Ultrafast Formation of ZnO Nanorods via Seed-Mediated Microwave Assisted Hydrolysis Process

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Abstract. One dimensional (1D) zinc oxide, ZnO nanostructures have shown promising results for usage in photodiode and optoelectronic device due to their high surface area. Faster and conventional method for synthesis ZnO nanorods has become an attention for researcher today. In this paper, ZnO nanorods have been successfully synthesized via two-step process, namely alcothermal seeding and seed-mediated microwave hydrolysis process. In typical process, the ZnO nanoseeds were grown in the growth solution that contained equimolar (0.04 M) of zinc nitrate hexahydrate, Zn (NO₃)₂·6H₂O and hexamethylenetetramine, HMT. The growth process was carried inside the inverted microwave within 5-20 s. The effect of growth parameters (i.e. concentration, microwave power, time reaction) upon the modification of ZnO morphology was studied. ZnO nanostructures were characterized by Field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD). The densities of nanorods were evaluated by the Image J analysis. It was found that the morphology (e.g. shape and size) of nanostructures has changed drastically with the increment of growth solution concentration. The density of ZnO nanorods was proven to increase with the increasing of reaction time and microwave power. We hypothesize that the microwave power might enhance the rate of nucleation and promote the faster nanostructure growth as compared with the normal heating condition due to the superheating phenomenon. This method might promote a new and faster alternative way in nanostructure growth which can be applied in currently existing application.

1. Introduction

Zinc oxide (ZnO) is a common material that is readily used in semiconductor fabrication especially in solar cell and gas sensor due to its special properties. ZnO is a wide energy band gap material (3.37 eV) that exhibits excellent optical, electrical and thermochromism properties. Recently, it has been demonstrated that ZnO readily self-assembles into diversity of nanocrystalline structures such as nanospines, tetrapods, nanorod [1-3].

Many approaches have been done to produce a vertical array of ZnO nanorods such as vapor-solid-liquid method, chemical vapor deposition and electrochemical growth method [4]. However, all of these methods consume a lot of energy and time. In order to synthesize a well-crystalline nanostructure in an economical way, hydrothermal process was introduced. Wang et.al [5] have reported the formation of various ZnO nanostructures via hydrothermal process. The effect of growth conditions
(i.e. concentration, pH and growth time) was studied. It was found that an interesting structure called latch-like structure was formed at higher pH: 8.0 and 120 °C for 4 h. Nevertheless, this method was time consuming and cannot produce a uniform homogeneous sample due to the existence of temperature gradient between the vial and growth solution during the convection heating process.

A fast and easier way which is called as microwave hydrothermal process was introduced in recent years. Microwave radiation synthesis is a method that applies the electromagnetic radiation to alter the dipole moment of the molecule and induce formation of nanostructure through the superheating mechanism. This method has been widely used in medical science, organic polymerization and nanomaterial synthesis [6, 7] due to its accelerate synthesis and high yield of the nanostructure. Recently, we have synthesized the ZnO nanoplate via the reflux microwave oven inside microwave transparent vial (i.e. sealed Teflon) [8]. This method has shown a rapid growth of nanostructure in homogeneity distribution within minute. Unfortunately, the special design microwave is costly which retards the mass reproduction. Considerable attention has also been given to reaction time and growth rate of nanostructure in recent research. Mahpeykar et al. [9] have synthesized ZnO nanowire in rapid growth rate of 200 nm min$^{-1}$ by the ammonia assisted growth process. Several reports have suggested the effective increment of growth rate of nanostructure synthesized directly in solution form. However, the coverage of nanostructure spin coated from the as-grown solution on to the substrate is very difficult to control.

Our group have been actively involved in the synthesis of ZnO nanostructure directly on the surface with controllable shape and morphology [10, 11]. Here, we report the growth of ZnO nanostructure on the surface of FTO via ultrafast microwave seed assisted method within 10-20 s. This experiment was carried in two-step synthesis process, namely alcothermal seeding and microwave-assisted hydrolysis process. An equimolar (0.04 M) of zinc nitrate hexahydrate, Zn (NO$_3$)$_2$.6H$_2$O and hexamethylenetetramine, HMT was used as a growth solution. The effect of precursor concentration, microwave power and the reaction time was studied. The optimum and high density of ZnO nanorods was obtained at microwave power of 1100 W in growth solution with concentration of 0.04 M for 20 s. This technique has been shown to be a simple and faster way in producing vertically aligned ZnO nanorods. This result could be potentially used in rapid production of ZnO nanorods.

