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Fabrication and Characterization of the ZnO Nanoparticles by Controlled Decomposition

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ABSTRACT

ZnO nanoparticles having different size and morphology were obtained by thermal decomposition method with long chain amine ligand and their physical and chemical characterization were comprehensively investigated. Zinc complexes were synthesized by two phase method and this precursor was used for the synthesis of ZnO nanoparticles in high temperature environment. Decomposition behaviour of the mixture with long chain amine precursor was monitored by Fourier Transformed Infrared Technique together with X-Ray Diffraction patterns to analyze the crystal features of the obtained nanocrystals. Transmission Electron Microscopy unveiled the morphological behaviour and crystalline properties of the nanoparticles which show a great homogeneity and monodispersity from the geometrical perspective. Long chain amine precursor concentration was great actor on the formation and growth behaviour of the ZnO nanoparticle as results indicated.

Keywords: Nanoparticle, nanostructures, thermal degradation, ZnO.

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Kontrollü Bozundurma Tekniği İle ZnO Nanopartikül Üretimi ve Karakterizasyonu

ÖZ

Farklı boyut ve morfolojiye sahip ZnO nanopartikülleri uzun zincirli amin ligandı kullanılarak termal bozundurma yöntemi ile elde edilmiş ve fiziksel ve kimyasal karakterizasyonları kapsamlı bir şekilde gerçekleştirilmiştir. Çinko kompleksleri iki fazlı yöntemle sentezlendikten sonra bu öncü reaktif yüksek sıcaklık kullanılarak ZnO nanoparçacık üretimi için vektörleştirildi. Uzun zincirli amin kimyasalını da içeren karışımın bozunma davranışları ve aynı zamanda elde edilen nanokristal özelliklerinin tayini için Fourier Dönüşümlü Kızılötesi Tekniği ile X-Işını Kırınım metotları kullanıldı. Transmisyon Elektron Mikroskobu, geometrik açıdan homojenlik ve monodispersite gösteren nanoparçacıkların morfolojik davranışlarını ve kristal özelliklerini ortaya koymuştur. Sonuçların gösterdiği gibi, uzun zincirli amin kimyasalının konsantrasyonu, ZnO nanoparçacığının oluşumu ve büyüme davranışı üzerinde büyük bir aktördür.

Anahtar Kelimeler: Nanopartikül, nanoyapılar, termal bozundurma, ZnO.

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1. Introduction

Among the nanostructure synthesis methods, thermal techniques were successfully progressed in the production of nano based structures lately. This is largely motivated due to the distinctive features of these nanoparticles depending on their bulk counterparts. Especially hot injection method, hydrothermal-solvothermal method, microwave technique and thermal decomposition gained large interest driven by aim to modulate and investigate nanoparticle by different methods to detect physical and chemical properties as a vector of nanoparticle size and geometry [1-6]. Therefore monodispersed and homogeneous nanoparticles of inorganic and organic structures (e.g., metal, metal oxide, semiconductors, organic nanostructures) can be obtained with exquisite control over nanoparticle size and geometrical shape [7-8].
Production techniques involving the increased temperature of complex or organometallic structures in high boiling organic solvents with or without surface modifying groups in an oxygenless atmosphere provided by Ar, N_2, He is a versatile platform for the fabrication of nanosized structures. Since huge control over the nanoparticle modulation, polydispersity index, surface features and morphology can be achieved through thermal decomposition methods. We also aimed to synthesize ZnO nanoparticles by controlling the aforementioned properties. After the production of the Zn-carboxylate precursor, long alkyl chain amine was utilized to conduct the high temperature decomposition by amide formation to synthesize the ZnO nanoparticles [9-11].

