

Ultrasound assisted green synthesis of zinc oxide nanorods at room temperature

D V Pinjari^{1,*}, A B Pandit¹ & S T Mhaske²

¹Chemical Engineering Division, Institute of Chemical Technology, Matunga,
Mumbai 400 019, India

²Polymer and Surface Engineering Division, Institute of Chemical Technology, Matunga, Mumbai 400 019 India
E-mail: dv.pinjari@ictmumbai.edu.in

Received 12 May 2014; accepted 4 June 2014

Nanostructured ZnO (without stabilizers) has been synthesized using conventional (non-ultrasound i.e. NUS) as well as sonochemically assisted (US) synthesis method. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide (NaOH) have been used as raw materials (synthesis precursors). Zinc nitrate hexahydrate reacts with sodium hydroxide at room temperature ($35 \pm 2^\circ\text{C}$) to form ZnO powder. It is found that equilibrium conversion occurred in a shorter time in sonochemically (US) assisted method when compared to conventional (NUS) method. The ZnO powders synthesized by both the methods have shown to have nanometric-sized crystallites. It was found that the crystallite size of the sonochemically (US) synthesized ZnO and conventionally (NUS) synthesized ZnO are 23 ± 1 nm and 32 ± 1 nm respectively. The FTIR spectra analysis confirms the occurrence of the reaction to form Zinc Oxide by both NUS and US methods. Needle shaped structures agglomerated in the forms of bundles were also found in SEM micrographs. It was found that sonochemical synthesis method have saved more than 90% of energy utilized by conventional synthesis method along with the reduced in the reaction duration by 110 minutes.

Keywords: Inorganic compounds (ZnO), Nanostructures, Chemical synthesis (acoustic and conventional method), X-ray diffraction (XRD), Thermogravimetric analysis (TGA)

The development of new functional materials on the geometric length scale of approximately 1-100 nm has become the focus of the recent investigations due to the progress in all the areas of nano-material research in industry and development and scale of nanotechnology¹. These nanomaterials have unique properties and their functions and properties, are substantially different from those of bulk materials mainly due to their small size and large surface area per unit mass^{2,3}. Parameters such as size, size distribution and morphology are known to significantly alter the electrical, optical and magnetic properties, which determine the practical and industrial applications of the nanomaterials⁴.

Zinc oxide (ZnO), an inorganic compound, is widely used for a variety of applications because of its unique photo catalytic, electrical, electronic, optical, dermatological, and antibacterial properties⁵⁻¹¹. For these applications, the ZnO nano-particles need to be dispersed homogeneously in different matrices. Number of new synthetic strategies^{12,13} have been developed and deployed in order to prevent particles agglomeration, and increase the stability of ZnO nano-particles dispersions depending on its final

applications. There are several researchers worldwide had worked on the synthesis of ZnO using precipitation methods¹⁴⁻¹⁷. Zinc nitrate/zinc chlorides have been used as a precursor while other reacting materials have been varied from ammonium carbonate, ammonium hydroxide, sodium oleate etc. Davood (2013) has also reported the effect of various calcination temperatures on the photoluminance of the synthesized ZnO nanoparticles.

The sonochemically assisted synthesis method has been proved to be a useful technique to obtain novel materials¹⁸. The chemical effects of ultrasonic irradiation arise from the phenomenon acoustic cavitation, namely, the formation, growth and implosive collapse of bubbles in a liquid medium, resulting into a spontaneous reaction of short time high temperature and pressure pulse¹⁹. These special conditions of high temperature, pressure coupled with local intense micromixing facilitated by acoustic cavitation lead to many unique properties in the irradiated solution and particle precipitated from the same²⁰.

In this paper, nanostructured ZnO was synthesized using conventional (NUS) method (described later)

and sonochemically (US) assisted synthesis method. The effect of ultrasound on ZnO particles such as % crystallinity, crystallite size and morphology has been studied to understand the role of ultrasound (ultrasonic energy) in the synthesis process of ZnO nanoparticles.

Experimental Section

Materials

Zinc nitrate hexahydrate (GR) was purchased from Lobachemie India Pvt. Ltd. Mumbai, India. Sodium hydroxide (AR) in the dry pellet/flakes form was obtained from S. D. Fine Chemicals Ltd, Mumbai, India.

