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Temperature and Solvent Impact on Zinc Oxide Nanostructures Synthesized via Hydro-Solvo-Thermal Technique

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Abstract: ***This work presents temperatureimpact on ZnO nanostructures growth when synthesized via solvo-thermal technique. For a temperature range of:70, 100, 130 and 160 ºC, and precursors of Zinc acetate dihydrate and sodium hydroxide (both dissolved in methanol)we noticed an obvious temperature impact on the grain size and hence an obvious variation on the corresponding band gap energy. Having the fact that ZnO is a semiconductor; variation of ZnO nanostructures band gap energy means variation of quantum confinement effect; which is considered to be an essential parameter to tune semiconductors optical and electrical properties. This work also presents solvent impact on ZnO nanostructures growth when synthesized via hydro-solvo-thermal technique at temperatures of 70 ºC and 150ºC, and precursors of Zinc acetate dihydrate and sodium hydroxide; both dissolved in H2O:Methanole solution mixtures of: 1:3,2:2, 3:1 and 1:3. Again, we noticed an obvious solvent impact on ZnO nanostructures shapes and sizes. Morphology, crystalline structure and optical properties of ZnO nanostructures were determined using field emission scanning electron microscopy (FE-SEM), X-ray diffraction crystallography (XRD) and UV-Vis spectroscopy. SEM measurements showed particles sizes increment as temperatures increase. XRD measurements showed hexagonal crystalline-wurtzite phase structures in all temperatures. UV-vis measurements showed red shifts absorptions as a result of particles sizes increment, and hence, decrement for the corresponding band gap energy in comparison with the bulk one.Average sizes of ZnO nanostructures varied between 50 to 500nm.***

Keywords: ZnO nanostructures, ZnO-XRD, ZnO-UV-vis,ZnO-SEM, ZnO-hydrothermal

1. Introduction

Nanomaterials are materials of the recent era. Since the discovery of SEM in 1960s [1, 2] the potential of small hidden world start to be exposed. Today this small hidden world is known as the world of nanomaterials. A milestone scientific revolution started when researchers discovered the possibility and flexibility to create endless lists of shapes and sizes of nanomaterials using cheap or expensive, simple or complex methodologies to rationally synthesis materials with the desired electronic and optical properties[3-7]. Interestingly, the matter has not limited to nanomaterials synthesis, thought, researchers started to go yet beyond nature to create their own nanomaterials, and hence it was the discovery of metamaterials; enormous scientific materials with enormous potentials widely being used in military, industrial and health sectors [8-14].General concepts of nanomaterials and metamaterials are far beyond the limitation of this work. This work may only considers the impact of temperature and solvent on ZnO nanostructures growth level when synthesized via hydro-solvo-thermal technique[15,16].Law temperature-based methodology of solvothermal (or Hydrothermal if water is used as a solvent) is a cheap and powerful technique widely used to synthesize wide ranges of nanostructures starting from single crystal molecules up to nanowires. In this technique, essential parameters such as growth temperature, incubation time, solvents species, precursors species and precursors concentrations are needed to be determined in order to produce well-designed nanostructures in a controlled manner.ZnO is a semiconductor with wide semiconducting-based band gap energy averaged as 3.3 eV and large exciton binding energy namely as 60 meV[17-19]. As such, the variation of ZnO nanostructures shapes and sizeswould affect the band gap energy and hence, affect the quantum confinement effect. The latest is considered to be an essential parameter to rationally tune semiconductors optical and electrical properties. ZnO nanostructures are widely used as: UV light emitters at room temperature[20], photo catalysts in solar cells[21], corrosion inhibitors[22], biosensors and gas sensors[23,24].

