

Research Article

The Effect of Solvents, Acetone, Water, and Ethanol, on the Morphological and Optical Properties of ZnO Nanoparticles Prepared by Microwave

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HDA-capped ZnO nanoparticles were prepared by solvothermal method using solvents of different polarities. A number of parameters were kept constant such as temperature, pressure, time, and pH while solvents were varied, that is, water, ethanol, and acetone. The TEM was used for the structural properties and morphologies such as spheres, mixture of rods, and spheres and stars were obtained in ethanol, acetone, and water, respectively, in a given reaction time of 15 minutes. Both ethanol and acetone gave rods with high aspect ratio primarily because of the lengths of the rods. Water and ethanol have the hydroxyl groups which interact with nanoparticles from nucleation, growth, and termination giving rise to nonspherical shapes. The hydroxyl group promotes growth in a nonuniform way resulting in stars and rods. The optical features were typical of ZnO nanoparticles with excitonic peaks in the range 368 to 374 nm from their absorption spectra. The XRD patterns of the particles gave the most stable form of ZnO which is the hexagonal phase, with high degree of crystallinity and with the 101 plane predominant in all solvents.

1. Introduction

Semiconductors in a nanoscale level have attracted a great deal of interest due to their unique properties [1]. One of the unique characteristics of the nanoparticles is their size dependent electrical and optical properties known as the quantum confinement effect [2, 3]. ZnO is one of the few semiconductors which exhibit quantum confinement effect. ZnO is a wide band gap (3.34 eV) material and it has found applications in various fields [4]. It is an environmental friendly oxide, because of its nontoxicity and the ability to absorb in the UV range. It is as such used as a UV absorbent in the sunscreens and in solar energy conversion [5].

Other applications of ZnO include photovoltaic devices, gas sensors, photocatalysis, transparent conducting coating, and electrostatic transducers, [4]. It is well documented that the shape and size of the material strongly affect the

properties and the applications of the material [6–9]. Hence, much effort is being dedicated on controlling the size and shape of the particles; however this still remains a challenge in synthetic chemists in the nanoscience field. Different factors such as time, temperature, concentration, precursors, capping molecule, solvents, and others are reported to affect the shape and size of the nanoparticles [7, 8].

ZnO is an interesting metal oxide because it can exist in diverse convoluted morphologies [10, 11]. Herein we report on the effect of solvent effect on the shape of ZnO nanoparticles. Solvents play a crucial role in a reaction; they provide a means of temperature control by determining the highest temperature at which the reaction will occur. ZnO has been prepared by different methods. A novel sol-gel technique for the synthesis of stable zinc oxide colloids composed of nano-sized wurzite crystal was reported by Bahnemann et al. [12] and Spanhel and Anderson [13].

Other methods for the preparation of the metal oxide semiconductor nanoparticles reported to date include double-jet precipitation [14], flow through supercritical water method (FT-SCW) [15], and reverse micelles [16]. A nonhydrolytic single source precursor for the synthesis of the different metal oxide was reported by Rochengerger et al. [17] where a metal cupferron complex acts as a single source precursor for the various metal oxides. In a solvothermal synthesis, a solvent acts as a reaction medium that allows the relatively high temperature required for crystallisation of inorganic material [18]. It has proven to be the most efficient and easiest method for the production of ZnO nanoparticles. The choice of solvent used for the reaction has been reported to affect the shape of ZnO nanoparticles formed. Tonto and coworkers showed that by using organic solvents of different chain lengths, single crystalline ZnO nanoparticles of different aspect ratio can be prepared [18].

Another recent work on solvothermal synthesis is that reported by Linping Xu and coworkers. They reported that by using solvents of different saturated vapour pressures morphologies such as cauliflower, truncated, hexagonal, conical, spheres, rods, tubular, hour glass ZnOs are attained in solvents such as THF, decane, acetone, ethanol, water, and toluene, respectively [19]. However, the shapes were attained using conventional heating while microwave heating is also gaining importance in synthetic chemistry due to its unique effects such as rapid and selective heating, high reaction rate, increased product yield, and energy saving, and it has been used in the synthesis of ZnO nanoparticles [20–22]. Previously a mixture of hexadecylamine and oleic acid through hot reduction of zinc halide by superhydride followed by oxidation was reported to produce ZnO nanocrystals with low-size dispersion [23]. Herein we report on the effect of solvents polarity on the morphology and optical properties of ZnO nanoparticles produced by microwave irradiation.