Ultrasound Set-up

Ultrasound for sonochemically synthesis of ZnO was generated with the help of ultrasonic instrument set up (horn type). The Animated representation of the set up is given in Fig. 1. The specification and details of the experimental set up, processing parameters used during the experiments are: Make: Ace, USA; Operating frequency: 22 kHz; Rated output power: 750 W; Diameter of stainless steel tip of horn: 1.3×10^{-2} m; Surface area of ultrasound irradiating face: 1.32×10^{-4} m²; Expected ultrasound intensity: 3.4×10^5 W/m².

Synthesis of ZnO by conventional method (NUS)

Zinc nitrate hexahydrate, 3.72 g (0.1 mol) was dissolved in 125 mL of distilled water and 1 g, (0.2 mol) Sodium hydroxide was dissolved in 125 mL distilled water separately and kept ready. Sodium hydroxide solution was added drop wise in the zinc nitrate hexahydrate solution under constant stirring

using an overhead stirrer (Remi-India make, propeller type impeller, rotating at 500 rpm). The addition time of sodium hydroxide solution into zinc nitrate hexahydrate solution was 2 min. The aqueous clear solutions turned milky white colloidal suspension on addition of sodium hydroxide solution without any visible particulate precipitation. The reaction was allowed to proceed for further 2 h after the complete addition of sodium hydroxide under constant stirring at room temperature ($35 \pm 2^\circ\text{C}$). The temperature of the process was maintained at $35 \pm 2^\circ\text{C}$ by means of supplying water to jacketed reactor, used for synthesis. The solution was centrifuged at 12000X g for 10 min to separate the product and the settled and pelleted product was washed thrice using distilled water (50 mL each time) to remove the byproducts and unreacted reactants. In the washing process, particles of ZnO get suspended so it was again centrifuged using same parameter (at 12000X g for 10 min) mentioned above. After complete washing, the product was dried at 80°C for 3 h for complete conversion of $\text{Zn}(\text{OH})_2$ to ZnO ²¹. After the complete drying and dehydration to ZnO, the powder obtained was (milky white in nature), cooled, grounded by mortar, checked for yield and was characterized using XRD, FTIR and SEM. The synthesis of ZnO material by conventional method (NUS) was replicated thrice and the results reported here are computed by averaging the individual results with error bar (\pm variation) for yield%, crystallinity% and crystallite size.

Synthesis of ZnO by sonochemical method (US)

Zinc nitrate hexahydrate, 3.72 g (0.1 mol) was dissolved in 125 mL of distilled water and 1 g, (0.2 mol) Sodium hydroxide was dissolved in 125 mL distilled water separately and kept ready. Sodium hydroxide solution was added drop wise in the zinc nitrate hexahydrate solution under sonication using an Ultrasonic Horn (ACE 22 KHz) at 40% amplitude for 2 min with a 5 sec ON and 5 sec OFF cycle from time $t = 0$ hour. After addition, the solution was again exposed to acoustic cavitation (by using ultrasonic horn) for further 8 min to complete the reaction of Zinc nitrate hexahydrate and Sodium hydroxide to $\text{Zn}(\text{OH})_2$ formation. The temperature of the process was maintained at $35 \pm 2^\circ\text{C}$ by means of supplying water to jacketed reactor, used for synthesis. The rest of the procedure was same as described before in synthesis of ZnO by conventional method (NUS).

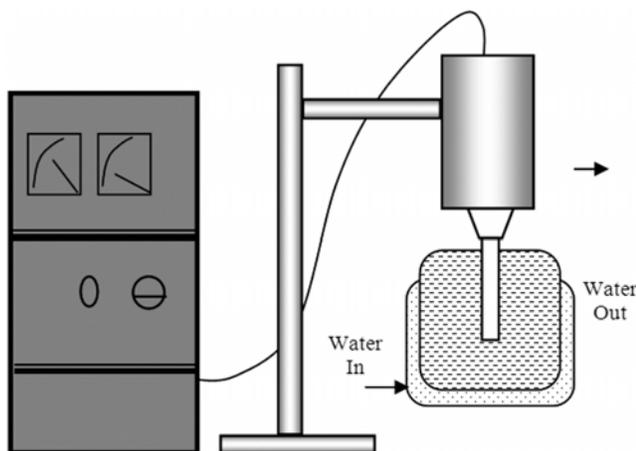


Fig. 1 — Ultrasonic Equipment (animated)

Characterization

The dried ZnO samples (powder form) were first characterized by studying their X-Ray diffraction patterns on a Rigaku Mini-Flex X-Ray diffractometer. XRD patterns were recorded at angles between 2° and 80°, with a scan rate of 2°/min. Particle sizes were determined using the Debye-Scherrer equation. Fourier Transform Infra Red Spectroscopy (FTIR) spectra of the ZnO samples were recorded on IRPrestige-21®. Sample was prepared by diluting ZnO into potassium bromide (KBr) in the ratio of 1:100.

