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Chemical Growth of Spherical Zinc Oxide Nanoparticles and Their Structural, Optical Properties

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ABSTRACT

A simple wet chemical method has been successfully used to fabricate Spherical zinc oxide nanoparticles. The structural characteristics were investigated through X-ray diffraction. The crystal unit cell of the nanoparticles was found to be hexagonal. The morphology of the nanostructures was studied using transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM). SAED pattern of the sample confirms the uniform distribution of nanoparticles. UV-visible spectrum was used to calculate the band gap of the nanoparticles. The value of the band gap also suggests the quantum confinement effect. The photoluminescence spectrum shows shallow deep level visible emission due to various defect states. Thus, our investigation will be very helpful in the development of ZnO based optoelectronic device applications.

***Keywords*:** ZnO nanoparticles; Absorption; Photoluminescence; XRD; TEM; FESEM

1. Introduction

ZnO is very well known multifunctional wide and direct band gap semiconductor having excellent size dependent tunable optical property which is of great interest in the NPs based drug delivery, bio-imaging, and biomedical research [1,2,3]. Due to large direct band gap ZnO being used in many optoelectronic devices [4,5,25] like short wavelength light-emitting[6], UV lasing[7], and It also exhibits other interesting properties, like magnetic properties [28], piezoelectricity [8], photovoltaic devices and optical solar cells [9], gas sensing[10], These properties depend on the morphology of the nanostructures. Various methods, such as physical and chemical-vapor deposition [11], hydrothermal growth [12, 13], pulsed-laser deposition [14] have already appeared in the literature to fabricate various types of ZnO nanostructures. Some of the above-mentioned methods have some drawbacks. Used precursors are unstable causing environmental hazards and require very high temperature, low pressure, control rate of carrier flow and many more. These methods are not cost effective also. Here, we report the fabrication of ZnO nanoparticles by a simple and cost-effective wet-chemical method. We next investigated

the structural and morphological behavior of such ZnO nanoparticles .The optical absorption and emission property of the ZnO nanoparticles was also investigated.

2. Experimental

In the synthesis of zinc oxide nanoparticles (NP^s) at room temperature, we followed the conventional wet chemical method for synthesis of ZnO nanostructures as reported in [15]. All the chemicals of the synthesis of ZnO NP^s were used as supplied (Merck- 99.99 % pure). In a typical synthesis process, 0.25 M of zinc acetate di-hydrate ($Zn(CH_3COO)_2.2H_2O$) was dissolved in methanol to prepare 100 ml solution. NaOH solution was prepared by dissolving predetermined amount of NaOH in methanol to prepare 0.25 M NaOH solution. Then under constant stirring, the zinc acetate solution was added drop-wise to the NaOH solution and the stirring was continued further for 4 hour. At the end of the reaction, a white colloidal solution was obtained. The solution was then filtered and the precipitate was dried at 100^0c through 2 hour in an ordinary furnace for further structural and optical characterization. X-Ray diffraction (XRD) data were collected in a Rigaku X-ray diffractometer using Cu-Kα radiation of wavelength 1.54 Å over the angular range $20°<2\theta<80°$. Scanning electron microscope (SEM) images were recorded in a Zeiss SEM operating at 5 kV. For TEM study a very small amount of the powder sample was first dispersed in alcohol by ultra-sonication. A drop of that solution was taken on a carbon coated grid for TEM imaging. Optical absorption measurements were carried out by using Shimadzu-Pharmaspec-1700 UV-VIS in the range 200–800 nm. Room temperature photoluminescence (PL) data were recorded in a PERKIN ELMER LS-55 spectrometer using Xenon lamp as a source of excitation at 330 nm.

3. Results and discussions

3.1. UV-visible spectroscopy

UV-visible spectroscopy was carried out to study further the optical property of the nanoparticles. The room temperature UV-absorption spectra of the ZnO nanoparticles dispersed in water is shown in figure 1(A). ZnO NPs shows a prominent exciton band at 366 nm due to excitonic transition at room temperature [20, 30]. This absorption in the visible range of wavelength implies that there exist more defect energy levels in the synthesized ZnO nanostructures that are due to the specific experimental synthesis conditions. Optical absorption coefficient has been calculated in the Wavelength region 200–900 nm. The bandgap of the as-prepared nanoparticles are are determined from the relation [21]

$$(\alpha h\nu)^2 = c(h\nu - E_g)$$

where C is a constant. E_g is the band gap of the material and α is the absorption coefficient. Figure 1(B) shows the plot of $(\alpha h\nu)^2$ vs. energy ($h\nu$) and it is used to determine band gap. The band gap of the sample is found to be 3.78 eV (figure 1(B)), which is greater than the bulk ZnO (3.37 eV) [22-23].

