Original Article

Visible light mediated photocatalytic activity of cobalt doped Bi$_2$O$_3$ nanoparticles

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ABSTRACT

Herein, we suggest a novel chemical precipitation method to prepare different concentrations (0.05–0.25 M) of cobalt doped Bi$_2$O$_3$ nanoparticles. The prepared products exhibit excellent structural and optical properties. The influence of doping on the morphology of Bi$_2$O$_3$ was analyzed by FE-SEM and confirmed by HR-TEM. Furthermore, the photocatalytic activities of the samples were studied in the degradation of methylene blue under visible light irradiation. Compared to bare Bi$_2$O$_3$, 3% of cobalt doped Bi$_2$O$_3$ showed the highest degradation in 15 min of irradiation.

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1. Introduction

Recent past semiconductor oxides in the nano regime have consumed ample space in the development activities of modern science. The use of semiconductor oxides in nanoscale provides many unique advantages. Due to large volume–surface ratio, nano-sized materials show different physical and chemical properties in comparison to bulk materials [1]. Among the semiconductor oxides, Bi$_2$O$_3$ finds application in gas sensors, fuel cells and photocatalysis [2–8]. However, the higher band gap of Bi$_2$O$_3$ (2–3.9 eV) needs UV light for photodegradation, which prevents the usage of natural source sunlight. Therefore, the band gap tailoring is an important fact and can be achieved by metal ions doping. Generally, the metal ion doping makes radical changes in optical, electrical and magnetic properties of host material by altering its electronic structure. Many approaches have been followed so far to prepare Bi$_2$O$_3$ including co-precipitation, sol–gel, hydrothermal and colloid emulsion [9–12]. Among the different methods, chemical precipitation is cost effective and less time consuming [13]. Many reports have been published on Bi$_2$O$_3$ for photocatalytic applications; however, reports on the sunlight mediated photocatalytic activity of Bi$_2$O$_3$ are limited. Recently, Mail Schlesinger et al. have demonstrated the photocatalytic degradation of methylene blue by Bi$_2$O$_3$ nanostructure under visible light irradiation [14]. Hicham Oudghiri-Hassani et al. have reported the photocatalytic activity of α-Bi$_2$O$_3$ nanoparticles in the degradation of rodamine B under UV light irradiation [15]. Sini Kuriakose et al. have shown that cobalt doped ZnO nanorods exhibit highly enhanced methylene blue degradation than pure ZnO nanorods [16].
Herein, we present a chemical precipitation approach to synthesize different levels of cobalt doped \( \alpha \)-Bi\(_2\)O\(_3\) nanoparticles. The synthesized products were analyzed for their structural, optical and morphological characterizations. Furthermore, the prepared products were analyzed under sunlight irradiation by degradation of organic dye methylene blue (MB).

### 1.1. Synthesis of undoped and transition metals doped bismuth oxide nanoparticles

In the present study bismuth nitrate penta hydrate (Bi\(_2\)(NO\(_3\))\(_5\)·5H\(_2\)O), sodium hydroxide (NaOH), cobalt nitrate (Co(NO\(_3\))\(_2\)·6H\(_2\)O) were used. All chemicals were used as received in analytical reagent (AR) grade.

For the preparation of 0.05 M of cobalt doped Bi\(_2\)O\(_3\), 1.0 M of bismuth nitrate penta hydrate was dissolved in 50 ml of deionized water and then stirred the solution vigorously. Then, 0.05 g of cobalt dissolved in 50 ml of deionized water was mixed. Finally, 0.1 M of sodium hydroxide dissolved in 50 ml of deionized water was added drop wise to the above solution under stirring. The entire solution was stirred continuously for 4 h at 80°C until a light yellow precipitate was formed. Then, the obtained precipitate was washed repeatedly with deionized water and then filtered. The precipitate was dried in hot air oven at 100°C for 1 h, and then annealed at 500°C in a muffle furnace for 4 h to get phase pure cobalt doped bismuth oxide nanopowders. The same procedure was repeated for other concentrations of doping. In the preparation of pure Bi\(_2\)O\(_3\), the above stated procedure was adopted in the absence of cobalt.