We therefore report a reproducible synthesis of ZnO nanoparticles with controlled morphology, crystal property and chemical properties through controlled proportion of reactants and incorporation of long alkyl chain for well characterized nanoparticles. The most salient feature of this article is the production of anisotropic ZnO nanoparticles which was obtained by controlled thermal decomposition and the effect of the long chain amine compound which attaches to the nonpolar growing facets of the ZnO nuclei and provide elongated nanostructures. Since amine and long chain acid together form an equilibrium that dominates the selective facet growing, it is possible to modulate the morphologies of the ZnO nanostructures. Results basically reveal that nanoparticles consist of high crystallline structures with varying shapes providing a deep insight on the ZnO nanoparticle formation by thermal decomposition method.

2. Material and Method

2.1. Materials and Precursor Synthesis

Production of ZnO nanoparticles were conducted through zinc-oleate complex 1:2 equivalent amounts of zinc chloride (ZnCl2, Acros, 98%) and sodium oleate (Sigma Aldrich, 99%)) were reacted. In a specific method it follows the addition of 5.0 g of zinc chloride into 24.35 g of sodium oleate (80 mmol, Sigma Aldrich, 99%) which were mixed and vigorously stirred.

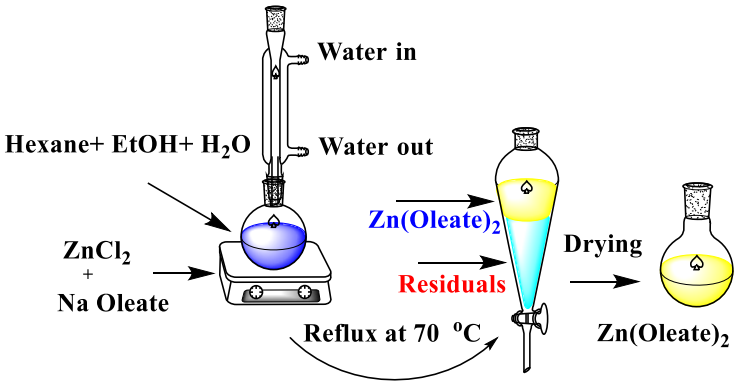

Figure 1. Two phase method for the $Zn(Oleate)_2$ precursor synthesis

A solvent mixture composed of 80/60/140 EtOH/H_2O/Hexane was utilized. This two phase solution was brought to 70 °C and reflux was conducted at the same temperature for 4-5 h [12]. When the reaction is ended, the zinc-oleate complex at upper organic layer concentrated by rotavapor (Figure 1) and purified by distilled water and dried. Precursor reaction was investigated by FT-IR analysis.

Reaction was clearly shown in Figure 2.

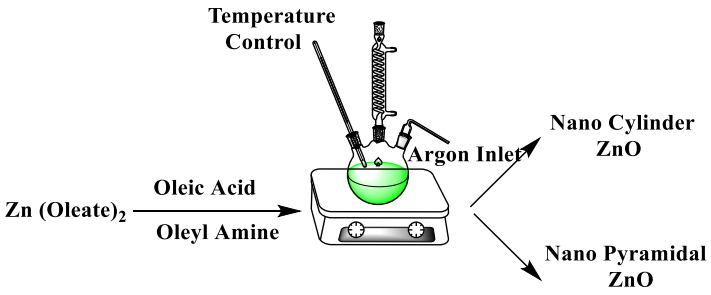

Figure 2. Thermal decomposition technique for the synthesis of ZnO nanoparticles

2.2. Material Analysis

For the detection of morphology and sizes, Transmission electron microscopy (TEM) was performed by Tecnai G2 20 (FEI) on cupper grids. Specimens for TEM was prepared by dropping a colloid solution on a 400 mesh copper grid coated by an carbon structure. XRD patterns were measured by STOE-STADI MP vertical system using Cu Kα (α=0.15406 nm) radiation. For the analysis by FT-IR, Perkin Elmer 400, 4000-400 cm^{-1} range were used and simply platform on ATR Universal Sampling Accesory, Statistical analysis were performed by Image J on the TEM images by counting 50-100 particles. Thermal analysis of the prepared structures was investigated in between 30 to 500°C with a heating rate of 10°C/min by applying nitrogen atmosphere (flow rate; 25 ml/min) in Mettler Toledo TGA/DSC 1 Stare systems.

