Hierarchical and Complex ZnO Nanostructures by Microwave-Assisted Synthesis: Morphologies, Growth Mechanism and Classification

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ABSTRACT

Zinc Oxide is an important and multi-purpose material in various industries due to its particular chemical and physical properties. Discovering a cheap, fast, clean, safe, and easy to use method, to synthesize this oxide nanoparticle has attracted a lot of attention in recent applications. The unique properties of the microwave and its special heating capabilities have yielded desirable outcomes by combining different synthesis methods. In the recent years, the vast majority of studies focus on the microwave-assisted synthesis of zinc oxide nanoparticles. This review article attempts to go over the recent advancements on the synthesis of zinc oxide nanoparticles with the aid of microwave, different morphologies and applications obtained by this method. Various microwave-assisted synthesis methods are classified, including the solution-based methods such as hydrothermal, sol-gel, and combustion methods. Morphology of the nanoparticles can affect the properties, and subsequently, applications of these nanoparticles. On the other hand, there is great diversity of morphological and synthesis conditions of zinc oxide nanoparticles. Thus, categorizing the synthesis techniques and providing features of them, facilitates the selection of appropriate method for designing new hierarchical structures with potential properties for future applications. Also it is endeavored to focus on the formation mechanisms of these methods. Finally, the various morphologies obtained under microwave radiation and their formation mechanisms are discussed and the effective factors in the synthesis are analyzed and presented. The potential and suitable fields of development and progress in the future studies are also proposed.


KEYWORDS

Zinc oxide nanoparticles; microwave-assisted synthesize; growth mechanisms; hierarchical structure

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1. Introduction

The significant improvements in the production and detection of nanoparticles, and discovering new chemical and physical properties of them has opened new prospect for applications of materials.\(^1\)\(^,\)\(^2\) Therefore, the synthesis of inorganic nanocrystallites is now a research field in new materials because of the applications of the nanocrystallites in catalysis, optoelectronics, microelectronics, and biology.\(^3\)\(^-\)\(^8\) Nowadays, the extensive use of nanoparticles in the field of research and industry is obvious; hence the production of nanoparticles in various sizes and shapes in the shortest time with the highest efficiency is extremely important.

Zinc oxide is recognized as a multi-purpose material because of unique physical and chemical properties such as high chemical, thermal, and mechanical stability,\(^9\)\(^-\)\(^11\) electrical,\(^12\)\(^,\)\(^13\) optical,\(^13\)\(^-\)\(^17\) and piezoelectric\(^18\) properties. In materials science, ZnO is classified as a semiconductor belonging to the group II-VI.\(^19\) The direct band gap of 3.37 eV at room temperature and high exciton energy of 60 meV have caused zinc oxide to be considered desirable for potential use in nanoscale electronic and optoelectronic devices.\(^20\) Piezoelectric and pyroelectric properties of ZnO\(^21\) enables it to be used in gas sensors,\(^22\)\(^-\)\(^27\) glucose sensor,\(^22\) catalysts,\(^28\)\(^,\)\(^29\) optoelectronic,\(^30\)\(^,\)\(^31\) and piezoelectric\(^32\) devices and solar cells.\(^33\)\(^-\)\(^35\) Bio-dependent properties such as low toxicity, biocompatibility and biodegradability\(^18\)\(^,\)\(^36\) make zinc oxide an interesting material to be used in biomedicine, and ecological systems.\(^37\)\(^-\)\(^39\) Structural diversity of zinc oxide nanoparticles makes them classifiable among new common materials.

Nowadays, we are confronted by a wide range of challenges that make the use of nanoscale devices inevitable. Therefore, new, reliable and cheap methods of synthesizing new nanomaterials for biological and nanoelectronic applications are vital.\(^40\) Among the various methods of producing nanoparticles, the distinct features that lead to the superiority of a method in comparison to other similar methods are: 1- controlling the particle size, shape, structure, and uniform distribution in size and composition, 2- improving the purity of nanoparticles, 3- preventing the agglomeration of particles, 4- the stability of physical properties, 5- the ease of reproduction, 6- the
possibility of higher mass production and lowering the costs, adhering to the green chemistry principles, and quick implementation of the reactions. From the treatment duration and the energy consumption point of views, conventional heating is not suitable for the production of nanoparticles. However, the unique abilities of microwave which lead to prepare the appropriate ground for the rapid and homogeneous reaction, can provide the requirements mentioned above easily.