Thermogravimetric analysis (TGA) studies were performed using thermal analyser (TA Instruments, USA). The sample was heated in nitrogen atmosphere in alumina crucible at the rate of 20 K/min. Sample preparation for Scanning Electron Microscopy (SEM) includes the deposition of platinum on ZnO powder. Scanning Electron Microscopy of the samples was carried out on a JOEL JSM 680LA 15 KV SEM to estimate the surface characteristics of the sample. Together, the XRD and SEM methods are expected to provide exact knowledge regarding the particle size and crystalline characteristics of the synthesized ZnO.

Results and Discussion

Yield and reaction time

The reaction time for the conventionally synthesized ZnO was 2 h while reaction time used for sonochemically synthesized ZnO was 10 min. The percentage yield of the reaction was estimated on the basis of initial weight of the raw materials taken and final weight of product obtained after the complete drying (compared to the stoichiometric expected quantity). During the washing of synthesized ZnO material, unreacted raw materials present in the reaction and byproduct formed was separated. It was observed that yield of the reaction in the case of sonochemically (US) synthesized ZnO (73.22 ± 1.92 %) was higher than in the case of conventionally (NUS) synthesized ZnO (48.13 ± 2.68 %). The impact of acoustic cavitation was evident in not only in the increased yields (yield is increased by 35% with a

saving 110 min) but also the reduction in average particle size (Table 1). This is due to the rapid micromixing and resulting faster reaction (also possibly due to the formation of hot spots) to form nano ZnO.

Crystallinity and particle size of ZnO

From the XRD patterns (Fig. 2), it is also possible to compute the % crystallinity and crystallite size. The amorphous phase fraction of the sample may be determined by taking the ratio of the amorphous area of the X-ray diffractograms to the total area. The area covered by the amorphous region means that the area of the diffractograms not contained by any sharp diffraction peaks. A method for estimation of amorphous phase fraction from XRD patterns have been developed by K. Prasad *et al.*¹⁸ in the earlier publication.

Crystallite size of the ZnO samples may be obtained using the Debye-Scherrer equation. Vigneshwaran *et al.*^{21,22} have used the Debye-Scherrer equation successfully for the estimation of size of nano ZnO in the past. The same procedure has been repeated here.

The Debye-Scherrer equation is used frequently in X-ray analysis of materials, particularly powder diffraction of metal oxides. It relates the peak breadth of a specific phase of a material to the mean crystallite size of that material. It is quantitative

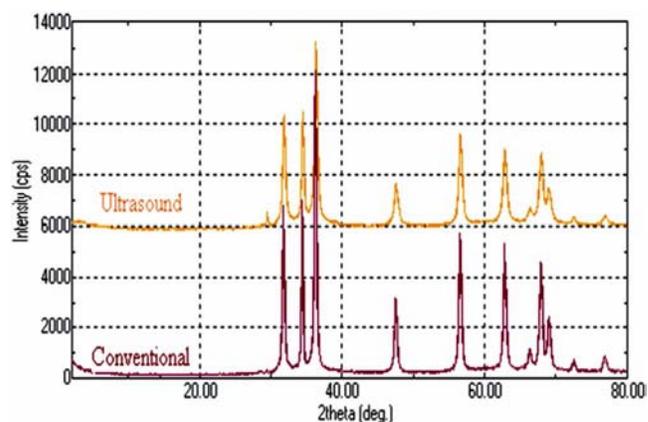


Fig. 2 — XRD pattern of the conventionally (NUS) and sonochemically (US) synthesized ZnO.

