

Synthesis and Characterization of ZnO Nanotubes by Hydrothermal Method

Nehal A. Salahuddin^{1*}, Maged El-Kemary², Ebtisam M. Ibrahim²

¹ Department of Chemistry, Faculty of Science, Tanta University, 31527, Tanta, Egypt

²Nanotechnology center, Department of Chemistry, Faculty of Science, KafrElSheikh University, 33516, KafrElSheikh, Egypt

Abstract- zinc oxide nanotubes were prepared by a hydrothermal method using zinc nitrate as a precursor. The synthesized nanotubes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and their optical properties were characterized using UV-visible spectroscopy. The XRD analysis confirmed that the ZnO nanotubes have the hexagonal wurtzite structure. UV-vis absorption spectrum showed a typical spectrum of pure ZnO nanotubes. According to TEM analysis, the mean length and average outer diameter of the ZnO NTs were about 2.4 μm and 200 nm, respectively.

Index terms- ZnO nanotubes, Hydrothermal, TEM, SEM

I. INTRODUCTION

Zinc oxide is an n-type semiconductor of hexagonal wurtzite structure with optical transparency in the visible range [1]. Zinc oxide (ZnO) is a self-activated crystal of hexagonal wurtzite structure with direct wide band gap energy of 3.37 eV at room temperature [2-4], and has strong excitonic emission in the ultraviolet range even at room temperature due to its larger excitonic binding energy of 60 meV which is significantly larger than other materials [5]. ZnO has attracted much interest as one of the multifunctional inorganic nanoparticles due to its unique combination of superior chemical, physical, optical, biological, electrical, long-term environmental stability, biocompatibility, low cost and non-toxic properties. Therefore, nano-ZnO can potentially be applied to photocatalyst for degradation of waste water pollutants, catalysts, gas sensors, semiconductors, varistors, piezoelectric devices, field-emission displays, ultraviolet (UV) photodiodes, surface acoustic wave (SAW) devices, UV-shielding materials, rubber, medical and dental, pigments and coatings, ceramic, concrete, antibacterial and bactericide, and composites [6-13]. Various morphology of ZnO nanostructures have been realized, such as nanoparticles, nanorods, nanowires, nanobelts, nanotubes, nanobridges, nanowalls, nanohelices, mesoporous single-crystal nanowires, and polyhedral cages [9, 14]. On the other hand, one-dimensional (1D) nanostructures such as rods, wires, belts and tubes have attracted much attention in recent years, due to their many unique properties and the possibility that may be used as building blocks for future electronics and photonics, as well as for life-science applications. 1D nanostructures are expected to play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical and electromechanical

nanodevices. Among the 1D nanostructures, ZnO rods (NRs) and nanotubes (NTs) have been widely studied because of their easy nanomaterials formation and device applications [15]. Recently different synthesis methods have been devised for ZnO nanostructures such as vapor transport process [16, 17], spray pyrolysis [18, 19], thermal decomposition [20], hydrothermal synthesis [21, 22], sol-gel processing [23], direct precipitation and co-precipitation [24-26]. Among these methods, vapor deposition (PVD) and chemical vapor deposition (CVD) have been developed to synthesize ZnO nanoparticles into complex structures such as flower-like and web-like agglomerates. However, in order to obtain the final structure these methods usually require multiple steps, sophisticated equipment and high temperature. In contrast, low-temperature wet chemical processes such as, hydrolysis, precipitation and hydrothermal process are cost-effective and scalable and have been used for preparation a wide variety of ZnO nanostructures [27]. Hydrothermal technique is a promising alternative synthetic method for nanostructure materials because of the low process temperature and very easy to control the particle size. The hydrothermal process have several advantage over other growth processes such as use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and less hazardous. The low reaction temperatures make this method an attractive one for microelectronics and plastic electronics. This method has also been successfully employed to prepare nanoscale ZnO and other luminescent materials [28]. In brief, the particle properties such as morphology and size can be controlled via the hydrothermal process by adjusting the reaction temperature, time and concentration of precursors. The aim of this work was to find a simple route to prepare ZnO nanotubes (powder) via hydrothermal method and characterize the final product using several techniques.

II. EXPERIMENTAL

2.1. Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99% Sigma-Aldrich), sodium hydroxide pellets (NaOH, 99% Merck), Ethylene Diamine (EDA $\text{C}_2\text{H}_8\text{N}_2$; 99%, Merck), Ethanol ($\text{C}_2\text{H}_5\text{OH}$, 95%, Pio chem) were used as received.

