SAKARYA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ DERGİSİ

Sakarya University Journal of Science
SAUJS

ISSN 1301-4048 e-ISSN 2147-835X Period Bimonthly Founded 1997 Publisher Sakarya University
http://www.saujs.sakarya.edu.tr/

Title: Two Significant Factors Affecting the Dimensions of the ZnO Nanorods During Chemical Bath Deposition: Precursor Solution Concentration and HMTA Content

Authors: Memnune KARDEŞ, Koray ÖZTÜRK

Recieved: 2023-01-20 00:00:00

Accepted: 2023-02-24 00:00:00

Article Type: Research Article

Volume: 27
Issue: 4
Month: August
Year: 2023
Pages: 757-767

How to cite
Memnune KARDEŞ, Koray ÖZTÜRK; (2023), Two Significant Factors Affecting the Dimensions of the ZnO Nanorods During Chemical Bath Deposition: Precursor Solution Concentration and HMTA Content. Sakarya University Journal of Science, 27(4), 757-767, DOI: 10.16984/saufenbilder.1241020
Access link
https://dergipark.org.tr/en/pub/saufenbilder/issue/79486/1241020

Sakarya University Journal of Science 27(4), 757-767, 2023

Two Significant Factors Affecting the Dimensions of the ZnO Nanorods During Chemical Bath Deposition: Precursor Solution Concentration and HMTA Content

Memnune KARDEŞ*[1], Koray ÖZTÜRK[1]

Abstract

The effects of zinc ion concentration and hexamethylene tetramine (HMTA) content of the aqueous precursor solution on the aspect ratios of the one-dimensional (1D) ZnO nanorods during chemical bath deposition (CBD) were investigated. The ZnO nanorods were grown on these seeded substrates by the low-temperature CBD method at 95 °C for 5 h. In the first part of this investigation the zinc nitrate hexahydrate (ZNH) to HMTA molar ratio was kept constant at a ratio of 1:1 for each of the CBD solutions prepared with different Zn^{+2} ion concentrations of 0.025, 0.035, 0.050, and 0.075 M. The number densities of the nanorods (i.e., number of nanorods per unit area) were increased with the increasing concentration. In the second part, the ZNH to HMTA molar ratio was varied to differ from the 1:1 value and, in turn, to obtain the precursor solutions relatively rich in Zn^{+2} or OH^{-}ions. Here, the concentration of the precursor solution was kept constant at 0.05 M. The lateral growth perpendicular to the c-axis of the ZnO nanorods was found to be suppressed with the increasing HMTA content (e.g., for the ZNH to HMTA molar ratio of 0.4: 1) due to its capping effect. However, the precursor solution containing an excessive amount of HMTA led to a decrease in the probability of crystal growth, which has been attributed to the OH^{-} ion enrichment.

Keywords: ZnO nanorods, CBD, HMTA, aspect ratio, crystal growth

1. INTRODUCTION

One-dimensional (1D) ZnO nanorods are promising candidates among nanomaterials, which have been the building blocks of many electronic, optoelectronic, photovoltaic, and photocatalytic applications in recent years [1, 2]. Especially in photocatalytic applications, it is important to increase the surface-to-volume ratio as the efficiency increases when the molecules are adsorbed on (relatively) larger catalyst surface area. The surface-to-volume ratio of ZnO nanorods is extremely high, and their structure (along the rod growth direction) is more conducive to charge carrier transfer and the effective separation of electron-hole pairs [3, 4]. ZnO nanostructures have been synthesized by a wide variety of methods, including spray pyrolysis, chemical vapor transport (CVT), chemical vapor deposition (CVD), pulsed laser deposition (PLD), sol-gel, chemical bath deposition

* Corresponding author: memnunedaglar@gtu.edu.tr (M. KARDEŞ)
[1] Gebze Technical University, Materials Science and Engineering Department
E-mail: k.ozturk@gtu.edu.tr
ORCID: https://orcid.org/0000-0002-5073-6564, https://orcid.org/0000-0003-1795-0777

