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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 $3\ x\ 10^{13}$ 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 Zn^{2+} and O^{2-} 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]. Hydrothermal synthesis technique exhibits several benefits such as simple technique, low temperature (between 60–100ºC), high yield and more controllable process. The crystal could growth in diverse dimensions and shapes which relied on the composition of starting mixture, process temperature and pressure. Thus it provides high purity material with high degree of crystallinity [13]. This method is based on solution phase synthesis, which can be done in an aqueous solution at temperatures lower than the boiling point of water. Because of its simplicity, tolerable growth conditions and low cost, it is a preferred synthesis approach over gaseous phase synthesis [14].

Extensive research on growing ZnO nanorods on different platforms, including glass substrates, aluminium foil, plastic optic fibre, and silica microfiber, has been proven. It's also been shown on flexible platforms including PEN substrates, paper substrates, polyimide substrates and ITO/PET substrates. Despite numbers of nanostructures such as nanoflowers, nanospheres and nanowires have been introduced, one dimensional (1-D) nanorods have a specific attribute for sensing application such as reducing the electron-hole pair recombination possibilities, direct charge transport along with ZnO arrays, higher surface-to-volume ratio and chemically reactive surface [15]. Furthermore, high concentrations of oxygen vacancies allow many active sites for molecules adsorption [16]. However, the problem of producing optimum nanorods physical structure which vertically growth is it required thorough and precise procedure. There were numerous studies on improving the ZnO nanostructures growth by optimization of the synthesis process such as concentration alterations [17], [18], growth duration [19], growth temperature [20] and solvent variations [21]. Growth duration is one of the most important parameters because it influences the nanorods dimension such as density, length and optical scattering cross section. These dimensions could change the optical response of the nanostructures in term of attenuation coefficients and scattering [22].

This paper would explain comprehensive step by step hydrothermal synthesis process in order to produce well aligned vertical growth direction of ZnO nanorods on the glass substrates based on the most optimal parameters found in the literature. It is start with the elaboration of the optimum synthesis parameters for the ZnO nanorods growth, following by the results and discuccion and eventually the conclusion.

2. OPTIMUM GROWTH OF ZNO NANORODS VIA HYDROTHERMAL METHOD ON GLASS SUBSTRATES

Hydrothermal synthesis process was employed for ZnO nanorods coating onto microscope glass (Heathrow Scientific LLC, USA). The synthesis process required three major steps which are glass substrate preparation, seeding and growth process.

2.1. Preparation og glass substrate

For the ultrasonic cleaning procedure, standard microscope glass substrates (Heathrow Scientific LLC, USA) were submerged in a container of soap water for 15 minutes. The soap water was then dumped, and the washing procedure was resumed with pure water for another 15 minutes. The glass substrates were then submerged in acetone [CH3COCH3] (Bendosen Laboratory Chemical, Germany) using water bath process for 15 minutes before being put in an oven at 90 ˚C for 1 hour to remove organic material. Figure 1 summarises the preparation method.

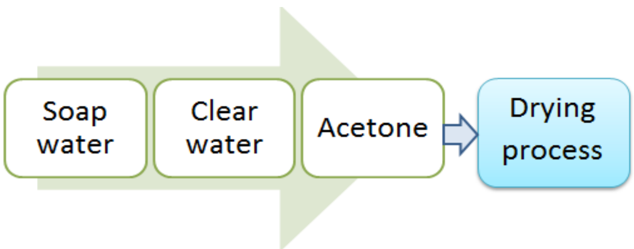


Figure 1. Glass substrates preparation process

2.2. Seeding process

Figure 2 shows the seeding procedure, which was carried out on the glass substrates. This is this to create nucleation centers for ZnO nanorods growth. The uniformity, diameter, length and density of the ZnO nanorods are highly reliance to this procedure. It involves three main steps which are seeding solution preparation, forming nucleation centers on glass substrates and annealing.

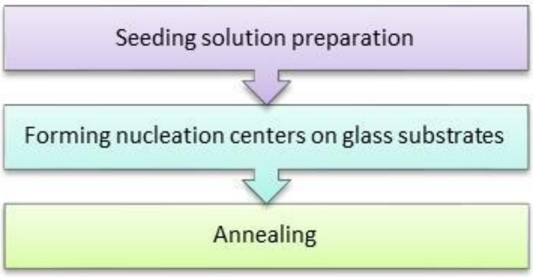


Figure 2. Seeding procedure on the glass substrates

Initially, two set of solutions were prepared which are ZnO nanoparticles solution and pH control solution. The first solution was synthesized by adding zinc acetate dehydrate [$Zn(O_2CCH_3)_2.2H_2O$] (Friendemann Schmidt, Germany) in ethanol [C_2H_5OH] (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 [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].

