Effect of pH on Crystal Size and Photoluminescence Property of ZnO Nanoparticles Prepared by Chemical Precipitation Method

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Received: 30 April 2014 / Revised: 18 August 2014 / Published online: 23 January 2015
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Abstract The effects of pH value on crystal size and optical property of zinc oxide nanoparticles prepared by chemical precipitation method were investigated. Prepared samples have been characterized by means of X-ray diffraction, scanning electron microscopy, ultraviolet–visible spectrometer and photoluminescence spectrometer. From X-ray diffraction profile, it is found that the particle size of sample increases from 13.8 to 33 nm when the pH value of the solution was increased from 6 to 13. Microstructural study also shows that the particle size increases with pH value. Hexagonal shape of the zinc oxide nanoparticle has been confirmed by the scanning electron microscopy image. The recorded ultraviolet–visible spectrum shows excitonic absorption peaks around 381 nm. The energy gap of the prepared samples has been determined from the ultraviolet–visible absorption spectrum, effective mass model equation and Tauc’s relation. It was found that the energy gap of the prepared samples decreases with increase in pH value. The recorded blue shift confirmed the quantum confinement effect in the prepared zinc oxide samples. Photoluminescence spectrum infers that the increase in pH value shifts the ultraviolet–visible emission but not the violet and green emissions.

KEY WORDS: Zinc oxide nanoparticles; pH value; Crystal structure; Microstructure; Energy gap; Photoluminescence

1 Introduction

Zinc oxide (ZnO) is one of the promising non-toxic and II–VI group semiconductor materials [1, 2]. In recent years, many researchers are working on solution-grown ZnO nanomaterials due to its extraordinary electrical and optical characteristics, required for nanoscaled electronic and optoelectronic devices [3–6]. In comparison with other wide band gap semiconductors, ZnO possesses a band gap of 3.37 eV with large exciton binding energy of 60 meV which ensures an efficient ultraviolet (UV) and blue emission at

room temperature [4, 5]. It is reported that ZnO possesses higher quantum efficiency, good stability against photo-corrosion and photochemical properties, and ability to grow high-quality single crystal with cost effectiveness. Also, it is an inexpensive luminescent and bio-friendly oxide semiconductor material. As a result of the properties affirmed above, ZnO is expected to have an extensive applications in UV laser [7], biosensors [8], bio-imaging [9], drug delivery [10], piezoelectric transducers [11], dye-sensitized solar cells [12], high sensitivity chemical gas sensor [13], volatile organic compound sensor [14], DNA sequence sensor [15], short wavelength (green, blue, UV) optoelectronic devices [16], light-emitting diodes [17] and field-effect transistors [18]. Recent development in nanotechnology uses the ZnO nanostructure as cantilever in scanning electron microscope (SEM) with a size that is 500 times smaller than the conventional cantilever, which offers improved sensitivity and mechanical flexibility [19].

Available online at <http://link.springer.com/journal/40195>

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In the area of bioengineering, ZnO has been investigated for the growth control of *Saccharomyces cerevisiae* bacteria [20, 21] and microalgae [22]. As it is biocompatible and biodegradable, ZnO wires are used in biosensors and biological systems [23]. With the alertness of the anticancer effect of photo-excited ZnO, guided delivery of ZnO-based drugs has become a topic of interest [24]. It is envisaged that magnetic ZnO composites in the form of capsules or nano-submarines can be magnetically guided to a desired location of a human body. As a result, there would be significant enhancement of ZnO efficiency and large reduction in dosage and cost. Because of these interesting features, many research groups have chosen this material.

A wide range of physical and chemical methods have been adopted by different research groups for the synthesis of ZnO nanoparticles such as chemical precipitation, sol-gel synthesis, hydrothermal reaction and electrochemical routes. Extensive literature assessment infers that chemical precipitation method is the foremost method for the synthesis of ZnO nanoparticles. As chemical precipitation is a low-temperature process, and its easy procedure to control the particle size and its low cost, this method finds suitable application in microelectronics and plastic electronics also. It is reported that [25] precipitation method yields the smallest nanoparticle with best optical and photocatalytic activity, compared with other methods mentioned above. Due to these reasons, precipitation method has been adopted for the present work.

Apart from synthesis procedure, some other parameters like reaction temperature, pH value of the solution, aging time, concentration of the precursors, amount of modifier, type of modifier and the solvent used also play a key role in nucleation and growth of ZnO nanoparticles. A number of investigations have been focused on the synthesis and characterization of ZnO nanoparticles, but only a very few articles deal with the effect of pH value on crystal size and energy gap of ZnO nanoparticles prepared by chemical precipitation method. For example, Li *et al.* [26] investigated the effects of temperature, pH value and precursors on the particle size. They found that pH of the solution has a certain effect on scheming the particle size. In similar study, Zhang *et al.* [27] reported that pH value is the main factor that influences the morphology of the nanoparticles. Since, pH value affects the formation of nuclei and growth environment of ZnO. Lu and Yeh [28] observed the remarkable variation in the morphology of ZnO powder from an ellipsoidal shape to a rod-like shape, as the pH value of the solution increased from 9 to 12 in a hydrothermal reaction. They considered that the nucleation profoundly depends on the pH of the starting solutions. In similar fashion, Rani *et al.* [29] found to increase in crystalline size (14 nm) with pH value from 6 to 9, thereafter the crystalline size decreases to around 12 nm when the pH value of the solution was further increased to 11. Conversely, Alias

et al. [30] investigated the effect of pH value on the structural and optical properties of ZnO nanopowders synthesized by sol-gel centrifugation method without capping agent. Based on their result, they concluded that the particle size decreases with increase in pH value. It is clear from these earlier reports that a few authors claimed that the particle size of ZnO nanoparticles increases with pH value and few authors found that it decreases with pH value.

