

DNA Assisted Synthesis, Characterization and Optical Properties of Zinc Oxide Nanoparticles

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Abstract—Recently biosynthesis of metal oxide nanoparticles had attracted much attention because of the necessity to develop new clean, ecofriendly and cost effective synthesis techniques. Zinc oxide nanoparticles were prepared by co-precipitation, using DNA, a biomaterial, as capping agent. The nanoparticles obtained are characterized using XRD, SEM, and FTIR. The XRD confirms the crystalline nature and formation of nanoparticle. The optical properties were studied using Photoluminescence spectroscopy and UV-Vis absorption studies. Band gap of the material obtained is 3.63eV higher than the bulk value (3.37eV). Broad and intense luminescence emissions make the material suitable for blue lazing applications. The results are compared with Zinc Oxide nanoparticles prepared using EDTA as capping agent and found to be of better quality in many aspects. If metal oxide nanoparticles can be synthesized using DNA as capping agent will it favor the synthesis of medically useful metal oxide directly into human body?

Index Terms—biosynthesis, DNA, nanoparticles, bandgap, Photoluminescence

I. INTRODUCTION

Synthesis of semiconductor nanoparticles having a controlled size distribution has attracted significant interest in research because of their quantum size effects, luminescent properties and other important physical and chemical properties. The broad area of applications include optoelectronic devices, solar energy conversion, molecular and cellular imaging and trace detection. A major feature of semiconductor nanoparticles is the quantum confinement effect, which leads to spatial enclosure of charge carriers within the nanocrystal. Because of this effect we can tune the light emission from the media throughout the ultraviolet, visible, near infrared and mid infrared spectral regions. For instance, by adjusting the appropriate size of the semiconducting particle band gap is tunable over a wide range of wavelength. More over the fluorescent emission spectra of quantum dots can be tuned continuously by changing the particle size, and a single wavelength can be used for

the simultaneous excitation of all different sized quantum dots [1]-[5].

ZnO is one of the most important II-VI semiconductor compound having excellent optical properties. It is a direct bandgap material of bandgap 3.37eV at 300K. Considerable amount of effort has been devoted to the synthesis and study of optical property of ZnO related nanoparticles and quantum dots. Highly monodispersed ZnO nanocrystal can be synthesized via size restricting growth methods. Adding surface capping organic materials to the solution is one of the ways to achieve the size restriction. This simple preparation technique has opened the way towards tunable light emitting devices and low voltage display devices. There is a significant change in the properties when the dimensions of the nanocrystallites become comparable to Bohr radius of excitons corresponding to widening of the energy gap as size decreases. Among the different techniques used by researchers to synthesize ZnO nanoparticles chemical method is a simple and really cost effective method.

Among biological molecules DNA have been extensively used as a bio template to grow inorganic quantum confined structure and to organic non biological building blocks into extended hybrid materials because of their physicochemical stability and unique structure [6]-[8]. The integration of nanotechnology and biology and medicine is expected to produce major advances in molecular biology and bio engineering. Using biomolecules as a templating agent to synthesize inorganic nanoparticles is an effective method to fabricate functional materials with well-defined structure and controllable dimensions. We adopted the precipitation technique using DNA as capping agent to synthesize ZnO nanoparticles. Samples of Zinc oxide nanoparticles using same preparation conditions with another capping agent (EDTA) is also synthesized as a part of this work to compare the properties exhibited by them.

The most important and famous biomaterial known to man is DNA (Deoxy ribo nuclic acid) that carries the genetic code in all living organisms. During the last two decade, DNA “the molecule of life” has been attracting attention of researchers in diverse area of science and technology. Recently it is reported that DNA molecules

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can be used as a data storage medium. DNA memory, utilizing DNA molecules and DNA reactions for data processing, has been proposed as a high capacity and high density memory. Another application for DNA is being explored in the field of nano biotechnology. Establishing a tie between biotechnology and nanotechnology resulted in a new field called nano biotechnology. DNA can be used as a bio template to grow inorganic quantum confined structures like quantum dots, quantum wires, metallic nanoparticles, metal oxides and sulphides etc.