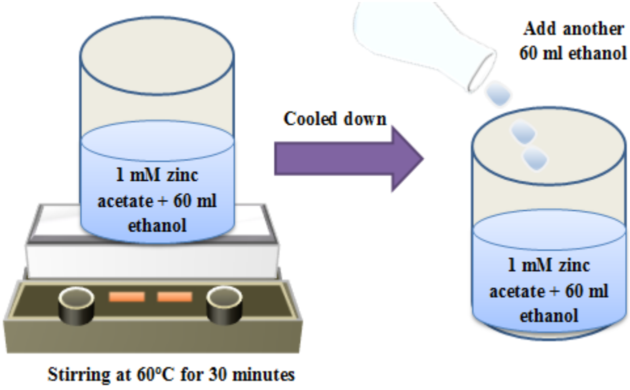


Figure 3. Preparation of the ZnO nanoparticles solution

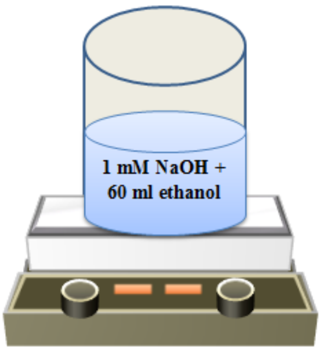


Figure 4. Preparation of the pH control solution

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 (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.

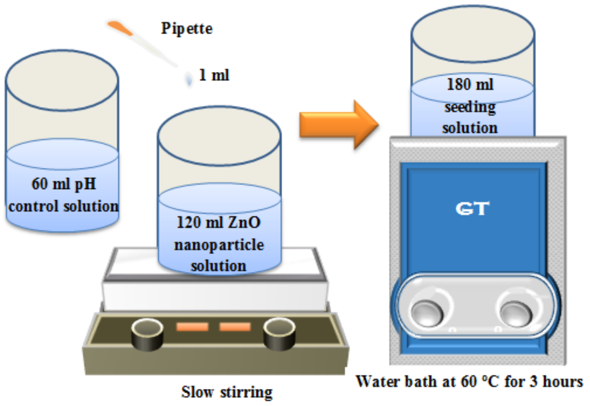


Figure 5. Drop and stir technique for alkaline process to prepare seeding solution

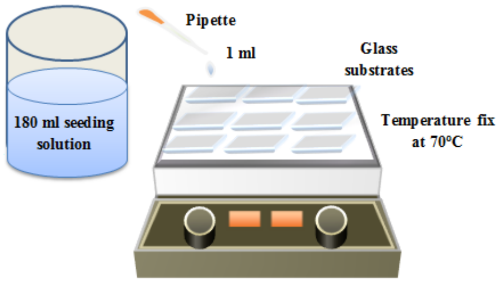


Figure 6. Drop and dry technique on the glass substrates

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)2·6H 2O] (Sigma-Aldrich) and 0.7 g of hexamethyleneteramine or HMT [(CH 2)6N4] (Sigma-Aldrich) were dissolved in 500 mL of deionized (DI) water and stirred for 10 minutes. Zinc Nitrate Hexahydrate $Zn(NO_2)_3$ 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 Zn^{2+} 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 Zn^{2+} 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].

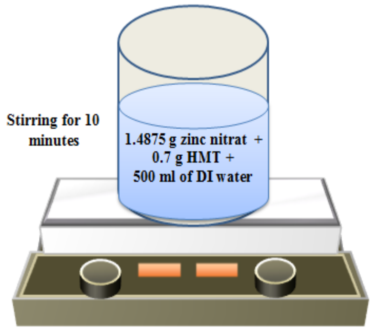
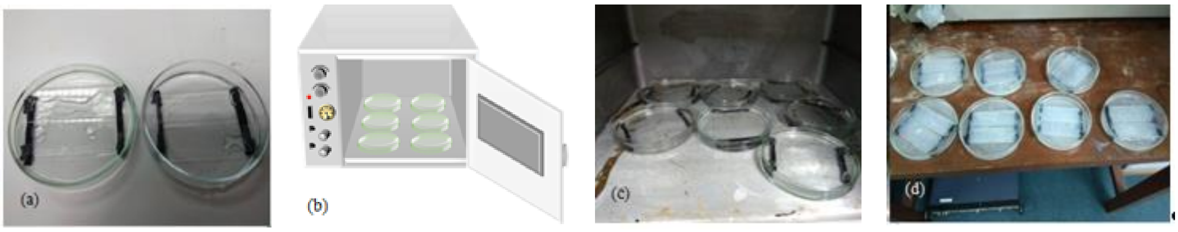


Figure 7. Preparation of 10 mM ZnO growth solution



(a) (b) (c) (d)

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 (3×10^{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.

