Aligned vertical growth of zinc oxide nanorods on glass substrates using optimum hydrothermal synthesis technique

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ABSTRACT

This paper reported an optimized hydrothermal synthesis technique to grow zinc oxide (ZnO) nanorods vertically on the normal microscope glass. ZnO nanorods exhibited various advantages such as strong binding energy, non-toxicity, large surface to volume ratio and versatility for optical detections. However, the growth of nanorods which aligned vertically on the glass substrates is rather complicated. It required a thorough process based on optimized concentration, growth duration, growth temperature and solvent variations. The morphological structure result has shown an exceptional vertical growth of the nanorods on the glass surfaces which increase the nanorods density. The optimized synthesis technique produced high density ZnO nanorods up to $3 \times 10^{13}$ nanorods/m² which is double as compared to conventional synthesis technique.

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1. INTRODUCTION

Zinc oxide (ZnO) nanorods is an essential functional material. At ambient temperature, it has a substantial exciton binding energy (60 meV) and a wide bandgap of 3.4 eV. When exposed to the surrounding response, the nanomaterial works as a receptor layer. It causes a change in its optical characteristics, which the evanescent field detects. The optical change is determined by the interaction's affinity constant [1]. One of the many nanostructures of Zinc oxide (ZnO) that has become a suitable nanomaterial in many applications is single crystalline of ZnO nanorods. It is a semiconductor material that is frequently employed in a range of integrated nano-systems such as resonators, solar cells, and antenna [2]-[8].

Zinc oxide has hexagonal structure with lattice parameters $a = 0.3296$ and $c = 0.52065$ nm. It is an alternating planes comprised of tetrahedrally coordinated Zn²⁺ and O²⁻ ions that stacked alternately along c-axis [9]. Because of its dynamic structure, wide range of morphologies, and surface chemistry, it stands out among other metal oxide semiconductors [10], [11]. Hydrothermal synthesis technique has become preferable synthesis method due to its simple growth condition. It uses alcohol as a medium to expedite the nucleation and growth as compared to water. Furthermore, it is environmental friendly method as it does not required additional organic solvents or procedure such as calcination and grinding [12].
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Initially, two sets of solutions were prepared which are ZnO nanoparticles solution and pH control solution. The first solution was synthesized by adding zinc acetate dehydrate \([\text{Zn(O}_2\text{CCH}_3)_2\cdot2\text{H}_2\text{O}]\) (Friendemann Schmidt, Germany) in ethanol \([\text{C}_2\text{H}_5\text{OH}]\) (HmbG Chemical, Germany) under continuous stirring at temperature of 60 °C for 30 minutes. After the mixture was cooled down to the ambient temperature, the solution was then further diluted by adding another 60 ml of pure ethanol slowly to produce 120 ml uniform ZnO nanoparticle solution as shown in Figure 3. Ethanol is capable to expedite the nucleation and growth rate of the nanorods as compared to water.

For pH control solution, aliquots of 0.003g of sodium hydroxide pellets \([\text{NaOH}]\) (Friendemann Schmidt Chemical, Germany) was added into 60 ml of pure ethanol under continuous stirring at temperature of 60 °C for 30 minutes as shown in Figure 4. This control solution is essential to determine the ZnO properties via hydrothermal process. The growth of the nanorods will improve when the pH of the ZnO nanoparticles solution increase to alkaline. The pH value could affect the nuclei and environment of the ZnO growth [23].

The pH control solution was included into ZnO nanoparticles solution after 10 minutes. It was conducted by using drop and stir technique where the ZnO nanoparticles solution was stirred for every single 1 ml pH control solution drop using pipet for around 1 minute as shown in Figure 5. This process was repeated until the pH increases from ~4 to ~9. This step is crucial to provide more hydroxyl ions \((\text{OH}^-)\) [14]. The combination was then placed in a water bath at 60 °C for 3 hours, or until the colour of the solution changed from clear to milky.

Figure 6 shows the procedure of forming nucleation sites on the glass substrates. Firstly, the glass substrates were placed on a hot plate at a fixed temperature of 70 °C. ZnO nanorods were grown on the cleaned glass surfaces. An amount of 1 ml of the seeding solution was drop on the glass substrates by using a pipette. Drop and dry technique was used because it is the most effective seeding method. To ensure that the seeds were properly adhered, the solvent was allowed to evaporate for 5 minutes. To ensure optimal seed dispersion on the surface of glass substrates, the technique was repeated ten times. The samples were then annealed for 3 hours at 300 °C.

Figure 2. Seeding procedure on the glass substrates

Figure 3. Preparation of the ZnO nanoparticles solution

Figure 4. Preparation of the pH control solution

Figure 5. Drop and stir technique
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2.3. Growth process

