© Universiti Tun Hussein Onn Malaysia Publisher's Office

IJIE

Journal homepage: http://penerbit.uthm.edu.my/ojs/index.php/ijie
ISSN : 2229-838X e-ISSN : 2600-7916

The International Journal of Integrated Engineering

Experimental the Influence of Growth Solution on Zinc Oxide Crystal Structures via Hydrothermal Method

Nasha Emieza Ruhaizat[1], Ainun Rahmahwati Ainuddin[1]*, Zakiah Kamdi[1]

[1]Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia, 86400, Batu Pahat, Johor, MALAYSIA

*Corresponding Author

DOI: https://doi.org/10.30880/ijie.2021.13.02.026
Received 1 January 2020; Accepted 3 December 2020; Available online 28 February 2021

Abstract: The properties of Zinc Oxide (ZnO) such as broad direct band gap (3.37eV), good crystallinity and inexpensive materials had gain interest of many researchers. This project is prone to investigate the role of growth solution in the formation of ZnO structures. The objective of this project is to growth the ZnO hexagonal rods structure on the seed layer coated glass substrate and to investigate the influence of ZNH and HMT precursor on structural and morphological properties by varying its molar ratio. Firstly, the ZnO were coated on the microscope glass substrate for five layers using sol gel spin coating techniques. The dimension of the microscope glass substrate used were 2.5cm x 2.5cm. The ZnO seed layer coated substrates then undergo low cost hydrothermal method for the growth of ZnO structures. Different concentration of ZNH:HMT growth solution were used during hydrothermal method at molar ratio 1:1, 1:2 and 2:1 so that the influence of HMT and ZNH in the formation of ZnO structures can be further investigate. Several types of machine were used for the characterization properties of ZnO structures such as X-ray diffraction spectrophotometer (XRD), field emission scanning electron microscopy (FESEM), and energy dispersive x-ray spectroscopy (EDS). XRD analysis revealed that the ZnO samples exhibited hexagonal rods structure. The higher concentration of HMT shows higher intensity of diffraction peaks at the plane (101), (100) and (002) of ZnO structures. FESEM images showed that uneven size of ZnO structure at higher ZNH concentration while large size of ZnO structures can be seen at higher HMT concentration. EDS proved that the elemental composition of Zn and O do exist in the sample.

Keywords: Zinc Oxide (ZnO), zinc nitrate hexahydrate (ZNH), hxamethylenetetramine (HMT), hydrothermal

1. Introduction

Zinc oxide (ZnO) nanostructures which is transparent semiconductor oxide is a promising material [1] that has been studied widely due to its properties such as wide bandgap (3.37 eV) and high exciton binding energy of 60 meV [2], environmental-friendly material [3] and can be produce abundantly due to its low cost of material. ZnO has various types of nanostructures, such as nanorods, nanowires, nanoparticles, nanobelts, nanopillars nanoflowers, and nanotubes [4-5]. The different types of ZnO nanostructures, size, morphology, and shape resulted in different application [6]. The potential application of ZnO nanostructures, such as gas sensor may occur due to its piezoelectric and pyroelectric properties [7]. ZnO nanostructures also suitable for electronic and laser technology due to its high thermal and mechanical stability at room temperature [8]. ZnO is suitable for biomedicine and in the pro-ecological system due to its low toxicity, biocompatibility, and biodegradability properties. This study is focusing on analyzing the growth of ZnO structures by varying the molar ratio of ZNH and HMT during the hydrothermal process. The size of ZnO rods differs at different concentration of growth solution [9]. A high concentration of HMT in growth process resulting in a high density of ZnO nanorods while a high density of zinc salt concentration causes the bigger size and larger surface area of ZnO nanotubes and slowly changing into other morphology [10]. Flake-like and rod-like ZnO structure in a high concentration of HMT

