

ORIGINAL ARTICLE

Impact of Transition Metal Doped Bismuth Oxide Nanocomposites on the Bandgap Energy for Photoanode Application

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ABSTRACT

Chemical co-precipitation approach has been successfully used to synthesize Bi₂O₃ and Zn/Bi₂O₃ nanoparticles. Bi₂O₃ exhibited a band gap energy of 1.78 eV, and Zn/Bi₂O₃ at 1 & 5% and band gaps of 1.83 eV & 1.99 eV respectively. The statistics unambiguously demonstrate that adding zinc dopant widens the energy gap. The cubic lattice structure of this crystal is produced by a powerful synergy between the zinc ions and bismuth oxide ions. The peaks showed well-aligned conspicuous diffraction peaks of the material with crystalline peaks at the (110) plane. The Bi₂O₃ patterns verified that the cubic crystal structure was successfully formed. With a classified orientation at the (110) plane, the synthesized material showed prominent peaks. The most noticeable peaks, with a strong orientation on the (110) plane, were recorded by the bismuth oxide material that was 1% doped. The FTIR peak at 811 cm⁻¹ indicates association with the Bi-O bond, thus verifying the existence of bismuth oxide. Additionally, the peak at 1394 cm⁻¹ corresponds to the C-H bond. The stretching vibrations of O-H were detected within the range of 3200 to 3445 cm⁻¹. The presence of a peak at 1635 cm⁻¹ indicates the utilization of H₂O in the experimental procedure, while vibrations of water molecules are observed in the range of 2311 to 2331 cm⁻¹.

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1 Introduction

Due to its wide range of possible applications in numerous fields, including sensors, supercapacitors, photovoltaics, photoanode, and photocatalysis, bismuth oxide has attracted substantial attention in scientific research [1].

Several methods have been used to synthesize the bismuth oxide. These include electrodeposition [2], chemical vapor deposition [3], thermal decomposition [4], sol-gel [5], flame spray pyrolysis [6], laser ablation [7], microwave [8], hydrothermal [9], solvothermal [10], solution combustion [11], thermal oxidation [12], and co-precipitation method [13].

Co-precipitation among all these methods is highly preferred. Using this method, the size of the nanoparticles can be controlled efficiently. It is the most convenient, inexpensive, and industrially viable technique for the preparation of NPs [14]. Among other metal semiconductor materials [15]–[27], bismuth oxide material has a wide range of application with excellent optical and structural properties.

A p-type semiconductor with a direct band gap of 2.8 eV is bismuth oxide. Unfortunately, when utilized alone, Bi₂O₃ shows little activity under visible light [28]. To enhance the visible light activity of Bi₂O₃ and improve the material's optical characteristics, it is therefore of significant interest to dope this material.

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Furthermore, when evaluating these materials for optoelectronic applications, the bandgap of Bi_2O_3 is quite important. Bismuth oxide has been seen to change into a major transition metal oxide with a variety of desirable characteristics when dopants are added. Doped bismuth oxide has a lot of promise for use in optical coatings, sensors, electrolyzes, ceramic membranes, solar cells, fuel cells, transparent ceramic glass production, and ceramic membranes.

As a result, the precise tuning of the bandgap in bismuth oxide depends critically on the presence of dopants [29]. Lithium [30], cerium [31], coumarin [32], ytterbium [33], vanadium [34], dysprosium and tantalum [35], and rare earth metals [28] have all been used as dopants in attempts to dope Bi_2O_3 for a range of purposes.

The objective of the current work is to use the chemical co-precipitation approach to examine the impact of transition metal zinc doping on the structural and optical characteristics of bismuth oxide. To do this, both the pure and doped nanoparticles have been examined using a variety of characterization techniques, such as X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), and UV-visible Spectroscopy. These methods enable a thorough investigation of the structural and optical modifications brought about by the zinc doping procedure in bismuth oxide.

2 Experimental Section

2.1 Materials

As starting materials, sodium hydroxide (NaOH), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), and bismuth nitrate ($\text{Bi}_2(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) were all employed. All the chemicals were of analytical grade and used as received from Sigma-Aldrich.

