Sonochemical synthesis of zinc oxide nano particles

Nandini Sharma, Ranjana Jha[*]

Research Lab for Energy Systems, Department of Physics, Netaji Subhas Institute of Technology, University of Delhi, Dwarka, New Delhi-110078, India

[*]Corresponding author: Tel: (+91) 9654573775; E-mail: nandinis304@gmail.com

Abstract

Zinc oxide nanoparticles were synthesized utilizing a green and simple sonochemical route. The synthesized ZnO nanoparticles were characterized for the analysis of structural and optical properties. Characterization with XRD and TEM shows that the synthesized particles were uniformly distributed, crystalline in nature with spherical shape and narrow size distribution of particles (48-50 nm). UV-Vis and PL spectra shows optical band gap to be 3.5 eV and ZnO sample possess fewer defect states. ZnO nanoparticles synthesized shows good optical properties and was observed to be a promising candidate to be used in thin film solar cells. Copyright © 2017 VBRI Press.

Keywords: Zinc oxide, nanoparticles, sonochemical, acoustic cavitation, green route.

Introduction

Zinc Oxide (ZnO) is a thoroughly studied n- type wide band gap (3.37eV) semiconductor with a large binding energy of 60 meV at room temperature and chemically stable [1][2][3]. The zinc oxide nano particles are widely used in comparison to the bulk [4] for various applications as it exhibits various interesting physical properties like more surface active sites [5]. There are several chemical methods reported by researchers to synthesize metal oxide nanoparticles [6]. Oxidation process [7], polymerization method[8], hydrothermal [9], solvothermal[10], sol–gel combustion[11], precipitation and sol–gel synthesis are the various methods[12][13] that are used to grow ZnO nanostructures. These methods employ complicated protocols and conditions like high temperature, long reaction time. Recently, Sonochemical method [14][15] was used to synthesize various types of nanomaterials with unusual properties. In this process, ultrasound is applied to the reactant solution to initiate the chemical reactions. Sonochemistry originates from acoustic cavitation phenomena, that is, the formation, growth and implosive collapse of bubbles inside the solution[16]. Ultrasound waves produced by horn or bath type sonicator is induced directly or indirectly into the prepared solution[17]. Using horn type sonicator is an energy efficient method, as less reaction time is required [18]. A series of longitudinal waves are generated into the reaction solution by virtue of the presence of the ultrasound waves. Cavitation bubbles are developed when the rarefaction cycles are greater than the compressive forces inside the liquid molecules. Mechanical and chemical energies are generated by implosions inside the reaction mixture when the bubbles are collapsing as a result of cavitation.

Reports are available on the sono-chemical synthesis of various nanomaterials[19][20][21][22][23][24][25] with good optical and structural properties. Manickam [26] in his paper has mentioned the advantages of this facile route over the other chemical routes. The reduced reaction time, moderate reaction conditions (low temperature) and consumption of non-toxic solvent are the main features of Sonochemical route. Almost all the chemical reactions like oxidation, reduction, dissolution, decomposition, and hydrolysis are induced under ultrasonic radiation[27]. The reaction activity of the reactants increases considerably by the presence of more free radicals generated inside the system.

Sonochemical synthesis of Transition metal oxides nanoparticles [28] and the effect of solvent ratio on their size, morphology was studied [6][29]. In 2011[30], ZnO of crystal size 57.5 nm was prepared sonochemically but sodium hydroxide was used as an alkali material. In 2013, hierarchical ZnO nanostructures have been synthesized using base like sodium hydroxide and ammonia water in Sonochemical process [31] .

Nanostructures of ZnO with controlled morphology have been synthesized by Sonochemical method using a cationic surfactant[32][33]. A simple Sonochemical route was demonstrated for the shape-selective preparation of ZnO nanorods, nanocups, nanodisks, nanoflowers, and nanospheres depending on the concentration of precursor chemicals, the kind of hydroxide anion-generating agents, the ultra-sonication time, and the use of a capping agent [34]. Bang and Suslick reviewed applications of

ultrasound in the synthesis of nanomaterials **[35]**. To the best of our knowledge, sonochemical growth of good quality spherical ZnO nanoparticles (well separated, no agglomeration, low defect states, crystallinity with no impurity phase) without making use of any template or surfactant has not been reported previously.

