https://doi.org/10.31436/iiumecp.v1i1.3001

ROLE OF HYDROXYL IONS IN THE GROWTH OF 1-D ZINC OXIDE ON WIRE USING DIRECT HEATING METHOD

ANH THI LE[1,2], THI DUY HANH LE[2], NGUYEN ANH TUAN HUYNH[2], KUAN-YEW CHEONG[1], CHEE-MENG KOE[1], WAI-KIAN TAN[3], SUMIYYAH BINTI SABAR[1], SWEE-YONG PUNG[1]*

[1]*School of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia*

[2]*Faculty of Chemical and Food Technology, Ho Chi Minh City University of Technology and Education (HCMUTE), No. 1 Vo Van Ngan, Thu Duc City, Ho Chi Minh City, Vietnam*

[3]*Institute of Liberal Arts and Sciences, Toyohashi University of Technology, Toyohashi, 441-8580, Aichi, Japan*

**Corresponding author: sypung@usm.my*

ABSTRACT: One dimensional zinc oxide (1-D ZnO) array has been utilized for various application such as photocatalytic, solar cells, and light emitting diode. Low-temperature solution-based methods including hydrothermal, chemical bath deposition, and precipitation methods have been frequently employed for the growth of 1-D ZnO nanostructures. These methods are easy to handle, less expensive, and environmental friendly. However, the main drawback of solution-based methods is the long growth duration of ZnO nanostructures varying from 2 to 12 hours. Direct heating method enables ZnO nanostructures to grow rapidly (less than 1 hour) on a metal substrate by employing the Joule heating effect. Under direct heating condition, the effect of hydroxyl ion (OH^-) on the formation of 1-D ZnO is crucial to investigate. In this work, ZnO submicron-rods were grown on kanthal wire with different OH^- concentrations. The formation of ZnO submicron-rods was verified by FESEM, TEM and XRD analyses. At low OH^- ion concentration, $Zn(OH)_2$ precipitates were formed in the bulk solution. With the increase of OH^- ion concentration, $[Zn(OH)_4]^{2-}$ complexes were formed, which initiated the nucleation of ZnO on the kanthal wire surface. After direct heating for 10 minutes using 1.2M of OH^- ion, ZnO submicron-rods were fully grown on the wire with an average diameter of 304 ± 78.6 nm. In conclusion, tailoring the OH^- ion concentration eliminated the formation of $Zn(OH)_2$ precipitates and increased the $[Zn(OH)_4]^{2-}$ complexes which was favorable for the growth of 1-D ZnO in a controlled manner using direct heating method.

KEYWORDS: *ZnO, Direct heating; Hydroxyl ion; Kanthal wire*

1. INTRODUCTION

One dimensional zinc oxide (1-D ZnO) array has been attracted much attention in advanced applications including light-emitting devices [1], solar cells [2], gas sensors [3], and photocatalysis [4]. It is known that the optical and electrical properties of ZnO nanostructure are highly dependent on shape, size, and orientation [5]. ZnO arrays has been commonly synthesized by two-steps hydrothermal with long growth duration (3h to 12h) [6]. Developing a rapid and simple method has been attracted much attention for synthesizing 1-D ZnO arrays on supportive substrate.

https://doi.org/10.31436/iiumecp.v1i1.3001

Low-temperature (65 – 95°C) solution-based methods including hydrothermal [6], chemical bath deposition [7], or precipitation [8] methods were frequently employed for the growth of ZnO nanostructures. These methods are easy to handle, low temperature (60-100°C), less expensive, and environmental friendly. However, long growth duration and randomly orientation of ZnO crystal are the main drawback of solution-based methods. Direct heating method had been adapted for growing 1-D ZnO nanorods/nanowires on printed circuit board [9], and stainless steel mesh [10]. By employing the Joule heating effect, the substrate is directly heated when the current is passing through. Under direct heating condition, the effect of hydroxyl ions (OH^-) on formation of 1-D ZnO nanostructures on the heated substrate is crucial to investigate. Thus, in this study, the structure and morphology of ZnO was examined to evaluate the role of hydroxyl ions on the growth of ZnO on kanthal wire.