In this context, an attempt has been made to investigate the effect of pH on crystalline size, microstructure and bandgap of ZnO nanoparticles synthesized via precipitation method. For this, pH value of solution has been adjusted in a wide range from 6 to 13. Our result favors for the increase in particle size with pH value. The crystallite size and microstructure of the synthesized nanopowders found to depend strongly on the pH value of solution. The novelty of the present work is that the chemical precipitation method is a suitable method for producing the ZnO nanoparticles of size around 14 nm. Our investigation carries further information that the preparation approach discussed here is suitable for the construction of violet emission optoelectronic and nano-photonic devices.

2 Materials and Methods

2.1 Synthesis of ZnO Nanopowder

ZnO Nanoparticles were successfully synthesized by an extremely simple precipitation method using analytical grade zinc acetate di-hydrate [$\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ 99.5%, Merck] and sodium hydroxide (NaOH, Merck). These chemicals were used without further purification. Four samples were synthesized for the present study by varying the pH value of the solution. A transparent 0.2 mol/L zinc acetate di-hydrate [$\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$] solution was prepared in ethanol (99.7% purity) under vigorous stirring at room temperature (30 °C) and the same solution was used for all the four samples. For the synthesis of ZnO sample at pH value of 6, 150 mL of 0.2 mol/L zinc acetate di-hydrate solution was taken in a beaker. With this solution, certain amount of sodium hydroxide (NaOH) pellets was directly dropped into the solution till the pH value of the solution reaches 6. Elico LI 120 digital pH meter was used to measure the pH value of the solution. The milky white solution obtained so was stirred with magnetic stirrer for 7 h. Following this, 2 mL of polyethylene glycol (PEG MW: 400), capping agent, was added to the mixture of zinc acetate and sodium hydroxide solution, and the same was kept in an airtight container for a day towards the slow crystallization. Consequently, ZnO precipitation settled down at the bottom of the beaker. Then, the sodium acetate [$\text{Na}(\text{CH}_3\text{COO})$] transparent solution

was removed, and the particles were washed with ethanol several times. The particles thus obtained was filtered and dried at 80 °C for 10 h in a hot air oven to remove the remaining water content from the sample. Since the ethanol has longer chain length and it fastens the nucleation and growth of nanoparticles, the ethanol has been chosen as solvent. This is the reason for synthesizing samples with ethanol. Similar procedure was followed for the synthesis of samples at pH values of 8, 12 and 13. The overall reaction involved in the synthesis process can be written as

2.2 Characterization of ZnO Powder

Crystalline nature of the samples was acknowledged using Philips Analytical X-ray diffractometer (Model No. PW1830) equipped with Ni-filtered CuK_α radiation ($\lambda = 0.154187$ nm) for $2\theta = 30^\circ$ – 80° , with scanning rate of $5^\circ/\text{min}$ operated at 40 kV/30 mA. Topographical and elemental information of the samples were examined by using a scanning electron microscope (SEM—U9320A 8500: Agilent Technologies, Inc. USA) operated at 20 kV/20 mA. For SEM observation, powder was uniformly sprayed on a carbon tape pasted on the specimen holder. In order to avoid charging while observation, the powder was coated with a thin layer of osmium tetroxide (~ 10 nm). JEM-1010 transmission electron microscope (TEM) was used to study the sample morphology and size. Synthesized nanopowders were dispersed in double distilled water, and then, the absorption and transmittance properties were studied by using Lambda 35 (PERKINELMER: USA) Ultraviolet–visible (UV–Vis) spectrophotometer. The functional group of the synthesized ZnO nanoparticles was characterized by the Fourier transform infrared (FTIR) spectroscopy in the range of $4,000$ – 400 cm^{-1} . The photoluminescence (PL) measurements were carried out at room temperature by means of PL spectrometer (Kimon, SPEC-14031K, Japan) with a He–Cd laser line of 325 nm as the excitation source.

3 Results and Discussion

3.1 X-ray Diffraction Analysis and Energy Gap Calculation

The result of room temperature X-ray diffraction pattern (XRD) of the prepared samples is shown in Fig. 1. The

Fig. 1 XRD spectra of ZnO nanoparticles synthesized via precipitation method at different pH values

sharp and most intense peaks observed here indicate that the synthesized ZnO nanoparticles are of high crystalline nature with single phase. The strong diffraction peaks appear at 31.8° , 33.4° , 36.2° , 47.5° , 56.5° , 62.8° , 66.3° , 67.9° , 69° , 72.6° and 76.9° corresponding to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes matches well with those of the wurtzite structure of ZnO crystal. It should be noted that except the diffraction peaks of ZnO, no other peaks of impurity (or) unreacted phase could be observed. The average crystallite size, D , has been obtained from the highest diffraction peak along the $\langle 101 \rangle$ plane using the Debye–Scherrer formula [31] as follows:

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (1)$$

where λ is the wavelength of the employed CuK_α radiation (0.154 nm), β is the full width at half-maximum (FWHM) of the peaks, and θ is the Bragg angle obtained from 2θ value corresponding to maximum intensity peak in XRD pattern. The average crystallite size calculated across 13.8, 18.0, 24.7 and 33 nm for the samples obtained at pH values of 6, 8, 12 and 13, respectively. Calculation depicts that the average crystallite size increases with increase in pH value of the solution just like the case of increase in diameter of the ZnO nanorods grown in similar method [4]. Also, it clearly shows that an increase in pH value helps in nucleation and growth of nanoparticles. As a matter of fact that the acid can restrain the hydrolysis and alkali can accelerate the hydrolysis in a chemical reaction. The low pH value of 6 corresponds to acidic nature of the solution and it could restrain the particle growth. When the pH

value is greater than 7, totally alkali environment supports in hydrolysis and this enhances particle growth, thereby increasing the particle size. Similar increase in particle size with pH value has also been reported [32, 33]. Based on the recorded XRD pattern, synthesized ZnO nanopowders are indexed as wurtzite hexagonal closely packed structure (space group: p63 mc) and its lattice constants a and c were determined from the following equation using the interplanar distance d and (hkl) values of the XRD profile.

$$\frac{1}{d^2} = \frac{4}{3} \left\{ \frac{h^2 + hk + l^2}{a^2} \right\} + \frac{l^2}{c^2}. \quad (2)$$

The calculated lattice parameters, shown in Table 1, are very close to those available in standard JCPDS data No. 36-1451 ($a = 0.3251$ nm and $c = 0.5212$ nm). It is interesting to note that the intensity of the (100) and (101) peaks found to increase with pH value. In all the samples, intensity of (101) peak is maximum. However, the intensity of (002) peak of pH value of 6 is higher than that of pH value of 13; i.e., intensity of the (002) peak decreases with the increase in pH value of the solution. This infers that increase in pH value limits the accumulation of atoms in (002) plane.

In general, energy gap of nanoparticles are inversely proportional to its radius. Therefore, the energy gap of the ZnO nanoparticles have been evaluated from the effective mass model expression [34], as given below

$$E_g^{\text{nano}} = E_g^{\text{bulk}} + \frac{\hbar^2}{8er^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi r \epsilon \epsilon_0} - \frac{0.124e^3}{\hbar^3 (4\pi \epsilon \epsilon_0)^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]^{-1}, \quad (3)$$

where, the first term, E_g^{bulk} corresponds the energy gap of bulk ZnO (3.37 eV), second term corresponds the quantum confinement effect and the third term is related to coulomb interaction. Here, r is the radius of the crystal calculated from the XRD analysis, m_e^* is the effective mass of the electron ($0.24 m_0$), m_h^* is the effective mass of hole ($0.59 m_0$), m_0 is the rest mass of the electron (9.110×10^{-31} kg), ϵ is the relative permittivity (8.66), ϵ_0 is the permittivity of

free space (8.854×10^{-12} F/m), $\hbar$ is Planck's constant (6.626×10^{-34} Js), and e is the charge of the electron (1.602×10^{-19} C). By substituting these values, the above Eq. (3) can be simplified as

$$E_g^{\text{nano}} = E_g^{\text{bulk}} + \frac{1.6}{r^2}. \quad (4)$$

The energy gap calculated to be 3.42, 3.40, 3.39 and 3.38 eV for the samples prepared at pH values of 6, 8, 12 and 13, respectively. As the sample prepared at pH value of 6 has smaller particles, its energy gap is greater than that of the sample prepared at pH value of 13. It proves that energy gap of the nanoparticle is inversely proportional to its radius. Therefore, from the XRD analysis, it is confirmed that chemical precipitation method is a suitable method for the synthesis of ZnO nanoparticles, and it provides a generic approach for producing the high-quality ZnO nanoparticles.

3.2 Dislocation Density and Micro-Strain Calculation

The dislocation density, S , is a measure of amount of defects and vacancies in the crystal which can be determined from the crystallite size (D) using the formula

$$S = \frac{1}{D^2}. \quad (5)$$

It can be seen from Table 1 that S increases from 5.3×10^{15} to 9.2×10^{15} with increasing pH value. It indicates that the lattice imperfection increases with particle size. Similarly, micro-strain (ϵ) has also been calculated using the formula

$$\epsilon = \frac{\beta \cos \theta}{4}. \quad (6)$$

From Table 1, it can be found that the micro-strain of the sample increases with pH value from 6 to 8, thereafter it decreases. On the whole, variation in micro-strain may be due to the change in microstructure, size and shape and defects of the particles. The increase in strain at pH value increases from 6 to 8 may be due to the creation of defects in the lattice. But the atoms trapped in the non-equilibrium