Here, we report the green and template-free sonochemical method to synthesize the ZnO nanoparticles. The obtained nanoparticles possess uniform size distribution with controlled morphology and reduced surface defect sites. The experiment was carried out at very low temperature (55°C), devoid of surfactant or toxic chemical. The pH was maintained at 7 value throughout the experiment. The size, crystallinity, morphology and optical properties of the synthesized nanoparticles were studied using different characterization techniques.
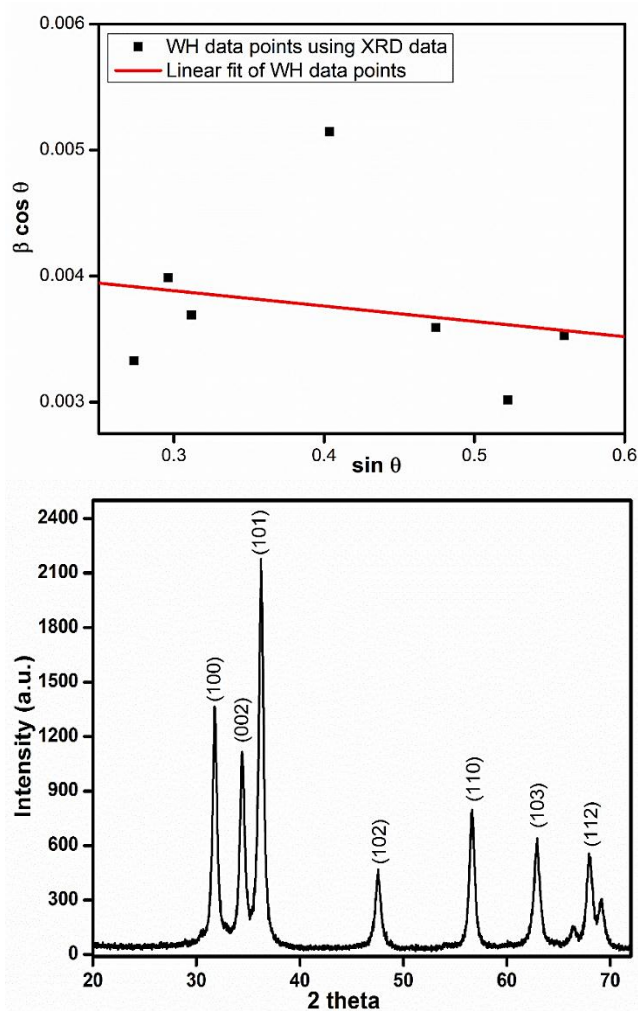

Fig. 1: XRD graph of ZnO nanoparticles and WH analysis of XRD data

Experimental

Zinc oxide nanoparticles were synthesized by ultra-sonication of aqueous – alcohol (composed of methanol, ethanol and distilled water) solution of Zinc acetate in the absence of alkali, by maintaining the neutral pH, i.e., 7 and at temperature 55°C.

Materials

All the reagents used in the present study, were of analytical grade. Zinc acetate (Dihydrate) 99.5 %, from Loba Chemie, Laboratory reagents and Fine chemicals (Molecular weight 219.50), ethanol (99.7%) from Merck, Solution for Leishman's stain from Loba Chemie, Laboratory reagents and Fine chemicals (Molecular weight 32.04) and double distilled water were used directly without any further purification.