2.2. Preparation of ZnO NTs

ZnO NTs were synthesized according to the method proposed by Bin Liu *et al* [22]. Firstly, 40 g of NaOH pellets and 14.874 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 ml of deionized water to prepare a precursor clear solution with a

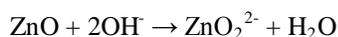
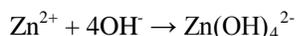
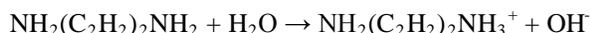
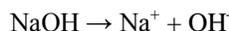
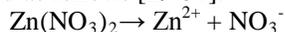
molar ratio of $Zn^{2+}:OH^-$ of 1:20. Then 6 ml of this solution ($Zn^{2+}:OH^- = 1:20$) was mixed with 10ml of distilled water. After that, 50 ml of pure ethanol was added, followed by 10 ml of ethylene diamine. The mixture was then kept in an ultrasonic water bath for 40 minutes and subsequently transferred to a Teflon-lined stainless steel autoclave. The autoclave was kept inside an electric oven set at 180 °C for 2 h and cooled. The precipitate (ZnO NTs) was separated by centrifugation and washed several times with deionized water and pure ethanol. The collected product was dried in a vacuum oven at room temperature for 24 h.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra were measured by FTIR -4100 spectrometer, JASCO with a frequency range from 4000 to 400 cm^{-1} , using KBr disks. The crystallinity and phases of the ZnO nanostructures were characterized by X-ray diffractometer, XRD-6000, Shimadzu, Japan with $Cu-K\alpha$ radiation ($\lambda = 1.5412 \text{ \AA}$), 40 Kv, 30 mA) in the 2θ range of 10-80° with 2°/min scanning rate. The crystallite size (D) of selected samples were estimated using the Scherer's equation, $D = k\lambda / (B \cos\theta)$ where: $k = \text{constant}$ ($0.89 < k < 1$), $\lambda = \text{wavelength of the X-ray}$, $B = \text{FWHM (Full Width at Half Maximum) width of the diffraction peak}$, $\theta = \text{diffraction angle}$. The morphological feature of the nanostructures was observed by a scanning electron microscope SEM-EDS, JSM-6360 LA, JEOL, Japan and a high-resolution transmission electron microscope (HRTEM), JEM-2100, JEOL. The samples for SEM were coated with gold and the samples for TEM analysis were prepared by dropping dilute suspension of ZnO nanostructures onto copper grids. The optical properties of prepared ZnO NTs were analyzed via UV-visible Spectrophotometer (Shimadzu, UV-2450).

III. RESULTS AND DISCUSSION

In general wet synthesis is more attractive compared to dry approaches, because it is able to produce high quality nanomaterials at low cost, and thus promises large-scale production of novel ZnO materials. The usages of a high basic condition and an alcoholic environment are the two crucial keys in ensuring the formation of ZnO_2^{2-} and a controlled release of this species from the alcohol-water mixture phase to the growing ZnO nanostructures. Ethylene diamine acts as chelating ligands to the Zn^{2+} cations in the precursor solution, inhibiting the radial enlargement of the rods. It is believed that the ultrasonic pretreatment of the solution mixture is an important step prior to the hydrothermal reactions at 180°C, which may generate a suitable amount of ZnO cluster nuclei for the subsequent hydrothermal growth [22]. The whole reaction process can be described as follows [29-31]:



3. 1. Fourier Transform infrared spectroscopic analysis

FT-IR spectrum of ZnO nanotubes, (Figure 1) shows the characteristic absorption bands at 508 and 404 cm^{-1} . These two absorption peaks correlate with the bulk To-phonon frequency and the Lo-phonon frequency [32]. The absorption band at 3500 cm^{-1} was assigned to the OH groups on the surface of ZnO.

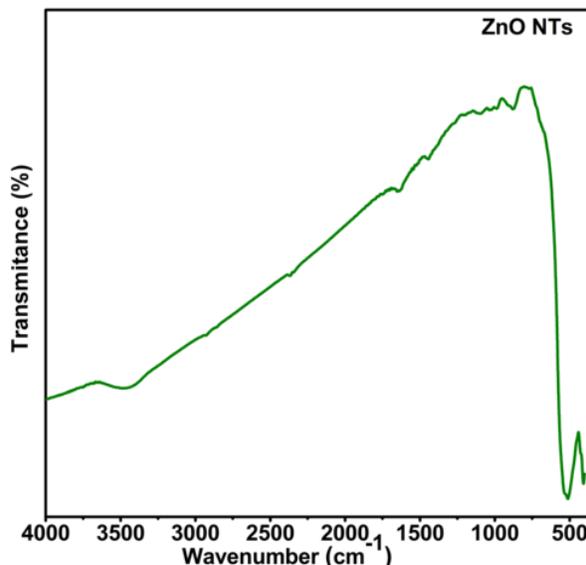


Figure 1 FT-IR spectrum of ZnO nanotubes.