2.3. Synthesis of the ZnO Nanoparticles

Fabrication process for the ZnO nanocrystals were conducted by heating the (290-300 °C) reaction mixture of $Zn(Oleate)_2$/Oleylamine (% 80-90 Riedel Haen)/Oleic acid (Riedel Haen) in a flask (Figure 2). By changing the concentrations and ligant combinations, it was possible to obtain nanocylinder and pyramid like ZnO nanostructures which were analyzed thoroughly. In a typical fabrication procedure, the required amounts of zinc-oleate complex with oleylamine and oleic acid were placed in a flask and this mixture was heated with 5 °C/min heating range under the argon protection untill the desired set-temperature (290-300 °C). According to the reactions equivalence amounts were 1:2:10 and 1:2:6 for the order of $Zn(Oleate)_2$:Oleic acid:Oleylamine. Increased oleylamine amounts varied the morphology of the obtained ZnO nanostructures. After reaching to desired temperature,medium was kept at this temperature for 1 h and milky, white-yellow solution of suspensions were clearly observed. After the cooling procedure till room temperature, EtOH was added for precipitation aim and nanostructures were separated by centrifuge at 11 000 rpm. Additionally washing procedure was applied 4-5 times by EtOH and nanostructures were dried under vacuo.

3. Results and Discussion

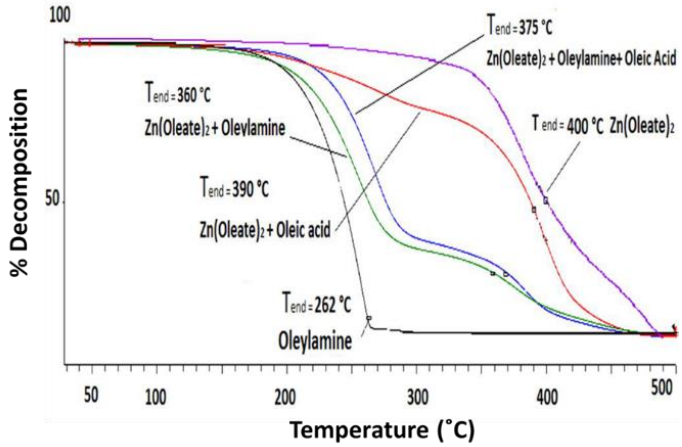

Figure 3. Thermal decomposition profiles of the reaction mixture components

Thermal analysis results in Figure 3 showed that, it is clear that Oleylamine (black) shows a thermal loss by 60 ˚C which continues till 260 ˚C. After this point, slight prominent peak which can be labelled as exothermic is detected and attributed to the residual organic structures of the composunds. $Zn(Oleate)_2$+Oleylamine (green) and $Zn(Oleate)_2$+Oleylamine+Oleic Acid (blue) thermogravimetric behaviours are analog but a slight change in decomposition shape is seen. This basically shows that reaction highly dependent on the amine attack onto the $Zn(Oleate)_2$. Oleic acid can be introduced but amine attack is still crucial for the formation of ZnO nanoparticles by amide formation. Interestingly, $Zn(Oleate)_2$+Oleic Acid (red) mixture shows another loss of weight which almost ends at 390 ˚C. This aspect is due to the new formed compound and its relative stability against to thermal decomposition. Actually addition of oleylamine ligant, triggers the decomposition of the $Zn(Oleate)_2$ complex in the reaction environment around 210 ˚C which is confirmed by molecular observation (Figure 4) of the precursor mixtures. It is detected that if oleylamine ligand is available in the reaction mixture, it causes a quick start for decomposition due to the thermal effect of amine functional group and its attack onto the Zn-ester group leading to the amide formation.

