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NANOSTRUCTURAL AND OPTICAL PROPERTIES OF HIERARCHICAL ZnO GROWN VIA HYDROTHERMAL METHOD

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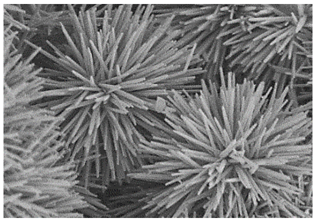
Graphical abstract



Abstract

A simple hydrothermal method was employed to synthesize 3D hierarchical ZnO nanorods deposited on Si (100) substrate at different growth temperatures (110 and 90°C) within 3 h. The structure, mode and composition of hierarchical ZnO nanorods were investigated by XRD, FESEM and EDX spectroscopy. The polycrystalline ZnO nanostructures products were indexed as hexagonal wurtzite structured, while the morphology was urchin like ZnO nanorods with different aspect ratio of nanorods and stoichiometric. The photoluminescence (PL) properties were studied of as-grown ZnO samples dependent on various growth temperatures. The PL results after UV excitation source were shown a single broad Vis emission peak for both samples with absents of UV emission peak. The emission edge of Vis peak was exhibited blue-shift due to increase temperature growth, and that suggest enhancement in hierarchical ZnO nanorods crystallinity. Oxygen deficiency is evidence on the creation various defects types in hierarchical ZnO nanorods. It is responsible on Vis emission bands. The results demonstrate promising future for the hierarchal ZnO nanostructure which could be applied in optoelectronics and gas sensing.

Keywords: Hierarchal ZnO nanorods, photoluminescence, hydrothermal

Abstrak

Satu kaedah hidroterma ringkas telah digunakan untuk mensintesis hierarki 3D rod nano ZnO yang dienapkan kepada substrat Si (100) pada suhu pertumbuhan yang berbeza (110 dan 90°C) dalam masa 3j. Struktur, mod dan komposisi hierarki rod nano ZnO dikaji menggunakan spektroskopi XRD, FESEM dan EDX. Produk struktur nano ZnO polihabluran telah diindeks sebagai struktur wurtzit heksagon, manakala morfologi rod nano ZnO seperti landak laut dengan nisbah aspek rod nano dan stoikiometri yang berbeza. Sifat-sifat kefotopendarcahayaan (PL) dikaji sebagai sampel ZnO dewasa bersandar kepada pelbagai suhu pertumbuhan. Keputusan PL selepas sumber pengujaan UV ditunjukkan sebagai puncak tunggal luas pancaran Vis untuk kedua-dua sampel tanpa kehadiran puncak pancaran UV. Hujung puncak pancaran Vis dipamerkan sebagai anjakan biru disebabkan oleh peningkatan suhu pertumbuhan, dan ini menunjukkan peningkatan dalam hierarki rod nano ZnO penghabluran. Kekurangan oksigen adalah bukti kepada kewujudan pelbagai jenis kecacatan dalam hierarki rod nano ZnO. Ia bertanggungjawab ke atas pancaran jalur Vis. Keputusan menunjukkan potensi hierarki struktur nano ZnO yang boleh digunakan dalam optoelektronik dan pengesanan gas.

Kata kunci: Hierarki rod nano ZnO, kefotopendarcahayaan, Hidroterma

1.0 INTRODUCTION

Zinc oxide is one of important kinds of metal oxide semiconductor due to it wide band gap of 3.36 eV, large exciton binding energy of 60 meV and a hexagonal wurtzite crystal structure. Undoped ZnO nanostructure is generally exhibited (n-type) properties; this material has good optical and electrical properties and its bio-safety. Because of the unique physical and chemical characteristics of ZnO nanostructure it has potential applications in different fields such as photo-detectors, gas sensors, solar cells, wave resonators and varistors (Cho *et al*., 2009; Zhang *et al*., 2014) etc.

ZnO nanostructures have been synthesized via different techniques including pulsed laser deposition, atomic layer deposition, sol-gel, molecular-beam epitaxy, hydrothermal and sputtering method etc. Different dimensions (1D, 2D and 3D) of ZnO nanostructures have been reported such as nonorods, nanosheets and nanoflower etc. However, the hydrothermal solution method is a simple, economic and easily controllable for fabricating ZnO nanostructures. In order to synthesis ZnO nanostructures in liquid solution, the effects of aqueous solution concentration of zinc salt, pH, substrate type, growth temperature, and growth time are the important factors in controlling the ZnO nanostructure properties (Liu *et al*., 2015; Song and Lim, 2007).