*Corresponding author: ainun@uthm.edu.my

also had been reported [11]. ZnO structure grown via hydrothermal method was indexed to hexagonal wurtzite structure [12]. Initially, ZnO seed layer must be deposited onto the substrate such as micro slide glass substrate [13], indium tin oxide (ITO) substrate [4], zinc substrate [14], Si substrate [15] and soda-lime glass substrate [16]. There are different method deposition of ZnO seed layer onto the substrate, such as spin coating [17], dc-magnetron sputtering [18], and thermal deposition [19]. Next, ZnO structures are grown via different methods, such as chemical vapor deposition, electrochemical deposition, vapor-liquid-solid, and hydrothermal [20]. Among all of these methods, hydrothermal are consider the most favorable method due to the simplest procedure methodology and cost-effectiveness for large scale of ZnO structures production [21]. Unlike other methods, hydrothermal does not require pressure and high temperature to fabricate ZnO structures makes them the most economical method. The influence of hexamethylenetetramine (HMT) and zinc nitrate hexahydrate (ZNH) molar ratio on the growth of ZnO structures are analyzed.

2. Experimental Methods

2.1 Preparation of seed solution using the sol-gel technique

A mixture solution of zinc acetate (ZnAc), diethanolamine (DEA), Isopropanol (IPA) and distilled water was prepared by sol-gel technique. ZnAc which act as a precursor to synthesis ZnO seed was dissolved in IPA alcoholic solvent. The function of using IPA alcoholic solvent is to reduce the viscosity of the solution without altering the end product of ZnO seed. By using magnetic stirrer, the solution was stirred continuously for about 30 minutes. Next, DEA which act as a stabilizer and distilled water was added drop by drop into this mixture solution containing ZnAc and IPA to obtain a clear solution. The solution was stirred again at 60 – 70 °C until the cloudy color solution turns colorless and aged for 24 hours to yield homogenous mixture. The mixture composition of ZnO sol-gel was summarized as Table 1 below:

Table 1 - The mixture composition of zinc oxide sol-gel

Material	Molecular weight (g/mol)	Ratio	Molecular weight to the ratio (g/mol)	Weight ratio	Weight (g)	Mol
ZAD	219.50	1.00	219.50	0.14	7.00	0.03
DEA	105.14	1.00	105.14	0.07	3.50	0.03
IPA	60.10	20.00	1202.00	0.78	39.00	0.65
H_2O	18.02	1.00	18.02	0.01	0.50	0.03
Total			1544.66	1.00	50	0.74

2.2 Preparation of Microscope Slide Glass Substrate

Microscope slide glass with dimension 2.5 cm x 2.5 cm was prepared. Glass cutter had been used to cut the microscope slide glass substrate to obtain the desired dimension. Every piece of the glass substrate should have the same size. Next, the glass substrates were cleaned using acetone follow by rinsing using distilled water. For further cleaning, the substrates then were cleaned again by using ethanol and rinsing using DI water and dry using air blower. It is essential to clean the glass substrate to ensure no residual attached to the glass substrate that can affect the result of ZnO crystal.

2.3 Deposition of ZnO Seed Layer

Deposition of ZnO seed layer was obtained by using sol-gel spin coating deposition techniques. Spin coating is a process where the seed layer is deposited onto the flat surface of the glass substrate. Put the prepared solution drop by drop on the glass substrate until it's fully covered the surface of the glass substrate and spin coating at 3000 rpm for 30 s. Heat-treated then were applied to the glass substrate at 250 °C in air for 5 minutes. The deposition method was repeated for five times to get 5 layers on the same substrate. For the final layer, ZnO seed layer was heated on the hot plate at 250°C for 1 hour to obtain a uniform seed layer. Fig. 1 shows an experimental set-up for deposition of ZnO seed layer using a spin coating technique.

