

Synthesis and Characterization of Nanocrystalline Zinc Oxide Thin Films via Green Chemistry

Sharma Bhasha^{a*}, Santosh Singh^b, Purnima Jain^a and Parul Malik^a

^a NSIT-Netaji Subhash Institute of Technology, Dwarka Sec-3, New Delhi, India

^b CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi, India

Abstract

Green chemistry is an alternative route of which has overcome the limitations of other chemical methods. Nanocrystalline zinc oxide (NC-ZnO) with different structures have been grown on quartz plates by spin coating method by the use of plant extracts of *Citrus aurantifolia* which can be a cost effective and eco-friendly approach.. The present exploration describes the synthesis and characterization of ZnO nanoparticles thin films were characterized by XRD, SEM and AFM and Raman techniques to reveal their structural, morphological and optical details.

Keywords: ZnO Nano particles; *Citrus aurantifolia* Extracts; X-RD;TEM; SEM; AFM; FTIR; Green Chemistry.

© 2015 Published by Journal of Nanoanalysis.

1. Introduction

Green synthesis of ZnO nanoparticles was efficient method using *Citrus aurantifolia* extracts for the ecofriendly development of novel technologies. Zinc oxide (ZnO) nanoparticles have importance due to their vast area of applications, e.g., gas, chemical and bio-sensors, cosmetics, storage, optical and electrical devices, window materials for displays, solar cells, and drug-delivery [1-5]. ZnO is an attractive material for short-wavelength opto-electronic applications owing to its wide band gap 3.37 eV, large bond strength, and large exciton binding energy (60 MeV) at room temperature [6]. As a wide band gap material, In addition, due to its non-centrosymmetric crystallographic phase, ZnO shows the piezoelectric property [7-8], which is highly useful for the fabrication of devices, such as electromagnetic coupled sensors and actuators. ZnO have extensive applications in water purification [9]. ZnO nanoparticles have been used to remove arsenic, sulphur from water even though bulk zinc oxide cannot absorb arsenic because nanoparticles have large surface area. ZnO is inexpensive n-type semiconductor [10]. Nanostructures made of ZnO have attracted significant attention due to their proposed applications in the low voltage and

* Corresponding author. Tel: +91-8588018269 E-mail address: sharmabhasha@gmail.com

short-wavelength 368 nm electro-optical devices transparent ultraviolet UV protection films and gas sensors. Therefore, several new routes have been developed to synthesize ZnO-NPs, such as, sol-gel, sol-gel combustion, chemical precipitation [24-25], hydrothermal, solvothermal, chemical vapor deposition (CVD), a sonochemical method, and thermal oxidation [11-19]. Sol-gel method is widely adopted for the fabrication of transparent and conducting oxide due to its simplicity, safety, no need of costly vacuum system and hence cheap method for large area coating. Some of these methods have limitations. Optoelectronic properties of ZnO nanostructures depend strongly upon their crystalline structure, morphology, defects and impurity contents. Structure & morphology are derived from the XRD and SEM measurements. ZnO is nontoxic it can be used as photo catalytic ZnO is an excellent material for the manufacture of sunscreen, because it absorbs ultraviolet (UV) rays and combat the potential problems associated with sun exposure. Degradation materials of environmental pollutants. The aim of this work is to grow nanostructures of ZnO with good crystalline quality, low structural and electronic defects.

1.1. Structure

Zinc oxide crystallizes in a wurtzite structure with alternating planes of tetrahedral coordinated Zn²⁺ and O²⁻ bonded alternately along c-axis of hexagonal unit cell with $a_0 = 0.3250$ nm and $c_0 = 0.5207$ nm. The cause for the natural N-type nature of ZnO is due to the sensitiveness of ZnO lattice constants to the presence of structural point defects (vacancies and interstitials) and extended defects (threading/planar dislocations) that are commonly found in ZnO resulting in a non-stoichiometric compound Zn_{1+d}O with an excess zinc.

Zinc oxide crystallizes in a wurtzite structure with alternating planes of tetrahedral coordinated Zn²⁺ and O²⁻ bonded alternately along c-axis of hexagonal unit cell with $a_0 = 0.3250$ nm and $c_0 = 0.5207$ nm. The cause for the natural N-type nature of ZnO is due to the sensitiveness of ZnO lattice constants to the presence of structural point defects (vacancies and interstitials) and extended defects (threading/planar dislocations) that are commonly found in ZnO resulting in a non-stoichiometric compound Zn_{1+d}O with an excess zinc. The end product in Green synthesis method was pale white precipitate. The calcinated powders are studied using different characterization techniques. Confirmation of pure ZnO phase is verified by XRD analysis.

