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# ZnO Nanowire Hydrothermal Synthesization: Parameters Affecting Their Growth Direction and Surface Morphology

Shrok Allami

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## Abstract

ZnO nanowires (or nanorods) have been widely studied due to their unique material properties and remarkable performance in electronics, optics, and photonics. This chapter presents a review of the current research of ZnO nanowires (or nanorods) synthesized by hydrothermal method. We discussed the mechanism of its nucleation and growth taking the effect of different parameters on its growth direction and their final morphology into account. A mixture of zinc nitrate and hexamine as precursor is the most popular. We reported the effect of precursor type and concentration, pH of the growth solution, bath temperature, substrate type and seeded layer, and duration time.

**Keywords:** ZnO nanowires, morphology, synthesized, hydrothermal method

## 1. Introduction

Recently, nanomaterials have attracted much attention due to their high performance in electronics, optics, and photonics. Nanomaterials can be classified into three groups—zero dimensional, one dimensional, and two dimensional—due to their aspect ratio. Zero-dimensional nanostructures are referred to as quantum dots or nanoparticles with an aspect ratio near unity. One-dimensional nanostructures such as nanowires, nanorods, nanofibers, nanobelts, and nanotubes find perfect application in semiconductor materials and device. Two-dimensional nanomaterials, as thin films, are used as an optical coating, corrosion protection, and semiconductor thin film devices.
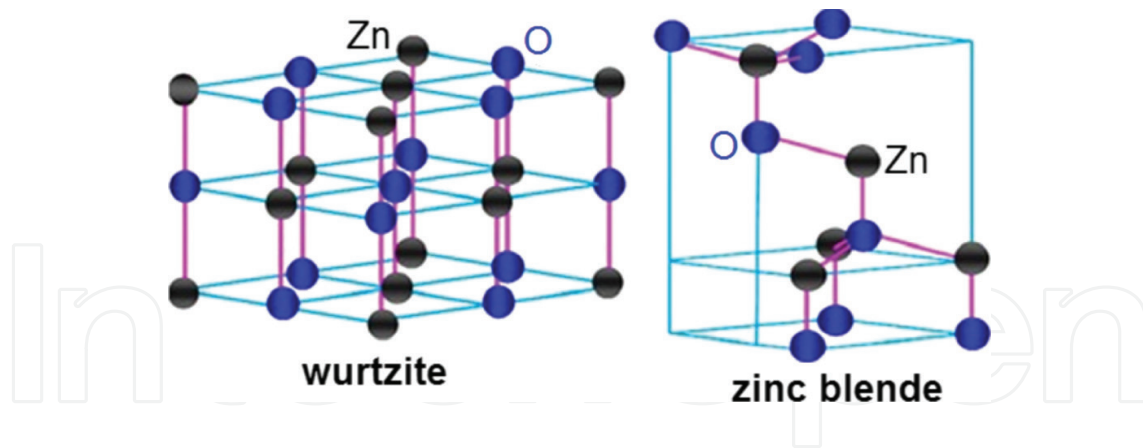
**Figure 1.** Two types of ZnO crystal structure.

Currently, one-dimensional zinc oxide (ZnO) nanowire is one of the most interesting nanomaterials for researchers [1]. It is a semiconductor material with a direct wide band gap energy (3.37 eV) and a large excitation binding energy (60 meV) at room temperature [2]. ZnO exists in two main crystalline structure, hexagonal wurtzite and cubic zinc, blended as shown in **Figure 1**.

The hexagonal crystalline structures with about 1.60 of $c/a$ ratio is close to the hexagonal cell ideal $c/a$ value = 1.633 [10]. Its structure could be described as a number of alternating planes composed of tetrahedrally coordinated of $O^{2-}$ and $Zn^{2+}$ stacked along the $c$-axis (**Figure 1**) [3].

Due to their remarkable performance in electronics, optics, and photonics, ZnO nanowires are attractive candidates for many applications such as UV lasers [4], light-emitting diodes [5], solar cells [6, 7], gas sensors [8], photodetectors [9], and photocatalysts [10]. ZnO nanowires also are used increasingly as photocatalysts to inactivate bacteria and viruses and for the degradation of environmental pollutants such as dye pesticides and volatile organic compounds [11, 12].

## 2. ZnO nanowire synthesis

ZnO nanowires can be synthesized mainly by two methods: vapor phase and solution phase. Solution phase synthesis has many advantages over vapor phase synthesis, as low cost, low synthesis temperature (<200°C), scalability, and ease of handling. This allows using different kinds of substrates including inorganic and organic, an aqueous or organic solution, or a mixture of them in the growth process [13, 14].

## 3. Hydrothermal method

The solution phase synthesis processes carried out in an aqueous solution, under high vapor pressure and temperature [4, 15]. Hydrothermal method among all of the synthesis methods is found to be the most attractive synthesis technique to obtain well-aligned ZnO nanowires, hierarchical or branched nanowires. Since no need for high-temperature manufacturing and

vacuum processing in hydrothermal method that would offer the potential for much lower processing cost. A lot of effort has been made to investigate the effect of synthesis parameters on the density, dimensions, and quality of ZnO nanowires [3, 4, 6, 7, 15, 16]. Many focused on seeding layer effect [10, 17–20], chemical reagent, and their concentration effect on ZnO nanowire density [21], morphology [22], growth time, and temperature [22]. We think that, there are still need to study the effect of additives under different fabrication conditions on ZnO nanostructure morphology.

The general process for vertically aligned ZnO nanowires grown on a seeded or unseeded substrate by the hydrothermal method is done using mixture aqueous solution as a precursor (or growth solution) that contains an alkaline reagent and $Zn^{2+}$ salt ($Zn(NO_3)_2$, $ZnCl_2$, etc.). The alkaline reagents that have been used to supply $OH^-$ during the reaction process are NaOH, hexamethylenetetramine (HMTA), $Na_2CO_3$, ammonia, and ethylenediamine. Elevated temperatures (>100°C) and pressures in a Teflon-sealed stainless autoclave [24–27] are required when NaOH, KOH, or $Na_2CO_3$ is chosen to supply $OH^-$ in the synthesis process. HMTA, ammonia, or ethylenediamine has been chosen in the synthesis process which can reduce the synthesis temperatures (<100°C) and pressure to an atmospheric pressure [28].

It was found that the key parameters for controlling nucleation and morphology of ZnO nanowires can be achieved by controlling the supersaturation reaction and reactant stability that depends on solution temperature and pH, precursor concentration, and duration growth time. Another important parameter is the nature of the substrate on which ZnO nanowires nucleate and grow over. Seeding of ZnO particles is usually used to prompt the nucleation process and improve ZnO particles adhesion, their distribution, and alignment. Without a ZnO seeding layer, ZnO nanowires could be grown also on a seedless substrate by using Au and introducing a suitable content of ammonium hydroxide into the precursor solution. Au is used as an "intermediate layer" to assist the growth of ZnO nanowires after treating the layer [29].
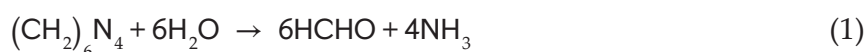
## 4. ZnO nanowire synthesis mechanism

Hexamethylenetetramine (($CH_2)_6N_4$ or HTMA) and $Zn(NO_3)_2$ are the most often used in producing high-quality ZnO nanowires [28].
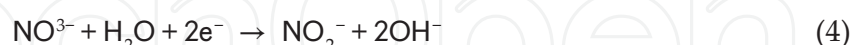
Nanowire formed after ZnO cluster can be precipitated on the substrate when the growth solution attained saturation when the production of anion and cation exceeds the solubility of the reactants [29].

