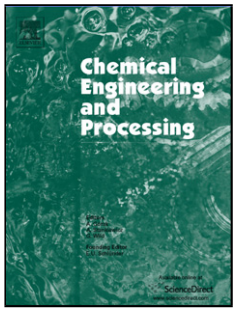

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Effect of pH on sonication assisted synthesis of ZnO nanostructures: Process details

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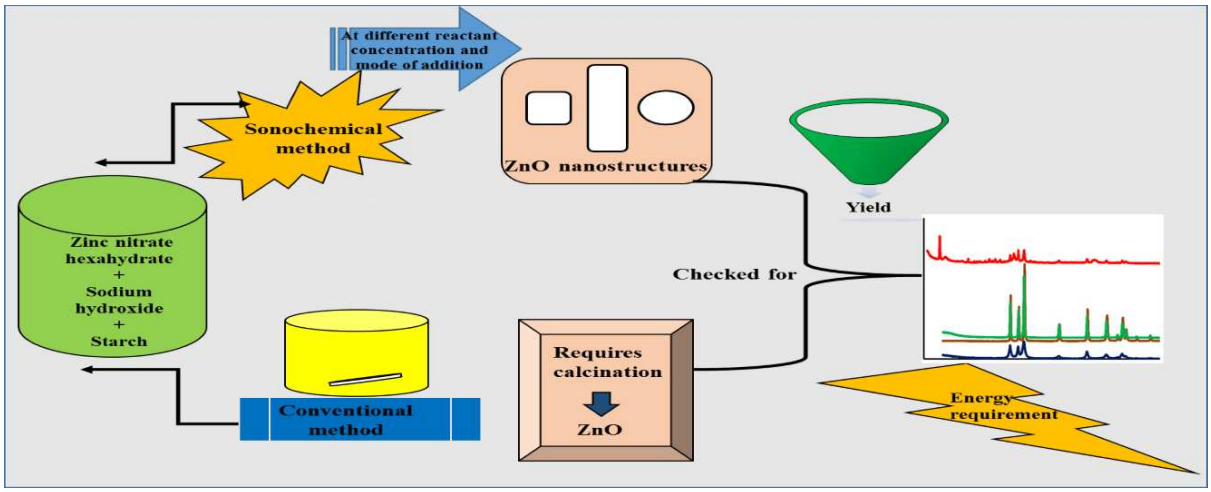
Graphical abstract



Highlights

- Elucidates sonochemical synthesis of ZnO nanostructures due to change in pH
- Mixing time has been determined to decide rate of addition of precursor
- Effect of pH on yield, crystallite size and band gap energy are investigated
- Microthermal heating in sonication method assist the direct synthesis of ZnO
- The energy delivered during sonication and conventional process has been computed

ABSTRACT

A facile sonication assisted fabrication of zinc oxide nanostructures (plate, rod and spherical) were successfully accomplished by changing the pH of the reaction mixture (acidic, neutral and basic). Starch was used as a capping agent. Mixing time was determined to decide the rate of addition of $Zn(NO_3)_2$ solution into the NaOH base solution. In a sonication method, the system was irradiated by ultrasound for a total duration of 20 min. The effect of pH on the yield (%), crystallite size, crystallinity (%), structures and band gap energy of ZnO were measured and compared using different characterization tools. The yield evaluated accounts for material balance in sonochemically prepared ZnO sample. A probable mechanism was proposed to explain the formation of tailored ZnO morphology based on the concentration of zinc species present in the solution. It was revealed from the X-ray diffraction data, that conventional magnetic stirring technique needs calcination for ZnO formation. However, sonochemical method leads to direct synthesis of ZnO. It was observed that the quantum of energy required for sonochemical method of synthesis is comparable to the energy required for agitation and calcination (together) during conventional method of ZnO synthesis.

Keywords: Zinc oxide, Nanostructures, Sonication, pH

1. Introduction

Synthesis of nanoparticles using efficient methodology is the first requirement of any novel study of nanoparticles. Zinc oxide nanoparticles can be grown on substrate or synthesized independently.

Nano ZnO structures are most attractive material due to their unique electrical and optical properties. Their use has been explored in the field of heterogeneous catalyst for synthesis of derivatives [1], photocatalyst for dye degradation [2], enzyme immobilization [3], and photoelectrocatalyst [4]. Researchers have reported numerous methods for zinc oxide nanostructures synthesis such as sonication [5], solvothermal [6], hydrothermal [7] and polymerization [8] etc. Among them sonication is very promising and efficient method for rapid synthesis of metal oxide nanoparticles with uniform morphology and improved phase purity as proposed by Bang and his colleagues [9]. Sonication assisted nanoparticle preparation have been reported for ZnO, $ZnFe_2O_4$ and $LaFeO_3$ by Sivakumar et al. [10, 11, 12]. The physical effects of ultrasound such as shock waves and microjets produced from formation, growth and implosive collapse of bubbles have been utilized for emulsification and surface damage [13, 14]. The chemical effects of ultrasound resulted by sonolysis of water producing free radicals have been applied in various reactions as oxidants and reductants species [9].

There are some reports [15, 16, 17] giving information about the morphology evolved by varying the pH of the reaction mixture solution during zinc oxide synthesis. This has been

accomplished with different concentrations of NaOH, KOH, HCl and $Zn(NO_3)_2$ precursors, employing technique such as magnetic stirring, reflux and microwave. Swaroop and his colleagues have obtained hexagonal rod and plate like zinc oxide nanostructure at pH=7, 9 and at pH=10.5, 12.5, respectively at different concentrations of NaOH [15]. Wahab et al. [16] have reported a synthesis procedure with starting material zinc nitrate hexahydrate and hydroxyl amine hydrochloride. Evidence of disk shaped zinc oxide at solution pH 6, 7, 8 and 9 while microflower zinc oxide nanostructure at pH=10, 11 and 12 have been observed by Wahab and his coworkers. Nano zinc oxide rods have been synthesized with different aspect ratio by Sangari and Devi at pH= 9, 11 and 13, from zinc nitrate and potassium hydroxide [17].

Research articles addresses following details about evolved ZnO structures. Shi et al. [18] have achieved different nanosheets based hierarchical structures (HSs) by varying reactant concentration of NaOH and $Zn(NO_3)_2$ as 0.25:0.05,0.5:0.10,2.50:0.50 and 0.50:0.05. The produced HSs have appeared as spheres, cylinders, smoother and also sparsely arranged and some parallel nanosheets assembled on flat trunks. Mishra et al. [19] have proposed the synthesis of flower like ZnO nanostructure with the aid of starch and ultrasonication employing precursors such as zinc acetate and sodium hydroxide. This work suggested that agglomeration of ZnO nanostructures can be prevented by the use of starch. Vigneshwaran et al. [20] have synthesized ZnO with different concentrations of starch.

Previous review of the literature on nanostructure of the synthesized ZnO elucidates limitations viz. excessive reaction time, higher temperatures, lower yields and inadequate discussion about the variation in crystallite size, percentage crystallinity and band gap energy. Mechanism involved in the formation of different morphologies and energy calculation for the ZnO structures synthesized by sonochemical and conventional technique have not been sufficiently established in previous reports. In current study, different morphologies of ZnO

viz. plate, rod, and spherical shaped have been fabricated with starting materials NaOH and Zn $(NO_3)_2.6H_2O$ in the presence of starch as a capping agent in the ultrasonic field. The varying concentration of precursors with its mode of addition (reverse and inverse addition) was correlated with the final pH (acidic, neutral and basic) of the solution. Further a study on mixing time, yield (%), crystallite size, crystallinity (%) and band gap energy along with the mechanism involved in the formation of different morphologies has been examined for the ZnO structures synthesized by sonochemical technique.

A simple and rapid sonochemical method of ZnO synthesis has been compared with conventional magnetic stirring method. The work also gives the information of energy delivered during the conventional stirring and during calcination process.

2. Materials and methods

2.1 Materials

The following chemicals, zinc nitrate hexahydrate (98 % purity, Thomas Baker, Mumbai, India), sodium hydroxide (97% purity, S. D. Fine Chemicals Ltd., Mumbai, India, AR grade), potato soluble starch (99.4 % purity, S. D. Fine Chemicals Ltd., Mumbai, India,) and methanol (LR grade) were procured and used without further purification. Milli-Q water (0.22µm Millipore filtered) was used throughout the experiment.