(CBD), and hydrothermal synthesis [5–8] CBD is one of the most widely used methods because of its low cost and temperature requirement. The most important advantage of the CBD method is that almost any substrate can be used for the growth of vertical ZnO nanorods by forming a ZnO seed layer [9, 10]. The quality of the crystal growth depends on the growth time and temperature, and on the chemical bath conditions, such as the nature and concentrations of chemicals, the pH of the growth solution, and the control of additives to control the structural morphology of ZnO nanorods [11]. Previous studies have revealed that it is possible to control the aspect ratio of ZnO nanorods on the substrate by varying the bath temperature in the CBD process. Poornajar et al. [12] reported that the aspect ratio (length/diameter) of ZnO nanorods increased as the growth temperature (80-90°C) increased. Abdulrahman et al. investigated [13] the effects of different growth temperatures (65-115°C) on the crystal structure of ZnO nanorods and emphasized that the aspect ratio increased with growth temperature up to 95°C and it tended to decrease with increasing temperature to 115 °C. Zn^{2+} and O^{2-} ions tend to be adsorbed into polar planes such as (001) to minimize the surface energy during the ZnO nanorod growth process. Temperatures that provide sufficient thermal energy (e.g., 95 °C) lead to anisotropic growth of ZnO nanorods along the c-axis. However, at low temperatures, sufficient thermal energy may not be supplied for the ions to be adsorbed on polar surfaces. Therefore, the ions will adsorb randomly in different crystallographic planes such as (101) and (100) [14, 15]. Moreover, the reaction rate in the CBD process results in the formation of structures of different sizes and irregular morphology. Therefore, it is required to control the chemical reaction by using convenient additives such as organic ligands and surfactants. Amine molecules such as hexylamine, ethylenediamine, trimethylamine and butylamine are frequently used as additives in the CBD precursor solution [16]. Hexamethylenetetramine (HMTA) is a nonionic, heterocyclic tertiary amine that is highly soluble in water and often preferred as a reducing agent and pH regulator among amine molecules. In recent studies, it has been revealed that HMTA acts as a capping agent that promotes anisotropic growth along the c-axis in addition to its OH^- ion provider (pH regulator) effect [17, 18]. Considering the importance of surface area in photocatalytic reactions, studies with different molar ratios will be carried out to determine the effect of HMTA concentration in the precursor solution on ZnO nanorods morphology.

In this study, the effects of precursor solution concentration and HMTA content on the growth of ZnO nanorods were investigated. To facilitate effective crystal growth, all nanorod arrays to be characterized were grown on the seeded chemically stable and optically transparent glass lamella. The five-step wet chemical dip-coating technique was used to provide complete coverage of the glass surfaces with the ZnO seed layer. ZnO nanorods were successfully grown on the seeded glass substrate by a low-temperature (~95 ℃) CBD method. The molar ratio of Zn^{2+}/OH^- is crucial in the morphology control of ZnO nanostructures. The multiple roles of HMTA were revealed by examining in detail the structural properties of grown ZnO nanorods by non-equimolar zinc nitrate hexahydrate (ZNH) and hexamethylenetetramine (HMTA) concentrations over a wide range.

2. METHODS

The surface must be clean (free of impurities) and suitable for chemical bonding. For this purpose, glass lamellas (2.5 cm x 1cm x 7.5 cm) were placed vertically in the chalet. It was kept overnight at 70 °C (oven) in an aqueous solution of hydrochloric acid (HCl, Merck 36.7%) prepared at a ratio of 1:5 by volume. Then, the lamellas were washed with distilled water, and they were kept in 0.2 M NaOH (Merck) aqueous solution at 70 °C for 4 hours. The glass surface was activated after

washing with distilled water and drying at 80 °C for 1 hour. The presence of active nucleation sites lowers the thermodynamic barrier and supports the nucleation and crystal growth stages. Therefore, a two-step seed-mediated process was followed to grow ZnO nanorods. ZnO seed solution was prepared by stirring 0.1 M zinc acetate dihydrate ($Zn(C_2H_3O_2).2H_2O$, Merck) (ZAD) and 0.2 M $NaOH$ in 100 mL of ethanol at 60 °C for 2 hours (pH~10.1). Activated glass surfaces were coated using dip-coating technique at a speed of 100 mm/min and dried at 130 °C for 5 minutes. It has been reported that optimum seed thickness is obtained by 4-6 dip-coating cycles to promote crystallization and alignment of ZnO nanorods [19, 20]. Therefore, this coating step was repeated 5 times. In our previous study [21], the effect of different annealing temperatures (250-400 °C) of the seed layer on the crystallinity and orientation of the ZnO nanorods was investigated. Good crystallinity and sufficient seed densities were obtained at 400 °C. Therefore, the seeded samples were annealed at 400 °C in the present study.

CBD precursor solutions were prepared by mixing zinc nitrate hexahydrate (ZNH) ($Zn(NO_3)_2 \cdot 6H_2O$, Sigma Aldrich) and hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$, Merck) aqueous solutions at room temperature. The molar ratio of the solution was fixed at 1:1, whereas concentrations are set as 0.025, 0.035, 0.050, and 0.075 M. The effect of HMTA concentration in the precursor solution on the aspect ratios of ZnO nanorods was evaluated by changing the ZNH: HMTA molar ratios. For this, precursor solutions rich in Zn^{+2} ions (1:1/4 (Z4), 1:1/2.5 (Z2.5), 1:1/1.5 (Z1.5) and 1:1 (Z1) (ZNH: HMTA)) and vice versa OH^- ions (1/4:1 (Z0.25), 1/2.5:1 (Z0.4) and 1/1.5:1 (Z0.6) (HMTA: ZNH)) were prepared. The value corresponding to state 1 for each sample was fixed at 0.05 M. ZnO nanorods were synthesized by CBD method in 5 hours at 95 °C on the seeded glass substrates. At the end of the reaction, the samples were washed several times with acetone and distilled water, respectively. Finally, samples were kept in an oven at 150 °C for 30 minutes to evaporate the excess water. The crystal structures of all samples were determined by X-ray diffraction analysis (XRD, Rigaku DMax 200) using Cu-Kα radiation with a scanning range of $2\theta = 20 - 70°$ and a wavelength of $\lambda = 1.5406$ nm. In addition, the morphologies of the ZnO nanorods were investigated using scanning electron microscopy (SEM, Philips XL30SFEG). Before and after the CBD process, the pH values of the precursor solutions were measured by the pH meter (Ohaus Starter 300).