Table 1 Summary of the characteristics of the ZnO nanoparticles synthesized at various pH values

pH value	2θ (101) (°)	FWHM (°)	D (nm)	d (nm)	a (nm)	c (nm)	V (nm ³)	V (nm ³)	S	ϵ (10 ⁻³)	L (Å)
6	36.15	0.60	13.8	0.2821	0.3258	0.5218	1,377	0.144	5.3	1.03	1.8935
8	36.17	0.46	18.0	0.2822	0.3233	0.5260	3,055	0.142	3.1	1.49	1.8995
12	36.21	0.35	24.7	0.2818	0.3259	0.5218	7,893	0.144	1.6	1.41	1.8939
13	36.16	0.25	33.0	0.2823	0.3233	0.5260	18,822	0.143	9.2	0.99	1.8935

D is average particle size; d is (101) plane space; V is the volume of the particle; v is the volume of the unit cell; $S = (1/D^2) \times 10^{15}$ is the dislocation density; ϵ is micro-strain; and L is bond length

position could shift toward equilibrium position, and it could release the strain. Hence, the micro-strain decreases as the pH value increases from 8 to 13. Furthermore, the observed decrease in FWHM may be due to the particle size or micro-strain or both [35]. Meanwhile, the crystalline quality of samples has been found to increase constantly with the pH value. It is evident that the decrease in strain causes the increase in crystal size through line broadening.

In order to strengthen the XRD analysis, further, the volume of the nanoparticles has been calculated from the relation $V = (4/3)\pi(D/2)^3$ and the volume of hexagonal unit cell from $v = (3a^2c)/2$. Then, the ratio V/v gives the number of unit cell present in a particle, which has been calculated from the equation $n = 1.621(D^3/a^2c)$. Further, the Zn–O bond length (L) has been calculated by the relation,

$$L = \sqrt{0.3a^2 + (0.5 - u)^2c^2}, \quad (7)$$

where $u = \frac{a^2}{3c^2} + 0.25$.

In this equation, u is known as internal parameter (z -coordinate of the oxygen atoms) of the wurtzite structures. Zn–O bond length was found to be 1.8935, 1.8895, 1.8939 and 1.8895 Å for the pH value of 6, 8, 12 and 13, respectively. All the details calculated from XRD pattern is given in Table 1.

3.3 Analysis of UV–Vis Absorption Spectrum

The optical absorption spectrum of the prepared samples recorded at visible and ultraviolet region is shown in Fig. 2. The recorded absorption peak (λ_{ab}) for the samples prepared at pH value of 6, 8, 12 and 13 are 361, 368, 374 and 381 nm, respectively. As seen, λ_{ab} increases gradually with the pH value. The absorption peaks of all the samples reported here are lower than that of bulk ZnO (388 nm), which corresponds to the blue shift in the spectrum. This blue shift in the excitonic absorption favors for the little quantum confinement effect [36], since the size of the nanoparticle under study is much larger than the Bohr radius of ZnO (approximately 2.34 nm) [37]. Furthermore, the energy gap of the nanoparticles has been calculated using the relation $E_g = (1.243/\lambda_{ab})$, and it was found to be 3.43, 3.37, 3.32 and 3.25 eV for the samples of pH value of 6, 8, 12 and 13, respectively. As the energy gap is inversely proportional to λ_{ab} , measurement demonstrates that the sample synthesized at pH value 6 has the largest energy gap of 3.43 eV, whereas the sample synthesized at pH value of 13 has the lowest energy gap of 3.25 eV. Thus, the energy gap measurement relays that the particle size increases with pH value.

The spectrum also indicates that the sample synthesized by chemical precipitation method has a very high level of

purity. The presence of any contaminants would have acted as dopants in the ZnO, causing lower energy (higher wavelength) transitions, which would appear as small peaks or drops in the UV–Vis spectrum. But the spectrum shows a smooth line beyond the original drop. It proves that the precipitation method provides high purity ZnO nanoparticles.

3.4 Transmittance Spectrum and Tauc's Relation

Optical transmittance spectrum of the prepared samples is shown in Fig. 3. From the figure, it is clear that the pH value has some influence on the optical transmittance of the ZnO nanoparticles. Obviously, the sample synthesized at pH value of 6 has the minimum transmittance of 20%, and the sample synthesized at pH value of 8 has the maximum transmittance of 65%. Further increase in pH value decreased the transmittance and finally it reached $\sim 30\%$ at pH value of 13. It is interesting to note that the transmittance is almost uniform between 250 and 750 nm for the samples synthesized at pH value of 6, 12 and 13. But for the pH value of 8, the transmittance is low below 350 nm and it increases exponentially, till 750 nm. This obvious trend suggests that the ZnO nanoparticles prepared at pH value of 6 can act as a strong UV absorber for wavelengths shorter than 350 nm.

In addition to the correlation between pH value and transmittance, energy gap of the prepared samples has also been evaluated using the Tauc's relation [38]

$$(\alpha h_\nu)^2 = A (h_\nu - E_g),$$

where A is a constant, h_ν is the energy of the photon, α is the absorption coefficient ($\alpha = 4\pi k/\lambda$; k is the absorption index), E_g is the energy gap of the nanoparticles under investigation, which is shown in the Fig. 4. It is estimated from the intercept of the linear portion of the curve on x -axis. Estimated E_g to be 3.42 eV for the sample at pH value of 6 and it decreases to 3.39 3.38 and 3.38 eV on further increase in pH value to 13, which are very close to our earlier report [39, 40]. The energy gap measurement from the UV–Vis absorption spectrum and effective mass model equation is in good agreement with Tauc's relation and is shown in Table 2.

