Visible light responsive heterostructured α-Bi$_2$O$_3$/ZnO doped β-Bi$_2$O$_3$ photocatalyst for remediation of organic pollutants

Gurpreet Kaur*, Seema Sharmab,*, Priti Bansalc,*

αResearch Scholar of I.K. Gujral Punjab Technical University, Jalandhar-Kapurthala Highway, Kapurthala 144603, India, Tel. +91 91158 45087, email: gurpreet.kaur5087@gmail.com (G. Kaur)

bDepartment of Chemistry, Maharaja Ranjit Singh Punjab Technical University, Bathinda 151001, India, Tel. +91 94171 14169, email: paperpubseema@gmail.com (S. Sharma)

cDepartment of Applied Sciences, YCoE, Punjabi University Guru Kashi Campus, Talwandi Sabo 151302, Bathinda, India, Tel. +91 94175 40285; Fax +91 1655 220253; email: preet2anand@yahoo.co.in (P. Bansal)

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ABSTRACT

Novel visible-light active α-Bi$_2$O$_3$/ZnO doped β-Bi$_2$O$_3$ (ZB) photocatalyst was synthesized at different temperatures 400°C (ZB4), 500°C (ZB5), and 600°C (ZB6) by modified sol–gel method. The structural, morphological, compositional, and optical properties of synthesized photocatalyst were characterized using X-ray powder diffraction, field emission scanning electron microscopy, energy dispersive X-rays spectroscopy, Fourier transform infrared spectroscopy, and UV-vis spectroscopy. With an increase in calcination temperature, the bandgap of the prepared photocatalyst increases, and metastable β-phase Bi$_2$O$_3$ changes to α-phase. The photocatalytic activity was evaluated using Alizarin Red S (ARS) as a model organic compound. The rate of degradation was estimated from residual concentration spectrophotometrically. The results revealed that with an increase in calcination temperature, the photocatalytic activity of synthesized ZB photocatalyst decreases. Maximum decolorization efficiency (88%) was shown by the photocatalyst prepared at 400°C which is 29% and 37% higher than that of photocatalyst prepared at 500°C and 600°C, respectively.

Keywords: ZnO; Bi$_2$O$_3$; Photocatalyst; Alizarin Red S; Visible light

1. Introduction

Inorganic semiconductor-based photocatalysis has emerged as a “green” technology for the photocatalytic degradation of recalcitrant organic water pollutants [1,2]. Many semiconductor metal oxides such as TiO$_2$, ZnO, Bi$_2$O$_3$, WO$_3$, Nb$_2$O$_5$, CuO, MgO, Fe$_2$O$_3$, SnO$_2$, UV/Fe$_2$O$_3$, Fe$_2$O$_3$/sunlight [3–7], and metal sulfides such as ZnS, CdS, Bi$_2$S$_3$ [8–10] have been employed as photocatalyst for pollutants degradation. Among them, TiO$_2$ and ZnO have been extensively used as photocatalysts due to their excellent optical and electronic properties [11–13]. But, TiO$_2$ and ZnO can be stimulated by ultraviolet (UV) light due to their wide bandgap (3.37 eV) and this factor greatly limits their photocatalytic application under visible light irradiations [14–16]. Bi$_2$O$_3$ is another widely used photocatalyst, exists in six crystallographic polymorphic forms symbolized as α-, β-, γ-, δ-, ε-, and ω and has bandgap ranging from 2.0 to 3.96 eV depending upon the crystalline phase formed [17–21]. But Bi$_2$O$_3$ shows poor photocatalytic activity due to hasty recombination of the photoinduced electron-hole pairs [22,23].
The photocatalytic activity of Bi\textsubscript{2}O\textsubscript{3} is improved by doping with metal ions. Doping of semiconductor oxides helps to increase the lifetime of photogenerated electrons and holes which act as trapping centers close to the conduction band [24]. Bi\textsubscript{2}O\textsubscript{3} doped with transition metal (Pb\textsuperscript{2+}, V\textsuperscript{5+}, Ag\textsuperscript{+}, and Co\textsuperscript{2+}) showed higher photocatalytic activity than bare Bi\textsubscript{2}O\textsubscript{3} under visible light [25]. The metastable Bi\textsubscript{2}O\textsubscript{3} has been proved to be the best photocatalytic crystalline form due to its lower bandgap energy (~2.5 eV) [26]. Photocatalytic activity of β-Bi\textsubscript{2}O\textsubscript{3} can be further enhanced by introducing metal atoms such as Ag, Fe, Au, Pb, and C [27]. The best results for metal doping can be obtained when the radius of doping metal is close to that of other metal, to enable its incorporation into lattice sites [28]. A few studies have been reported related to the doping of Bi\textsubscript{2}O\textsubscript{3} semiconductor with ZnO. Chen et al. [29] have examined the photocatalytic activity of ZnO doped Bi\textsubscript{2}O\textsubscript{3} prepared by spray pyrolysis method for the treatment of methyl orange. Hou et al. [30] investigated the photocatalytic decomposition of methylene blue using Bi\textsubscript{3}ZnO\textsubscript{5} synthesized by a solid-state reaction method.