Synthesis of zinc oxide nanoparticles by ultrasonic method

ZnO nanoparticles were prepared via the ultrasonic method. 0.1M solution of zinc acetate dihydrate was prepared in 200ml aqueous alcohol (180 ml DI water, 10 ml ethanol and 10 ml Solution for Leishman's stain). The solution was stirred on magnetic stirrer for 10 minutes to obtain a clear solution. Then, the beaker containing clear solution was kept in a bath type sonicator (150 Watts at 20 KHz frequency, of Transonic Company) and sonicated at 55°C for 2 hours to obtain a turbid solution. pH value of solution was measured throughout the experiment using Decibel DB-1003 digital pH meter and it varied from 6 (clear solution) to 7 (turbid solution). Then the turbid solution was filtered using micron filter paper to obtain the residue on filter paper. The obtained residue was kept in hot air oven for 4 hours at 140°C in order to evaporate the excess solvent, ions and get dry powder. The dry powder was again washed with a mixture of 1:1 ethanol and methanol, followed by drying at 100°C again under hot air oven for 3 hours.

Characterizations/ measurements

High Resolution X-Ray Diffraction (HR-XRD) measurements of the sample was performed on the machine D8-Advance model of Bruker Inc. using monochromatic CuK_α line (λ=0.154056 nm) and was compared with the available Joint Committee on Powder Diffraction Studies (JCPDS card no.89-1397) data files to confirm the size and phase. The sample was characterized using Transmission electron microscopy to confirm the size and morphology. Optical properties were measured by Ultraviolet Visible spectroscopy (Analytik Jena Specord 250) and Photoluminescence spectroscopy techniques. pH was monitored using Decibel DB-1003 digital pH meter.

Results and discussion

Sono chemically synthesized Zinc oxide nanoparticles were characterized by several analytical techniques and instruments to study structural, optical and morphological properties.

Structural studies

The obtained XRD pattern of the ZnO matches well with the JCPDS card no. 89-1397. The crystallite size of the ZnO was estimated by Debye Scherer equation**[36]**, i.e., $D=(k\,\lambda\,/\,\boldsymbol{\beta}\cos\theta)$ where D is the crystallite size, $\boldsymbol{\lambda}$ is the
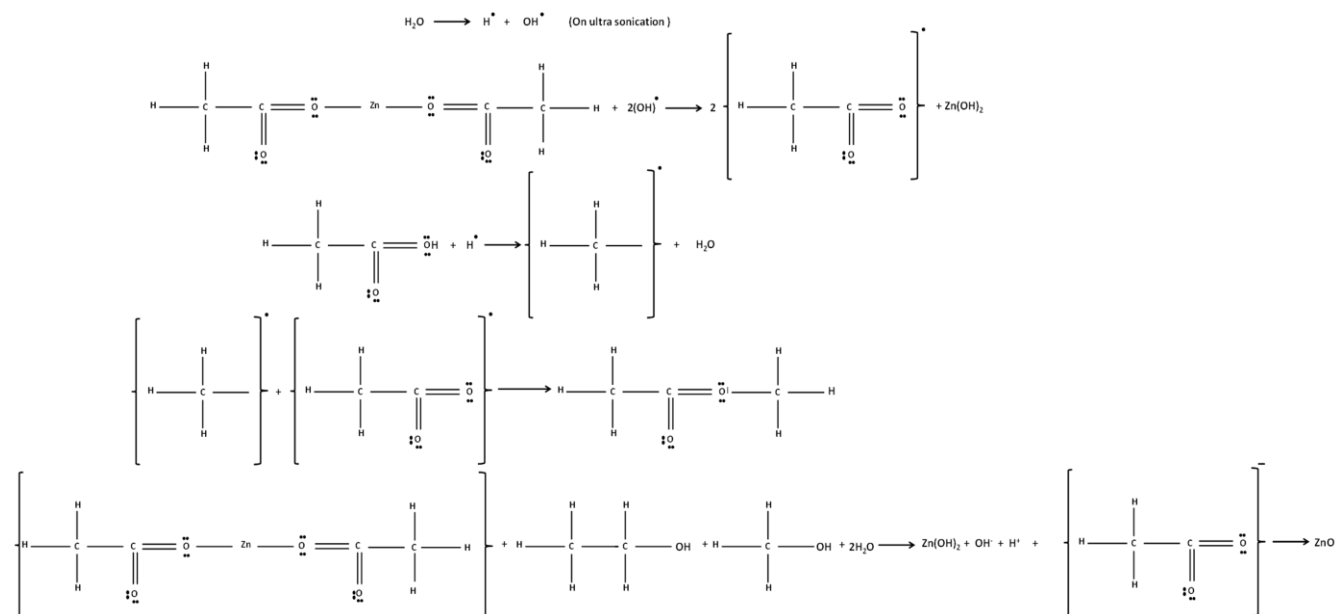
Scheme 1: Reaction mechanism of ZnO nanoparticles formation

wavelength of incident X-ray (1.54 Å for CuK_α), k is a constant equal to 0.93, **β** is the peak width at half maxima intensity and θ is the Bragg diffraction peak position. The estimated crystallite size was 48 nm.