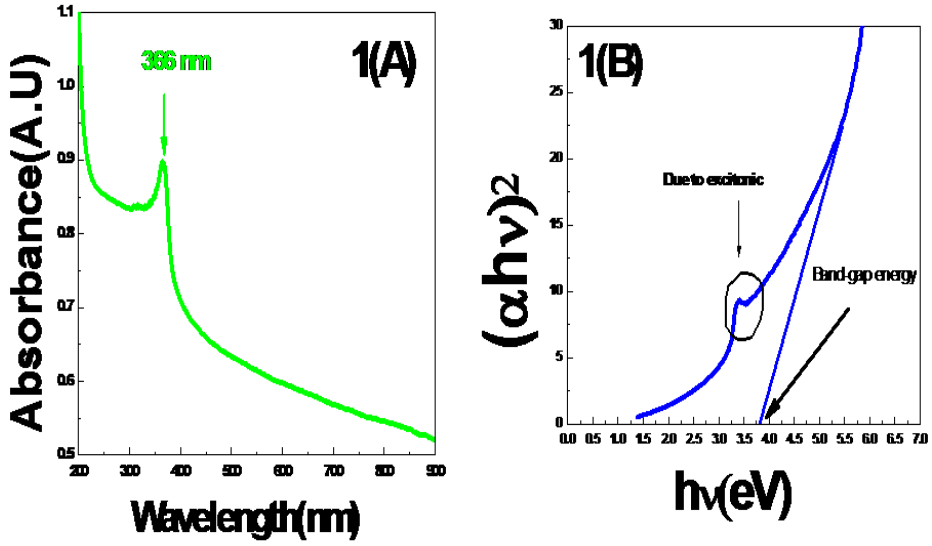

Figure 1: (A) UV-VIS absorption spectra of the ZnO nanoparticles, (B) Tauc's plot for the determination of the band gap of the ZnO nanoparticles.

3.2. Photoluminescence spectroscopy

The PL emission spectra of the ZnO nanoparticles shown in figure 2 consist of five emission peaks, these are a strong blue emission at ~395 nm, a blue-green emission at ~485 nm, and a weak green emission at 530 nm. The 395 nm peak can be attributed to the interstitial zinc or oxygen [16]. The green emission of the ZnO prepared corresponds to the singly ionized oxygen vacancy in ZnO, and this emission is a result of capturing of a photo-generated hole by the oxygen vacancy [17]. The 451nm, 530 nm and 595nm peak corresponding to the surface states [18]. The blue-green emissions at 485 nm might be due to surface defects in the ZnO powder [19].

3.3. X-ray diffraction (XRD)

From XRD pattern (figure 3), the unit cell of the crystal was found to be hexagonal with the presence of the peaks (100), (002), (101), (102), (110), (103), (200), (112), and (201).The diffraction pattern indicates that the planes are randomly oriented [26].
We have also calculated the crystallite size (here we mean by crystallite size as the dimension of the coherent diffracting domains) using Scherrer formula [27] and are given by

$$\text{Crystalline size: } R_{hkl} = \frac{0.89\lambda}{\beta \cos\theta}$$

In this calculation, the highest intensity (101) peak was analyzed and considered it to be Gaussian. The crystallite size was found to be ~18 nm. Besides, no impurity peaks were detected which indicates that the fabricated ZnO nanomaterials are highly pure.