DNA can be used as a guiding template for polymerization of conducting polymers. For example polypyrrole and ployaniline are synthesized on DNA template by the interaction of cationic monomers to the backbone of DNA immobilized on a Si surface. This approach has potential for fabrication of high density conducting polymer nanowires with a predetermined position and orientation on a Si surface [9]. The method of synthesizing Zinc oxide nanoparticles using DNA is being reported for the first time and these nanoparticles may be more biocompatible and suitable for direct applications in the field of medicine.

II. SYNTHESIS AND CHARACTERIZATION

A. Preparation Technique

All Chemicals and DNA powder were obtained from commercial sources (SRI, Merck). In the first method we used aqueous solutions of DNA powder as capping agent to control the particle size. Here 0.1M solution of Zinc acetate, 0.1M solution of Sodium hydroxide are added drop wise into 0.01 wt.% of DNA solution at the rate of 10ml per hour under constant stirring using a magnetic stirrer. A white precipitate is formed at the end of reaction. The precipitate obtained is washed several times using distilled water to remove traces of mother chemicals. The precipitate is filtered, dried in a hot air oven kept at 60 °C and then ground, into fine powder. In the second method EDTA was used instead of DNA and the procedure was repeated with same molar solutions of Zinc acetate and sodium hydroxide. The samples obtained from the two methods will hereafter be referred as Z1 and Z2.

B. Characterization

X-ray diffraction (XRD) spectra of samples are recorded with a PAN Analytical Model X'pert pro X-ray diffractometer employing CuK α radiation at 40KV and 100mA at a scanning rate of 8° min $^{-1}$ in the range 20-70°. The scanning electron micrographs (SEM) of the samples are recorded with a Hitachi model S-3000H scanning electron microscope. The FTIR studies of all the samples were carried out in a Perkin-Elmer FTIR Spectrophotometer between 300cm $^{-1}$ and 4000cm $^{-1}$. The absorption spectra of this material were taken at room temperature with the help of a Jasco V 550UV/Vis-NIR spectrophotometer.

III. RESULTS

A. Structure and Morphology

The precipitate in both process are white in colour. The energy dispersive analysis (EDAX) gives information about the elements present in the sample as well as approximate stoichiometry. The results of EDAX of the sample Z1 (Fig. 1) shows that there is no impurity and there is no traces of the chemicals used. The percentages of Zinc and Oxygen in the two samples (Z1, Z2) are given in Table I.

TABLE I. RESULT OF EDAX ANALYSIS SHOWING THE PERCENTAGE OF ZN AND O IN THE SAMPLE

Element	Mass%		Atom%	
	Z1	Z2	Z1	Z2
O K	6.67	9.1	22.61	29.04
Zn K	93.33	90.9	77.39	70.96
Total	100	100	100	100

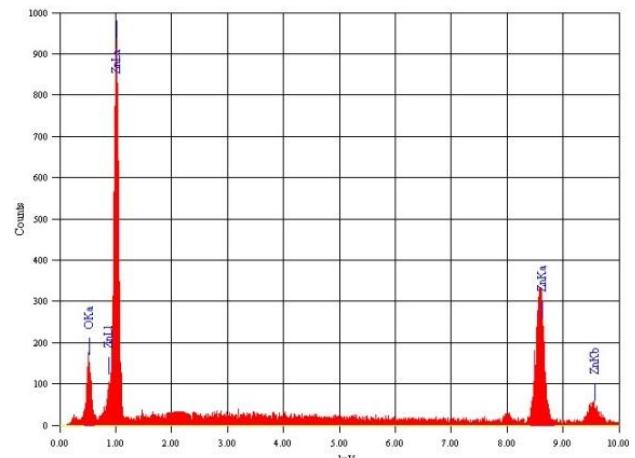


Figure 1. Edax spectrum of sample Z1.