3.5 Morphology and Compositional Analysis

SEM images of the prepared ZnO nanoparticles are shown in Fig. 5. A strong effect of pH value on the crystalline growth is clearly observed from the micrograph. It is found that the surface morphology of the particle is improved with increasing pH value. At lower pH value, the size distribution of particles appears to be less homogenous. It

Fig. 2 UV-Vis absorption characteristics of ZnO nanoparticles synthesized at different pH values: **a** pH 6; **b** pH 8; **c** pH 12; **d** pH 13

Fig. 3 Optical transmittance versus wavelength of ZnO samples synthesized at different pH values

is well known that nanoparticles are prone to aggregate due to the surface area to volume ratio; many primary nanoparticles combined themselves during the crystallization, which results in large bulk particles with severe agglomeration at pH value of 6. Such kind of agglomeration was previously reported [30, 32].

Morphology of particles is found to be roughly spherical and homogenous and some of the particles have agglomerated even when the pH value is increased to 8. Further increase in pH value to 12 resulted nanoparticles of different size; a few of them are spherical but majority of the particles are in rod-like structure. At pH value is 13, there is no agglomeration and all the particles are individual and

uniform in size. Most interesting thing to be considered here is that the sample prepared at pH value of 13 contains the particles of hexagonal facet. Magnified version of one such hexagonal facet, enclosed by dotted circle, is highlighted in the inset. Measurement reveals that the average particle size is 23, 36 and 43 nm for samples synthesized at the pH value of 8, 12 and 13, respectively. Particle size measured with SEM is in close agreement with that of XRD analysis. SEM analysis also reveals that the particle size increases with the increase in pH value. This observation is exactly opposite to some other experiment. For instance, as stated in introduction, Rani *et al.* [29] noticed a decrease in particle size when pH value higher than 9. They suggested that the dissolution of ZnO would take place at higher pH value, thereby decreases the particle size. But in our case, particle size increases consistently till pH value reach 13. Therefore, we believed that dissolution of ZnO didn't occur even at higher pH value of 13. As a result, many smaller nanocrystals combined themselves and formed a larger particle. Figure 6a shows a typical TEM image of ZnO nanoparticles grown at pH value of 12, from which the sphere-like morphology could be identified clearly and the average size of the nanoparticles are estimated to be about 25 nm.

Energy dispersive spectra (EDS) shown in the Fig. 6b–d depict the results of composition analysis of the samples prepared at pH values of 6, 8 and 13. Seeing that similar spectrum was recorded for all the samples, only three spectra are displayed here. The spectra corresponds the

Fig. 4 Energy gap of the ZnO nanoparticles synthesized at different pH values

peaks of zinc (Zn), oxygen (O) and carbon (C). Moreover, there are some other small peaks which show that the synthesized samples contains small amount of impurity still. It is evident that the synthesized nanoparticles have Zn and O. Result of composition analysis is given in Table 3.

3.6 FT-IR Studies

Result of FT-IR analysis of prepared ZnO particles is displayed in Fig. 7. A series of absorption peaks from 4,000 to 1,000 cm^{-1} can be found, corresponding to the vibration modes of impurities such as hydroxyl, carboxylate, carboxyl and alkane present in the nanopowders. To be more specific, the spectra show main absorption bands at 3,290–3,420 cm^{-1} represents O–H stretching vibration of water [41] from NaOH (used as a precursor) and those at 2,934 cm^{-1} represents the C–H stretching vibrations of alkane groups. The peak at about 2,201–2,358 cm^{-1} arises from the atmospheric CO_2 on the metallic cations. However, this peak hasn't been observed at pH 12. The peak observed around 1,707 cm^{-1} of samples prepared at pH value of 6 and 12 are due to carboxyl group. Small peaks recorded between 1,646 and 1,542 cm^{-1} are probably from C=O band. Similarly, the absorption peaks at 1,425–1,495 cm^{-1} represents the carboxylate group (COO^-). The band around 1,388 cm^{-1} is the representative of bending

vibration of $-\text{CH}_2$. Moreover, the band at $\sim 1,273 \text{ cm}^{-1}$ corresponds the O–H symmetric bending. The C–H in plane bending vibration has been noticed at 1,112 cm^{-1} only from the sample prepared at pH value of 13. The peaks around 1,020–1,044 cm^{-1} depict the stretching vibration of C–O attributed to zinc acetate. The band centered at 815, 883 and 914 cm^{-1} is attributed to bending mode of carbonate.

In the infrared region, characteristic Zn–O stretching mode was found at the wave number between 482 and 595 cm^{-1} . This difference in wavenumber may be due to difference in particle sizes and the frequencies are consistent with those reported in the literature [42]. These stretching mode peaks are indicative of the successful synthesis of ZnO nanoparticles. IR Peak assignments for various functional groups are displayed in Table 4. As the size of the nanoparticles increases, the FTIR signature of these impurities decreases.