2.2 Synthesis of Zn-doped Bismuth Oxide Nanocomposites

Zinc-doped (1 and 5 mol %) Bi_2O_3 was made by mixing 30 mL of deionized water with 1 M bismuth nitrate. After that, 30 mL of deionized water containing the stoichiometric amount of zinc acetate was added while being stirred magnetically.

Additionally, the above-mentioned solution had 30 mL of deionized water and 0.1 M NaOH dissolved in it added dropwise while being stirred. A light-yellow precipitate formed after being magnetically agitated for 5 hours at 80°C with this mixed solution. The precipitate was then filtered after being repeatedly rinsed with deionized water. To create Zn-doped (1 and 5 mol%) Bi_2O_3 NPs, the precipitate was first dried for two hours at 100°C in an oven and then further annealed for three hours at 500°C in a muffle furnace. The same procedure was used to make pure Bi_2O_3 NPs without the use of zinc acetate.

3 Results and Discussions

3.1 Optical study of Bi_2O_3 and $\text{Zn}/\text{Bi}_2\text{O}_3$

Figure 1 displays the plots of the absorbance, transmittance, and reflectance data for the produced nanoparticles at various

zinc dopant molarities. All of the produced nanoparticles showed a similar pattern in the absorbance plot (Figure 1(S1)), with elevated absorbance data in the UV region and a drop in absorbance as the wavelength moved toward the visible-near infrared region.

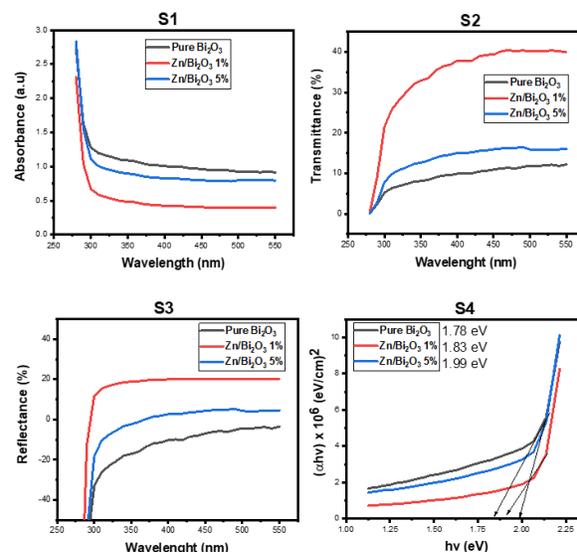


Figure 1: (S1-absorbance), (S2-transmittance), (S3-reflectance), and (S4-bandgap energy)

In comparison to undoped Bi_2O_3 , it was discovered that adding a small amount of zinc (1%) as a dopant reduced the absorbance of the Bi_2O_3 nanoparticles throughout the electromagnetic spectrum. Even beyond the (1%) doped zinc absorbance data, further increases in the zinc dopant (to 5%) dramatically enhance the absorbance data. The absorbance of the material rises with increasing electromagnetic light radiation and zinc molar concentration, which causes an increase in the absorbance of $\text{Zn}/\text{Bi}_2\text{O}_3$ at high doping levels. Bi_2O_3 doped with 5% zinc has a strong UV absorbance, which makes the material appropriate for p-n junction formation in solar cells and photovoltaic applications in general. Equation (1) was used to extrapolate the absorbance result to the transmittance data for all nanoparticles.

$$T = 10^{-A} \quad (1)$$

Figure 1(S2) depicts the transmittance plot of pure Bi_2O_3 and $\text{Zn}/\text{Bi}_2\text{O}_3$ nanoparticles produced at various zinc dopant molarities. The 1% transmittance rose as the wavelength increased in all synthesized nanoparticles, showing a consistent pattern. Bi_2O_3 materials were found to have much lower transmittance data when a higher concentration of zinc dopant (5%) was added, notably in the visible-near-infrared region. This makes it a good material for solar energy collectors and optical devices.

