

Research Article

Synthesis, Characterization, and Spectroscopic Properties of ZnO Nanoparticles

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ZnO nanoparticles have been synthesized by precipitation method from Zinc nitrate. The powder was characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, selected-area electron diffraction, UV-vis optical absorption, and photoluminescence spectroscopy analyses. XRD patterns showed that ZnO nanoparticles have hexagonal unit cell structure. SEM and TEM pictures reveal the morphology and particle size of prepared ZnO nanoparticles. The UV-vis absorption spectrum shows an absorption band at 355 nm due to ZnO nanoparticles. The photoluminescence spectrum exhibits two emission peaks one at 392 nm corresponding to band gap excitonic emission and another located at 520 nm due to the presence of singly ionized oxygen vacancies. The synthesis method has potential for application in manufacturing units due to ease processing and more economical reagents.

1. Introduction

Nowadays, there has been an increasing demand for the development of nanosized semiconductors due to their significant electrical and optical properties which are highly useful in fabricating nanoscaled optoelectronic and electronic devices with multifunctionality [1–3]. Among various semiconducting materials, zinc oxide (ZnO) is a distinctive electronic and photonic wurtzite n-type semiconductor with a wide direct band gap of 3.37 eV and a high exciton binding energy (60 meV) at room temperature [4, 5]. The high exciton binding energy of ZnO would allow for excitonic transitions even at room temperature, which could mean high radiative recombination efficiency for spontaneous emission as well as a lower threshold voltage for laser emission. The lack of a centre of symmetry in wurtzite, combined with a large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and hence the use of ZnO in mechanical actuators and piezoelectric sensors [6, 7]. ZnO is potential candidate for optoelectronic applications in the short wavelength range (green, blue, UV), information

storage, and sensors as it exhibits similar properties to GaN [8–10]. ZnO nanoparticles are promising candidates for various applications, such as nanogenerators [11], gas sensors [12], biosensors [13], solar cells [14], varistors [15], photodetectors [16], and photocatalysts [17]. From the literature survey, it was found that various approaches for the preparation of ZnO nanopowders have been developed, namely, sol-gel, microemulsion, thermal decomposition of organic precursor, spray pyrolysis, electrodeposition, ultrasonic, microwave-assisted techniques, chemical vapor deposition, and hydrothermal and precipitation methods [18–27]. Most of these techniques were not extensively used on a large scale, but chemical synthesis has been widely used due to its simplicity and less expensive. In the present study, we report the synthesis of ZnO nanoparticles using chemical method and the characterization of ZnO nanoparticles using X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), UV-vis absorbance, and photoluminescence spectra is discussed.

2. Experimental Methods

Zinc nitrate, sodium hydroxide, and ethanol were purchased and used without further purification. Zinc oxide nanoparticles were synthesized by wet chemical method using zinc nitrate and sodium hydroxide precursors. In this experiment, a 0.5 M aqueous ethanol solution of zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was kept under constant stirring using magnetic stirrer to completely dissolve the zinc nitrate for one hour and 0.9 M aqueous ethanol solution of sodium hydroxide (NaOH) was also prepared in the same way with stirring of one hour. After complete dissolution of zinc nitrate, 0.9 M NaOH aqueous solution was added under high speed constant stirring, drop by drop (slowly for 45 min) touching the walls of the vessel. The reaction was allowed to proceed for 2 hrs after complete addition of sodium hydroxide. The beaker was sealed at this condition for 2 h. After the completion of reaction, the solution was allowed to settle for overnight and further, the supernatant solution was separated carefully. The remaining solution was centrifuged for 10 min, and the precipitate was removed. Thus, precipitated ZnO NPs were cleaned three times with deionized water and ethanol to remove the byproducts which were bound with the nanoparticles and then dried in air atmosphere at about 60°C . During drying, $\text{Zn}(\text{OH})_2$ is completely converted in to ZnO . The prepared ZnO nanoparticles were characterized for their optical and nanostructural properties. X-ray diffraction pattern for the ZnO NPs was recorded using an X-ray diffractometer (PANLYTICAL) using Cu K_α radiation of wavelength $\lambda = 0.1541$ nm in the scan range $2\theta = 20\text{--}90^\circ$. Morphology of the sample was investigated using scanning electron microscope (SEM with EDXA, Sirion) which also has been used for compositional analysis of the prepared ZnO nanoparticles. The optical transmission/absorption spectra of ZnO dispersed in water were recorded using a UV-VIS spectrophotometer (Hitachi, U-3010). The photoluminescence (PL) spectrum of the ZnO nanoparticles dispersed in water has been measured using a spectrofluorimeter (F-2500 FL Spectrophotometer, Hitachi).

