Room temperature chemical synthesis of Bi$_2$O$_3$ nanoparticles

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Abstract
In this article, room temperature synthesis of Bi$_2$O$_3$ nanoparticles in a single-pot reaction is reported. The nanoparticles were synthesized by reducing Bi(NO$_3$)$_3$$^\cdot$5H$_2$O with NaBH$_4$ as a reducing agent, SDS and oleic acid as stabilizing agents. The synthesized nanoparticles were characterized using UV-vis absorption spectroscopy, FTIR spectroscopy, XRD, and HR-TEM. The crystalline nature of the synthesized nanoparticles was confirmed through XRD and HR-TEM data analysis. An average particle size of 14 nm (with quasi-spherical morphology) and a wide band gap were measured for the synthesized nanoparticles. HRTEM image confirmed a highly crystalline growth at individual nanoparticle level. Dielectric measurement indicates a rapid reduction of both real and imaginary dielectric constants as the frequency increases to higher values. The potential application of the synthesized nanoparticles has been demonstrated in photocatalytic degradation of pollutants present in the industrial waste-water.

1 | INTRODUCTION
Bi$_2$O$_3$ is widely used in micro-electronics [1–3], fuel cell [4], optical coating [5], oxide electrolyte [6, 7], gas sensors [8, 9], and as a catalyst [10]. Bi$_2$O$_3$ has a high refractive index (2.6 at 500 nm) [11] and a large energy gap. Bi$_2$O$_3$ nanoparticles (NPs) exhibit a blue shift in the absorption spectrum and display a strong photoluminescence and photoconductivity. It is found in five different polymorphic forms ($\alpha$, $\beta$, $\gamma$, $\delta$, and $\omega$) [12], each having different physical properties and crystalline structure. The stability of Bi$_2$O$_3$ polymorphic forms varies with temperature and doping. $\alpha$-phase is stable at low temperature [13]; $\delta$-phase is stable at high temperature. The phase transition temperature from $\alpha$-phase to $\delta$-phase is $T_t \sim 725^\circ$C [14] and other phases are metastable.

Several synthesis methods, such as thermal decomposition, flame spray pyrolysis, microemulsion-based technique, have been utilized in the past in order to synthesize Bi$_2$O$_3$ NPs. In all these conventional wet-chemical methods, high pressure and temperature conditions are required. The synthesis of metal-oxide nanoparticles such as Bi$_2$O$_3$ at room temperature, without using multi-step reaction, is a challenging task. In the present study, we synthesized Bi$_2$O$_3$ nanoparticles at room temperature in a single-pot reaction, using bismuth(III) nitrate 5-hydrate $\{\text{Bi(NO}_3)_3$$^{\cdot}$5H$_2$O$\}$ as the precursor salt, NaBH$_4$ as a reducing agent, sodium dodecyl sulfate (SDS) and oleic acid as stabilizing agents. The size and shape of these nanoparticles were characterized using transmission electron microscopy (TEM), the crystallinity of NPs was analysed using powder X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM). Further characterization was performed using UV–vis spectroscopy, photoluminescence spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. Dielectric properties of the NPs were investigated using an LCR meter. A model application of synthesized NPs in the treatment of industrial waste-water via photocatalytic degradation of pollutants present in the water has also been demonstrated in this work.

2 | MATERIALS AND METHODS
Bismuth(III) nitrate 5-hydrate (Bi(NO$_3$)$_3$$^\cdot$5H$_2$O), sodium dodecyl sulphate (SDS: C$_{12}$H$_{25}$NaO$_{4}$S), sodium borohydride (NaBH$_4$), and oleic acid (C$_{18}$H$_{34}$O$_2$) were obtained from Fisher Scientific and Ranken. All chemicals used in the synthesis were of high purity analytical grade. Other reagents and solvents used in the synthesis were obtained from commercial suppliers and were used as received. All aqueous solutions were prepared

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FIGURE 1 (a) UV-Vis plot, (b) Tauc plot from UV-Visible spectroscopy data showing the band gap of Bi$_2$O$_3$ nanoparticles

using ultra-pure water obtained from a customized Mili-Q water system.