The observed peaks in diffraction pattern corresponds to reflection planes (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) and indicates a wurtzite structure for the sample under study. The lattice constants of the prepared sample were a = b = 3.26047 Å, c = 5.23650 Å which was found to be slightly larger than those of pure ZnO (a = b = 3.249 Å, c = 5.206 Å).

Williamson-Hall analysis resulted in the average distribution of crystallite size to be 39 nm as calculated from the y-intercept of the graph, as shown in Figure 1. The average particle size of ZnO nanoparticles evaluated from Scherer's formula and W-H plot analysis are inter correlated.

Formation mechanism of ZnO nanoparticles

The formation mechanism of ZnO nanoparticles is stated in **Scheme 1.** In **Fig. 2**, Zinc hydroxide is formed in the medium after sonication in the presence of methanol and ethanol. It is the product of hydrolysis of the zinc acetate precursor. The chemical reaction shows that the addition of methanol is helpful in increasing the hydrolysis rate and provides hydroxyl ion to the solvent medium during sonication. As reported by various researchers **[25][37]**, that locally generated high temperature and high pressure in a sonicated aqueous medium, leads to splitting of water molecules (H. (atom) and OH free radical). Some of the splitted water molecules again recombine to form water molecule. The growth of ZnO particles is due to dehydration of Zincate ions in the presence of ultrasound waves. The shape of the particles is being solely tuned by ultrasound energy dissipated.
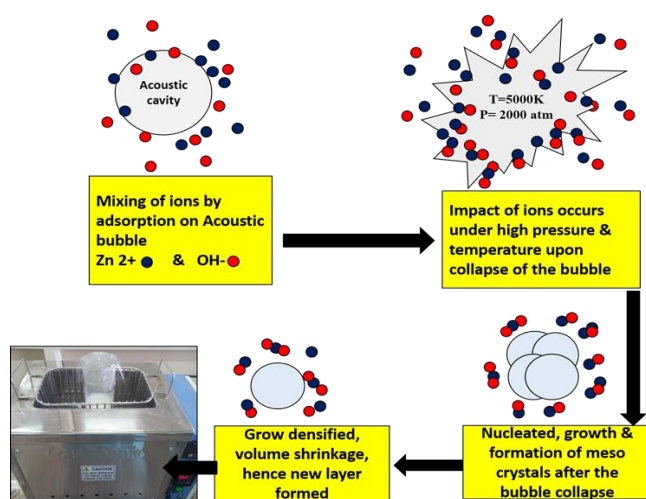

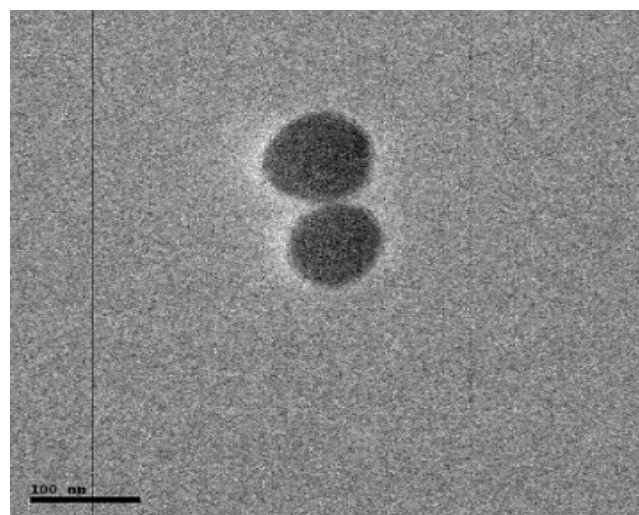**Fig. 2**. Schematic representation of sonochemical process.

