ISSN 2349-4506
Impact Factor: 2.265

Global Journal of Engineering Science and Research Management

OPTICAL PROPERTIES OF ZnO NANOMATERIALS SYNTHESIZED BY THERMAL METHOD

Tumpa Paul[*1] Partha P Saikia[2] Mrinal K Baruah[3]
[*1]Department of Chemistry, Darrang College, Tezpur - 784001, Assam, India.
[2]Department of Chemistry, NNS College, Titabar – 785630, Assam, India.
[3]Department of Chemistry, NNS College, Titabar – 785630, Assam, India.

KEYWORDS: XRD analysis, SEM analysis, EDX analysis & UV-Visible analysis.

ABSTRACT
Nano-sized ZnO materials have been synthesized by thermal method, at temperature800^{O}C, in presence of an anionic surfactant, sodium dodecyl sulphatr (SDS). The nanoparticles were characterized by X-Ray diffraction (XRD), Scanning Electron Microscope (SEM), and Electron Dispersive X-Ray (EDX) methods. XRD study show that ZnO crystals have hexagonal closed packed structure. SEM result reveals dumb-bell-like and rod-like morphologies of the nanomaterials which are found to be heterogeneous in nature. Optical properties of the nanomaterials were examined by UV-visible analysis and the band gap and the average radius of the particles have been found to be 3.27 eV and 3.57 nm, respectively.

INTRODUCTION
Zinc oxide occurs in two crystalline forms- hexagonal wurtzite structure and cubic zincblende structure. The common structure is wurtzite structure which is most stable at ambient conditions. It has a hexagonal unit cell with two lattice parameters; each anion is surrounded by four cations at the corners of the tetrahedron, thus showing the tetrahedral coordination [1]. The zincblende structure can be stabilized by growing ZnO on substrates with cubic lattice structure. The radii of Zn^{2+} ion is 0.074 nm and for O^{2-} ion, it is 0.140 nm this property accounts for the preferential formation of wurtzite structure rather than zinc blende structure [2].

A common property of nanomaterial's is that the properties exhibited by the nanomaterial's are quite different from their bulk dimension. Various methods, e.g., precipitation, thermal, microwave, emulsion, sol-gel, hydrothermal, etc., have known in literature but ZnO nanmomaterials sysnthesized by zinc salt with organic anion is not much. Mostly acetate salt of zinc has been largely known [3-12]; however, oxime and acetylacetonate complexes of zinc have been reported [13]. Recently, zinc formate has been used for the synthesis of ZnO nanomaterials [14]. Various morphologies of these nanoparticles viz. nanorods, nanotubes, nanobelts, nanoflowers, nanowires, polyhedrals, nanoflakes, nanoballs, etc. have been known. However, based upon the morphologies of ZnO nanoparticles, diversified range of their application could be achieved [15-19].

In the present study, our aim is to synthesize ZnO nanomaterials by thermal method using zinc formate as the precursor. Characterization of the nanomaterials and their optical properties will also be studied.

MATERIALS AND METHODS
Materials
For the synthesis of ZnO nanomaterials, zinc formate, $Zn(HCOO)_2$ was used. Sodium dodecyl sulphate (SDS), an anionic surfactant, in aqueous solution as a surfactant and NaOH as an alkali were used here.

Thermal method
The thermal method has been reported elsewhere. Briefly, 1.65g zinc formate salt was dissolved in 60 ml distilled water and poured in a silica crucible. The crucible was heated in a muffle furnace at 5^{O}C per minute up to 800^{o}C. Then the crucible was allowed to cool to room temperature and finally kept in a dessicator. The white material was stored in a polypropylene bottle.

Instrumental methods
X-Ray Diffraction (XRD) study was undertaken using a Bruker AXS and the X-ray diffraction was determined with CuKα radiation with wavelength, λ= 1.54178A^{o} at the Bragg angle (2 theta) ranging from 10 – 100^{o} at a scan rate of 5^{o} 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).

Global Journal of Engineering Science and Research Management

Optical measurement of the nanomaterial's, dispersed in ethanol, was carried out using a UV-visible spectrometer in the range 200 – 700 nm wavelength

RESULTS AND DISCUSSION

XRD analysis

The crystalline nature of the synthesized ZnO nano material was verified by the XRD measurements. ZnO nanomaterials exhibit diffraction pattern in the 2θ range from 10-100^o. The XRD pattern of the synthesized nanomaterials is presented in Figures 1. The diffraction peaks are well matched with the Joint Committee on Powder Diffraction Standards (JCPDS-36-1451) for bulk ZnO.

