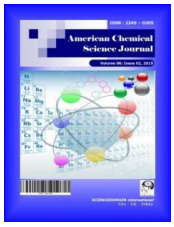

American Chemical Science Journal
11(4): 1-10, 2016, Article no.ACSJ.22660
ISSN: 2249-0205

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Synthesis of ZnO Nanoparticles from Zinc Formate and Their Optical Properties

Susmita Boruah[1], Syeda Mustafiza[1], Devojit Saikia[1], Heerok Jyoti Saikia[1], Partha P. Saikia[1] and Mrinal K. Baruah[1*]

[1]Department of Chemistry, NNS College, Titabar-785630, Assam, India.

Authors' contributions

This work was carried out in collaboration between all authors. Authors SB, SM, DS and HJS performed all the experiments. Authors PPS and MKB designed, analyzed, interpreted data and wrote the whole manuscript. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACSJ/2016/22660
Editor(s):
(1) Georgiy B. Shul'pin, Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia.
Reviewers:
(1) Alexandre Gonçalves Pinheiro, Ceará State University, Brazil.
(2) Nelcy Della Santina Mohallem, Universidade Federal de Minas Gerais, Brazil.
(3) Ryan D. Corpuz, Mindanao State University, Philippines.
Complete Peer review History: http://sciencedomain.org/review-history/12602

Original Research Article

Received 17th October 2015
Accepted 30th November 2015
Published 9th December 2015

ABSTRACT

Zinc oxide nanoparticles were successfully synthesized by alkaline precipitation method from zinc formate dihydrate and sodium hydroxide using sodium dodecyl sulphate (SDS) as a surface active agent. In another experiment, the zinc salt was heated at 600℃ for comparison with the synthesized ZnO nanoparticles by precipitation method. Defined morphological characteristics of complex nanomaterial such as spherical, nanoflex, dumb-bell like and rod-like shapes have been obtained. The nanoparticles were characterised by X-ray diffraction (XRD). The morphologies of synthesized zinc oxide nanoparticles were determined by scanning electron microscope (SEM). The elemental composition of the nanoparticles was carried out by SEM attached Energy Dispersive X-ray Diffractometer (EDX). Optical properties of prepared ZnO nanoparticles were studied by UV-visible spectrophotometer. It has been found that band gap of the nanoparticles are in the range 3.36 – 3.65 eV and the radii of the particles are in the range 1.48 – 2.73 nm.

Keywords: Zinc oxide nanoparticles; zinc formate; precipitation; thermal.

**Corresponding author: E-mail: drmkbaruah@yahoo.com;*

1. INTRODUCTION

Nanotechnology is a rapidly developing branch of material science which has been attracting a large number of scientists and technologists throughout the world since the last part of the twentieth century. The progress of this technology is mainly due to its potential benefits in varieties of fields including food, medicine, energy, optical, electrical, textile, and such others. ZnO is an inorganic compound and is a white powder. It occurs in nature in the form of mineral zincite. The powder is widely used as an additive in numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g., car tires), lubricant, paints, ointments, adhesives, sealants, pigments, foods batteries, ferrites, fire retardants, and first aid tapes. The nanoparticles have been reported to form various shapes. Thus variation of morphology of zinc oxide nanoparticles depends on the starting materials as well as on the methods and conditions of synthesis. There are a number of processes of synthesis of ZnO nanoparticles reported in literature involving various methods such as precipitation [1-8], sol-gel [9-11], emulsion [12-15], thermal [16-18], microwave [19], hydrothermal [20-24], mechanochemical [25-27] etc. In this paper, we report herein a novel method for synthesis of zinc oxide nanoparticles by precipitation and thermal method using zinc formate as the precursor. Further optical properties of the synthesized ZnO nanoparticles are also aimed at.

2. MATERIALS AND METHODS

2.1 Materials

In this study, ZnO nanoparticles were prepared from zinc formate, Zn $(HCOO)_2$ which is used as a precursor. Two compounds - Sodium dodecyl sulphate (SDS) as a surfactant and NaOH as an alkali were used here.