Hexamethylenetetramine (HMT) was responsible for the production of ammonia ($NH_3$) that played the role of complexion agent. That is, complexion agent aided the yield of Zinc tetramine ($Zn(NH_3)_4^{2+}$) complexion in alkaline medium. The reaction that occurs in the bath is shown in the chemical equations [30]:

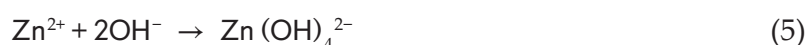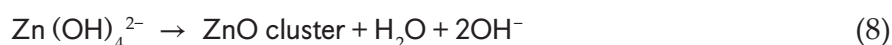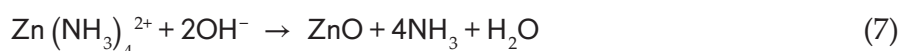Decomposition reaction:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \tag{1}$$

Hydroxyl supply reaction:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{2}$$

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \tag{3}$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \tag{4}$$

Supersaturation reaction:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_4^{2-} \tag{5}$$

$$Zn^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} \tag{6}$$

ZnO nanowire growth reaction:

$$Zn(NH_3)_4^{2+} + 2OH^- \rightarrow ZnO + 4NH_3 + H_2O \tag{7}$$

$$Zn(OH)_4^{2-} \rightarrow ZnO\ cluster + H_2O + 2OH^- \tag{8}$$

In the growth solution, the hexamethylenetetramine is first hydrolyzed (Eq. (1)). $NO_3^-$ ions from $Zn(NO_3)_2$ decomposition acquire electrons and are reduced to $NO_2^-$ ions, inducing the increase of $OH^-$ concentration (Eq. (4)) [32]. $OH^-$ ions are combined with $Zn^{2+}$ ions to form an intermediate growth unit of $Zn(OH)_4^{2-}$ (Eq. (5)), while Zinc tetramine ($Zn(NH_3)_4^{2+}$) is formed from the combination of $Zn^{2+}$ ions with $NH_4^+$. Due to dehydration of the complex in the alkaline medium, ZnO clusters are formed by the electrostatic repulsion of ionic species ($Zn^{2+}$ and $OH^-$) (Eqs. (7) and (8)). It is well known that solution supersaturation is a prerequisite for ZnO growth and is also intimately connected with their growth and morphology evolution. As the reactions continue, more ZnO clusters appear in solution. When the solution becomes supersaturated, nucleation cluster of molecules formed undergo rapid decomposition, and particles combine to produce film thickness, where ZnO nanowire is formed in the solution via the substrate.

One of the key parameters for the growth of ZnO nanowires is controlling the reactant supersaturation. It is believed that high supersaturation levels favor nucleation and low supersaturation levels favor crystal growth. With a short explanation for this, they reported that if a lot of $OH^-$ is produced in a short period, the $Zn^{2+}$ ions in the solution will precipitate out quickly, and therefore, $Zn^{2+}$ would contribute little to the ZnO nanowire growth and result in the fast consumption of the nutrient and prohibit further growth of the ZnO nanowires. Thus, the concentration of $OH^-$ should be controlled in the solution to maintain s suitable per saturation levels during the whole nanowire growth process [32].

HMTA control growth direction due to its ability to attach the nonpolar facets of the ZnO nanowires and prevent attracting access $Zn^{2+}$ ion, thus leaving only the polar (001) face for epitaxial growth [32].

# 5. Parameters affecting ZnO nanowire growth and morphology

## 5.1. Precursor concentration

Wang et al. reported that unless the average diameter and length of ZnO nanorods increases with the precursor concentration increases (**Figure 2**), it was found that the changes in the $[Zn(NO_3)_2]/[C_6H_{12}N_4]$ ratio have no significant effect on the diameters of the ZnO nanorods (**Figure 3**).

It was found also that using unity ratio leads to achieve the maximum value of aspect ratio of ZnO nanorod array [33].

Xu et al. synthesized ZnO nanowires using equimolar concentrations of the zinc salt and HMTA; the nanowire density increased till reaching steady state with the precursor concentration. The authors referred that to the increase of zinc chemical potential with zinc concentration in the solution. To balance this increment, more nucleation sites on the substrate surface will be generated, and, therefore, the density of the ZnO nanowires will increase. However, when the density reaches saturation rate, any increase in the solution concentration may not increase the density of the nanowires anymore [8].
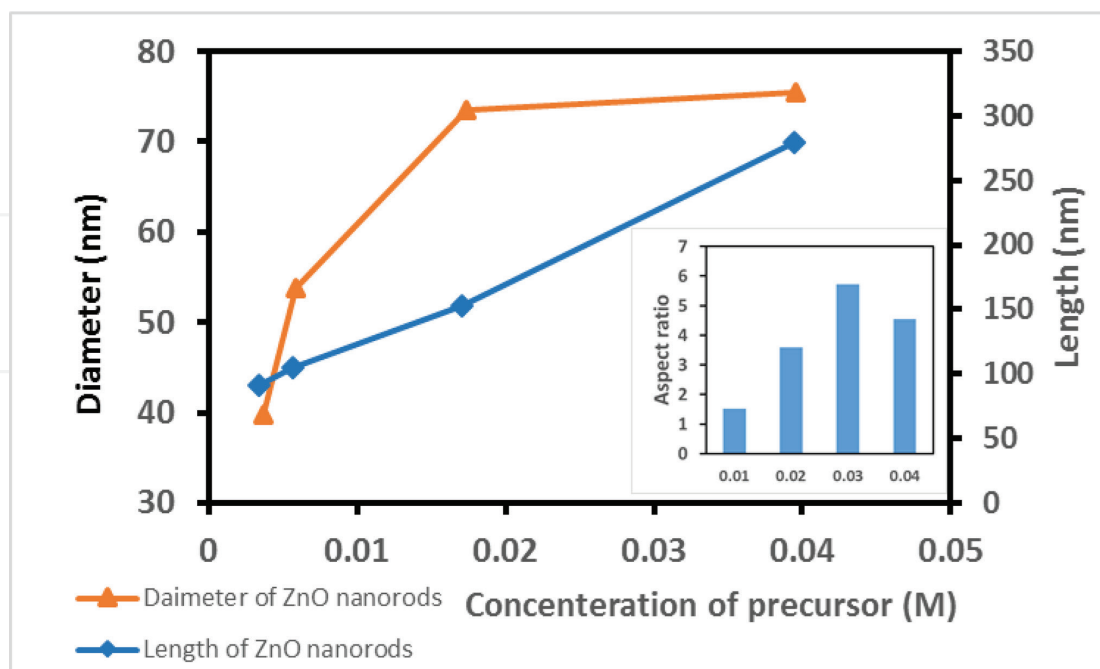


**Figure 2.** Average diameters, lengths, and aspect ratios of ZnO nanorods prepared from various precursor concentrations with a $Zn(NO_3)_2/C_6H_{12}N_4$ ratio of 5 (image from [33] ©2008 The American Ceramic Society).
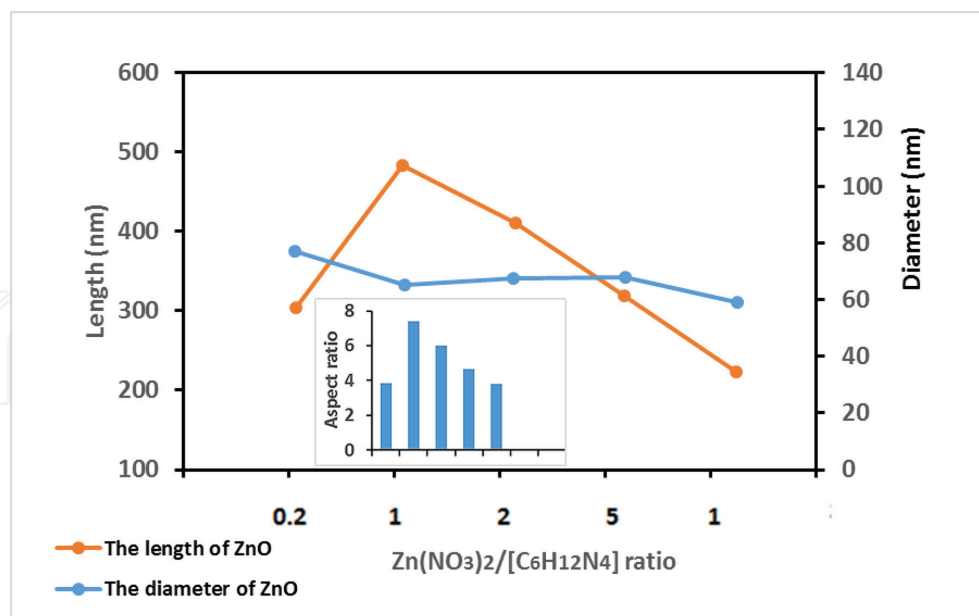
**Figure 3.** Average diameters, lengths, and aspect ratios of ZnO nanorods prepared in a 0.04 M precursor solution with various $Zn(NO_3)_2/C_6H_{12}N_4$ ratios (image from [33] ©2008 The American Ceramic Society).

Kim et al. reported that precursor concentration plays a role in ZnO nanowire structure and increasing the concentration could change ZnO nanorod growth from single crystals with low density and variable orientations to polycrystals due to the supersaturated $Zn^{2+}$ source [34].

Gokarna et al. achieved well-aligned, highly crystalline, small-diameter urchin-like ZnO NWs on PS beads which were pre-coated with a ZnO seed layer. They found that the average diameter of ultra-thin ZnO NWs that are produced from salt precursor dissolved in water with the small addition of $NH_4OH$ as growth solution could be controlled by varying the concentration of zinc acetate in the growth solution. Smaller size is obtained with lower concentration. XRD patterns showed that the NWs had a wurtzite hexagonal structure and (001) preferred growth direction [35] (**Figure 4**).