3. Results and Discussion

As part of our research programme, we synthesize nanoparticles with enhanced particle properties using chemical routes that help in controlling the surface energy. The functionalized particles were characterized by the following techniques.

3.1. X-Ray Diffraction (XRD). Figure 1 represents the X-ray diffraction pattern of ZnO nanopowder. A definite line broadening of the XRD peaks indicates that the prepared material consist of particles in nanoscale range. From this XRD patterns analysis, we determined peak intensity, position and width, full-width at half-maximum (FWHM) data. The diffraction peaks located at 31.84° , 34.52° , 36.33° , 47.63° , 56.71° , 62.96° , 68.13° , and 69.18° have been keenly indexed as hexagonal wurtzite phase of ZnO [28, 29] with lattice constants $a = b = 0.324$ nm and $c = 0.521$ nm (JPCDS card number: 36-1451) [30], and further it also

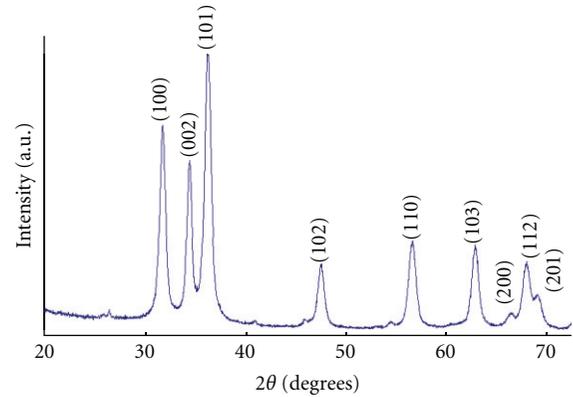


FIGURE 1: XRD pattern of prepared ZnO nanoparticles.

confirms the synthesized nanopowder was free of impurities as it does not contain any characteristics XRD peaks other than ZnO peaks. The synthesized ZnO nanoparticle diameter was calculated using Debye-Scherrer formula [31]

$$d = \frac{0.89\lambda}{\beta \cos\theta}, \quad (1)$$

where 0.89 is Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle, and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane (101). The average particle size of the sample was found to be 16.21 nm which is derived from the FWHM of more intense peak corresponding to 101 plane located at 36.33° using Scherrer's formula.

3.2. SEM/TEM Pictures. Figure 2 represents the SEM pictures of ZnO nanoparticles at different magnifications. These pictures confirm the formation of ZnO nanoparticles. These pictures substantiate the approximate spherical shape to the nanoparticles, and most of the particles exhibit some faceting. From the pictures, it also can be seen that the size of the nanoparticle is less than 10 nm which was in good agreement with the particle sizes (8.32 nm) calculated from the Debye-Scherrer formula. The selected area electron diffraction (SAED) pattern (Figure 3) shows distinct bright rings which confirm the preferential orientation of nanocrystals instead of irregular [29, 32]. Transmission electron microscopic pictures (Figures 4(a), 4(b), and 4(c)) have also revealed the ZnO nanoparticles formation produced at different magnifications by confirming the hexagonal plane to the prepared nanoparticles.