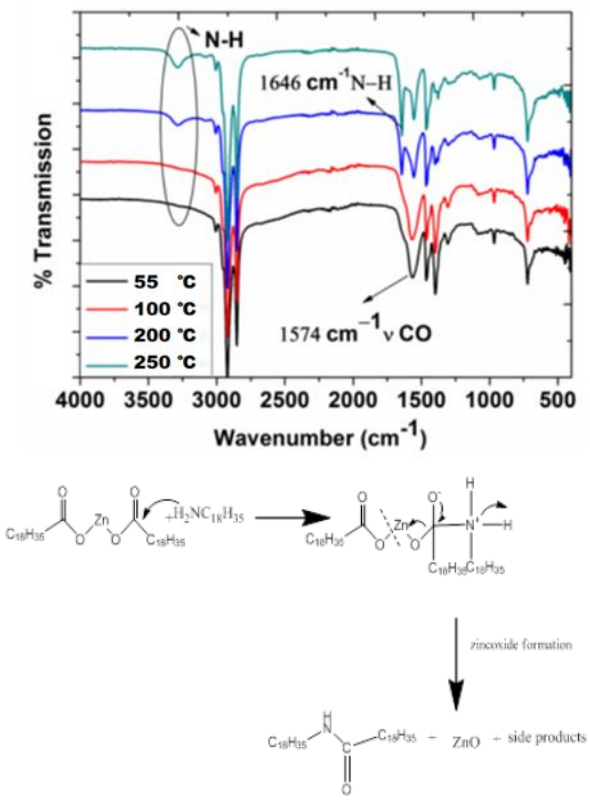

Figure 4. Amide formation during the ZnO nanoparticle production and reaction mechanism

Other decomposition curves reveal that if oleylamine precursor is absent, reaction composition becomes highly resistant to the thermal change which requires high nucleation and growth temperature in the environemnt. Consequently, a thermal decomposition which is focused at 290-300 ˚C would provide ZnO uniform nanostructures as the analysis indicated. For a proper control of the decomposition, it is important to detect which point provides more suitable decomposition conditions for the precursor mixture. Therefore thermal analysis was conducted for the reaction mixture and single precursors. Therefore, oleylamine and $Zn(Oleate)_2$ were analyzed as single components and additionally other mixture examples such as $Zn(Oleate)_2$+Oleylamine, $Zn(Oleate)_2$+Oleic acid $Zn(Oleate)_2$+Oleic acid+Oleylamine were analyzed accordingly. It is seem that $Zn(Oleate)_2$+Oleic acid+Oleylamine mixture starts decompose at 290- 300 C where can be accepted as the nanoparticle formation point. Other mixtures such as $Zn(Oleate)_2$+Oleic acid and $Zn(Oleate)_2$+Oleylamine also supports this specific temperature detection.

As analysis revealed, mechanism of the ZnO nanoparticle formation is a non-hydrolytic decomposition route and it can be monitored by FT-IR spectroscopy. Nanoparticle formation was detected by the amide bond by the amine attack on the Zn-oleate complex. Since amine attack is leading the formation

of oleyl substituted amide structure, peaks which arises at around 3280 cm-1 after 200˚C is the primary reactsion result for the observable nanoparticle formation. This peak shows a clear N-H formation while it was not observable before lower temperatures. Also carbonyl peak at 1574 cm-1 disappears with the reaction.