3 | SYNTHESIS OF Bi$_2$O$_3$ NPS

Bismuth nitrate pentahydrate (10$^{-3}$ M) was dissolved in 100 ml distilled water. The solution was mixed with 1 ml (1% oleic acid) and 10 ml (10 % SDS) in a 250 ml beaker on a magnetic stirrer at 500 rpm speed for 5–6 min. Thereafter, sodium borohydride solution (0.1 M) was mixed into the solution drop-by-drop until a dark black colour appeared. Thus, a highly simplified chemical synthesis of Bi$_2$O$_3$ nanoparticles was achieved in a single-pot reaction at room temperature. The as-prepared solution was centrifuged three times at 8000 rpm for 10 min to remove all unreacted reducing and capping agents as well as precursor salts. The dark colour precipitate obtained after the centrifugation was dried for further characterization. The dried powder was greyish in colour.

4 | CHARACTERIZATION OF Bi$_2$O$_3$ NPS

UV–vis spectroscopy measurements of Bi$_2$O$_3$ nanoparticles were performed using an Agilent dual-beam spectrophotometer operated at a resolution of 1 nm in the wavelength range of 200–800 nm. Distilled water was used as the solvent for the measurement. Fluorescence spectroscopy measurements were carried out at room temperature by employing a 488 nm line of an argon ion laser. The PL spectrum was obtained using a Perkin Elmer LS 55 fluorescence spectrometer. The size and shape analysis of the Bi$_2$O$_3$ nanoparticles were performed using TEM and HR-TEM with JEOL, JEM-2010 operated at an acceleration voltage of 200 kV. For these measurements, samples were prepared by ultrasonically dispersing the powder of nanoparticles in methanol and drop-casting the material on the carbon-coated copper-grids with a time lapse to let the solvent evaporate. To confirm the crystallinity of the synthesized Bi$_2$O$_3$ nanoparticles, XRD data were recorded from the dried powder of the as-prepared solution using Rigaku Miniflex-II X-ray diffractometer equipped with high-intensity Cu-K$_\alpha$ radiations ($\lambda = 1.5406$ Å) operated at a voltage of 30 kV and a current of 15 mA at the scan rate of 2$^\circ$/min in the 2$\theta$ range of 20–80$^\circ$. FTIR spectroscopy measurement on the sample using KBr pellet was performed by using a Perkin-Elmer Spectrum One instrument. The spectrometer was operated in the diffuse reflectance mode at a resolution of 2 cm$^{-1}$. To obtain a good signal-to-noise ratio, 128 scans of the powder were taken in the range of 450–4000 cm$^{-1}$.

Dielectric properties of the synthesized NPs were studied using a Hioki 3532-50 LCR Hi-Tester. The dried powder of the synthesized NPs was pelletized using KBr press. The diameter and the thickness of the pellets were 13 and 0.7 mm, respectively. The outer faces of the prepared pellets were coated with high conductivity silver paste to minimize the contact resistance.

The photocatalytic activity of the synthesized Bi$_2$O$_3$ NPs was explored through the photocatalytic degradation of an aqueous solution containing an organic dye under direct sunlight. The NPs were mixed 0.1% in 100 ml in an organic pollutant model dye (Eosin Blue). The mixed solution was stirred in the dark for 30 min, followed by irradiation with sunlight. At regular intervals of time, about 3 ml of the reaction mixture was taken into a quartz cuvette and the absorbance of the samples was measured using an Agilent Cary-5000 UV–vis–NIR spectroscope.

5 | RESULTS AND DISCUSSION

In Figure 1a, UV-Vis absorption spectra of the synthesized Bi$_2$O$_3$ nanoparticles dissolved in water is presented. An absorption peak is observed at 260 nm wavelength, which is consistent with the reported values in the literature [15]. In Figure 1b, the energy band gap is measured using the Tauc Plot. As presented in the figure, the calculated value of the band gap is 3.4 eV.