2. Experimental

2.1. Materials. Zinc nitrate hexahydrate ($\text{ZnNO}_3 \cdot 6\text{H}_2\text{O}$) 99%, sodium hydroxide pellets (NaOH), hexadecylamine (HDA), ethanol, and acetone were reagents from Sigma-Aldrich and were all used without further purification.

2.2. Synthesis of Zinc Oxide Nanoparticles. Zinc oxide nanoparticles of various morphologies were synthesized using the method reported by Bahnemann et al. [12]. In a typical synthesis, 2.5 g of HDA, zinc nitrate hexahydrate (0.3 M), and sodium hydroxide (0.3 M) prepared by dissolving in either acetone, ethanol, or deionised water was placed into the teflon reaction vessels of the Multiwave 300. The mixture was reacted at 120°C for 15 min in all solvent medium.

2.3. Characterisation

2.3.1. Optical Properties. Absorption spectra were acquired on a Analytikjena Specord 50 UV-Vis spectrophotometer. The particles were dissolved in methanol, and solution was placed in a quartz cuvettes with 1 cm path length. A Perkin

Elmer LS 45 Fluorimeter was used for the photoluminescence of the nanoparticles dissolved in methanol.

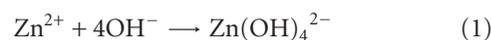
2.3.2. Electron Microscopy. Transmission electron microscopy was acquired on the Hitachi Jeol 100S operated at 80 keV. A drop of nanoparticles dissolved in methanol was placed on a copper grid.

2.3.3. Powder X-Ray Diffraction. XRD patterns of the powdered samples were obtained on a Phillips X'Pert materials research diffractometer using secondary monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$) at 40 Kv/50 mA. Samples were supported on a glass slide. Measurements were taken using a glancing angle of incidence detector at an angle of 2 for 2θ values over 10–80 in steps of 0.05 with a scan speed of 0.012.

2.3.4. Fourier Transform Infrared (FTIR) Spectroscopy. The FT-IR spectrum of the nanoparticles was recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer. The powder sample was placed on a sample holder and the spectrum was recorded.

3. Results and Discussions

The synthesis of ZnO nanoparticles was made in various methods to study the effects on conditions such as precursors, temperature, time, and concentration on the morphology and properties of nanoparticles. The solvents have not been investigated to explore their effects in the morphologies and optical properties. In the work various solvents with varying degree of polarities were used. One of the general morphologies obtained from aqueous media is star-shaped nanoparticles, and different morphologies were obtained in solvents acetone, water, and ethanol due to the solvent interactions with the precursor, zinc nitrate salt in the presence of hexadecylamine to stabilize the particles. Microwave technique was used to ensure that the precursor is soluble in all solvents and hexadecylamine also was dispersed to allow both kinetic and thermodynamic control in the growth of nanoparticles. The interaction between solvents, hexadecylamine, and the precursor becomes critical in influencing the growth of particles. The addition of a base sodium hydroxide is generally known to generate an intermediate hydroxide $\text{Zn}(\text{OH})_4^{2-}$ upon reaction with the zinc salt (1). The conversion of the hydroxides into ZnO (2) is promoted by excess of sodium hydroxide in the presence of solvent medium either water, ethanol, or acetone. Water has the least solubility towards HDA whereas in acetone and ethanol solubility is increased and allowing more interaction between the particles and the capping molecule:



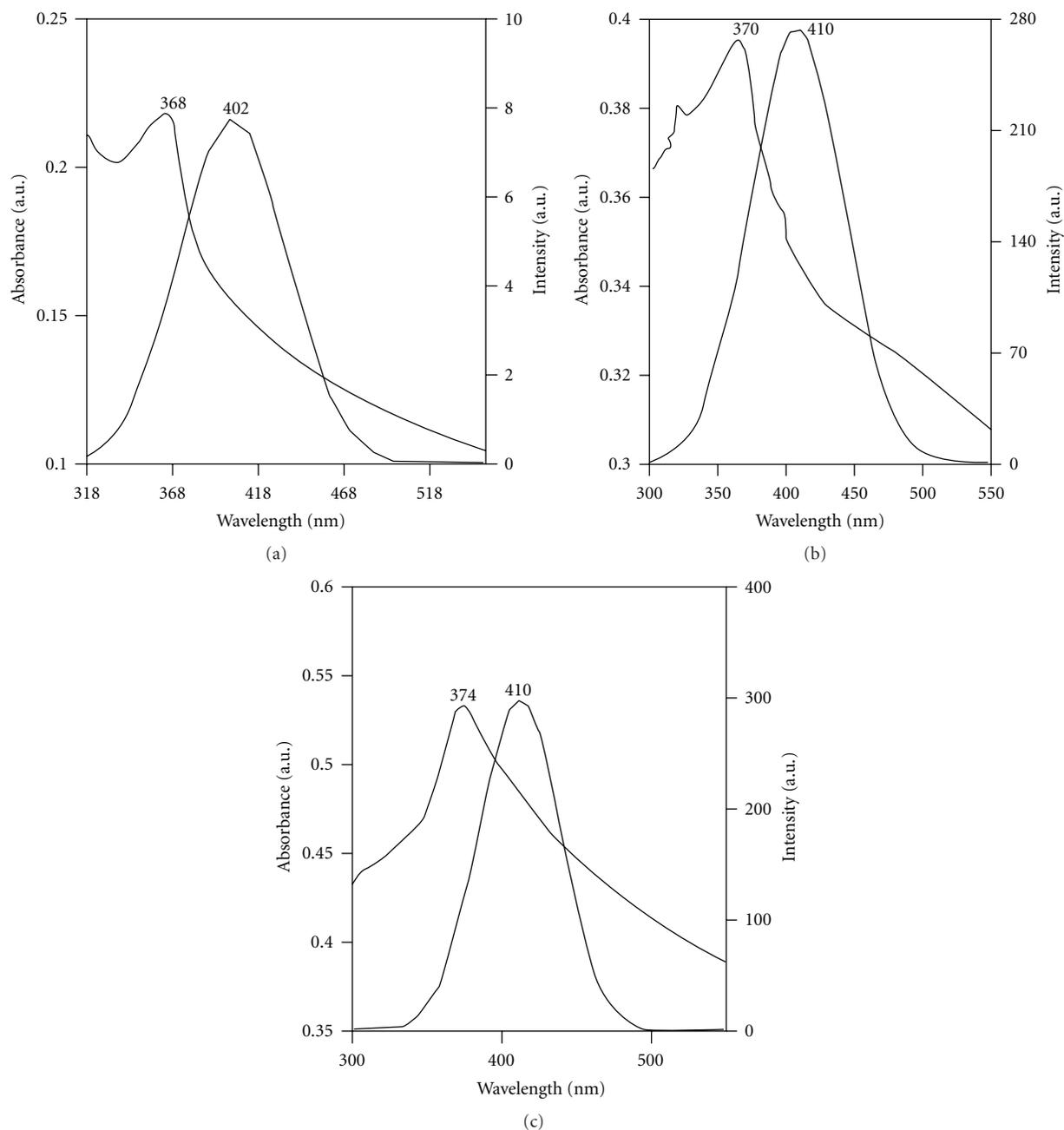


FIGURE 1: Absorption and emission spectra of ZnO nanoparticles synthesised in ethanol (a), acetone (b), and water (c) at 120°C and time of 15 minutes under microwave.

3.1. Optical Properties. The optical properties of ZnO nanoparticles in ethanol as a solvent are shown in Figure 1(a). ZnO normally exhibits two emission peaks; one is a broad green emission in the region between 500 and 530 nm [10] which is due to the oxygen vacancy. The other gave much narrow ultraviolet emission band at around 400 nm which is due to the excitons recombination. A well-defined excitonic peak appears at 368 nm and is slightly blue shifted when compared to the bulk which appears at 370 nm. One of the impressive features of semiconductor nanoparticles is their ability to emit light upon excitation

with shorter wavelength of equivalent to the absorption onset, an electron is promoted from valence band to the conduction band, and on relaxation a photon is emitted.

The emission peak at 402 nm is associated with the excitons recombination corresponding to the band edge emission of ZnO (Figure 1(a)). The wavelength maximum emission is red shifted from the absorption peak and this is a typical feature of well-passivated nanoparticles. The absorption spectrum of ZnO nanoparticles prepared in acetone is presented in Figure 1(b). The excitonic peak appears in 369 nm, blue shifted compared to the bulk. The blue shift