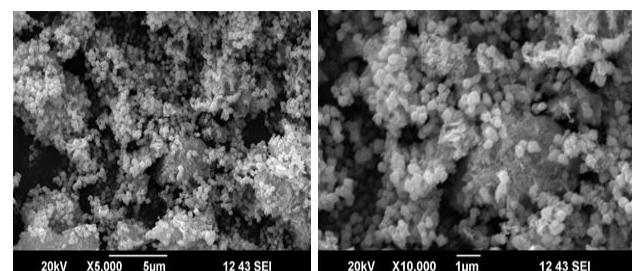


Figure 2. SEM images of the Zinc oxide nanoparticles (Z1) synthesized using DNA (different resolutions)

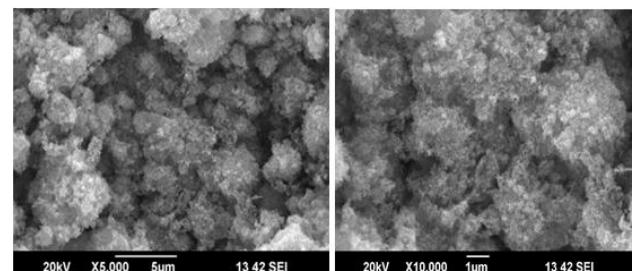


Figure 3. SEM images of the Zinc oxide nanoparticles (Z2) synthesized using EDTA (different resolutions)

The morphology of the precipitates is obtained from the scanning electron micrographs of Z1 and Z2. The Fig.

2 shows the surface morphology of sample Z1 for two resolutions. The particles are homogeneous in shape and size.

The surface morphology of the sample Z2 prepared using EDTA as capping agent is given in Fig. 3.

The homogeneity in shape and size of the nanoparticles in the sample Z1 appears to be better than that of Z2 under the resolutions taken. But the sizes calculated using XRD shows a good homogeneity in size in the case of Z2 in comparison with that of Z1. The crystal phase identification of the precipitate is done by comparing the X-ray diffraction spectra with reported crystal diffraction data by JCPDS. The Fig. 4 and Fig. 5 shows distinctive peak at (100), (002), (101), (102), (110), (103), (200), (112) and (201) that are in good agreement with wurtzite ZnO.