3.3. UV-Vis Absorption Spectrum. The size of the nanoparticles plays an important role in changing the entire properties of materials. Thus, size evolution of semiconducting nanoparticles becomes very essential to explore the properties of the materials. UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nanosized particles. The absorption spectrum of ZnO nanopowder is shown in Figure 4. It exhibits a strong absorption band at about 355 nm [33]. An excitonic

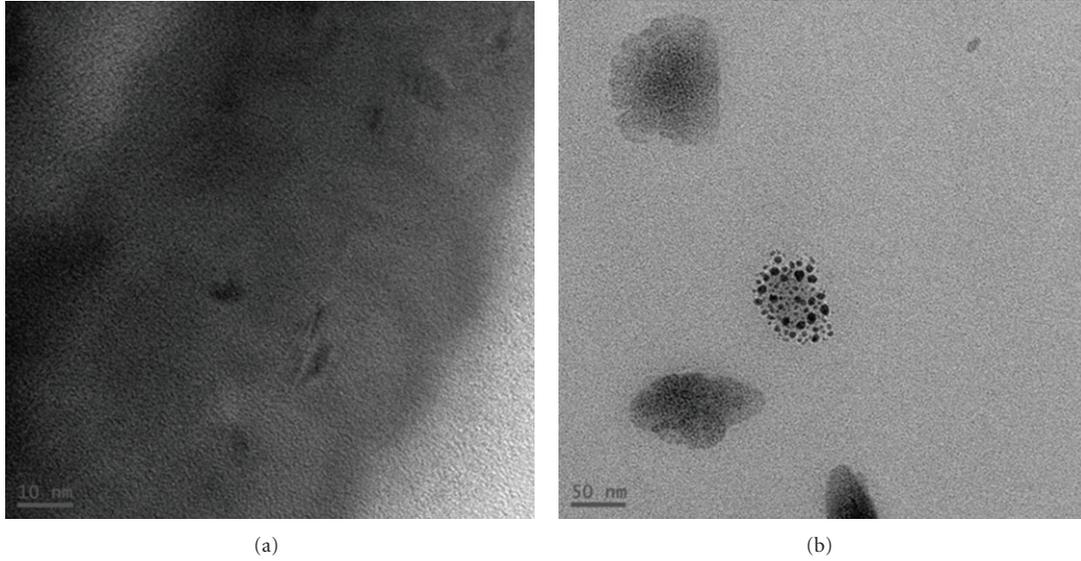


FIGURE 2: SEM pictures of ZnO nanoparticles at different magnifications.



FIGURE 3: SAED patterns of prepared ZnO nanopowder.

absorption peak is found at about 258 nm due to the ZnO nanoparticles which lie much below the band gap wavelength of 358 nm ($E_g = 3.46$ eV). It is also evident that significant sharp absorption of ZnO indicates the monodispersed nature of the nanoparticle distribution [8].

The average particle size in a nanocolloid can be calculated from the absorption onset from UV-vis absorption spectra by using effective mass model (Figure 5) [34, 35] where the band gap E^* can be approximated by

$$E^* = E_g^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2er^2} \left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right) - \frac{1.8e}{4\pi\epsilon\epsilon_0 r} - \frac{0.124e^3}{\hbar^2 (4\pi\epsilon\epsilon_0)^2} \left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right)^{-1}, \quad (2)$$

where E_g^{bulk} is the bulk band gap expressed in eV, \hbar is Plank's constant, r is the particle radius, m_e is the electron effective mass, m_h is the hole effective mass, m_0 is free electron mass, e is the charge on the electron, ϵ is the relative permittivity, and ϵ_0 is the permittivity of free space. Due to the relatively small effective masses for ZnO ($m_e = 0.26$, $m_h = 0.59$), band gap enlargement is expected for particle radii less than about 4 nm [34, 35]. The following equation was derived from the effective mass model given above with small mathematical simplification [36] which is used to find the size of the particle from the absorbance spectra,

$$r \text{ (nm)} = \frac{-0.3049 + \sqrt{-26.23012 + 10240.72/\lambda_p \text{ (nm)}}}{-6.3829 + 2483.2/\lambda_p \text{ (nm)}}, \quad (3)$$

where λ_p is peak absorbance wavelength in nm. The prepared ZnO nanoparticles exhibit an absorbance peak at about 258 nm which corresponds to the particle size of 2.07 nm. This result has also been confirmed by the SEM pictures.