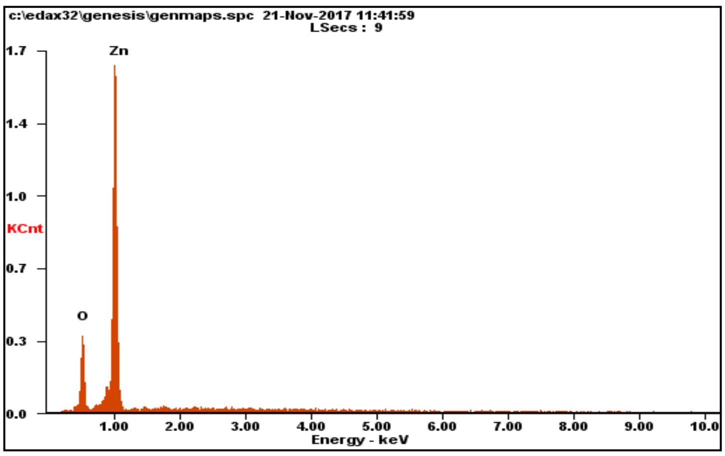
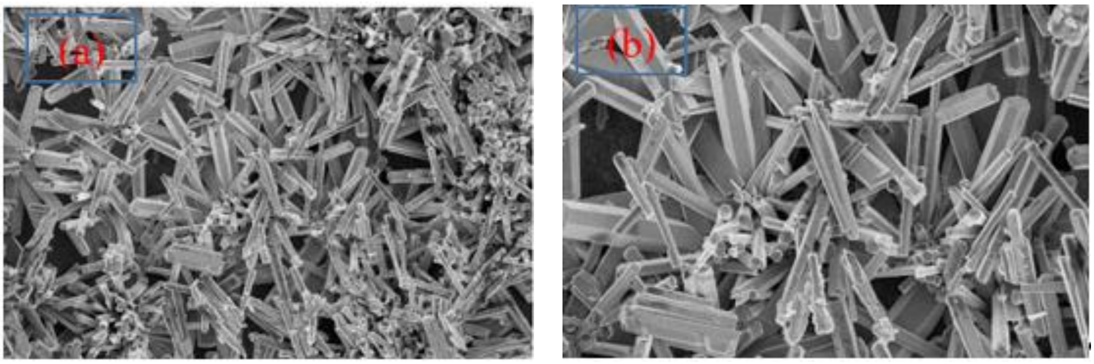
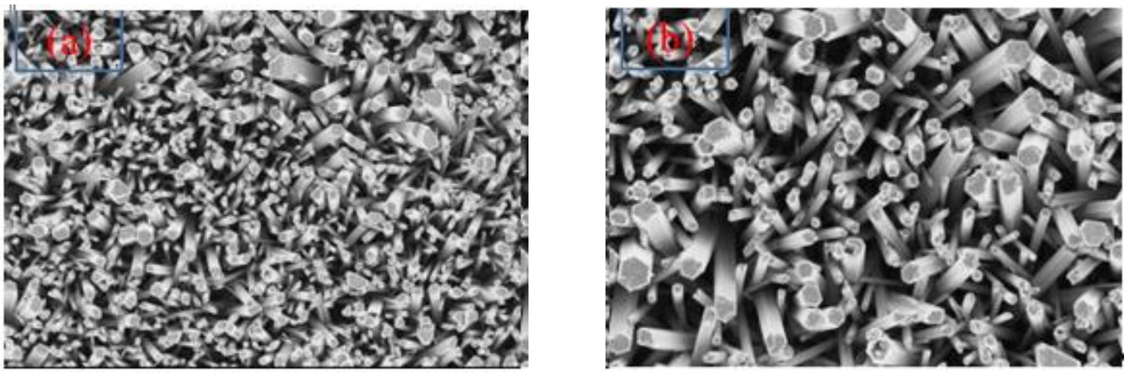


Figure 91. The samples solely contain zinc and oxygen, according to EDX elemental analysis



(a) (b)

Figure 10. ZnO nanorods coated glass grow in horizontal direction using conventional synthesis process; (a) 5kX magnification and (b) 10kX magnification



(a) (b)

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 $3\,x\,10^{13}$ 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 nanrods. 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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