2.2 Ultrasound set-up

Ultrasonic instrument (horn type) was used for synthesis of nano zinc oxide in sonochemical method. The specifications of the instrument are given below:

Make: Ace, USA.

- Diameter of stainless steel tip of horn: 1.3×10^{-2} m
- Calorimetric efficiency: 9 %

- Operating frequency: 22KHz
- Rated output power: 750W
- Surface area of ultrasound irradiating face: 1.32×10^{-4} m^2
- Expected ultrasound intensity: 2.27×10^6 W/m^2 at 40% power amplitude

2.3 Reaction scheme for ZnO synthesis

$$Zn(NO_3)_2.6H_2O + 2\,NaOH \longrightarrow Zn(OH)_2 + 2NaNO_3 + 6\,H_2O$$

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$

It is a two-step, instantaneous and co-precipitation type of reaction. In conventional techniques (magnetic stirring systems), the decomposition of zinc hydroxide to zinc oxide has been achieved by heating the obtained precipitate at 260 °C as suggested by Kumar et al. [21]. Zinc hydroxide to zinc oxide conversion occurs by the microthermal heating generated out of sonication energy (cavitational hot spots) which differentiates sonication from conventional technique [22].

2.4 Mixing time calculation experiment

Mixing time was determined to decide the rate of addition of one of the precursors (zinc nitrate hexahydrate acid) into the other precursor (sodium hydroxide base). This is a decolourisation method in which base solution was colored by phenolphthalein indicator and was subsequently decolorized by the addition of five percent excess of acid. The time from start of the addition of acid to the disappearance of pink color of last colored trace is considered and color change can be observed in captured video. This time corresponds to the 95% mixing time for the specific volume and agitation speed and is termed as θ_{95}. [23, 24].

Zinc nitrate hexahydrate precursor, five percent excess (9.366 g, 0.0314 mol) with 1.5 g starch, dissolved in 100 ml water was kept ready in a glass measuring cylinder which forms

acidic solution. Sodium hydroxide precursor (2.4 g, 0.06 mol) 100 ml, being basic in nature was colored pink with 2-3 drops of phenolphthalein indicator and was kept ready in 250ml beaker under magnetic stirring at 500 rpm. Acid solution (100 ml) was subsequently added to the base solution in beaker kept under magnetic stirring and mixing time was measured as described above. Mixing time θ_{95} was found to be 1-2 s for the total of 200 ml volume precursor solution and at 500 rpm of magnetic stirrer speed without sonication. Thus it can be concluded that the rate of addition of next precursor drop should be after every 1-2 s so that the previous drop gets thoroughly mixed and reacts completely. In correspondence to mixing time measured, we decided to keep the addition time of 100ml of zinc nitrate hexahydrate solution of 30 min in both sonication as well as conventional method of synthesis. The constant dropwise addition of 100ml zinc nitrate hexahydrate to sodium hydroxide solution was maintained by peristaltic pump and required 30min for complete addition of zinc nitrate hexahydrate solution to sodium hydroxide solution.

2.5 Synthesis of ZnO by sonochemical method

In a typical synthesis procedure, concentration of precursor zinc nitrate hexahydrate and sodium hydroxide were varied to tailor the morphology of ZnO. Table 1 gives the details of precursor concentration and mode of addition employed in various experiments and the samples are termed as Z1 to Z4.

Starch solution was prepared for ZnO synthesis and details of preparation of starch solution is given in supplementary information. Starch contains branched structured amylopectin and linear structured amylose. Both are held by hydrogen bonds. Amylose form complexes with Zn^{2+} as amylose has high number of co-ordinating functional groups [25]. Amylose has gluing property and has a tendency to form coil so it binds onto ZnO nuclei [19].

2.5.1 Experimental procedure for ZnO synthesis

Zinc nitrate hexahydrate precursor was weighed and dissolved in 100 ml cooled starch solution by magnetic stirrer at 500 rpm for 10 min to form clear zinc nitrate hexahydrate in starch solution. Sodium hydroxide precursor was weighed and dissolved separately in 100 ml Milli-Q water by magnetic stirrer at 500 rpm for 10 min and was kept ready. The sodium hydroxide solution was then added dropwise to zinc nitrate hexahydrate solution (containing starch) under sonication using an Ultrasonic Horn (ACE operating at a frequency of 22kHz) at 40% power amplitude from time t = 0 h (from start of addition) over 30 min with a 5s on pulse and 5s off cycle. Addition was done continuously without any pause. The zinc nitrate hexahydrate solution turns turbid as soon as sodium hydroxide solution was added. After complete addition of sodium hydroxide solution to zinc nitrate hexahydrate solution in the first 30 min, whole mixture (zinc nitrate hexahydrate+ starch+ sodium hydroxide) was again exposed to acoustic irradiation by the same ultrasonic horn for further 10 min (without altering sonication parameters, same as that used during addition) to ensure complete conversion of precursors into zinc oxide. The initial temperature of reactant solution was measured as 28°C which increased to 40°C (due to acoustic energy input) at the end of the reaction i.e. at 40 min [30min addition+10min of further sonication]. Z1, Z2 and Z3 samples were synthesized by the above procedure while for Z4 synthesis, addition was reversed i.e. zinc nitrate hexahydrate solution was added to sodium hydroxide solution keeping all the parameters same as described earlier during sonication, to explore the morphology of nano ZnO formed in basic environment. No external cooling has been provided during the addition or reaction. Precursor pH was recorded by pHep pocket sized pH Meter (Hanna instrument) at the start of the reaction. For the stoichiometric precursor concentrations, pH values are given below.

pH of only starch solution =6.0

pH of only zinc nitrate hexahydrate solution= 4.0

pH of (zinc nitrate hexahydrate + starch) solution =4.1

pH of only sodium hydroxide solution =12.8

The pH of the reaction mixture after the completion of reaction i.e. at 40 min time was measured in each experiment. The measured values of pH were 7.1, 9.2, 11.3 and 7 for Z1, Z2, Z3 and Z4 samples respectively. The pH changes from acidic to neutral, acidic to slightly basic, acidic to basic and basic to neutral in case of Z1, Z2, Z3 and Z4 samples respectively. It can be attributed to the change in concentration of zinc species which is discussed further in the section 4.4.

The resultant solution after sonication was centrifuged with Beckman Coulter Rotor RJ-20 being set at 10000 rpm (14896×g) rotation speed and for 20 min of operating time. The white precipitated product pellet formed at the bottom of the centrifuge tube was separated, reslurried in Milli-Q water by an ultrasonic horn for 5 min to completely remove soluble impurities and by product $NaNO_3$ before the next stage of centrifugation. Again the reslurried solution was centrifuged at 10,000 rpm for 20 min and the product pellet obtained was dispersed in small amount of methanol. When methanol gets evaporated, product was dried at 150°C for 12 h in oven and analyzed (yield, XRD). This was followed by calcination in furnace (Nabertherm Gmbh) conducted at 600°C, for 6 h of calcination time with ramping rate 5°C/min in order to achieve maximum crystalline product ZnO and to remove any residual starch. Alkaline degradation of starch can also eliminate starch from ZnO samples but samples were calcined in order to remove residual starch and to make them comparable for analysis with conventionally synthesized samples. The calcined product i.e. bare ZnO was checked for yield and then characterized by X-ray diffractometer, Field emission gun scanning electron microscopy and Ultraviolet-visible spectroscopy instruments.

Above described procedure depicts the samples Z1, Z2, Z3 and Z4 synthesized in first set of experiments. To know the effect of sonication on ZnO synthesis, second set of experiments were carried out in the absence of starch, by keeping all the experimental conditions same as in first set of experiment for Z2 sample. The obtained yield was nearly quantitative (100 %) based on stoichiometry. Z2 sample synthesized in the absence of starch was characterized by XRD instrument.

2.6 Synthesis of ZnO by conventional method

In the conventional method of synthesis, magnetic stirrer was employed substituting the ultrasonic horn for synthesizing ZnO. Sample NZ2, synthesized by conventional method involves the use of same concentrations of reactants as that were used for Z2 sample, synthesized in the first set of sonication experiments without employing starch.