Figure 1(S3) shows the graphical data of the reflectance versus wavelength for materials produced from Bi_2O_3 and $\text{Zn}/\text{Bi}_2\text{O}_3$ at different zinc dopant molarities. It appears that $\text{Zn}/\text{Bi}_2\text{O}_3$ and Bi_2O_3 have low reflecting properties. Most materials' low

reflectivity makes them suitable for anti-reflective coatings and a potential component of solar control coatings.

The energy band gap (E_g) of Bi_2O_3 and $\text{Zn}/\text{Bi}_2\text{O}_3$ at varied zinc dopant molarity was deduced via Equation (2).

$$(ahv)^2 = A(hv - E_g) \quad (2)$$

Figure 1 (S4) shows a plot of $(ahv)^2$ against hv for Bi_2O_3 and $\text{Zn}/\text{Bi}_2\text{O}_3$ at varied zinc dopant molarity. The materials' energy band gap was calculated from this plot by projecting the straight section of the curve down to the hv axis at $(ahv)^2 = 0$. Bi_2O_3 exhibited a band gap energy of 1.78 eV, and $\text{Zn}/\text{Bi}_2\text{O}_3$ at 1% & 5% had band gaps of 1.83 eV & 1.99 eV respectively. The statistics unambiguously demonstrate that adding zinc dopant widens the energy gap. Bi_2O_3 and $\text{Zn}/\text{Bi}_2\text{O}_3$ are excellent promising materials for solar cell manufacturing, according to band gap statistics.

3.2 Structural study of Bi_2O_3 and $\text{Zn}/\text{Bi}_2\text{O}_3$

The synthesized nanoparticles' structural layout is shown in Figure 2. The cubic crystal structure in Figure 2's X-ray diffractograms has the JCPDS card number 01-074-2276. The cubic lattice structure of this crystal is produced by a powerful synergy between the zinc ions and bismuth oxide ions.

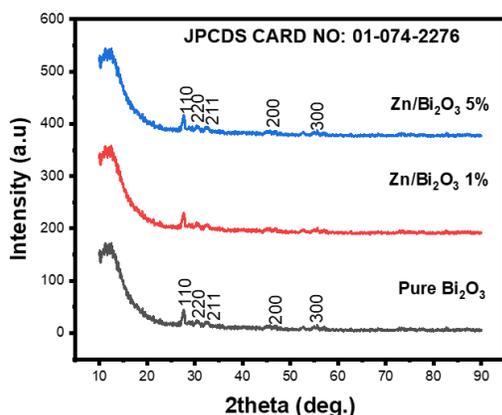


Figure 2: XRD patterns of Bi_2O_3 and $\text{Zn}/\text{Bi}_2\text{O}_3$

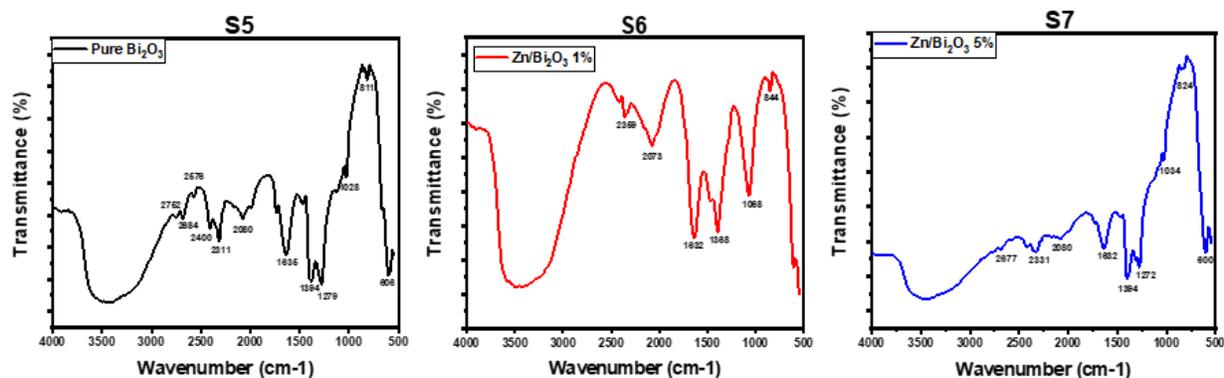


Figure 3: (S5-FTIR of Bi_2O_3), (S6- FTIR of $\text{Zn}/\text{Bi}_2\text{O}_3$ 1%), and (S7- FTIR of $\text{Zn}/\text{Bi}_2\text{O}_3$ 5%)