The synthesis of ZnO nano- and microparticles via various methods such as hydrothermal, sol-gel, electrochemical decomposition, combustion, vapor phase deposition, and precipitation from aqueous solution has been focused on by some researchers. Compared to conventional methods of heating, the combination of microwaves with some methods has attracted a high attention in materials science as a new method of heating. The main reason for such a wide attention paid to this technique is attributed to its numerous benefits such as rapid volumetric heating, high speed, shorter reactions, reduced side reactions, enhanced reaction selectivity, energy saving, and increased production efficiency.

Besides, due to the size, shape, morphology, purity, crystallinity and chemical composition-dependent properties, controlling the morphology of ZnO nanoparticles is an important issue. The combination of synthesis methods with microwave heating makes the synthesis process of nanoparticles, convenient, simple, and efficient task which facilitates the controlling of the morphology. In addition, the precursors, solvents, and additives play the important role in the morphology and shape of final obtained nanostructure. However, the addition of catalysts, surfactants, or templates to the reaction medium leads to the presence of heterogeneous impurities in the product as well as increasing the cost of production, which may limit the product application and development. So, designing an inexpensive and additive-free method is of high necessity.

Recent progresses made in relative fields indicate that combining these oxide nanoparticles with others as hybrid composites, doped nanoparticles and core-shell structures can improve the properties. Designing and engineering new hierarchical structures has recently attracted much attention. Understanding the basis of this flexible method and categorizing the synthesis methods can greatly contribute to achieving hierarchical structures with outstanding properties. A great deal of studies has been carried out about the microwave-assisted synthesis of ZnO and different morphologies. According to studies done by this group, there is no comprehensive and exhaustive overview on the microwave-assisted synthesis of ZnO nanoparticles up to this date. Therefore, it is the aim of this review to provide a quick and easy understanding of this technique. A conceptual diagram is provided to summarize the key points of the review in Figure 1.

2. Microwave heating

2.1. Heating mechanisms

Microwaves are located in-between infrared and radio waves with a wavelength within 1 mm to 1 m and a frequency ranging from 0.3 to 300 GHz. To prevent interference of the communication waves and microwaves, the industrial and domestic microwave devices are set to operate within the wavelength of 12.2 cm equal to the frequency of 2.45 GHz.

Microwave-assisted synthesis provides the opportunity to carry out the reaction within a short span of time, no more than a few minutes, due to the microwaves’ ability to transfer energy directly to the reactive components, which is not possible in the conventional heating methods. As a result of the molecular alignment in the same direction of the applied microwave field under the impact of microwave frequency, the polar end of molecules tends to change direction and make the oscillation proportional to that of the microwave electromagnetic field. Thus, heat is produced by the molecular collisions and friction and temperature increases rapidly.

The ability of the molecules in a liquid to align with the applied electrical field varies in different frequencies and viscosities. At low-frequency radiation, molecules rotate with the electric field oscillation. With this behavior, the molecules gain some energy, but the overall heating effect, in this case, is low. At high frequencies of the electrical field, the dipoles do not have enough time to respond to the oscillating field and so they do not rotate. Therefore, no energy transfer or heating occur. If the applied field is within the range of microwave radiation, then the frequency of the applied radiation will be sufficiently low to provide the dipoles with enough time to respond to the variable field, and so they are able to continuously re-align themselves along the direction of the applied field. On the other hand, the frequency is not high enough to allow the dipoles to precisely pursue the field oscillation. Therefore, if the dipolar molecule tends to spin again and ends up to be consistent with the oscillating field, the field is rotated and a phase difference is formed between the rotating dipole and field that leads to the dipole energy loss through friction and collisions in the heat form. In solutions containing ions, the ions in the solution move under the influence of the electrical field and, as a result of an increase in collision velocity, the kinetic energy is converted in to heat.
As explained above, the components are affected via dipolar polarization and ionic conduction mechanisms. In the dipolar polarization mechanism, the dipolar molecules try to re-align along the rapid change of the microwave electromagnetic field. In comparison, in the ionic conduction mechanism, the electrical field results in the free mobility of ions or ionic species in the material which in turn, causes ions to follow the rapid changes in the field. The rotational motion of molecules results in energy transfer. These phenomena are clearly demonstrated in Figure 2.

By increasing the polarity of molecules, their alignment with the microwave field will be more effective. Thus, the heating process by microwave is independent of the thermal conductivity of the reaction vessel and a thermal gradient develops from the solution to the walls of the vessel. The input power, heating frequency, and on-off radiation cycle are the key parameters of the microwave system and each of them seemingly have a great influence on the structure and properties of nanoparticles. Furthermore, in microwave-assisted synthesis, another decisive factor is the polarity property of solvent. The higher the possibility of molecule/ion alignment with microwave field is, the more effective heating would be.