2.2 Preparation of Nanoparticles

Two methods – precipitation method and thermal method were used for the synthesis of ZnO nanoparticles.

2.3 Precipitation Methods

The zinc oxide nanomaterials were obtained from hydrolysis of zinc formate solution in water using NaOH solution. 7.771 g zinc formate was dissolved in 100 ml distilled water. 4.0 g NaOH was dissolved in 100 ml distilled water. The zinc salt solution, taken a beaker, was kept on a water bath; the temperature was maintained at 70-75℃ under continuous electric stirring condition. Sodium dodecyl sulphate (SDS) was used as a surfactant and 2 g of it was added to the zinc salt solution. Then NaOH solution was added dropwise from a burette to the zinc formate solution until the pH attained at 10.5. The resulting turbid solution was placed on the water bath for additional two hours at the same reaction temperature under continuous stirring condition. Thus white material was separated out which was washed first with distilled water and finally with ethanol. The white material was made into two parts.

One part of the white material was allowed for two days to dry at laboratory temperature. This ZnO nanomaterial is designated as ZnO_{24} for our convenience. The other part of the white material was kept in an electric oven and the temperature was maintained at 75℃ for three hours. This ZnO nanomaterial is designated as ZnO_{75} for our convenience. Each nanomaterial was stored in a polypropylene bottle.

2.4 Thermal Method

Zinc formate solution in water was prepared by dissolving 1.65 g zinc formate in 60 ml distilled water. The solution was poured in a silica crucible. The crucible was kept in a muffle furnace, the rate of heating was maintained at 5℃ per minute. The crucible was heated up to 600℃. After attaining 600℃, the crucible was removed from the furnace, allowed to cool to room temperature and finally kept in a dessicator. This ZnO white material is designated as ZnO_{600} for our convenience. The nanomaterial was stored in a polypropylene bottle.

2.5 Instrumental Methods

The crystalline nature of the synthesized ZnO nano material was verified by X-Ray Diffraction (XRD) pattern. The XRD measurements of the particles was carried out using a Bruker AXS and the X-ray diffraction was determined with CuKα radiation with wavelength, $\lambda = 1.54178A^{o}$ at the Bragg angle (2θ) ranging from 10 – 80° at a scan rate of 5° min^{-1}.

The Scanning Electron Microscope (SEM) analysis was carried out using LEO 1430 VP Scanning Electron Microscope coupled with Oxford EDX system (INCA X-ray microanalysis).

UV-visible absorption spectroscopy is widely used to understand the optical properties of nanoparticles. The synthesized ZnO nanomaterials were insoluble in water and almost in all organic solvents. For this study, the nanoparticles were dispersed in ethanol. Optical measurements were carried out using a UV-visible spectrometer in the range 200 – 700 nm wavelength.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Charaterisation of the nanoparticles by X-ray diffraction (XRD) has shown diffraction pattern in the 2θ range from 10-80°. The XRD spectra for three ZnO nanoparticles (ZnO_{24}, ZnO_{75} and ZnO_{600}) are presented in Figs. 1-3. All the diffraction peaks are well matched with the Joint Committee on Powder Diffraction Standards (JCPDS-36-1451) for bulk ZnO. Nevertheless the results provide valuable information. The lattice parameters of ZnO are: a = 0.3249 nm and c = 0.5206 nm. These parameters are quite similar to Suresh and Sandhu [28] who reported lattice constants a = b = 0.32 nm, c = 0.52 nm for Wurtzite geometry of ZnO. The ratio c/a has been reported to be 1.633 for an ideal hexagonal closed packed structure. Our result of c/a ratio is 1.6023 which is almost close to the ideal value (1.633) of hexagonal cell. The major reflections between 30° and 40° (2 θ values) indicate more crystallinity regions of the nanoparticles. Less intense other peaks (2θ values) also reveals crystallinity. Further, the peaks in all the three spectra have shown high intensity and narrower spectral width, thus strongly suggesting good crystallinity of the nanomaterials. All the observed peaks correspond very well to the literature data of the wurtzite structure of ZnO [29].