The morphologies of ZnO structures based photoluminescence (PL) spectra are limited in two regions with one or several of the following emission bands: firstly in the UV region centred at around 380 nm and secondly in the visible (Vis) region with green emission band centred at around 510 nm, a red emission band centred at around 640 nm and an IR emission band centred at around 730 nm. The UV emission peak of ZnO nanostructure is attributed to the radiative recombination of excitonic centers. The origin of Vis peak is due to the surface and deep-level defects, such as zinc and oxygen vacancies and oxygen interstitials (Djurišić and Leung, 2006; Tang *et al*., 2014; Yao *et al*., 2000).

On the other hand, clarifying the origins responsible on the various type of PL emissions peaks from ZnO nanostructure is an important and a controversial issue, which is need further study (Djurišić and Leung, 2006; Lee *et al*., 2010). ZnO nanostructures have improvement in the optical properties comparing with the bulk materials due to their large specific surface area to volume ratio, quantum confinement, morphology, and size effect (Djurišić and Leung, 2006; Vinodkumar *et al*., 2014; Yang *et al*., 2014).

In this study, the thin film of hierarchical ZnO nanorods was grown by using simple hydrothermal method on silicon (Si) substrate. The PL properties of ZnO nanostructure was studied depending on growth temperature. The structure, mode and composition of ZnO nanostructures were investigated by XRD, FESEM and EDX spectroscopy. Photoluminescence (PL) properties at room temperature of as-synthesis ZnO nanostructures samples were studied by using a photoluminescence spectroscopy (PL) at room temperature.

2.0 EXPERIMENTAL

Zine oxide precursor solution was prepared by using zinc nitrate, hexamethylenetetramine (HMT) and deionized water as the raw materials to produce a 0.1 M of precursor. All the chemical reagents used in the experiments were analytical grade without further purification. Certain dosage of (NH_3) was added to increase the pH value of precursor solution at 10 values. This solution was stirred for 15 min for homogenization. Later, the mixture of precursor was transferred to autoclave. Si (100) substrates were used to deposit hierarchical ZnO nanorods. The substrates were cleaned by ethanol and acetone with ultrasound bath, prior immersed into solutions for growing ZnO nanostructures. The mixture was hydrothermally heated at (90 and 110^{0}C) for (3 h). Finally the hierarchical ZnO nanorods were successfully grown on the substrate and the oven cooled down at room temperature. Next, the samples were washed with ethanol, distilled water and dried at 65°C for 30 min. Structure, mode and stoichiometric ratio of hierarchical ZnO nanorods were characterized by FESEM equipped with an energy-dispersive (EDX) and an X-ray diffraction (XRD) techniques. The optical properties of the hierarchical ZnO nanorods were studied using room temperature photoluminescence spectroscopy (PL) at an excitation wavelength of 350 nm.

3.0 RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of hierarchical ZnO nanostructures dependent on temperature growth (110 - 90^{o}C) and time growth of (3 h). As shown in the figure, the samples were polycrystalline and all diffraction peaks demonstrated as ZnO crystals with a hexagonal wurtzite structure according to the standard card (JCPDS card no.36-1451). In additional, XRD spectra were appeared ZnO samples without any impurity peaks. The variation of growth temperature leads to the intensity of diffraction peaks of the ZnO nanostructure were changed simultaneously. The slightly enhanced in intensity and narrowed spectral width of (FWHM) of oriented in c-axis (002) diffraction peak with increase growth temperature indicating that high crystallinity of the hierarchical ZnO nanorods. The above mentioned properties of hierarchical ZnO nanorods can be attributed to the anisotropic growth of the ZnO crystals, (Hai-Bo *et al*., 2012; Yang, *et al*., 2014).

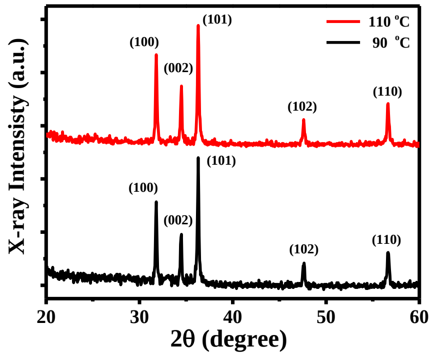


Figure 1 XRD patterns of hierarchical ZnO nanorods grown at (90 and 110ᵒC), 0.1 M and 3 h