The capacity of a solvent for absorbing microwave radiation and converting the electromagnetic energy into heat, and the capability of a solvent for heating is defined by the
loss tangent component \((\tan \delta = \frac{\varepsilon''}{\varepsilon'})\); in which \(\varepsilon''\) is the dielectric loss factor which represents the efficiency of transforming absorbed energy to heat, and \(\varepsilon'\) is the dielectric constant which represents capability of a material to be polarized as the result of the external electrical field. Hence, the high value of \(\tan \delta\) for a solvent indicates its great ability to absorb microwaves and convert it to heat.\(^{57,58,65,66}\)

Since the frequency of the microwave devices is set on a constant value (2.45 GHz), its dielectric constant only changes with temperature, in which by increasing solvent temperature, dielectric constant decreases. It has been stated by Pimentel et al.,\(^{67}\) even though the presence of some probable additives such as precursor and surfactant naturally reduces the pressure and temperature of the solvent as compared to the pure state, the increase in temperature should be avoided in general by incorporating some additional systems such as water circulation system. It has been said that non-polar solvents are not heated through microwave irradiation. Addition of a little amounts of a polar solvent with a high loss tangent can provide them to be heated. Another way for speeding up the warming process is to add salt to the solvent. In this case, the solubility problems can arise because many organic solvents form a heterogeneous mixture.\(^{68}\) Ionic solvents can be a suitable solvent in microwave-assisted synthesis for organic and inorganic compounds, due to their good dielectric properties, low vapor pressure, low melting temperature, the high-temperature range in the

**Figure 2.** Schematic representation of polar molecules’ behavior in the presence of microwave radiation during synthesis.
liquid state (up to 400°C), low toxicity, non-flammability and high ionic conductivity. These solvents not only act as a suitable solvent for precursors, but also as the stabilizing agent of the formed morphology. Furthermore, some ionic solvents are soluble in organic, non-polar solvents that may solve the polarization problem. The use of ionic solvents such as 1-butyl-3-ethylimidazolium tetrafluoroborate, 1-butyl-3-ethylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, glutamic tetrafluoroborate, 1-n-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide, 1-decyl-3-methylimidazolium hexafluorophosphate is reported in the microwave-assisted synthesis of ZnO nanoparticles.

2.2. Accelerating mechanisms

As mentioned earlier, the main advantage of microwave-assisted synthesis is its shorter reaction time. Lidström et al.60 reported the microwave impact on the rate of chemical reaction based on the Arrhenius equation (Eq. 1).

\[ K = A e^{-\Delta G / RT} \]  

In which K, A, \( \Delta G \), R and T refers to rate constant, pre-exponential constant, activation free energy, universal gas constant and temperature, respectively. According to Eq. 1, two mechanisms are proposed for speeding up the chemical reactions. A possible mechanism is to increase the constant A, which depends on mobility of molecules and their oscillation at the reaction side. Microwave can cause oscillation by aligning the molecules along its field, and affect the constant A. Another possible mechanism is to influence the activation free energy (\( \Delta G \)). However, what is certain is that the effect of microwave could be due to its special heating capabilities which is not provided in the conventional heating. Bilecka et al.77 reported that the microwaves’ acceleration effect is mainly influenced by the kinetic factors, and there is no evidence based on the reduced activation free energy (\( \Delta G \)) of the esterification reactions.

It is known that using silicon carbide (SiC) vessels results in absorption in the GHz range, therefore it can also be used for electromagnetic wave absorption. Baghbanzadeh et al.79 investigated the role of microwave on accelerating the reactions. Nanoparticles were synthesized under microwave irradiation by the hydrothermal method under the same conditions in two separate SiC and Pyrex vessels. By Using the SiC vessel, any microwave electromagnetic effects are removed and the possibility of distinguishing thermal and non-thermal effects is thus provided. In this study, it is reported that no difference is observed in the shape, size, and size distribution of particles, and the effects of the microwave on the quality of the final product are strictly related to the thermal effects of microwave, and the high rate of the reaction is merely due to high reaction temperature. Huang et al.18 stated that the effect of microwave could lead to the quick hydrolysis of precursor which in turn facilitates the nucleation and crystallite growth. Moreover, it is proposed that the rapid increase in the temperature or pressure, leads to an increase in the movement speed of the particles and the particle integration at the collision point. The merging of the adjacent particles or the primary particles in the surface layers of nanostructures forms complex structures.