2. Synthesis of ZnO nanostructures

ZnO nanostructures were synthesized using zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and sodium hydroxide (NaOH) as precursors. This to prepare ZnO via Zinc hydroxide oxidation under severe conditions of high temperature and high pressure using Teflon lined stainless steel autoclave hydrothermal system, see Figure1. In fact, ZnO is formed as a result of the following reaction:

$$Zn(CH_3COO)_2 + NaOH \longrightarrow Zn(CH_3COO)(OH) + NaCH_3COO + H_2O \quad \ldots\ldots 1$$

$$Zn(CH_3COO)(OH) + NaOH \longrightarrow ZnO + NaCH_3COO + H_2O \quad \ldots\ldots 2$$

Using methanol as a solvent, a solution of 0.5M $Zn(CH_3COO)_2.2H_2O$ was mixed at a molar ratio of 1:10 with 5M NaOH under continuous magnetic stirring. The mixture was then transferred into a Teflon-lined-stainless steel autoclave, well-sealed and heated at temperatures range of: 70, 100, 130 and 160°C for 24 hours. The reactor was then cooled to room temperature, and the product was filtered and washed with de-ionized water until the pH of

final solution was 7.0. It was then had the final wash with ethanol to eventually dried at 100 °C for 12h.

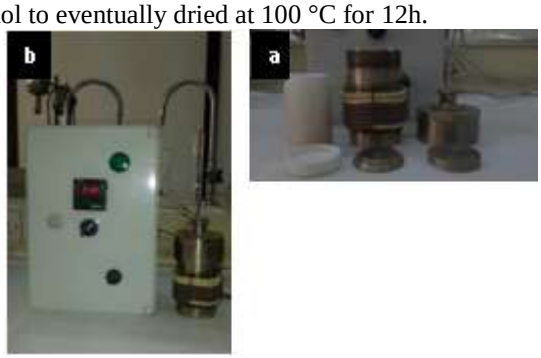


Figure 1: Autoclave Teflon lined stainless steel: apart (a) and attached to the control unit in the hydrothermal system (b).

3. Characterizations

UV-vis spectra showed absorption peaks at: 364, 368, 370 and374nm for: 70, 100, 130 and 160 °C, respectively, see Figure 2. Absorption peaks are used to be highly affected by several factors such as: band gap energy, oxygen deficiency, crystal size and structure, surface roughness in addition to impurity centres[25].

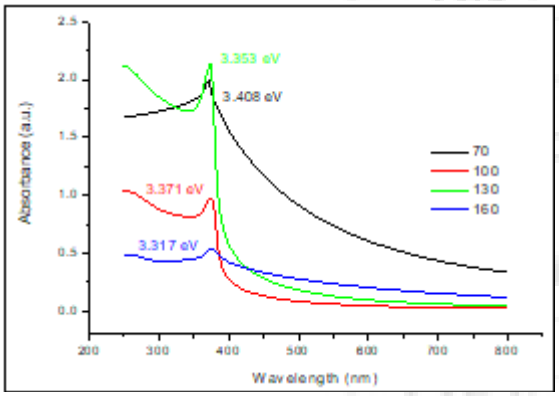


Figure 2: UV-vis absorption spectra at the region of (250-800) nm for ZnO nanostructures synthesized via hydrothermal technique at temperatures rang of (70-160) °C. Note the absorption peaks of: 364, 368, 370 and 374 for: 70, 100, 130, and 160 °C, respectively, indicating red shifts as a result of particles sizes increment i.e. decrement for the band gap energy namely as: 3.408, 3.371, 3.353 and 3.317eV, respectively.

From equation $E = h.C/\lambda$(where h is the Plank constant = 4.135667 x10-15 eV.s, C is the speed of light = 3.00x108 m/s and λ is the maximum wavelength of the absorption peaks), values of band gap energy were found to be equal to: 3.408, 3.371, 3.353 and 3.317eV ata temperatures range of: 70,100,130 and160°C, respectively, see Figure 3.Obviously, values of band gap energy decrease as the wavelength of absorption peaks increasewheretemperatures increase. From SEM images, shown in Figure 4, when temperatures increase the grain sizes increase as well. This implies that as grain sizes increase the band gap energy decrease;and this is how tomanipulate the efficiency of semiconducting properties. Our results come to an agreement with Karmakar group [26].From other hand,relation in Figure 3 could be expressed using a polynomial fit of:$Y = 218.86567 - 1.72638X + 0.00463X^2 - 4.16667E\text{-}6X^3$; anexpression which was generated using polynomial fit tools form software package of Origin 6.1. Via this relation, it is possible to estimate, in advance, the band gap energy (and hence electrical and optical properties) for ZnO nanostructures at a particular range of temperatures or sizes.