In this method, zinc nitrate hexahydrate, 8.92 g (0.03 mol) was dissolved in 100 ml Milli-Q water and 2.4 g (0.06 mol) sodium hydroxide was dissolved in 100ml Milli-Q water separately and was kept ready. The sodium hydroxide solution (as before) was then added dropwise to the zinc nitrate hexahydrate solution under magnetic stirring. As this is an instantaneous reaction, reaction does not need any additional time beyond 40 min, for complete conversion. Also, mixing time explains the addition time required for adding the reactant sodium hydroxide into zinc nitrate hexahydrate solution to attain complete mixing of the reactants. The reaction was performed at the room temperature and the rest of the procedure (centrifugation, washing, drying and calcination) was same as described in the sonochemical method. NZ2 sample prepared by conventional technique was checked for yield before and after calcination. Uncalcined NZ2 sample was characterized by XRD to check the type of the product formed i.e. $Zn(OH)_2$ or ZnO or any other.

3. Characterization

The samples synthesized by sonochemical technique were checked for the yield obtained and characterized by X-ray diffractometer (XRD), Field emission gun-scanning electron microscopy (FEG-SEM) and Ultraviolet-visible (UV-vis) spectroscopy instruments. The samples synthesized by conventional technique were checked for the yield and characterized by XRD instrument. The samples synthesized by sonochemical and conventional technique were first characterized by XRD (Bruker D8 Advance, Germany) with Nickel filtered Cu-Kα radiation source of wavelength 1.54 Å and with step size 0.02^o per 0.2 s in 2θ scan range of 10^o to 80^o. A beam current of 40mA and voltage 40KV were used during XRD analysis. The surface morphology of the calcined ZnO samples synthesized by sonication assisted precipitation technique have been analyzed by using FEG-SEM (Mira 3 Tescan) and micrographs are shown in Fig. 2. Absorption spectra of the ZnO samples were recorded in the wavelength range of 200-600 nm by using Shimadzu UV 3600 UV-vis-NIR spectrometer (Shimadzu Corporation, Kyoto, Japan) at room temperature and are demonstrated in Fig. 6.

4. Results and discussion

4.1 Percentage yield of sonochemically and conventionally synthesized ZnO samples

Table 2 displays yield (%) of sonochemically (in the first and second set of experiments) and conventionally prepared calcined and uncalcined ZnO samples. The yield was computed by taking a ratio of actual weight of calcined ZnO (gm) to the stoichiometric expected product weight (gm).

The yield was checked before (100.02%) and after calcination (96.79 %) for the sample "Z2 without starch" shown in the Table 2 and the difference in the yield was found to be negligible. The negligible difference in yield was due to the removal of moisture from the sample. The yield obtained in the absence of starch for the sonochemically synthesized sample was found to be stoichiometric. Stoichiometric yield (92.3% excluding losses and

98.3% including losses) has been obtained for the calcined sample NZ2 synthesized by the conventional technique. So, the yield was observed to be stoichiometric only after calcination of the NZ2 sample synthesized by conventional technique. This may be ascribed to decomposition of the intermediate product like $Zn(OH)_2$ into ZnO by calcination. This concludes that conventional technique does not lead to a direct ZnO formation unless it is calcined. From this it can be inferred that we directly got ZnO, with sonication and without starch. This can be attributed to the fact that local temperatures generated during acoustic cavitation in sonication method converts all the reactants into the product ZnO without forming any intermediate products like $Zn(OH)_2$.

For Z1, Z2, Z3 and Z4 samples synthesized sonochemically in the presence of starch, yield obtained was more than 100% which can be attributed to the residual starch and moisture which gets eliminated only after calcination of the samples to form pure ZnO product. So, the yield measured after calcination of those samples was for pure ZnO and was not more than 100% (Table 2). Yield obtained for the uncalcined Z1 and Z2 sample (131.68% and 144.03% respectively) are more than the uncalcined Z3 and Z4 sample (111.52 % and 102.14% respectively). This may be because of induced solubilization of starch by progressive increase in the negative charge at alkaline pH [26]. This results into intermolecular repulsion of starch chains degrading the starch (possibly due to microthermal heating generated during sonication and resultant cavitation) and leading to higher uncalcined yield for Z1 and Z2 than Z3 and Z4 samples. The yield obtained for all the calcined samples synthesized in the first set of experiments by sonication method was observed to be around 98 % (Table 2) including losses (approximately 4% of 2.43g stoichiometric ZnO quantity i.e. 0.09g ZnO of losses were observed) and including around 3% precursor impurities (3% of 2.43g stoichiometric ZnO quantity i.e. 0.07g ZnO).

4.2 Crystallite size and crystallinity analysis using X-ray Diffraction data

X-ray diffraction patterns were determined to elucidate product identity and for investigating the % crystallinity, phase purity and crystallite size of the synthesized samples. All the diffractograms shown in Fig.1 (a) exhibit nine prominent peaks and are in good accordance with Joint Committee on Powder Diffraction Standards (JCPDS- 79-0208) card for bulk ZnO. As per the JCPDS data, sharp and intense peaks at 2θ values are 31.619°,34.335°, 36.10°, 47.367°, 56.313°, 62.646°, 66.033°,67.641° and 68.738° which corresponds to crystal planes (h k l) of (100), (002), (101), (102), (110), (103), (200), (112) and (201) respectively [27]. It can be noticed from the Fig. 1(a) that all the calcined samples synthesized by sonication technique have sharp and intense XRD peaks due to the removal of moisture, impurities as well as the residual starch. The 2θ values in Fig. 1(a) exactly matches with each other and with the JCPDS data. This confirms the formation of well crystalline, hexagonal, wurtzite ZnO product in sonochemical technique.

Fig. 1(b) reveals the XRD pattern of sonochemically synthesized, Z3 sample before calcination, Z3 after calcination and sample Z2 without starch after calcination. Their 2θ values matches with each other and with JCPDS data which confirms that sonochemical technique independently produces ZnO (ascribed to hot spots generation) without employing the calcination process. The obtained peaks appeared to be less prominent with reduced intensity for uncalcined sample Z3 than the peaks obtained in the case of same sample Z3 after calcination. This is because after calcination, sample Z3 crystals get consolidated due to the removal of any impurities to give sharp and intense peaks. Also, peak broadening in the case of uncalcined sample Z3 shown in the Fig.1 (b) for sample "Z3 before calcination" indicates the formation of small nanocrystals of size 11.82 nm present in it as against 34.85 nm size nanocrystals formed in the calcined sample Z3.

XRD pattern of uncalcined NZ2 sample in Fig. 1(b) indicates some additional peaks which does not match with the JCPDS data of ZnO. 2θ value of NZ2 sample does not match with

the 2θ values obtained for the samples synthesized by sonication method. XRD analysis of NZ2 sample indicates unknown intermediate product formation other than ZnO. The analysis clearly concludes that the conventional technique does not result into only ZnO production but have formed intermediates like zinc hydroxide nitrate hydrate. The reason could be, there exist no microthermal heating in the conventional method as in sonication method of synthesis which assist the direct ZnO production [22].

Debye-Scherrer formula has been used in literature for crystallite size estimation [28]. Formula is given as $D=K\lambda/\beta \cos\theta$

Where K is constant and is 0.91, λ is Cu Kα radiation wavelength used in XRD analysis and is 0.154 nm, β is full width at half maximum in radians and θ is the scattering angle in degree.

For crystallite size calculation, highly intense and sharp peak at $2\theta = 36.10°$ corresponding to the (101) lattice plane of hexagonal wurtzite ZnO phase was employed. Z1 and Z2 were prepared under near neutral and slight basic environment respectively while Z3 and Z4 were formed in basic environment and so were compared with their XRD data. Crystallite size of Z2 (24.81 nm) is larger than Z1 (16.24 nm) which can be ascribed to more alkalinity in Z2 giving rise to some $[Zn(OH)_4]^{-2}$ units formation along with more concentration of $Zn(OH)_2$ species formed during synthesis of Z2 sample. Higher concentration of $Zn(OH)_2$ species are responsible for smaller crystallite size as described in section 4.4 for the sample Z1.The crystallite size of Z3 is greater than Z4. It may be attributed to the higher alkali concentration, producing $[Zn(OH)_4]^{-2}$ units, accounting for crystal growth in Z3 sample and excess OH^- concentration (exceeding saturation limit) existing in Z4 sample preventing the growth rate of rod in axial direction to form smaller crystals as explained in section 4.3.