3.4. Photoluminescence Spectrum. It is worth mentioning that the physical properties of semiconducting materials undergo changes when their dimensions get down to nanometer scale known as the "quantum size effects." For example, quantum confinement increases the band gap energy of ZnO, which has been observed from photoluminescence [37]. The photoluminescence originates from the recombination of surface states. The strong PL implies that the surface states remain very shallow, as it is reported that quantum yields of band edge will decrease exponentially with increasing depth of surface state energy levels [38, 39]. Figure 6 shows the photoluminescence spectrum of ZnO nanopowder with excitation wavelength 320 nm at room temperature. The spectrum exhibits two emission peaks, one is located at around 392 nm (UV region) corresponding to

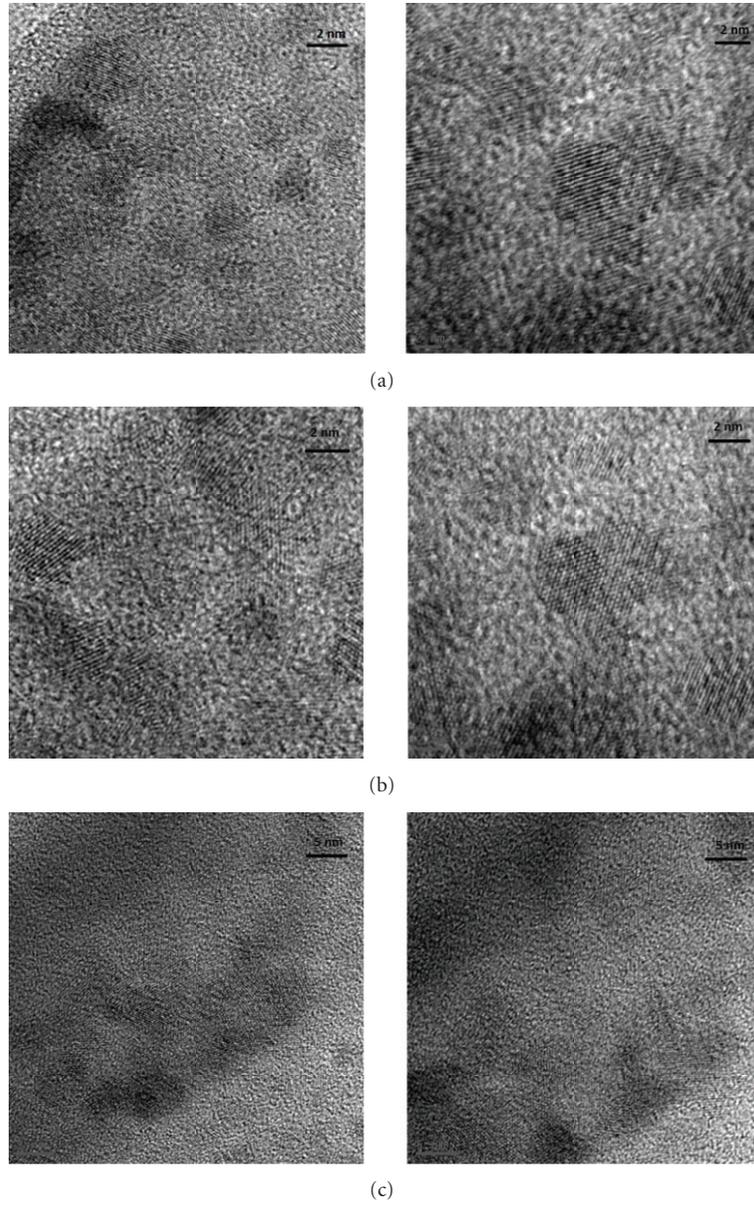


FIGURE 4: High-resolution transmission electron microscopic pictures of ZnO nanoparticles.