The NPs were irradiated with an excitation of wavelength 280 nm to study the photoluminescence peak(s). In the PL spectrum, as presented in Figure 2, a strong photoluminescence peak was observed at 310 nm. The PL emission peak suggests a near ultraviolet (deep bluish) photoluminescence [16]. The peak in this region is indicative of photoluminescence from a wide band gap material. In comparison to bulk, the Bi$_2$O$_3$ nanoparticle displays strong photoluminescence effects owing to the confinement effects. The emission spectra signify high recombination of the electron hole pair [17].
To investigate the formation, shape and size of the synthesized Bi$_2$O$_3$ nanoparticles, TEM imaging was carried out. Presented in Figure 3a is a TEM micrograph of the NPs that reveals the formation of NPs. A scale bar of 20 nm is presented in the image to estimate the size of NPs in the image. The synthesized nanoparticles are of different shape with an overall quasi-spherical morphology. The particle size histogram of the NPs is presented in Figure 3b. It shows that the average size of nanoparticles is about 14 nm and the particles are mostly within the range of 11–17 nm. The NPs appear to be uniform and dispersed.

The HRTEM micrograph presented in Figure 4 was obtained for a precise investigation of crystallinity in the synthesized nanoparticles. From the figure, it can be seen that the lattice plane exhibits d-spacing of about 2.71 Å, which corresponds to (120) lattice plane. It also demonstrates single crystallinity in the synthesized NPs.

To assess overall crystallinity of the Bi$_2$O$_3$ NPs, we conducted powder X-ray diffraction (XRD) measurement. The data is presented in Figure 5. In the bulk form, bismuth oxide is known to show four main structural polymorphs, which possess distinct crystalline structures and physical properties [15]. In the diffraction, pattern peaks are matched with the monoclinic phase of Bi$_2$O$_3$, which is matched with JCPDS (Joint Committee on Powder Diffraction Standards) #41-1449 [18]. The crystallinity of Bi$_2$O$_3$ nanoparticles has already been complemented with HRTEM analysis.

In the synthesis of Bi$_2$O$_3$ nanoparticles, we used oleic acid solution (1%) and SDS solution (10%) which work as the surfactant and stabilizing (and capping) agent, respectively. In Figure 6, the FTIR spectrum of Bi$_2$O$_3$ nanoparticles is displayed. The representative peaks of bismuth oxide nanoparticles, including 3447 cm$^{-1}$ corresponds to the normal O-H stretching vibration of H$_2$O molecules. The appearance of the absorption bands at 2929 cm$^{-1}$ and 2842 cm$^{-1}$ represents the C-H aliphatic stretching and absorption band at 1474 cm$^{-1}$ and 829 cm$^{-1}$ are due to the $-$CH$_2$ bending mode, whereas the band at 1383 cm$^{-1}$ corresponds to a CH$_3$ deformation due to the
FIGURE 4 HR-TEM images of Bi$_2$O$_3$ nanoparticles showing interplanar distance

FIGURE 5 XRD graph of Bi$_2$O$_3$ nanoparticles

FIGURE 6 FTIR spectrum of Bi$_2$O$_3$ NPs

presence of the SDS surfactant. The spectrum exhibits several distinct asymmetric and symmetric stretching bands of -OSO$_3$. The band at 1235 cm$^{-1}$ corresponds to asymmetric S-O stretching, whereas the peaks at 1072 and 989 cm$^{-1}$ result from symmetric S-O stretching. Meanwhile, the bands at 1647 cm$^{-1}$ and 1217 cm$^{-1}$ marked the presence of C-H bending and C-O stretching modes, respectively, attributing to the presence of oleic acid. However, the peak at 721 cm$^{-1}$ corresponds to the oxalate group [19–21]. The FTIR peaks at 586 and 630 cm$^{-1}$ represents the characteristic O-B-O group stretching mode.