### 1.2. Characterizations

The crystalline phase and particle size of undoped and Co doped Bi\(_2\)O\(_3\) nanoparticles were analyzed by powder X-ray diffraction (XRD) measurement which was carried out at room temperature by using the XPERT-PRO diffractometer system (scan step of 0.05° 2\(\theta\), counting time of 10.16 s per data point) equipped with a Cu tube for generating Cu K\(_\alpha\) radiation (\(k = 1.5406\) Å) as an incident beam in the 2\(\theta\)-theta mode over the range of 10–80°, operated at 40 kV and 30 mA. The band gap energy was measured at wavelength in the range of 250–900 nm by using UV–vis–NIR spectrophotometer Varian/carry 5000 equipped with an integrating sphere and the baseline correction was performed using a calibrated reference sample of powdered barium sulphate (BaSO\(_4\)). The photoluminescence (PL) emission spectra of the samples were recorded with a Spectrofluorimeter (Jobin Yvon, FLUOROLOG-FL3-11). The functional groups were determined by a SHIMADZU-8400 Fourier transform infrared spectrometer in which the IR spectra were recorded by diluting the milled powders in KBr and the wavelength between 4000 and 400 cm\(^{-1}\). The morphological analysis was performed by a JEOI: JSM-6390 scanning electron microscope (SEM) with the operating voltage of 20 kV and confirmed by JEOI transmission electron microscope (TEM) with operating voltage of 120 kV. Energy-dispersive spectrum (EDS) analysis of the products was performed during SEM measurements. The UV–vis absorption measurements of the products during photocatalytic measurements were recorded in the wavelength range of 400–800 nm using a Shimadzu UV1800 spectrometer.

### 1.3. Photocatalytic activity experiment

Photocatalytic activity of undoped and Co doped Bi\(_2\)O\(_3\) nanoparticles, was evaluated by studying photodegradation of MB dye solution under sunlight radiation. The undoped and Co doped Bi\(_2\)O\(_3\) nanoparticles (0.15 g) were taken in separate open borosilicate glasses of 250 mL capacity. 100 mL of BG dye solution of initial concentration (5 mg/L) were then added to those vessels and the contents were stirred keeping irradiated under sunlight. All the experiments were conducted between 11.00 am and 02.00 pm under direct sunlight and the solar intensity (1250 × 100 Lu ± 100) was almost constant. After predetermined time intervals, adequate quantity of solutions were taken out and centrifuged (Remi centrifuge, Model No: C-85414 with 3000 rpm). The concentration of BG in supernatant was analyzed using a Shimadzu UV1800 spectrophotometer by measuring the absorbance at respective \(\lambda_{\text{max}}\) of 646 nm. The percentage of degradation of BG dye was calculated from the following equation [17].

\[
\text{Percentage of degradation} = \frac{C_0 - C_t}{C_0} \times 100
\]

where \(C_0\) is the initial concentration of BG dye solutions (mg/L), \(C_t\) is the concentration of dye after irradiation after selected time interval (mg/L).

### 2. Results and discussion

#### 2.1. Structural studies

Fig. 1 shows the diffraction patterns of undoped and Co-doped \( \alpha \)-Bi\(_2\)O\(_3\) nanoparticles. All the products show the reflections from (120), (121), (112), (041), (321) and (220) planes enlightening the monoclinic crystal structure of Bi\(_2\)O\(_3\) (ICPDS: 71-0465). No reflections related to cobalt or oxides of cobalt are noted enlightening the formation of pure phase of Bi\(_2\)O\(_3\). However, the effect of doping implies a non monotonic shift in the diffraction patterns toward the higher angle region exhibiting the successful incorporation of cobalt in to Bi\(_2\)O\(_3\). The average crystallite sizes of the products were calculated using Scherer’s formula [17]. The calculated crystallite sizes and

![Fig. 1 – The magnified characteristic peaks of undoped and different concentrations of Co-doped \( \alpha \)-Bi\(_2\)O\(_3\) nanoparticles.](image-url)
2.2. UV–vis absorption spectra

