Synthesis of $\alpha$-Bismuth oxide using solution combustion method and its photocatalytic properties

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Abstract. The monoclinic bismuth oxide was prepared by the solution combustion method using bismuthyl nitrate as the raw material and citric acid as fuel. The synthesis process consisted of the formation of a clear transparent solution and the formation of white powder after heating the mixture at 250 °C for 2 hours. The yellow pale crystalline materials were obtained after calcination of the white powder at 600 °C for 80 minutes. Furthermore, the photocatalytic activity of the product was also studied using methyl orange as a model pollutant. The result showed that the coral reef-like bismuth oxide was able to degrade 50 mL methyl orange (5 ppm) by 37.8 % within 12 hours irradiation using 75-watt tungsten lamp.

1. Introduction

Use of inorganic semiconductor catalysts for the degradation of environmental wastes has gained extensive research interest recently [1, 2]. Bismuth oxide is one of the non-TiO$_2$ semiconductor catalysts that have shown effective catalytic properties for the degradation of environmental wastes [2-5]. Bismuth oxide (Bi$_2$O$_3$) is a pale yellow solid, having a melting point of about 825 °C [6] and very easily reduced to Bi-metal when being heated with carbon or hydrogen [7]. Bismuth oxide (Bi$_2$O$_3$) has excellent optical and electrical properties such as wide band-gap, high refractive index, high dielectric permittivity and high photoconductivity [8]. Other than photocatalysis bismuth oxide can also be used in various other applications such as gas sensing [9] and superconductors [10].

Bismuth oxide exists in five different polymorphs, $\alpha$-Bi$_2$O$_3$, $\beta$-Bi$_2$O$_3$, $\gamma$-Bi$_2$O$_3$, $\delta$-Bi$_2$O$_3$ and $\epsilon$-Bi$_2$O$_3$ respectively, wherein each polymorph has different properties [7]. The variation of the properties among the types closely relates to the stability of the material to the temperature. In the low temperature, the type of $\alpha$-Bi$_2$O$_3$ (monoclinic) is formed, while there are four phases of Bi$_2$O$_3$ stable at high temperatures (more than 600 °C) i.e. $\beta$-Bi$_2$O$_3$ (tetragonal), $\gamma$-Bi$_2$O$_3$ (body centred cubic), $\delta$-Bi$_2$O$_3$ (face centred cubic) and $\epsilon$-Bi$_2$O$_3$ (triclinic) [11]. $\delta$-Bi$_2$O$_3$ phase transforms into $\beta$-Bi$_2$O$_3$ or $\gamma$-Bi$_2$O$_3$ if being heated at 650 °C or 639 °C, respectively. Both $\alpha$-Bi$_2$O$_3$ and $\delta$-Bi$_2$O$_3$ phases are correspondingly stable at low and high temperature. In contrast, the other phases are metastable; however, stabilization of these materials can be conducted by doping with impurities [12]. Various transitional metals have been doped in Bi$_2$O$_3$ to observe its catalytic properties [4, 5, 13]. The $\beta$-Bi$_2$O$_3$ is one of the most commonly used polymorph for photocatalytic applications [1, 4, 13, 14] whereas use of $\alpha$-bismuth oxide has just been recently reported [15].
Bismuth oxide can be synthesised by several methods that include sol-gel [6], deposition [16], solution combustion [17], hydrothermal [18], and fusion spray method [19]. Solution combustion has several advantages such as easy processing, use of low temperatures, easy to control the particle size leading to shorter reaction times, high product purity, crystallinity and nanosized powder with high specific surface area [20]. In the current study bismuth oxide is synthesised by solution combustion method using bismuthyl nitrate as a raw material and citric acid as a fuel. The obtained bismuth oxide was characterized for its morphology, crystal structure and surface functional groups using SEM-EDX, XRD and FTIR respectively. Furthermore, the photocatalytic activity of the bismuth oxide particles was demonstrated by degradation of methyl orange dye.