2. MATERIALS AND METHODS

The materials used to synthesize ZnO were sourced from Merck including zinc acetate dehydrate (CAS-383058) and sodium hydroxide (CAS-1064981000). Kanthal wire (Vapour Tech, 20Ga, coil 30 feet) was used as a supportive substrate for the growth of ZnO.

Direct heating method was used to synthesize ZnO on kanthal wire as reported in previous study [11]. Firstly, kantal wire was cut, coiled into a string and ultrasonic cleaned using ethanol and dried at 80°C. Secondly, solutions of 0.1M zinc acetate dehydrate and sodium hydroxide with various concentrations of 0.8M, 1M and 1.2M were prepared separately using distilled water. Zinc acetate dehydrate solution was added dropwise into sodium hydroxide under vigorous stirring for 15 min at room temperature. Both ends of the kanthal coil were connected with electrical power supply of 30W. The kanthal coil was dipped into the as-prepared precursor mixture. The coil was heated up when applying the power of 30W for 10min. The temperature of the wire was measured by a digital thermometer. After 10 min of direct heating, the coil was washed with distilled water and dried at 80°C. The as-synthesized samples were designated as ZnO/wire-0.8M, ZnO/wire-1M, and ZnO/wire-1.2M corresponding to the OH^- concentration of 0.8M, 1M, and 1.2M, respectively.

The structure and morphology of as-synthesized samples were analyzed using X-ray Diffraction (XRD, Bruker D8, accelerating voltage of 40kV, Cu K_a radiation k = 1.5406 Å) and Field Emission Scanning Electron Microscope (FESEM, Zeiss Supra 35VP, WD = 5mm, accelerating voltage of 10kV, and InLens detector), Transmission Electron Microscope (TEM, Tecnai G220 S-Twin, 200kV field emission gun) analyses, respectively. The average length and diameter of ZnO rods were measured from FESEM images using ImageJ software with the sample size of 10.

3. RESULTS AND DISCUSSION

Figure 1 shows XRD spectra of bare kanthal wire and as-synthesized ZnO/wire grown at various OH^- concentration of 0.8M, 1M, and 1.2M. The bare kanthal wire had diffraction peaks of Aluminum Chromium (Al_8Cr_5, Hexagonal, ICDD. no. 98-000-0411) and Aluminum Chromium Iron ($Al_{0.5}Cr_{0.5}Fe$, Cubic, ICDD. no. 98-006-5697). After growing ZnO with OH^- concentration of 0.8M and 1M (sample ZnO/wire-0.8M and ZnO/wire-1M) most of the diffraction peaks of bare kanthal wire were suppressed. Only main diffraction peaks of Al_8Cr_5 (at 29.29° and 47.33°) and $Al_{0.5}Cr_{0.5}Fe$ (at 44.85°, 65.02°, and 82.34°) were found at ZnO/wire-1M sample. When OH^- concentration was increased to 1.2M (sample ZnO/wire-1.2M) additional diffraction peaks at 34.4°, 36.6°, and 63.1° matched the crystallographic (002), (011) and (013) planes of ZnO hexagonal Wurtzite structure (ICDD no.: 98-010-5281), respectively. Similar diffraction patterns of ZnO was reported by Amin et al. [12], where ZnO nanorods

https://doi.org/10.31436/iiumecp.v1i1.3001

were grown on silicon substrate at 90°C for 5h using hydrothermal method. The crystallographic (002) plane had the strongest diffraction peak of ZnO/wire-1.2 sample, indicating that ZnO was preferably grown in [001] direction [13].