3. 2. Powder X-ray diffraction (XRD) studies

Figure 2. Illustrates the XRD patterns of the as-prepared ZnO NTs. It is apparent that, the diffraction lines are consistent with the values reported in the database of ZnO (JCPDS) card no. PDF 2010: 01-071-6424, providing clear evidence for the formation of hexagonal wurtzite-type structure with cell constants of $a=0.324 \text{ nm}$ and $b=0.520 \text{ nm}$, and no diffraction peaks of any other phases were detected [33]. The average crystalline size of ZnO NTs was calculated according to Scherer's equation and the result was found to be 209.4 nm.

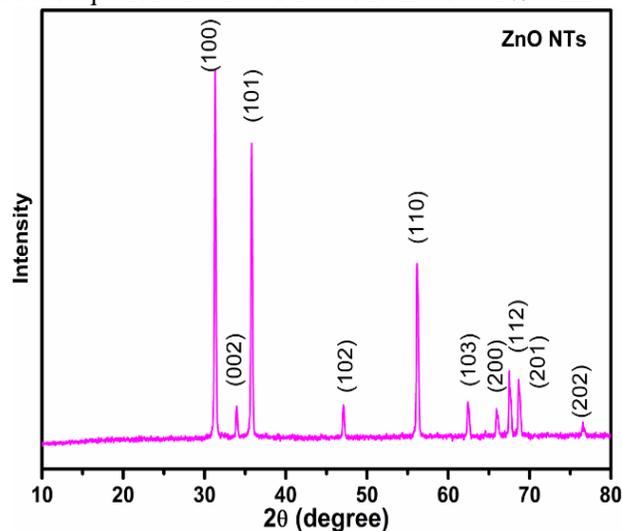


Figure 2. XRD patterns of ZnO nanotubes (ZnO NTs).

3.3. SEM analysis

Figure 3. Shows the SEM images of the ZnO NTs at different magnifications. The images clearly show that uniform ZnO NTs were obtained and most of the nanotubes are parallel to each other. The magnified image shows hollow core structure of the ZnO NTs with single-crystalline, densely packed, faceted hexagonal tabular shape. The average outer diameter and length of the ZnO NTs were about 200 nm and 3 μ m, respectively.

3.4. TEM analysis

Further studies on the structure of the ZnO NTs were done using transmission electron microscope. On the basis of high-resolution TEM the formation of ZnO NTs was further confirmed and the analysis shows that the hollow ZnO NTs grow with a single-crystalline structure and the axial direction is along the [001] as shown in Figure 4. The mean length and wall thickness of the ZnO NTs were about 2.4 μ m and 200 nm, respectively.

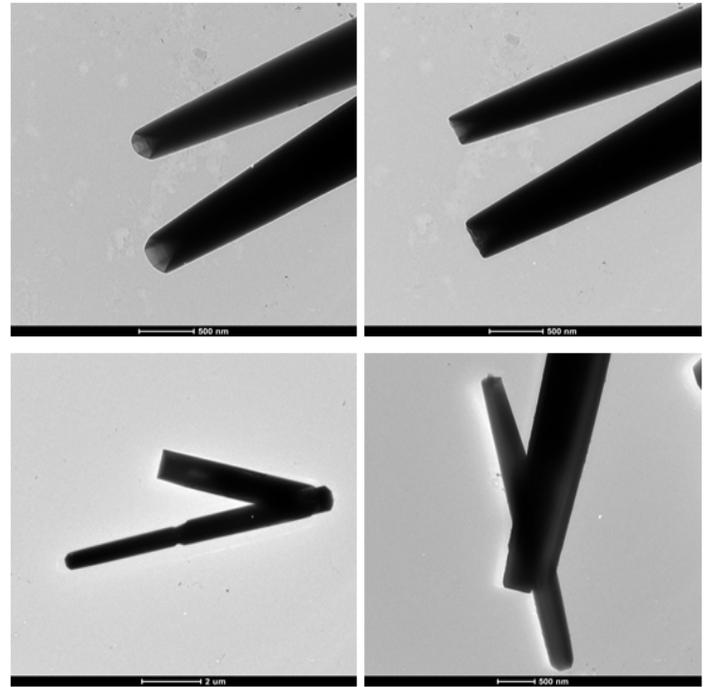


Figure 4 TEM images of ZnO NTs at different magnifications.