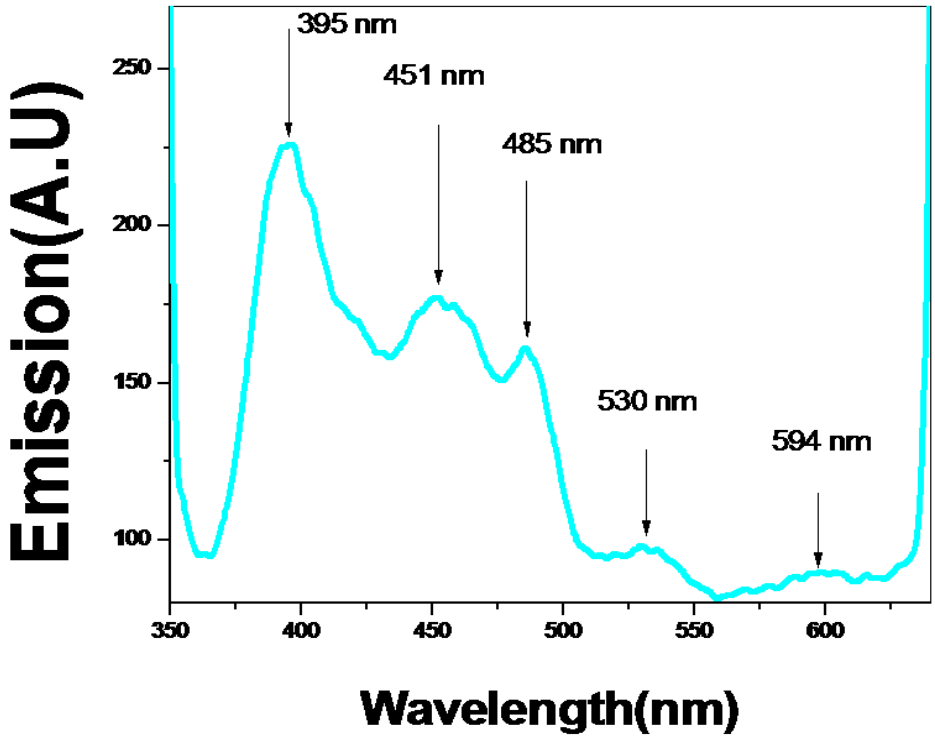

Figure 2: Room-temperature photoluminescence spectrum of the ZnO nanoparticles.

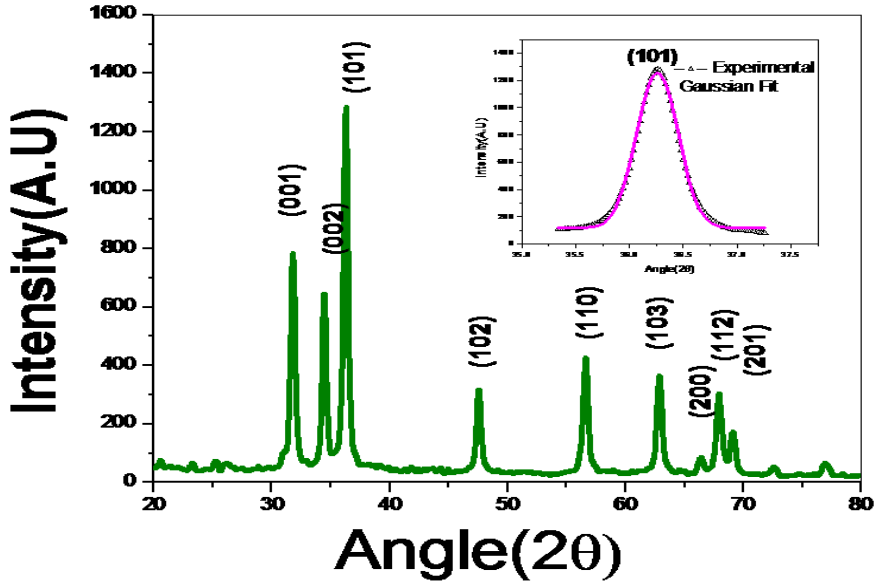

Figure 3: XRD pattern of the ZnO nanoparticles ; inset shows the Gaussian fitting of the (101) peak of ZnO nanoparticles

3.4. Transmission electron microscopy study

Further studies on the structure of the ZnO nanoparticles were done using transmission electron microscopy. Figure 4 (A) shows the TEM image of the synthesis nanoparticles. The average diameter of a nanoparticle is ~20 nm. The corresponding selected area electron diffraction (SAED) pattern is also shown in figure 4(B), which reveals the crystalline nature of the nanoparticle (24-25, 29).