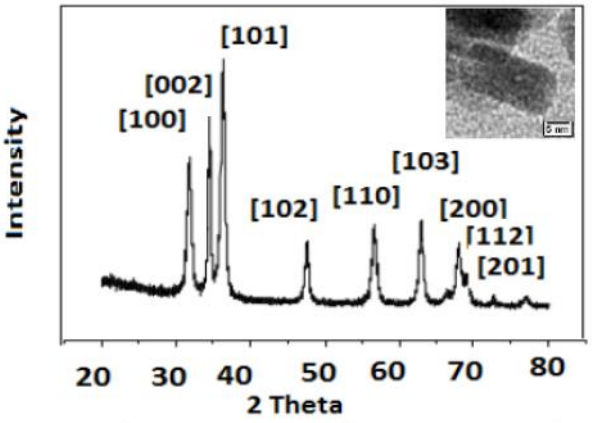

Figure 5. XRD patterns of the cylindirical ZnO nanoparticles

Nonhydrolytic thermal production of nanoparticles slightly varies from hot injection synthesis since temperature control and way of using temperature is different. [13-14]. Thermal heating procedure generally starts at room temperature with all components and heating rate may change the geometrical and surface characteristics of obtained structures.

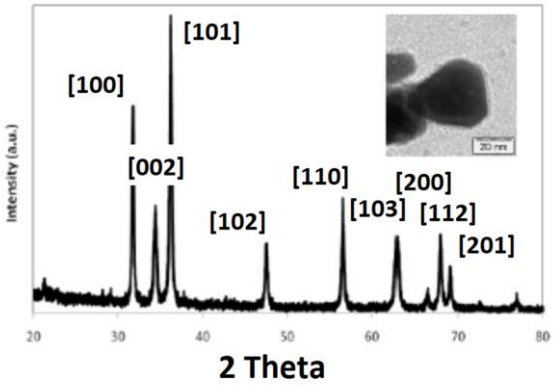

Figure 6. XRD patterns of the triangle shaped ZnO nanoparticles

Suitable temperature starts the crystallization, and when completed other reaction components are removed for obtaining the final nanostructures. Nonhydrolytic decomposition has technical advantages over hot injection method and necessary compositions must be prepared carefully for the desired nanostructure formation. Especailly hot injection method needs the separation of formed nucleus in critical diameter from their growth procedure. Still thermal heating procedure enables the upscaling of nanostructures and size uniformity can also be realized with high standarts and uniformity.

Table 1. 2Theta positions of the cylindirical and pyramidal ZnO compared with standart ZnO

Miller Indices	JCPDS (36-1451) 2Theta	Cylinder ZnO 2Theta	Pyramid ZnO 2Theta
[100]	31.770	31.75	31.76
[002]	34.422	34.42	34.41
[101]	34.553	34.56	34.55
[102]	47.539	47.54	47.54
[110]	56.635	56.60	56.61
[103]	62.864	62.87	62.86
[200]	66.378	66.38	66.37
[112]	67.961	67.95	67.96
[201]	69.100	69.11	69.10

It is widely known that amine ligants can attach to the nonpolar facets of the ZnO nuclei in the early stages of the nanoparticle formation. This will provide a selective growth and anisotropic nanostructures are obtained. Diffraction patterns of produced cylindirical ZnO nanoparticles are illustrated in Figure 5 and peak positions were were compared with standart ZnO as shown in Table 1. According to analysis observed peaks can be indexed to the würtzite phase of hexagonal ZnO (JCPDS No. 36-1451). After the investigation it is clear that there is no unpredictable peak of different phase of ZnO structure. Also no impurities were observed that confirms the great purity of the produced ZnO nanoparticles. By X-ray line broadening it was able to calculate the average particle size by Scherrer equation and found as 26 nm. Due to the nano size effect, patterns were slightly broadened and it was detected that the diffraction line (002) was narrower than the line (101) indicating an asymmetry in the crystallite shape. Interestingly in Figure 6, if diffraction patterns of the pyramidal ZnO nanoparticles is analyzed, intensity of the (002) peak is lower when compared to (001). Therefore one can easily derived that changing the amine concentration in reaction, it was possible to change the crystalline growth habits of the ZnO nanoparticles. Also there is no unknown or unpredictable peak among the observable peaks which shows the high purity of pyramidal ZnO nanoparticles. X-ray broadening technique (Figure 6) was used for calculating the particle size of the pyramidal ZnO nanostructures and found around 48 nm as also conducted before, using Scherrer equation;

$D = k\lambda / (\beta \cos\theta)$

where D is is accepted as size in nm, λ is source wavelength (1.54056 Å for CuKα radiation), k is 0.9, β is width at half-maximum intensity and θ can be titled as position for peak.