Table 1 — Crystallinity, crystallite size and yield of the conventionally (NUS) and sonochemically (US) synthesized ZnO

Method	Crystallinity (%)		Crystallite size d(nm)		Yield (%)		Specific surface area (m ² g ⁻¹)	Energy (J)	Power Input (W)
	Average	± variation	Average	± variation	Average	± variation			
Conventional	51.14	0.43 ≈ 1	32	0.35	48.12	2.68	33.45	-	-
Sonochemical	44.67	0.37 ≈ 1	23	0.26	73.22	1.92	46.53	19565	32.60

equivalent of saying that the larger the material's crystallites are, sharper are the XRD peaks. According to the full width at half-maximum (FWHM) of the diffraction peaks, the average size of the particles (crystallite) can be estimated from the Scherrer equation:

The equation takes the form:

$$B_{hkl} = K\lambda / (D_{hkl} \times \cos\theta_{hkl}) \quad \dots(1)$$

Specific surface area of the sample was calculated from the formula²³

$$S = 6 \times 10^3 / \rho L \quad \dots (2)$$

where, S is the specific surface area ($\text{m}^2 \text{g}^{-1}$); L is the average crystallite size; ρ is the density of the Zinc Oxide (5.606gcm^{-3})

All the computed results including %crystallinity, crystallite size and specific surface area have been tabulated in Table 1. Zinc oxide crystallites generally exist in three forms: hexagonal wurtzite, cubic zinc blended, and rarely observed cubic rocksalt. The wurtzite structure is most stable at ambient conditions and thus, is most common. In Fig. 2, XRD pattern indicates the formation of hexagonal wurtzite phase of ZnO (International Center for Diffraction Data, JCPDS 36-1451) which is in agreement with the electron diffraction results. The peaks at different crystal planes of US synthesized ZnO matches exactly with that of NUS synthesized ZnO indicating essentially no difference in the two products. The peak broadening in the XRD pattern (for both samples) clearly indicates that very small nanocrystals are present in the samples. The crystallinity of all the samples is still substantial because of the inherent characteristics of the sonically assisted process. It was found that NUS synthesized ZnO shows more crystallinity (by 6.5%) than US synthesized ZnO. This may be because of adverse environments created during sonication and facilitating faster reaction, not allowing crystal to form properly. The high energy generated due to cavitation phenomenon and micromixing caused by the same may increase the randomness of the brownian motion of the ZnO molecules not allowing regular crystal formation. This reduces the ability of the molecules to remain in a stable lattice positions for long, leading to the lowering of crystallinity. Crystallite size of the US synthesized ZnO was found also to be lower than NUS synthesized ZnO. It could also be due to the reduction in crystallinity. As the crystallinity of metal oxide reduces, its crystallite size is also known to reduce, which is consistent with this observation¹⁸.

Fourier Transform Infra Red Spectroscopy (FTIR)

Figure. 3 show the FTIR spectrum of the conventionally (NUS) and sonochemically (US) synthesized ZnO respectively. The dried powder obtained gives an absorption band near 3400cm^{-1} representing O-H mode. The absorption band at 480 and 532cm^{-1} confirm the sample as ZnO²⁴. The result of the FTIR spectrum of ZnO particles is generally influenced by particle size and morphology²⁵.

Thermogravimetric analysis

The thermo gravimetric (TGA) analysis shows the weight loss of synthesized ZnO sample. The first weight loss occurs at 144°C for NUS synthesized ZnO and at 139°C for US synthesized ZnO, when the water molecules (H_2O) start to dissociate itself from $\text{Zn}(\text{OH})_2$ due to extreme temperature and pressure conditions generated by ultrasound exposure. It was noticed that that the second weight loss occurs when the material starts to decompose at 249°C for NUS synthesized ZnO and at 220°C for US synthesized ZnO. There was no weight losses observed after 250°C for NUS system and 220°C for US system. After this, synthesized ZnO was very stable upto 600°C . It was also observed that weight loss occurred in case of US synthesized ZnO is more than NUS synthesized ZnO. Enomoto *et al.*²⁶ have reported that