3.2 SEM Analysis

The surface morphology of ZnO nanoparticles were examined by scanning electron microscope (SEM). The images are shown in Figs 4-6. The images reveal the formation of ZnO nanostructures. The materials are of varying sizes and are not homogeneous.

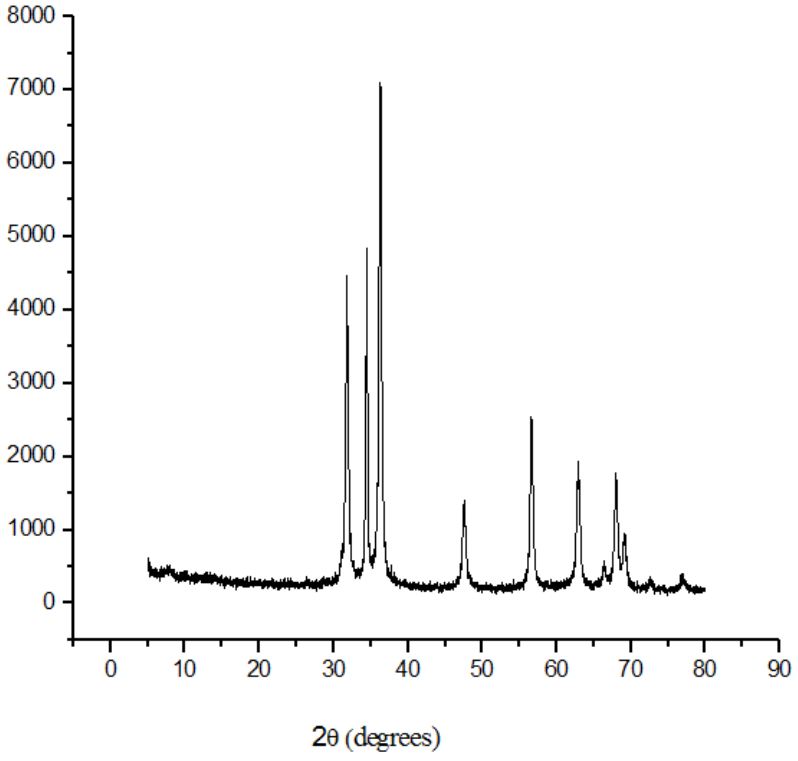

Fig. 1. XRD pattern for ZnO_{24}

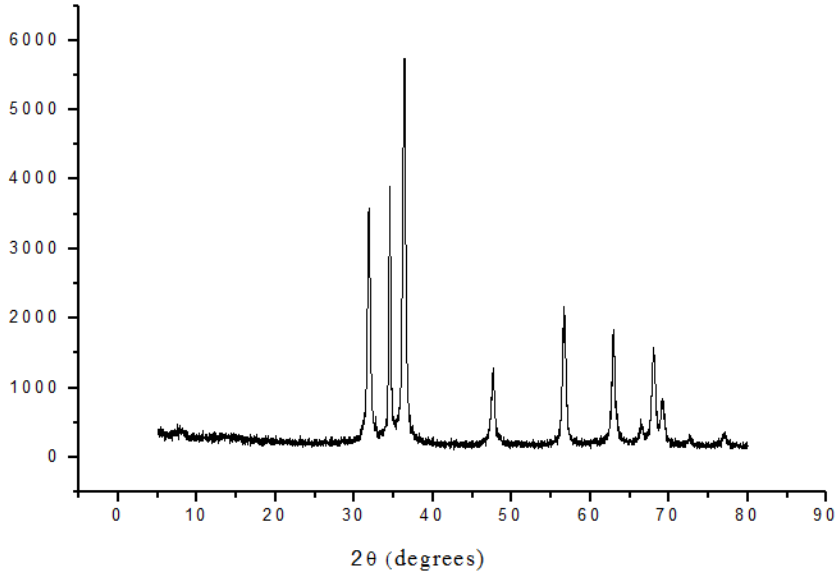

Fig. 2. XRD pattern for ZnO_{75}

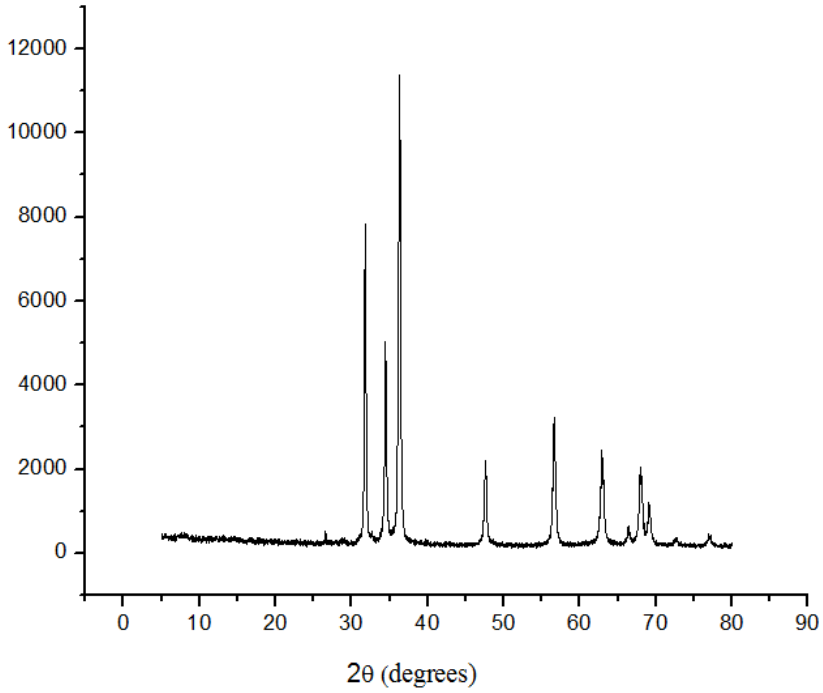

Fig. 3. XRD pattern for ZnO_{600}

Fig. 4 shows the SEM image of ZnO nanoparticles prepared by precipitation method at room temperature. The image shows approximate spherical shape to ZnO nanoparticles.

The SEM image of ZnO nanoparticles prepared by precipitation method at room temperature which was dried in oven at 75℃ is shown in Fig. 5. Fig. 6 shows the SEM image of ZnO nanoparticles prepared by thermal method at 600℃. SEM images revealed approximate dumb bell-like characteristics to the synthesised nanoparticles.