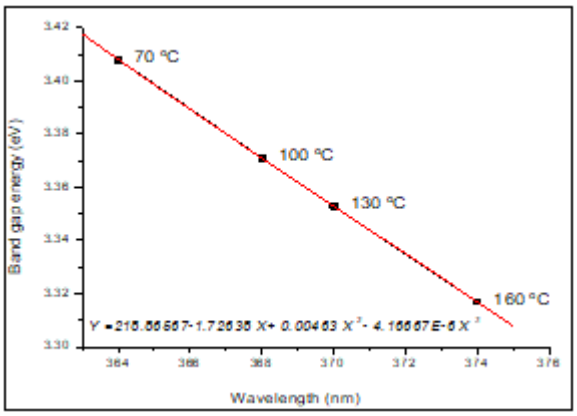


Figure 3: The relation of band gap energy (calculated from $E = h.C/\lambda$) and the corresponding absorption wavelengths peaks taken from Figure2. Note how the values of the band gap energy decrease as the wavelength of absorption peaks increase. This could be expressed using a polynomial fit of:$Y = 218.86567 - 1.72638\ X + 0.00463\ X^2 - 4.16667E\text{-}6\ X^3$. By means of this relation,one can estimate the band gap energy, and hence, predict the electrical and optical properties for ZnO nanostructures at a particular range of temperatures or sizes.

FE-SEM images showed an obvious temperature and solvent impacton ZnO nanostructures growth leveland morphology. This is consistent with others who derived the same conclusion but with different range of temperatures and different solvents; indicating an enormous flexibility on tuning electrical and optical properties for such cheap and powerful materials[26]. Generally speaking, as temperature increase the grain size increase as well; an effect which could be attributed to the natural trend of ZnO molecules to assemble and bond at high temperatures. Figure4. shows SEM images for ZnO nanostructures growth starting from >100nm polygonal like shapescondensed horizontally along two dimensions at 70 °C to >100nm polygonal like shapes irregularly aggregated along three dimensions at 100 °C; then developed to >100nm polygonal and spherical like shapes condensed vertically along three dimensions at 130 °C; and then to>500nm rode like shapes at 150 °C; to end up with a combination of >500nm rode like shapes and>1000nm octahedron like shapes at180 °C.Regarding solvent effect, Figure 5 shows SEM images for ZnO nanostructures variation starting from (100-500)nm cubes and hexagonal prisms like shapes in aqueous solutions to >100nm polygonal like shapes a mixture solution of 1:3 H2O:Methanole.