ZnO growth was performed after the seeding process completed. At first the growth solution was prepared as shown in Figure 7. A 1.4875 g zinc nitrate hexahydrate [Zn(NO3)2·6H2O] (Sigma-Aldrich) and 0.7 g of hexamethyleneteramine or HMT [(CH2)6N4] (Sigma-Aldrich) were dissolved in 500 mL of deionized (DI) water and stirred for 10 minutes. Zinc Nitrate Hexahydrate Zn(NO3)2 has been used as an aqueous solution for hydrothermal synthesis of ZnO nanorods growth as reported in the literature [24]. It acts as a source of Zn2+ ions when the growth was conducted in a temperature range between 100 to 150 °C. It was reported that ZnO powder is nucleated in a heterogeneous system and zinc hydroxide precursors would dissolve partially at pH level less than 11. While at pH level more than 11, the zinc hydroxide precursors are wholly dissolved to form a clear solution. HMT that acts as surfactant play a significant role in modification of ZnO particles. There are another two important variables in ZnO nanorods preparation via hydrothermal technique which are temperature and time. It was reported that the ZnO particles increase as the HMT concentrations, process time and temperature rise [25]. HMT not only provide hydroxyl ions to generate the precipitation reaction but also represent as a buffer when the hydrolysis rate reduced with increasing pH increases and vice versa. Other literature described the function of HMT in different perspective [26]. It has been mentioned that the HMT would attach to the non-polar facets of zincite crystal to produce a long chain polymer and a non-polar chelating agent. This avoids the excess of Zn2+ ions that resulted in only the side of polar (0001) leave for epitaxial growth. Thus, HMT would play a role as a shape inducing polymer surfactant rather than as a buffer as described earlier. Therefore, the ZnO morphologies could be controlled by altering the amount of pH, soft surfactant and ethylenediamine of the mixture of sodium hydroxide, zinc acetate and surfactant. Homogeneous growth achieved at pH of 12 and it becomes inhomogeneous when the pH level decreased. It was reported that the sample with 1:1 molar ratio of the precursor exhibits the highest photocatalytic efficiency. It was also found that 1:1 molar ratio of zinc nitrate and HMT produce good quality nanorods [18].

Prior of the growth procedure on the glass substrates, the setup for the stage of the samples needs to be prepared. The purpose of the stage is to ensure a gap between the seeded area of the glass substrates and the bottom surface of the petri dish. Eventually the seeded glasses were placed on the stages inside the petri dish with the seeded area were positioned facing downwards to the bottom of the petri dish as shown in Figure 8(a). After that, the seeded glass substrates were submerged in 200 ml of the solution and cooked in a 90 °C oven in a Figure 8(b) and (c). To maintain a consistent growth rate, the synthesis solution was changed every 5 hours. The ZnO nanorods were developed for 12 hours in the experiment. The 12h growth time was chosen because it increases the numbers of nanorods density as compared to the other growth hour sample which allow maximum light scattering and limit the backscattering which enhanced the coupling efficiency. The growth procedure was completed by extracting the samples and washing them in DI water several times. Figure 8 depicts the coated glass with ZnO nanorods (Figure 8(d)). Due to the quicker thermal breakdown of hexamine and the release of more OH– at high temperatures, the synthesis temperature impacts the growth rate of ZnO nanorods. It has been found that process temperature of 90 °C displayed the highest photocatalytic efficiency and produced better array of ZnO nanorods as compared to other temperature level. It is due to the higher surface area generated on the sample [18].
Figure 7. Preparation of 10 mM ZnO growth solution

Figure 8. ZnO nanorods growth procedure; (a) seeded glass immerse in growth solution, (b) samples put in oven, (c) heated process in the oven and (d) ZnO nanorods coated glass at the end of the process

3. RESULTS AND DISCUSSIONS

The Hitachi model 3400N was used to examine the morphology of ZnO nanorods growing on glass surfaces using field emission scanning electron microscopy (FESEM). Meanwhile, the chemical constituents of the samples were determined using energy dispersive X-ray (EDX). Figure 9 depicted the EDX elemental analysis of the coating samples consist of only zinc and oxygen [27]. Overall FESEM images of the nanorods on the glass surface at 5kX and 20.00 kX magnifications using conventional synthesis process are shown in Figure 10(a) and (b). Where as FESEM images of the nanorods on the glass surface at 5kX and 20.00 kX magnifications using optimum synthesis process are shown in Figure 11(a) and (b). It can be observed that ZnO nanorods morphological structures growth in aligned vertical direction as compared to the conventional process where the growth directed horizontally. It also shows that the density ($3 \times 10^{13}$ nanorods/m$^2$) of the optimum synthesis process improve by a factor of 2 as compared to the recent method [28]. The forward and backward scattering into the nanorods was affected by these physical structures, resulting in different light transmission behaviour inside the microfibre. As a result, the output light intensity would vary depending on the configuration of the nanorods.

Figure 9. The samples solely contain zinc and oxygen, according to EDX elemental analysis
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Figure 10. ZnO nanorods coated glass grow in horizontal direction using conventional synthesis process; (a) 5kX magnification and (b) 10kX magnification

Figure 11. ZnO nanorods grow in uniform and vertically align with optimum synthesis process; (a) 5kX magnification and (b) 10kX magnification

4. CONCLUSIONS
In summary, an optimum hydrothermal synthesis technique to grow aligned zinc oxide (ZnO) nanorods vertically on the glass substrates has been successfully demonstrated. It is performed by employing optimized concentration alterations, growth duration, growth temperature and solvent variations. Based on the nanostructure characterization, the nanorods growth has been directed upwards vertically compared to the conventional process. This produced higher ZnO nanorods density up to $3 \times 10^{13}$ nanorods/m$^2$ which is double improvement as compared to conventional synthesis technique. It shows the optimum hydrothermal technique is effective to produce a good quality nanorods. Therefore, the work contributes to the investigation of the most optimum synthesis process to grow a well align ZnO nanorods which grow vertically and produce higher density of nanorods. Thus, for future research direction, the ZnO nanorods could be applied in variety integrated nano-systems such as resonators, medical devices, optoelectronics and RT gas sensor.

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