Chapter 2

2. Synthesis and Physico-chemical characterization of different sized uncapped and capped ZNPs by several conventional and novel processes.

2.1. Introduction:

Ultrahigh surface area and unique properties in the nanoscale have been the main motivations for researchers to develop highly efficient nanomaterials for different modern applications. In recent years, there has been a great deal of interest in the use of zinc oxide nanoparticles (ZNPs) as a material for a wide range of applications. ZnO is a key technological material. The lack of a centre of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors. In addition, ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60meV) in ZnO crystal can ensure efficient excitonic emission at room temperature and room temperature ultraviolet (UV) luminescence.

![Figure 1. The wurtzite structure model of ZnO. The tetrahedral coordination of Zn–O is shown.](image)
In this chapter, synthesis and physico-chemical characteristics of different types of uncapped and capped ZNPs are described.

2.2. Synthesis and Physico-chemical Characterizations of ZNPs [ZNP (N)] from zinc nitrate:

50 ml of 0.5M sodium hydroxide solution is heated at 70°C. 50 ml of 0.5M solution of zinc nitrate solution is added drop wise for 30 minutes to the sodium hydroxide solution under constant stirring. After 3 hr reaction, a white precipitate is deposited at the bottom. The precipitate is washed several times and dried overnight to get ZNPs [1].

ZNP(N) was characterized by using Scanning Electron Microscopy (SEM) [Carl Zeiss], Transmission Electron Microscopy (TEM) [FEI] and Energy dispersive spectroscopy (EDAX) analysis. Scanning electron microscope was used to study the size and surface morphology of ZNPs. Due to small size of the particles the morphology was not quite clear from SEM micrograph [Figure 2a]. However the size of the particles was ~50 nm. Composition of the sample was confirmed by Energy-dispersive X-ray spectroscopy. EDAX analysis showed that the sample contained Zn and O as the elemental composition of synthesized ZNP (N) [Figure 2(a) inset]. Distinct size and shape (50 nm) was confirmed by TEM micrograph [Figure 2(b)].

Figure 2. (a) Scanning electron microscopic image of ZNP(N); (b) Transmission electron micrograph of ZNP(N) and energy-dispersive X-ray analysis of ZNP(N)(inset).
2.3. Synthesis and Physico-chemical Characterizations of ZNPs \([\text{ZNP(C)}]\) from zinc acetate:

Cetyl trimethyl ammonium bromide (CTAB) is added in Zinc acetate solution under constant stirring. 10 ml sodium hydroxide solution (2M) is then added to it and the mixture is refluxed at 120°C for 3 hrs. The solution is filtered and washed with distilled water and ethanol to get ZNPs[2]. SEM image [Figure 3a] indicated size and surface morphology of ZNP(C). TEM image clearly indicated the size of ZNP(C) which lies between 80-120 nm[Figure 3b]. Zn and O are the elemental composition of synthesized ZNP (C) which was confirmed by EDAX analysis [Figure 3b inset].

![Figure 3. (a) Scanning electron microscopic image of ZNP(C); (b) Transmission electron micrograph of ZNP(C) and energy-dispersive X-ray analysis of ZNP(C) (inset).](image)

2.4. New synthesis and Physico-chemical Characterizations of ZNPs \([\text{ZNP (T)}]\) from zinc acetate in presence of TRIS buffer:

This synthesis process involves a single step reaction. First 0.05 M zinc acetate solution and 20% TRIS solution are separately prepared in water. Then zinc acetate and TRIS solution are mixed vigorously for 1 minute. Then the mixture is placed in microwave for heating 3 minutes. The resultant product is centrifuged at 10000 rpm and washed several times with deionized water to remove excess of TRIS buffer. Finally the product is dried at 80°C for overnight [3]. Detailed physicochemical characterizations are described below.
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Hydrodynamic radius and zeta potential of ZNP(T) was analyzed using dynamic light scattering (DLS) in Malvern Zetasizer. UV-VIS absorbance of ZNP(T) was measured in a Shimadzu (model no. 1760) UV-VIS spectrometer. Powder sample XRD of ZNP(T) was carried out in Bruker D8 instrument applying a primary beam monochromator to select the Kα1 component of the employed copper radiation (wavelength of 1.54056 Å). FTIR spectra were recorded in Perkin-Elmer Spectrum 100. Photoluminescence spectrum (PL) was recorded in Hitachi spectrofluorimeter (model no: F-7000). The topography of ZNP(T) was obtained by Atomic Force Microscope (AFM) of NTegra, NT-MDT (TS-150) in tapping mode. Morphology of the synthesized ZNP(T) was studied in SUPRA 40 Field Emission Scanning Electron Microscope (FESEM) of Carl Zeiss, operated at acceleration voltage of 5.0 kV; EDX analysis was carried out with the same instrument. Particle size of ZNP(T) was obtained from High Resolution Transmission Electron Microscope (HR-TEM) (FEI) at an operational voltage of 200 kV. Stability of the ZNP(T) with increase in temperature through a wide range was obtained from TG-DTA analysis carried out in Diamond TG/DTA pyris series with a heating rate of 10°C per minute under nitrogen atmosphere.