The lattice parameters of ZnO are: a = 0.3249 nm and c = 0.5206 nm and the ratio of c/a is 1.633 for an ideal hexagonal closed packed structure. The result obtained in this study for c/a ratio is 1.6023 which is almost close to the ideal value (1.633) of hexagonal cell. It is important that the major reflections at around 32, 35 and 37 ^{O} in the region 30$^-$40^O (2θ values) indicate more crystallinity of the nanoparticles. Moreover, high intensity and narrow spectral width strongly suggest good crystallinity of the nanomaterial's.

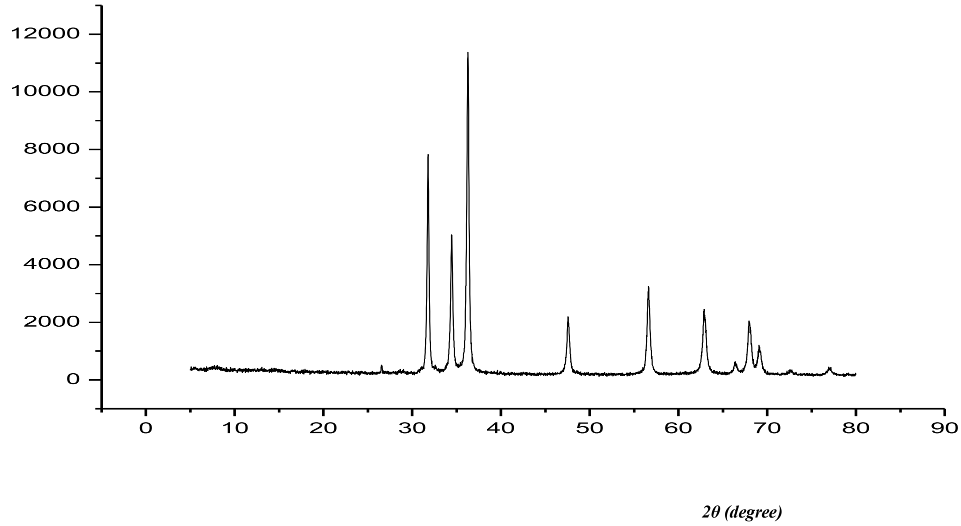


Figure 1. XRD pattern of ZnO nanoparticles

SEM analysis

Scanning electron microscope (SEM) provides good information regarding the surface morphology of nanoparticles. In this study, SEM analysis has been done and the image of the synthesized nanomaterials is presented in Figure 2. The SEM image reveals heterogeneous nature of the ZnO nanomaterials. Different morphological pattern have been found in the SEM image (Figure 2); however, dumb-bell like and rod-like morphologies are apparent.