3. CONCLUSIONS AND DISCUSSION

3.1. The Effect of Molar Concentration

The crystallographic structures of ZnO nanorods grown with 0.025, 0.035, 0.05, and 0.075 M concentrations are shown in Figure 1a. All observed diffraction peaks in the XRD patterns are consistent with the standard diffraction peaks of the hexagonal wurtzite phase of ZnO (JCPDS No. 36-1451). No other impurity diffraction peaks were represented. The strong diffraction peaks are located at $2\theta = 34.4°$, $2\theta = 31.7°$, and $2\theta = 36.2°$, and the corresponding planes of ZnO are (002), (100) and (101), respectively [22, 23]. The texture of ZnO nanorods for all samples were achieved along the polar c-axis corresponding to the (002) plane of ZnO. It was observed that the orientation along the c-axis increased with increasing molar concentration. The peak intensities of the sample of Z35 (0.035 M) were considerably higher than the other samples (Figure 1b). On the other hand, the orientation was partially impaired when the concentration increased from 0.050 to 0.075 M. The deformation of orientation was due to the impact of HMTA on the growth characteristics of ZnO nanorods.

Furthermore, the preferred orientation of ZnO nanorods was evaluated according to the texture coefficient (TC) expressed in Equation 1:

$$TC_{(002)} = \frac{I_{(002)}/I^{\circ}_{(002)}}{I_{(002)}/I^{\circ}_{(002)} + I_{(101)}/I^{\circ}_{(101)}} \quad (1)$$

where $I_{(h\,k\,l)}$ is the obtained XRD peak intensity corresponding to (h k l) plane and $I^{\circ}_{(h\,k\,l)}$ is the intensity of the (h k l) plane related to the standard powder diffraction intensities of the (h k l) plane [12, 24]. The calculated $TC_{(002)}$ values of all samples are listed in Table 1. The degree of c-orientation of the Z35 sample is ~0.92 which validates a high preferential orientation of ZnO nanorods along the c-axis. However, the $TC_{(002)}$ value of ~0.72 of the Z25 sample confirmed its random orientation (Figure 1b).

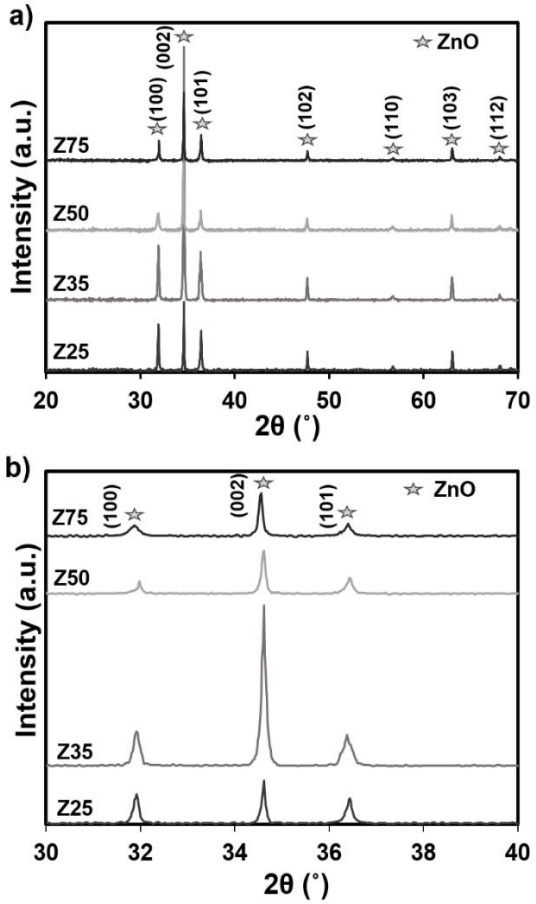

Figure 1 a) XRD patterns of ZnO nanorods grown at different molar concentrations (i.e., 0.025, 0.035, 0.05, and 0.075 M) and b) Enlargement of the region between 30-40°

Table 1 The texture coefficient of (002) plane ($TC_{(002)}$) of ZnO nanorods grown at different concentrations (i.e., 0.025, 0.035, 0.05, and 0.075 M)

Samples	$TC_{(002)}$
Z25	0.79
Z35	0.92
Z50	0.88
Z75	0.85

Top and cross-sectional SEM views of ZnO nanorods were grown by CBD with 0.025, 0.035, 0.05 and 0.075 M concentrations are shown in Figure 2. ZnO nanorods with the hexagonal cross-section were successfully grown in all samples, while lengths and diameters of nanorods were slightly varied.