The % crystallinity was computed by taking a ratio of integral area of the peak (area under the peak without baseline correction) to the total area of the peak (area under the peak with

baseline correction). The integral area and total area values are obtained from the software present with Rigaku Mini Flex X-ray diffractometer instrument. The % crystallinity was found to be consistent with the crystallite size for all the ZnO samples displayed in Table 3. From the Table 3 it can be inferred that the crystallite size of zinc oxide reduces with % crystallinity which is in accordance with the observations reported in our previous work, for the synthesized nano calcium carbonate [29]. XRD results of all the calcined samples prepared by the sonication method are comparable with FEG-SEM images obtained in section 4.3.

4.3 Investigation of ZnO morphology by Field emission gun-scanning electron microscopy (FEG-SEM)

All the FEG-SEM micrographs reveals different morphology of ZnO solids obtained, depending upon the different pH conditions during their synthesis process. It can be inferred from FEG-SEM images (Fig. 2a-d) that the reactant concentration and the method of addition plays a vital role in tailoring the morphology of ZnO. Lesser agglomeration is observed in all FEG-SEM images of ZnO samples which may be attributed to loss of active surface charge due to shockwaves generated by acoustic cavitation. The Z1 (Fig. 2a) and Z2 (Fig. 2b) attained plate (three dimensional) like structures. These morphologies could be credited to large $Zn(OH)_2$ species compared to $[Zn(OH)_4]^{-2}$ units formed during ZnO synthesis. These $Zn(OH)_2$ species, constrained growth in the axial direction which result into plate like morphologies.

The Z3 (Fig. 2c) and Z4 (Fig. 2d) sample indicates that the basic pH conditions of the solutions affect the length (L) and diameter (D) of nano ZnO rod (Z3 sample: Average L=181.25 nm and Average D= 72.5 nm, Z4 sample: Average L=102.95 nm and Average D= 89.64 nm) without significantly changing their morphology which is elaborated further. Z3

sample (Fig. 2c) shows rod shaped (two dimensional) morphology. It can be ascribed to large number of $[Zn(OH)_4]^{-2}$ units compared to $Zn(OH)_2$ species, formed during the synthesis which allow the growth of ZnO in the axial direction (Fig. 3) resulting into rod shaped morphology.

Z4 sample (Fig. 2d) demonstrates short rod shaped morphology. In Z4, zinc nitrate hexahydrate precursor was added to sodium hydroxide precursor i.e. reverse addition was carried out under sonication so ZnO structure formed were in highly basic environment where OH^- i.e. $[Zn(OH)_4]^{-2}$ concentration exceeds a saturation limit thereby preventing the growth of rod to give more or less spherical shaped (zero dimensional) ZnO nanostructure. Even crystallite size determined from XRD data for Z3 and Z4 sample are in good agreement with FEG-SEM images. Crystallite size for Z4 sample is lower (17.55 nm) than crystallite size of Z3 sample (34.85 nm).

4.4 Possible growth mechanism involved in ZnO synthesis

At low and medium concentration of the alkali, sodium hydroxide, it was considered that both $Zn(OH)_2$ and $[Zn(OH)_4]^{-2}$ species are present in the solution as shown in Fig. 4. For sample Z1 and Z2, where concentration of alkali was low and average respectively, plate like structures were obtained as seen in FEG-SEM analysis. The formation of large number of plate like morphologies and very little growth in the axial direction of ZnO indicates a large number of spurious nuclei formation of $Zn(OH)_2$ and comparatively minor constituents of $[Zn(OH)_4]^{-2}$ growth units responsible for the growth of ZnO along the axial direction [30] as demonstrated in Fig. 4.

At higher concentration of alkali as in Z3, it was assumed that a large number of $[Zn(OH)_4]^{-2}$ units are formed which act as growing nuclei for the rod like structure formation of ZnO. Rod like feature was exhibited in FEG-SEM analysis for Z3 sample as the nuclei growth is along

c-axis i.e. along lattice plane (0001) direction and growth is much faster than the other faces. The faster growth rate makes evident the rapid production of $[Zn(OH)_4]^{-2}$ units in Z3 sample synthesis as observed in Fig. 4. Reichle et al. [31] experimented and found the fraction of zinc species existing in zinc hydroxide solution over a range of pH at 25°C (Fig.5.) and our possible mechanism can be correlated with it.

When OH^- concentration of $[Zn(OH)_4]^{-2}$ units exceeds a saturation limit (Fig. 4), growth units are protected by the excess OH^- ions before they are integrated into crystal unit and hence growth rate of rod is highly inhibited to give more or less spherical structured morphology in Z4 sample.

The role of acoustic cavitation in the mechanism described can be speculated as follows. ZnO nanostructures with uniform size and shape were directly obtained in sonochemical method of synthesis requiring no calcination step. Possible justification and the significance of sonication technique can be linked to similar findings reported in the previous studies. As described by Sanoop and his co-workers, sonication method converts zinc hydroxide to zinc oxide by the microthermal heating generated out of sonication energy whereas in the conventional technique, conversion to ZnO requires 500°C of calcination temperature [22]. It has been suggested by Shi and his colleagues earlier, that tremendous energy and high-speed microjet generated in sonication, accelerates the nucleation process. Also, as stated, local homogenous nucleation and growth was found to be effective to form uniform and pure nanocrystals in sonication method as compared to the traditional method of synthesis [18].

4.5 Ultraviolet-Visible spectroscopy (UV-vis spectroscopy)

Fig. 6 shows UV-vis absorption spectra of calcined ZnO samples prepared by sonication technique. The sonochemically synthesized ZnO samples were heated to 600°C to get pure

ZnO (does not contain any starch and moisture) and pure ZnO samples were analysed by UV-vis spectrometer. 0.1 g ZnO was added to 5 ml deionized water and sonicated for 1 min before UV-vis measurement.

Fig. 6 exhibits that all the samples calcined at 600°C gave a maximum absorption at around 385 nm which is the characteristic band absorption of hexagonal wurtzite crystalline structure of nano ZnO as previously reported [32]. Hence, they are likely to have optical properties. These results are in good agreement with the previous reports where the ZnO sample heated at 600°C was observed to have strong absorption at 384 nm. The effect of annealing temperature on ZnO structures has been studied by Pudukudy et al. [32]. They have observed change in ZnO nanostructures from quasi spherical to capsules with an increase in the annealing temperature.

The band gap energy results are in accordance with a study reported earlier which gave a clear evidence of decrease in band gap energy attributed to large particle size and increased crystallinity of ZnO [32].

Band gap energy (E_g) can be determined by formula, $E_g = 1240/\lambda$

where E_g = Band energy in eV, λ= wavelength in nanometer

Band gap energy of sonochemically prepared calcined ZnO samples were determined with the Band gap energy formula and are illustrated in Table 4.

4.6 Energy efficiency

A sample example reported in Appendix A shows energy calculations. The energy required for ZnO synthesis during sonication and during calcination was calculated separately and compared. In a synthesis of ZnO by sonication method, it is already explained that 20 min irradiation time gave nearly 100 % yield and XRD has confirmed the ZnO formation. Net energy utilized in sonication method at 40 % power amplitude for 20 min irradiation time by 750-watt horn having horn efficiency 9% was calculated as 13613.44 J/g of product. Overall

energy supplied for processing of material using sonochemical method was found to be 151260. 50 J/g as calculated in appendix A.1. We performed an experiment to check the yield, with 10 times larger quantity than that used in Z3, in sonochemical method of ZnO synthesis (rest all other parameters were same) with 1s on pulse and 1s off cycle. Yield obtained was quantitative and so the overall energy was reduced to 15000 J/g. Further, when tried to check the yield in the experiments with more than 10 times reactant quantity and larger reaction volume, stoichiometric yield could not be obtained. To know the cause of nonstoichiometric yield, atomic absorption spectroscopy of procured zinc nitrate hexahydrate was performed. Zinc composition in zinc nitrate hexahydrate will not change. So, on the basis of this, 1 and 0.1 ppm zinc nitrate hexahydrate sample were prepared to validate the zinc composition in zinc nitrate hexahydrate compound which will thereby validate the hexahydrate form of the compound. The absorbance obtained in the Atomic absorption spectroscopy (Table 5) has matched the standard samples of zinc so it made evident that the zinc nitrate hexahydrate was in the hexahydrate form.