Very diluted test solution of the ZNP(T) was used for DLS measurements which showed good sampling with its hydrodynamic radius centering at around 100 nm however this hydrodynamic radius was higher compared to its actual radius (Figure 4).

![Size Distribution by Intensity](image)

**Figure 4.** Measurements of hydrodynamic radius of ZNP(T) by using DLS.

UV-VIS absorbance of ZNP (T) exhibited a hump shaped curve with the peak centered at 363 nm (Figure 5a) [4]. Powder XRD (Figure 5b) of the ZNP(T) exhibited ten characteristic peaks with \( 2\theta = \)
Surface functional groups of ZNP (T) were confirmed by FTIR spectra (Figure 6a). The stretching frequency which centered at around 3400 cm$^{-1}$ was due to O-H stretching and marginally for N-H stretching. Both the stretching frequencies overlapped with each other resulting in a broad peak. The peak at 1632 cm$^{-1}$ was for the C=O stretching of carbonyl group. Stretching frequencies centered at 1462 cm$^{-1}$ and 1400 cm$^{-1}$ were attributed to N-H bending and -O-H bending respectively. Stretching frequencies obtained at lower wave number was the characteristic peak of Zn-O stretching frequency of ZNP(T)[7].

Zeta potential measurements validated surface functionality of ZNP(T) which was earlier measured by FTIR analysis. Zeta potential analysis showed that the particle had very small negative zeta potential at lower pH range. Low zeta potential at acidic pH 3 (-0.60 mV) was attributed to the presence of $^\prime$NH$_3$ from the ionization of NH$_3$ group along with O-H group. Increased zeta potential (of -13.6 mV at pH 9) at alkaline pH was due to ionization of $^\prime$O from O-H group (Figure 6b).

Figure 5. (a) UV-VIS absorbance spectra of synthesized ZNP(T), (b) X-ray diffraction pattern of ZNP(T).

31.60°, 34.21°, 36.02°, 47.37°, 56.51°, 62.76°, 66.15°, 67.70°, 68.89° and 76.85°. These ten peaks could easily be indexed to (100), (002), (101), (102), (110), (113), (200), (112) and (201) diffraction planes of ZnO with hexagonal structure [JCPDS card no. 034477][5]. Hexagonal structure with highest intense (101) plane suggested the possible growth of ZNP (T) along [0001] direction[6].
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Figure 6. (a) FTIR spectra of ZNP(T), (b) Measurement of zeta potential as a function of pH.

FE-SEM (Figure 7a) images showed that the particles were nearly spherical and had homogenous morphology. The EDX spectrum revealed that Zn and O were the main chemical components (Figure 5 (a) inset) of ZNP(T). Conclusively HR-TEM micrograph (Figure 7b) illustrated that ZNP(T) with average particle size 15-20 nm were nearly spherical and uniform. AFM study of ZNPs showed size, shape, and surface roughness (~0.45 nm) of the particles (Figure 8).

Figure 7. (a) Morphological analysis of ZNP(T) by FESEM; inset indicating the EDX spectrum of ZNP(T), (b) HR-TEM image of ZNP(T).
TG analysis revealed that the ZNP (T) retained stability through a temperature range of 50°C to 700°C (figure 9a). The sample underwent 0.48% of weight loss up to the temperature of 140°C due to the loss of free water molecules from the surface and weight loss above 400°C was due to dead sorption of bound water molecules [8]. No considerable weight loss was observed up to higher temperature of 700°C. Photoluminescence (PL) property of ZNP (T) (figure 9b) showed two peaks in PL curve when it was excited at 340 nm. The first was the sharp one centering at 383 nm while the broad second one was centered at 438 nm [9]. The lower band was attributed to recombination of excitons [10] while the broad peak could be indexed to singly ionized oxygen vacancy in ZnO, resulting from recombination of a photon-generated hole with single ionized charge state of defect [11].
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Figure 9. (a) Thermogravimetric weight loss of ZNP(T) as a function of temperature, (b) PL spectra of ZNP(T).