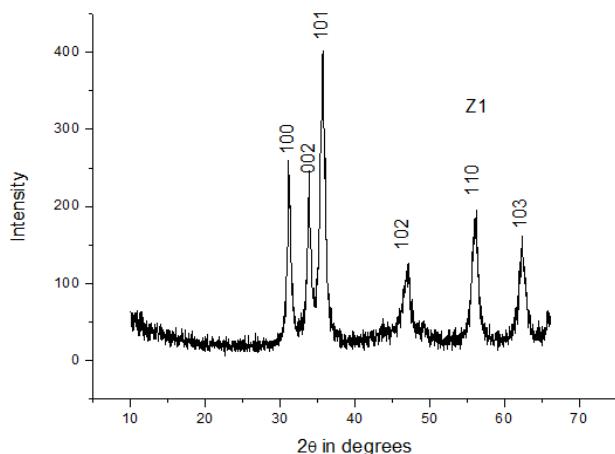


Figure 4. XRD spectrum of Zinc oxide nanoparticles of sample Z1

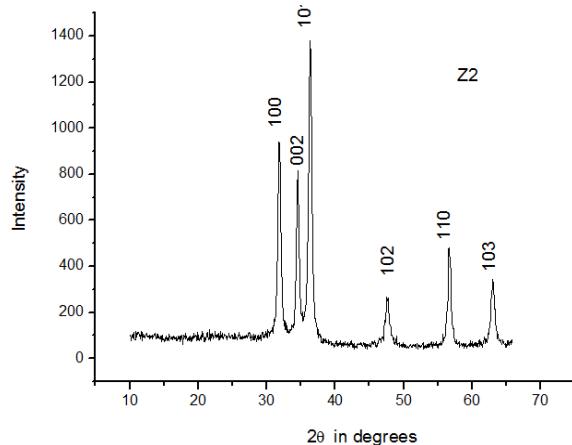


Figure 5. XRD of Sample Z2

The diffraction pattern of sample Z1 is in close agreement with reported values in card no 75-1533 (lattice parameter $a=3.351$, $c=5.226$). The 2theta values at which the diffraction peaks of sample Z2 obtained in good match with the reported values in JCPDS card 75-0576 (lattice parameters, $a= 3.242$ and $c=5.194$). The Debye Scherer's Eq. (1) can be used to evaluate the particle size d , where k is a constant and is 0.9 for spherical particles. The microstrain e , and dislocation density D , can be calculated using Eq. (2) and Eq. (3).

$$d = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

$$e = \left(\frac{\lambda}{d \cos \theta} - \beta \right) \left(\frac{1}{\tan \theta} \right) \quad (2)$$

$$D = \frac{1}{d^2} \quad (3)$$

where λ is the wavelength of X-ray, β full width at half maximum and θ the Bragg's angle of diffraction. Using Eq. (1) the average particle size obtained for ZnO nanoparticle is 13nm in Green synthesis using DNA while the size of nanoparticles obtained using EDTA is 20nm. The micro strain for the samples Z1 and Z2 are, calculated using equation (2), 3.09×10^{-3} and 2.5076×10^{-3} respectively. The strain also contributes to broadening of peaks in the XRD. The dislocation density was also found out, using equation (3), and obtained as 6.869×10^{15} and 2.437×10^{15} lines/m² for samples Z1 and Z2 respectively.

B. FTIR Studies

The FTIR spectra of sample Z1 is given in Fig. 6.

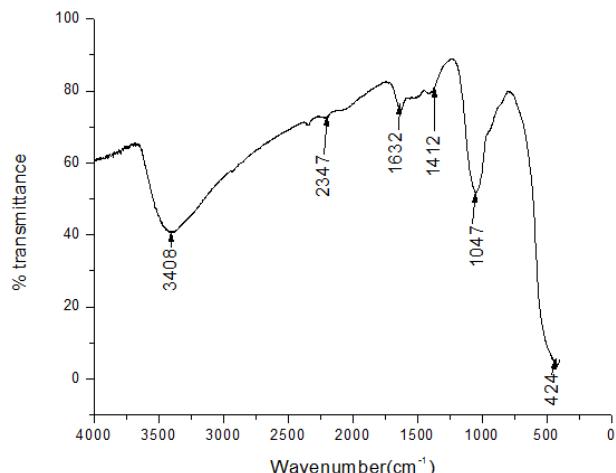


Figure 6. FTIR spectrum of Z1

The band at 3408cm^{-1} is due to the asymmetric stretching of OH bond and the band at 2347cm^{-1} is valence vibration of occluded water. The bands near 1631cm^{-1} indicates the presence of aromatic ring and here this band can be due to C=O stretching in the amide and the band at 1047cm^{-1} is due to the C-O stretching vibration. The presence of these bands indicates the presence of some carbonaceous material. The bands between around 1400cm^{-1} can be attributed to presence of carbonaceous material and the band at 424cm^{-1} is the changes in the interaction between oxygen and Zinc ion.

The FTIR spectrum of Z2 (Fig. 7) shows lesser bands and the bands at 510cm^{-1} and 863cm^{-1} are indicative of Zn-O vibrations. The small bands between 1410cm^{-1} - 1490cm^{-1} indicate the presence of some carbonaceous material and the band at 3423cm is due to the stretching vibration of OH bond. The presence of carbonaceous material shows that repeated washing of the precipitate was not so successful in removing the traces of chemicals used completely.