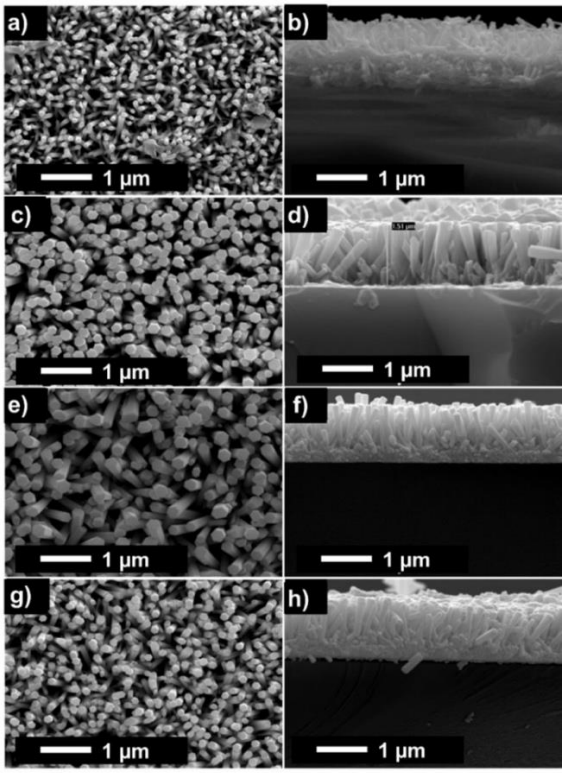

Figure 2 The top and cross-sectional SEM views of ZnO nanorods synthesized at a, b) 0.025, c, d) 0.035, e, f) 0.05, and g, h) 0.075 M

It has been seen that ZnO nanorods with low molar concentration (0.025 M) were randomly oriented and the number of nanorods per unit area is relatively less (Figure 2a, b). The vertical alignment of nanorods improved with increasing molar

concentration (Figure 2c-h). During growth in a solution containing 0.025 M HMTA, the HMTA concentration in the solution at the bottom of the nanorods gradually decreases and this reduces the steric hindrance effect. The higher the HMTA concentration, the more controlled growth occurs. On the other hand, the number of nanorods for the sample of Z75 (Figure 2e, f) was quite high and this negatively affected the alignment.

The diameters, lengths, and aspect-ratios of ZnO nanorods synthesized at different concentrations measured via SEM images are listed in Table 2. All values were the arithmetic mean and standard deviation of 10 measurements. The average diameters of ZnO nanorods were 120, 250, 200, and 175 nm for the sample of Z25, Z35, Z50, and Z75, respectively. The average length of ZnO nanorods were 660, 1450, 1220, and 1040 nm for the sample of Z25, Z35, Z50, and Z75, respectively. The mean diameter and length values of the Z35 sample were quite high compared to the other samples, and these data confirm that the peak intensities are high in XRD patterns. However, the maximum aspect-ratio was achieved with the sample with 0.05 M concentration.

Table 2 The diameters, lengths, and aspect-ratios of ZnO nanorods grown at different concentrations (i.e., 0.025, 0.035, 0.05, and 0.075 M) calculated via SEM images

Samples	Diameter (nm)	Length (nm)	Aspect-Ratio
Z25	120 ± 20	660 ± 100	5.6
Z35	250 ± 18	1450 ± 90	5.8
Z50	200 ± 17	1220 ± 80	6.2
Z75	175 ± 19	1040 ± 80	5.9

3.2. The Effect of HMTA Content

The effect of hexamethylenetetramine (HMTA) concentration used as a reducing agent and pH regulator in CBD precursor solution on ZnO nanorods morphology was investigated. Top and cross-sectional SEM images of ZnO nanorods grown with different ZNH: HMTA molar ratios are shown in Figure 3 and Figure 4. It has been seen that ZnO nanorods were successfully grown for all ZNH:HMTA ratios rich in Zn^{2+} ions (i. e., 1:1/4 (Z4), 1:1/2.5 (Z2.5), 1:1/1.5 (Z1.5), and 1:1 (Z1)) (Figure 3). It was clearly seen that the lengths of the nanorods increased, and their alignment improved with decreasing $[Zn^{2+}: OH^{-}]$ molar ratio.