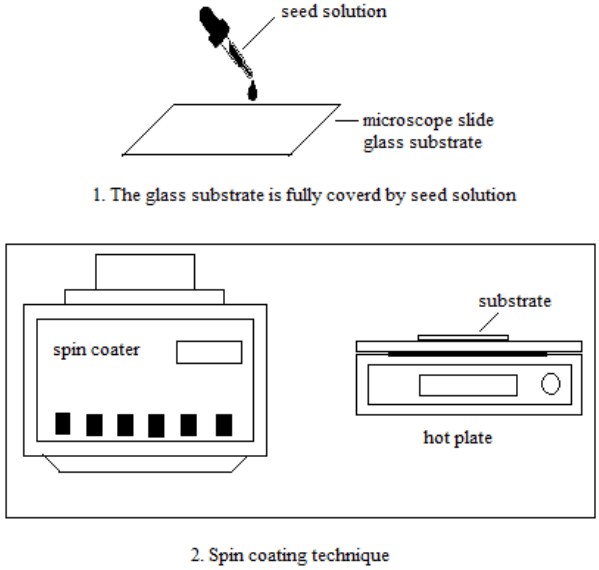


Fig. 1 - Deposition of ZnO seed layer via spin coating technique

2.4 Preparation of ZnO Crystal using the Hydrothermal Method

ZNH and HMT were used synthesis ZnO hexagonal rod. ZNH and HMT with various molar ratio were mixed in 50 ml distilled water under room temperature to form a mixture solution. The molar ratio for ZNH:HMT used in this study are 1:1, 1:2, and 2:1. The solution then was poured inside Teflon-lined autoclave. Table 2 below shows the weight composition of precursors for molar ratio 1:1, 1:2, and 2:1.

Table 2 - The weight composition of precursor for molar ratio 1:1, 1:2 and 2:1

Weight composition of ZNH: HMT for molar ratio 1:1					
Material	Molecular weight (g/mol)	Ratio	mM	Mol	Mol x molar mass = weight (g)
ZNH	297.48	1	10	0.01	2.97
HMT	140.19	1	10	0.01	1.40
Weight composition of ZNH: HMT for molar ratio 1:2					
Material	Molecular weight (g/mol)	Ratio	mM	Mol	Mol x molar mass = weight (g)
ZNH	297.48	1	10	0.01	2.97
HMT	140.19	2	20	0.02	2.80
Weight composition of ZNH: HMT for molar ratio 2:1					
Material	Molecular weight (g/mol)	Ratio	mM	Mol	Mol x molar mass = weight (g)
ZNH	297.48	2	10	0.01	2.97
HMT	140.19	1	5	0.005	0.70

ZnO seed layer coated substrate was kept inside autoclave in a vertical position. The autoclave then was sealed and maintained at 90 °C for 3 hours in the oven. Next, the sample was taken out from the autoclave and wash using distilled water to remove any residual materials. The sample was put on the hot plate for post heat treatment at 90 °C for 5 minutes. Fig. 2 shows an experimental set-up image for the position ZnO seed layer coated substrate inside the autoclave.

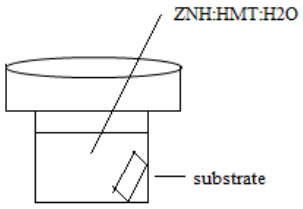


Fig. 2 - The vertical position of ZnO seed layer coated substrate inside an autoclave

3. Results and Discussion

X-ray diffraction (XRD) range pattern between 20 - 80° was used to analyze the crystal structure of ZnO synthesis at a different molar ratio of ZNH:HMT using the hydrothermal method. The diffraction peak to be indexed to the Joint Committee on Powder Diffraction Standards (JCPDS) card no 36-1451 which drive the ZnO sample to exhibit hexagonal wurtzite structure. Fig 3 shows the intensity and diffraction peaks of each sample.

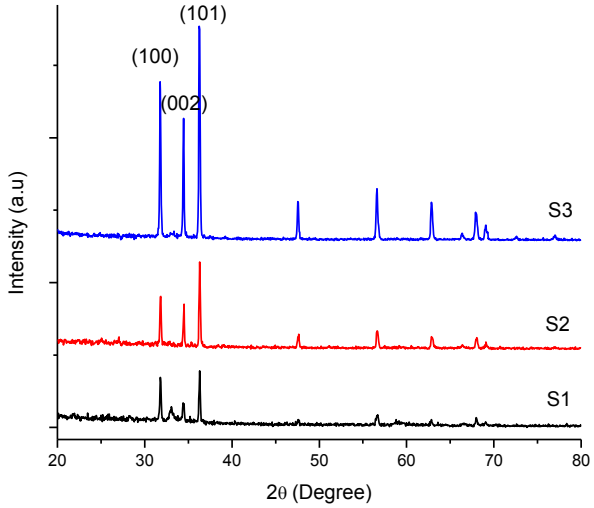


Fig. 3 - XRD pattern of ZnO samples for the different molar ratio of ZNH:HMT at 90°C for 3 hours; (S1) 2:1, (S2) 1:1, and (S3)1:2