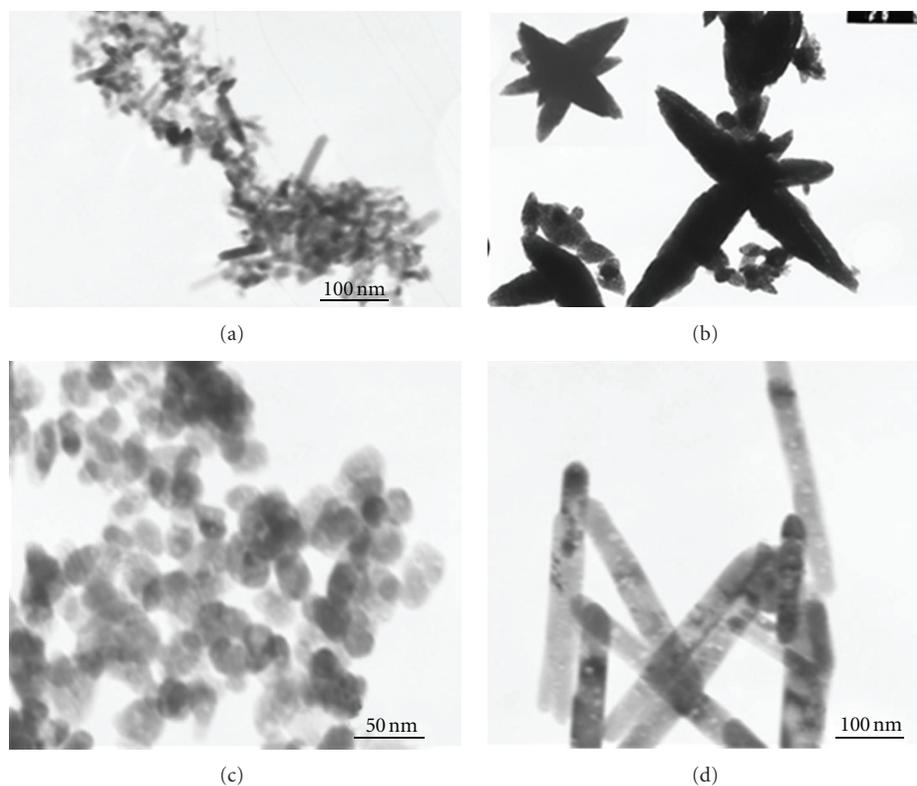


FIGURE 2: TEM images of ZnO nanoparticles synthesised in various solvents, ethanol (a), acetone (b, c), and water (d) at 120°C and time of 15 minutes under microwave.

is due to the particles nanosize regime exhibiting quantum confinement effect. The photoluminescence spectra show a broad emission due to the wide distribution of the particle size. The large particle size and shape of the particles synthesised in water as a solvent influenced the appearance of the absorption peak (Figure 1(c)). The absorption peak for water is also much more tailing compared to the peak of acetone and ethanol.

3.2. Structural Properties

3.2.1. TEM and IR Spectral Analysis. In the alkyl containing solvents, ethanol, and acetone, a mixture of rods and spheres was formed. It has been reported that organic solvents promote the formation of spheres and rods [19]; therefore a similar trend was observed with ethanol and acetone (Figures 2(a), 2(b, c)), respectively. Particles formed when ethanol was used as a solvent in Figure 2(a) have spheres ranging from 20 to 60 nm and rods with aspect ratio of 8–60. Since nanoparticles are so small, they are very unstable and tend to agglomerate. Over the years the problem has been overcome by using an organic molecule that is going to introduce steric hindrance between the particles thereby preventing agglomeration. Hexadecylamine (HDA) has proven to be a good capping agent over the years. It is versatile and is mobile enough to readily add to monomer but stable enough to prevent agglomeration [6]. Even though HDA is such a good capping agent, particles obtained in ethanol appear to have

agglomerated. It is well documented that ZnO contains the fastest growing plane 0001. Therefore in the beginning of the reaction, spheres are formed which contains the high energy 0001. Because of the high energy, the plane that elongates faster than the other planes resulting into the formation of rods [24].

Particles formed in acetone (Figures 2(b) and 2(c)) have spheres with sizes ranging from 45 to 100 nm and rods with aspect ratio which ranges from 37 to 94, and particles are bigger and longer than those formed in ethanol. Acetone has the lowest boiling point compared to ethanol; therefore particles formed in acetone are heated to a lower temperature, and because of the low dielectric constant compared to ethanol, it interacts the least with the electromagnetic radiation of the microwave. Therefore particles formed in acetone were expected to be much smaller. Long rods also formed in acetone a phenomenon established when nonalcoholic solvents are used in solvothermal synthesis [25] of ZnO nanoparticles. The influence in the formation of long rods could be resulting from the one-dimensionality of the interaction with the amine group of the HDA. HDA is known to promote growth along one plane through the bonding interaction between the NH_2 group and the ZnO nanoparticles. Therefore the solubility of HDA in acetone at the given temperature (120°C) allows the formation of both spheres and rods under the microwave treatment. Using water as solvent, star-shaped particles were formed (Figure 2(d)). The star-shaped nanoparticles have also been