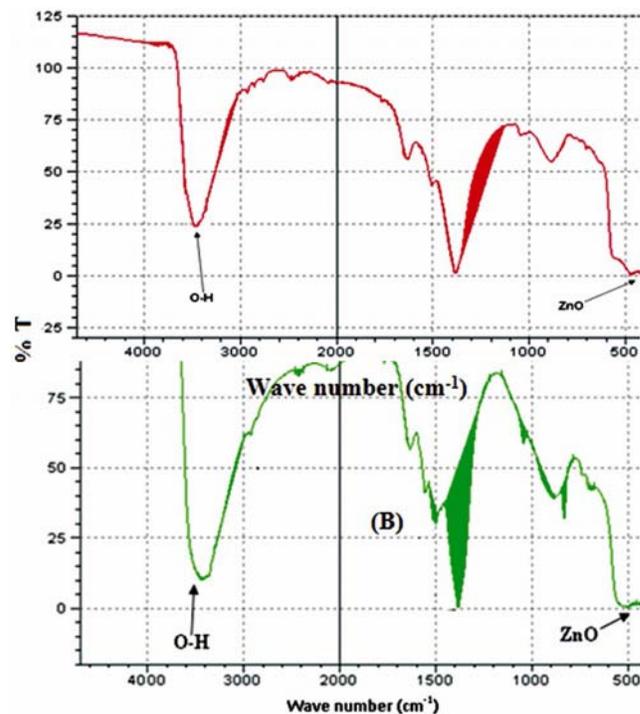
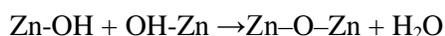


Fig. 3 — FTIR spectrum of (A) conventionally (NUS) synthesized ZnO particles and (B) sonochemically (US) synthesized ZnO particles.

due to ultrasound irradiation, system consisting of suspended particles can cause agglomerations. This is attributed to the formation of Zn-O-Zn bonds by combination reaction of Zn-OH bonds present on the surface of the particle species. This reaction is referred to as water condensation^{26,27}.



These bonds are created by ultrasound enhanced collisions occurring between these particles in solution. The above mentioned observation of higher weight loss in the case of US synthesized sample could be due to this phenomenon. However, more work needs to be carried out before it can be conclusively say so.

Scanning Electron Microscopy

From the SEM micrographs (Figs 4 and 5) of the NUS and US synthesized ZnO samples some observations have been made, that supported the results observed from the XRD patterns. The SEM image results of the ZnO for NUS (Fig. 4A) and US

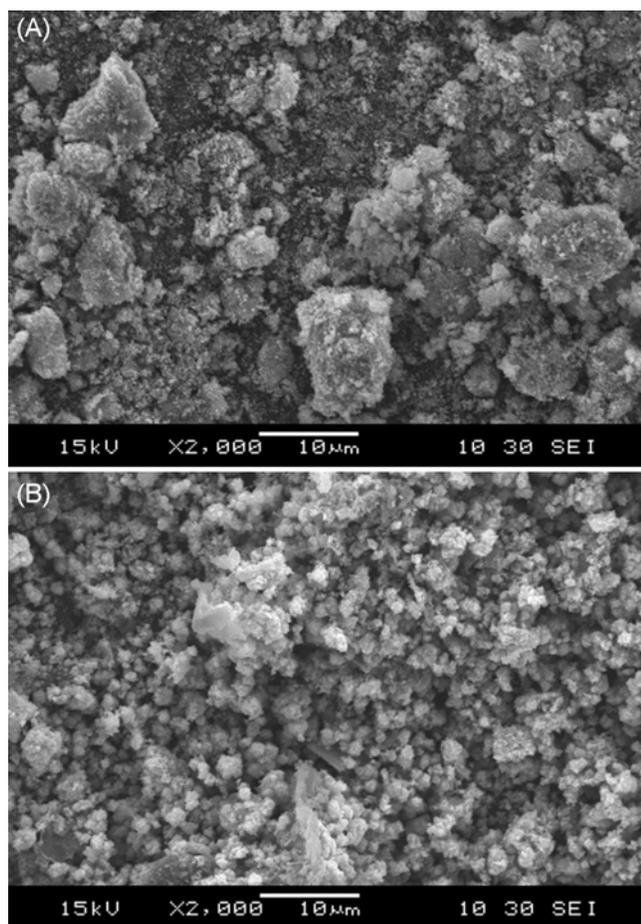


Fig. 4 — SEM Micrograph of synthesized ZnO at 2000X: (A) Conventionally (NUS); (B) Sonochemically (US)