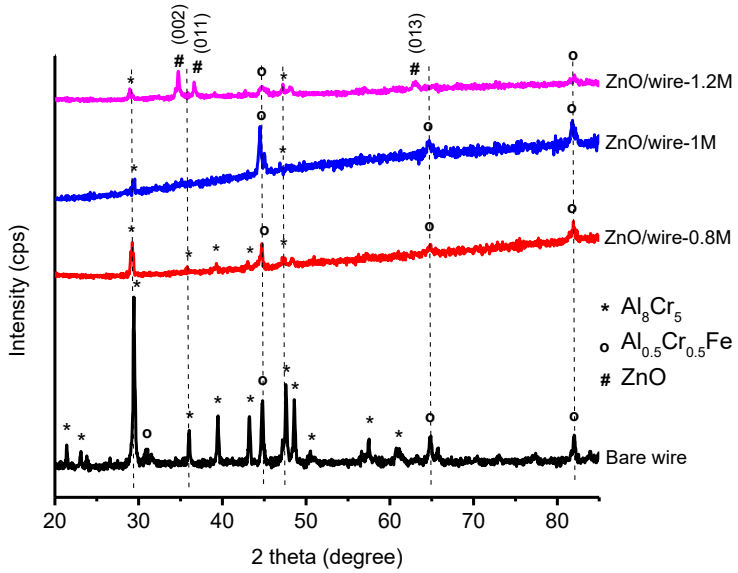

Figure 1. XRD spectra of bare kanthal wire and as-synthesized ZnO/wire grown at various OH- concentration of 0.8M, 1M, and 1.2M.

The role of OH^- ions on the growth of ZnO on kanthal wire was further investigated via morphology evolution using FESEM analysis as shown in Figure 2. After direct heating the wire at 30W for 10min the solution temperature was 73 ± 5°C. Figure 2a shows the morphology of ZnO/wire-0.8M sample, containing wo kinds of distinct products i.e., flower-like ZnO and octahedral $Zn(OH)_2$. The average diameter and length of flower-like ZnO were 67.2 ± 4.8um and 619.4 ± 180.9nm, respectively. The average size of octahedral $Zn(OH)_2$ particles was 2.7 ± 0.6µm which were aggregated from smaller microcrystals. Similar observation was found at the study of phase transformation of $Zn(OH)_2$ to ZnO particles at 80°C for 2h using hydrothermal method [14]. When the OH- concentration increased to 1M (Figure 2b), more ZnO nucleus was started growing on kanthal wire. At OH^- concentration of 1.2M, ZnO rod-shaped was fully grown on the wire surface with average diameter of 304 ± 78.6nm as depicted in Figure 2c. The FESEM images ZnO/wire-1.2M are consistent with the XRD spectra in Figure 1, showing that ZnO sub-micron rods grew on kanthal wire along [001] (c-axis) direction. Figure 2d & 2e shows TEM images of ZnO/wire-1.2M. The lattice fringes of the ZnO rods were 0.26 nm which corresponds to the (002) plane of the wurtzite ZnO. Similar lattice fringes spacing of ZnO was observed in the study of Hsu et al., in which ZnO nanorods were grown on stainless steel mesh by hydrothermal method [15].

Based on the XRD spectra, FESEM and TEM images, it can be concluded that the OH- ions play a major role for the growth of 1-D ZnO structure on kanthal wire. The OH^- ions created the super-saturation of aqueous solution of zinc acetate and sodium hydroxide, which was the key driving force for the growth of ZnO during direct heating. At relatively low OH^- concentration (0.8M), $Zn(OH)_2$ precipitates were mainly formed in the solution rather than growing on the kanthal wire surface. With the increase of OH- concentration to 1.2M, $Zn(OH)_2$ precipitates were dissolved forming soluble $[Zn(OH)_4]^{2-}$ complexes which were favorable for the nucleation of ZnO during direct heating the wire [14]. It is well known that that the hexagonal wurtzite ZnO was the polar crystal; and polar face (002) with surface dipoles were

https://doi.org/10.31436/iiumecp.v1i1.3001

thermodynamically less stable [4]. Thus, $[Zn(OH)_4]^{2-}$ ions could be adsorbed on the positively charged (002) plane of ZnO, promoting the crystal growth on [001] direction for forming 1-D ZnO submicron rod shape.