The optical property of undoped and Co-doped α-Bi₂O₃ was studied by UV–vis absorption spectra. Fig. 2 displays the UV–vis absorption results of undoped and Co-doped α-Bi₂O₃. As seen in figure, on increasing the concentration of doping the absorption edges are shifted toward the longer wavelength region indicating decrease in the band gap of Bi₂O₃ on doping [18]. Furthermore, the intensity of absorption also increases as the concentration of doping increases. The band gap energies of undoped and cobalt doped α-Bi₂O₃ particle were explored by wavelength obtained from UV–vis absorption spectra using the usual equation [14] and the obtained values are presented in Table 2. As reported in the table, the value of band gap decreases gradually with an increase in the level of doping. As supportive information the doping concentration versus band gap graph was drawn and is presented as Fig. 2a.

2.3. Photoluminescence

For semiconductors, the photoluminescence (PL) spectra are related to the transfer behavior of the photo induced electrons and holes, so that it can reflect the separation and recombination of photo induced charge carriers [19]. Fig. 3 shows the room temperature photoluminescence spectra (excitation wavelength at 330 nm) of the undoped and different levels (0.05–0.25 M) of Co²⁺ doped α-Bi₂O₃ nanoparticles. It can be observed that all the samples show a bluish green emission peak centered at 466 nm, which could be ascribed to slight structural defect of the prepared samples [20]. However, the intensity of the bluish green emission decreases with an increase in the concentration of doping. Actually, transition metal doping can introduce shallow donor or acceptor levels, which may be responsible for quenching of band edge luminescence in the case of doped α-Bi₂O₃ nanostuctures. Generally, at a high Co²⁺ incorporation, the cobalt atoms have a tendency to form clusters around oxygen. The formation of these clusters will cause passivation of the surface of α-Bi₂O₃ and may provide competitive pathways for recombination.
resulting quenching of broad bluish green emission, which means that the structural defect concentration in Co\textasciitilde{}doped samples decreases with higher Co content.

2.4. Functional group analysis

Fourier transform infrared spectra of undoped and Co-doped \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} were recorded in the range of 4000–400 cm\textsuperscript{-1} as depicted in Fig. 4. All the samples show peaks of bending and stretching vibrations. The peak at about 566 cm\textsuperscript{-1} represents the Bi–O bonds and was shifted to a new position of 577 cm\textsuperscript{-1} on higher concentration of doping. The shifting can be ascribed to the change in the bond length that occurs when Co\textsuperscript{2+} ions substitute Bi\textsuperscript{3+} ions in the Bi\textsubscript{2}O\textsubscript{3} lattice. The obtained band shift on doping is exactly matched with the result reported by other research group [21]. Furthermore, the appearance of Peaks near 830 cm\textsuperscript{-1} and 1370–1390 cm\textsuperscript{-1} are representing the existence of nitrate (NO\textsubscript{3}) ion [22].

The presence of peaks between 1620 and 1640 cm\textsuperscript{-1} are due to the bending vibration of the absorbed water, and the peaks at around 3400–3500 cm\textsuperscript{-1} are attributed to the stretching vibration of absorbed hydroxyl function groups [23].

2.5. Field emission scanning electron microscopy (FE-SEM)

The surface morphology of the pure and Co-doped (0.15 M) \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} nanostructures was analyzed by FE-SEM. Fig. 5a clearly shows that pure Bi\textsubscript{2}O\textsubscript{3} shows the nano-sheet like morphology, whereas the Co-doped (0.15 M) \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} composed of many inter connected narrow nanoplates (Fig. 5c). The EDX spectrum (Fig. 5b) reveals no extra peaks related to elements other than constituents. Furthermore, the EDX result of doped product confirms the presence of dopant (cobalt) in the matrix in the nominal value (Fig. 5d).

Further, the morphology confirmation was made by TEM analysis. Fig. 6a shows the HR-TEM image of the \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} sample. As observed in the figure, the appearances of fringe patterns exhibit the growth of \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3}. Whereas, the HR-TEM image of doped \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} shows the presence of well resolved fringe patterns of \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} (Fig. 7a). The TEM micrograph of \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} exhibits sheet like morphology (Fig. 6b), whereas, the doped \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} shows the needle like particles with a little agglomeration (Fig. 7b). Furthermore, the SAED patterns of undoped and Co-doped \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} exhibit the diffraction rings corresponding to (121), (112), (041), (321) and (220) planes of \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} (Figs. 6c and 7c).