Fig. 3. TEM image of ZnO nanoparticles.

Morphological characterizations

The morphology, structure and size of the prepared sample were investigated by Transmission Electron Microscopy (TEM). **Fig. 3.** indicates that the morphology of the ZnO particles is almost spherical with uniform size distribution (48-50 nm). Separate grain boundaries are observed in the TEM image with no agglomeration or clustering of nanoparticles. The crystallite size as observed from TEM graph is in good agreement with the result estimated from XRD and W-H analysis.

Optical properties

Fig. 4. depicts the observed UV-Vis absorption spectra of ZnO at room temperature. Before performing the UV-Vis measurement, the ZnO was dispersed in ethanol with a concentration of 0.1 weight %. The observed spectrum shows a characteristic absorption peak of ZnO due to the electron transitions from the valence band to the conduction band ($O_{2p} \rightarrow Zn_{3d}$) at wavelength of 350nm for the synthesized sample. From the observed peak at 350 nm, the intrinsic band gap of ZnO was calculated to be 3.5eV. It is also evident that significant sharp absorption of ZnO indicates the monodispersed nature of the nanoparticle distribution.
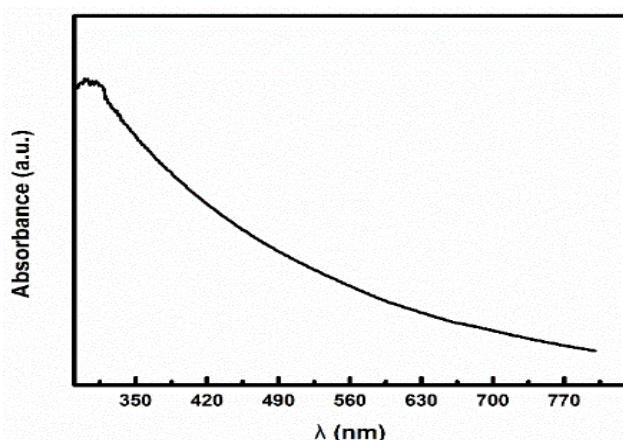

Fig. 4. Ultraviolet-Visible spectra of ZnO nanoparticles.

Fig. 5. shows the room temperature PL properties of ZnO nanoparticles synthesized by Sonochemical route at excitation wavelength of 350 nm. Several emission bands, including band edge emission at 396 nm (~3.12 eV), ultraviolet emission at 403 nm (3.07 eV), violet emission at 428 nm (~ 2.89 eV) and blue emission at 453 nm (~2.73 eV), were observed.

The band edge emission at ~396 nm attributes for the recombination of excitons. Ultra violet emission depicts free excitonic emission. Whereas, visible emission ZnO corresponds to different intrinsic defects such as Oxygen vacancies V_O, Zinc vacancies V_{Zn}, Oxygen interstitials O_i and Zinc antisites Z_{ni}. The violet emission at 428 nm (2.89 eV) refers to an electron transition from a donor level of neutral Z_{ni} to the top level of the valence band[38]. As the violet photoluminescence is present at 2.89 eV which indicates that, the donor level of the Z_{ni} is present at