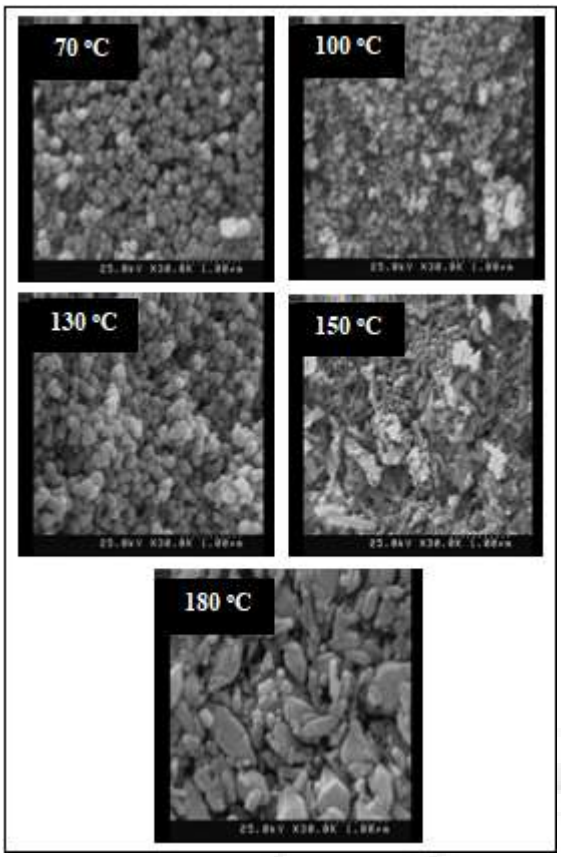
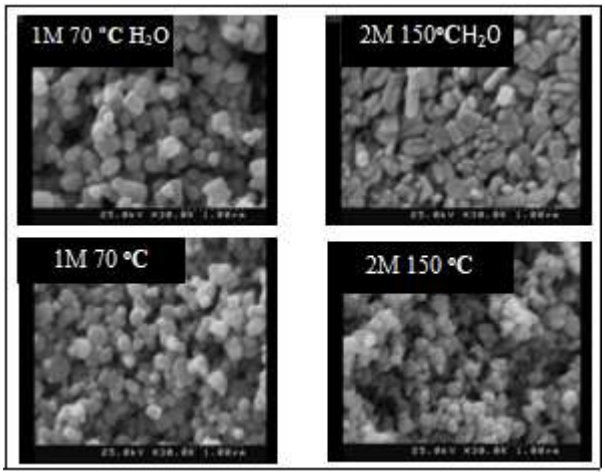


Figure 4: SEM images for ZnO nanostructures synthesized at different temperatures using Teflon lined stainless steel autoclave hydrothermal system. Note the impact of temperature rise on nanostructures shapes and sizes. Nanostructures growth start from >100nm polygonal like shapes condensed horizontally along two dimensions at 70 °Cto >100nm polygonal like shapes irregularly aggregated along three dimensions at 100 °C;then developed to >100nm polygonal and spherical like shapes condensed vertically along three dimensions at 130 °C; and then to >500nm rode like shapes at 150 °C; to end up with a combination of >500nm rode like shapes and >1000nm octahedron like shapes at 180°C.



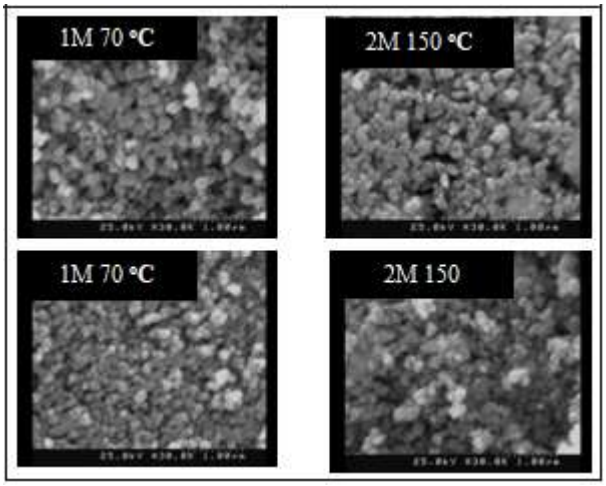


Figure 5: SEM images for ZnO nanostructures synthesized via autoclave hydro-solvo-thermal technique using solution mixtures of H_2O:Methanole of: 1:3, 2:2, 3:1 and 1:3. Note the solvent effect on ZnO nanostructures shapes and sizes. Shapes and sizes variation start from (100-500) nm cubes plus hexagonal prisms like shapes in aqueous solutions to >100 nm polygonal like shapes in a mixture solution of 1:3 H_2O:Methanole. Temperatures and NaOH concentration are shown in-set.