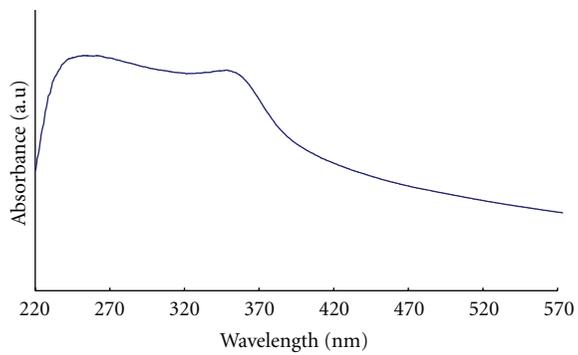


FIGURE 5: UV-vis absorption spectrum of ZnO nanoparticles.

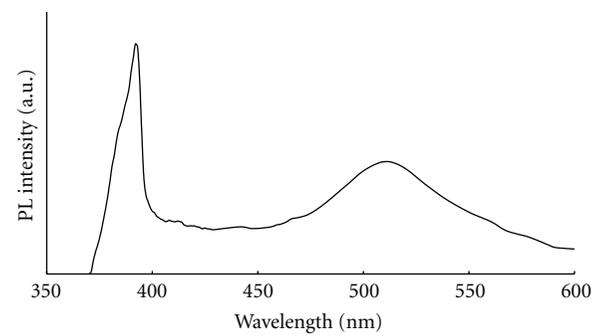


FIGURE 6: Photoluminescence spectrum of prepared ZnO nanoparticles ($\lambda_{\text{exc}} = 320 \text{ nm}$).

the near band gap excitonic emission [40] and the other is located at around 520 nm attributed to the presence of singly ionized oxygen vacancies [41]. The emission is caused by the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy [28, 40]. Further, the spectrum also reveals the narrow size distribution of nanoparticles in the powder as the luminescence peak full-width half-maximum (FWHM) is only in few nanometers [42].

4. Conclusions

ZnO nanoparticles have been prepared using wet chemical synthesis method and were characterized by XRD, SEM, SAED, UV-vis absorption, and photoluminescence spectroscopy. XRD and SEM studies confirmed the nanostructures for the prepared ZnO nanoparticles. SAED pattern consists of bright uniform rings confirming preferential orientation for nanocrystals instead of random orientation. From UV-vis absorption spectrum, the calculated average size of the prepared ZnO nanoparticles is found to be 2.2 nm for peak absorbance wavelength. The prepared ZnO nanoparticles exhibit ($\lambda_{\text{exc}} = 320 \text{ nm}$) sharp UV band corresponding to near band gap excitonic emission and broad green emission band due to the oxygen vacancy at room temperature. These ZnO nanoparticles can be used in different industrial applications, namely, luminescent material for fluorescent tubes, active medium for lasers, sensors, and so forth.

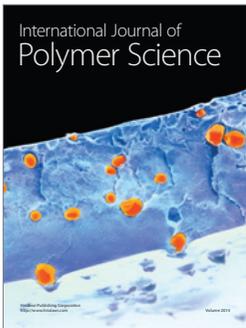
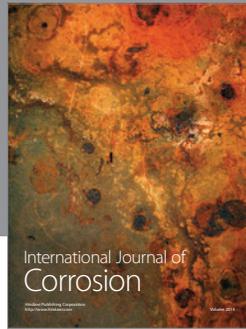
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