(Fig. 4B) have been compared at the same magnification of 2000X. The US synthesized ZnO show not only comparatively smaller particle size but also considerably less agglomeration. Fig. 4 depicts the SEM micrograph of synthesis of ZnO by NUS and US method. The micrographs of the synthesized ZnO samples (Fig. 5) are also displayed at the same magnification of 10000X. A cluster of needle shaped structure (fairly organized) is observed in the US samples (Fig. 5B) that is absent in the NUS samples (Fig. 5A). Lesser agglomeration and sharply defined structures are observed in the case of the US samples in general. It is also seen in Fig. 5 that length of the needles shaped ZnO are approximately 500 nm in length and diameter is less than 100 nm (aspect ratio of nearly 5). However, crystallite size are found to be 23 nm for US synthesized ZnO particle and 32 nm for NUS synthesized ZnO particle, as reported in Section 3.2.

Growth rate of the crystal planes, which can be different due to differences in surface free energies,

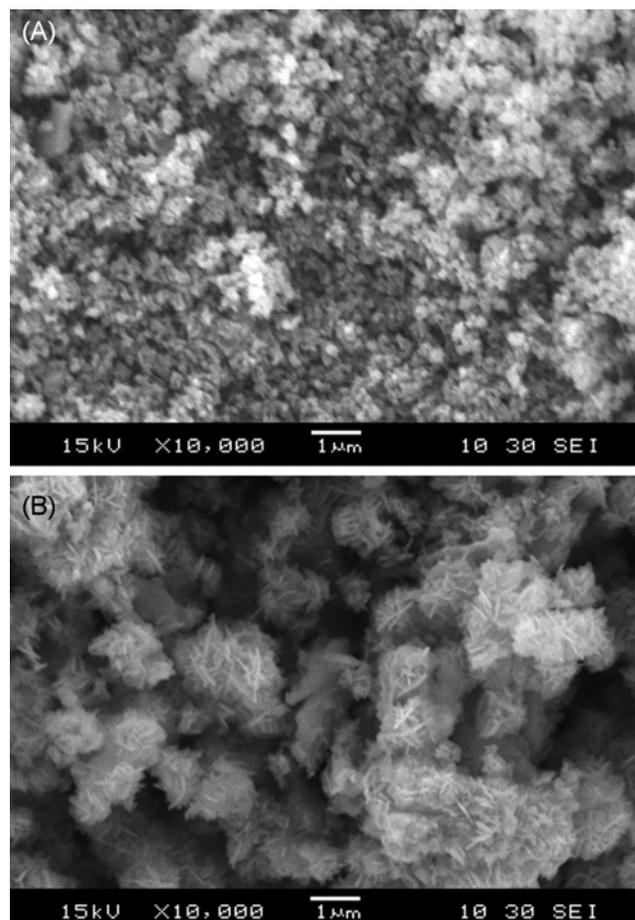


Fig. 5 — SEM Micrograph of synthesized ZnO at 10000X: (A) Conventionally (NUS); (B) Sonochemically (US).

determines the final crystal morphology²⁸. Although, wurtzite (ZnO) crystal structure is polar with different growth rate of the crystal planes. Spherical shaped ZnO particles (Fig. 4A and Fig. 5A) will be relatively easily developed due to the Ostwald ripening process^{29,30} and due to the cavitation conditions applied for synthesis of ZnO material, needle shaped structure may be formed.

Use of cavitation as a reaction aid has had its influence in the reaction step by considerably reducing their particle size and increasing the packing these particles into other composite systems. This not only helps in improving its effect on material properties by increasing the effective surface area, reducing the overall reaction time but also aids in increasing the different types of crystals formed.

Efficacy of energy utilization

For the comparison of the energy required for these two synthesis methods (conventional (NUS) and sonochemical (US)) to obtain ZnO nanomaterials, a sample calculation is reported in Appendix (I). The energy utilized for the synthesis of ZnO nanomaterial is the total energy supplied (kJ) per unit weight of the material processed/obtained (gm). It is already explained in section 3.1 that reaction time to synthesize ZnO were 10 min for US method and 2 hours NUS method. Total energy required per unit weight of the material obtained to synthesize ZnO is 23.04×10^{-3} (kJ/gm) for US synthesis method and 240.55×10^{-3} (kJ/gm) for NUS synthesis method.

Thus, US synthesis method has proved to be an energy efficient method which saved more than 90% of energy utilized by NUS synthesis method along with the reduced in the reaction duration.