Besides doping, more attention has been given to the design and synthesis of heterostructured catalysts. To date, large numbers of efficient heterostructures have been developed and used for photocatalytic degradation of various organic pollutants because of the advantage over their corresponding single components. For example, AgI/WO\textsubscript{3} [31], g-C\textsubscript{3}N\textsubscript{4} [32], and rGO/TiO\textsubscript{2} [33] photocatalysts have been prepared for the degradation of different organic pollutants. MoSe\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} heterojunction exhibits enhanced photocatalytic activity because of high oxygen evolution [34]. So far, a variety of Z-scheme photocatalysts have been constructed and explored for energy and environmental applications. For example, Bi\textsubscript{3}S\textsubscript{5}/BiVO\textsubscript{4}/MgInS\textsubscript{3} [35], Ag/g-C\textsubscript{3}N\textsubscript{4}(CN)/Bi\textsubscript{2}TaO\textsubscript{6}(BTO) [36], and MoS\textsubscript{2}/QD/g-C\textsubscript{3}N\textsubscript{4} [37] showed excellent photocatalytic activity for the degradation of carbamazepine, sulfamethoxazole, and rhodamine B, respectively. g-C\textsubscript{3}N\textsubscript{4}/Ag/MeO\textsubscript{2}/Ag\textsubscript{3}PO\textsubscript{4} composite photocatalyst exhibits superior solar-driven oxygen evolution [38].

To the best of our knowledge, the synthesis, characterization and application of heterostructured α- and β-form of Bi\textsubscript{2}O\textsubscript{3} doped with ZnO photocatalyst has not been reported. In the present work, heterostructured α-Bi\textsubscript{2}O\textsubscript{3}/ZnO doped β-Bi\textsubscript{2}O\textsubscript{3} has been prepared and characterized. Its photocatalytic activity has been evaluated using ARS as a model pollutant.

### 2. Experimental

#### 2.1. Catalyst preparation

The photocatalyst was prepared by modified sol-gel method with a molar ratio of Bi:Zn fixed at 1:0.25, using bismuth nitrate pentahydrate (Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O), zinc nitrate hexahydrate (Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), dextrose (C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}), ammonium solution (25% with specific gravity 0.91), and nitric acid (98 wt.%) (AR grade, Loba Chemie Pvt., Ltd.). Bismuth nitrate pentahydrate was dissolved in 100 mL of HNO\textsubscript{3} solution (60% v/v, HNO\textsubscript{3}) to avoid hydrolyzation of Bi\textsuperscript{3+} ions. Further 80 mL of ammonia solution was added under constant stirring, the white precipitate formed was washed with double distilled water several times and was refluxed at 80°C for 4 h in 200 mL solution prepared by adding 100 mL of 0.25 M dextrose solution and 100 mL of 0.25 M zinc nitrate solution. After refluxing, the solution was evaporated on a water bath until the formation of shiny chocolate colored gel. The resulting gel was calcined at different temperatures (400°C, 500°C, and 600°C) for 1 h to obtain a yellow colored powder.