3.7 PL Spectrum of the ZnO Nanoparticles

Photoluminescence study helps to find out the structural defects in nanoparticles. It is well known that the PL intensity depends on the particle density in the solvent. In order to analyze the impact of pH value on PL intensity, 150 mg of ZnO nanopowder from each sample has been dispersed in 15 mL double distilled water, and then, the

spectrum has been recorded. Figure 8 displays the PL spectra of samples under study. As expected, each curve depicts the variation of PL intensity with respect to pH value. A considerable decrease in PL intensity with pH is observed. This variation in PL intensity reveals the transmittance spectra. It can be seen that four emission bands were observed in all the samples such as (1) UV emission (<400 nm) band, (2) violet emission (430 nm) band, (3) blue emission (487 nm) band and (4) a weak but broad green emission (513 nm). Of these, UV emission is known as a near-band-edge (NBE) emission, which originates from the recombination of free exciton through an exciton–exciton collision process.

The characteristic UV emission (399 nm) of ZnO nanoparticles has been observed at 399 nm in all the cases. It can be seen that, the UV region starts widen with pH value and it is wider at pH value of 13. It shows that the sharp UV peaks can be obtained at lower pH value. Also, it is clear that UV

emission is dominant at lower pH value of 6 whereas the violet emission dominates when the pH value higher than 8. It is due to the fact that the lower pH value correspond the higher concentration of H^+ ions which facilitates higher concentration of hydrogen dopants incorporated into the lattice of ZnO [4] which further contributes to the stronger UV (NBE) intensity as hydrogen dopants [5]. The violet emission band observed in all the samples between 423 and 448 nm is attributed to the presence of zinc interstitials (Zn_i) shallow donors, which have a 0.22 eV energy gap below the conduction band. Exciton recombination between the electrons localized at the zinc interstitials and holes in the valence band leads to this violet emission. This type of violet emission band was also observed in the ZnO nanoneedle arrays reported by Ahn *et al.* [43]. In addition to violet, blue emission has been observed sharply around 487 nm in all the samples. Meanwhile, the weak green emission covers a wide of 513–540 nm. From the present study, it is clear that increase of pH value i.e., increase of particle size is favorable for the violet emission and it widens the UV emission range from 399 to 417 nm (Refer curve d in Fig. 8), but it does not affect blue and green emissions. Therefore, the photoluminescence study reported here concludes that the type of emission from the ZnO nanoparticles, i.e., whether UV (or) violet is determined by the pH value of the solution. Also, the strong violet and weak blue bands emitted by the samples confirm that the prepared samples contain the ZnO nanoparticles.

Table 2 Energy gap (in eV) measurements from different methods of the ZnO nanoparticles synthesized at various pH values

pH value	Effective mass model	UV–Vis spectrum	Tauc's relation
6	3.42	3.43	3.42
8	3.40	3.37	3.39
12	3.39	3.32	3.38
13	3.38	3.25	3.38

Fig. 5 SEM images of ZnO nanoparticles synthesized at various pH values: **a** pH 6; **b** pH 8; **c** pH 12; **d** pH 13

Fig. 6 TEM image of the ZnO nanocrystals synthesized at pH 12 **a**, EDS spectra of ZnO nanocrystals synthesized at pH 6 **b**, pH 8 **c**, pH 13 **d**

Table 3 Results of elemental analysis of the ZnO nanoparticles synthesized at various pH values

pH value	Zn K (wt%)	O K (wt%)
6	60.28	39.72
8	63.18	36.82
12	66.77	33.23
13	68.83	31.17

Fig. 7 Typical FTIR spectrum and their peak assignments of ZnO nanoparticles synthesized at various pH values: *a* pH 6; *b* pH 8; *c* pH 12; *d* pH 13

Several groups have reported different defect centers in ZnO that are responsible for the blue and green visible emissions [44]. This visible emission is due to an electronic

transition from a level close to the conduction band edge to a defect associated trap state, such as an oxygen vacancy. According to Vanheusden *et al.* [45], visible luminescence of ZnO is mainly originated from the defect states such as oxygen vacancies and zinc interstitials. Oxygen, normally, exhibit three types of charge states such as V_o^0 , V_o^+ , and V_o^{2+} . The oxygen vacancies are situated below the bottom of the conduction band (CB) in the series of V_o^0 , V_o^+ , and V_o^{2+} , from top to bottom. It was recently reported that the transition involving zinc vacancy would result in blue emission [46]. Here, a sharp blue emission peak has been noticed exactly at 487 nm, and this peak occupies the same position irrespective of the pH value. A broad green emission band between 513 and 540 nm, known as a deep-level emission, is related to the deep-level defect states [47]. This green emission originates from the recombination of a photo-generated hole with an electron, occupying the oxygen vacancy and interstitials of zinc. Shallow acceptor levels lie at 0.3 and 0.4 eV above the top of the valance band (VB) due to zinc vacancy (V_{zn}) and oxygen interstitial (O_i), respectively. Again, Zinc interstitial (Zn_i) produces a shallow donor level at 0.5 eV below the bottom of CB [48]. The position of different defect levels is illustrated in Fig. 9. In this study, the less intense green emission peaks were observed 513–540 nm in all the samples. As a result, the present PL study infers that pH of the solution has high impact on the luminescence property of the ZnO sample.