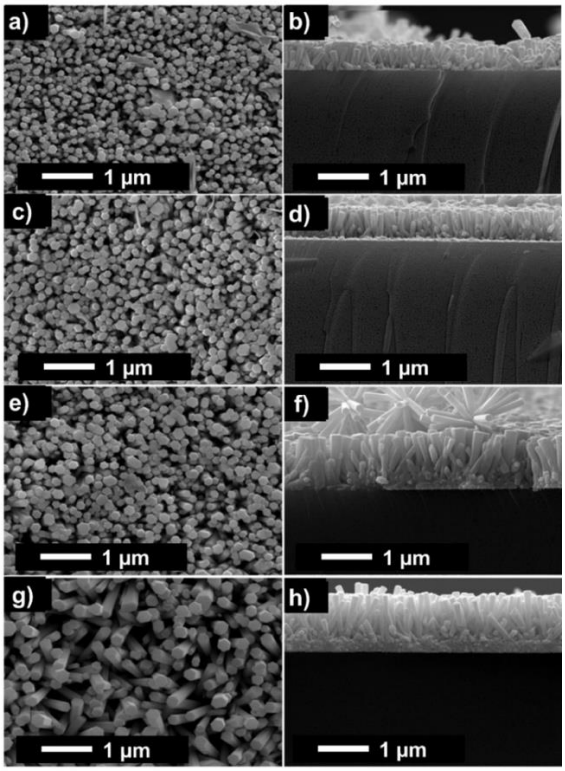

Figure 3 Top (a-g) and cross-sectional (b-h) SEM views of ZnO nanorods grown using solution with ZNH: HMTA molar ratios of a, b) 4, c, d) 2.5, e, f) 1.5 and g, h) 1

On the other hand, SEM images for ZNH:HMTA ratios rich in OH^{-} ions (i.e., 1/4:1 (Z0.25), 1/2.5:1 (Z0.4), and 1/1.5:1 (Z0.6)) are shown in Figure 4. ZnO nanorods were able to be grown for the ZNH:HMTA ratio of 0.6. However, the molar ratios of 0.25 and 0.4 were insufficient for the nucleation of nanorods (Figure 4a-d). Moreover, ZnO nanorods were almost absent at the higher molar ratio of 0.4 (Figure 4c, d), while the crystal growth was partially present at the 0.25 molar ratio (Figure 4a, b).

The diameter, length, and aspect-ratios of ZnO nanorods were measured for all samples

using top SEM views and the values (the arithmetic mean and standard deviations of 10 measurements) were listed in Table 3. Also, the pH values before and at the end of the CBD reaction as a function of the ZNH: HMTA ratio are shown in Figure 5.

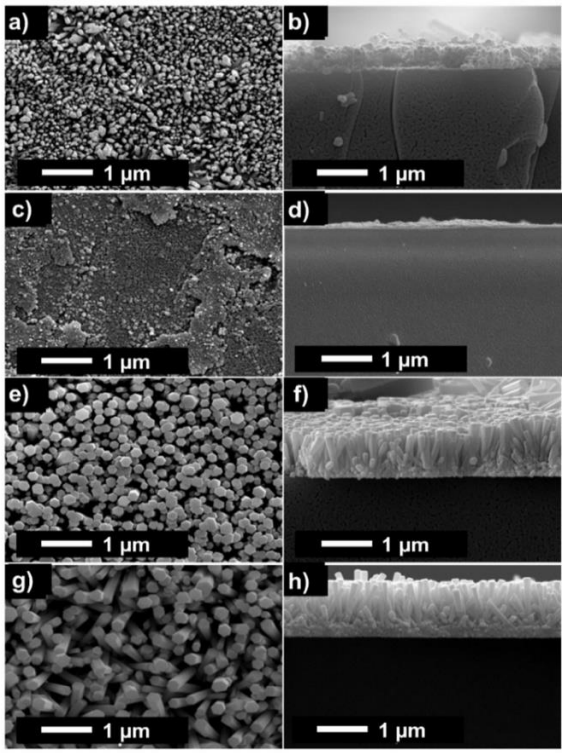

Figure 4 Top (a-g) and cross-sectional (b-h) SEM views of ZnO nanorods grown using solution with ZNH: HMTA molar ratios of a, b) 0.25, c, d) 0.4, e, f) 0.6 and g, h) 1

It has been observed that the lengths of ZnO nanorods increased rapidly when the ZNH: HMTA molar ratio decreased from 4 to 1. On the other hand, the pH values of the solutions rich in Zn^{2+} ions (i.e., ZNH:HMTA ratio between 1 and 4) almost remained constant at values of ~6.8 and ~6.4 before and after the CBD process, respectively. However, the lengths of nanorods were decreased when the molar ratio decreased below 1. The pH values of the solutions rich in OH^- ions (i.e., ZNH:HMTA ratio between 0.25 and 1) before and after the CBD process are strongly decreased from ~7.0 to ~7.8 and ~7.0 to ~7.5, respectively (Figure 5). The diameters of the ZnO nanorods reached the largest value in the sample with a molar ratio of 0.6 ZNH: HMTA (ZS0.6).

Table 3 The diameters, lengths, and aspect-ratios of ZnO nanorods grown at different concentrations (i.e., 0.025, 0.035, 0.05, and 0.075 M) calculated via SEM images

Samples	Diameter (nm)	Length (nm)	Aspect-Ratio
Z4	180 ± 21	500 ± 80	2.7
Z2.5	190 ± 18	600 ± 100	3.1
Z1.5	250 ± 17	920 ± 100	3.6
Z1	200 ± 17	1220 ± 80	6.1
Z0.6	180 ± 20	1010 ± 100	5.6
Z0.4	-	-	-
Z0.25	130 ± 22	230 ± 50	1.7

The aspect ratios of ZnO nanorods reached to a maximum value of 6.1 for the Z1 coded sample. When the HMTA concentration is increased further, the solution is enriched with OH^- ions and the Zn^{2+} ion concentration decreases. Thus, the probability of nucleation is reduced. Moreover, the decrease in the diameter of nanorods with increasing HMTA ratio is direct evidence that HMTA significantly suppresses radial growth and promotes axial growth. While HMTA acts as a pH regulator, it also plays multiple roles with a steric hindrance effect that inhibits lateral growth.