~0.61 reV below the conduction band. Radiative transition of an electron from the donor level of Z_{ni} to an acceptor level of neutral V_{Zn} for the prepared material corresponds to a blue emission at ~2.73 eV. The emissions as observed from the PL spectra for the violet and blue emission in the visible region, it is calculated that acceptor level of V_{Zn} is located at ~0.16 eV above the valence band, which indicates surface defects of ZnO nanostructure[39].
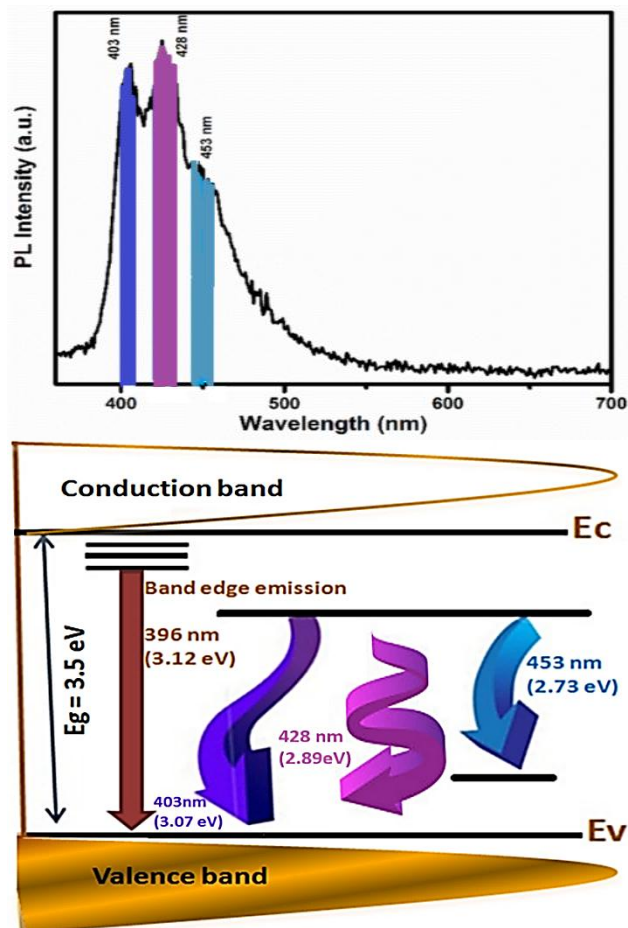

Fig. 5. (a) shows PL spectra of the ZnO nanoparticles   and, (b) the Energy level Diagram showing emission from ZnO nanoparticles.

There is quenching of green and yellow emission peaks as observed by other researchers[40][41][42] at excitation wavelength of 350 nm . This signifies absence of heterogeneity of the surface traps and oxygen interstitials respectively in the prepared sample. As seen from the PL spectrum, there is narrow size distribution of nanoparticles in the powder as the luminescence peak full-width half-maximum (FWHM) is only in few nanometers with less emission peaks in visible region[43][44].

Conclusion

A green ultrasonic assisted route for the growth of nanoparticles of ZnO. ZnO nanoparticles are synthesized by a single-step reaction which is a direct conversion mechanism of Zinc acetate to ZnO nanoparticles without

using any alkaline material. ZnO nanoparticles having enhanced morphology with reduced surface defects are formed. TEM analysis shows that obtained ZnO nanoparticles are having a consistent grain size of 50 nm and uniform spherical shape. Recombination centers are reduced from the synthesized ZnO powder as there is no agglomeration as depicted in TEM analysis. Only two trap state visible emission peaks (blue and violet) in PL spectra which indicates less surface defects. Ultrasonic assisted synthesized ZnO nanoparticles having unique properties as discussed above are compatible with the required parameters of photoanode for high efficiency thin film solar cells.