Large reactant quantity (here more than 10 times the reactant quantity) requires larger reaction volume to reduce the viscosity of the reaction solution in the experiment. Higher reaction volume lowers the cavitational intensity (power dissipation per unit volume decreases) and active cavitational volume is restricted to small area around the horn [33]. But it is possible to get quantitative yield by using larger tip diameter of the horn (2.1 cm, Dakshin horn) while processing more than 10 times the reactant quantity.

Power consumption refers to the electrical energy over time supplied to operate an electrical furnace. “Info” menu present with the furnace (Nabertherm Gmbh) demonstrates all the details of active/last program run, including the power consumption value. Power consumption was found to be 11.7 KWh delivered by 6300cc capacity furnace during calcination of conventionally synthesized NZ2 sample having density 0.64g/cc, for the

furnace being operated at 600°C for 6h with 5°C/min ramping rate. KWh is a measure of energy and KW is a measure of power and 1KWh energy expenditure represents 3.6×10^6 J. Energy required for stirring to form 4032 g NZ2 sample and energy required for its calcination was evaluated as 4200.24 and 9399.80 J/g of product respectively, given in Appendix A.2. It can be inferred from section A.1 and A.2, excess energy consumed in sonication method was 9.33%.

Conclusions

From the systematic studies of ZnO synthesis on pH variation in a simple sonochemical method, it was found that morphology of ZnO depends on the pH of the reaction mixture. The morphology was tuned by changing concentration of reactants and the method of addition of one precursor solution to the other. Sonication has resulted into uniform structures of ZnO as demonstrated. A variation from plate like to rod like morphology was observed when pH value of the reaction mixture (measured at the end of the reaction) varied from acidic to basic, during zinc oxide synthesis. Reverse addition of precursor solution resulted into more or less spherical shaped morphology of zinc oxide. Mixing time was evaluated to decide the rate of addition of zinc nitrate hexahydrate solution into sodium hydroxide solution and was found to be 30 min. The yield was around 98% for all the sonochemically synthesized calcined ZnO samples. The probable mechanism was described schematically for the different ZnO morphologies obtained by FEG-SEM analysis based on the concentration of zinc species present during ZnO synthesis. Variation in the crystallite size, % crystallinity and band gap energy of calcined ZnO samples was illustrated by XRD data and UV-vis absorption spectra respectively, in sonochemical synthesis method. It was evidenced from XRD data that conventional technique yield (for NZ2 sample) intermediates like zinc hydroxide [$Zn(OH)_2$] and zinc hydroxide nitrate hydrate [$Zn_5(OH)_8(NO_3).2(H_2O)$] and forms ZnO product only after calcination of these intermediates while sonochemical method forms

direct ZnO product. Quantitative energy calculation shows marginal energy consumption difference between sonication and conventional method of synthesis to obtain zinc oxide.

Acknowledgement

Financial support from University Grants Commission (UGC), India is gratefully acknowledged.

Appendix A. Energy calculations

A.1 Energy delivered during sonication method

- Energy required to synthesize ZnO material= Energy delivered by ultrasonic horn during sonication
- Efficiency of ultrasonic horn used for ZnO synthesis = 9% (calculated independently using calorimetric method)
- Net energy used by 750-watt capacity ultrasonic horn at 40 % power amplitude for 20 min pulse on time with 9% horn efficiency= 750 × 0.4× 0.09× 20× 60

  = 32400 J
- Net energy used (J/g of product) = 32400/2.38 (for 98% yield)

  =13613.44J/g

Overall energy estimation

- Energy delivered during sonication using 750-watt capacity horn for 20 min at 40 % power amplitude = 750 × 0.4 × 20× 60

  = 360000 J
- Overall energy supplied for processing of material using sonochemical method = Energy delivered by the horn using sonication/Quantity of the material obtained

  = 360000 J/2.38g (for 98% yield)

  = 151260. 50 J/g

- For 10 times larger quantity, Overall energy supplied = 360000J/24g =15000J/g

A.2 Energy delivered during calcination

- Power consumption during calcination of conventionally prepared NZ2 sample as displayed by the furnace (Nabertherm Gmbh), being operated at 600°C for 6h with 5°C/min ramping rate = 11.7 KWh = $11.7\times 3.6 \times 10^6$ J=4.212×10^7 J
- Power consumption for 90% efficiency furnace= $11.7 \text{ KWh} \times 0.9 = 3.79 \times 10^7$ J
- Net energy used (J/g of product) = 3.79×10^7 J/ 4032 g (for NZ2 sample having 0.64g/cc density and for 6300cc furnace volume accommodating 4032 g NZ2 sample)

$$= 9399.80 \text{ J/g}$$

- **Stirring energy required to form 4032 g NZ2 sample**

Stirring energy required to form 4032 g NZ2 sample is calculated from power number below.

Assuming Power number (P_o) required for 4 blade (45^o) pitched type impeller of w/d i.e. 3/13.5 = 0.22 as 1.94

Applied power (P) =$P_o \times \rho \times N^3 \times D^5$

where ρ=density of fluid in kg/m^3

N=Rotational speed in rev/s

D=Diameter of impeller in meters

P =$1.94 \times 1380 \times (500/60)^3 \times 0.135^5$ = 69.47 watt

Consider 24 g NaOH dissolved in 100ml D.I water and 89.2 g zinc nitrate hexahydrate dissolved in 50 ml D.I water as per done in sonochemical synthesis method for 10 times reactant quantities. So for 4032 g zinc hydroxide preparation, it requires 3244 g NaOH to be

dissolved in 13.51 L D.I water and 12062.40 g zinc nitrate hexahydrate to be dissolved in 6.761 L D.I water. So total reactor capacity should be 27.97 L. As 24 g NaOH dissolved in 100ml water requires 30 min addition time, 13.51 L NaOH solution will require 4053 min addition time with further stirring time of 10 min. These reactant quantities can be processed by keeping diameter of the reactor (T) equal to height of reaction mixture (H) in the reactor. Therefore, height and diameter of the reactor should be equal to 40.5 cm. Diameter of the pitched blade stirrer (D), width of the baffle (W) and height of stirrer from the bottom of the reactor should be T/3, T/12 and T/3 respectively [34].

- So energy required for stirring 4032 g NZ2 sample = 69.47 watt × (4063×60) s

  $= 1.69\times10^{7}$ Joules

- Stirring energy required to form 4032 g NZ2 sample= 1.69×10^{7} J/4032 g

  = 4200.24 J/g

- Overall energy required for stirring and calcination of 4032 g NZ2 sample= 9399.80 + 4200.24 = 13600.047 J/g