ISSN 2349-4506
Impact Factor: 2.265

Global Journal of Engineering Science and Research Management

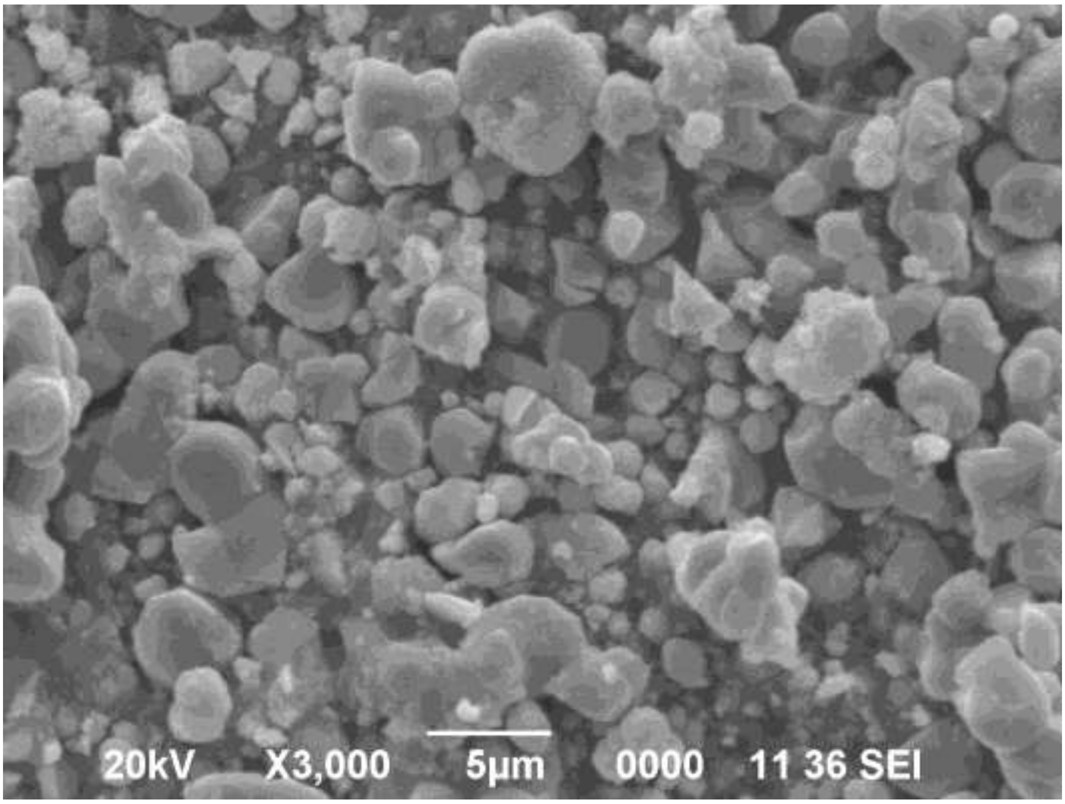
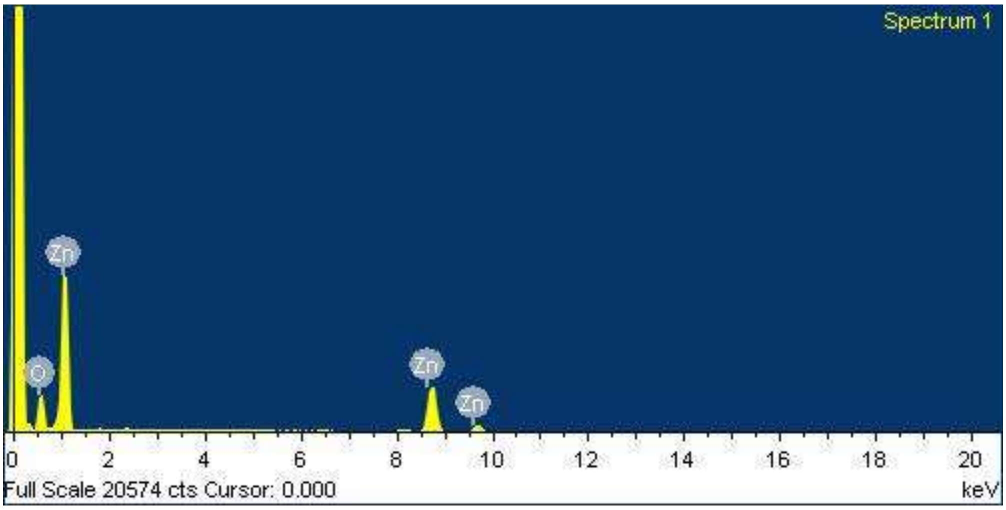


Figure 2. SEM image of ZnO nanoparticles

EDX analysis

Coupled to SEM, EDX spectroscopy gives an important quantitative information regarding elemental composition of the nanomaterials. The EDX spectrum the synthesized nanomaterials is given in Figures 3. In the spectrum, distinct peaks for zinc atom and oxygen atom have been observed revealing high purity of the synthesized ZnO nanomaterials. The elemental composition (as weight % and atomic %) for zinc and oxygen atoms are also recorded and are given below.



Element	Weight%	Atomic%
O K	37.44	70.98

ISSN 2349-4506
Impact Factor: 2.265

Global Journal of Engineering Science and Research Management

Zn K	62.56	29.02
Totals	100.00	

Figure 3. EDX image and elemental composition of ZnO nanomaterials.