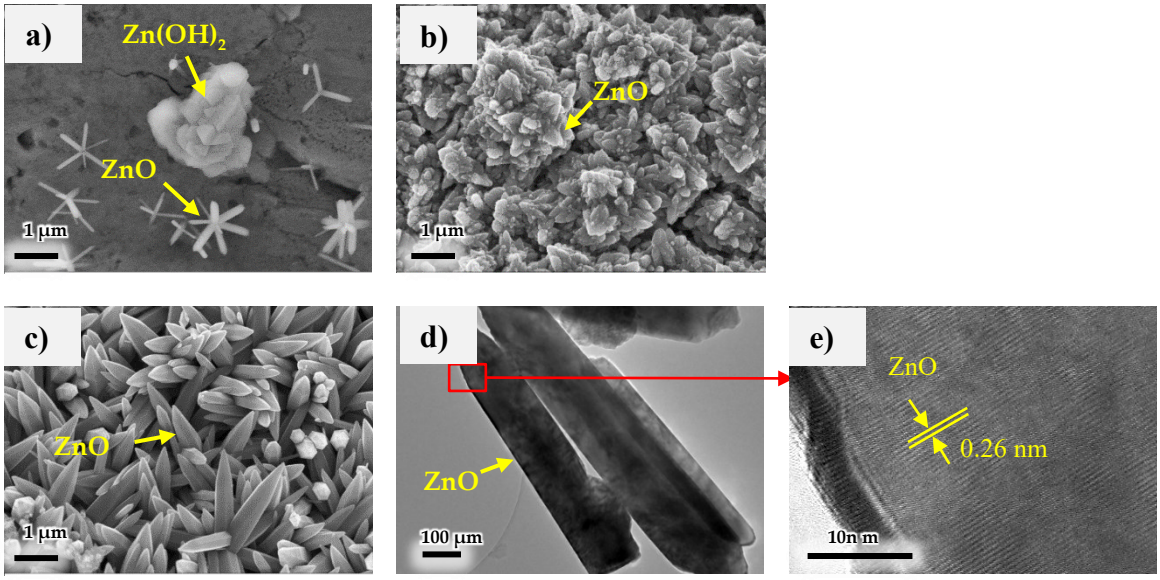

Figure 2. Morphology of ZnO/wires. a) – c) FESEM images of ZnO/wire samples synthesized at OH- concentrations of a) 0.8M, b) 1M, and c) 1.2M; and d) – e) TEM/HRTEM of ZnO/wire-1.2M

4. CONCLUSION

ZnO sub-micron rods with average diameter of 304 ± 78.6nm were fully grown on the kanthal wire by direct heating method with the control of OH^- ions concentration. At low OH- concentration, $Zn(OH)_2$ precipitates were formed in the solution rather than growing onto kanthal wire surface. With the increase of OH^- concentration, the nucleation of ZnO nuclei from $[Zn(OH)_4]^{2-}$ complex was initiated on the kanthal wire surface under direct heating. Tailoring the OH^- ion concentration eliminated the formation of $Zn(OH)_2$ precipitates and increased the $[Zn(OH)_4]^{2-}$ complexes which was favorable for the growth of 1-D ZnO in a controlled manner using direct heating method.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of Ministry of Higher Education, Malaysia for providing the research funding under Fundamental Research Grant Scheme (FRGS) (FRGS/1/2020/TK0/USM/02/27) to conduct this project and the support from the USM Fellowship and Faculty of Chemical and Food Technology, HCMC University of Technology and Education.

REFERENCES

[1] Han, W., S. Oh, C. Lee, J. Kim, and H.-H. Park, (2020). ZnO nanocrystal thin films for quantum-dot light-emitting devices, ACS Applied Nano Materials, 3(8):7535-7542.