2. Experimental Measurements

Nanocrystalline (NC) ZnO thin films grown by sol-gel process [11-16] from citrus aurantifolia fruits obtained from the market were peeled and the pulps were sliced into small pieces and blended in Distilled water. The blended pulps were then filtered by using muslin cloth to remove solid particles. The liquid was further filtered using syringe filter. Zinc acetate was dissolved in 100 ml of the filtered C. aurantifolia liquid extracts using zinc acetate as precursor on quartz plate by using 10%, 15% and 25% concentrations of zinc acetate [Zn(CH₃COO)₂·2H₂O].

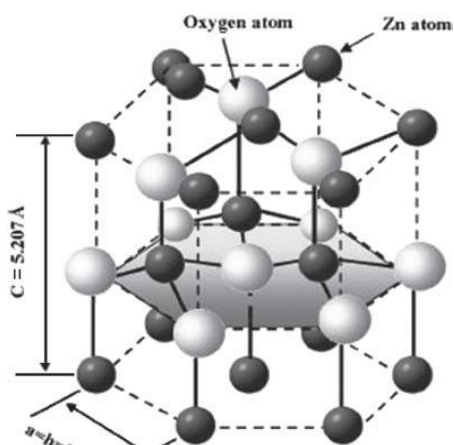


Figure 1. Structure of ZnO

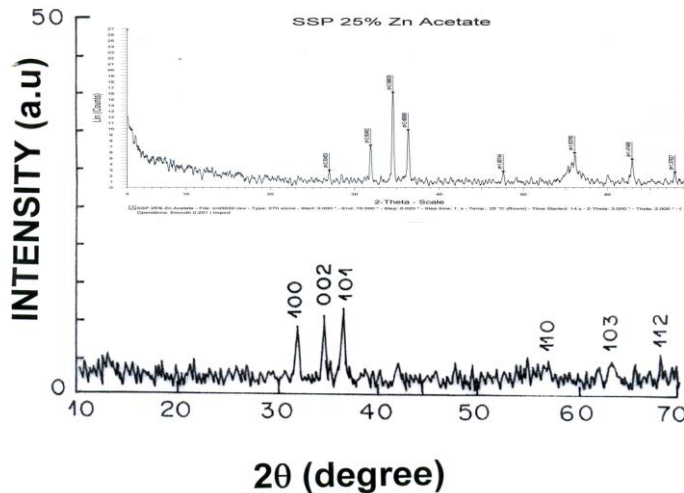


Figure 2. ZnO thin film derived from 5% and 25% sol

The pH value of the solution was between 3.7 and 4.0. The mixtures were heated at 80 °C under continuous stirring for 3 hr. after which precipitate occurred. Then the solution is left for 30 minutes which results in the formation of white bulky solution. The solution is then washed 8-10 times with distilled water and filtered in a filter paper. The residue obtained is put for drying in oven at a temperature of about 95°C for 8 hr. The precipitates were recovered, thoroughly rinsed in distilled water followed by drying wafer at 100o C and subsequent annealing at 100o C, 200o C, 300o C and 400o C for one hour to optimize temperature suitable for good quality ZnO films. Ten coatings were done to obtain the optimum thickness of the film needed for characterization. The spherical zinc oxide nanoparticles were produced using different concentration of zinc acetate which was used as the zinc source by simple sol gel method which is short time process and cost effective. The film thickness were 250 nm, 256 nm and 334 nm by ellipsometric investigations. Bruker AXS D8 Advance diffractometer which has in built Diffracplus software using CuK α radiation for XRD measurements. LEO-440 SEM for morphological study.

3. Results & Discussions

3.1 XRD Pattern

Synthesized NC-ZnO particle analyzed on the basis of their crystallinity, crystallite size, band gap and structural properties. X-Ray Diffraction pattern Figure 2 is used to calculate crystallite size and variation in band gap. Unique characteristic X-ray diffraction pattern of each crystalline solid gives the designation of “fingerprint technique” to XRD for its identification.