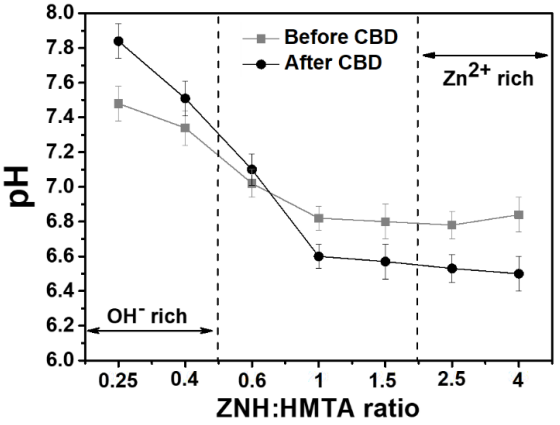

Figure 5 Evolution of the pH values before (gray dots) and after (black dots) CBD as a function of the [ZNH: HMTA] ratio

In the photocatalysis process, the organic pollutant molecules are adsorbed on the photocatalyst sample surfaces. The catalytic reactions take place on the surfaces of the catalyst. Therefore, the geometric factors

such as diameter, length, and surface area of ZnO nanorods are crucial in the photocatalytic degradation rates. In previous studies, it was revealed that a high aspect ratio supplied more adsorption sites for the efficient catalytic reaction [25, 26]. Reduced aspect ratios, however, lead to the adsorption of molecules mostly on the top surfaces. On the other hand, excessively lengthened nanorods may prevent UV light penetration on entire surfaces. Therefore, the aspect ratio of ZnO nanorods is expected to be at an optimum level for adequate interactions with UV light [21].

3.3. Growth Mechanism of ZnO nanorods

The preferential growth mechanism of ZnO nanorods by CBD is explained by thermodynamic considerations. The top and lateral faces of ZnO nanorods are composed by polar c-planes with lower surface energy and non-polar m-planes, respectively. Total free energy is minimized when the surface area of non-polar m-plane vertical lateral faces is improved by promoting axial growth at the expense of radial growth [27, 28]. The axial growth rate typically exceeds the radial growth rate due to kinetic factors. Therefore, ZnO nanorods is generally terminated with a polar c-plane due to the electrostatic interactions of Zn^{2+} and OH^{-} ions in the precursor solution. However, it should be noted that growth rates are limited by the mass transport of chemicals in the precursor solution [29]. The priority of binding to the polar surfaces of ZnO by chelating HMTA molecules is due to the capping agent effect. HMTA can bind to the crystal surfaces of ZnO in two ways. It occurs by hydrogen bonding between ammonium cations and O^{-2} crystal ions, or by a covalent bond between basic N atoms and the acidic Zn^{2+} region. HMTA prevents Zn^{2+} entry to the lateral surfaces and facilitates its anisotropic growth in the [001] direction by binding to the non-polar lateral surfaces of ZnO [30]. Commonly, it provides $-OH$ ions to regulate the pH of the acidic solution because of Zn^{2+} hydrolysis. HMTA can play an active role in the morphology of ZnO nanorods, both as a capping agent and as a pH regulator depending on the molar ratio of ZNH:HMTA. The HMTA source decomposes to form formaldehyde and ammonia with sufficient thermal energy by reaction (2). Ammonia reacts with water to provide OH^{-} ions dissolved in water through reaction (3) and (4), and these ions can react with Zn^{2+} to form ZnO by reaction (5) and (6). Typical reactions are described below [10]:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCOH + 4NH_3 \quad (2)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (3)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (4)$$

$$Zn(NO_3)_2 \rightarrow Zn^{2-} + 2NO_3^- \quad (5)$$

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O \quad (6)$$

4. CONCLUSION

The multiple roles of HMTA content and the concentration of CBD solution on the dimension of ZnO nanorods were investigated in this study. ZnO nanorods were successfully grown on the glass substrate by seed-mediated approach using the low-temperature CBD method. The effects of zinc ion concentration and HMTA content of the CBD solution on the crystal orientation and aspect ratios of ZnO nanorods were investigated. The crystallinity and morphological analysis indicated that the orientation and number densities of the nanorods (i.e., the number of nanorods per unit area) were increased with the increasing molar concentration from 0.025 to 0.05. Moreover, ZNH: HMTA molar ratio of precursor solution is critical in the growth of ZnO in liquid phase by CBD. It was found that increasing HMTA content promoted the growth of ZnO nanorods along the c-axis, and the lateral growth was suppressed by the capping effect of HMTA. It is revealed that the largest axial growth rate of ZnO nanorods was reached for the [ZNH: HMTA] ratio of 1. HMTA induces vertical growth of ZnO

nanorods along the c-axis through a steric hindrance effect that inhibits lateral growth. However, excessive HMTA content led to a reduced probability of crystal growth attributed to OH^- ion enrichment.