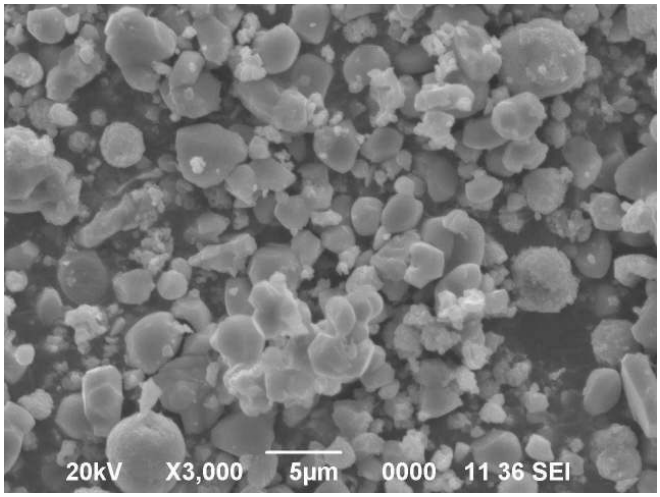

Fig. 4. SEM image of ZnO_{24}

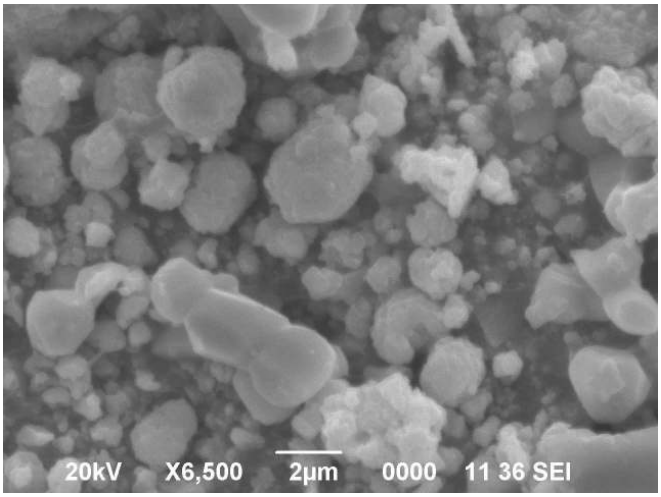

Fig. 5. SEM image of ZnO_{75}

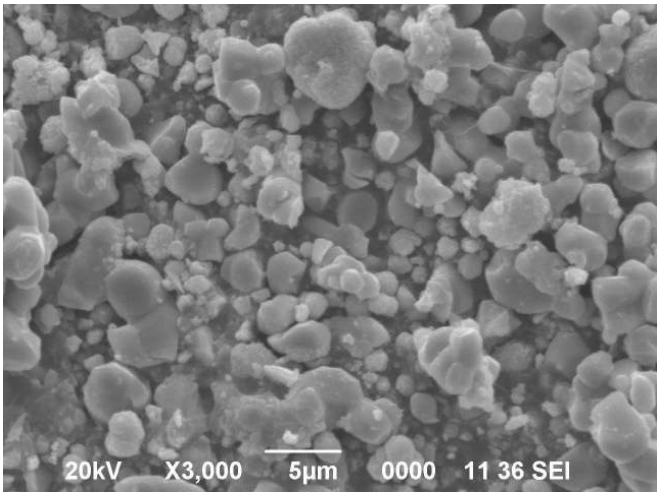

Fig. 6. SEM image of ZnO_{600}

3.3 EDX Analysis

The EDX spectra of ZnO_{24}, ZnO_{75} and ZnO_{600} nanomaterials synthesized in this study are shown in Figs. 7-9. All the spectra have shown distinct peaks for zinc atom and oxygen atom. As there appears no peak for other elements, this strongly suggests high purity of the synthesized ZnO nanomaterials. The weight percentage determined by EDX spectroscopy for zinc and oxygen atoms almost similar in case of ZnO_{24} and ZnO_{75} samples but considerable change has been found in the ZnO_{600} sample (Tables 1-3).