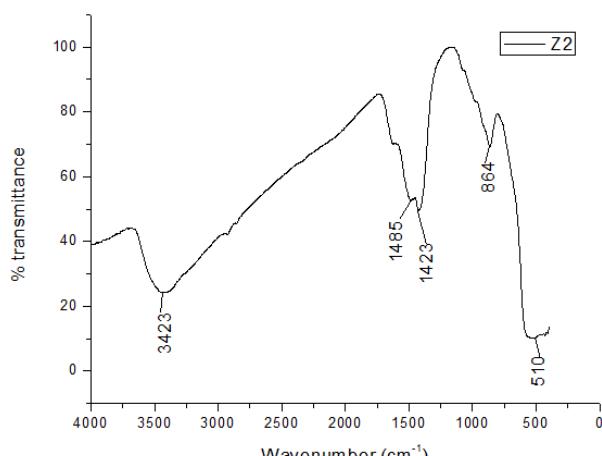


Figure 7. FTIR spectra of sample Z2

C. UV-Vis Absorption Spectroscopy

The nature of UV-Vis absorption spectra of both samples is similar with peak slightly shifted. Rather than directly converting the wavelength corresponding to maximum value of absorption to find band gap, drawing Tauc plot between $h\nu$ in eV versus $(\alpha h\nu)^2$ gives better linearity extrapolation of which gives band-gap is preferred. Fig. 8 and Fig. 9 gives the Tauc plot of absorption of sample Z1 and Z2. The band gaps obtained from graph are 3.63eV and 3.52eV respectively, which again confirms that particle size of crystallites formed using DNA is smaller than that for synthesized using EDTA and hence a wider band gap.

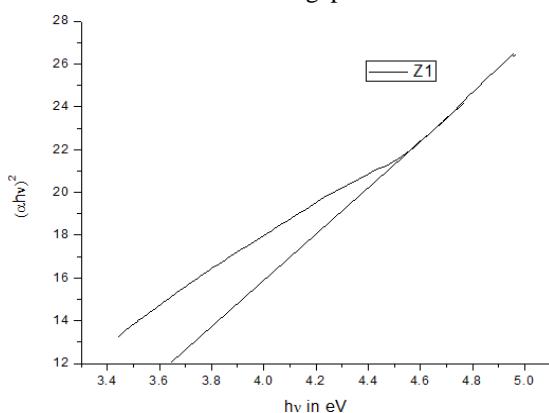


Figure 8. Tauc Plot of the absorption spectra of sample Z1

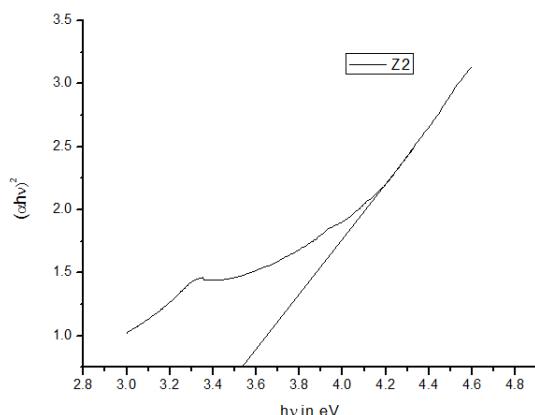


Figure 9. Tauc plot of the absorption spectra of sample Z2

The optical properties of a semiconductor are dependent on both the intrinsic and the extrinsic defects in the crystal structure. The defects can be of various types, like due to interstitial atoms, vacancies etc. If foreign atoms such as impurities are involved in the defects then these defects are called extrinsic point defects. If the defects only consist of host atom, then these defects are called intrinsic atoms. Intrinsic optical recombination takes place between the electrons in the conduction band and holes in the valence band [10].

D. Photoluminescence Studies

Both intrinsic and extrinsic point defects contribute to the luminescence properties in ZnO [10]. Generally a sharp ultra-violet (UV) emission band and a broad emission band are observed. The UV emission band is commonly attributed to transition recombination of free excitons in the near band-edge of ZnO. The broad emission band in the visible region (420nm-750nm) is attributed to deep level defects in ZnO. There are many different deep level defects in the crystal structure of ZnO and they affect the optical and electrical properties of ZnO.

