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Synthesis of nanoscale Bi_2O_3 with rectangular rod-like geometry using *Manilkara zapota* fruit extract

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Abstract

The plant product mediated synthesis of nanomaterials has gained immense attention from researchers due to its eco-benign, low cost and less time-consuming properties. It provides immense opportunities to synthesize nanomaterials with diverse size ranges and a wide variety of morphologies just through control of reaction parameters. In this study, for the first time, we report the synthesis of nanoscale Bi_2O_3 with rectangular rod-like geometry from Bismuth nitrate solution through the mediation of *Manilkara zapota* fruit extract. The morphological characterization of as-synthesized yellow-colored Bi_2O_3 powder was confirmed using the scanning electron microscope (SEM) method. X-ray diffraction (XRD) analysis showed crystalline nature for the synthesized Bi_2O_3. Energy-dispersive X-ray spectroscopy (EDX) studies revealed a very high purity for synthesized Bi_2O_3 with an elemental composition of 87.98% and 12.02% for Bi and O respectively. Fourier Transform Infra-Red (FTIR) spectroscopic analysis was performed to analyze the bond stretching vibrations of Bi_2O_3 and to identify the functional groups of capping molecules in the leaf extract. The FTIR spectral analysis revealed the signals corresponding to Bi-O and Bi-O-Bi bond stretching vibrations. From the results of SEM, XRD, EDX and FTIR, we conclude that it is possible to synthesize nanoscale Bi_2O_3 with rectangular rod-like geometry using bismuth nitrate solution and *Manilkara zapota* fruit extract.

Keywords: *Green synthesis, Nanoscale Bi_2O_3, Nanorods, Manilkara zapota, Leaf extract.*

1. Introduction

Metal oxide nanostructures are the most versatile and richest class of semiconducting materials due to their extensive structural, physical, chemical properties and functionalities. These materials possess tunable bandgap and display unique optical, optoelectronic, magnetic, electrical, mechanical, thermal, catalytic and, photochemical properties[1]. These properties make them excellent candidates for various high-level technological applications in fuel cells, batteries, ceramics, sensors, solar cells, supercapacitors, optical devices, memory devices, capacitors, photocatalysis, etc [1].

Bismuth and its compounds are considerably less toxic and harmless among the heavy metals and have earned the status of 'green element' [2]. Bismuth trioxide (Bi_2O_3) is an important commercial oxide of bismuth which exist in distinctive polymorphism forms such as α-Bi_2O_3(monoclinic), β-Bi_2O_3 (tetragonal), γ- Bi_2O_3 (body-centered cubic) and ω- Bi_2O_3 (triclinic) [3]. α- Bi_2O_3 is poorly water-soluble and stable at room temperature. It has potential applications in the field of biomedicine as dental materials, antiseptic, astringent and emollient agents [4, 5]. As it is non-toxic to human tissue, it can be used for temperature sensing, dual-modal imaging and drug delivery [6].

Various physical and chemical methods have been reported for the synthesis of Bi_2O_3 nanostructures of varying morphologies [7]. However, there is an urgent need for developing a feasible green synthesis approach that used non-toxic precursors and mild reaction conditions [8]. The use of plant extract can be a viable option, as reducing and stabilizing agents present in it can assist the synthesis of a wide variety of advanced metal and metal oxide nanostructures. The plant metabolites such as alkaloids, phenolic compounds, flavonoids, terpenoids and catechins act as the reducing agents [9-11]. Moreover, plant-mediated synthesis is the safest, most cost-effective and ideal method for the large-scale production of nanoparticles. Several authors have already reported the synthesis of Bi_2O_3 nanoparticles, nanorods and nanowires using green routes [12, 13]. However, the development of new green methods for the synthesis of Bi_2O_3 nanomaterials with different morphologies such as nano rectangular geometries is not widely reported.

In the present work, we have green synthesized nano Bi_2O_3 with rectangular rod-like geometry using *Manilkara zapota* (sapota) fruit extract as both reducing and capping agent. The characterization was carried out to confirm the nano Bi_2O_3 with rectangular rod-like geometry.