In our previous work, we studied ZnO nanowire structure and morphology by varying the precursor concentration with equimolar concentrations of the zinc salt and HMTA on the seedless substrate. We found that increasing precursor concentration might provide a lot of ZnO nuclei and densify nanorods. For samples fabricated at low precursor equimolar solution (5 mM), nonalignment, small aspect ratio, low densities, and prism-like ZnO nanorods were achieved, **Figure 5a**. Increasing precursor concentration to 10 Mm leads to decreased aspect ratio and increased density of nonalignment prism-like-shaped nanorods, **Figure 5b**. **Figure 5** shows the surface morphology of the above samples [37].

## 5.2. Growth temperature

ZnO nanowire growth by a hydrothermal process is a thermo-activated process; nanowire formation must be activated by the heating of growth solution to the desired temperature. A minimum temperature of ~60°C is required to obtain ZnO nanowires. Cesar and his group [38] reported that the starting temperature of ZnO growth solution on seeded substrate plays a role
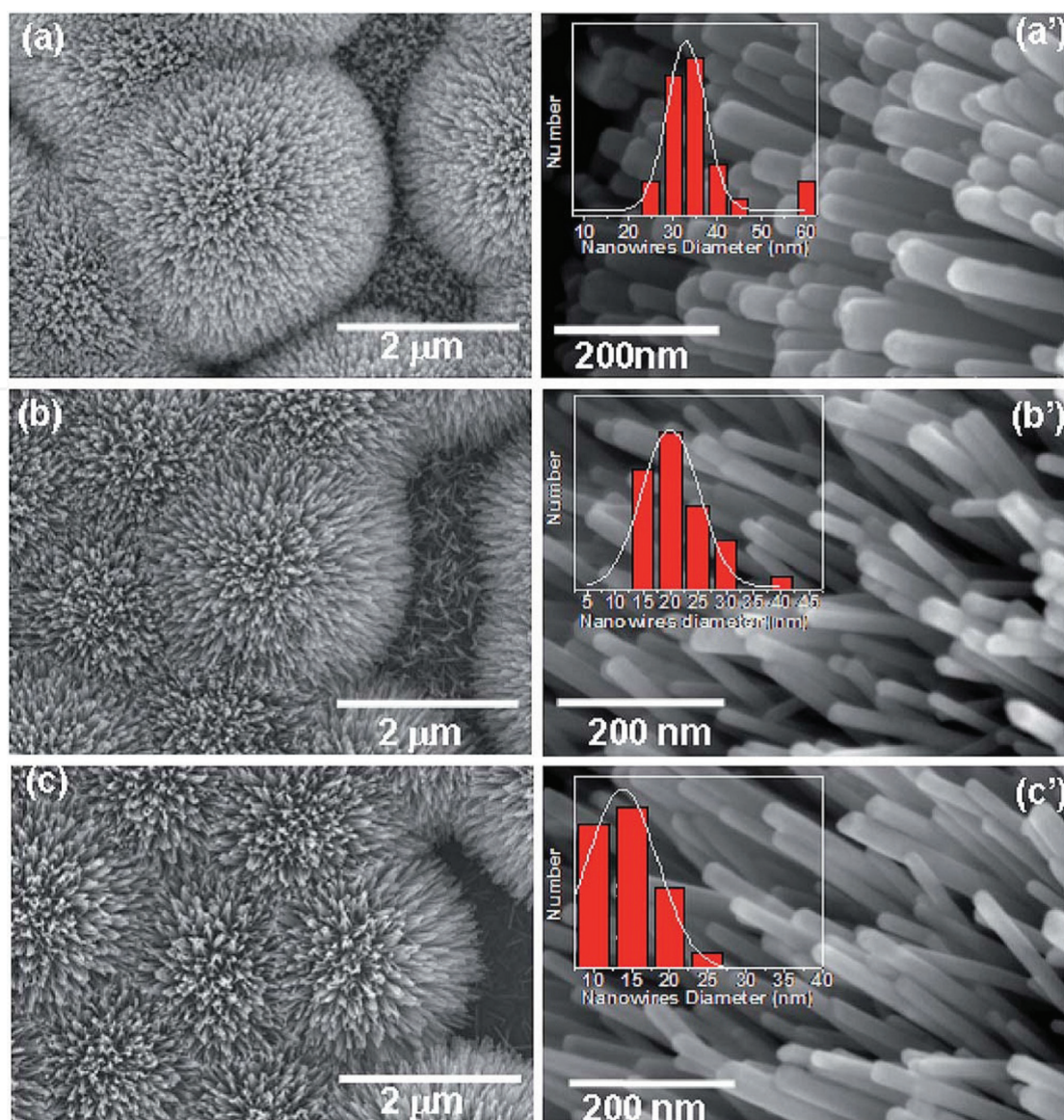
**Figure 4.** SEM images of ZnO NWs grown as a function of varying solution concentration. (a, a′) 0.029 M, (b, b′) 0.02 M, and (c, c′) 0.018 M, respectively. (a, b, c) are at low magnification; (a′, b′, c′) are at high magnification of the NWs with the diameter distribution of the NWs. The white line on the histograms represents the corresponding fitted Gaussian distributions (image from [35]).

in their resultant morphologies. Bigger nonaligned ZnO nanowires with a slight coneshaped achieved when the growth solution heated from room temperature to the required temperature during synthesization process, while vertically aligned small-diameter ZnO nanowires achieved when pre-heated solution used in the synthesization process. They put an explanation for that as shown in **Figure 6**. During the heating process, the ZnO seeds begin firstly to coalesce to form larger ZnO seeds. Those larger seeds are responsible for obtaining the larger ZnO nanowire diameters. They concluded that at low-temperature range (60–80°C), both lateral and axial growth are promoted, while at the high-temperature range ($T > 80°C$), the axial growth is mainly supported. That means the temperature plays an important role in the growth kinetic along the $c$-axis [0001], more than the other directions. **Figure 7** represents the evolution of the average length with the growth temperature for a fixed growth time (2 hours).
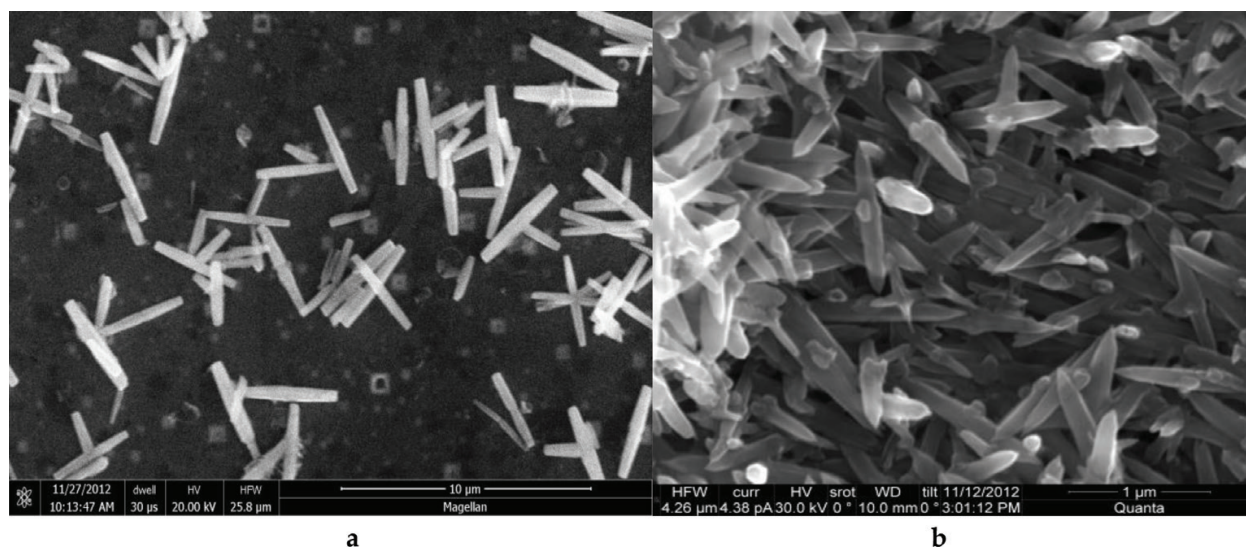
**Figure 5.** SEM image of ZnO grown at precursor equimolar solution: (a) (5 mM) and (b) (10 mM) (image from [37]).
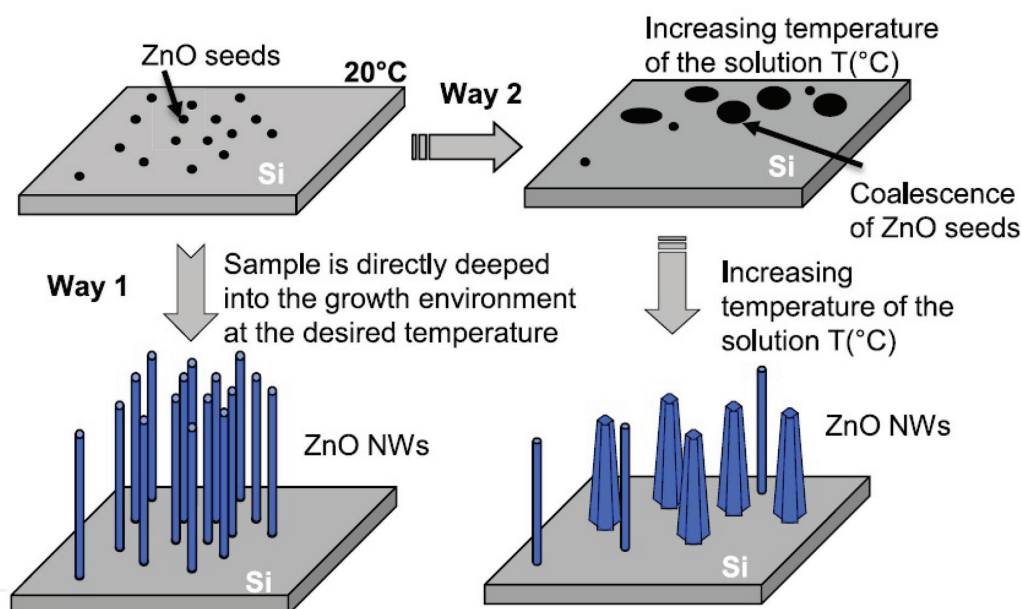