The XRD pattern consists of a single (002) peak which occurred due to ZnO crystals and grows along the c-axis. High purity and crystallinity of the prepared ZnO NPs confirms the sturdy and clear peak. For other impurities no characteristic peak was accessible [19]. The deviation of the lattice parameters is caused may be due to presence of various point defects such as zinc antisites, oxygen vacancies, and extended defects, such as threading dislocation. With increasing calcinations temperature peak height increases and FWHM decreases as result diffraction peaks become stronger and sharper, thereby indicating that the crystal quality has been improved and the size of particles become bigger. Moreover, all diffraction peaks of the product show stronger peak intensities, indicating that the obtained ZnO nanoparticles have high crystallinity.

3.2. Raman Spectra

Characteristic peaks of ZnO is between ~335, ~380 ~430, ~450, ~570, and ~610 cm⁻¹ are seen. The peak at ~335 cm⁻¹ is assigned to the bending vibration while the other two peaks are attributed to the stretching vibrations. It may be noted that, the Raman bands at ~335 and 610 cm⁻¹ gets significantly reduced. The band at 540- 417 cm⁻¹ point out ZnO nanoparticles [20-22].

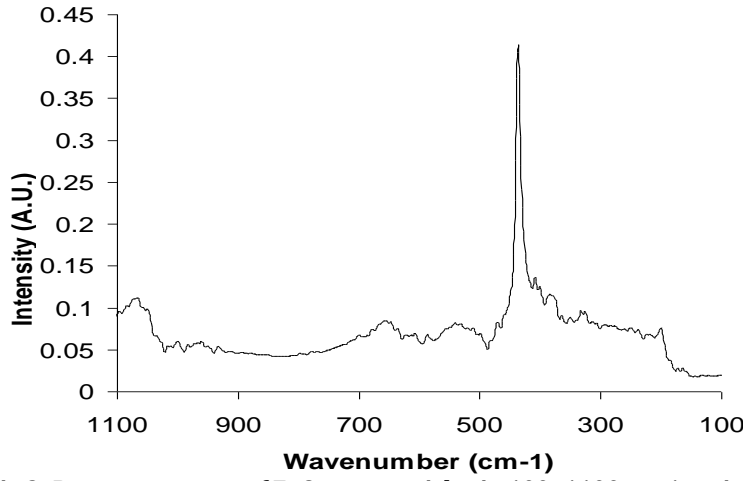
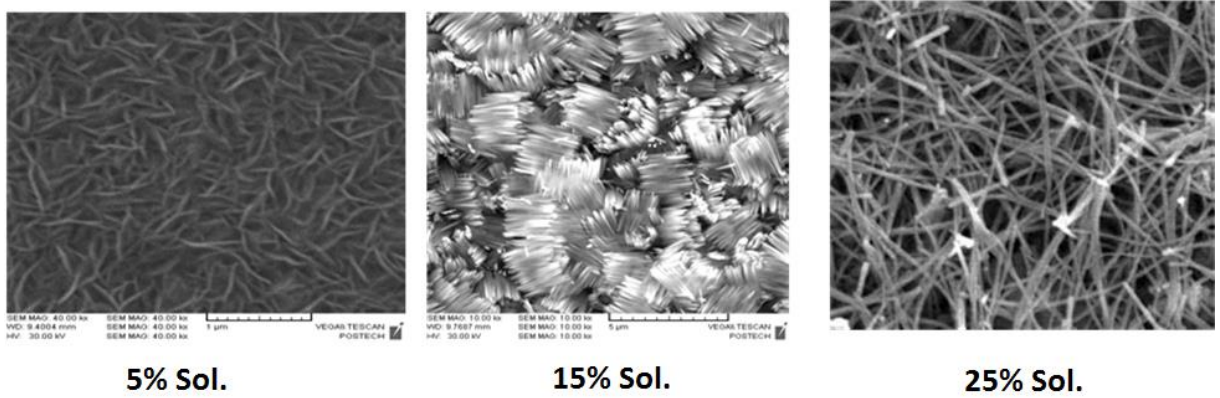