2. Materials and Methods

2.1 Materials and Reagents

The ripen fruits of *Manilkara zapota* used in experiments were collected from a local garden. Bismuth nitrate, nitric acid, ethanol and other chemicals used in the study were of analytical grade purchased from Sigma Aldrich and Fischer Chemicals Ltd.

2.2 Preparation of fruit extract

The fruits of ripening *Manilkara zapota* were thoroughly washed in distilled water and peeled off. About 25 g peeled fruit is crushed into a paste with the help of mortar and pestle in 100 mL distilled water, and the resulting juicy extract was first filtered through a muslin cloth and later using Whatman filter paper. The filtered fruit extract was later used in experiments.

2.3 Synthesis of rectangular rod-like nano Bi_2O_3

Bismuth nitrate solution was prepared by dissolving 2.425 g of bismuth nitrate salt in 50 mL of 10% nitric acid by slow addition of nitric acid to salt. The dissolved salt solution was further diluted to 100 mL using distilled water.

For the synthesis, 50 mL of the above bismuth nitrate solution was taken in a 200 mL beaker and 50 mL fruit extract was added to it slowly over for 20 minutes with continuous stirring. The mixture turned from colorless to light brown. The reaction mixture was later transferred to a 200 mL reagent bottle and autoclaved at 121°C and 15 lb for 20 mins. After autoclaving, the color of the solution changed to pale yellow and a white precipitate was formed. The reagent bottle was removed from the autoclave, cooled to room temperature and precipitate was isolated by centrifugation followed by filtration. The white residue was washed two to three times with distilled water and ethanol, and dried in a hot air oven at 75 °C for about 30 mins. The white precipitate was annealed in a muffle furnace at 300 °C for about 2 hrs 30 mins to get yellow-colored Bi_2O_3 powder. The overall synthesis process was completed in about 8-9 hrs. The photograph of synthesized yellowish Bi_2O_3 powder is shown in Fig. 1. The obtained Bi_2O_3 powder was stored in culture tubes and later subjected to characterization.

Fig. 1. *The Bi_2O_3 powder synthesized using Manilkara zapota*

2.4 Characterization of nano Bi_2O_3

The characterization of biosynthesized nano Bi_2O_3 was performed using XRD, FTIR, EDX and SEM methods. The X-ray diffraction (XRD) pattern was measured on Brunker AXS D2 phaser diffractometer using Cu Kα radiation. FTIR studies on the samples were carried out using Jasco FTIR 4100 (Japan) in the wavenumber range of 600-4000 cm^{-1}. SEM has been performed on a ZEISS EVO40EP (Germany) microscope.

3. Results and discussion

3.1 SEM analysis

The morphology of the synthesized nanomaterial was studied through SEM analysis. The SEM microscopic image of Bi_2O_3 nanomaterial is shown in Fig 2. SEM image reveals the formation of the numerous three-dimensional rectangular rod-like structures. It also reveals that the individual rods have a varied size distribution.