A.3 Excess energy consumed in sonication method from section A.1 and A.2 = 9.33%

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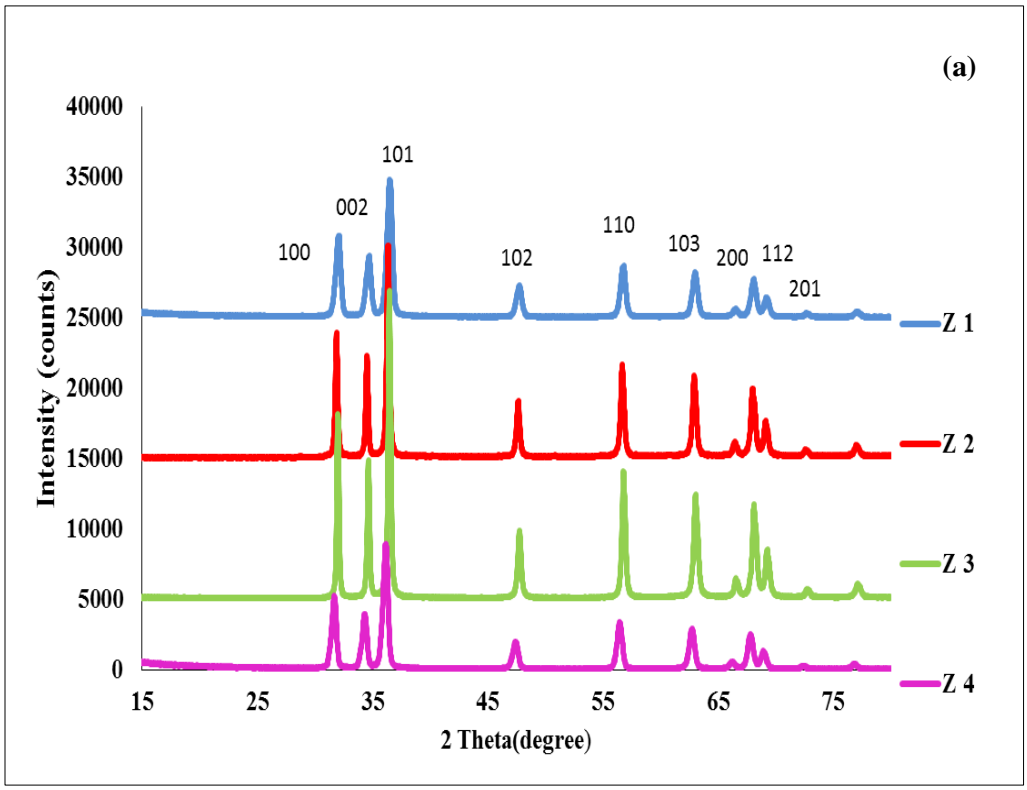


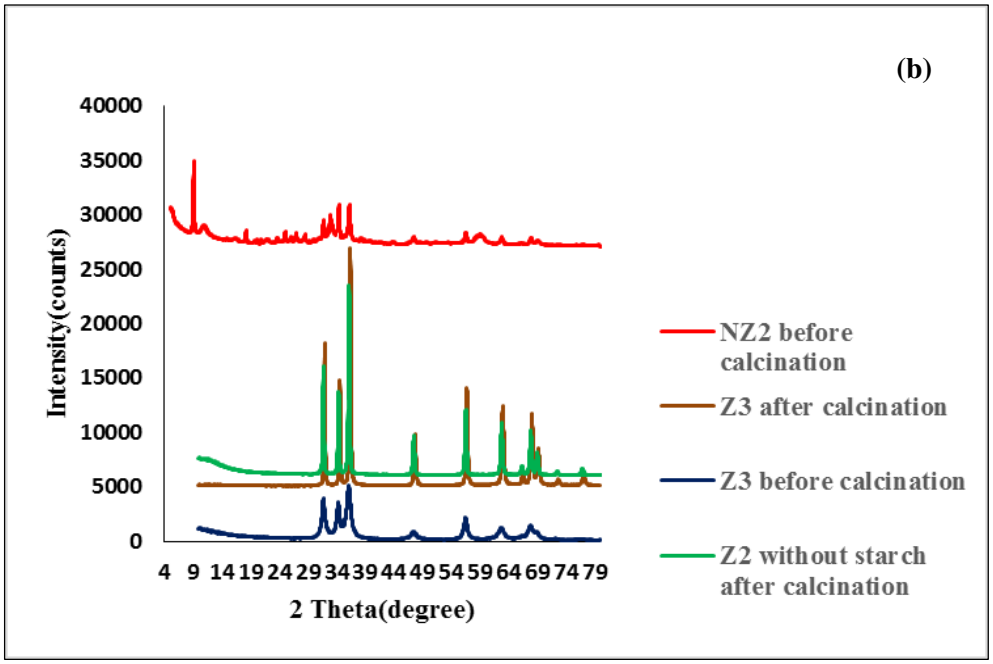
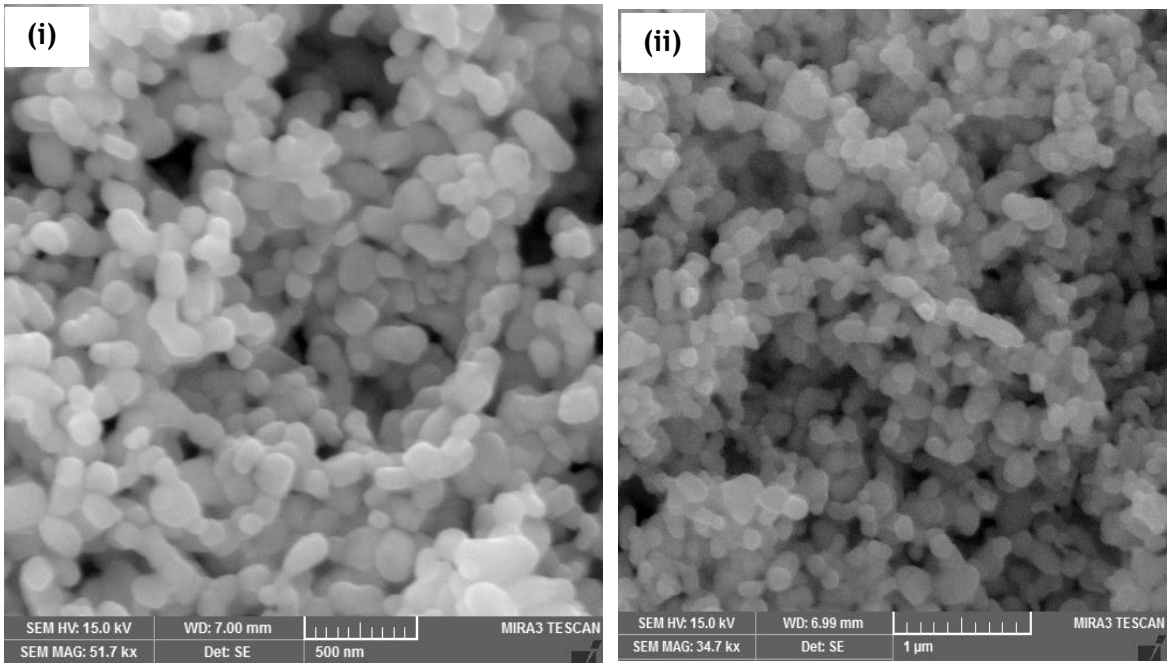
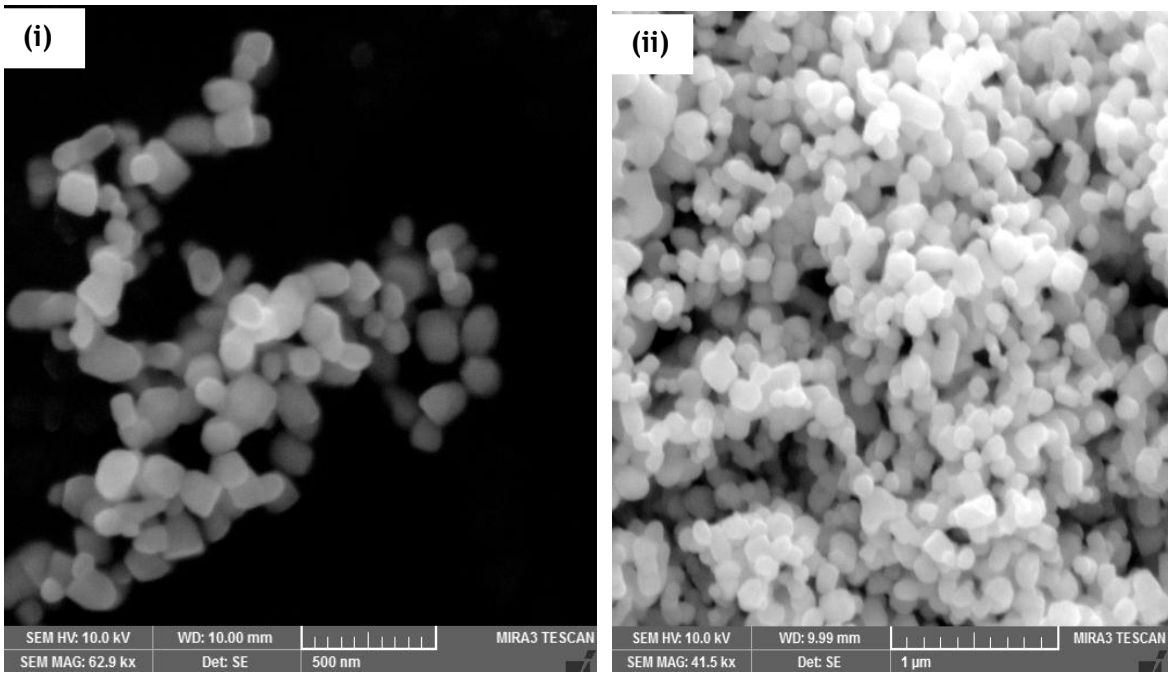