#### 2.2. Characterization

X-ray diffraction (XRD) pattern of the prepared photocatalyst was recorded in the 20 scan range of 20°–80° using APEX-II CCD diffractometer, Bruker, United States (Cu Ka radiations) operated at 40 kV and 30 mA. The morphology of the samples was examined with field emission scanning electron microscopy (FE-SEM, Carl Zeiss SMARTSEM® V05.06, Carl Zeiss, Germany) with energy dispersive spectra (EDS, XFlash® 6/1100, Bruker, United States). The chemical structure and composition of the prepared samples were analyzed by Fourier transform infrared (FTIR) spectroscopy using Spectrum 2, Perkin-Elmer, United States spectrometer. The UV-vis absorbance spectra were obtained using UV-1650PC spectrophotometer, Shimadzu, Japan in the range of 200–800 nm.

#### 2.3. Photocatalytic studies

Photochemical degradation experiments were carried in 500 mL vessel equipped with water circulation system placed in a specially designed four-chambered photoreactor, each chamber equipped with 23 W LED bulbs (2,300 lm) with emission in the wavelength range between 480 and 600 nm. During the irradiation, magnetic stirrers and aquarium aerators were used for homogeneous mixing and aeration of the reaction mixture, respectively. The irradiance remains constant throughout the experiment and was found to be 90 μmol/m²/s. The absorption spectra of the dye solution were recorded using a UV-vis spectrophotometer. For the photocatalytic activity measurements, 0.1 g of photocatalyst (ZB4, ZB5, and ZB6) was added into 100 mL of ARS dye solution (20 mg/L at pH = neutral (6.7)). Before the illumination under visible light, the solution was stirred in dark for 20 min to obtain good dispersion and establish adsorption/desorption equilibrium between the photocatalyst and ARS dye. The solution under constant stirring and aeration was illuminated for 13 h under visible light irradiation. During the experiment, at certain time intervals, samples were withdrawn with the help of a syringe and filtered through a 0.45 μm Whatman syringe filter to record absorption spectra of degraded dye solution using UV-vis spectrophotometer. The degradation efficiency (%) was calculated by using the following equation:

\[
\text{Degradation efficiency } (\%) = \left(1 - \frac{A}{A_0}\right) \times 100 \tag{1}
\]

where \(A_0\) is the initial absorbance of ARS dye and \(A\) is the variable absorbance of ARS dye after different intervals of photo-irradiation [39, 40].
3. Results and discussion

3.1. XRD analysis

The crystallinity, crystal phases of synthesized nano photocatalyst, and the effect of calcination were examined by XRD as shown in Fig. 1. From XRD pattern and corresponding 20 values of diffraction peaks, it can be confirmed that heterojunction of α-Bi₂O₃ (JCPDS card number 71-2274) and ZnO doped β-Bi₂O₃ (JCPDS card number 43-0449) is formed at temperature 400°C. Zn²⁺ (0.74 Å) can substitute Bi³⁺ ionic sites (1.17 Å) because of its smaller ionic radius [29]. However, with an increase in calcination temperature the metastable β-Bi₂O₃ changes slowly to α-Bi₂O₃ which is confirmed as the intensity of peak at 27.4 increases in ZB6 sample in comparison to ZB4 and ZB5. Moreover, peak at 37.6° (1 1 2) appears in ZB5 corresponding to α-Bi₂O₃ and its intensity increases in ZB6. Two more peaks at 35° (2 1 0) and 62.9° (0 5 2) corresponding to α-Bi₂O₃ appear in ZB6. The crystallite size was estimated by applying the Scherrer equation \(D = \frac{K \lambda}{\beta \cos \theta}\) to the full width at half-maximum (FWHM) of the (2 0 1) peak, where \(\beta\) is the half-height width of the diffraction peak, \(K = 0.89\) is a coefficient, \(\theta\) is the diffraction angle (27.96°), and \(\lambda\) is the X-ray wavelength corresponding to the Cu Kα radiations (\(\lambda = 1.5406 \, \text{Å}\)) [40,41]. The mean size of nanoparticles calculated by the Debye–Scherrer formula was found to be ~ 40–50 nm.