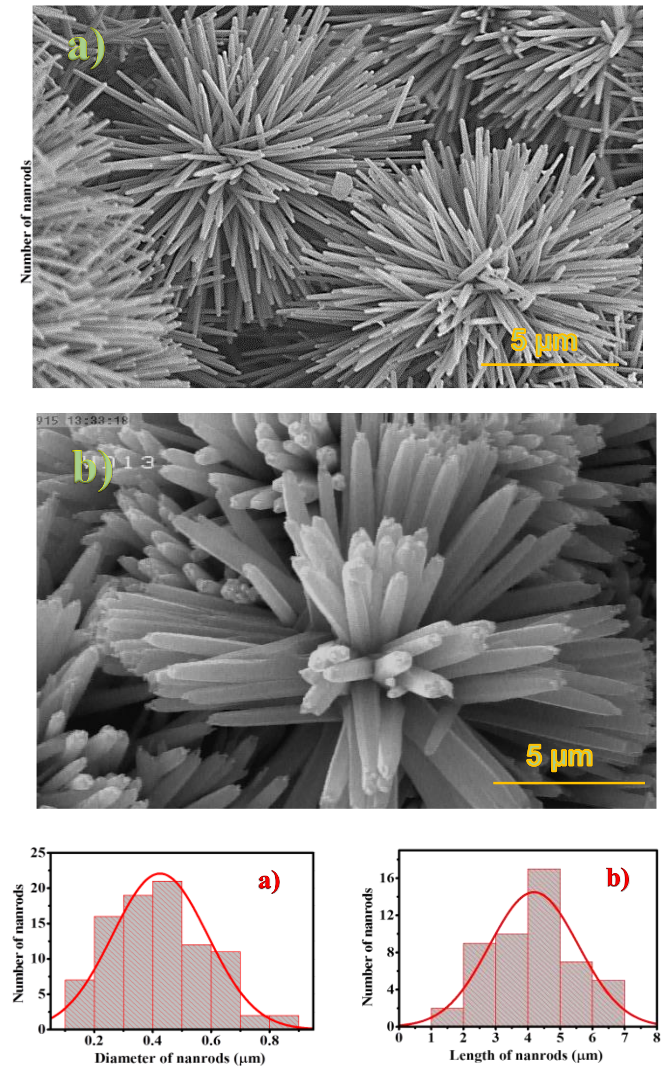


Figure 2 (a and b) FESEM images of hierarchical ZnO nanorods grown at (90 and 110ᵒC), 0.1 M for 3 h. The histogram of nanorods-dependent hierarchical ZnO nanostructures grown under (a) 90ᵒC and (b) 110ᵒC, curves are the Gaussian fits

The morphology, composition and size of ZnO nanostructures were characterized by FESEM equipped with an energy-dispersive EDX. Figure 2 (a and b), appear FESEM images of uniform hierarchical shapes like urchin-like ZnO nanorods were samples consisted of different geometry average size about (0.144 - 0.44 µm in diameter and 2.01 to 4.3 µm in length) under different temperatures growth between (90 and 110ᵒC) respectively. FESEM results demonstrated different aspect ratio of nanorods dependent of hierarchical ZnO nanostructures which was affected by changing temperature growth. The diameter and length of ZnO nanorods were increased with increased the temperature of growth from 90 to 110 ᵒC. These results are good agreement with previous literature review, (Solís-Pomar *et al*., 2011; Sorayaie *et al*., 2015).

Figure 3 (a and b), demonstrate composition of hierarchical ZnO nanostructures films which was grown on Si substrate under different temperatures growth using EDX spectroscopy. The figures confirm the presence of O, Zn, and Si as the elemental compositions, where, Si element can be attributed to substrate. EDX spectra for ZnO samples shows the Zn/O atomic ratios were determined to be approximately 3.03 and 2.88 for ZnO nanostructures grown under different temperature growth (90 – 110ᵒC) respectively. That suggest the oxygen deficiency its presence in the crystal structure of hierarchical ZnO nanorods, and was confirmed by EDX spectra. Thus, creation of different crystal defects with different ratios in hierarchical ZnO nanostructures due to changing in temperature growth of samples.