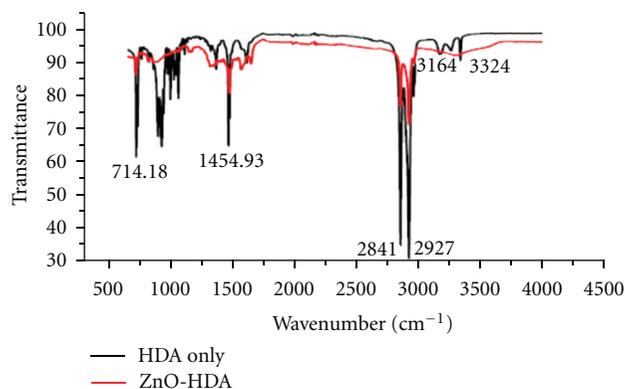


FIGURE 3: FTIR spectra of ZnO nanoparticles synthesised using zinc nitrate in water at 120°C and time of 15 minutes under microwave.

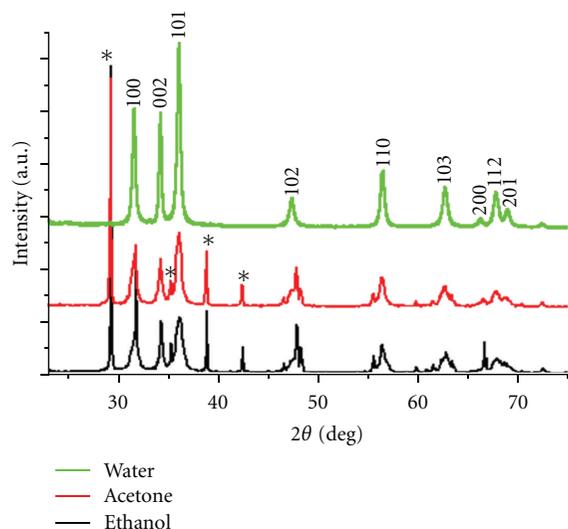


FIGURE 4: XRD pattern ZnO nanoparticles synthesised using zinc nitrate in different solvents, water, acetone, and ethanol at 120°C and time of 15 minutes under microwave.

reported using conventional heating; their shape which is due to the coalescence of several nuclei and water has the tendency of forming star-shaped particles [24].

Under normal conditions, HDA will not dissolve in water; however the microwave might induce the dissolution of HDA in water therefore capping the particles effectively. To confirm that HDA passivated the particles formed in water, the IR was used. The FTIR in Figure 3 illuminates the evolution of surface-bonded molecule on ZnO nanoparticles. In HDA only, the peaks at 3181.87–3336 cm^{-1} are due to N–H stretching of the primary amine. The C–H and C–N–H stretching appears at 2850 and 2916 cm^{-1} . In ZnO capped with HDA, the N–H vibration disappears and the peak broadens; this can be possible due to the OH stretching of some water on the surface of ZnO nanoparticles. The C–C (714.8 cm^{-1}) and CH₂ wagging (1454.3 cm^{-1}) vibrations are highly intense in HDA due to the high number of CH₂'s in the molecular structure of HDA; however the

introduction of ZnO nanoparticles weakens the peaks. The presence of similar peaks from both ZnO–HDA and HDA cannot conclusively denote the interaction of HDA with ZnO nanoparticles but it does indicate the presence of HDA in the sample.

3.2.2. XRD Analysis. To confirm the purity and determine the phase of the particles, X-ray diffractometry was used. The XRD diffraction peaks were indexed to hexagonal phase ZnO. The morphologies from acetone and ethanol (Figure 4) have similar diffraction patterns except for the relative intensities due to their random orientation. XRD pattern for water was indexed to pure hexagonal phase ZnO without any trace of Zinc Nitrate, while ethanol and acetone show some impurities marked with an asterisk. The impurities are from unreacted zinc nitrate; however the peaks are broad in both solvents compared to water which has narrow and more intense peaks. The broadness of the peaks is due to the small size of the particles.

4. Conclusions

The synthesis of ZnO nanoparticles capped with hexadecylamine (HDA) was carried out with $\text{Zn}(\text{NO}_3)_2$ and NaOH as the base in acetone, ethanol, and water. Reaction in ethanol results in the formation of rods and spheres which are of smaller sizes with respect to those formed in acetone as a solvent under similar conditions. Water as a solvent forms highly crystalline ZnO nanoparticles which are star shaped. The solvent influence was observed to drive for the interaction of HDA with ZnO nanoparticles growth with both thermodynamic and kinetic controls considered under the microwave irradiation. The polar characteristic of the solvent was proposed to be the main factor that affects both nucleation and growth of ZnO nanoparticles and, consequently, determines the shape, size, and aspect ratio of the products.

Acknowledgments

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