Acknowledgments
Memnune Kardeş also acknowledges the scholarship from the domestic PhD Scholarship Program (2211/C) of The Scientific and Technological Research Council of Turkey (TÜBİTAK) intended for priority areas.

Funding
The author (s) has no received any financial support for the research, authorship or publication of this study.

Authors' Contribution
The authors who have made substantial contributions to the work reported in the manuscript are:

M.K.: Term, Conception and design of study, Visualization, Writing - Original Draft, Data Curation, Investigation, Formal analysis, Validation, Methodology.
K.Ö.: Supervision, Project administration, Term, Conceptualization, Writing- Original Draft, Data Curation, Investigation, Formal analysis, Validation, Methodology.

The Declaration of Conflict of Interest/ Common Interest
No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval
This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics
The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

REFERENCES

[1] I. Udom, M. K. Ram, E. K. Stefanakos, A. F. Hepp, D. Y. Goswami, "One dimensional-ZnO nanostructures: Synthesis, properties and environmental applications", Materials Science in Semiconductor Processing, vol. 16, no. 6, pp. 2070–2083, 2013.

[2] M. Samadi, M. Zirak, A. Naseri, M. Kheirabadi, M. Ebrahimi, A. Z. Moshfegh, "Design and tailoring of one-dimensional ZnO nanomaterials for photocatalytic degradation of organic dyes: a review", Research on Chemical Intermediates, vol. 45, pp. 2197–2254, (2019).

[3] C. J. Chang, M. H. Hsu, Y. C. Weng, C. Y. Tsay, C. K. Lin, "Hierarchical ZnO nanorod-array films with enhanced photocatalytic performance", Thin Solid Films, vol. 528, pp. 167–174, 2013.

[4] T. Cossuet, E. Appert, J. L. Thomassin, V. Consonni, "Polarity-Dependent Growth Rates of Selective Area Grown ZnO Nanorods by Chemical Bath Deposition", Langmuir, vol. 33, no. 25, pp. 6269–6279, 2017.

[5] B. Astinchap, R. Moradian, M. N. Tekyeh, "Investigating the optical properties of synthesized ZnO nanostructures by sol-gel: The role of zinc precursors and annealing time", Optik, vol. 127, no. 20, pp. 9871–9877, 2016.

[6] A. A. Mohd Raub, J. Yunas, M. A. Mohamed, B. Bais, A. A. Hamzah, J. Ridwan, J. Kazmi, M. A. Hassan, "Synthesis and characterization of ZnO NRs with spray coated GO for enhanced photocatalytic activity", Ceramics International, vol. 48, no. 13, pp. 18238-18245, 2022.

[7] N. Lepot, M. K. Van Bael, H. Van den Rul, J. D'Haen, R. Peeters, D. Franco, J. Mullens, "Synthesis of ZnO nanorods from aqueous solution", Materials Letters, vol. 61, no. 13, pp. 2624–2627, 2007.

[8] L. Xu, Y. L. Hu, C. Pelligra, C. H. Chen, L. Jin, H. Huang, S. Sithambaram, M. Aindow, R. Joesten, S. L. Suib, "ZnO with different morphologies synthesized by solvothermal methods for enhanced photocatalytic activity", Chemistry of Materials, vol. 21, no. 13, pp. 2875–2885, 2009.

[9] N. T. Son, J. S. Noh, S. Park, "Role of ZnO thin film in the vertically aligned growth of ZnO nanorods by chemical bath deposition", Applied Surface Science, vol. 379, pp. 440-445, 2016.

[10] M. Kardeş, G. Başaran Dindaş, H. C. Yatmaz, N. Dizge, K. Öztürk, "CBD grown pure and Ce-doped ZnO nanorods: Comparison of their photocatalytic degrading efficiencies on AR88 azo dye under visible light irradiation", Colloids Surface A Physicochemical Engineering Aspects, vol. 607, pp. 125451, 2020.

[11] K. Mosalagae, D. M. Murape, L. M. Lepodise, "Effects of growth conditions on properties of CBD synthesized ZnO nanorods grown on ultrasonic spray pyrolysis deposited ZnO seed layers", Heliyon, vol. 6, no. 7, pp. e04458, 2020.

[12] M. Poornajar, P. Marashi, D. H. Fatmehsari, M. K. Esfahani, "Synthesis of ZnO nanorods via chemical bath deposition method: The effects of physicochemical factors", Ceramics International, vol. 42, no. 1, pp. 173–184, 2016.

[13] A. F. Abdulrahman, S. M. Ahmed, S. M. Hamad, A. A. Barzinjy, "Effect of Growth Temperature on Morphological, Structural, and Optical Properties of ZnO Nanorods Using Modified Chemical Bath Deposition Method", Journal of Electronic Materials, vol. 50, pp.1482–1495, 2021.