UV-Visible analysis

In order to understand the size, shape, concentration, agglomeration state, etc. of nanoparticles, UV-Visible analysis is an important method in which the optical property of the materials are precisely known. The nanoparticles interact with specific wavelength of light and give maximum absorption at a particular wavelength and the information band gap energy. The magnitude of band gap of materials is an essential property of semiconductor, nanomaterial's, insulators, etc.

The band gap is the difference of energy between the highest occupied state in the valence band and the lowest unoccupied state in the conduction band. The band gap refers to the minimum energy difference between the top of the valence band to the bottom of the conduction band. The wavelength at maximum absorption obtained in the UV-visible spectrum is taken for the determination of band gap.

The UV-visible spectrum of the synthesized ZnO nanoparticle in the range 240-700 nm is presented in Figure 4. Maximum absorption is observed at 380 nm wavelength. The band gap of the nanoparticles have been found to be 3.27 eV.

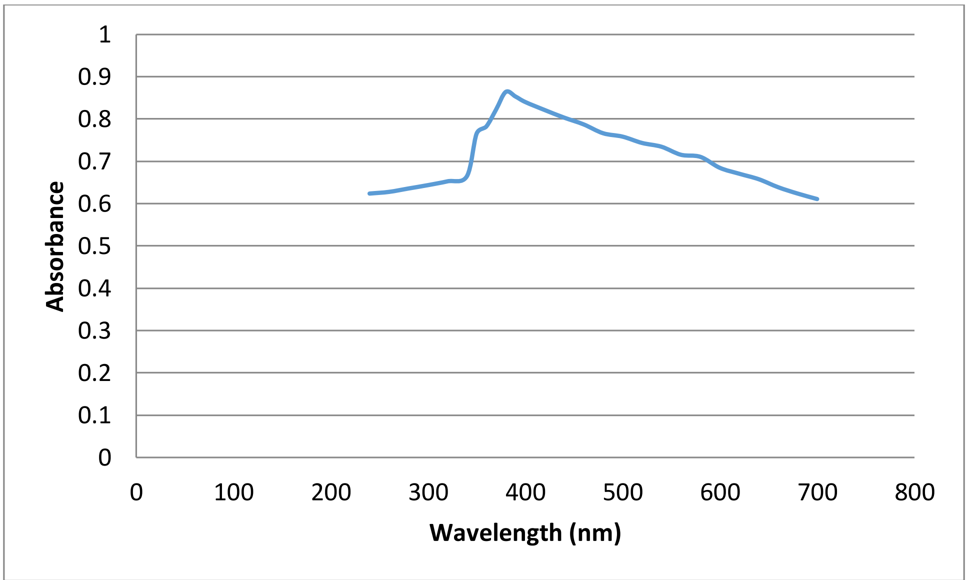


Figure 4. UV-Visible spectrum of synthesized ZnO nanomaterials.

Soosen et al [20] reported an equation, derived by using an effective mass model, which they used to determine particle size (r, radius) as a function of peak absorbance wavelength (p) for monodispersed ZnO nanoparticles. The radius of the nanomaterials has been calculated and found to be 3.57nm. The distinction between a semiconductor and an insulator is not precise, but it is considered that the band gap energy for insulators is > 4.0 eV, thus the nanomaterials synthesized in this study possess semiconductor properties.

CONCLUSIONS

It can be concluded that the simple thermal method, presented here, using zinc formate as a precursor in the presence of a surfactant, sodium dodeccyl sulphate (SDS), impurity free hexagonal crystals of dumb-bell-like and rod-like morphologies of the nanomaterials with hexagonal configuration have been found. Optical properties of ZnO nanomaterials, viz. band gap and average radius of the particles, have been calculated; these show the semiconductor property of the nanomaterials and would find applications in different fields.