**Figure 6.** Schematic sketch of two possible routes for ZnO nanowire array synthesis (image from [38]).

Unless Sugunan et al. did not significant any difference in the nanowires morphology for different hydrothermal growth bath temperatures carried out with low precursors concentration [31]. We found an important role of the synthesization temperature on ZnO nanowires nucleation and growth, without changing their hexagonal shape [37]. Small aspect ratio, low densities, and nonalignment hexagonal-shaped ZnO nanorods were achieved, when ZnO nanorods are synthesized at low precursor equimolar solution (5 mM) and low temperature (65°C) (**Figure 8a**). Elevating growth temperature to 85°C increases nanorod density but affects their shape to become prism-like and branched with growth advancement as shown in **Figure 8b**. As we can see from Eq. (1), seven moles of reactants produce 10 moles of products; increasing the reaction temperature leads to increase in HMTA hydrolysis and push the
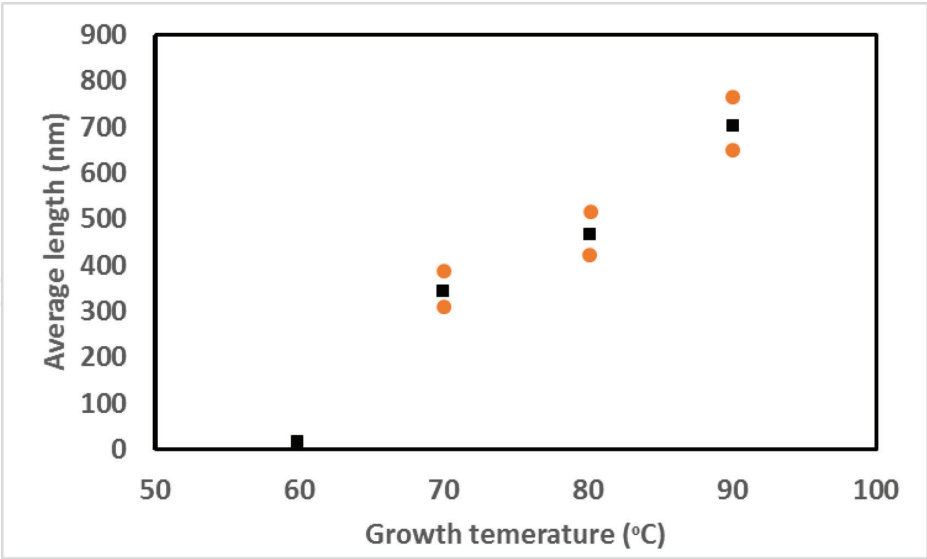
**Figure 7.** Average length of ZnO nanowires as a function of the growth temperature (image from [38]).
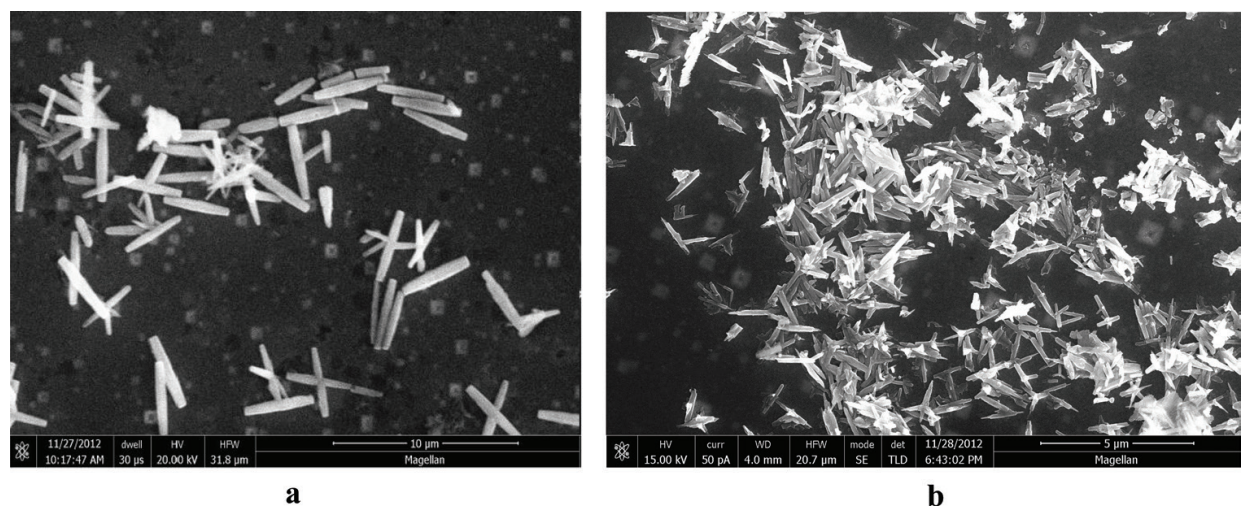


**Figure 8.** SEM images for ZnO synthesized in (a) 65°C and (b) 85°C (images from [37]).

equilibrium forward associated with increased system entropy [39, 40]. It can be recognized that increasing temperature provides more $OH^-$ ions with mobile energy that enhance ZnO nucleation to minimize their free energy. During the growth, process nanorod shape changed from hexagonal to prism-like shape; it was probably due to increasing the electrostatic reaction between the solution ions and ZnO polar surfaces with temperature and increasing erosion reaction on the top of the nanorods.

## 5.3. The seedless substrate and ZnO seeding layer

It was found that via hydrothermal synthesis method, any substrate can be used for the growth of vertical ZnO nanowires by using ZnO seeding layer. In this way, ZnO nanowires can grow on flat surface regardless of the substrate (polymer, glass, semiconductor, metal,

polydimethylsiloxane (PDMS), polystyrene (PS), polyethylene terephthalate (PET), polyethylene fibers, microfibers, polyurethane, polyimide, and paper, only controlling the growth conditions). Typical pre-seeding methods include deposition of ZnO seed on the substrate by spin coating of ZnO nanoparticles, sputter deposition, and physical vapor deposition. In order to improve ZnO particle adhesion to the substrate and nanowire vertical growth, ZnO seeds from zinc acetate must be annealed at a certain temperature. The texture, thickness, and crystal size of ZnO seed layers also affect the quality of ZnO nanowire growth. Greene et al. [41] studied the minimum annealing temperature required to form textured seeds from zinc acetate on a silicon substrate. The results suggest that temperatures between 150 and 200°C are needed for seed alignment, whereas higher temperatures promote seed crystallinity and growth. While Baruah and Dutta [22] have reported that a very uniform thin layer of ZnO nanoparticles could be observed when ZnO seeds are annealed at 350°C. ZnO crystallized into nanoparticles as well as nanorod-like structures when the annealing temperature was further increased to 450°C. Ghayour et al. [42] investigated the effect of seed layer thickness on alignment and morphology of ZnO nanorods. The results showed that the diameter increased, the density decreased, and the length of the nanorods slightly decreased when the thickness of the seed layer increased (**Table 1**). Wu et al. [43] studied the effects of seed layer characteristics on the synthesis of ZnO nanowires. The density of nanowires decreased when the thickness increased, and the diameter of the nanowires was found to increase with the seed layer grain size. Ji et al. [44] found that the average diameter of nanowires increased and the density decreased when the seed layer thickness changed from 20 to 1000 nm. Baruah and Dutta [42] reported that the nanorods grown on seeds crystallized from a zinc acetate solution have a higher aspect ratio (of the order of 3) than those grown using nanoparticle-seeded substrates.