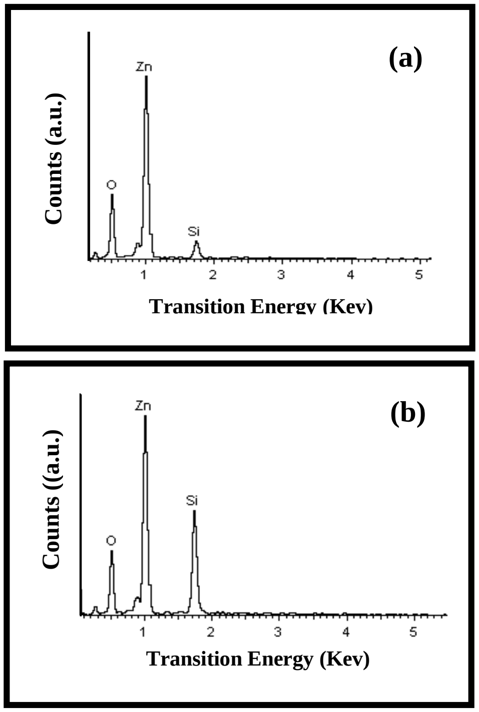


Figure 3 EDX spectra of hierarchical ZnO nanorods grown with 0.1 M for 3 h at temperature (a) 90°C and (b) 110°C

The room temperature photoluminescence (PL) of the hierarchical like urchin like ZnO nanorods grown under various temperatures growth were presented in Figure 4. The emissions spectra of samples presents the two broad visible (Vis) emissions bands centered at 432 nm and the second bands centered about 410 nm, which are grown under (90 and 110 °C) respectively. The visible spectrum of ZnO nanostructures is produced by the radiative recombination, which is attributing to surface defects and defects related to deep level emission such as oxygen vacancies and zinc interstitials, (Ding *et al*., 2011; Gondal *et al*., 2009). The results of PL spectra dependent on temperature growth were indicated to blue-shift of emission edge of hierarchical ZnO nanostructures with increased temperature growth as well as associated with highest intensity of Vis emission peak as shown in Figure 4. Furthermore, it is noticed that disappear of UV emission peak of hierarchical ZnO samples. Thus, these results are confirmed that the presence defects in ZnO nanostructures based on EDX spectra of Figure 3, which allow concluding that the Vis emission likely to attributed from these defects. The most important, the increase in the temperature growth of hierarchical ZnO nanostructures thus indicates that the improvement in crystallinity of the ZnO sample. This is validated through the increases of Vis intensity and the blue-shift of Vis emission edge as shown in Figure 4. These results were in agreement with researchers, (Hai-Bo, *et al*., 2012; Li *et al*., 2014; Zhu *et al*., 2007). The emission edge of ZnO nanostructure was increased and shifted toward UV emission edge that means ZnO nanostructures have been enhancement in the quality of ZnO nanostructure crystallinity.

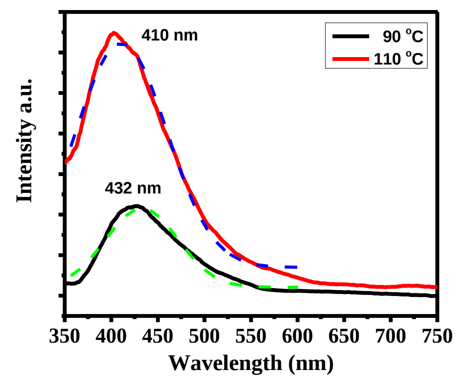


Figure 4 PL spectra of hierarchical ZnO nanorods grown at (90 and 110°C), 0.1 M and 3 h, curves are the Gaussian fits

4.0 CONCLUSION

In present work, hexagonal hierarchical of ZnO nanorods was synthesized via a liquid precipitation route under different low temperatures growth. The change in the temperature growth of ZnO nanostructure was induced to change in the aspect ratio of nanorods-dependent of hierarchical ZnO nanostructures. The temperature growth of the ZnO crystal was proved to play an important role in PL properties of hierarchical ZnO nanorods due to the change in composition ratio of oxygen and zinc atoms. Oxygen deficiency which produces surface defects and defects related to deep level emission in hierarchical ZnO nanostructures were strongest evidence. These defects are responsible on the Vis emission bands. Also, the slightly increase in temperature growth from 90 to 110°C leads to improvement in hierarchical ZnO nanorods crystallinity due to Vis emission intensity increase and blue-shift of the Vis emission edge toward UV region. This work provides a viable and low coast method to control on the morphology dimension and PL properties of hierarchical ZnO nanorods by controlling the crystal temperature growth. These results can be promising future of hierarchiel ZnO nanorods in different application.