Conclusion

Semi-crystalline nanostructured ZnO particles are successfully synthesized, at room temperature, without stabilizers, by conventional (NUS) and sonochemical method (US). Detailed structural characterizations demonstrate that the US synthesized products are wurtzite hexagonal phase, and the needle shaped-like ZnO crystals have a novel layered structure. The sonochemical synthesis method has saved substantial energy (more than 90%) for the synthesis of ZnO. Thus, the sonochemical synthesis technique is fast, simple, convenient, time saving, economical, and environmentally benign. This method promises a future large-scale synthesis possibly for the desirable particle size and shape of

ZnO nanoparticles for many applications in nanotechnology.

Acknowledgement

Authors are thankful to Department of Science and Technology, Government of India for providing financial assistance.

References

- Gleiter H, *Acta Mater*, 48 (2000) 1.
- Cushing B L, Kolesnichenko V L & O'Connor C J, *Chem Rev*, 104 (2004) 3893.
- Alivisatos A P, *J Phys Chem*, 100 (1996) 13226.
- Lisiecki I, Size, *J Phys Chem B*, 109 (2005) 12231.
- Pan Z W, Dai Z R & Wang Z L, *Science*, 291 (2001) 1947.
- Arnold M S, Avouris P, Pan Z W & Wang Z L, *J Phys Chem B*, 107 (2003) 659.
- Sawai J, *J Micro Methods*, 54 (2003) 177.
- Xiong M, Gu G, You B & Wu L, *J Appl Poly Sci*, 90 (2003).
- Behnajady M A, Modirshahla N & Hamzavi R, *J Hazard Mater*, 133 (2006) 226.
- Tang E, Cheng G, Ma X, Pang X & Zhao Q, *Science*, 252 (2006) 5227.
- Tang E, Cheng G & Ma X, *Powder Tech*, 161 (2006) 209.
- Guo L, Yang S, Yang C, Yu P, Wang J, Ge W & Wong G K L, *Chem Mater*, 12 (2000) 2268.
- Kwon Y J, Kim K H, Lim C S & Shim K B, *J Am Ceramic Soc Proc Res*, 3 (2000) 146.
- Davood R, *Renewable Energy*, 50 (2013) 932.
- Chen C, Liu P, & Lu C, *Chem Eng J*, 144 (2008) 509.
- Li C, Yu Z, Fang S, Wang H, Gui Y & Xu J, *J Alloy Compd*, 475 (2009) 718.
- Siqingaowa Z & Yao H, *Front Chem China*, 1 (2006) 277.
- Prasad K, Pinjari D V, Pandit A B & Mhaske S T, *Ultrason Sonochem*, 17 (2010) 409.
- Moholkar V S, Sable S P & Pandit A B, *AICHE J*, 46 (2000) 684.
- Patil M N & Pandit A B, *Ultrason Sonochem*, 14 (2007) 519.
- Vigneshwaran N, Sampath K, Kathe A A, Varadarajan P V & Prasad V, *Nanotechnology*, 17 (2006) 5087.
- Chandramouleeswaran S, Mhaske S T, Kathe A A, Varadarajan P V, Prasad V & Vigneshwaran N, *Nanotechnology*, 18 (2007) art. no. 385702.
- Senthilkumaara S, Porkodia K & Vidyalakshmi R, *J of Photochem and Photobiology A: Chem*, 170 (2005) 225.
- Yong J K, Kyoung H K, Chang S L & Kwang B S, *J Ceram Process Res*, 3 (2002) 146.
- Ristic M, Music S, Ivanda M & Popovic S, *J Alloys Compd*, 397 (2005) L1.
- Enomoto N, Koyano T & Nakagawa Z, *Ultrason Sonochem*, 3 (1996) S105.
- Frost R L, Lisa M & Huaiyong Z, *J Coll Interf Sci*, 316 (2007) 72.
- Andelman T, Gong Y, Polking M, Yin M, Kushovsky I, Neumark G & O'Brien S, *J Phys Chem B*, 109 (2005) 14314.
- Gao X, Li X, & Yu W, *J Phys Chem B*, 109 (2005) 1155.
- Xu L, Guo Y, Liao Q, Zhang J & Xu D, *J Phys Chem B*, 109 (2005) 13519.