In seedless substrate thin layer of Au over a thin layer of Ti in order to overcome mismatching between substrate used and the ZnO particles then are annealed at 350°C under argon atmosphere. The formation of ZnO nuclei on Au surface is a complicated task to accomplish. For this, different techniques are employed to introduce the negative charges over the Au surface to attract the positively charged zinc (II) complexes, formed during Eqs. (3) and (6). It was reported that the surface roughness of the substrate has shown a major effect on the orientation and quality of the NW produced. The smooth Au (111) surface is ideal for the growth of highly aligned ZnO NWs [36].

It was found that Au provides the proper sites for nanowire ZnO nucleation on its grain boundary, **Figure 9** [38].

| Thickness of the seed layer (nm) | Diameter of ZnO nanorods (nm) | Density of ZnO nanorods ($\mu m^{-2}$) | Length of ZnO nanorods (nm) |
|---|---|---|---|
| 20 | 30 | 213 | 1052 |
| 40 | 36 | 209 | 1007 |
| 160 | 51 | 184 | 998 |
| 320 | 72 | 169 | 967 |

**Table 1.** The diameter, density, and length of ZnO nanorods corresponding to the thickness of the seed layer (from [42]).
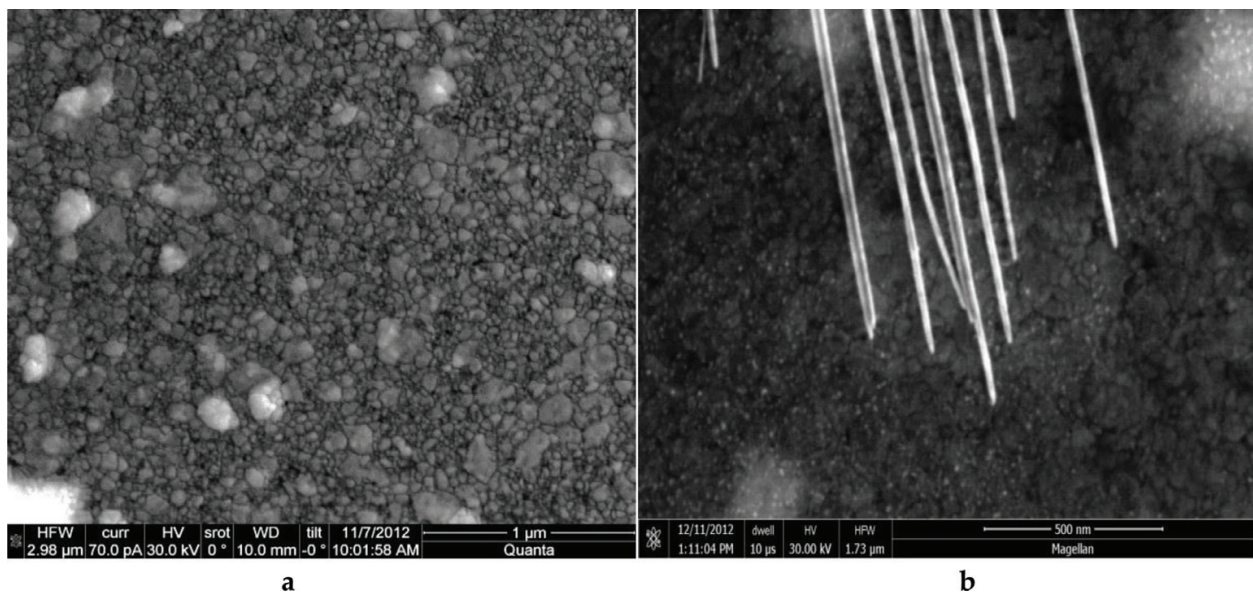
**Figure 9.** SEM images for seedless substrate: (a) after annealing and (b) ZnO nanowire growth on Au grain boundary. From [37].

## 5.4. Growth solution pH value

Recently, it was found that the introduction of ammonium hydroxide into the growth solution as an additive could efficiently affect ZnO nanowire morphology and their aspect ratio on pre-seeding and seedless substrate. Baruah and Dutta [45] synthesized ZnO nanorods on pre-seeded glass substrates using equimolar concentration of zinc nitrate and HTMA as the precursors. Flower petal-like ZnO nanostructures were obtained when the growth process is initiated in basic condition (pH 8–12). Akhavan et al. [46] studied the effect of pH change in basic range on the growth of ZnO nanorods by using zinc nitrate and NaOH as precursors. They reported that the diameters of the nanowires are increased with pH until they formed a ZnO film when the pH value reached 11.44 with a fast growth rate of ZnO nanorods on the seeded layer.

On seedless Au substrate, Boubenia et al. [36, 47] controlled both ZnO NW density and their electrical properties via developed low-cost and scalable bottom-up hydrothermal growth process using $NH_4OH$ addition. They found that small increase in pH value leads to increase the NW densities, **Figure 10**. They put an explanation that depends on the formation of Zn (II) complexes in the solution, which will largely decrease the Zn solubility and lead to a supersaturation large enough to initiate a large number of ZnO nuclei both in the solution and onto the Au-coated substrate. They reported that $NH_4OH$ addition has no effect on preferred growth direction of the resultant, a perfect hexagonal prism-shaped NW, and their arrays exhibit a strong preferential c-axis orientation vertically to the growth substrates.

In order to adjust the pH value of the growth solution on a seeded substrate for 2 hours at 90°C, Cesar et al. [38] added HCl or NaOH to the growth solution. They observed that the ZnO nanowires are well oriented quasi-perpendicularly to the substrate and have a quite homogeneous diameter distribution for all the pH values used. But they found that pH affected ZnO nanowire morphologies. Different morphologies could be obtained: hexagonal
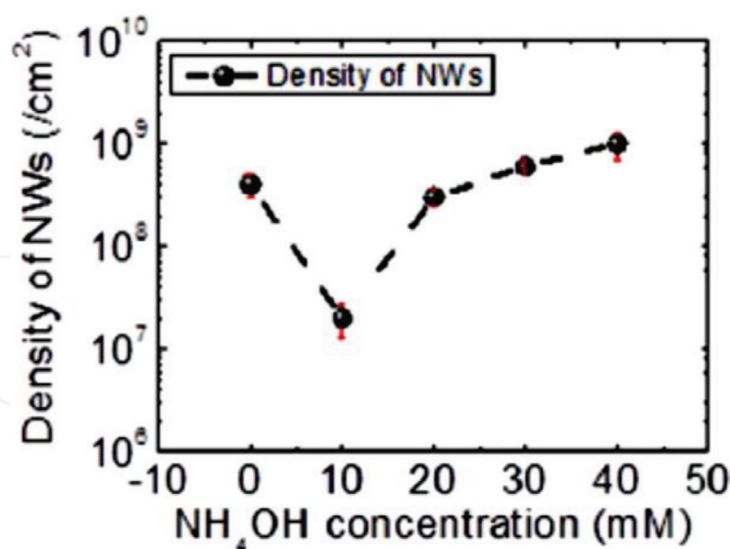
**Figure 10.** The variation of ZnO NW density with the change in NH₄OH concentration (from [36]).

nanorods for pH = 7, double cone-shaped tip nanorods for pH = 8, nanoprisms for pH = 10, and nanoflowers for pH = 12. For the pH value in the acid range (pH < 7.0), an attack on the seed layer leads to an inhomogeneous surface.

Igori Wallace [30] confirmed the ZnO nanowire shape changing with pH raising from 8.1 to 9 and 10 from hexagonal shape to tapered flower-like shape, respectively. They referred this change to the competition between growth and erosion. As is well known, the hexagonal wurtzite ZnO crystal is a typical polar crystal with a dipole moment in the direction of c-axis; the 0001 crystal plane represents the polarity and is metastable, but the side planes are non-polar and relatively stable. The metastable polar top planes are able to attract hydroxyl ion $OH^-$ from the solution which contributes to the nanowire growth. Upon the addition of aqueous ammonia, $OH^-$ was increased, and its total amount was not consumed completely during the growth. The rest of the $OH^-$ in solution took part in the erosion reaction at the same time. So the relative erosion process became intensive as the pH was increased.