2. Experimental details

2.1. Synthesis of ZnO nanostructures

One dimensional (1D) hexagonal nanorods were synthesized via two-step route method, namely alcothermal seeding and hydrothermal growth process. Alcothermal seeding [12] was used to prepare uniform nanoseed particles. In typical procedure, 20 mL of ethanolic solution (Sigma Aldrich, Reagent grade) of zinc acetate (0.01 M) was prepared. The solution was then spin coated on a FTO substrate with 3000 rpm for 30 s. After that, the as-coated substrate was heated on a hotplate at 100 °C for 15 min. This process was repeated for 3 times to obtain a high density of nanoseed particles. Finally, the substrate was transferred into the horizontal tube furnace (VT Furnace) and annealed in air for 1 h at 350 °C. Using this process, ZnO nanoseeds with size of 5-10 nm in high density were obtained.

Hexagonal ZnO nanorods were grown from the nanoseeds in a growth solution that contained equimolar (0.04 M) of zinc nitrate hexahydrate, Zn (NO$_3$)$_2$.6H$_2$O and hexamethylenetetramine, HMT (Reagent grade, Sigma Aldrich) via microwave assisted hydrolysis process. A Panasonic inverted home application microwave system (NN-GD577M, 1100 W, 2.45 GHz) was used in this study. In typical process, the seeded substrate was placed inside the glass vial that consisted of 5 mL of growth solution. After that, the glass vial was put into the Teflon container and positioned on the centre of microwave during the growth process. Lastly, the sample was taken out from the system. The as-grown nanorods were cleaned with copious of distilled water and dried with a jet of nitrogen gas. Effect of structural growth of ZnO was studied by varying the growth solution concentration (0.01-0.05 M), microwave power (180-1100 W) and reaction time (5-20 s).
2.2. Characterization

The morphology of the nanostructures was examined using Field emission scanning electron microscope (FESEM, ZEISS Supra .55 VP) that was operated at the pressure of $10^{-5}$ Pa and acceleration voltage, EHT of 5 kV. The crystallinity and purity of the sample were characterized by using advanced x-ray diffraction spectrometer (XRD, Bruker D8) with CuKα radiation. Diffraction angle of 30-50˚ and scanning rate of 0.002˚/s was thus studied.

3. Results and discussion

3.1 Effect of Concentration

Figure 1 shows the FESEM image of ZnO nanorods grown at different growth solution concentrations, namely 0.01 M-0.05 M in 1100 W for 20 s. ZnO nanorods were successfully grown on the surface using this present approach. As seen from Figure 1, the nanorods diameter was found to be dependent on the growth solution concentration. In typical results, the diameter increased from c.a. 30 nm to 80 nm with the increasing concentration up to 0.04 M. But it decreased to c.a. 50 nm once the concentration exceeded 0.05 M. Besides, it was found that the density of nanorods also changed with the concentration. The density of the sample increased exponentially with the concentration. The densities of the sample were 0.54, 0.58, 0.63, 0.74 and 0.91 nanorods/um², respectively. Furthermore, it was noticed that the present nanorod end showed a rough surface. This phenomenon contradicts with the other reports that nanorods synthesized via usual hydrothermal method only showed a flat hexagonal surface. The existence of rough surface might be caused by the Ostwald ripening which will be discussed later. Figure 1 (G) shows the XRD spectra of the samples grown at different growth solution concentrations, namely 0.01 M-0.05 M. A dominant peak correlated to (002) plane of ZnO hexagonal wurtzite structure (JCPDS No file: 36-1451) was obtained at around 2θ of 34.4˚ in all the samples. Besides that, it was noticed that three small peaks which denoted the (100), (101) and (102) planes were obtained at 2θ of 31.3˚, 36.2˚ and 47.5˚, respectively. The Bragg intensity increased with the concentration due to the increment of diameter and density of nanorods. This result is in good agreement with the FESEM image of nanorods. Apart from ZnO and FTO peaks, there was no other Zn complex peak appeared in the spectrum. From this result, it was confirmed that the pure ZnO nanostructures were successfully grown on the substrate by using the current method.

The effect of precursor concentration on the nanorods diameter and density can be considered as follows. In the microwave-assisted hydrolysis process, the microwave radiation directly heated the whole volume of the solution and induced the hydrolysis process of the Zn complex. In the growth process, the ionic species aligned within the electrical field and nucleated on the nanoseeds surface in an effort to minimise the surface energy. The growth process only occurred when the critical size of nanoseeds was obtained. The nanoseeds then grew until reaching the critical size that promoted to vertically-aligned nanorods growth (refer Figure 2). For the case of concentration of 0.01 to 0.04 M, the nanorods diameter and density increased with the increasing of concentration. This can be understood as the result of quick formation of critical size on most of the nanoseeds on the surface due to the increasing precursors. Amount of the nanoseeds which resulted in nanorods growth increased accordingly, leading to higher density of the sample. Since the nanostructure growth was toward all directions including long and short axis of nanorod, the diameter also increased with the increasing of concentration. However, at relatively high concentration i.e. 0.05 M, the nanorods diameter decreased as compared to those prepared at lower concentration. This could be due to the rapid growth process at such high concentration, where the critical size was expected to be smaller than those in the lower concentration. Hence smaller diameter and higher density nanorods were obtained.