Nowadays, the increase in the production speed and quality of the product in terms of uniform size distribution, high purity, and low surface defects, along with the importance of ZnO in various industries have developed an interest in this method of heating and its combination with different ZnO nanoparticle synthesis routes.

3. Fabrication methods of nano- and micrometric zinc oxide

Synthesis of ZnO nanoparticles is reported to be done through various methods, including vapor deposition, hydrothermal and solvothermal, sol-gel, deposition from microemulsion and mechanochemical methods. According to numerous studies, microwave-assisted synthesis includes the hydrothermal18,37,47,68,79–96 solvothermal67 sol-gel77,79,97–99 combustion100–102 and other solution-based synthesis methods103–105 which involve the preparation of precursors solution (PS), microwave radiation of the PS (within the autoclave, flux, and crucible, depending on the type of method), cooling, separation, particle washing, drying and, in some cases, aging before the separation, calcination81,83 and annealing107. The general procedure of the formation mechanism and growth of ZnO with different morphologies consists of three stages: (1) reaction between Zn2+ and OH− species in PS, (2) rapid and homogeneous nucleation of ZnO under microwave irradiation, and (3) oriented attachment of the formed ZnO nuclei in the preferred direction depending on the presence of various factors. In this regard, \([\text{Zn(OH)}_4]^{2-}\), which acts as the growth units, is either available in the solution, or is produced as a result of \(\text{Zn(OH)}_2\) dissolving.108–110 The decomposition kinetic of these complexes and the
morphology of nucleation sites determines the size and shape of the nanoparticles.\textsuperscript{111} General reactions that are commonly reported in all of the formation mechanisms for ZnO are reactions 2 to 4.\textsuperscript{118,82,88,100,112–114}

\begin{align*}
Zn^{2+} + 2OH^- &\rightarrow Zn(OH)_2 \tag{2} \\
Zn(OH)_2 + 2OH^- &\rightarrow [Zn(OH)_4]^{2-} \tag{3} \\
[Zn(OH)_4]^{2-} &\rightarrow ZnO + H_2O + 2OH^- \tag{4}
\end{align*}

The precipitation reaction is one of the most common liquid phase reactions leading to the formation of the solid phase, which is widely used for the synthesis of zinc oxide powder on large scale. When the aqueous solution of zinc salts undergoes a reaction, compounds with less solubility are derived from the solution. Zinc oxide powder can then be obtained after washing, drying, and calcination of the deposits.\textsuperscript{115}

Precipitation process typically starts with formation of Zn(OH)\textsubscript{2} followed by its conversion into ZnO. According to Wang et al.,\textsuperscript{108} phase transformation mechanism of Zn(OH)\textsubscript{2} to ZnO is based on three methods, including dissolution-precipitation, in-situ crystallization, and solid-solid phase transformation. According to dissolution-precipitation mechanism, the Zn(OH)\textsubscript{2} microcrystallites are dissolved in alkaline solution and produce [Zn(OH)\textsubscript{4}]\textsuperscript{2-} ions that act as the growth units for the nucleation and ZnO growth in the solution (Figure 3).\textsuperscript{116}

Through the in-situ crystallization mechanism of ZnO from Zn(OH)\textsubscript{2}, the ZnO nucleation occurs in Zn(OH)\textsubscript{2} matrix and the outward rapid crystal growth occurs. Through this process, Zn(OH)\textsubscript{2} easily dissolves in the defected sites and a cavity is formed. Zn(OH)\textsubscript{2} dehydration in the cavity leads to the formation of ZnO nuclei. In addition, the obtained [Zn(OH)\textsubscript{4}]\textsuperscript{2-} growth units through the dissolution of Zn(OH)\textsubscript{2} can make their ways to the nucleus and accelerate the growth of ZnO nuclei.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{system.png}
\caption{Schematic representation of the formation stages of ZnO nucleus and its further growth as a result of the dissolution of Zn(OH)\textsubscript{2} phase and achieving the growth units.}
\end{figure}
While the ZnO growth occurs, the remaining source of Zn(OH)$_2$ acts as a template for keeping the ZnO crystals until its complete dissolution. This mechanism demonstrates the fact that this method involves growing inside the pattern which is associated with the precipitation mechanism. Through the solid-solid transformation mechanism, nucleation and crystal growth of ZnO follows the dissolution-precipitation mechanism before nanoparticles make contact with the surface of Zn(OH)$_2$. However, as soon as they reach the Zn(OH)$_2$ surface, they penetrate into the matrix. At this stage, more growth follows the direct solid-solid Zn(OH)$_2$ transformation to ZnO. Since the two solid phases are in contact with each other perfectly, there is no possibility for the alkaline solution to reach the phase boundary and accelerate the growth through the dissolution-precipitation mechanism. The dehydration process during solid-solid transformation mechanism seems to occur between every two adjacent hydroxyl groups on the Zn(OH)$_2$ lattice. After dehydration, each oxygen ion forms a tetrahedral coordination with four zinc ions and vice versa.