2. Experimental Methods

2.1. Materials
Bismuth(II) subnitrate (Bi$_5$O(OH)$_9$(NO$_3$)$_4$), nitric acid (65%, v/v), NH$_4$OH (25%, v/v), polyethylene glycol (PEG 20000), citric acid, methyl orange and aquadest were of analytical grade (except for aquadest) were purchased from Merck Index, Indonesia.

2.2. Synthesis of Bismuth Oxide using Solution Combustion Method
The synthesis procedure for Bi$_2$O$_3$ follows the solution combustion method reported by La et al. [20] with some modifications. 2.91 g Bi$_5$O(OH)$_9$(NO$_3$)$_4$ and 1.471 g citric acid were dissolved in 10 ml HNO$_3$. The mixture was then added 0.04 g PEG 20000 and stirring 350 rpm for 5 minutes. A clear transparent solution was formed, that was subsequently heated at 250 °C for 2 hours. A turbid white suspension was formed that was air cooled to room temperature. The white precipitant was filtered from solution and washed using distilled water to remove all the acid. The white powder was then dried in the oven for 24 hour at 110 °C. The sample was later calcined at 600 °C for 80 minutes. A yellow powder was obtained after calcination and used for further characterisation.

2.3. Characterisation of the Samples
The starting material bismuth(II) subnitrate and yellow powder were characterized to observe complete conversion. The characterisation techniques used were XRD, SEM-EDS and FTIR. X-ray diffractogram was obtained using XRD Bruker with CuK radiation ($\lambda = 0.15418$ nm) at 40 kV and 30 mA, and with 20 ranging from 10° to 60°. The morphology of the samples were identified using SEM-EDX (JEOL-JSM-G510LV). The FTIR spectra were recorded using FTIR Prestige 21 (Shimadzu) between wavenumber (400-4000 cm$^{-1}$).

2.4. Photocatalytic Activity on Methyl Orange Degradation
The absorbance peak of methyl orange was determined by observing the absorbance in the visible range of 300-700 nm using a UV-Vis spectrophotometer (Shimadzu UV-1201). The maximum absorbance was observed at a wavelength of 462 nm which further used for monitoring the reaction end point.

Photocatalytic activity of the synthesised Bi$_2$O$_3$ particles was conducted using the following procedure. 0.1 g sample bismuth oxide was added into 50 mL methyl orange solution (5 ppm) and stirred 600 rpm. This sample was then irradiated with tungsten lamp 75 watt (1.4-3.6 eV) and analysed after a time interval of 2 hours for maximum reaction time of 12 hours. A control was carried out with the degradation experiment without any Bi$_2$O$_3$ particles. The Bi$_5$O(OH)$_9$(NO$_3$)$_4$ was also tested as a control to observe any catalytic activity (only one experiment for 12 hours was carried out for Bi$_5$O(OH)$_9$(NO$_3$)$_4$). All experiments were performed in duplets.

3. Results and Discussion

3.1. Synthesis of bismuth oxide using combustion method
Synthesis of bismuth oxide using bismuth(II) subnitrate as the raw material produced pale white powder after drying it in oven for 24 hour at 110 °C as shown in Figure 1a. The color of the powder turned to be yellow when calcination at 600 °C for 80 minutes was applied as shown in Figure 1b. This yellow color powder indicated that bismuth oxide was formed.

Figure 1. a) The white powder product after heating at 110 °C for 24 hour in oven, b) The yellow powder product after calcination of the white powder product at 600 °C for 80 minutes.

3.2. X-Ray Diffraction (XRD)

Figure 2 presents the diffractograms of bismuth(II) subnitrate and bismuth oxide, respectively. The XRD pattern in Figure 2a shows three intense peaks at 2θ values of 25.0°, 27.8° and 42.0° respectively, corresponding to bismuth(II) subnitrate [21]. However the pattern in Figure 2b shows intense peaks at 2θ values of 27.5°, 33.2° and 33.4° corresponding to that of α-bismuth oxide [22]. The α-bismuth oxide thus synthesised has a monoclinic structure having the lattice and the angular parameters as \(a = 5.8499(3), b = 8.1698(4),\) and \(c = 7.5123(3)\) are \(\alpha = 90°, \beta = 112.988(4)°\) and \(\gamma = 90°\) respectively (JCPDS No: 76-1730). These lattices are consistent with the product formed. This results are also in good agreement with previous literature [15]. The absence of peaks at 25.0° in Figure 2b indicates absence of the bismuth(II) subnitrate in the product.