From Fig. 3, the primary diffraction peaks observed at 2θ value with higher intensity value are 36.3°, 31.8° and 34.4° corresponding to the planes (101), (100) and (002). Since all the ZnO sample major peaks are indexed to the plane (101), (100) and (002) refer to the JCPDS card no 36-1451, it is indicated that the result obtained from ZnO sample exhibit hexagonal wurtzite structure with good crystallinity particles [21]. S1 had lower intensity peaks compare to S2 while S3 had higher intensity peaks compare to S2. This is because S1 had a higher concentration of ZNH compare to S2, while S3 had a higher concentration of HMT compare to S2. This observation showed that S3 had the best crystalline structure among the samples. The crystalline structure of the ZnO hexagonal rods structure had a strong dependency on the concentration of ZNH and HMT. The higher concentration of ZNH and the lower concentration of HMT in S1 cause Zn^{2+} unable to react with OH^- comes from HMT to form ZnO crystal. ZnO chemical reaction is as below:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6CH_2O + 4NH_3 \quad (1)$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

$$2OH^- + Zn^{2+} \leftrightarrow ZnO + H_2O \quad (3)$$

Upon heating, HMTA decomposes to form formaldehyde and ammonia. Ammonia then reacts with water to produce OH^- which is the main factor of crystallization of ZnO [9]. There was an impure peak between the plane (100) and (002) in S1 graph which strongly supports the idea that Zn^{2+} unable to react with OH^- to form ZnO crystal. The impure peaks exist in S1 between the plane (100) and (002) may due to the free Zn^{2+} in the sample. Meanwhile, S3 had higher intensity diffraction peaks than S2 due to the high concentration of HMT in S3. The formation of ZnO crystal structure involved a reaction between 2 mol of OH^- and 1 mol of Zn^{2+}. The high concentration of HMT and enough amount of zinc precursor

determination guide the orientation and lateral growth of ZnO structures [22]. Fig. 4 shows FESEM image is used to analyze ZnO sample surface morphology of ZNH:HMT precursors at molar ratio 2:1, 1:1, and 1:2.

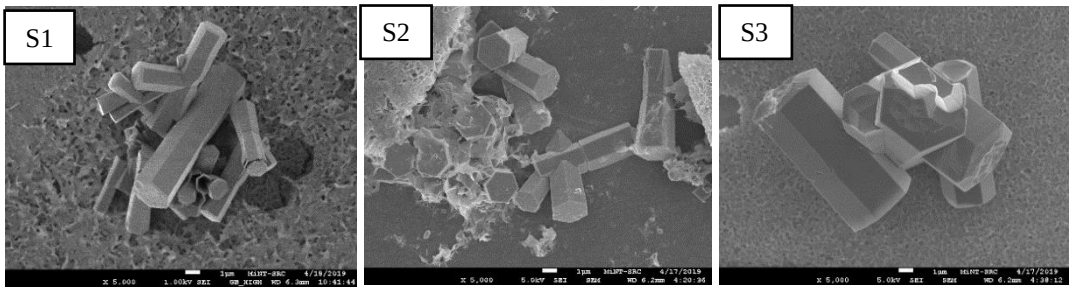
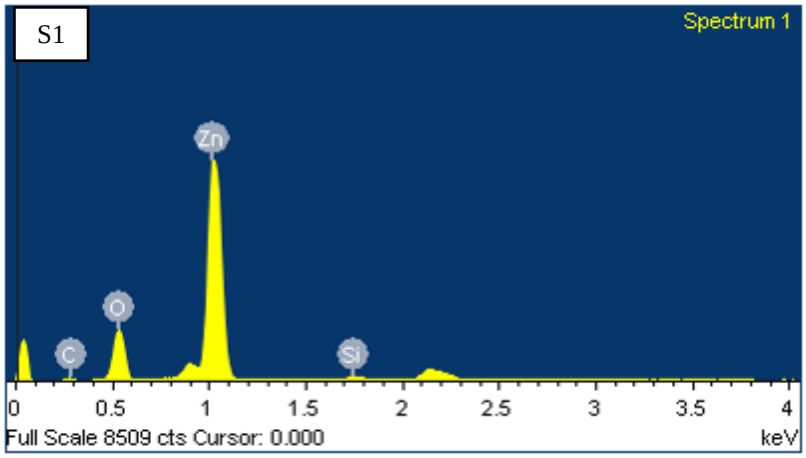