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References

[1] Cho, D. H., Kim, J. H., Moon, B. M., Jo, Y. D. and Koo, S. M. 2009. Control of A- and C-plane Peferential Orientations of ZnO Thin Films. *Applied Surface Science*. 255(6): 3480-3484.

[2] Ding, M., Zhao, D., Yao, B., Li, B., Zhang, Z. and Shan C. 2011. The Surface Defect-Related Electroluminescence from the ZnO Microwire. *Journal of Physics D: Applied Physics*. 44(7): 075104.

[3] Djurišić, A. B. and Leung, Y. H. 2006. Optical Properties of ZnO Nanostructures. *Small*. 2(89): 944-961.

[4] Gondal, M., Drmosh, Q., Yamani, Z. and Saleh, T. 2009. Synthesis of ZnO2 Nanoparticles by Laser Ablation in Liquid and Their Annealing Transformation into ZnO Nanoparticles. *Applied Surface Science.* 256(1): 298-304.

[5] Hai, B. F., Xin, L. Z., Si, S. W., Zhi, G. L. and He, B. Y. 2012. Zn/O Ratio and Oxygen Chemical State of Nanocrystalline ZnO Films Grown at Different Temperatures. *Chinese Physics B*. 21(3): 038101.

[6] Lee, J., Chung, J. and Lim, S. 2010. Improvement of Optical Properties of Post-Annealed ZnO Nanorods. *Physica E: Low-Dimensional Systems and Nanostructures*. 42(8): 2143-2146.

[7] Li, H., Jiao, S., Gao, S., Li, H. and Li, L. 2014. Dynamically Controlled Synthesis of Different ZnO Nanostructures by a Surfactant-Free Hydrothermal Method. *Cryst. Eng. Com*. 16(38): 9069-9074.

[8] Liu, Y., Li, C., Wang, J., Fan, X., Yuan, G. and Xu, S. 2015. Field Emission Properties of ZnO Nanorod Arrays by Few Seed Layers Assisted Growth. *Applied Surface Science*. 331: 497-503.

[9] Solís, P. F., Martínez, G. E., Meléndrez, C. M. and Pérez, T. E. G. 2011. Growth of ZnO Nanowires Using Au/Pd Nanoparticles as Catalyst. *Proceedings of the 2011 Journal of Nano Research*. 145-154.

[10] Song, J. and Lim, S. 2007. Effect of Seed Layer on the Growth of ZnO Nanorods. *The Journal of Physical Chemistry C*. 111(2): 596-600.

[11] Sorayaie, P., Yusefi, M.-H., Fallah, H.-R. and Parsanasab, G.-M. 2015. Growth of a Seven Pointed Star Shaped of Vertical and Uniform ZnO Nanostructures on Optical Fiber Via Catalyst-free VLS Mechanisms. *Applied Physics A*. 118(2): 519-524.

[12] Tang, J. F., Su, H. H., Lu, Y. M. and Chu, S. Y. 2014. Controlled Growth of ZnO Nanoflowers on Nanowall and Nanorod Networks via a Hydrothermal Method. *Cryst. Eng. Comm*. 17(3): 592-597.

[13] Vinodkumar, R., Navas, I., Porsezian, K., Ganesan, V., Unnikrishnan, N. and Pillai, V. M. 2014. Structural, Spectroscopic and Electrical Studies of Nanostructured Porous ZnO Thin Films Prepared by Pulsed Laser Deposition. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 118: 724-732.

[14] Yang, B., Zuo, X., Yang, X., Zhou, L. and Li, G. (2014). Effects of pH Values on Crystal Growth and Photoluminescence Properties of ZnO Hexagonal Rods with Cones. *Materials Letters.* 130: 123-126.

[15] Yao, B., Shi, H., Bi, H. and Zhang, L. 2000. Optical properties of ZnO Loaded in Mesoporous Silica. *Journal of Physics: Condensed Matte*r. 12(28): 6265.

[16] Zhang, J., Guo, E., Yue, H., Wang, L. and Zhang, C. 2014. Effect of Ultrasonic Treatment Before and After Hydrothermal Process on the Morphologies and Formation Mechanism of ZnO Nanorods. *Applied Physics A.* 114(2): 521-528.

[17] Zhu, B., Zhao, X., Su, F., Li, G., Wu, X., Wu, J., *et al*. 2007. Structural and Optical Properties Of Zno Thin Films on Glass Substrate Grown by Laser-ablating Zn Target in Oxygen Atmosphere. *Physica B: Condensed Matter*. 396(1): 95-101.