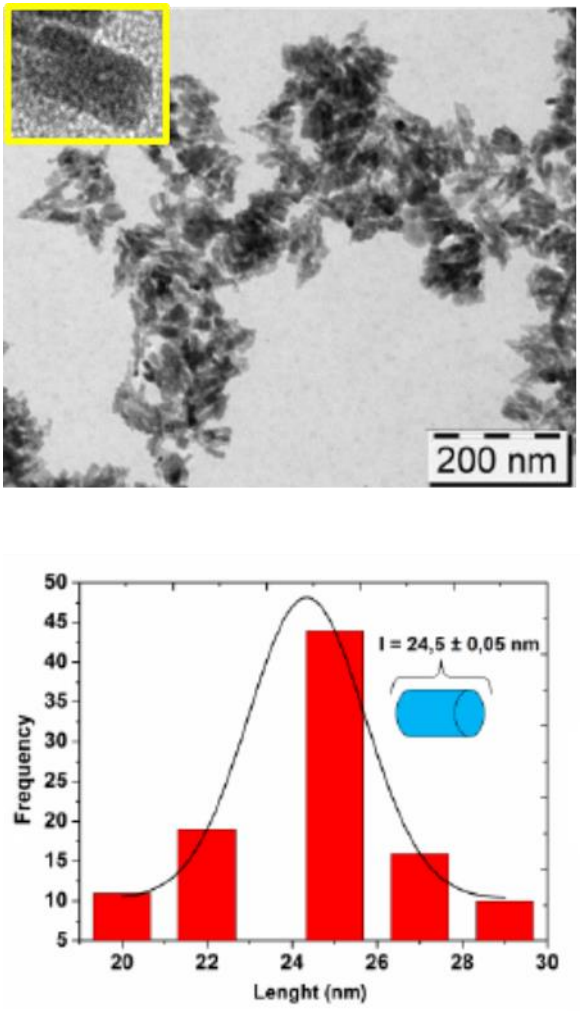

Figure 7. TEM image of cylindirical ZnO nanoparticle and length calculation of the nanostructures

The TEM images of cylindirical and pyramidal ZnO nanoparticles are shown in Figure 7 and Figure 8 with calculated size statistics. The TEM study was conducted to expand the deep characteristics of crystallinity together with morphology and magnitude of the ZnO nanoparticles. Selected TEM pictures of ZnO nanoaprticles confirmed that if the reactant proportions are 1:2:10; cylindirical ZnO

nanoparticles with averagely 25 nm in length and 12 nm in diameter were obtained. Cylindirical character is easily seen with enlarged images. Interestingly TEM images also show that cylindirical nanoparticles are attached to each other forming a self assembly when closely analyzed. The average particle size for cylindirical ZnO nanoparticles by histogram was found to be 24.5 nm. As for the pyramidal ZnO nanoparticles, 1:2:6 proportion of reactants seem the main reason of anisotropy which was confirmed by the TEM images. Since Debye–Scherrer poisitons can be assigned (100), (002), (011), (012), (110), (103) respectively in the XRD patterns, TEM image simply confirmed the calculated primary particle size.