Fig. 4 - FESEM images of ZnO sample for the various molar ratio of ZNH:HMT at 90°C for 3 hours; (S1) 2:1, (S2) 1:1, and (S3)1:2

The images result from Fig.4 can be concluded that the ZnO sample had a strong dependency on ZNH:HMT molar ratio. Different growth solution molar ratio had different length and diameter size of ZnO samples. However, all the ZnO samples exhibit hexagonal rod-like shape structure. The length and diameter size of S1 ranging between 3.83 to 9.74 µm and 1.25 to 2.96 µm, respectively. The significant difference between structure range size explained that S1 had an uneven size of ZnO structures. Various size of ZnO hexagonal rod structure exists in S1. This may due to the low concentration of HMT in growth solution resulted in an insufficient supply of OH^- to react with Zn^{2+} to form ZnO hexagonal rod structures. The previous study stated that ZnO hexagonal nanorods were grown unevenly at 1.5:1 molar ratio of Zn^{2+}:HMT ranging size between 60 to 70nm [10]. The growth of ZnO hexagonal structure depending on OH^- supply from the decomposition of HMT. The length and diameter size of S2 ranging between 6.69 to 7.04µm and 2.32 to 2.58µm, respectively. There were not much different in length and diameter of ZnO hexagonal rod structures. The size of ZnO hexagonal rod structures was considered much similar to each other. The length size of S3 ranging between 8.48 to 9.89 µm and the diameter size ranging between 5.41 to 6.58 µm. The length and diameter size of S3 was considered larger than S2 due to the higher concentration of HMT in S3. The size of ZnO rods depends on the concentration of HMT because of critical monomers diffusion and limited growth [9]. Table 3 and Fig. 5 shows that EDS analysis is used for the elemental analysis to confirm the presence of ZnO hexagonal rod-like shape on the glass substrate.

Table 3 - Percentage of weight element composition of ZnO sample for different ZNH: HMT molar ratio at 90°C for 3 hours; (S1)2:1, (S2)1:1 and (S3)1:2

S1		S2		S3	
Element	Weight (%)	Element	Weight (%)	Element	Weight (%)
O	22.37	O	22.72	O	22.40
Zn	72.44	Zn	71.89	Zn	73.39