Until now, microscopic details of the nucleus formation have not been effectively understood. Besides, it has not been precisely mentioned that which mechanism is responsible for the arrangement of nanoparticles. However, it is logical to assume that the orientation and growth of the nanoparticles are controlled through the nucleation and the growth of several zinc and oxygen layers in the preferred direction. The growth process is performed by the perfect fit of the tetrahedral structure of [Zn(OH)$_4$]$^{2-}$ species with the polyhedral (0001) face (Figure 4).\textsuperscript{117}

Also, a series of reports have indicated the film growth of nanoparticles on different surfaces. In this case, the rapid microwave heating forms ZnO embryos with high free energy that bombard the surface immersed in the solution. These nuclei are formed because of heterogeneous nucleation and subsequently, lead to the formation of the film. The resulting arrays on the surface will grow in the preferred direction, depending on the available conditions (Table 1). In vapor-based methods for film growth on surfaces, high temperatures and catalysts are often required, which limits the pool of available choices in substrate. In order to make the selected method efficient in terms of economic and energy supply, the process temperature should be lower; thus, the solution-based methods are used. As a result, the epitaxial growth of nanoparticles in solution on the surface takes place at lower temperatures. Furthermore, considering that reaching the appropriate length of the arrays requires an extended period of time as well as refreshing the PS in conventional heating, microwave heating can solve these limiting problems of solution-based methods by quickly reaching to crystallization temperatures and increasing amount of homogeneous nucleation in the solution. In fact, consumption of the precursor as a result of high amounts of heterogeneous nucleation, which prevents the growth of nanoparticles, is the main reason of the aforementioned complications.