2.6. Evaluation of photocatalytic activity

The generation of photo induced electrons and holes as well as their separation, migration and capture by the reactive species is regarded as the basic process for the operation of semiconductor photocatalysts. Generally the photocatalytic activity of semiconductor photocatalysts not only depends on their electronic structure as well as depends on many other factors such as morphology, surface area and crystalline phase and size.

The photocatalytic activity of undoped and Co-doped (0.15 M) \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} was investigated using degradation of aqueous methylene blue (MB) dye solution. Fig. 8a and b shows the absorption spectra of MB dye using undoped and Co-doped \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} catalysts as a function of wavelength (400–800 nm) for various time intervals 0, 15, 30, 45, 60, 75, 90, 105, 120 and 135 min. The degradation effect was characterized by monitoring the absorption peak of MB dye centered at 664 nm.

From Fig. 9a and b, we can say that the maximum absorption peak (at 664 nm) decreases with increasing irradiation time. This illustrates that the MB dye concentration decreases in the presence of undoped and doped catalysts under solar light illumination. The decrease in the absorption of the mixed solution was due to the destruction of the homo and heteropoly aromatic rings present in the dye molecules.

The effect of doping on the catalytic performance of \( \alpha \)-Bi\textsubscript{2}O\textsubscript{3} was evaluated from the percentage degradation of the MB dye. The percentage of degradation was calculated from the usual formula. The Bi\textsubscript{2}O\textsubscript{3} doped with cobalt exhibits the best catalytic activity and the degradation of MB (97%) is almost complete after 135 min. In contrast pure Bi\textsubscript{2}O\textsubscript{3}...
Fig. 5 - SEM micrograph of (a) Bi$_2$O$_3$, (c) Co-doped Bi$_2$O$_3$ with (b and d) corresponding EDX spectrum.

Fig. 6 - (a) HR-TEM, (b) TEM and (c) SAED pattern of Bi$_2$O$_3$ nanoparticles.

Fig. 7 - (a) HR-TEM, (b) TEM and (c) SEAD pattern of Co-doped Bi$_2$O$_3$ nanoparticles.

degradation only 76.15% of MB after 135 min. The potential reason for the enhanced catalytic activity of doped Bi$_2$O$_3$ is its improved charge separation efficiency and larger amount of MB absorption. Along with this cobalt doping may extend the photoresponse to the visible region and improves the photocatalytic activity of Bi$_2$O$_3$. The process of photocatalytic degradation of an organic dye can be understood as follows. The initial stage involves adsorption of the organic dye onto
Fig. 8 – Time dependent UV absorption spectra of MB degradation by (a) undoped and (b) Co-doped α-Bi₂O₃ nanoparticles.

Fig. 9 – Photo catalytic degradation rates of MB under solar light irradiation and pseudo first order rate constant (K) for the photo decomposition of MB for (a) pure and (b) Co doped α-Bi₂O₃ nanoparticles.

the surface of Bi₂O₃ nanostructure. Irradiation of MB adsorbed Bi₂O₃ with sunlight leads to the pair creation (electron–hole). These photogenerated electrons in the conduction band of Bi₂O₃ interact with the oxygen molecules adsorbed on Bi₂O₃ to form superoxide anion radicals (O₂•⁻). The holes generated in the valence band of Bi₂O₃ react with the surface hydroxyl groups to form highly reactive hydroxyl radicals (OH•). The highly reactive hydroxyl radicals and superoxide radicals react with MB dye adsorbed on Bi₂O₃ and lead to its degradation resulting in its colorless form [24].

3. Conclusion

In summary, we report a simple chemical precipitation route for the fabrication of undoped and Co-doped α-Bi₂O₃ nanoparticles. The diffraction results confirmed the formation of Bi₂O₃. The morphologies of the products were analyzed by FE-SEM and confirmed by TEM analysis. The results of the photocatalytic activity reveal that Bi₂O₃ doped with cobalt is better able to degrade MB, due to its enhanced charge separation efficiency and visible light photosresponse.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