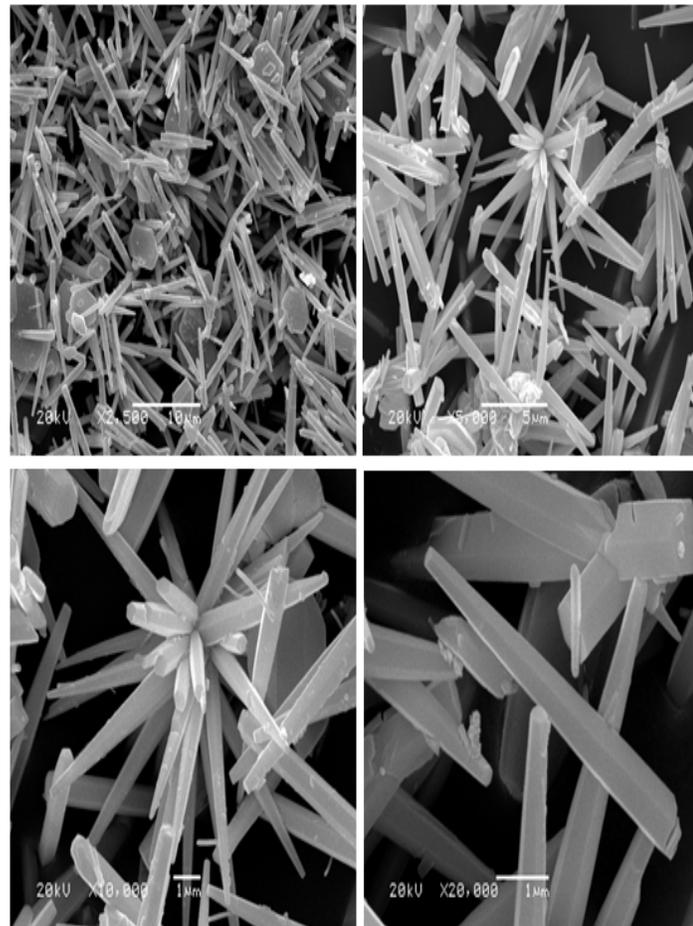


Figure 3 SEM Images of ZnO NTs at different magnifications.

3.5. UV analysis

Figure 5. shows the UV-vis spectra of ZnO NTs. A broad band at 367 nm is the characteristic band of pure ZnO nanotubes [34].

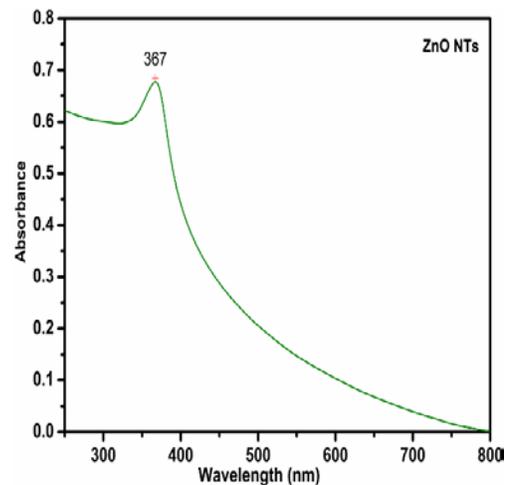


Figure 5 UV- absorption spectra of ZnO NTs.

IV. CONCLUSION

ZnO NTs with an average outer diameter and length of 200 nm and 2.4 μ m respectively were prepared by wet method (hydrothermal method). The FT-IR showed the characteristic absorption bands at 508 and 404 cm^{-1} . These two absorption peaks correlate with the bulk To-phonon frequency and the Lo-phonon frequency. The morphology was evaluated using XRD, SEM and TEM. The XRD analysis confirmed that the ZnO nanotubes have the hexagonal wurtzite structure. The optical properties were measured by UV-vis spectroscopy.