3.1. Microwave-assisted hydrothermal and solvothermal methods

3.1.1. Principles

Hydrothermal method is a subset of solvothermal methods which is widely used because of its advantages such as safety and biocompatibility (with respect to particle growth in an aqueous solution instead of organic solvents). In general, hydrothermal synthesis refers to reactions occurred under high-pressure/high-temperature conditions.\textsuperscript{128} The synthesis takes place inside an autoclave as the high-pressure reactor. The precursor mixture is gradually heated to temperature of 100–300°C and the reaction takes from several hours to several days to complete. Eventually, during the cooling, the crystallite nuclei are formed and begin to grow.\textsuperscript{42} One advantage of this approach is the possibility of performing reactions at low temperatures\textsuperscript{128} and being eco-friendly due to isolated system.\textsuperscript{129}
<table>
<thead>
<tr>
<th>Precursors</th>
<th>Substrate</th>
<th>Seed layer</th>
<th>Post treatment</th>
<th>Power</th>
<th>Holding time</th>
<th>Temperature</th>
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<th>Other effective parameters</th>
<th>Morphology &amp; size</th>
<th>References</th>
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<tbody>
<tr>
<td>Seeding solution: zinc acetate dehydrate; isopropyl alcohol (IPA). Growth solution: zinc nitrate hexahydrate, hexamine.</td>
<td>soda lime glass</td>
<td>300°C, 10 min</td>
<td>Heating: to 120°C</td>
<td>140 W</td>
<td>180 s</td>
<td>thin film consist of nanowires (D:20 nm, L:200 nm)</td>
<td>118</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seeding solution: zinc acetate dehydrate, ammonium hydroxide; water. Growth solution: zinc acetate dehydrate, ammonium hydroxide.</td>
<td>glass</td>
<td>100°C, 1 min</td>
<td>Calcination: 350°C, 30 min, air</td>
<td>4-80 min</td>
<td>100 W</td>
<td>nano-sheets (t: 30–50 nm) consist of nanoparticles (D: 15 nm) that are self-assembled to form sheets</td>
<td>119</td>
<td></td>
<td></td>
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<tr>
<td>Solution of tetra ammonium zinc complex [Zn(NH₃)₄⁺²⁺].</td>
<td></td>
<td>Aging: 20 s</td>
<td></td>
<td></td>
<td></td>
<td>nano-sheets (t: 500 nm) consist of rice shaped (D:250–350 nm)</td>
<td>120</td>
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<tr>
<td>Seeding solution: zinc acetate dehydrate; ethanol. Growth solution: zinc nitrate hexahydrate, hexamethylene tetramine (HMTA).</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Circular nanorods with rough surface</td>
<td>121</td>
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</tr>
<tr>
<td>Seeding solution: zinc acetate dehydrate; ethanol. Growth solution: zinc nitrate hexahydrate, hexamethylene tetramine (HMTA).</td>
<td>Si (100) substrate;</td>
<td>800°C, 5 min, air</td>
<td>Calcination: 350°C, 30 min, air</td>
<td>4-80 min</td>
<td>100 W</td>
<td>90°C</td>
<td>10.07, 10.46, 10.65, 10.79, 10.9</td>
<td>nanowires arrays with a narrow distribution of diameters but poor alignment, fully vertically aligned nanowires with a wide diameter distribution</td>
<td>122</td>
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</tr>
<tr>
<td>Seeding solution: zinc acetate dehydrate; 1-propanol. Growth solution: zinc nitrate hexahydrate, hexamethylene tetramine (HMTA); deionized water.</td>
<td>n-type silicon, glass substrate, polyethylene terephthalate (PET)</td>
<td>100°C, 1 min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nanowires with a narrow distribution of diameters but poor alignment, fully vertically aligned nanowires with a wide diameter distribution</td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>Seed material: Zn(OH)₂·PVAG. Growth solution: zinc nitrate hexahydrate, hexamethylene tetramine (HMTA).</td>
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<td></td>
<td></td>
<td></td>
<td>nanowires array</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>Seed layer deposition: sputtering. Growth solution: zinc nitrate hexahydrate, hexamethylene tetramine (HMTA).</td>
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<td></td>
<td></td>
<td>nanowires array</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>Seeding solution: zinc acetate dehydrate; ethanolamine, 2-methox ethanol. Growth solution: zinc nitrate hexahydrate, hexamethylene tetramine (HMTA).</td>
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<td></td>
<td>nanowires array</td>
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<tr>
<td>Seeding solution: zinc acetate dehydrate; selenium. Growth solution: zinc nitrate hexahydrate, hexamethylene tetramine (HMTA).</td>
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<td></td>
<td>nanowires array</td>
<td>127</td>
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</table>
In this method, the precursor solution contains zinc salts as a source of cations (Zn$^{2+}$) and precipitator ions (OH$^-$/CO$_3^{2-}$) and surfactants or morphology-modifying agents. Through this process, the precursor is eventually converted to ZnO using heat treatment operations. The most widely used precursors in the ZnO hydrothermal synthesis is the zinc acetate and zinc nitrate and other zinc salts such as zinc chloride. The widely used alkaline compounds that act as the precipitator are potassium hydroxide, sodium hydroxide, and ammonia. Divalent metal ion does not hydrolyze in an acidic medium, so the presence of alkaline solution is necessary to form ZnO nanoparticles. The formation of different nanostructures depends on the temperature of the process, the applied precursors, adding surfactants or morphology modifying agents, and the pH. It is worth noting that some materials act both as the reducing and complexing agents. Hydrazine hydrate is an example of these materials. However, the sodium hydroxide, under the same conditions, acts only as the reducing agent.

Morphologies such as chrysanthemum-like, nanosheets, nanorods, nanospheres, leaf-like, prism-like nanorods, (nanorod and nano-sheet bundle) flower-like structures, flower-shaped particles, nanopenels, quasi-cylindrical, round-shaped porous nanoparticles, hollow and porous nano and microspheres, star-like, nanowires, nanodisks, safflower-like, cauliflower-like, ixora-like, nanotips, micro-cups, micro-rings, urchin-like, bitter-melon-like microparticles, and nanopellet morphologies are produced by hydrothermal method with conventional heating. Some reports also show the growth of ZnO nanocrystals on the surface. Through this method, seeding of the surfaces is done by ZnO nanoparticles which provide the possibility of growth. Some examples in this regard include the growth of nanorods on the glass surfaces, and also the growth on silicon wafers coated with a ZnO thin film. During the growth process by the hydrothermal method, anisotropic nanostructures can be attached on all surfaces using a seed layer of ZnO. The noteworthy point is the changing morphology of the grains grown by changing the conditions (pH, temperature, and precursor concentration) during the growth process.