3.2. FESEM and EDX analysis

The surface morphology of prepared photocatalyst was analyzed by FESEM (Fig. 2). The FESEM images of prepared photocatalyst show the formation of irregularly shaped clusters of nanoparticles. With the increase in temperature, agglomeration increases. At 600°C, there is the appearance of a flowery arrangement constituted with a bean-shaped cluster decorated densely by nano-grain sized particles. The EDS spectrum of prepared photocatalyst showed Bi, Zn, O peaks indicating that the prepared sample was composed of Bi, Zn, and O elements (Fig. 2). Furthermore, no peak related to any impurity was detected in the EDS spectrum which confirms that the synthesized photocatalyst is pure.

3.3. FTIR analysis

The chemical composition of the prepared photocatalyst was examined by Fourier transform infrared (FTIR) spectroscopy (Fig. 3). The peak around 685 cm⁻¹ is assigned to the Bi–O stretching vibration of the non-bridging oxygen of the
3.4. UV-visible analysis

The optical properties of the synthesized photocatalyst were examined by UV-vis spectrum (Fig. 4) which depicts a strong absorption peak at 417, 409, and 403 nm (defined by the edge at the intersection of wavelength through extrapolation of the horizontal and sharply rising portions of the curves) for ZB4, ZB5, and ZB6, respectively [30]. The bandgap energy of the photocatalyst was calculated using the following equation:

\[
\text{Bandgap (eV)} = \frac{1,240}{\text{Wavelength (nm)}} \quad [4,44]
\]

The bandgap of ZB4, ZB5, and ZB6 sample is found to be 2.97, 3.03, and 3.07 eV from the absorption edge. The decrease in absorbance with an increase in calcination temperature is due to the change of β-form (bandgap 2.5 eV) to α-form (bandgap 2.9 eV) of Bi\(_2\)O\(_3\). Moreover, the bandgap of the prepared photocatalyst is more than the pure form of Bi\(_2\)O\(_3\) which confirms its doping with ZnO having bandgap 3.37 eV.

3.5. Photocatalytic activity of the prepared photocatalyst

The photocatalytic activity of prepared photocatalyst was evaluated by photo-degradation of widely used textile dye, Alizarin Red S (sodium alizarin sulfonate, C\(_{14}\)H\(_{6}\)Na\(_2\)O\(_7\)S) under visible light irradiation. It is a water-soluble anthraquinone dye and its release in the environment poses a threat to human beings and animal life [45–48]. The activities of the different (ZB4, ZB5, and ZB6) photocatalysts were evaluated by monitoring the UV-vis spectrum of irradiated ARS dye solution. Fig. 5 shows a time-dependent UV-vis spectrum of ARS dye during visible light photoirradiation with a significant decrease in absorption intensity with an increase in irradiation time. The spectra of ARS dye shows a peak at 516 nm in the visible region and two narrow peaks at 334 and 261 nm in the UV region. The rate of ARS decolorization was monitored for a decrease in the intensity of
prominent peak at $\lambda_{\text{max}} = 516$ nm indicating the degradation of chromatophoric groups of ARS dye [49,50]. The decolorization efficiency was maximum with ZB4 (88%) and only 59% and 51% decolorization was observed with ZB5 and ZB6 within 13 h, respectively. The degradation efficiency of the ARS dye was observed for the decrease in intensity of two narrow peaks at 334 and 261 nm (related to unsaturated bonds). It can also be seen that maximum degradation efficiency was found with ZB4 as compared to ZB5 and ZB6 as shown in Fig. 6.

3.6. Photocatalytic degradation mechanism

Fig. 7 shows the schematic illustration of the photocatalytic mechanism of ZB4 photocatalyst. The feasibility of a photocatalytic activity depends mainly on positions of the valence band maximum and conduction band minimum. The valence band (VB) and conduction band (CB) potentials can be calculated by using the following equation:

$$E_{CB} = X - E' - 0.5 E_g$$  \hspace{1cm} (3)

where $X$ is the absolute electronegativity of the semiconductor, (X value for Bi$_2$O$_3$ is 5.986 eV and for ZnO is 5.79 eV), $E'$ is the energy of free electrons on the hydrogen scale (~4.5 eV), $E_g$ is the bandgap energy of semiconductor and $E_{CB}$ can be determined by $E_{CB} = E_{VB} - E_g$ [26,51–53]. The conduction band (CB) and valence band (VB) potentials of ZnO, ZB4, ZB5, and ZB6 are given in Table 1.