[2] Wibowo, A., M.A. Marsudi, M.I. Amal, M.B. Ananda, R. Stephanie, H. Ardy, and L.J. Diguna, (2020). ZnO nanostructured materials for emerging solar cell applications, RSC Advances, 10(70):42838-42859.

[3] Wang, C.N., Y.L. Li, F.L. Gong, Y.H. Zhang, S.M. Fang, and H.L. Zhang, (2020). Advances in doped ZnO nanostructures for gas sensor, The Chemical Record, 20(12):1553-1567.

[5] Le, A.T., T.D.H. Le, K.-Y. Cheong, and S.-Y. Pung, (2022). Immobilization of zinc oxide-based photocatalysts for organic pollutant degradation: A review, J. Environmental Chemical Engineering, 10(5):108505.

[6] Saleem, S., M.H. Jameel, A. Rehman, M.B. Tahir, M.I. Irshad, Z.-Y. Jiang, R.Q. Malik, A.A. Hussain, A.u. Rehman, A.H. Jabbar, A.Y. Alzahrani, M.A. Salem, and M.M. Hessien, (2022). Evaluation of structural, morphological, optical, and electrical properties of zinc oxide semiconductor nanoparticles with microwave plasma treatment for electronic device applications, J. Materials Research and Technology, 19(2126-2134.

[7] Zhu, Y., L. Zhou, and Q. Jiang, (2020). One-dimensional ZnO nanowires grown on three-dimensional scaffolds for improved photocatalytic activity, Ceramics International, 46(1):1158-1163.

[8] Abdulrahman, A.F., S.M. Ahmed, N.M. Ahmed, and M.A. Almessiere, (2020). Enhancement of ZnO nanorods properties using modified chemical bath deposition method: effect of precursor concentration, Crystals, 10(5):386.

[9] Yasmeen, S., F. Iqbal, T. Munawar, M.A. Nawaz, M. Asghar, and A. Hussain, (2019). Synthesis, structural and optical analysis of surfactant assisted ZnO–NiO nanocomposites prepared by homogeneous precipitation method, Ceramics International, 45(14):17859-17873.

[10] Chew, Z.J. and L. Li, (2012). Localised zinc oxide nanowires growth on printed circuit board by in-situ joule heating, Materials Letters, 76(226-228.

[11] Lee, W.C., Y. Fang, D. Commandeur, R. Qian, Z.T.Y. Al-Abdullah, and Q. Chen, (2017). Ultra rapid direct heating synthesis of ZnO nanorods with improved light trapping from stacked photoanodes for high efficiency photocatalytic water splitting, Nanotechnology, 28(35):355402.

[12] Aziz, S.N.Q.A.A., K.C. Meng, S.-Y. Pung, Z. Lockman, A. Ul-Hamid, and W.K. Tan, (2022). Rapid growth of zinc oxide nanorods on kanthal wires by direct heating method and its photocatalytic performance in pollutants removal, J. Industrial and Engineering Chemistry,

[13] Amin, G., M. Asif, A. Zainelabdin, S. Zaman, O. Nur, and M. Willander, (2011). Influence of pH, precursor concentration, growth time, and temperature on the morphology of ZnO nanostructures grown by the hydrothermal method, J. Nanomaterials, (2011)269692.

[14] Doustkhah, E., M. Esmat, N. Fukata, Y. Ide, D.A.H. Hanaor, and M.H.N. Assadi, (2022). MOF-derived nanocrystalline ZnO with controlled orientation and photocatalytic activity, Chemosphere, 303(134932.

[15] Wang, M., Y. Zhou, Y. Zhang, S.H. Hahn, and E.J. Kim, (2011). From $Zn(OH)_2$ to ZnO: a study on the mechanism of phase transformation, Crystal Engineering Communications, 13(20):6024-6026.

[16] Hsu, M.-H. and C.-J. Chang, (2014). Ag-doped ZnO nanorods coated metal wire meshes as hierarchical photocatalysts with high visible-light driven photoactivity and photostability, J. Hazardous Materials, 278:444-453.