In our previous work [37], we found that $NH_4OH$ addition to the equimolar growth solution could change nanostructure shape and its growth direction on a seedless substrate using the hydrothermal process at 85°C. Adding $NH_4OH$ to low-concentration nutrient solution (5 mM) changed ZnO nanostructure shape from prism-like to hexagonal shape as shown in **Figure 11a** and **b**. While adding $NH_4OH$ to (10 mM) concentration nutrient solution, as we mentioned in the effect of precursor concentration, increase aspect ratio, nanorod density, and change their shape to typical hexagonal dumbbell-like, **Figure 12a** and **b**. XRD spectrums confirm the change in ZnO dominate growth surface from (002) to (112) under the addition of $NH_4OH$. ZnO grown on <111> oriented nano-gold layer has wurtzite structure along high energy polar surfaces and XRD spectrums (**Figure 2c**) also. $NH_4OH$ addition leads to reduce HMT hydrolysis and $Zn(OH)_4^{-2}$ formation (Eq. (5) while tended to increase reaction no. 7 which means increasing growth instead of nucleation. Branching of nanorods appears when a distortion in the nanorods takes place due to stress induced with the locally increased pH
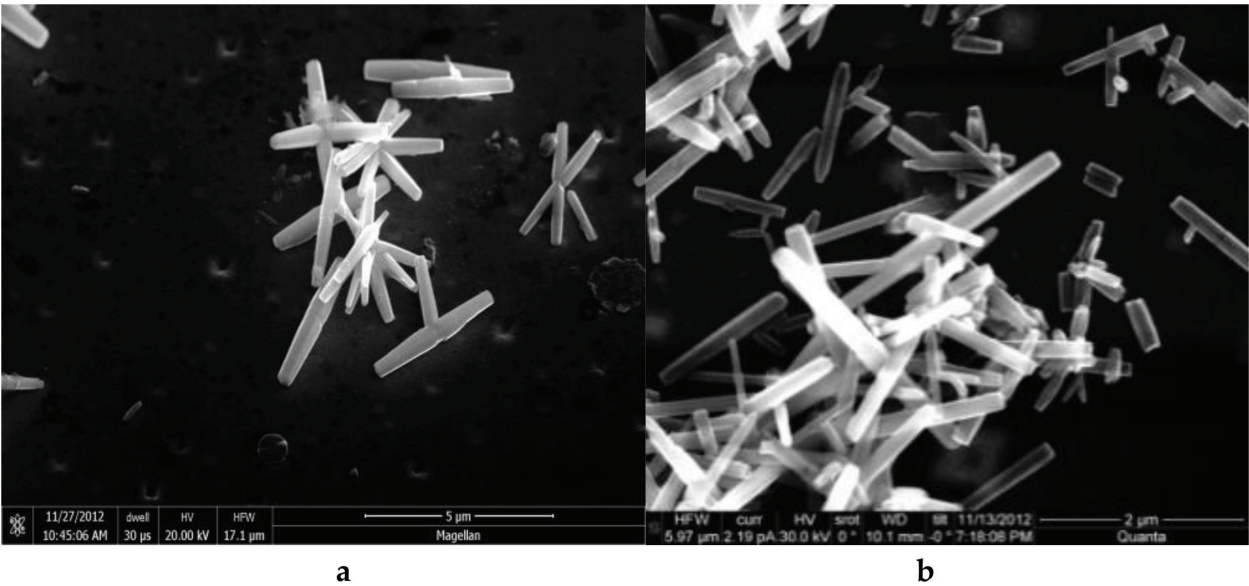
**Figure 11.** SEM images for ZnO shape change using equimolar growth solution 5 mM (a) without addition and (b) with the NH$_4$OH addition (image from [37]).
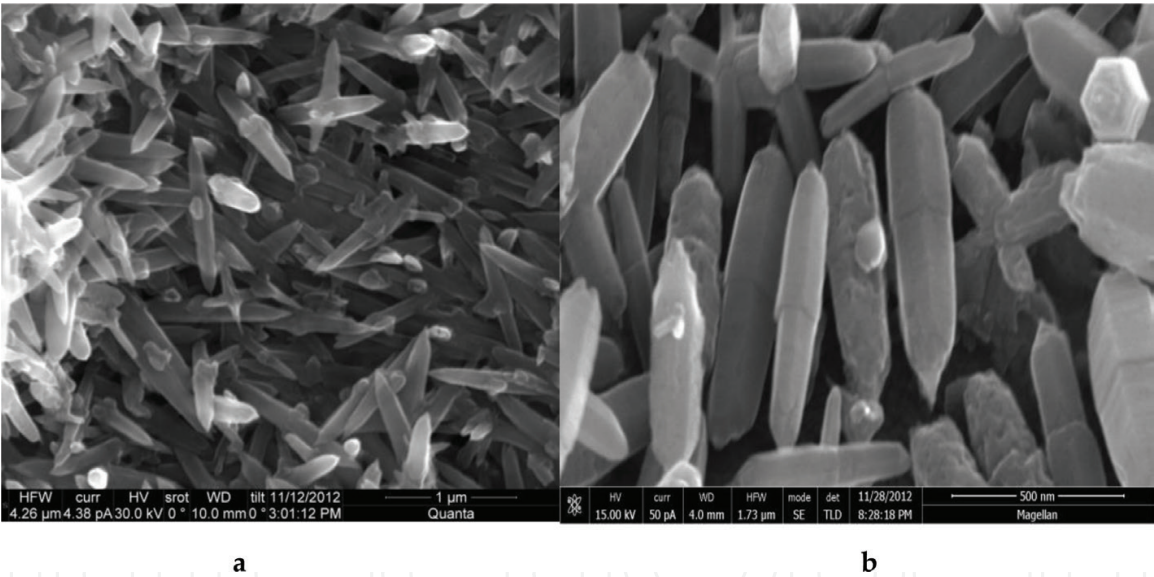


**Figure 12.** SEM images for ZnO shape change using equimolar growth solution 10 mM (a) without addition and (b) with the NH$_4$OH addition (image from [37]).

value near the interface between nanorods and solution that repulse Zn ions electrostatically in order to reduce the surface energy from this distortion.

Increasing nutrient to HMTA ratio to 2:1 (25 mM nutrient, 12.5 mM, and low amount of 0.35 mM NH$_4$OH) creates clear growth solution. Increasing Zn ion in the growth solution leads to fasten its precipitation as ZnO clusters on Au grain boundary of seedless substrate, **Figure 12a** and **c**. These clusters form very small-diameter nanowires grown fast as a forest-like structure. The fast depletion of Zn ions from the solution leads to increase OH$^-$ and then

pH value of the solution and at ZnO/solution interface which prompts the branching process. Increasing the amount of $NH_4OH$ in the above solution creates a milky-like solution producing high-density vertically aligned ZnO nanorods (**Figure 12b**), due to the effect of $NH_4OH$ in controlling HMT hydrolysis and fasting ZnO precipitation from the solution. With time Zn ion depletion increased which leads to increase in $OH^-$ and pH value creating very small-diameter nanowires with nanorods that eroded according to long-time exposure to alkaline media.

## 5.5. Growth duration time

Yuan et al. [23] reported that the average diameter and length of ZnO nanowires increased while the aspect ratio reduced with growth duration time till slowed down due to depletion of the precursor when ZnO nanowires are synthesized using equimolar (50 mM) zinc nitrate and HMTA at 93°C (**Figure 13**).