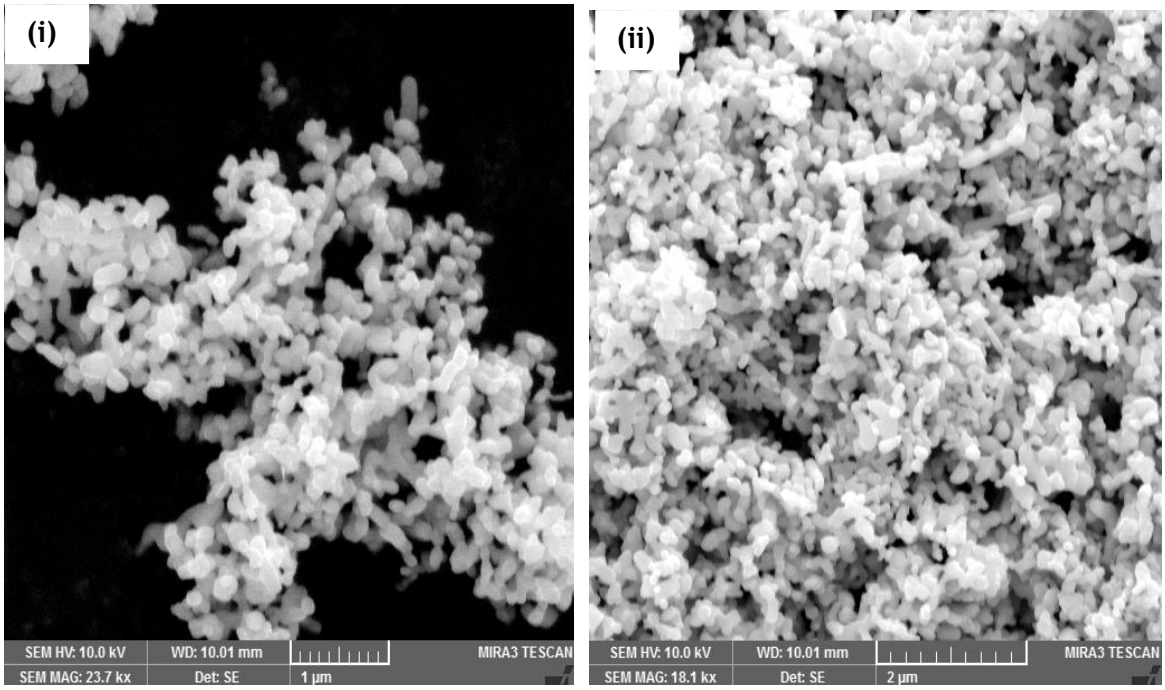
Fig. 1. X-ray Diffraction pattern of **(a)** Calcined ZnO samples synthesized by sonochemical method and **(b)** Comparison of the samples synthesized by conventional and sonochemical method



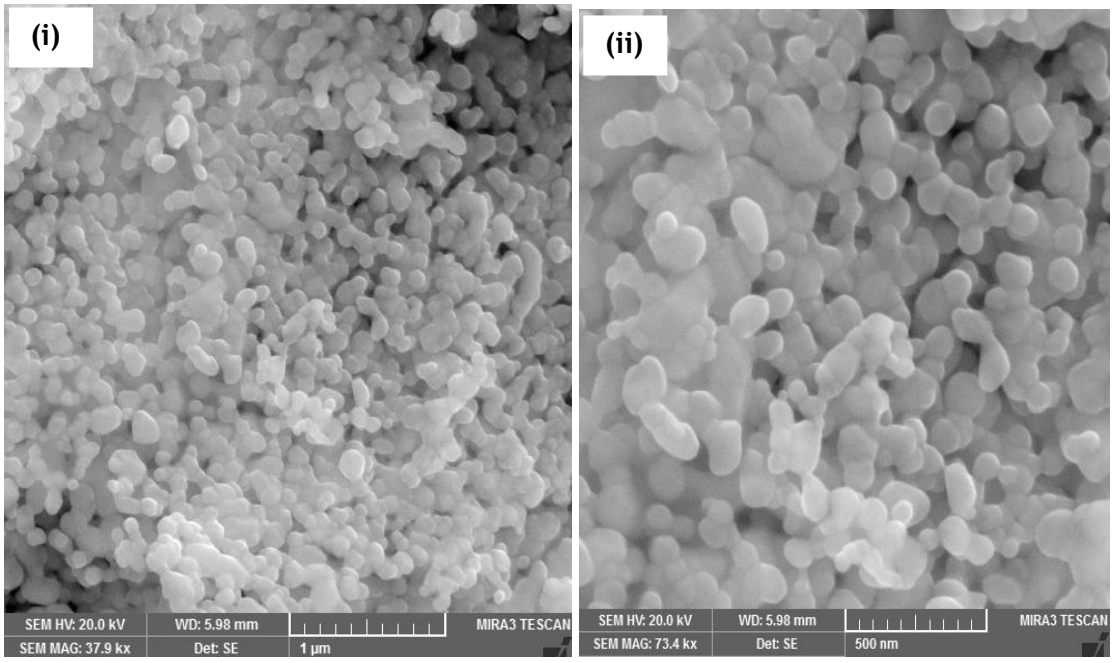
a) Z1 sample



b) Z2 sample



c) Z3 sample



d) Z4 sample

Fig. 2. Field emission gun-scanning electron microscopy (FEG-SEM) of sonochemically synthesized calcined ZnO samples (a) Z1 (b) Z2 (c) Z3 (d) Z4