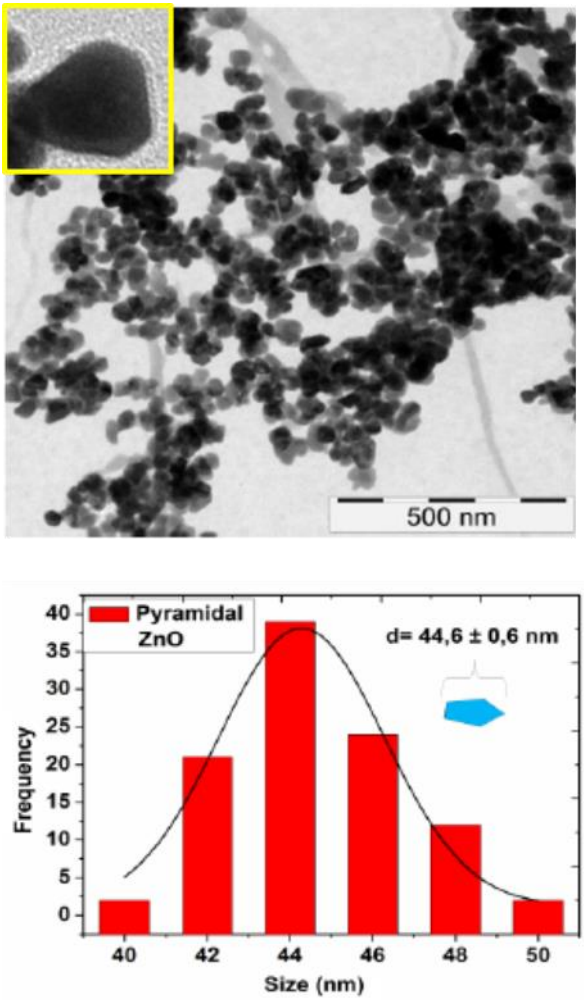

Figure 8. TEM image of pyramidal ZnO nanoparticle and statistical size calculation

The particle size detection by TEM analysis is slightly different to that of the XRD analysis. According to the TEM images dimond like pyramidal structures are clearly seen. It can be easily concluded that in the present work, the effect of the amine proportion on the ZnO nanoparticle morphology and crystallinity were investigated. By using different condiitons and reactant proportions it is possible to change the ZnO nanoparticle geometry [15].

ZnO nanoparticles find wide applications in cosmetic industry, creams, antibacterial applications, in pigment industry, photocatalytic industry, solar cell applications, theranostics and polymer industry for its filler and white color properties.It is known that varied shapes of ZnO nanostructures mostly places itself on the relative surface energy of the crystal facets. It is known that ZnO structures generally have three planes: a top and also quite polar zinc (0001) region, also six symmetric and also nonpolar {1010} regions where parallel to the [0001], and lastly a basal and also quite polar oxygen (0001) region. Polarities of these facets vary different mixtures of solvents together with surface modifying ligants, temperature and pH with synthesis techniques produce various size and shape of ZnO nanostructures. It is known that if there is any specific ligant or surface modifier having a specific affinity for a selected nanostructure facets, resulting nanostructure might be changed easily. Therefore

experimental results showed that by changing the concentration of amine ligant it is possible to change the growth habits of ZnO nanoparticles resulting with cylindirical or pyramidal geometry.

Conflict of Interest Statement

The authors declare that there is no conflict of interest

References

[1] D. Ílem-Özdemir, E. Gündoğdu, M. Elinci and M. Aşikoğlu, "Nanoparticles: from diagnosis to therapy," *International Journal of Medical Nano Research,* vol.3, no.1, pp. 1–5, 2016. doi:10.23937/2378-3664/1410015

[2]C. M. Donegá, P. Liljeroth and D. Vanmaekelbergh, "Physicochemical evaluation of the hot injection method, a synthesis route for monodisperse nanocrystals," *Small*, vol. 1, no.12, pp.1152-62, 2005. doi:10.1002/smll.200500239

[3] Y.Jun, J. Choi and J. Cheon, "Shape control of semiconductor and metal oxide nanocrystals through nonhydrolytic colloidal routes," *Angew Chem Int Ed Engl,* vol. 45, pp. 3414-39, 2006. doi:10.1002/anie.200503821