The microwave-assisted hydrothermal method is a development in conventional hydrothermal method for the short-term production of nanoparticles. This method was first used by Komarneni et al. to synthesize fine ceramic powders. The advantages of microwave heating over the conventional heating of autoclave are rapid heating to the crystallization temperature, uniform nucleation, and rapid super-saturation through the fast dissolution of the precipitated hydroxides which reduce the crystallization temperature and time. The minimum heating time in the hydrothermal method is reported as 60 minutes by Chen et al., whereas the maximum heating time is reported about 48 hours by Kumar et al. However, the minimum period of heating in hydrothermal method with microwave radiation is reported as 3 minutes by Pimentel et al. and maximum heating time is reported as 1 hour in several articles.

Also, in the microwave-assisted synthesis method, there is the possibility of controlling the morphology through nanoparticle synthesis by the continuous temperature control.

The particles produced during the microwave-assisted hydrothermal method are reported in numerous articles as micro/nano rods, flower-like structures (nanorod bundle), square-like nanosheets, nanosheets, nanowires, nano thruster vane, nanodandelion, nano spindle, tripods and tetrapods, spherical, rugby-like, sponge-like, star-shaped (nanorod bundle), marigold flower-like, needle-like, and ellipsoidal morphologies that are discussed in detail in the present work (Table 2). The steps involved in the formation of zinc oxide nanoparticles by the hydrothermal method are shown in Figure 5.

### 3.1.2. Formation mechanisms

The occurrence of competing precipitation and dissolution reactions, as well as the presence of complexing agents and surfactants along with morphology-modifying agents which prevent the growth in a certain direction (due to adsorption on the specific faces) will cause the specific mechanisms for the production of nanoparticles with specific morphologies. Some of the proposed mechanisms are mentioned in this section.

A formation mechanism was proposed by Gomes et al., for ZnO structures. Since ZnO is a polar crystal with polar (0001) faces terminated to Zn and (000T) faces terminated to O, it has anisotropic growth and different growth rates in different directions of the crystal. Nucleation of ZnO depends on the concentration of the reactants. Moreover, in the growth stage, according to the polarization properties of the crystal and adsorption of the agents on preferred faces, different growth rates in different directions and different morphologies can be obtained. According to Baghbanzadeh et al., the most preferred growth direction of rod nanoparticles is [10$ar{T}$1].
<table>
<thead>
<tr>
<th>Precursors</th>
<th>Post treatments</th>
<th>Power</th>
<th>Holding time</th>
<th>Temperature/ pH</th>
<th>Other effective parameters</th>
<th>Morphology &amp; size</th>
<th>Schematics</th>
<th>Crystallographic properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc nitrate, ammonia; water.</td>
<td>Calcination: 5 h</td>
<td>800 W</td>
<td>30 min</td>
<td>120°C/10</td>
<td>Flower-like structure (L: 100–150 nm)</td>
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<tr>
<td>Zinc acetate dehydrate, urea;</td>
<td>Calcination:</td>
<td>30 min</td>
<td>120°C/10</td>
<td></td>
<td>Rough microrod (L: 1–3 μm, W: 0.7–1 μm), Smooth microrod (L: 2–3 μm)</td>
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<td>water.</td>
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<tr>
<td>Zinc nitrate hexahydrate, ammonia;</td>
<td>Calcination:</td>
<td>15 min</td>
<td>220°C</td>
<td></td>
<td>Nanosheets (W: 70 nm, t: 12 nm)</td>
<td></td>
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<tr>
<td>water; cetyl trimethyl ammonium</td>
<td>400°C, 90 min</td>
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<tr>
<td>bromide (CTAB).</td>
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<tr>
<td>Zinc oxide, sodium hydroxide;</td>
<td></td>
<td>30 min</td>
<td>150°C</td>
<td></td>
<td>Flower-like (D: ~ 10 μm) consist of rod-like building block units (L: 5 μm, D: 1 μm, narrower at the end)</td>
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<td>ethanol; ethylene diamine (EDA).</td>
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<tr>
<td>Zinc acetate dehydrate, sodium</td>
<td></td>
<td>1 h</td>
<td>150°C</td>
<td></td>
<td>Nanorods (L: 1–2 μm, W: 100–150 nm)</td>
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<tr>
<td>hydroxide; water.</td>
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<tr>
<td>Zinc acetate, ammonia; water;</td>
<td></td>
<td>60 min</td>
<td>120°C</td>
<td></td>
<td>Spherical (D: 60–90 nm), Rugby-like (D: ~ 450 nm, L: ~ 700 nm)</td>
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<tr>
<td>triethanolamine (TEA).</td>
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<tr>
<td>Zinc acetate dehydrate, sodium</td>
<td></td>
<td>400 W</td>
<td>45 min</td>
<td>140°C</td>
<td>Nanorods (D: 60 80 nm, L: 250 nm)</td>
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<tr>
<td>hydroxide; water, ethanol.</td>
<td>(100%)</td>
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<tr>
<td>Zinc nitrate hexahydrate, sodium</td>
<td></td>
<td>600 W</td>
<td>15 min</td>
<td>120°C</td>
<td>Hexagonal platelets (D: 20–100 nm)</td>
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<tr>
<td>hydroxide; water.</td>
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<tr>
<th>Precursors</th>
<th>Power</th>
<th>Holding time</th>
<th>Temperature</th>
<th>Other effective parameters</th>
<th>Morphology &amp; size</th>
<th>Schematics</th>
<th>Crystallographic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc nitrate hexahydrate, sodium hydroxide; water, polyethylene glycol (PEG2000), ethanol.</td>
<td></td>
<td>30 min</td>
<td>180°C</td>
<td></td>
<td>Quasi-spherical microspheres (D: 1.5–20 μm) consist of nanorods (D: 300 nm, L: 1 μm)</td>
<td><img src="image1" alt="Schematic" /></td>
<td>Lattice constants: a = 0.3249 nm, c = 0.5206 nm</td>
</tr>
<tr>
<td>Zinc acetate dehydrate, sodium hydroxide; water; O- (m- or p-) nitrobenzoic.</td>
<td></td>
<td>10 min</td>
<td></td>
<td>with O- (m- or p-) nitrobenzoic, without O- (m- or p-) nitrobenzoic</td>
<td>Flower-like structures consist of sword-like nanorods (W: 60–100 nm, L: several micrometers), nanorods (D: ~200 nm, L: up to 4 μm)</td>
<td><img src="image2" alt="Schematic" /></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate hexahydrate, ammonia; water.</td>
<td></td>
<td>10 min</td>
<td>90°C</td>
<td></td>
<td>Porous polygonal nanoflakes</td>
<td><img src="image3" alt="Schematic" /></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate hexahydrate, dodecylamine (DDA); water.</td>
<td>150 W</td>
<td>15 min</td>
<td>80°C</td>
<td>DDA:Zn^{2+} molar ratio: 1:20</td>
<td>Hexagonal quasi-hour glasses</td>
<td><img src="image4" alt="Schematic" /></td>
<td></td>
</tr>
</tbody>
</table>
An example of chemical reactions for the formation of ZnO in aqueous solution from zinc acetate dehydrate and sodium hydroxide precursors is presented by Caglar et al.\textsuperscript{81} The process is performed based on the reactions (5) and (6):