2.5. Synthesis of capped ZNPs using different capping agents:

(i) Using starch as capping agent:

0.5 M Zinc nitrate is dissolved in 0.5% soluble starch solution and 1 M NaOH was dissolved in deionized water. Under constant stirring, the zinc nitrate solution was added drop wise for 30 min to NaOH solution which is maintained at 70°C. After 2-3 hrs, the white precipitate deposited at the bottom of the flask is collected, washed several times with absolute ethanol and distilled water. ZNP(S) is harvested by high-speed centrifugation (10000 rpm) and dehydration of the resultant pellet [12].

Figure 10. (a) Morphological analysis of ZNP(S) by FESEM; (b) HR-TEM image of ZNP(S).

FESEM image [Figure 10a] indicated size and surface morphology of ZNP(S). TEM image clearly indicated the size of ZNP(S) which lies between 80-120 nm [Figure 10b]. Zn and O are the elemental composition of synthesized ZNP(S) which was confirmed by EDAX analysis [Figure 10b inset]. Surface functional groups of ZNP(S) were confirmed by FTIR spectra (figure 11a). Stretching frequency observed at 3440 cm\(^{-1}\) was for the OH stretching. Similarly 2906 cm\(^{-1}\) and 2850 cm\(^{-1}\) denoted asymmetric and symmetric CH stretching of starch fragment. While stretching frequency obtained at 1640 cm\(^{-1}\) and 1384 cm\(^{-1}\) were for C=O stretching and OH bending respectively.
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Powder XRD (Figure 11b) of the ZNP(S) exhibited ten characteristic peaks with $\theta = 31.70^\circ$, 34.29°, 36.20°, 47.45°, 56.45°, 62.75°, 66.24°, 67.81°, 68.95° and 76.85°. These ten peaks could easily be indexed to (100), (002), (101), (102), (110), (113), (200), (112) and (201) diffraction planes of ZnO with hexagonal structure [JCPDS card no. 034-077] [5].

(ii) Using Poly ethylene glycol (PEG) as capping agent:

First ZNPs are synthesized by mixing zinc nitrate solution and NaOH solution. The reaction mixture is then vigorously stirred for 20 min at ambient temperature and PEG-400 is added as a surfactant during synthesis. The amount of added PEG 400 per unit gram of ZNPs are determined in such a way that it makes monolayer coverage over ZNP (P) [12].

Figure 11. (a) IR spectra and (b) XRD of ZNP(S).

Figure 12. (a) Morphological analysis of ZNP(P) by FESEM; (b) HR-TEM image of ZNP (P).
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FESEM image [Figure 12a] indicated surface morphology of ZNP (P). TEM image clearly indicated the size of ZNP(C) which lies between 120-150 nm [Figure 12b]. Surface functional groups of ZNP (P) were confirmed by FTIR spectra (figure 13a). Stretching frequency at 3410 cm\(^{-1}\) was for the OH stretching. Similarly stretching frequency obtained at 2914 cm\(^{-1}\) and 2862 cm\(^{-1}\) were for CH stretching which were very prominent. Stretching frequency centered at 1638 cm\(^{-1}\) and 1405 cm\(^{-1}\) were for CH stretching and C=O stretching respectively. Various stretching frequency obtained from 1250 cm\(^{-1}\) to 1098 cm\(^{-1}\) for C-O and C-O-C stretching which were very similar to spectral pattern of PEG. Powder XRD (Figure 13b) of the ZNP(P) exhibited ten characteristic peaks with 20 = 31.53°, 34.29°, 36.09°, 47.45°, 56.40°, 62.58°, 66.24°, 67.81°, 68.95° and 76.92°. These ten peaks indexed hexagonal crystal structure of ZNP (P) [JCPDS card no. 034477] Therefore crystal structure of ZNP was unchanged in both the cases even after surface capping by starch and PEG respectively.

![Figure 13. (a)IR spectra and (b) XRD of ZNP(P).](image)

2.6. Conclusion:

This chapter provides an overview of a variety of physical and chemical methods that have been developed for synthesizing different types of ZNPs. Each method has its specific merits. This chapter also discussed a range of physicochemical properties associated with ZNPs, in the context of various intriguing applications are discussed in the next chapters.
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