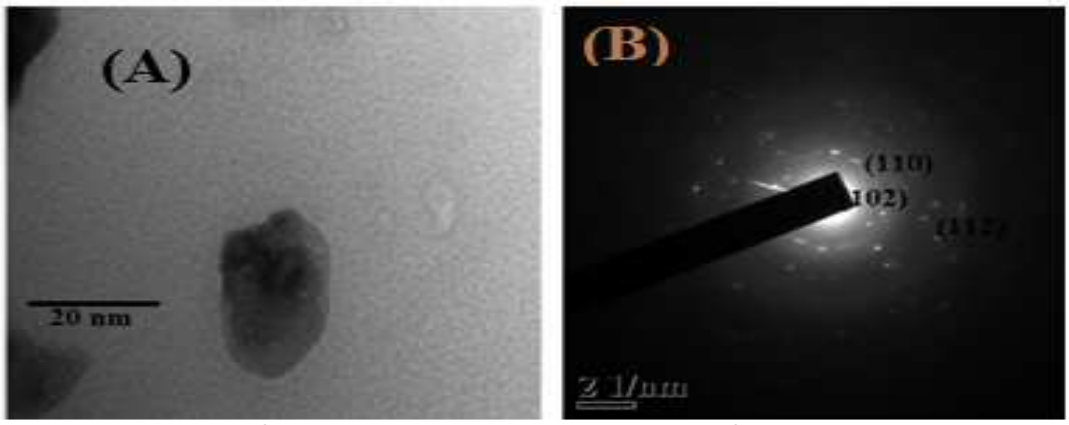

Figure 4: (A) TEM of ZnO nanoparticles, (B) SAED pattern of the ZnO nanoparticles

4. Field emission scanning electron microscope (FESEM) study

The morphology of the fabricated ZnO nanoparticles was observed in a ZEISS Field emission scanning electron microscope (FESEM) operated at 5 kV. Typical FESEM images (scale 200 nm) of the deposited material are shown in Fig. 5. Spherical ZnO nanoparticles were observed to form by the wet-chemical method. The EDX analysis revealed that the ZnO nanoparticles are composed of 88.25% of Zn and 11.751% Oxygen. Thus there is possibility of formation of interstitial zinc sites in the pyramidal ZnO nanocrystals.

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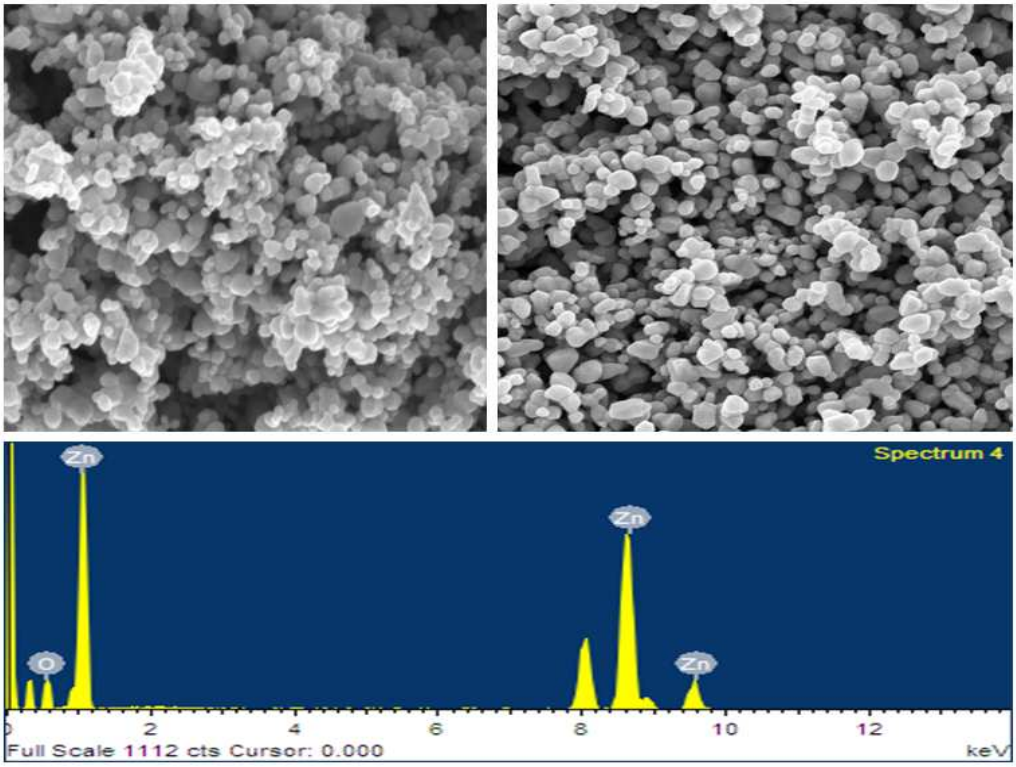

Figure 5: (a) & (b) FESEM of ZnO nanoparticles, (c) EDX pattern of the ZnO nanoparticles

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