For temperatures range of :70, 100, 130 and 160 ^oCXRD crystallography showed intense diffractionlines corresponding to plane configurations of: 100, 002, 101, 102, 110, 103, 200, 112 and 201; perfectly agree with the standard reference data of (JCPDS: 36-1451) card for ZnO powder; indicating hexagonal crystallite structures with wurtzite phase, see Figure 6.The effect of temperature variation on crystallites formation could be concluded when looking individually at XRD diffraction lines for each plane configuration appeared in Figure 6. Such effect could be concluded from the variation of XRD diffraction lines positions, widths and intensities,see Figure 7 (a-g). Having a closer look at diffraction lines of each plane configuration for each temperature one would conclude a uniform and nonuniform strain crystallite deformations. According to Khorsand Zak groupin addition to others[28-31], variation of diffraction line peak positionsindicate uniform strain crystallite deformations, while variation of diffraction line peak widths and intensities indicate nonuniform strain crystallite deformations. Diffractions at low Bragg`s angles with narrow intense peaks indicate decent crystallinity.

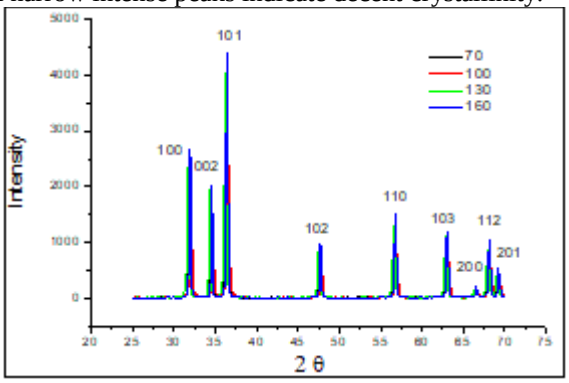


Figure 6: XRD crystallography for ZnO nanostructures at temperature range of :70, 100, 130 and 160 ^oC. Note the reflection peaks corresponding to plane configurations of: 100, 002, 101, 102, 110, 103, 200, 112 and 201. Spectra

pattern perfectly agree with standard reference data of (JCPDS: 36-1451) card for ZnO powder; indicating hexagonal crystallite structures with wurtzite phase.

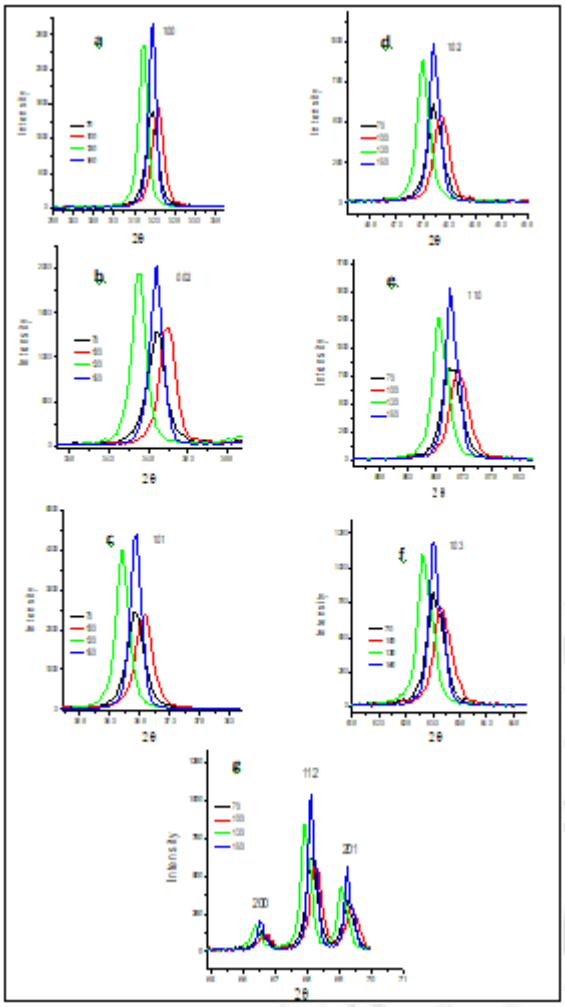


Figure 7(a-g): Zooming in XRD diffraction lines for each plane configurations appeared in Figure 6. Note the effect of temperature variation on crystallites formation. The effect of temperature variation could be concluded from the variation of XRD diffraction lines positions, widths and intensities.