In order to study the dielectric properties of the synthesized NPs, the pellets of NPs were fabricated as described in the sample preparation section. The pellets were investigated in the frequency range of 42 Hz–5 MHz. The dielectric constant of a material consists of a real ($\varepsilon'$) and an imaginary ($\varepsilon''$) part. The imaginary part, also called dielectric loss, can be calculated by multiplying the measured real part with the measured dissipation factor (D) or loss tangent [22]. In Figure 7a,b, real and imaginary parts of the dielectric constant are plotted versus frequency. Upto 1 kHz frequency, both $\varepsilon'$ and $\varepsilon''$ sharply decreased with increasing frequency. Beyond 1 KHz the variation and magnitude of both $\varepsilon'$ and $\varepsilon''$ were more or less saturated. In Figure 7c, the variation in the value of the dissipation factor (D) with increasing frequency is plotted. Initially, a substantial change in the D value was observed with increasing frequency upto 10 KHz. Beyond 10 KHz, the D value continued to decrease, but at a much lower rate with increasing frequency. 100 KHz onwards, there was almost no dissipation in the material, a fact reflected in the AC conductivity versus frequency plot presented in Figure 7d. The AC conductivity value was initially observed to increase gradually and then almost exponentially beyond 100 KHz. Such a variation pattern is very useful in applications such as high frequency switches.

In order to demonstrate an efficient photocatalytic activity of Bi$_2$O$_3$ NPs, 0.1% NPs were mixed in 100 ml in an organic pollutant model dye (Eosin Blue). The following reaction mechanism is given below:

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

$$\text{e}^- + \text{O}_2 \rightarrow \text{O}_2^-$$  \hspace{1cm} (2)

$$\text{h}^+ + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$$  \hspace{1cm} (3)

$$\text{H}^+ + \text{Dye} \rightarrow \text{Degradation products}$$  \hspace{1cm} (4)

$$\text{O}_2^- + \text{Dye} \rightarrow \text{Degradation products}$$  \hspace{1cm} (5)

$$\text{OH}^- + \text{Dye} \rightarrow \text{Degradation products}$$  \hspace{1cm} (6)
Presented in Figure 8 are the absorbance spectrum of the dye with and without the NPs at different time intervals. The absorption spectrum without NPs was first recorded and a characteristic absorbance peak at 530 nm was observed. Thereafter, the absorbance spectra were recorded after 15, 30 and 45 min of irradiation in direct sunlight to measure the photocatalytic activity of NPs [23, 24]. The degradation efficiency (%) was calculated using the following equation:

\[
\% \text{Photodegradation} = \left( \frac{C_0 - C(t)}{C_0} \right) \times 100
\]  

where \( C_0 \) and \( C(t) \) are the initial and final concentration of the Eosin blue dye, respectively after irradiation for \( t \) minutes. Peak values of the individual graphs have been used as the data for obtaining % photodegradation.

It can be observed from Figure 9 that about 51% photodegradation of eosiin blue was achieved in the first 15 min, followed by about 77% degradation in 30 min and nearly 90% degradation in 45 min. 77% photodegradation of the model organic pollutant within the first 30 min under freely available sunlight confirms an efficient photocatalytic activity of \( \text{Bi}_2\text{O}_3 \) NPs and this property can be utilized in applications including the treatment of industrial waste-water discharge.
6 | CONCLUSION

We have successfully demonstrated a simple, single-pot, chemical protocol for the synthesis of bismuth oxide nanoparticles at room temperature. The synthesized Bi$_2$O$_3$ nanoparticles were investigated with TEM, HRTEM, XRD, UV-Vis, PL, and FTIR spectroscopy. The band gap was measured 3.4 eV for the synthesized NPs. Observed PL peak at 310 nm is also consistent with the measured wide band gap value. The morphology of the as-synthesized Bi$_2$O$_3$ NPs was studied using TEM micrograph, which confirmed an overall quasi-spherical and dispersed NPs in the range 11–17 nm. The crystallinity of the NPs was confirmed using HRTEM and XRD. HRTEM image confirms highly crystalline growth at individual nanoparticle level with spacing of $d = 2.71$ Å for the lattice plane $(120)$. The XRD data indicates growth of the monoclinic $\alpha$-phase. A potential application was successfully demonstrated by utilizing Bi$_2$O$_3$ NPs in photocatalytic degradation of a model organic pollutant under direct sunlight irradiation.

ACKNOWLEDGEMENT

The authors would like to acknowledge Aligarh Muslim University for their financial support through INC departmental funds.

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