Fig 3 -Raman spectrum of ZnO nanoparticles in 100 -1100 cm-1 region

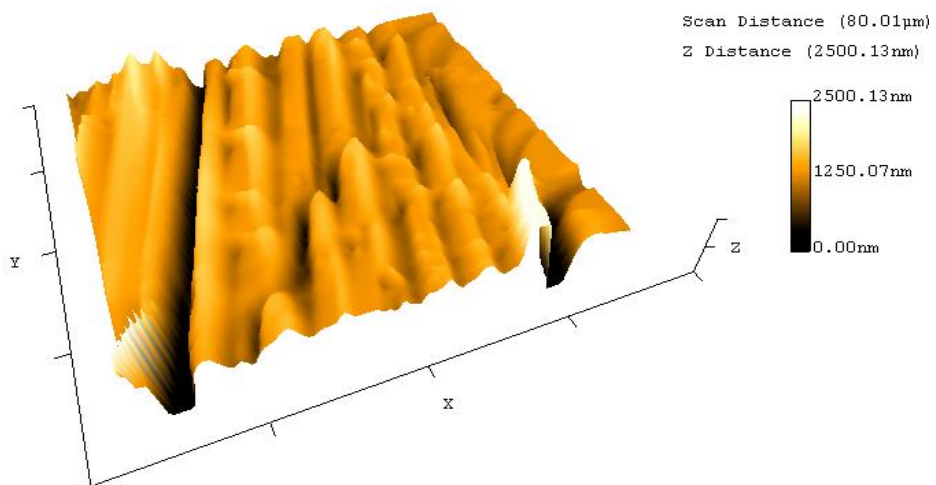


5% Sol.

15% Sol.

25% Sol.

Figure4 SEM images of Nanocrystalline ZnO thin film



Missing of plane & distortions at peripheries

3.3 SEM and AFM Images

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions: 1) acquiring elemental maps or spot chemical analyses using EDS, 2) discrimination of phases based on mean atomic number (commonly related to relative density).

(SEM) micrograph of ZnO thin film is shown in with presence of tightly packed grains. The nanocrystals are regularly distributed on the glass substrate and crystallite size. SEM micrograph of ZnO thin film shows that the small grains made a smooth and transparent surface.

SEM (Scanning Electron Micrograph) and AFM (Atomic Force Microscopy) images are shown clearly to see the particle size and grain size respectively.

3.4 Fourier transform infrared spectroscopy (FTIR) analysis

Fourier transforms infrared (FTIR) spectrometer. The spectroscopy merely based on the fact that molecules absorb specific frequencies that are characteristic of their structure termed as resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates.

In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. FTIR can be used to analyze a wide range of materials in bulk or thin films, liquids, solids, pastes, powders, fibers, and other forms. FTIR analysis can give not only qualitative (identification) analysis of materials, but with relevant standards, can be used for quantitative (amount) analysis.

3.5 TEM Analysis

Transmission electron microscope examination can yield the information like topography, morphology, composition as well as crystallographic information's.

In TEM there is no change in the refractive index of the medium when the illumination beam is deflected, the vacuum in the lens is the same as the vacuum in the column.