On irradiation with light conduction band electrons (e$^-$) and valence band holes (h$^+$) are generated in the photocatalyst. The conduction band (CB) of doped material is higher in position than ZB4 which can trap electrons (e$^-$) from conduction band (CB) of semiconductor for the photoreduction of O$_2$ to produce superoxide radical anion ($O_2^-$) and on protonation further yields HOOO$^*$. However, the formed photogenerated holes (h$^+$) reacts with OH$^-$ or H$_2$O and oxidize them into OH$^*$ radicals. The resulting OH$^*$ radicals, being highly active and strongly oxidizing species are responsible for the oxidation of ARS dye into simple end-products (such as CO$_2$, O$_2$, etc.). These reactions can be summarized in the following steps [27,46,54,55]:

$$\text{ZnO/Bi}_2\text{O}_3 \text{ + hv} \rightarrow e^- (\text{CB}) + h^+ (\text{VB})$$  \hspace{1cm} (4)

$$\text{OH}^- + h^+ (\text{VB}) \rightarrow \text{OH}^*$$  \hspace{1cm} (5)

$$\text{H}_2\text{O} + h^+ (\text{VB}) \rightarrow \text{OH}^* + \text{H}^+$$  \hspace{1cm} (6)

$$\text{O}_2 + e^- (\text{CB}) \rightarrow \text{O}_2^-$$  \hspace{1cm} (7)

$$\text{O}_2^- + \text{H}^+ \rightarrow \text{HO}_2^-$$  \hspace{1cm} (8)

$$\text{HO}_2^- + \text{HO}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}$$  \hspace{1cm} (9)

$$\text{H}_2\text{O}_2 + \text{O}_2^- \rightarrow \text{OH}^* + \text{OH}^- + \text{O}_2$$  \hspace{1cm} (10)
ARS dye $+ \text{OH}^-$ → Degradation products

ARS dye $+ \text{h}^+$ (VB) → Oxidation products

ARS dye $+ \text{e}^-$ (CB) → Reduction products

The difference in the photocatalytic efficiency of prepared catalysts at different calcination temperatures can be explained based on the position of the conduction band (CB) and valence band (VB) calculated as in Table 1. It is seen that the maximum difference in CB potential of ZnO and ZB4, that is, the trapped electrons ($\text{e}^-$) remain for a longer time in CB or other words maximum charge separation takes place in ZB4 which prevents electrons-holes recombination, hence maximum photodegradation was found to be with ZB4.

4. Conclusions

$\alpha$-Bi$_2$O$_3$/ZnO doped $\beta$-Bi$_2$O$_3$ photocatalyst at different calcination temperatures was synthesized by a modified sol–gel method. The results revealed that an increase in calcination temperature affects the phase and morphology of the prepared photocatalyst. The photodegradation efficiency of ZB4, ZB5, and ZB6 was evaluated using ARS dye as an organic pollutant under visible light irradiation. The maximum photocatalytic activity of ZB4 (88%) was observed as compared to ZB5 (59%) and ZB6 (51%) due to less bandgap (2.97 eV) and less phase transformation ($\beta$-Bi$_2$O$_3$ to $\alpha$-Bi$_2$O$_3$) at lower temperature, that is, 400°C. Therefore, ZB4 powder calcined at lower temperature, that is, 400°C acts as an efficient photocatalyst for the degradation of organic compounds in a neutral medium under visible light illumination.

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References


Table 1

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Bandgap (Eg) (eV)</th>
<th>Conduction band (CB) potential (eV)</th>
<th>Valence band (VB) potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>3.14</td>
<td>+2.860</td>
<td>−0.280</td>
</tr>
<tr>
<td>ZB4</td>
<td>2.97</td>
<td>+2.969</td>
<td>−0.001</td>
</tr>
<tr>
<td>ZB5</td>
<td>3.03</td>
<td>+3.001</td>
<td>−0.029</td>
</tr>
<tr>
<td>ZB6</td>
<td>3.07</td>
<td>+3.021</td>
<td>−0.049</td>
</tr>
</tbody>
</table>