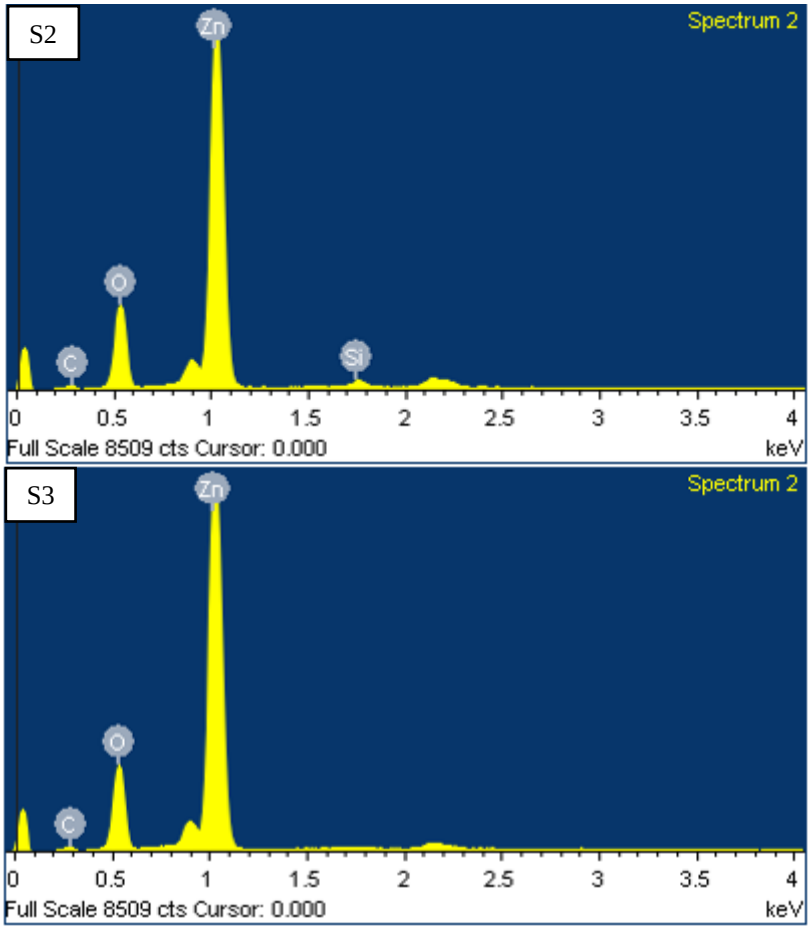


Fig. 5 - EDS analysis of ZnO sample for different ZNH: HMT molar ratio at 90°C for 3 hours; (S1)2:1, (S2)1:1 and (S3)1:2

All the samples above contain element Zn and O. The presence of higher weight percentage of Zn and O as the main element composition indicates that pure ZnO hexagonal rod-like shape does exist on the glass substrate meanwhile the present of Si may due to the element component on the glass substrate itself.

4. Conclusion

The result obtained can be summarized as follows:

1. It is indicated that the result obtained of ZnO sample exhibit hexagonal wurtzite structure with good crystallinity particles since all the ZnO sample major peaks are indexed to the plane (101), (100) and (002) refer to the JCPDS card no 36-1451.
2. SEM images showed that ZnO sample had a strong dependency on ZNH:HMT molar ratio. Sample S1 with a high concentration of ZNH showed uneven structure size meanwhile sample S3 with a high concentration of HMT showed more significant and constant ZnO structure.
3. The higher elemental percentage of zinc and oxygen confirmed the presence of ZnO hexagonal rod-like shape on the glass substrate.

Acknowledgement

The authors would like to thanks Ministry of Higher Education Malaysia and Universiti Tun Hussein Onn Malaysia Research Management Centre (RMC) for providing research funding support Grant (FRGS K202).

References

[1] W. Khan and S. D. Kim, "Optimum post-growth rapid thermal annealing temperature for the structural and optical properties of hydrothermal ZnO Nanorods," Proc. 2017 14th Int. Bhurban Conf. Appl. Sci. Technol. IBCAST 2017, no. 100, pp. 40–43, 2017

[2] D. B. Shinde, "Influence of Annealing Temperature on Photoelectrochemical Performance of ZnO Thin Films Prepared By Low-Temperature Aqueous Chemical Reflux Technique," no. 64259, pp. 32–36, 2018

[3] M. Thirumavalavan, K.-L. Huang, and J.-F. Lee, "Preparation and Morphology Studies of Nano Zinc Oxide Obtained Using Native and Modified Chitosans," Materials (Basel)., vol. 6, no. 9, pp. 4198–4212, 2013

[4] D. Phromyothin et al., "Growth of ZnO nanorods via low-temperature hydrothermal method and their application for Hydrogen production," Mater. Today Proc., vol. 4, no. 5, pp. 6326–6330, 2017

[5] S. Ilican, "Effect of Na doping on the microstructures and optical properties of ZnO nanorods," J. Alloys Compd., vol. 553, pp. 225–232, 2013

[6] K. A. Wahid, W. Y. Lee, H. W. Lee, A. S. Teh, D. C. S. Bien, and I. A. Azid, "Effect of seed annealing temperature and growth duration on hydrothermal ZnO nanorod structures and their electrical characteristics," Appl. Surf. Sci., vol. 283, pp. 629–635, 2013

[7] G. N. Narayanan and K. Annamalai, "Role of hexamethylenetetramine concentration on structural, morphological, optical and electrical properties of hydrothermally grown zinc oxide nanorods," J. Mater. Sci. Mater. Electron., vol. 27, no. 11, pp. 12209–12215, 2016