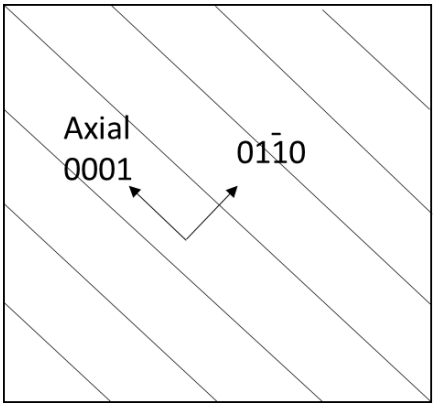


Fig. 3. Axial direction growth

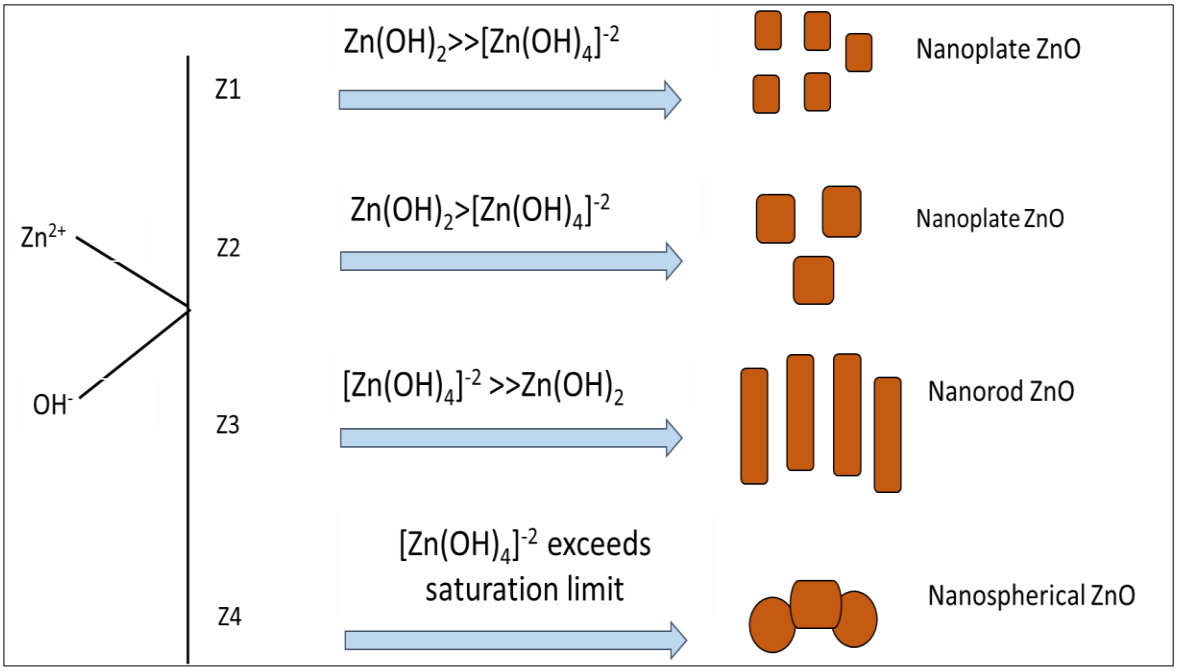


Fig. 4. Possible growth mechanism involved in ZnO synthesis

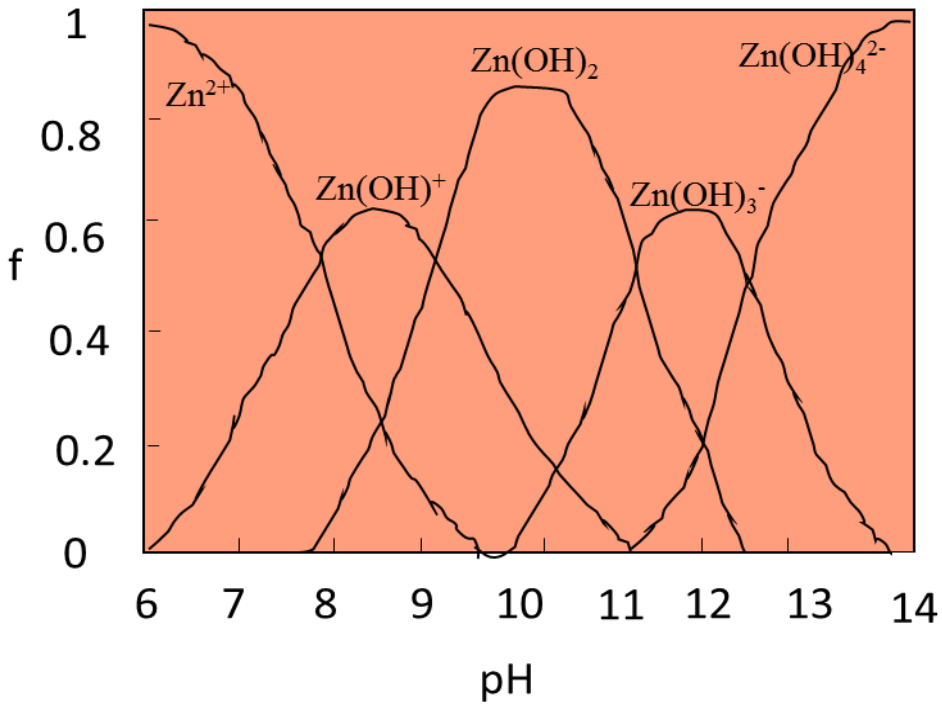


Fig. 5. Fraction of zinc species existing over a range of pH at 25°C [31]

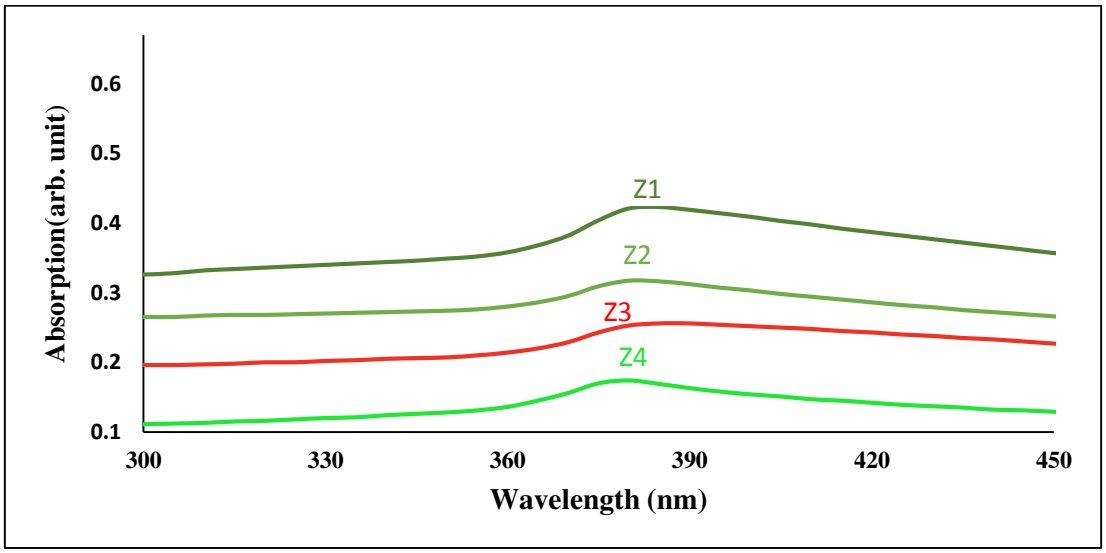


Fig. 6. UV-vis absorption spectra of sonochemically synthesized calcined ZnO samples

Table 1

Details of precursor concentration and mode of addition employed in sonochemical synthesis method

Sr. No.	Details (in terms of the stoichiometric ratio)	Zinc nitrate hexahydrate concentration	Sodium hydroxide concentration	Addition	Sample name
1.	15% excess zinc nitrate hexahydrate, stoichiometric sodium hydroxide	10.258g (0.34M)	2.4 g (0.6M)	Inverse addition i.e. Sodium hydroxide precursor solution was added to zinc nitrate hexahydrate precursor solution	Z1
2.	Both precursors in stoichiometric amount	8.92g (0.30M)	2.4 g (0.6M)	Inverse addition i.e. Sodium hydroxide precursor solution was added to zinc nitrate hexahydrate precursor solution	Z2
3.	Stoichiometric zinc nitrate hexahydrate,12.5 % excess sodium hydroxide	8.92g (0.30M)	2.7 g (0.67M)	Inverse addition i.e. Sodium hydroxide precursor solution was added to zinc nitrate hexahydrate precursor solution	Z3
4.	Both precursors in stoichiometric amount	8.92g (0.30M)	2.4 g (0.6M)	Reverse addition i.e. Zinc nitrate hexahydrate precursor solution was added to sodium hydroxide precursor solution	Z4

Table 2

Percentage yield of sonochemically and conventionally synthesized ZnO samples

Sr. No.	Sample name	Reaction time (min)	Yield (%) calculated before calcination	Yield (%) calculated after calcination at 600°C	
				excluding 4% losses and 3% precursor impurities	including 4% losses and 3% precursor impurities
1	Z1	40	131.68	89.65	96.65
2	Z2	40	144.03	91.76	97.76
3	Z3	40	111.52	92.79	98.79
5	Z2 without starch	40	100.02	89.79	96.79
6	NZ2	40	118.60	92.3	98.3

Table 3

Crystallite size and % crystallinity of calcined ZnO samples synthesized by sonochemical method

Sr. No.	Sample name	2θ value (degree)	FWHM value (in radian)	Crystallite size(nm)	% crystallinity
1	Z1	36.479	0.515	16.24	33.63
2	Z2	36.340	0.337	24.81	53.822
3	Z3	36.453	0.24	34.85	75.68
4	Z4	36.125	0.476	17.55	30.27

Table 4

Band gap energy of sonochemically synthesized calcined ZnO samples

Sr. No.	Sample name	Band gap energy (E_g in eV)
1.	Z1	3.26
2.	Z2	3.22
3.	Z3	3.17
4.	Z4	3.24

Table 5

Absorbance measurements of zinc present in zinc nitrate hexahydrate analyzed by Atomic absorption spectroscopy

Sample name	Concentration(ppm)	Absorbance
Standard 1	0.5	0.121
Standard 2	1.0	0.221
Standard 3	1.5	0.348
Sample 1	0.832	0.194
Sample 2	0.217	0.052