Baruah and Dutta [22] carried out ZnO nanowire experiments on zinc acetate-seeded substrates for different growth durations from 5 to 15 hours also confirmed increasing the length
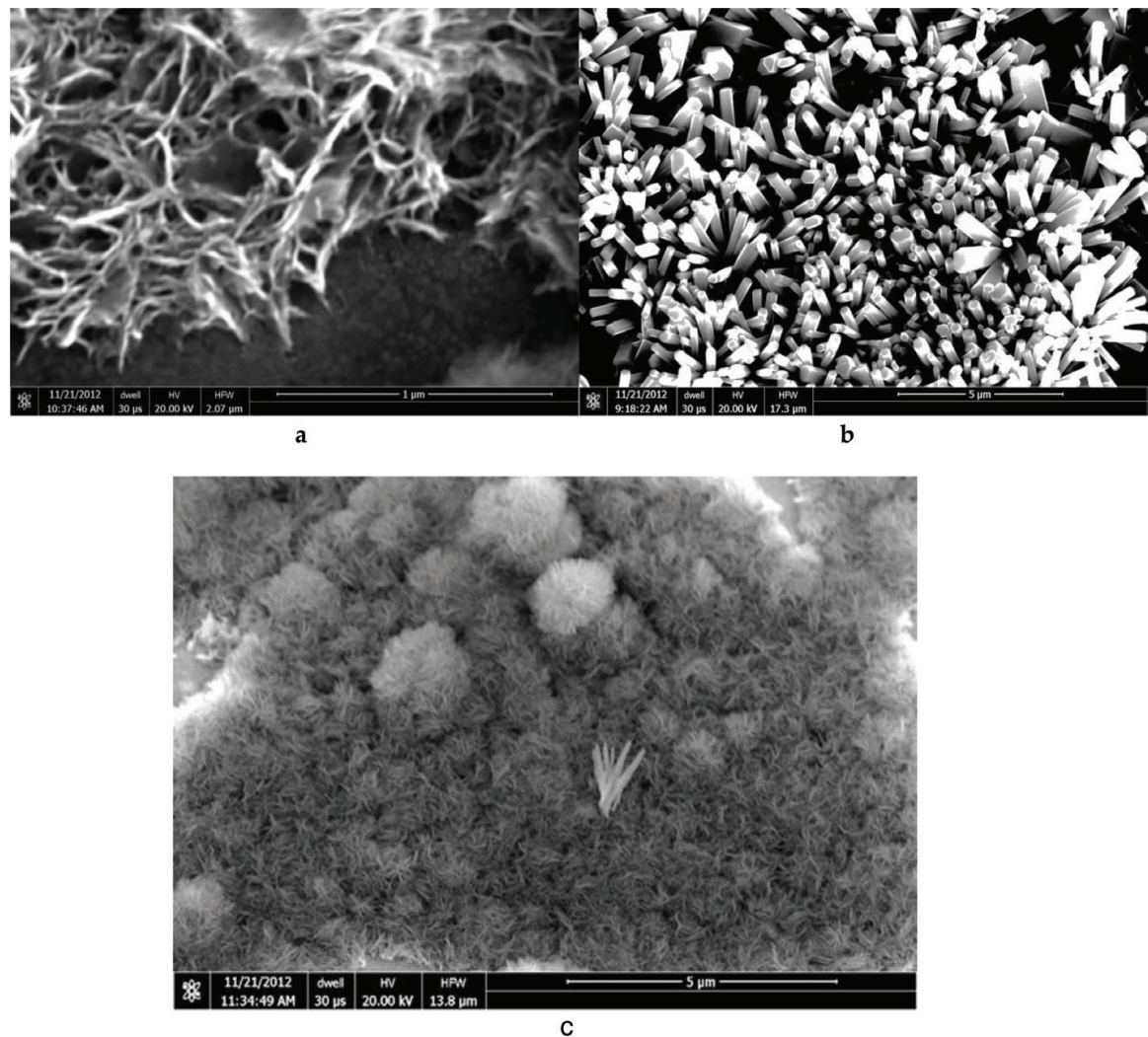


**Figure 13.** SEM images for ZnO nanorod morphology fabricated at 25 mM nutrient, 12.5 mM HMTA, and 0.35 mM $NH_4OH$: (a) clear, (b) milky, and (c) low magnification of clear (images from [37]).

and diameter of the ZnO nanowires with time. The nanowire growth slowed down after a certain period; to keep up the growth rate, they supply fresh solution to the growth solution (**Table 2**).

Cesar et al. [38] investigated the effect of the growth time on the ZnO nanowire morphology synthesized at 90°C with pH of 7.0 for a growth time from 30 min to 6 hours. There are two growth stages for the synthesis of ZnO nanowires: the first stage of about 13 nm/min growth rate until 1 hour and the second one with a slower growth rate of about 2.5 nm/min, the growth time situated between 1 and 6 hours (**Figure 14**).

ZnO nanostructure morphology would not be affected by increasing duration growth time when it was synthesized at low equimolar solution and growth temperature of 65°C. Activation energy is required to enhance the HMT hydrolysis and ZnO precipitation from the solution; it needs higher growth temperature. Extended duration growth time with rising growth solution temperature to 85°C leads the prism-like ZnO nanorods to branch. Advance growth time with $NH_4OH$ addition to 5 mM nutrient solution at 85°C changed the nonaligned hexagonal nanorods to a branched nanorod as shown in **Figure 15a**. Increasing the growth solution

| Growth time (h) | Average diameter (nm) |
|---|---|
| 0.5 | 35 |
| 1 | 37 |
| 1.5 | 55 |
| 2 | 90 |
| 2.5 | 100 |
| 3 | 100 |

**Table 2.** Average diameter of ZnO nanowire changes with growth time (data from [23]).
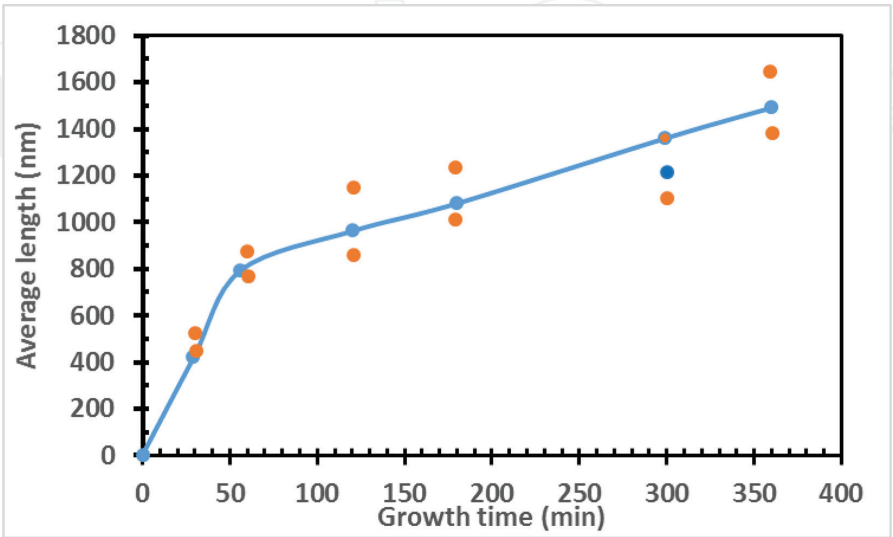