REFERENCES

1. Greenwood, N.N.; Earnshaw, A. Chemistry of the elements. Pergamon Press, , 1989.
2. Klingshirn CF, Meyer BK, Waag A, Hoffmann A, Geurts JMM Zinc Oxide: From Fundamental Properties Towards Novel Applications. Springer. 2010, pp. 9–10.
3. Kumra, K.M.; Mandal, B.K.; Naidu, E.A.; Sinha, M.; Kumar, K.S.; Reddy, P.S. Synthesis and characterization of flower shaped zinc oxide nanostructures and its antimicrobial activity. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2013, 104, 171–174.
4. Kołodziejczak-Radzimska, A.; Jesionowski, T.; Krysztafkiewicz, A. Obtaining zinc oxide from aqueous solutions of KOH and $Zn(CH_3COO)_2$. Physicochem. Probl. Miner. Process. 2010, 44, 93–102.
5. Hong, R.; Pan, T.; Qian, J.; Li, H. Synthesis and surface modification of ZnO nanoparticles. Chem. Eng. J. 2006, 119, 71–81.
6. Jia, W.; Dang, S.; Liu, H.; Zhang, Z.; Yu, Ch.; Liu, X.; Xu, B. Evidence of the formation mechanism of ZnO in aqueous solution. Mater. Lett. 2012, 82, 99–101.
7. Mahato, T.H.; Prasad, G.K.; Acharya, B.S.J.; Srivastava, A.R.; Vijayaraghavan, R. Nanocrystalline zinc oxide for the decontamination of sarin. J. Hazard. Mater. 2009, 165, 928–932.
8. Benhebal, H.; Chaib, M.; Salomon, T.; Geens, J.; Leonard, A.; Lambert, S.D.; Crine, M.; Heinrichs, B. Photocatalytic degradation of phenol and benzoic acid using zinc oxide powders prepared by sol-gel process. Alex. Eng. J. 2013, 52, 517–523.
9. Yue, S.; Yan, Z.; Shi, Y.; Ran, G. Synthesis of zinc oxide nanotubes within ultrathin anodic aluminum oxide membrane by sol-gel method. Mater. Lett. 2013, 98, 246–249.
10. Lu, C.H.; Yeh, C.H. Emulsion precipitation of submicron zinc oxide powder. Mater. Lett. 1997,33, 129–132.
11. Ismail, A.A.; El-Midany, A.; Abdel-Aal, E.A.; El-Shall, H. Application of statistical design to optimize the preparation of ZnO nanoparticles via hydrothermal technique. Mater. Lett. 2005, 59, 1924–1928.
12. Zhao, X.; Zheng, B.; Li, C.; Gu, H. Acetate-derived ZnO ultrafine particles synthesized by spray pyrolysis. Powder Technol. 1998, 100, 20–23.
13. Schneider, J.J.; Hoffmann, R.C.; Engstler, J.; Klyszcz, A.; Erdem, E.; Jakes, P.; Eichel, R.A.; Pitta-Bauermann, L.; Bill, J. Synthesis, characterization, defect chemistry, and FET properties of microwave-derived nanoscaled zinc oxide. Chem. Mater. 2010, 22, 2203–2212.
14. Boruah, S; Mustafiza, S; Saikia, D; Saikia, H.J.; Saikia, P.P. Baruah, M.K. Synthesis of ZnO nanoparticles from zinc formate and their optical properties. Amer. chem.. Sci. J. 11 (2016) 1-10.
15. Wahab, R.; Kim, Y.-S.; Shin, H.-S. Effect of Refluxing Time on the Morphology of Pencil like Zinc Oxide Nanostructures Prepared by Solution Method, Met. Mater. Int. 16(5) (2010) 767-772.
16. Ansari, S.G.; Wahab, R. ; Ansari, Z.A. ; Kim, Y.-S. ; Khang, G. ; Al-Hajry, A.; Shin, H.-S. Effect of nanostructure on the urea sensing properties of sol–gel synthesized ZnO, Sens. Actuators, B 137 (2009) 566-573.
17. Lu, J.; Ng, K.M.; Yang, S.H. Efficient, One-Step Mechanochemical Process for the Synthesis of ZnO Nanoparticles, Ind. Eng. Chem. Res. 47 (2008) 1095-1101.
18. Chang, W-Y.; Fang, Te-H.; Weng, C-I; Shin-Shing Y. Flexible piezoelectric harvesting based on epitaxial growth of ZnO, Appl. Phys. A 102 (2011) 705-711.
19. Mclaren, A.; Valdes-Solis, T.; Li, G.; Tsang, S.C. Shape and Size Effects of ZnO Nanocrystals on Photocatalytic Activity, JACS 131 (2009) 12540-12541.
20. Soosen, S.M.; Bose, L.; George, K.C. Optical properties of ZnO nanoparticles. Academic Review, XVI (2009) 57-65.