The electrical and optical properties of a semiconductor material can be controlled and modified by controlling the quantity and nature of the defects in it.

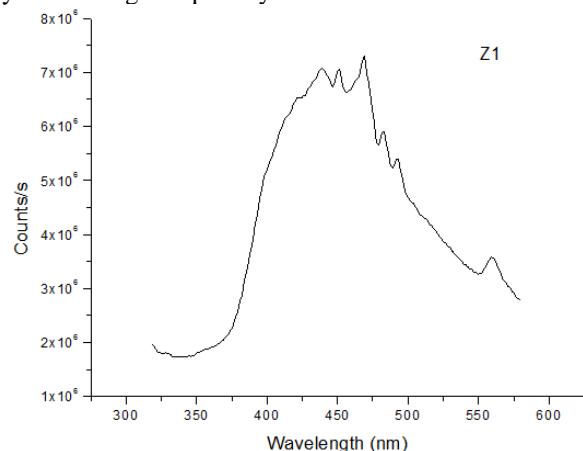


Figure 10. Photoluminescent spectrum of sample Z1

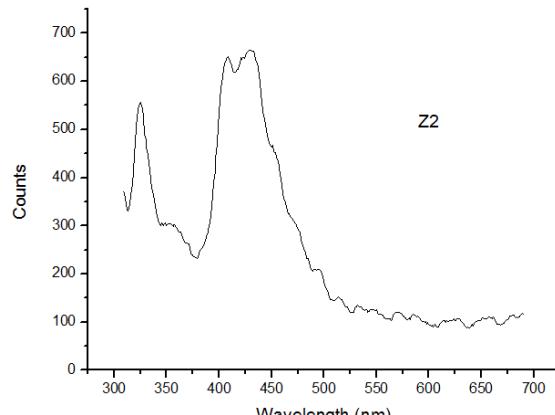


Figure 11. Photoluminescence spectrum of sample Z2

The deep level emission (DLE) band in ZnO has been previously attributed to different intrinsic defects in the

crystal structure of ZnO such as oxygen vacancies (VO) [11]-[14], oxygen interstitial (O_i) [15]-[18], zinc vacancies (VZn) [19]-[21], zinc interstitial (Zni) [22], [23] and oxygen anti-site (O_{Zn}) and zinc anti-site (Zn_o) [24]. The extrinsic defects such as substitution Cu and Li [16] are also suggested to be involved in deep level emissions.

The photoluminescence properties of the two samples Z1 and Z2 are different in nature even though common emissions are present. The luminescent spectra of Z1 are given in Fig 10. Show a broad and intense emission band in the blue region (420nm-470nm) with a small emission peak at green region. There are no other prominent peaks in the obtained spectra. But the emission spectra of sample Z2 (Fig. 11) is different from that of Z1 and shows two intense emissions, one sharp peak in the UV region, at 324nm and another broad band with two peaks at 410nm and 430nm, in the UV and Visible region. Since UV luminescence gets suppressed in the presence of blue emission band, and the blue luminescence is related to deep acceptor levels. The result reveals that the mechanism of blue luminescence in ZnO is by transition from near conduction band edge to deep acceptor levels. The luminescence spectra give qualitative information about the lattice defects.

IV. CONCLUSION

Nanoparticles of ZnO were successfully synthesized using green synthesis method utilizing DNA. The obtained nanoparticles were homogeneous in shape and size of the particles was 13nm. The Optical band gap and luminescent properties are explored. All the structural and optical property of nanoparticles synthesized using DNA was compared with the properties of ZnO nanoparticles synthesized using EDTA. The broad and intense blue violet emission band make the synthesized nanoparticles using DNA make them suitable for blue lazing applications.

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