Acknowledgements

References

1. Schmidt-Mende, L.; MacManus-Driscoll, J. L.; *Materials Today* **2007**, *10*, 40.
   DOI: 10.1016/S1369-7021(07)70078-0
2. Rajalakshmi, M. ; Arora, A. K. ; Bendre, B. S.; Mahamuni, S.; *Journal of Applied Physics* **2000**, *87*, 2445.
   DOI: 10.1063/1.372199
3. Wang, Z. L.; *Materials Today* **2004**, *7*, 26.
   DOI: 10.1016/S1369-7021(04)00286-X
4. Kołodziejczak-Radzimska, A.; Jesionowski, T. ; *Materials* **2014**, *7*, 2833.
   DOI: 10.3390/ma7042833
5. Liu, Y. ; Jian-er, Z. ; Larbot, A.; Persin, M.; *Journal of Materials Processing Technology* **2007**, *189*, 379.
   DOI: 10.1016/j.jmatprotec.2007.02.007
6. Kumar, R. V.; Diamant, Y. ; Gedanken, A.; *Chemistry of Materials* **2000**, *12*, 2301.
   DOI: 10.1021/cm000166z
7. Wang, Z. H.; Geng, D. Y.; Han, Z. ; Zhang, Z. D. ; *Materials Letters* **2009**, *63*, 2533.
   DOI: 10.1016/j.matlet.2009.08.044
8. Jajarmi, P.; *Materials Letters* **2009**, *63*, 2646.
   DOI: 10.1016/j.matlet.2009.08.062
9. Fang, X. ; Bando, Y.; Gautam, U. K.; Zhai, T.; Zeng, H.; Xu, X.; Liao, M.; Golberg, D.; *ZnO and ZnS Nanostructures: Ultraviolet-Light Emitters, Lasers, and Sensors*, **2009**, 34, 190.
   DOI: 10.1080/10408430903245393
10. Ehrentraut, D.; Sato, H.; Kagamitani, Y.; Sato, H.; Yoshikawa, A. ; Fukuda, T.; *Progress in Crystal Growth and Characterization of Materials* **2006**, *52*, 280.
    DOI: 10.1016/j.pcrysgrow.2006.09.002.
11. Shi, L.; Zeng, C.; Jin, Y. ; Wang, T. ; Tsubaki, N. ; *Catalysis Science and Technology* **2012**, *2*, 2569.
    DOI: 10.1039/C2CY20423A
12. Baruah, S.; Dutta, J. ; *Science and Technology of Advanced Materials* **2008**, *9*.
    DOI:10.1088/1468-6996/9/2/025009.
13. Xu, S.; Wang, Z. L. ; *Nano Research* **2011**, *4*, 1013.
    DOI: 10.1007/s12274-011-0160-7
14. Banerjee, P.; Chakrabarti, S.; Maitra, S.; Dutta, B. K.; *Ultrasonics Sonochemistry* **2012**, *19*, 85.
    DOI: 10.1016/j.ultsonch.2011.05.007
15. Sharma, N.; Jha, R.; Baghel, S.; Sharma,D.; J. Alloys and Comp. **2016**, *695*,270.
    DOI: 10.1016/j.jallcom.2016.10.194.
16. Kandjani, A. E. ; Tabriz, M. F. ; Pourabbas, B.; *Materials Research Bulletin* **2008**, *43*, 645.
    DOI:10.1016/j.materresbull.2007.04.005.
17. Mason, T. J.; Cintas, P.; *Handbook of Green Chemistry and Technology*, **2002**.
18. Xu, H.; Zeiger, B. W.; Suslick, K. S.; *Chemical Society reviews* **2013**, *42*, 2555.
    DOI: 10.1039/c2cs35282f.
19. Wongpisutpaisan, N. ; Charoonsuk, P. ; Vittayakorn, N.; Pecharapa, W.; *Energy Procedia*, **2011**, pp. 404–409.
    DOI: 10.1016/j.egypro.2011.09.044.
20. Vijayakumar, R.; Koltypin, Y.; Felner, I.; Gedanken, A.; *Materials Science and Engineering: A* **2000**, *286*, 101.
    DOI: 10.1016/S0921-5093(00)00647-X.
21. Xiong, H.-M.; Shchukin, D. G.; Möhwald, H. ; Xu, Y.; Xia, Y.Y.; *Angewandte Chemie (International ed. in English)* **2009**, *48*, 2727.
22. Okitsu, K.; *Theoretical and Experimental Sonochemistry Involving Inorganic Systems*, **2011**.
    DOI: 10.1007/978-90-481-3887-6.