4. Conclusion

In conclusion, we report temperatures impact on the grain size (with crystalline geometry remains constant as hexagonal with wurtzite phase) of ZnO nanostructures while synthesized. This means variation of temperatures could vary ZnO nanostructures electrical and optical properties. Essentially, ZnO nanostructures could be synthesized at as low temperature as 70 ^{o}C using cheap and simple technique of hyro-solvothermal.

5. Acknowledgment

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References

[1] D. McMullan, `Scanning electron microscopy 1928-1965`, *Scanning*, 2006, Vol.17, No.3, pp (175-185).

[2] D. McMullan, `Von Ardenne and the scanning electron microscope`, *Proc Roy Microsc.*, 2008, Vol.23, pp(283-288)

[3] X. Yang, `A Study on Antimicrobial Effects on Nanosilver for Drinking Water Disinfection`, *Springer Nature Singapore Pte Ltd.* 2017, ISBN:978-981-10-2901-1, Chapter 2.

[4] Y. Sun and Y. Xia, `Shape- controlled synthesis of gold and silver nanoparticles`, *Science*, 2002, Vol.298, pp(2176-2179)

[5] Y. Xia, Y. Xiong, B. Lim, S. Skrabalak, `Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics?`, *Angew. Chem. Int. Ed.*, Vol.48, pp(60-103)

[6] K. Kalishwaralal, V. Deepak, S. Ram Kumar Pandian, M. Kottaaisamy, S. Barathmanikanth, B. Kartikeyan and S. Gurnathan, `Biosynthesis of silver and gold nanoparticles using Brevibacteriumcasei.`, *Colloids Surf B Bio interfaces*, 2010 Vol.77, pp(257-262)

[7] Y. Kim, J. Song, `Synthesis of multi-walled carbon nanotube-Ag-nanoparticles composite nanomaterials using proton beam irradiation`, *J. NanosciNanotechnol*, 2014, Vol.14, pp(257-262)

[8] V. Vaselago, *Usp*, 1968, Vol.10, pp (509-514).

[9] J. Pendry, J. Holden, D. Robbins and W. Stewart, *Institute of Electrical and Electronic Engineering Transactions on Microwave Theory and Techniques*, 1999, Vol.47, pp (2075-2084).

[10] N. Engheta and R. Ziolkowski, "Metamaterials: Physics and Engineering Explorations", *Institute of Electrical and Electronic Engineering, Inc. Press, John Wiley & Sons*, 2006, printed book.

[11] N. Abdulrahman, `Nanotechnology and Chiroptical Spectroscopy to Characterise Optically Active Chiral Metamaterials`, *University of Glasgow Press*, PhD Thesis, 2014.

[12] F. Capolino, "Applications of Metamaterials", *CRC Press, Tylor & Francis Group*, 2009, printed book.

[13] N. Abdulrahman, Z. Fan, T. Tonooka, S. Kelly, N. Gadegaard, E. Hendry, A. Govorov and M. Kadodwala, ` Induced Chirality through Electromagnetic Coupling between Chiral Molecular Layers and Plasmonic Nanostructures`, *Nano Lett.*, 2012, Vol.12, pp (977−983).

[14] N. Abdulrahman, C.Syme, C. Jack, A.Karimuallh, L.Barron, N.Gadegaard and M. Kadodwala, ` The origin of off-resonance non-linear optical activity of a gold chiral nanomaterial`,*The Royal Society of Chemistry, Nanoscale*, 2013, Vol.5, pp(12651-12657).

[15] P. Aneesh, K. Vanaja, M. Jayaraj, `Synthesis of ZnO nanoparticles by hydrothermal method`, *Nanophotonic Materials IV*, 2007, Vol. 6639.

[16] X. Bai, L. Li, H. Liu, L. Tan, T. Liu and X. Meng, `Solvothermal Synthesis of ZnO Nanoparticles and Anti-Infection Application in Vivo`, *ACS Applied Materials & Interfaces*, 2015, Vol.7, pp (1308-1317).