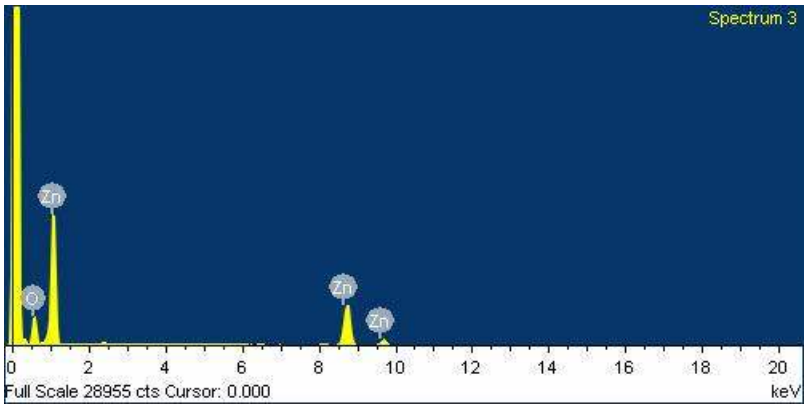

Fig. 7. EDX of ZnO_{24}

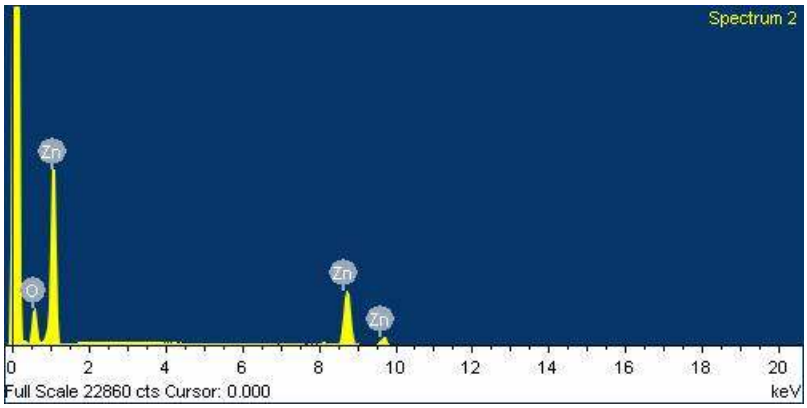

Fig. 8. EDX of ZnO_{75}

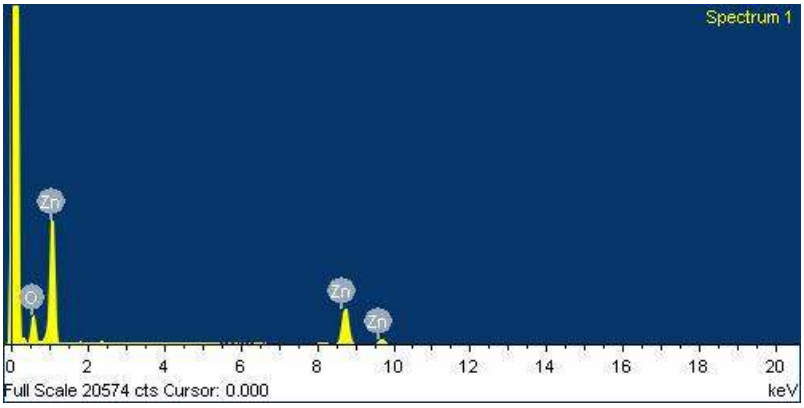

Fig. 9. EDX of ZnO_{600}

3.4 UV-visible Analysis

Optical property of nanoparticles is an important property which gives specific information of size, shape, concentration, agglomeration state, etc., near the surface of the particles. These particles interact with specific wavelength of light and show maximum absorption at a wavelength. An important study of the optical absorption from the UV-visible spectra of the nanoparticles is the determination of band gap. Measurement of band gap of materials is an essential property of semiconductor, nanomaterials, insulators, etc.

The UV-visible spectra of the synthesized ZnO nanoparticle in the range 250-600 nm are presented in Figs. 10-12. The absorption edges are observed at different wavelengths. The shifting of absorption edges is due to the quantum size effect. The band gap of the nanoparticles has been calculated using reported procedure [30] and are presented in Table 5. It is observed from the Table 5 that the wavelength of maximum absorption occurred in the range 340 - 370 nm and the band gap of the nanoparticles have been found to be in the range 3.36 – 3.65 eV. For bulk ZnO, the absorption edge appearing at 370 nm at room temperature and the band gap is 3.36 eV. Shifting of absorption edge to lower wavelength or higher energy reveals decreasing size of the nanomaterial. The radii of the systhesized ZnO nanoparicles have been determined and found that the radii range from 1.48 to 2.73 nm (Table 4). The nanoparticles prepared by thermal method at 600℃ yields smallest radius of the nanomaterials among others.