REFERENCES

- [1] D.Raoufi. Synthesis and photoluminescence characterization of ZnO nanoparticles. *Journal of Luminescence*, vol.134, pp. 213-219, 2013.
- [2] G.Z.Cao. Growth of zinc oxide nanorod arrays through sol electrophoretic deposition. *The Journal of Physical Chemistry*, vol. 108, pp.19921-19931, 2004.
- [3] W.D.Zhou, X.Wu, Y.C.Zhang. Solvothermal synthesis of hexagonal ZnO nanorods and their photoluminescence properties. *Materials Letters*, vol.61, pp. 2054-2057, 2007.
- [4] S-H.Hu, Y-C.Chen, C-C.Hwang, C-H.Peng, D-C.Gong. Development of a wet chemical method for the synthesis of arrayed ZnO nanorods. *Journal of Alloys and Compounds*, vol.500, pp.117-121, 2010.
- [5] X.Liu, A.Yamilov, X.Wu, J-G.Zheng, H.Cao, R.P.H.Chang. Effect of ZnO nanostructures on 2-dimensional random lasing properties. *Chemistry of Materials*, vol.16, pp.5414-5419, 2004.
- [6] D.W. Chase, B.C.Kim. Characterization on Polystyrene/ Zinc Oxide nanocomposites prepared from solution mixing. *Polymers for Advanced Technologies*, vol.16, pp.846-850, 2005
- [7] M.Xiong, G.Gu, B.You, L.Wu. Preparation and Characterization of poly(styrene butylacrylate) latex/nano-ZnO nanocomposites. *Journal of Applied Polymer Science*, vol.90, pp.1923-1931, 2003.
- [8] M.El-Kemary, H.El-Shamy, I.El-Mehasseb. Photocatalytic degradation of ciprofloxacin drug in water using ZnO nanoparticles. *Journal of Luminescence*, vol. 130, pp.2327-2331, 2010
- [9] A.Moezzi, A-M.McDonagh, M.B.Cortie. Zinc oxide particles: synthesis, properties and applications. *Chemical Engineering Journal*, vol.185-186, pp.1-22, 2012.
- [10] L.Schmidt-Mende, J.L.MacManus-Driscoll. ZnO-nanostructures; defects and devices. *Materials Today*, vol.10, pp.40-48, 2007.
- [11] X-Y.Ma, W-D.Zhang. Effects of flower-like ZnO nanowhiskers on the mechanical, thermal and antibacterial properties of waterborne polyurethane. *Polymer Degradation and Stability*, vol. 94, pp.1103-1109, 2009.
- [12] Y.Q.Li, S.Y.Fu, Y.W.Mai. Preparation and characterization of transparent ZnO/epoxy nanocomposites with high-Uv shielding efficiency. *Polymer*, vol.47, pp.2127-2132, 2006.
- [13] Y.O.Li, Y.Yang, S.Y.Fu. Photo-stabilization properties of transparent inorganic UV-filter/epoxy nanocomposites. *Composites Science and Technology*, vol.67, pp.3465-3471. 2007.
- [14] Y-B.Hahn. Zinc oxide nanostructures and their applications. *Korean Journal of Chemical Engineering*, vol.28, pp.1797-1813. 2011.
- [15] G-C.Yi, C.Wang, W.I.Park. ZnO nanorods: synthesis, characterization and applications. *Semiconductor Science and Technology*, vol.20, pp.22-34. 2005.
- [16] T.Charinpanitkul, K.Faungnawakij, W.Tanthapanichakoon.Review of recent research on nanoparticle production in Thailand. *Advanced Powder Technology*, vol. 19, pp. 443-457. 2008.
- [17] W.D.Yu, X.M.Li, X.D.Gao. Catalytic synthesis and structure characteristics of high-quality tetrapod-like ZnO nanocrystals by a modified vapor transport process. *Crystal Growth and Design*, vol.5, pp.151-155, 2005.
- [18] A.Ashour, M.A.Kaid, N.Z.El-Sayed, A.A.Ibrahim. Physical properties of ZnO thin films deposited by spray pyrolysis technique. *Applied Surface Science*, vol. 252, pp.7877-7848. 2006.
- [19] S.D.Lee, S-H.Nam, M-H.Kim, J-H.Boo. Synthesis and photocatalytic property of ZnO nanoparticles prepared by spray-pyrolysis method. *Physics Procedia*, vol.32, pp.320-326. 2012.
- [20] Y.Yang, H.Chen, B.Zhao, X.J.Bao. Size control of ZnO nanoparticles via thermal decomposition of zinc acetate coated on organic additives. *Journal of Crystal Growth*, vol.263, pp.447-453. 2004.