23. Zhu, S.; Zhou, H.; Hibino, M. ; Honma, I. ; Ichihara, M.; *Advanced Functional Materials* **2005**, *15*, 381.
    DOI: 10.1002/adfm.200400222.
24. Gedanken, A. ; *Ultrasonics Sonochemistry* **2004**, *11*, 47.
    DOI: 10.1016/j.ultsonch.2004.01.037.
25. Yadav, R. S.; Mishra, P. ; Pandey, A. C.; *Ultrasonics Sonochemistry* **2008**, *15*, 863.
    DOI: 10.1016/j.ultsonch.2007.11.003.
26. Manickam, S.; *Theoretical and Experimental Sonochemistry Involving Inorganic Systems*, **2011**, pp. 191–211.
    DOI: 10.1007/978-90-481-3887-6_8.
27. Bhatte, K. D.; Sawant, D. N.; Pinjari, D. V.; Pandit, A. B.; Bhanage, B. M.; *Materials Letters* **2012**, *77*, 93.
    DOI: 10.1016/j.matlet.2012.03.012.
28. Roy, A.; Maitra, S.; Ghosh, S.; Chakrabarti, S.; *Materials Research Bulletin* **2016**, *74*, 414.
    DOI: 10.1016/j.materresbull.2015.11.006
29. Wang, Y.; Yin, L.; Gedanken, A.; *Ultrasonics Sonochemistry* **2002**, *9*, 285. **DOI:** 10.1016/S1350-4177(02)00090-1
30. Askarinejad, A.; Alavi, M. A.; Morsali, A.; *Iranian Journal of Chemistry & Chemical Engineering* **2011**, *30*, 74.
31. Khorsand Zak, A.; Majid, W. H. A.; Wang, H. Z.; Yousefi, R.; Moradi Golsheikh, A. ; Ren, Z. F.; *Ultrasonics Sonochemistry* **2013**, *20*, 395.
    DOI: 10.1016/j.ultsonch.2012.07.001
32. Ghosh, S. ; Majumder, D.; Sen, A.; Roy, S.; *Materials Letters* **2014**, *130*, 215.
    DOI: 10.1016/j.matlet.2014.05.112
33. Stubbing, J. ; Brown, J.; Price, G. J.; *Ultrasonics Sonochemistry* **2016**.
    DOI: 10.1016/j.ultsonch.2016.04.036.
34. Jung, S. H.; Oh, E.; Lee, K. H. ; Yang, Y.; Park, C. G.; Park, W.; Jeong, S. H.; *Crystal Growth and Design* **2008**, *8*, 265.
35. Bang, J. H.; Suslick, K. S.; *Advanced Materials* **2010**, *22*, 1039.
    DOI: 10.1002/adma.200904093
36. Cullity, B. D.; *American Journal of Physics* **1957**, *25*, 394.
37. Capelo-Martnez, J. L.; *Ultrasound in Chemistry: Analytical Applications*, **2009**.
38. Mishra, S. K.; Srivastava, R. K. ; Prakash, S. G.; Yadav, R. S. ; Panday, A. C.; *Opto-Electronics Review* **2010**, *18*, 467.
    DOI: 10.2478/s11772-010-0037-4.
39. Klason, P. ; Berseth, T. Moe ; Zhao, Q. X.; Svensson, B. G.; Kuznetsov, A. Y.; Bergman, P. J.; Willander, M.; *Solid State Communications* **2008**, *145*, 321.
    DOI: 10.1016/j.ssc.2007.10.036.
40. Kang, H. S.; Kim, J. W.; Lim, S. H.; Chang, H. W.; Kim, G. H.; Kim, J. H.; Lee, S. Y.; *Superlattices and Microstructures* **2006**, *39*, 193.
    DOI: 10.1016/j.spmi.2005.08.042.
41. Simmons, J. G.; Foreman, J. V. ; Liu, J.; Everitt, H. O.; *Applied Physics Letters* **2013**, *103*.
    DOI: 10.1063/1.4829745.
42. Djuriic, A. B. ; Leung, Y. H. ; Tam, K. H.; Ding, L. ; Ge, W. K.; Chen, H. Y. ; Gwo, S.; *Applied Physics Letters* **2006**, *88*.
    DOI: 10.1063/1.2182096.
43. Talam, S.; Karumuri, S. R.; Gunnam, N.; *ISRN Nanotechnology* **2012**, *1*.
    DOI:10.5402/2012/372505.
44. Manoharan, D.; Loganathan, A. ; Kurapati, V.; Nesamony, V. J.; *Ultrasonics Sonochemistry* **2015**, *23*, *174*.
    DOI: 10.1016/j.ultsonch