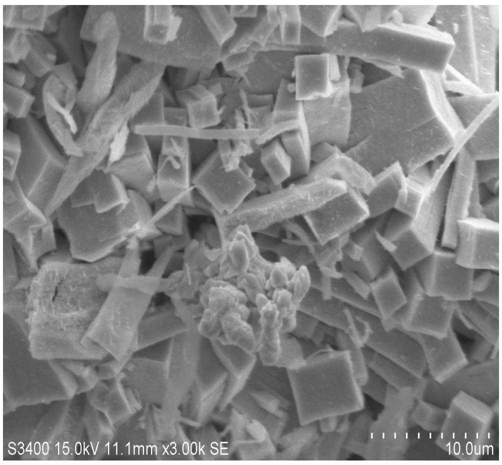

Fig. 2. *SEM image of rectangular rod like nano Bi_2O_3*

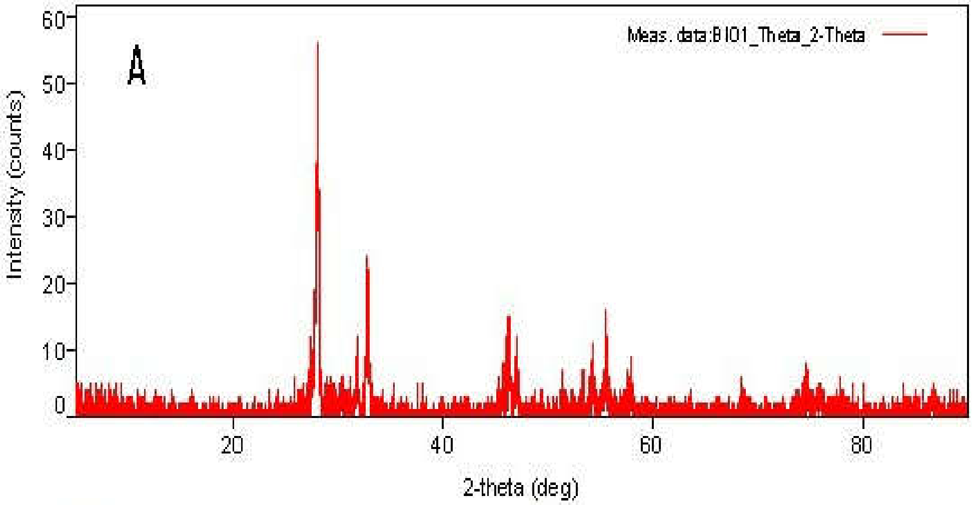

Fig. 3. *X-Ray diffraction pattern of synthesized Bi_2O_3*

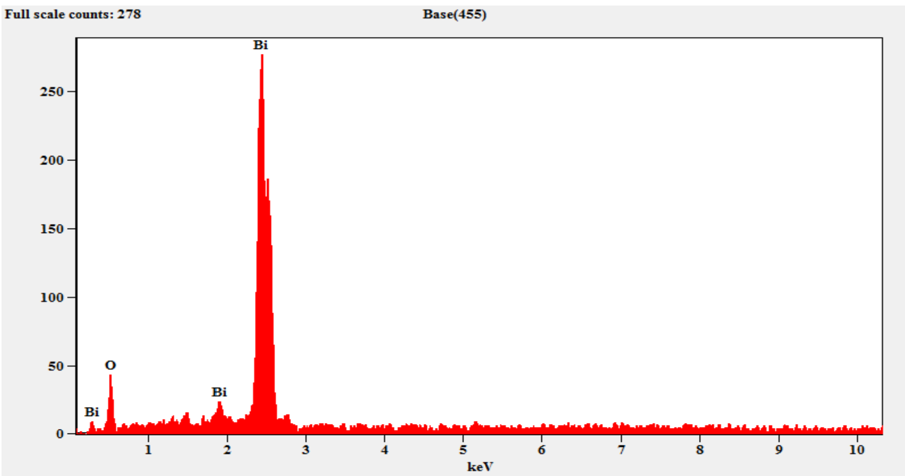

Fig. 4. *EDX spectrum of synthesized Bi_2O_3*

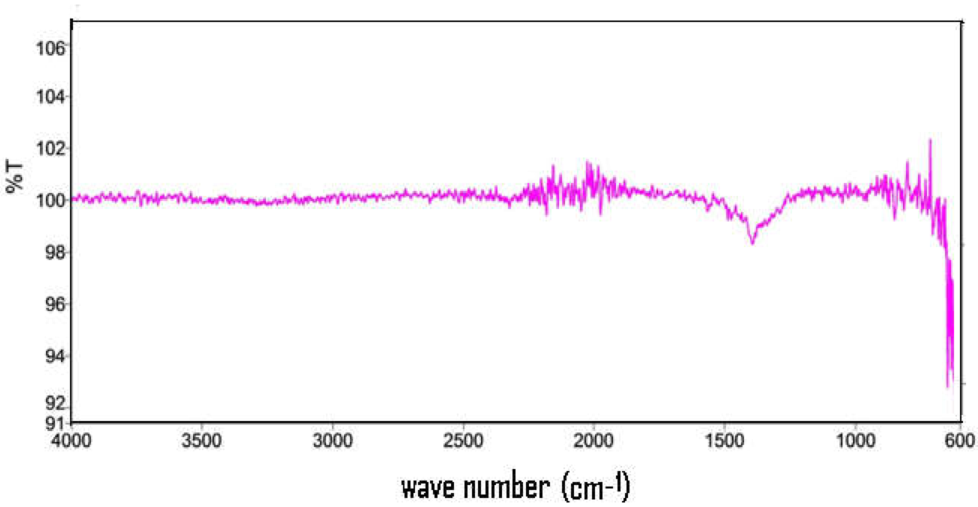

Fig. 5. *FTIR spectrum of synthesized Bi_2O_3 nanomaterial*

3.2 XRD analysis

The crystalline character of biosynthesized Bi_2O_3 was confirmed by the XRD analysis. The powder XRD spectral pattern of Bi_2O_3 nanorods is shown in Fig. 3. XRD spectrograph showed the major peaks at 2θ values 27.938, 31.782, 32.672, 46.97, 54.174, and 57.87 which may be identified with those of α-phase of Bi_2O_3 (JCPDS data, card no. 00-014-0699). The other peaks in the XRD spectrum are possibly contributed by impurities and the residue of the extract. The XRD data suggest a crystalline character for the nanomaterial which also agrees with the morphology revealed in SEM analysis.

3.3 EDX analysis

The analysis for the elemental composition of synthesized nanomaterial was performed using the EDX method. The EDX spectra and the corresponding elemental composition mapping of crude Bi_2O_3 are shown in Fig. 4. The EDX spectra reveal only signals corresponding to the spectral transitions from the elements Bismuth and Oxygen. The absence of signals other than Bi and O suggest that the prepared nanomaterial is of highest purity.

Table 1. *EDX elemental composition of Bi_2O_3 nanomaterial.*

Elements	Weight %	Atom %
O,K	12.02	64.09
Bi L	---	---
Bi M	87.92	35.91
Total	100.00	100.00