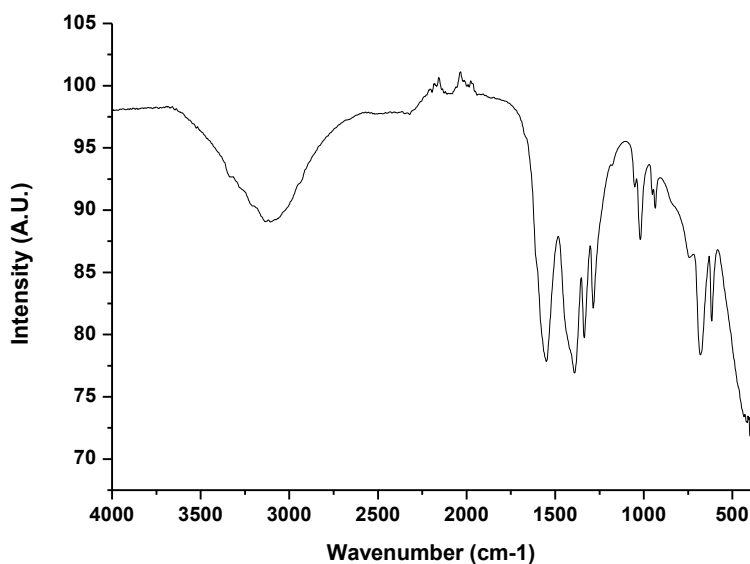


Figure 5. IR transmission spectrum of the ZnO-NPs

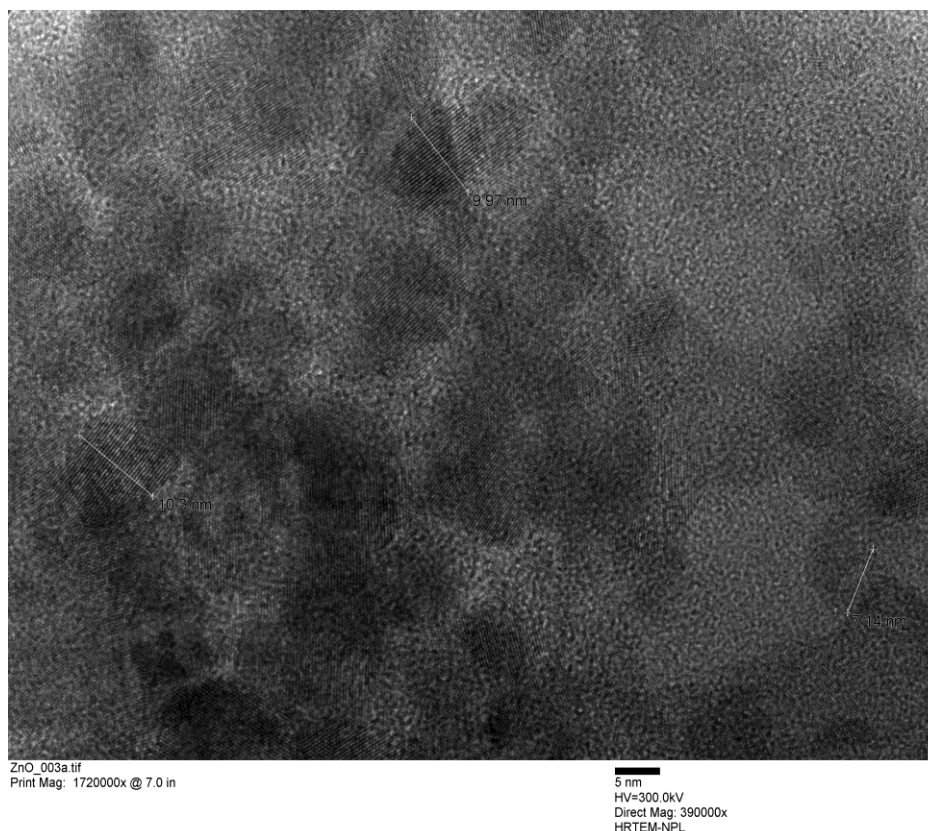


Figure 6. TEM images and electron diffraction patterns of ZnO nanoparticles at different temperatures. This image reveals that the product consist of spherical particles with the average size of 5-20 nm.

4. Conclusion

Synthesis of Zinc oxide nanoparticles via green chemistry has emerging field in nanotechnology to make nanomaterials which are eco-friendly; cost effective, stable particles for wide applications in the areas of electronics, medicine and cosmetics .ZnO nanoparticles have wurtzite structure. Employing plants in synthesis of nanoparticles are advantageous as compared to other conventional methods due to the presence of broad variability of bio-molecules which can increase the rate of reduction and stabilization of nanoparticles. XRD, AFM, Raman Spectra and SEM characterization reveals surface morphology and particles size of ZnO nanoparticles. It was observed that the band gap of the samples remains almost constant i.e. (3.17eV) for different calcinations temperature.

5. Acknowledgements

We are thankful to Prof. R.C. Budhani, Director, CSIR-National Physical Laboratory, and Delhi, India for permitting to carry out and publishing this work.

6. References

- [1]. J. B. Baxter and E. S. Aydil, Appl. Phys. Lett. 86, 53114 (2005).
- [2]. M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science 292,1897 (2001).
- [3]. J. Song, J. Zhou, and Z. L. Wang, Nano Lett. 6, 1656 (2006).
- [4] Z. L. Wang, Annu. Rev. Phys. Chem. 55, 159 (2004).
- [5] J. Sawai, H. Igarashi, A. Hashimoto, T. Kokugan, and M. Shimizu, J. Chem. Eng. Japan 29, 556 (1996).
- [6]. Q. Li, V. Kumar, Y. Li, H. Zhang, T. J. Marks and R. P. H. Chang (2005). J. Am. Chem. Soc. 17. 1001.

