures having a thickness of ~20±10 nm. Duan et al. [28] synthesized similar flower like structures using bismuth oxide formate. Alternatively, the Bi$_2$O$_3$ synthesized using NaOH has a honeycomb like flower structure as presented in Figure 6b. Previously, Zhou et al. [9] synthesized similar flower like structure using VO$_3$ as a precursor to get the desired shape of Bi$_2$O$_3$ particles. Comparing Figure 6a and 6b it can be seen that the sheets of Bi$_2$O$_3$ particles synthesized using NH$_4$OH are thicker than that of the particles synthesized using NaOH. As compared to the Figure 6a the particles in Figure 6b show a densely packed porous structure, having pore of 500-800 nm.

The photocatalytic activity of the synthesized Bi$_2$O$_3$ particles was evaluated by studying the degradation of aqueous solution of methyl orange under artificial solar irradiation.
tion. Figure 7a shows the photodegradation efficiency of methyl orange in absence and presence of the two flower like Bi\(_2\)O\(_3\) synthesized using NaOH and NH\(_4\)OH, respectively, as a function of irradiation time. It can be seen that there was \(~64\%\) degradation of methyl orange in the presence of Bi\(_2\)O\(_3\) synthesized using NaOH as compared to \(~78\%\) degradation of methyl orange in presence of Bi\(_2\)O\(_3\) synthesized using NH\(_4\)OH in 120 min.

The kinetic evaluation of the photocatalyst was carried out by using the Langmuir-Hinshelwood model, for pseudo-first order kinetics given by the Equation (1) [14,15,29].

\[
-ln\left(\frac{C}{C_0}\right) = kt
\]  

(1)

where, \(C_0\) is the initial concentration of methyl orange, \(C\) is the concentration of methyl orange at different irradiation time, \(k\) is the kinetic constant of the reaction, and \(t\) is the irradiation time. Figure 7b shows the linear plot of \(-ln(C/C_0)\) vs \(t\) for the two flower like Bi\(_2\)O\(_3\) catalysts, respectively. It can be seen from the Figure 7b that the Bi\(_2\)O\(_3\) synthesized using NH\(_4\)OH had a higher kinetic rate constant of \(12.5\times10^{-3}\) s\(^{-1}\) as compared to Bi\(_2\)O\(_3\) synthesized using NaOH of \(8.8\times10^{-3}\) s\(^{-1}\). The kinetic rate constant of the Bi\(_2\)O\(_3\) synthesized using NH\(_4\)OH was greater than that previously reported by Iyyapushpam et al. [14]. The reasons for the lower activity of Bi\(_2\)O\(_3\) synthesized using NaOH is the presence of the partial \(\gamma\)-Bi\(_2\)O\(_3\) phase. It is known that the \(\gamma\)-Bi\(_2\)O\(_3\) has lower activity (about one order of magnitude) than that of \(\alpha\)-Bi\(_2\)O\(_3\) [14,15]. The catalytic activity of the Bi\(_2\)O\(_3\) synthesized using NaOH had a higher activity than that of pure \(\gamma\)-Bi\(_2\)O\(_3\) of \(3.3\times10^{-4}\) s\(^{-1}\) [15] and \(1.1\times10^{-4}\) s\(^{-1}\) [6].

4. Conclusions

Synthesis of Bi\(_2\)O\(_3\) using the precipitation method with different precipitating agents was studied. The use weak base (NH\(_4\)OH) for Bi\(_2\)O\(_3\) precipitation resulted in formation of plate

Figure 6. SEM images of bismuth oxide synthesized using (a) NH\(_4\)OH and (b) NaOH, respectively

Figure 7. (a) Photodegradation of methyl orange in presence and absence of Bi\(_2\)O\(_3\), and (b) kinetic linear simulation curves of the degradation of methyl orange in presence of Bi\(_2\)O\(_3\) particles synthesized using NaOH and NH\(_4\)OH, respectively.
type structures arranged in the form of flowers. The use of strong base (NaOH) for precipitation of Bi$_2$O$_3$ led to formation of honeycomb like flower structure. Moreover, the photocatalytic activity of Bi$_2$O$_3$ synthesized using NH$_4$OH had better activity on degradation of methyl orange than the Bi$_2$O$_3$ synthesized using NaOH. The activity was dependent on the crystal structure of the Bi$_2$O$_3$.

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