The EDX data reveals a weight percentage of about 87.98% and 12.02% respectively for Bi and O. These results suggest that the synthesized nanomaterial is Bi_2O_3 and it is of highest purity.

3.4 FTIR of the Bi_2O_3 nanoparticles

The analysis for the functional groups and bonding vibrations in any compound can be analyzed through FT-IR spectroscopy. The FT-IR spectral profile of synthesized nanomaterial which showed several major peaks is shown in Fig:5. The peak at 600 cm 1 is probably assigned to Bi-O-Bi bending vibration and the peak located at 844 cm 1 is attributed to Bi–O–C vibration. The peak around 1381 cm 1 can be assigned for the Bi=O bond stretching vibration. The presence of Bi-O and Bi-O-Bi vibrational stretching frequencies in FT-IR spectra suggests that the compound is Bi_2O_3.

4. Conclusions

In this study, we have adopted a green synthetic approach to synthesize Bi_2O_3 nanorods with rectangular-rod-like geometry using bismuth nitrate solution and fruit extract of *Manilkara zapota.* The XRD pattern confirms the formation of Bi_2O_3 crystals and SEM analysis revealed the formation of rectangular rod-like structures. The EDX analysis suggests a high level of purity for the nanorods. FT-IR further confirms the presence of Bi-O and Bi-O-Bi bond structures which is a further confirmation of nano-level Bi_2O_3 rectangular rods. The synthesis involves a simple experimental procedure and is cost-effective as fruit extract is used, requires less time for the synthesis and produces non-toxic Bi_2O_3 rectangular rod-like nanomaterial. The synthesized material can find potential applications in the field of optics, electrochemistry and dye degradation.

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