The peaks showed well-aligned conspicuous diffraction peaks of the material with crystalline peaks at the (110) plane. The Bi_2O_3 patterns verified that the cubic crystal structure was successfully formed. With a classified orientation at the (110) plane, the synthesized material showed prominent peaks.

The most noticeable peaks, with a strong orientation on the (110) plane, were recorded by the bismuth oxide material that was 1% doped. Due to the modest ionic size of the zinc, the addition of zinc does not significantly alter the crystal structure; therefore, there is no discernible peak shift.

The material's crystallite size, D , the lattice constants (a), the interplanar distance (d), and the dislocation densities, $(1/D^2)$ as indicated in Table 1, were all calculated using Scherrer's equation ($D = k\lambda/\beta\cos\theta$). The variable lattice constants and dislocation densities were explained by the introduction of zinc and different crystallite sizes. The 2θ values rise and the lattice constant values change as a result of changes in the lattice sites brought on by an increase in crystallite size.

It has also been demonstrated that the lattice planes' interplanar distance varies over the orientation plane. The lattice structure changes as a result of distortions brought on by the introduction of the zinc, which allows the dopant to occupy the interstitial location. Peak broadening at larger 2θ values is explained by these aberrations.

3.3 FTIR Analysis

In the spectrum of Bi_2O_3 , as depicted in Figure 3(S5), the occurrence of the peak at 811 cm^{-1} indicates the association with the Bi-O bond, thus verifying the existence of bismuth oxide.

Additionally, the peak at 1394 cm^{-1} corresponds to the C-H bond [36]. The stretching vibrations of O-H were detected within the range of 3200 to 3445 cm^{-1} . The presence of a peak at 1635 cm^{-1} indicates the utilization of H_2O in the experimental procedure, while vibrations of water molecules are observed in the range of 2311 to 2331 cm^{-1} .

Table 1: Structural parameters of Bi₂O₃ and Zn/Bi₂O₃

Films	2θ (deg.)	Å	(Å)	(β)	(hkl)	D (nm)	σ (lines/m ² × 10 ¹⁶)
Pure Bi ₂ O ₃	27.36	3.256	5.640	2.0987	110	0.679	6.588
	30.38	2.939	5.878	2.0873	220	0.688	6.429
	32.66	2.739	5.478	2.0734	211	0.696	6.273
	47.04	1.930	4.315	2.0721	200	0.729	5.719
	55.60	1.651	4.045	2.0453	300	0.766	5.186
Zn/Bi ₂ O ₃ 1%	27.48	3.242	5.616	3.3313	110	0.428	1.659
	30.40	2.937	5.875	3.3311	220	0.431	1.637
	32.68	2.737	5.475	3.3310	211	0.433	1.618
	47.08	1.928	4.312	3.3291	200	0.454	1.475
	55.66	1.649	4.041	3.3288	300	0.471	1.373
Zn/Bi ₂ O ₃ 5%	27.48	3.242	5.616	3.4313	110	0.415	1.760
	30.40	2.937	5.875	3.4311	220	0.418	1.737
	32.68	2.737	5.475	3.4310	211	0.421	1.717
	47.08	1.928	4.312	3.4291	200	0.441	1.565
	55.66	1.649	4.041	3.4288	300	0.457	1.456

Table 2: Summary of observed FTIR peaks

S/No.	Wavenumber cm ⁻¹	Information
1	3000-3444	O-H stretching
2	2311-2331	Vibration of water molecules
3	1635	Water
4	1394	C-H bond
5	811	Bi-O bond vibration