Table 4 Peak assignments for the prepared ZnO nanoparticles synthesized at various pH values

Functional group	Wavenumber (cm ⁻¹)			
	pH 6	pH 8	pH 12	pH 13
O–H stretching of water	3,290	3,397	3,401	3,420
C–H stretching vibration	–	–	–	2,934
Existence of CO ₂	2,272	2,358	–	2,201
Carboxyl group	–	1,707	1,704	–
C=O band	1,585–1,509	1,573	1,646–1,542	1,633
Carboxylate group (COO ⁻)	–	1,495	1,425	1,465
Bending vibration of –CH ₂	–	1,383	1,372	–
O–H symmetric bending	1,273	1,224	1,225	–
C–H in plane bending vibration	1,112	–	–	–
Stretching vibration of C–O	1,020	1,040	–	1,044
Bending mode of carbonate	815	914	883	860
Stretching vibration of Zn–O	596	566	482	582

Fig. 8 Room temperature photoluminescence spectrum of the ZnO nanoparticles synthesized at various pH values: *a* pH 6; *b* pH 8; *c* pH 12; *d* pH 13 **Fig. 9** Schematic illustration of different defect levels in ZnO, which are responsible for the emission of different wavelength

4 Conclusions

In conclusion, nanocrystalline ZnO powders have been successfully synthesized by chemical precipitation method at four different pH values. The result presented here

confirms that pH value of the solution plays a major role in determining the structure, morphology and optical properties of the ZnO nanoparticles. The XRD pattern and SEM images confirmed the presence of crystalline wurtzite nanocrystals and also it confirmed that the particle size increases with pH value. TEM result also favors for the XRD analysis. The result of UV–Vis spectrum also justified that the prepared ZnO powders have particles in nanometer size. As the UV–Vis absorption of ZnO nanoparticles prepared at pH value of 6 is higher than the other particles, which concludes that ZnO nanoparticles with smaller size can be used as a UV absorber. From PL study, it is concluded that the pH value variation would affect the UV and Violet emission, but not the blue and green emissions. Finally, it is concluded that the ZnO nanoparticles prepared by chemical precipitation method at pH value of 13 is suitable for the construction of optoelectronic devices for violet emission.

References

- [1] M.A. Subhan, M.R. Awal, T. Ahmed, M. Younus, Acta Metall. Sin. (Engl. Lett.) **27**, 223 (2014)
- [2] Y. Yao, Q. Cao, Acta Metall. Sin. (Engl. Lett.) **26**, 467 (2013)
- [3] X. Huang, G. Li, B. Cao, M. Wang, C. Hao, J. Phys. Chem. C **113**, 4381 (2009)
- [4] X.H. Huang, C.B. Tay, Z.Y. Zhan, C. Zhang, L.X. Zheng, T. Venkatesan, S.J. Chua, Cryst. Eng. Commun. **13**, 7032 (2011)
- [5] X.H. Huang, Z.Y. Zhan, K.P. Pramoda, C. Zhang, L.X. Zheng, S.J. Chua, Cryst. Eng. Commun. **14**, 5163 (2012)
- [6] X.H. Huang, C. Zhang, C.B. Tay, T. Venkatesan, S.J. Chua, Appl. Phys. Lett. **102**, 111106 (2013)
- [7] C.Y. Luan, Y.K. Liu, Y. Jiang, J.S. Jie, I. Bello, S.T. Lee, J.A. Zapien, Vacuum **86**, 737 (2012)
- [8] A. Choi, K. Kim, H.I. Jung, S.Y. Lee, Sens. Actuators B **148**, 577 (2010)