[4] S. G. Kwon and H. Taeghwan, "Formation mechanisms of uniform nanocrystals via hot-injection and heat-up methods ," *Small*, vol. 7, no. 19, pp. 2685-702, 2011. doi:10.1002/smll.201002022

[5] M. Rajamathi and R. Seshadri, "Oxide and chalcogenide nanoparticles from hydrothermal / solvothermal reactions," *Current Opinion in Solid State and Materials Science*, vol. 6, no. 4, pp. 337-345, 2002. doi:10.1016/S1359-0286(02)00029-3

[6] J. A. Gerbec, D. Magana, A. Washington and G. F. Strouse "Microwave-Enhanced Reaction Rates for Nanoparticle Synthesis," *J.Am. Chem. Soc.*, vol. 127, pp. 15791-15800, 2005. doi:10.1021/ja052463g

[7] M. H. Huang, S. Mao, H. Feick, H.Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang, "Room-temperature ultraviolet nanowire nanolasers," *Science*, vol. 292, pp. 1897, 2001. doi:10.1126/science.1060367

[8] Y.E. Panfil, M. Oded and U. Banin, "Colloidal Quantum Nanostructures: Emerging Materials for Display Applications," *Angew Chem Int Ed Engl,* vol. 57, no. 16, pp. 4274-4295, 2018. doi:10.1002/anie.201708510

[9] G. Sharma and P. Jeevanandam, "Synthesis of self-assembled prismatic iron oxide nanoparticles by a novel thermal decomposition route," *RSC Adv.,* vol.3, pp.189-200, 2013. doi:10.1039/C2RA22004K

[10] T. Togashi, K. Tsuchida, S. Soma, R. Nozawa, J. Matsui, K. Kanaizuka and M. Kurihara "Size-Tunable Continuous-Seed-Mediated Growth of Silver Nanoparticles in Alkylamine Mixture via the Stepwise Thermal Decomposition of Silver Oxalate," *Chemistry of Materials,* vol.32, no. 21, pp. 9363-9370, 2020. doi: 10.1021/acs.chemmater.0c03303

[11] S. Chen, Y. Lu, T. Huang, D. Yan and C. Dong, "Oxygen Vacancy Dependent Magnetism of CeO2 Nanoparticles Prepared by Thermal Decomposition Method," *The Journal of Physical Chemistry C,* vol. 114, no. 46, pp. 19576-19581, 2010. doi:10.1021/jp1045172

[12] H. Damm, A. Kelchtermans, A. Bertha, F. Van den Broeck, K. Elen, J.C. Martins, R. Carleer, J. D'Haen, C. De Dobbelaere, J. Hadermann, A. Hardy and M. K. Van Bael, "Thermal decomposition synthesis of Al-doped ZnO nanoparticles: an in-depth study," *RSC Adv*., vol. 3, pp. 23745-54, 2013. doi:10.1039/C3RA43328E

[13] D. Wang, M. Xing, Y. Wei, L. Wang, R.Wang, and Q.Shen, "Modeling of Nucleation and Growth in the Synthesis of PbS Colloidal Quantum Dots Under Variable Temperatures," *ACS Omega*, vol. 6, no. 5, pp. 3701-3710, 2021. doi:10.1021/acsomega.0c05223

[14] S. A. McCarthy, R. Ratkic, F. Purcell-Milton, T.S. Perova, Y. K. Gunko, "Adaptable surfactant-mediated method for the preparation of anisotropic metal chalcogenide nanomaterials," *Sci. Rep*., vol. 8, pp. 2860, 2018. doi:10.1038/s41598-018-21328-7

[15] H.C. Morkoç and Ü. Özgür, Zinc Oxide: Fundamentals, Materials and Device Technology, Wiley-VCH Verlag GmbH & Co. KGaA, 2009.