Table 1. Elemental composition of ZnO_{24}

Element	Weight%	Atomic%
O K	34.49	68.27
Zn K	65.51	31.73
Totals	100.00	

Table 2. Elemental composition of ZnO_{75}

Element	Weight%	Atomic%
O K	34.06	67.85
Zn K	65.94	32.15
Totals	100.00	

Table 3. Elemental composition of ZnO_{600}

Element	Weight%	Atomic%
O K	37.44	70.98
Zn K	62.56	29.02
Totals	100.00	

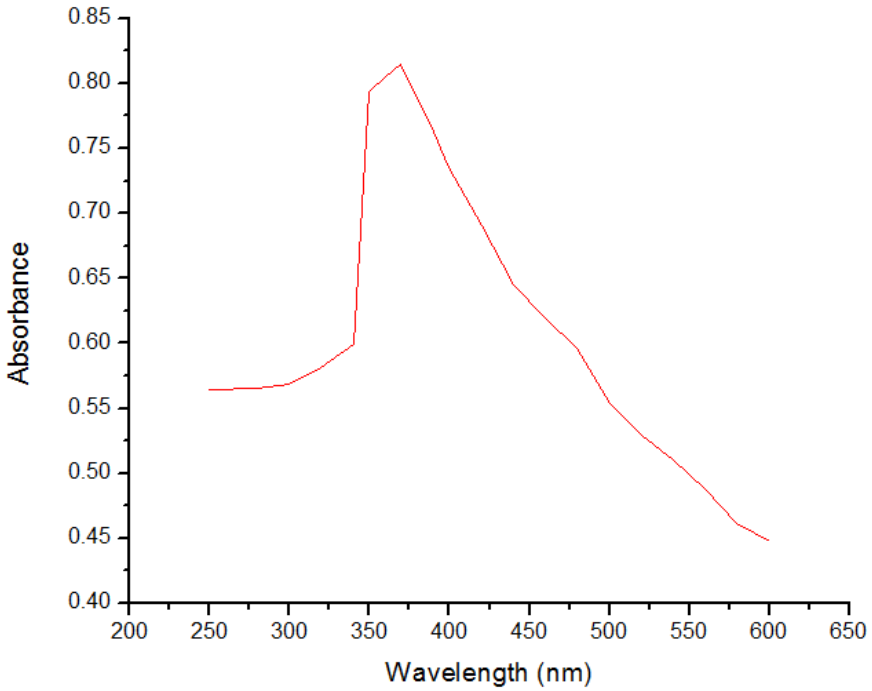

Fig. 10. UV-visible spectrum of ZnO_{24}

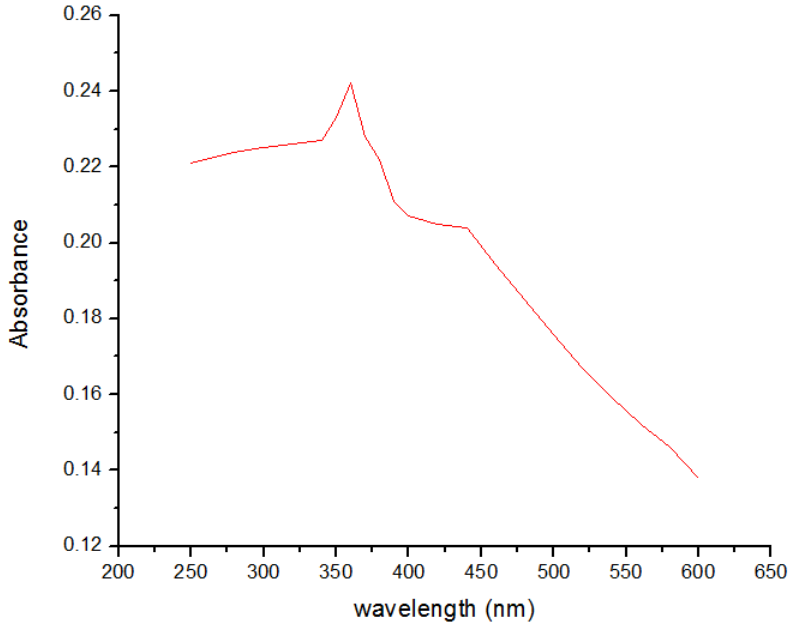

Fig. 11. UV-visible spectrum of ZnO_{75}

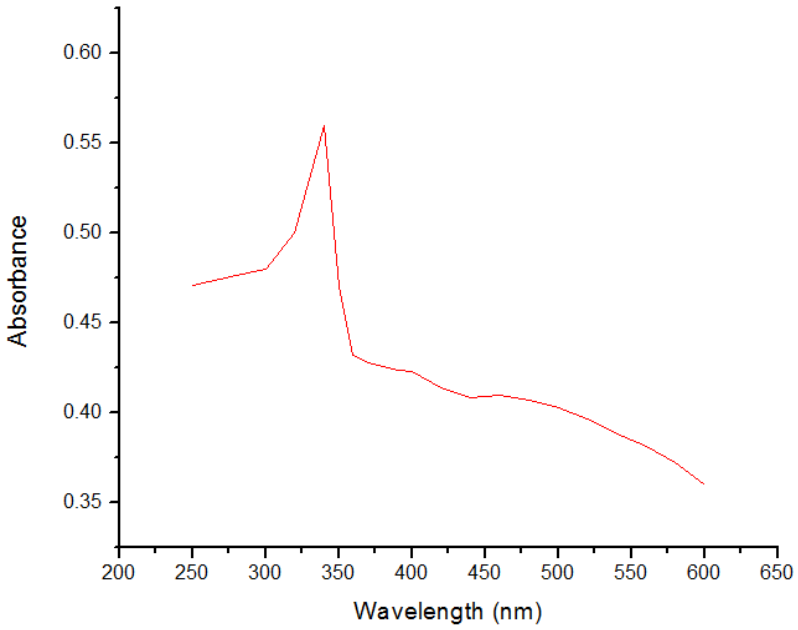

Fig. 12. UV-visible spectrum of ZnO_{600}

Table 4. Maximum absorption, band gap and radius of the ZnO nanoparticles

Sl. no.	ZnO sample	Maximum absorption	Band gap	Radius
1	ZnO_{24}	370 nm	3.357=3.36eV	2.73 nm
2	ZnO_{75}	360 nm	3.451=3.45eV	2.30 nm
3	ZnO_{600}	340 nm	3.654=3.65eV	1.48 nm

4. CONCLUSION

In this report, the synthesis of zinc oxide nanoparticles of different morphological characteristics has been carried out through different methods. The precursor was so selected that no literature has been noticed by us so far for synthesis of ZnO nanoparticles from zinc formate. Synthesis of nanomaterials through (i) a homogeneous phase reaction using zinc formate and sodium hydroxide at room temperature in water in presence of SDS furfactant. and (ii) thermal treatment of zinc formate solution in water at high temperature (600℃). The radii of the particles are ranges from 1.48 to 2.73 nm. The thermally synthesized ZnO particles have smaller radius than those synthesized by the precipitation method. The nanomaterials appear to be spherical, ellipsoidal, nanoflex, dumbbell-like and rod-like shaped. Analysis of nanomaterials was done by X-ray diffraction, Scanning Electron Microscope, Energy Dispersed X-ray and UV-visible spectroscopies. The band gap of the synthesized ZnO nanoparticles is in the range 3.36 – 3.65 eV. Fine crystalline and excellent pure ZnO nanomaterials have been evident in this study.

ACKNOWLEDGEMENTS

The authors are grateful to Dr L Baruah, Principal, NNS College, Titabar for providing facilities to carry out this work. Thanks are also due to Analytical division, Tezpur University and Institutional Biotech-Hub, NNS College for instrumental aanalysis. MKB is thankful to UGC-NERO for the financial support under MRP scheme (F.5-27/2013-14/MRP/NERO).

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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