[14] Q. Liu, T. Yasui, K. Nagashima, T. Yanagida, M. Hara, M. Horiuchi, Z. Zhu, H. Takahashi, T. Shimada, A. Arima, Y. Baba, "Ammonia-Induced Seed Layer Transformations in a Hydrothermal Growth Process of Zinc Oxide Nanowires", The Journal of Physical Chemistry C, vol. 124, no. 37, pp. 20563-20568.

[15] S. Guillemin, L. Rapenne, H. Roussel, E. Sarigiannidou, G. Brémond, V. Consonni, "Formation mechanisms of ZnO nanowires: The crucial role of crystal orientation and polarity", The Journal of Physical Chemistry C, vol. 117, no. 40, pp. 20738–20745, 2013.

[16] A. S. Kamble, B. B. Sinha, K. Chung, M. G. Gil, V. Burungale, C. J. Park, J. H. Kim, P. S. Patil, "Effect of hydroxide anion generating agents on growth and properties of ZnO nanorod arrays", Electrochimica Acta, vol. 149, pp. 386–393, 2014.

[17] A. F. Abdulrahman, "Study the optical properties of the various deposition solutions of ZnO nanorods grown on glass substrate using chemical bath deposition technique", Journal of

Ovonic Research, vol. 16, no. 3, pp. 181–188, 2020.

[18] V. Strano, R. Giovanni Urso, M. Scuderi, K. O. Iwu, F. Simone, E. Ciliberto, C. Spinella, S. Mirabella, "Double Role of HMTA in ZnO Nanorods Grown by Chemical Bath Deposition", The Journal of Physical Chemistry C, vol. 118, no. 48, pp. 28189–28195, 2014.

[19] B. Ikizler, S. M. Peker, "Effect of the seed layer thickness on the stability of ZnO nanorod arrays", Thin Solid Films, vol. 558, pp. 149–159, 2014.

[20] S. Guillemin, V. Consonni, E. Appert, E. Puyoo, L. Rapenne, H. Roussel, "Critical nucleation effects on the structural relationship between ZnO seed layer and nanowires", The Journal of Physical Chemistry C, vol. 116, no. 47, pp. 25106–25111, 2012.

[21] M. Kardeş, K. Öztürk, "Photocatalyst ZnO nanorod arrays on glass substrates: the critical role of seed layer in nanorod alignment and photocatalytic efficiencies", Chemical Engineering Communication, vol. 207, no. 11, pp. 1522-1535, 2020.

[22] J. Singh, S. S. Patil, M. A. More, D. S. Joag, R. S. Tiwari, O. N. Srivastava, "Formation of aligned ZnO nanorods on self-grown ZnO template and its enhanced field emission characteristics", Applied Surface Science, vol. 256, no. 21, pp. 6157–6163, 2010.

[23] P. Gu, X. Zhu, D. Yang, "Vertically aligned ZnO nanorods arrays grown by chemical bath deposition for ultraviolet photodetectors with high response performance", Journal of Alloys and Compounds, vol. 815, pp. 152346, 2020.

[24] Y. Kajikawa, S. Noda, H. Komiyama, "Preferred orientation of chemical vapor deposited polycrystalline silicon carbide films", Chemical Vapor Deposition, vol. 8, no. 3, pp. 99–104, 2002.

[25] A. Leelavathi, G. Madras, N. Ravishankar, "Origin of enhanced photocatalytic activity and photoconduction in high aspect ratio ZnO nanorods", Physical Chemistry Chemical Physics, vol. 15, no. 26, pp. 10795–10802, 2013.

[26] A. Das, R. G. Nair, "Effect of aspect ratio on photocatalytic performance of hexagonal ZnO nanorods", Journal of Alloys and Compounds, vol. 817, pp. 153277, 2020.

[27] K. M. McPeak, T. P. Le, N. G. Britton, Z. S. Nickolov, Y. A. Elabd, J. B. Baxter, "Chemical bath deposition of ZnO nanowires at near-neutral pH conditions without hexamethylenetetramine (HMTA): Understanding the role of HMTA in ZnO nanowire growth", Langmuir, vol. 27, no. 7, pp. 3672–3677, 2011.

[28] R. Parize, J. Garnier, O. Chaix-Pluchery, C. Verrier, E. Appert, V. Consonni, "Effects of Hexamethylenetetramine on the nucleation and radial growth of ZnO nanowires by chemical bath deposition", Journal of Physical Chemistry C., vol. 120, no. 9, pp. 5242–5250, 2016.

[29] W. Feng, B. Wang, P. Huang, X. Wang, J. Yu, C. Wang, "Wet chemistry synthesis of ZnO crystals with hexamethylenetetramine (HMTA): Understanding the role of HMTA in the formation of ZnO crystals", Materials Science in Semiconductor Processing, vol. 41, pp. 462–469, 2016.

[30] H. Avireddy, H. Kannan, P. Shankar, G. K. Mani, A. J. Kulandaisamy, J. B. B. Rayappan, "Non-mutually exclusive dual role of hexamethylenetetramine on the growth of ZnO nanostructures and their sensing footprints", Materials Chemistry and Physics, vol. 212, pp. 394–402, 2018.