**Figure 14.** Average length of ZnO nanowires as a function of the growth time (from [38]).
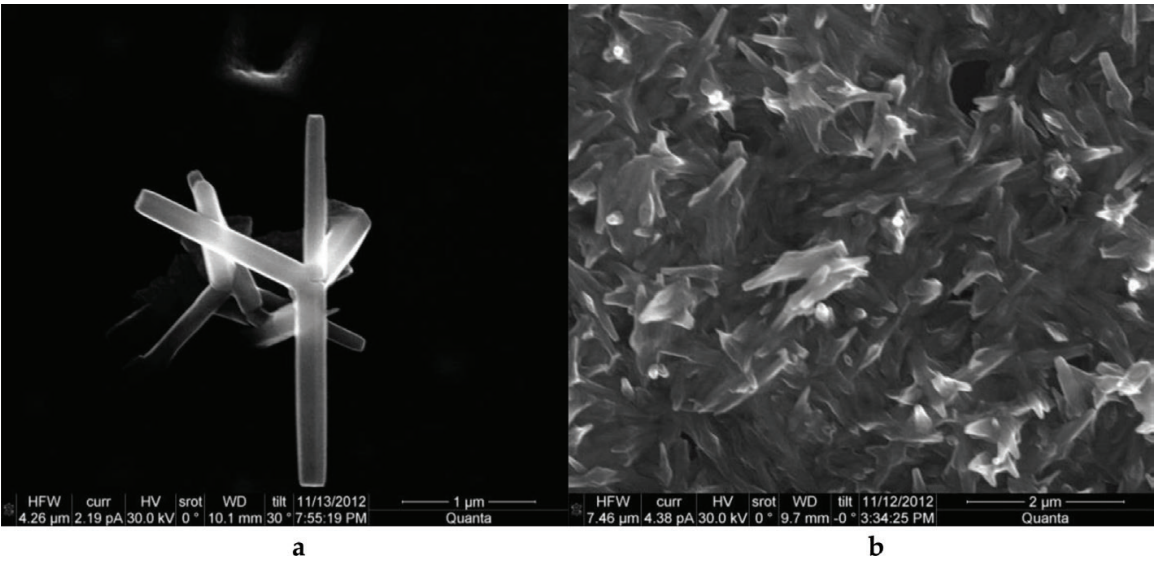
**Figure 15.** SEM images for ZnO nanostructure branched after long-time growth (a) with NH$_4$OH addition to 5 mM nutrient solution at 85°C and (b) without NH$_4$OH addition to 10 mM nutrient solution at 85°C (image from [37]).
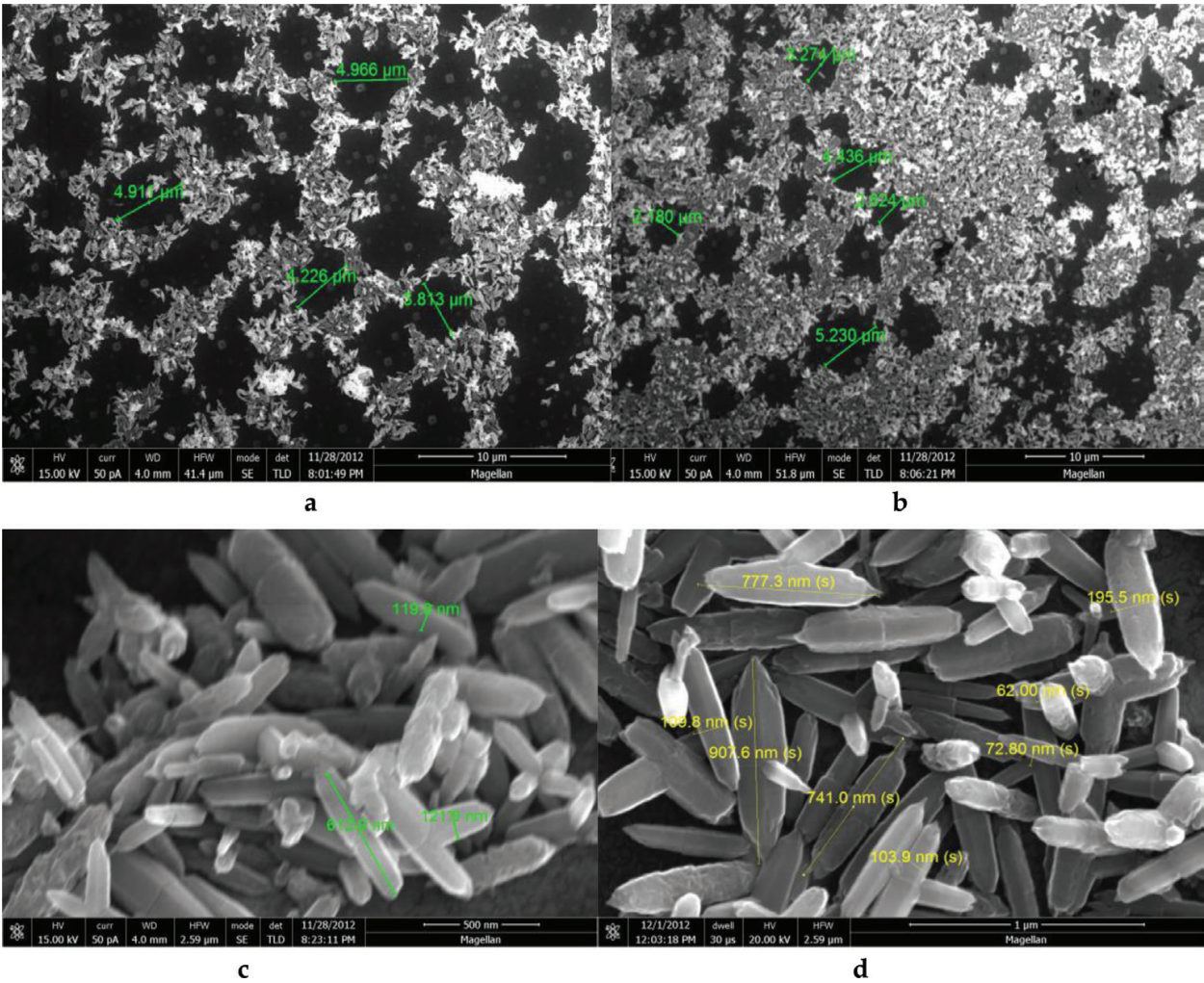


**Figure 16.** SEM images for ZnO nanostructure density and size for different growth NH$_4$OH addition to 10 mM nutrient solution at 85°C: (a) 10 hours, (b) 24 hours, (c) 10 hours, and (d) 24 hours (image from [37]).
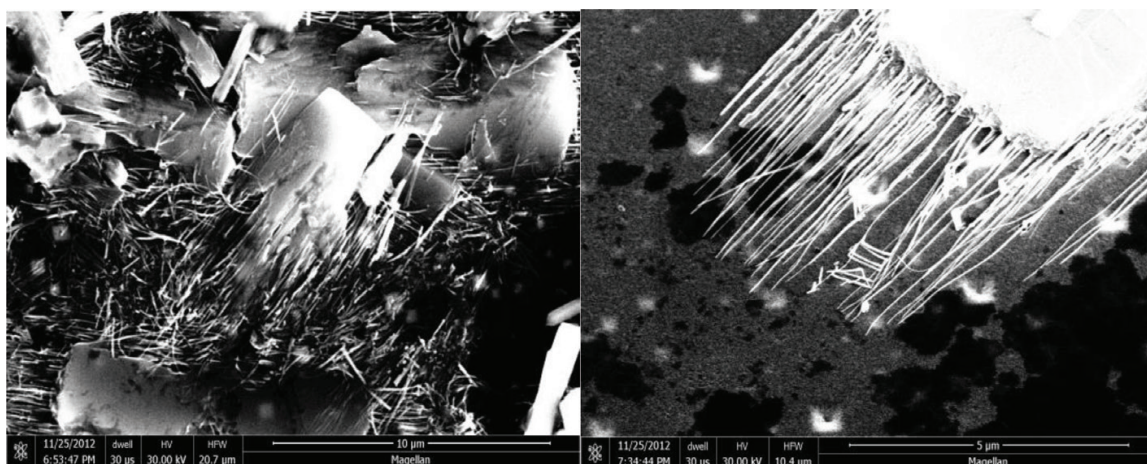
**Figure 17.** SEM images for ZnO nanorod morphology fabricated at 25 mM nutrient, 12.5 mM HMTA, and 0.35 mM NH₄OH milky color after long growth time (images from [37]).

concentration to 10 mM equimolar precursor's ratio, at 85°C solution temperature, leads the prism-like-shaped nanorods to branch early; lateral growth direction increased until getting continuous film after 24 hours as shown in **Figure 15b**. Advance growth with $NH_4OH$ addition changes the dominant growth surface to (112) from the first growth hours as shown in XRD spectrum; this replicated from nanorod shape change to a typical hexagonal dumbbell-like one.

Increasing growth time to samples in 10 mM nutrient solution at 85°C $NH_4OH$ addition leads to increase density and particle size as shown in **Figure 16**.

With growth duration time, $NH_4OH$ addition could prompt heterogeneous growth on the substrate, while the homogeneous nucleation in the bulk solution is suppressed so the growth could last for a long time without replenishing the solution [39]. Under this environment, an expectation of a local rise in pH value with growth time may assist initiation of more secondary nucleate branches on nanorod side surface [48]; this may explain the change in ZnO nanorod dominant growth surface and branching with $NH_4OH$ addition to the growth solution.

Long growth time for samples fabricated at 25 mM nutrient, 12.5 mM HMTA, and 0.35 mM $NH_4OH$ milky color leads to destruction of the ZnO nanowire structure due to long exposure to alkaline media, and increasing pH value in regions close to nanowires would erode their structure as shown in **Figure 17**.

## 6. Conclusion

This book chapter provides an overview of the ZnO nanowire synthesis by hydrothermal process, the simple and efficient method that has received increased attention. A mixture of zinc nitrate and hexamine as precursor is the most popular precursor used. In this chapter we tried to focus on the parameters affecting its morphology. We reported the effect of precursor type and concentration, pH of the growth solution, bath temperature, and duration time. It is a review from published works with our experience in ZnO synthesis by hydrothermal method.

In brief conclusion, increasing the precursor concentration and growth temperature could increase nanowire density and change their morphology. Precursor concentration has the ability to increase their sizes too. Growth starting temperature influenced the nanowire alignments and also affected the density and nanowire morphology. ZnO nanowires could be synthesized via hydrothermal synthesis method on any substrate, seeded or seedless. The thickness of these seed layers affects their diameter and density. Increasing duration growth time also could increase the diameter and length of the nanowires. $NH_4OH$ addition to the growth solution changes its pH value that could increase density and change nanostructure shape and its growth direction on a seeded and seedless substrate.

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