Meanwhile, for the case of concentration effect on the nanorods end surface roughness, Ostwald annealing process can be considered (refer Figure 2). It is agreed that the Ostwald annealing often occurs in the variation of time reaction. But in this experiment, we have applied a high power synthesis, which was 1100 W for the microwave growth process. This high power might increase the rate of nucleation. The precursor might be quickly consumed in a short period and cause a drastic drop
in the nucleation rate. This condition may cause the atom at the vertex site of nanorods surface to dissolve into the solution and then nucleate on the other site of the surface. This process is predicted to be more active at high concentration. Thus, the surface roughness of the nanorods end increased with the increasing concentration.

Figure 1. FESEM image of ZnO nanoseeds (A) and nanorods grown in 0.01 M (B), 0.02 M (C), 0.03 M (D), 0.04 M (E), 0.05 M (F) of growth solution at 1100 W for 20 s inside the inverted microwave and their corresponding XRD spectra (G). Scale bars are 100 nm.
3.2 Effect of microwave power

Figure 3 shows the FESEM and XRD results of the corresponding untreated and treated samples which were grown at microwave power of 187-1100 W. As seen from Figure 3(A), there was no nanostructure formed at 187 W. The nanorods formed as the power reached around 300 W. The diameter of the nanorods increased from c.a. 28 nm to 80 nm with the increasing microwave power. The density of nanostructures also increased from 0.49 to 0.74 nanorods/\text{nm}^2 as the synthesis power reached 1100 W. The surface roughness of the sample also increased with the microwave power. Effect of the power on crystalline structure of the sample was also studied here. The result is shown in Figure 3(G). It was found that the XRD profile on the sample prepared by different powers showed similar trend with that observed in Figure 1(G) without any shifting in the peak. This infers that there was no modification in the crystallinity of nanostructure in the application of microwave although different microwave powers were applied.

The effect of microwave power on the diameter, density and surface roughness can be explained as follows. Microwave power played an important role in determining the superheating state of the precursor solution in the nucleation process. The small microwave power was insufficient to generate dielectric heating for the hydrolysis process. As the power increased, the hydrolysis process happened more thoroughly in the solution. Indirectly, the ionic species concentration in the solution would be

Figure 2. Mechanism of ZnO nucleation process under microwave-assisted hydrolysis method.
affected. The phenomenon is similar to the concentration effect. As mentioned earlier, the density and the diameter of the nanorods might change with the critical size. Furthermore, the increment of surface roughness of the ZnO nanorods end might also be caused by the rate of microwave radiation emission besides the Ostwald ripening. As the power increased, the rate of microwave emission increased and caused the ionic species to oscillate in a higher speed. The collision between the dipolar ZnO molecules might also induce the defect on the nanorods end.

Figure 3. FESEM image of ZnO nanorods grown at 187 W (A), 363 W (B), 550 W (C), 748 W (D), 994 W (E) and 1100 W (F) for 20 s inside the inverted microwave and their corresponding XRD spectra (G). Scale bars are 100 nm.
3.3 Effect of reaction time
Figure 4 shows the FESEM image of ZnO nanostructure grown for different reaction times which were in the range of 5-20 s. As can be seen from Figure 4(A), none of the ZnO nanostructure was obtained on the surface. As the time prolonged to 8 s, the nanorods were found starting to grow and the growth solution turned into milky white colour after the synthesis process. The diameter and density of the ZnO nanorods increased proportionally with the extension of the reaction time, which were from c.a. 27 nm to 80 nm and from 0.44 to 0.74 nanorods/nm$^2$ for the growth time of 8-20 s, respectively. This could be related to the thermal energy required for initialisation of hydrolysis process. Thus, sufficient microwave irradiation time is needed. Based on this result, we predict that the hydrolysis could be started earlier than 8 s in the growth process. It was also found that the increasing of time also caused increase in the surface roughness of the nanorods end. This is a normal phenomenon as the Ostwald annealing process increased with the reaction time.

Figure 4. FESEM image of ZnO nanorods grown at 1100 W for 5 s (A), 8 s (B), 10 s (C), 15 s (D) and 20 s (E) inside the inverted microwave. Scale bars are 100 nm.

4. Conclusion
ZnO nanorods have been successfully synthesized using the ultrafast microwave-assisted hydrolysis method in 8-20 s. The diameter, density and surface roughness were found to depend on the concentration, microwave power and the reaction time. The presence approach should become an alternative strategy for rapid preparation of ZnO nanorods with a controlled-density, -diameter and -surface roughness for usage in currently existing applications.

Acknowledgment
We acknowledge the contribution of financial supports by the Malaysian Ministry of Higher Education under research grant ERGS/1/2011/STG/UKM/01/27 and FRGS/1/2012/SG02/UKM/02/3 and En. Mohamad Hasnul Naim B. Abdul Hamid and En. Idris in FESEM characterization.

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