[17] J. Xu, Z. Chen, J. Zapien, C. Lee and W. Zhang, `Surface engineering of ZnO nanostructures for semiconductor-sensitized solar cells`, *ADV Mater, Wiley-VCH Verlag GmbH & Co*, 2014, Vol.26, No.31, pp (5337-67).

[18] F. Fan, Y. Ding, D. Liu, Z. Tian and Z. Wang, `Facet-Selected Epitaxial Growth of Heterogeneous

Nanostructures of Semiconductor and Metal: ZnONanorods and Ag Nanocrystals`, *J. American Chemical Society*, 2009, doi:10.1021/ja9036324.
[19] L. Vines and H. Wenckstern, `ZnO-based materials and applications`, *Material Science in Semiconductor Processing*, 2017, Vol.69, pp (1-68).
[20] T. Voss, R. Siegfried and Walodvogel, `Hybrid LEDs based on ZnO nanowire structures`, *Material Science in Semiconductor Processing*, 2017, Vol.69, pp (52-56).
[21] A. Mauro, M. Fragala, V. Privitera and G. Impellizzeri, `ZnO for application in photocatalysis: From thin films to nanostructures`, *Material Science in Semiconductor Processing*, 2017, Vol.69, pp (44-51).
[22] F. Beshkar, H. Khojasteh and M. Salavati-Niasari, `Flowr-Like CuO/ZnO Hybrid Hirachial Nanostructures Grown on Copper Substrate: Glycothermal Synthesis, Characterization, Hydrophobic and Anticorrosion Properties.`, *Materials*, 2017, Vol.10, No.697.
[23] X. Sun, J. Wang, A. Wei, `Zinc oxide nanostructured biosensor for glucose detection`, *Journal of Materials Science and Technology-Shenyang*, 2008, Vol.24, No.4.
[24] J. Jonca, A. Ryzhikov, M. Kahn, K. Fajerwerg, B. Chaudret, A. Chapelle, P. Menini and P. Fau, `Shape-controlled ZnO nanostructures for gas sensing applications`, *Procedia Engineering*, 2014, Vol.87, pp (907-910).
[25] A. Ievtushenko, V. Tkach, V. Strelchuk, L. Petrosian , O. Kolomys, O. Kutsay, V. Garashchenko 2, O. Olifan, S. Korichev, G. Lashkarev and V. Khranovskyy, ` Solar Explosive Evaporation Growth of ZnO Nanostructures `, Appl. Sci., 2017, Vol.7, No. 383
[26] A. Kr Kalita, S. Karmakar, `Variation of Microstrain and Band gap of ZnO nanoparticle Thin Film Prepared by wet Chemical Method`, *International Journal of Innovative Research in Science, Engineering and Technology*, 2017, Vol. 6,No. 4, pp(5395-5401).
[27] M. Yousefi, M. Amiri, R. Azimirad , A. Moshfegh, `Enhanced photoelectrochemical activity of Ce doped ZnO nanocomposite thin films under visible light`, *Journal of Electroanalytical Chemistry*, 2011, Vol.661, pp (106–112).
[28] A. Zak, W. AbdMajid, M. Abrishami, R. Yousefi, `X-ray analysis of ZnO nanoparticles by Williamsone Hall and size-strain plot Methods`, *Solid State Sciences*, 2011, Vol.13, pp (251-256).
[29] V. Mote, Y. Purushotham and B. Dole, `Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles`, *Journal of Theoretical and Applied Physics*, 2012, Vol.6, No.6.
[30] E. Solati and D. Dorranian, ` Estimation of Lattice Strain in ZnO Nanoparticles Produced by Laser Ablation at Different Temperatures`, *Journal of Applied Spectroscopy*, 2017, Vol. 84, No.3.
[31] J. Chauhan, N. Shrivastav, A. Dugaya and D. Pandey, `Synthesis and Characterization of Ni and Cu Doped ZnO`, Journal of Nanomedicine & Nanotechnology, 2017, Vol.8, No.2.