Furthermore, the peak observed at 1261 cm⁻¹ can be attributed to the nitrate (NO₃⁻) group [37]. Apart from slight shifts in the wavenumbers, there is minimal distinction between undoped Bi₂O₃ and Zn/Bi₂O₃ (5%) nanoparticles. However, the Zn/Bi₂O₃ (1%) nanoparticles exhibit more pronounced O-H stretching within the range of 3000 – 3444 cm⁻¹, which is not observed in the undoped Bi₂O₃ or Zn/Bi₂O₃ (5%) samples. The observed FTIR peaks are presented in Table 2.

The FTIR spectrum shows that the peaks in Zn/Bi₂O₃ (1%) exhibit broadening, while there is a resemblance to undoped Bi₂O₃ as the zinc concentration in the nanoparticles increases to 5%. This behavior suggests a reduction in the crystallinity of the nanoparticles with an increasing concentration of zinc.

Additionally, the introduction of Zn doping leads to the emergence of an absorption peak in the visible region. This observation, as seen in Zn/Bi₂O₃ (1%), indicates that Zn doping has significantly improved the ability of Bi₂O₃ nanostructures to absorb visible light, thereby highlighting their potential for applications related to visible light-induced phenomena. These absorbance peaks due to doping can be attributed to transitions involving the dopant and the bismuth ions [29].

4 Conclusion

We have successfully used the chemical co-precipitation approach to synthesized Bi₂O₃ and Zn/Bi₂O₃. In comparison to undoped Bi₂O₃, it was discovered that adding a small amount of zinc (1%) as a dopant reduced the absorbance of the Bi₂O₃ nanoparticles throughout the electromagnetic spectrum. Even beyond the (1%) doped zinc absorbance data, further increases in the zinc dopant (to 5%) dramatically enhance the absorbance data. The 1% transmittance rose as the wavelength increased in all synthesized nanoparticles, showing a consistent pattern. Bi₂O₃ materials were found to have much lower transmittance data when a higher concentration of zinc dopant (5%) was added, notably in the visible-near-infrared region. Bi₂O₃ exhibited a band gap energy of 1.78 eV, and Zn/Bi₂O₃ at 1% & 5% had band gaps of 1.83 eV & 1.99 eV. The statistics unambiguously demonstrate that adding zinc dopant widens the energy gap. The cubic lattice structure of this crystal is produced by a powerful synergy between the zinc ions and bismuth oxide ions. The peaks showed well-aligned conspicuous diffraction peaks of the material with crystalline peaks at the (110) plane. The Bi₂O₃ patterns verified that the

cubic crystal structure was successfully formed. With a classified orientation at the (110) plane, the synthesized material showed prominent peaks. The most noticeable peaks, with a strong orientation on the (110) plane, were recorded by the bismuth oxide material that was 1% doped. The occurrence of the peak at 811 cm^{-1} indicates the association with the Bi-O bond, thus verifying the existence of bismuth oxide. Additionally, the peak at 1394 cm^{-1} corresponds to the C-H bond [23]. The stretching vibrations of O-H were detected within the range of 3200 to 3445 cm^{-1} . The presence of a peak at 1635 cm^{-1} indicates the utilization of H_2O in the experimental procedure, while vibrations of water molecules are observed in the range of 2311 to 2331 cm^{-1} .

Authors' Credit Statement

Shahbaz Afzal, Sidra Tehreem, Tahir Munir, Sakhi G. Sarwar: Original draft writing, methodology, reviewing and editing, conceptualization, data curation, software, **Shahbaz Afzal and Imosobomeh L. Ikhioya:** data collection, first-draft writing, conceptualization, data collection, methodology, software, reviewing, and editing, **Tahir Munir, Sakhi G. Sarwar, Imosobomeh L. Ikhioya:** visualization, data curation

Declaration of Competing Interest

Authors have declared no existing conflict of interest.

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