Figure 2. XRD patterns of a) bismuthyl nitrate and b) bismuth oxide synthesised using solution combustion method.
3.3. Fourier Transform Infrared (FTIR)
The IR spectra of the bismuth(II) subnitrate and bismuth oxide are shown in Figure 3. The peak at 3200-3600 cm\(^{-1}\) is a characteristic stretch vibration frequency of O-H [23]. This vibration mode is observed in both samples; however, the intensity of this peak decreases in the product. The presence of OH vibration mode observed in the product could be due to the incomplete reaction of raw material became bismuth oxide. Furthermore, significant decrease is also observed in the FTIR spectra of the product for vibration mode at 1200 – 1700 cm\(^{-1}\) which is a characteristic for NO\(_3\) - group even barely visible [6]. Meanwhile, the broad peak at 700 – 400 cm\(^{-1}\) originating from the metal-oxygen (Bi-O-Bi) vibration [6, 24] is still observed. Therefore, the FTIR results confirm the presence of bismuth oxide in synthesised in the product free of any unreacted bismuth(II) subnitrate.

![FTIR spectra of (a) bismuth(II) subnitrate and (b) bismuth oxide](image)

**Figure 3.** FTIR spectra of (a) bismuth(II) subnitrate and (b) bismuth oxide

3.4. Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)
Figure 4 shows the SEM images of bismuth(II) subnitrate and the resulting product of \(\alpha\)-bismuth oxide. It can be seen in Figure 4a that the shape of bismuth(II) subnitrate is briquette with the size of 8 \(\mu\text{m}\). Meanwhile, the morphology of \(\alpha\)-bismuth oxide synthesized using solution combustion method shows coral reefs like consisting of agglomerating small materials. Xia \textit{et al} [19] observed similar morphology for \(\alpha\)-bismuth oxide synthesized using fusion spraying method. The absence of wire-like structure of bismuth(II) subnitrate in Figure 4b shows complete removal of bismuth(II) subnitrate from the product. The in situ EDX analysis of \(\alpha\)-bismuth oxide shows absence of the nitrogen peak confirming the absence of bismuth(II) subnitrate in the product (figure 5).
3.5. Photocatalytic Activity

α-Bismuth oxide was tested as a photocatalyst for the degradation of methyl orange under different illumination time interval of 2 hours for reaction time of 12 hours under tungsten lamp irradiation. Photocatalysis was confirmed by studying the dye degradation using α-bismuth oxide without irradiation with tungsten lamp as compared to tungsten lamp irradiation. The result presented in the Figure 6 shows that the degradation (37.83%) of methyl orange using bismuth oxide during 12 hours under light tungsten irradiation. The maximum degradation was obtained after 12 hours irradiation which is the maximum of the time limit working. A linear trend is observed in the degradation of methyl orange in the presence of α-bismuth oxide.

A comparison to observe any catalytic activity of bismuth(II) subnitrate was also conducted. It was observed that the white bismuth(II) subnitrate turned orange in colour when suspended in 5 ppm methyl orange solution. This indicates that the dye is adsorbed on the surface of bismuth(II) subnitrate rather than degradation. No such change in colour of α-bismuth oxide (i.e. from yellow to orange) was observed confirming photocatalytic degradation of the dye. These results proved that the α-bismuth oxide synthesized using the solution combustion method can be used as a photocatalyst. The photocatalytic performance of α-bismuth oxide observed in this study is less than that observed for γ-bismuth oxide prepared by a simple chemical route [25].
4. Conclusion
Synthesis of bismuth oxide using solution combustion method produced α-bismuth oxide material which has a monoclinic structure with irregular shapes (coral reefs like structure) consisting of the small agglomerate particles. The synthesised α-bismuth oxide demonstrated photocatalytic activity in decomposition of methyl orange. The result indicates that this material is potential for photocatalyst for dye degradation.

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