- [7]. Sunandan Barua, Samir K. Pal and Joydeep Dutta, Nanostructured Zinc Oxide for Water Treatment, *Nanoscience and Nanotechnology-Asia*, 2, 90 (2012).
- [8] J. B. Webb, D. F. Williams, M. Buchanan, "Trans- parent and Highly Conductive Films of ZnO Prepared by RF Reactive Magnetron Sputtering," *Appl. Phys. Lett.*, vol. 39, No. 8, 1981, pp. 640-642. doi:10.1063/1.92815
- [9] S. J. Kang, J. Y. Choi, D. H. Chang and Y. S. Yoon, "A Study on the Growth and Piezoelectric Characteristics of ZnO Thin Film Using a RF Magnetron Sputtering Me- thod," *Journal of Korean Physics Society*, Vol. 47, No. 93, 2005, pp. S589-S594.
- [10].S. Chakrabarti and B. K. Dutta, "Photocatalytic Degrada- tion of Model Textile Dyes in Wastewater Using ZnO as Semiconductor Catalyst," *Journal of Hazardous Materi- als*, Vol. 112, No. 3, 2004, pp. 269-278.
- [11]. Zak AK, Majid WH, Abd Darroudi M, Yousefi R. Synthesis and characterization of ZnO nanoparticles prepared in gelatin media. *Mater Lett*. 2011; 65:70-73.
- [12]. Zak AK, Abrishami ME, Majid WH, Abd Yousefi R, Hosseini SM. Effects of annealing temperature on some structural and optical properties of ZnO nanoparticles prepared by a modified sol-gel combustion method. *Ceram Inter*. 2011; 37:393-398.
- [13]. Wang Y, Zhang C, Bi S, Luo G. Preparation of ZnO nanoparticles using the direct precipitation method in a membrane dispersion micro-structured reactor. *Powder Technol*. 2010; 202:130-136.
- [14]. Lu CH, Yeh CH. Influence of hydrothermal conditions on the morphology and particle size of zinc oxide powder. *Ceram Inter*. 2000; 26:351-357.
- [15]. Sangkhaprom N, Supaphol P, Pavarajarn V. Fibrous zinc oxide prepared by combined electrospinning and solvothermal techniques. *Ceram Inter*. 2010; 36:357-360.
- [16]. Yousefi R, Muhamad MR, Zak AK. Investigation of indium oxide as a self-catalyst in ZnO/ZnInO heterostructure nanowires growth. *Thin Solid Films*. 2010; 518:5971-5977.
- [17]. Cao Y, Liu B, Huang R, Xia Z, Ge S. Flash synthesis of flower-like ZnO nanostructures by microwave-induced combustion process. *Mater Lett*. 2011; 65:160-163.
- [18]. Mishra P, Yadav RS, Pandey AC. Growth mechanism and photoluminescence property of flower-like ZnO nanostructures synthesized by starch-assisted sonochemical method. *Ultrason Sonochem*. 2010; 17:560-565. [PubMed]
- [19]. Xu CH, Lui HF, Surya C. Synthetics of ZnO nanostructures by thermal oxidation in water vapor containing environments. *Mater Lett*. 2011; 65:27-30.
- [20]. Reza zamari, Azmi Zakaria, Hossein Abbastar Ahangar, Majid Darroudi, Alikhorsand Zak and Gregor P.C.Drummen, Aqueous starch as a stabilizer in zinc oxide nanoparticle synthesis via laser ablation, *Journal of Alloys and Compounds*, 516(5), 41-48 (2012)
- [21]. Kushal D. Bhatte, Dinesh. N. Sawant, Dipak V. Pinjari, Anirudha B. Pandit and Balchandra M. Bhange, One pot green synthesis of nanosized zinc oxide by sonochemical method, *Material Letters*, 77, 93-95 (2012)
- [22]. Reza zamari, Azmi Zakaria, Hossein Abbastar Ahangar, Majid Darroudi, Alikhorsand Zak and Gregor P.C. Drummen, Aqueous starch as a stabilizer in zinc oxide nanoparticle synthesis via laser ablation, *Journal of Alloys and Compounds*, 516(5), 41-48 (2012)
- [23]. Sankara Reddy B., Venkatramana Reddy S., Koteeswara Reddy N. and P ramoda Kumari, Synthesis, Structural, Optical Properties and Antibacterial activity of co-doped (Ag, Co) ZnO Nanoparticles, *Res. J. Material Sci.*, 1(1), 11-20 (2013)
- [24]. Xiao-lan Song, Peng Qu, Hai-pin Yang, Xi He, Guan-zhou Qiu, Synthesis of γ -Al₂O₃ nanoparticles by chemical precipitation method, *Journal of Central South University of Technology*. 12(5), 536-541(2012)
- [25]. srinivasa rao, rajesh kumar, rajagopal reddy, preparation and characterization of cds nanoparticles by chemical coprecipitation technique, *Chalcogenide Letters* 8, (3), 177-185 (2011).