- [21] W.L.Suchanek, R.E.Riman. Hydrothermal synthesis of advanced ceramic powders. *Advances in Science and Technology*, vol.45, pp.184-193. 2006.
- [22] B.Liu, H.C.Zeng. Hydrothermal synthesis of ZnO nanorods in the diameter regime of 50 nm. *Journal of American Chemical Society*, vol.125, pp. 4430-4431. 2003.
- [23] A.K.Zak, M.E.Abrishami, W.H.A.Majid, R.Yousef, S.M.Hosseini. Effect of annealing temperature on some structural and optical properties of ZnO nanoparticles prepared by a modified sol-gel combustion method. *Ceramic International*, vol.37, pp.393-398. 2011.
- [24] Y.Wang, C.Zhang, S.Bi, G.Luo. Preparation of ZnO nanoparticles using the direct precipitation method in a membrane dispersion micro-structured reactor. *Powder Technology*, vol.202, pp.130-136. 2010.
- [25] A.S.Lanje, S.J.Sharma, R.S.Ningthoujam, J-S.Ahn, R.B.Pode. Low temperature dielectric studies of zinc oxide (ZnO) nanoparticles prepared by precipitation method. *Advanced Powder Technology*, vol.24, pp.331-335. 2013.
- [26] C.C.Chen, P.Liu, C.h.Lu. Synthesis and characterization of nano-sized ZnO powders by direct precipitation method. *Materials Letters*, vol.65, pp.2059-2061. 2011.
- [27] D.Raoufi. Synthesis and microstructural properties of ZnO nanoparticles prepared by precipitation method. *Renewable Energy*, vol.50, pp.932-937. 2013.
- [28] A.R.Reddy, A.N.Mallika, K.S.Babu, K.V.Reddy. Hydrothermal synthesis and characterization of ZnO nanocrystals. *International Journal of Mining, Metallurgy & Mechanical Engineering*, vol.3, pp.52-55. 2015.
- [29] J.J.Hassan, Z.Hassan, H.Abu-Hassan. High-quality vertically aligned ZnO nanorods synthesized by microwave-assisted CBD with ZnO-PVA complex seed layer on Si substrates. *Journal of Alloys and Compounds*, vol.509, pp.6711-6719. 2011.
- [30] H.Hu, C.Deng, X.Huang. Hydrothermal growth of center-hollow multigonal star-shaped ZnO architectures assembled by hexagonal conic nanotubes. *Materials Chemistry and Physics*, vol. 121, pp. 364-369. 2010;
- [31] J.Yang, Y.Lin, Y.Meng, Y.Liu. A two-step route to synthesize highly oriented ZnO nanotube arrays. *Ceramics International*, vol. 38, pp. 4555-4559. 2012.
- [32] A.Anzlovar, Z.C.Orel, K.Kogej, M.Zigon. Polyol mediated synthesis of zinc oxide nanorods and nanocomposites with poly(methyl methacrylate). *Journal of Nanomaterials*, vol.2012, pp.1-9. 2012.
- [33] C.Li, X.Du, W.Lu, K.Liu, J.Chang, S.Chen, D.Yue, Z.Wang. Luminescent single-crystal ZnO nanorods: controlled synthesis through altering the solvents composition. *Materials Letters*, vol.81, pp.229-231. 2012.
- [34] A. Mostafaei, A.Zolriasatein. Synthesis and characterization of conducting polyaniline nanocomposites containing ZnO nanorods. *Progress in Natural Science: Materials International*, vol.22, pp.273-280. 2012.

AUTHORS

First Author – Nehal A. Salahuddin, Department of Chemistry, Faculty of Science, Tanta University, 31527, Tanta, Egypt.

Second Author – Maged El-Kemary, Nanotechnology center, Department of Chemistry, Faculty of Science, Kafrelsheikh University, 33516, Kafrelsheikh, Egypt.
(elkemary@yahoo.com)

Third Author – Ebtisam.M.Ibrahim, Nanotechnology center, Department of Chemistry, Faculty of Science, Kafrelsheikh University, 33516, Kafrelsheikh, Egypt.(ebtisam_mi@yahoo.com)

Correspondence Author – Nehal. A. Salahuddin, Department of Chemistry, Faculty of Science, Tanta University, 31527, Tanta, Egypt. email address, salahuddin.nehal@yahoo.com, (nehal.ataf@science.tanta.edu.eg), Tell: (002) 01154296713.