- [9] Y.L. Wu, C.S. Lim, S. Fu, A.I.Y. Tok, H.M. Lau, F.Y.C. Boey, *Nanotechnology* **18**, 215604 (2007)
- [10] H. Hong, J. Shi, Y. Yang, Y. Zhang, J.W. Engle, R.J. Nickles, X. Wang, *Nano Lett.* **11**, 3744 (2011)
- [11] B. Kumar, S.W. Kim, *Nano Energy* **1**, 342 (2012)
- [12] J. Han, F. Fan, C. Xu, S. Lin, M. Wei, X. Duan, Z.L. Wang, *Nanotechnology* **21**, 405203 (2010)
- [13] M. Chen, Z. Wang, D. Han, F. Gu, G. Guo, *J. Phys. Chem. C* **115**, 12763 (2011)
- [14] C. Wongchoosuk, S. Choopun, A. Tuantranont, T. Kerdcharoen, *Mater. Res. Innov.* **13**, 185 (2009)
- [15] R. Niepelt, U.C. Schroder, J. Sommerfeld, I. Slowik, B. Rudolph, R. Moller, B. Seise, A. Csaki, W. Fritzsche, C. Ronnin, *Nanoscale Res. Lett.* **6**, 511 (2011)
- [16] F. Yakuphanoglu, S. Mansouri, *Microelectron. Reliab.* **51**, 2200 (2011)
- [17] D.I. Son, B.W. Kwon, D.H. Park, W.S. Seo, Y. Yi, B. Angadi, C.L. Lee, W.K. Choi, *Nat. Nanotechnol.* **7**, 465 (2012)
- [18] W.K. Hong, S. Song, D.K. Hwang, S.S. Kwon, G. Jo, S.J. Park, T. Lee, *Appl. Surf. Sci.* **254**, 7559 (2008)
- [19] Z.L. Wang, *Adv. Mater.* **15**, 432 (2003)
- [20] K. Kasemets, M. Romet, A. Ivask, A. Kahru, *Toxicol. Lett.* **180**, S22310 (2008)
- [21] M. Heinlaan, A. Ivask, I. Blinova, H.C. Dubourguier, A. Kahru, *Chemosphere* **71**, 1308 (2008)
- [22] V. Aruoja, A. Kahru, H.C. Dubourguier, *Toxicol. Lett.* **180S**, S220 (2008)
- [23] J. Zhou, N.S. Xu, Z.L. Wang, *Adv. Mater.* **18**, 2432 (2006)
- [24] D.D. Guo, C.H. Wu, H. Jiang, Q.N. Li, X.M. Wang, B.A. Chen, *J. Photochem. Photobiol. B* **93**, 119 (2008)
- [25] C. Chena, B. Yua, P. Liub, J.F. Liua, L. Wang, *J. Ceram. Process. Res.* **12**, 420 (2011)
- [26] W.J. Li, E.W. Shi, T. Fukuda, *Cryst. Res. Technol.* **38**, 847 (2003)
- [27] H. Zhang, D. Yang, X. Ma, Y. Ji, J. Xu, D. Que, *Nanotechnology* **15**, 622 (2004)
- [28] C.H. Lu, C.H. Yeh, *Ceram. Int.* **26**, 351 (2000)
- [29] S. Rani, P. Suri, P.K. Shishodia, R.M. Mehra, *Solar Energy Mater. Solar Cells* **92**, 1639 (2008)
- [30] S.S. Alias, A.B. Ismail, A.A. Mohamad, *J. Alloys Compd.* **499**, 231 (2010)
- [31] X.H. Huang, Z.Y. Zhan, X. Wang, Z. Zhang, G.Z. Xing, D.L. Guo, D.P. Leusink, L.X. Zheng, T. Wu, *Appl. Phys. Lett.* **97**, 203112 (2010)
- [32] K. Sivakumar, V. Senthil kumar, N. Muthukumarasamy, M. Thambidurai, T.S. Senthil, *Bull. Mater. Sci.* **35**, 327 (2012)
- [33] S. Manafi, A. Rouhani, S. Joughedoust, A. Salehi, in *Paper Present in 2nd International Conference on Nanotechnology (NANOCON 2010)*, Olomouc, Czech Republic, EU, 12–14 Oct 2010
- [34] K.F. Lin, H.M. Cheng, H.C. Hsu, L.J. Lin, W.F. Hsieh, *Chem. Phys. Lett.* **409**, 208 (2005)
- [35] A. Jagannatha Reddy, M.K. Kokila, H. Nagabhushan, R.P.S. Chakradhar, C. Shivakumar, J.L. Rao, B.M. Nagabhushan, *J. Alloys Compd.* **509**, 5349 (2011)
- [36] U. Koch, A. Fojtik, H. Weller, A. Henglein, *Chem. Phys. Lett.* **122**, 507 (1985)
- [37] Y. Gu, I. Kuskovsky, M. Yin, S. O'Brien, G.F. Neumark, *Appl. Phys. Lett.* **85**, 3833 (2004)
- [38] Tauc. J. (ed.), *Amorphous and Liquid Semiconductor* (Plenum Press, New York, 1974)
- [39] K. Pushpanathan, S. Sathya, M. Jay Chithra, S. Gowthami, R. Santhi, *Mater. Manuf. Process.* **27**, 1334 (2012)
- [40] M. Jay Chithra, K. Pushpanathan, M. Loganathan, *Mater. Manuf. Process.* **29**, 771 (2014)
- [41] D.M. Fernandes, R. Silva, A.A.W. Hechenleitner, E. Radovanovic, M.A.C. Melo, E.A.G. Pineda, *Mater. Chem. Phys.* **115**, 110 (2009)
- [42] F. Ahmed, S. Kumar, N. Arshi, M.S. Anwar, B.H. Koo, C.G. Lee, *Funct. Mater. Lett.* **4**, 1 (2011)
- [43] H.A. Ahn, Y.Y. Kim, D.C. Kim, S.K. Mohanta, H.K. Cho, *J. Appl. Phys.* **105**, 013502 (2009)
- [44] A.B. Djuricic, Y.H. Leung, K.H. Tam, L. Ding, W.K. Ge, H.Y. Chen, S. Gwo, *Appl. Phys. Lett.* **88**, 103 (2006)
- [45] K. Vanheusden, C.H. Seager, W.L. Warren, D.R. Tallant, J.A. Voigt, *Appl. Phys. Lett.* **68**, 403 (1996)
- [46] K.H. Tam, C.K. Cheung, Y.H. Leung, A.B. Djuricic, C.C. Ling, C.D. Beling, S. Fung, W.M. Kwok, D.L. Phillips, L. Ding, W.K. Ge, *J. Phys. Chem.* **110**, 20865 (2006)
- [47] D. Wang, H.W. Seo, C.C. Tin, M.J. Bozack, J.R. Williams, M. Park, N. Sathitsuksanoh, A.J. Cheng, Y.H. Tzeng, *J. Appl. Phys.* **99**, 113509 (2006)
- [48] P.S. Xu, Y.M. Sun, C.S. Shi, F.Q. Xu, H.B. Pan, *Nucl. Instrum. Methods Phys. Res. B* **199**, 286 (2003)