[8] A. J. Haider, F. I. Sultan, and A. Al-Nafiey, "Controlled growth of different shapes for ZnO by hydrothermal technique," AIP Conf. Proc., vol. 1968, 2018

[9] W. Feng, B. Wang, P. Huang, X. Wang, J. Yu, and C. Wang, "Wet chemistry synthesis of ZnO crystals with hexamethylenetetramine(HMTA): Understanding the role of HMTA in the formation of ZnO crystals," Mater. Sci. Semicond. Process., vol. 41, pp. 462–469, 2016

[10] L. Roza, K. A. J. Fairuzy, P. Dewanta, A. A. Umar, M. Y. A. Rahman, and M. M. Salleh, "Effect of molar ratio of zinc nitrate: hexamethylenetetramine on the properties of ZnO thin film nanotubes and nanorods and the performance of dye-sensitized solar cell (DSSC)," J. Mater. Sci. Mater. Electron., vol. 26, no. 10, pp. 7955–7966, 2015

[11] H. Li, S. Jiao, H. Li, and L. Li, "Growth and characterization of ZnO nanoflakes by hydrothermal method : effect of hexamine concentration," pp. 2569–2573, 2014

[12] E. S. Babu, S. Hong, T. S. Vo, J. Jeong, and H. K. Cho, "Photoelectrochemical Water Splitting Properties of Hydrothermally-Grown ZnO Nanorods with Controlled Diameters," vol. 11, no. 1, pp. 65–72, 2015

[13] H. A. Wahab, A. A. Salama, A. A. El-Saeid, O. Nur, M. Willander, and I. K. Battisha, "Optical, structural and morphological studies of (ZnO) nano-rod thin films for biosensor applications using sol gel technique," Results Phys., vol. 3, pp. 46–51, 2013

[14] R. Shi, P. Yang, X. Dong, Q. Ma, and A. Zhang, "Growth of flower-like ZnO on ZnO nanorod arrays created on zinc substrate through low-temperature hydrothermal synthesis," Appl. Surf. Sci., vol. 264, pp. 162–170, 2013

[15] J. Rouhi, M. Alimanesh, R. Dalvand, C. H. R. Ooi, S. Mahmud, and M. R. Mahmood, "Optical properties of well-aligned ZnO nanostructure arrays synthesized by an electric field-assisted aqueous solution method," Ceram. Int., vol. 40, no. 7 PART B, pp. 11193–11198, 2014

[16] E. Pourshaban, H. Abdizadeh, and M. R. Golobostanfard, "ZnO Nanorods Array Synthesized by Chemical Bath Deposition: Effect of Seed Layer Sol Concentration," Procedia Mater. Sci., vol. 11, pp. 352–358, 2015

[17] A. M. Holi et al., "Effect of hydrothermal growth time on ZnO nanorod arrays photoelectrode performance," Optik (Stuttg)., vol. 127, no. 23, pp. 11111–11118, 2016

[18] S. Pokai et al., "Influence of seed layer thickness on well-aligned ZnO nanorods via hydrothermal method," Mater. Today Proc., vol. 4, no. 5, pp. 6336–6341, 2017

[19] M. Poornajar, P. Marashi, D. Haghshenas Fatmehsari, and M. Kolahdouz Esfahani, "Synthesis of ZnO nanorods via chemical bath deposition method: The effects of physicochemical factors," Ceram. Int., vol. 42, no. 1, pp. 173–184, 2016

[20] M. Wang, C. Xing, K. Cao, L. Meng, and J. Liu, "Alignment-controlled hydrothermal growth of well-aligned ZnO nanorod arrays," J. Phys. Chem. Solids, vol. 75, no. 7, pp. 808–817, 2014

[21] P. N. Mbuyisa, O. M. Ndwandwe, and C. Cepek, "Controlled growth of zinc oxide nanorods synthesised by the hydrothermal method," Thin Solid Films, vol. 578, pp. 7–10, 2015

[22] H. Avireddy, H. Kannan, P. Shankar, G. K. Mani, A. J. Kulandaisamy, and J. B. B. Rayappan, "Non-mutually exclusive dual role of hexamethylenetetramine on the growth of ZnO nanostructures and their sensing footprints," Mater. Chem. Phys., vol. 212, pp. 394–402, 2018