\[
\begin{align*}
\text{Zn}(	ext{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} & \rightarrow \text{Zn(OH)}_2 + \text{CH}_3\text{COONa} + 2\text{H}_2\text{O} \\
\text{Zn(OH)}_2 & \underset{\text{MW}}{\rightarrow} \text{ZnO} + 2\text{H}_2\text{O}
\end{align*}
\]  

Reaction (5) is the hydrolysis of Zn(CH\textsubscript{3}COO)\textsubscript{2} \cdot 2H\textsubscript{2}O to form complex compounds of zinc, while reaction (6) is the formation of ZnO under microwave radiation. This is while Pimentel et al.\textsuperscript{40} pointed to the formation of the [Zn(OH)]\textsubscript{4}\textsuperscript{2–} growth units under reaction (7) instead of reaction (6) and subsequently decomposition in to ZnO. In fact, Zn(OH)\textsubscript{2} is dissolving to form Zn\textsuperscript{2+} and OH\textsuperscript{−}. Later, by raising the concentrations of these species to the supersaturation amount, the nucleation of ZnO nucleus begins.

\[
\text{Zn(OH)}_2 + 2\text{H}_2\text{O} \underset{\text{MW}}{\rightarrow} [\text{Zn(OH)}_4]^{2–} + 2\text{H}^+ \tag{7}
\]

Chen et al.\textsuperscript{137} studied the microwave-assisted solvothermal synthesis using acetate precursor and water/ethylene glycol (EG) solvent in the absence of the alkaline agent and ZnO formation mechanism is proposed as reactions (8) and (9):

\[
\begin{align*}
\text{CH}_3\text{COO}^- + \text{H}_2\text{O} & \rightarrow \text{CH}_3\text{COOH} + \text{OH}^- \tag{8} \\
\text{Zn}^{2+} + 2\text{OH}^- & \underset{\text{MW}}{\rightarrow} \text{ZnO} + \text{H}_2\text{O} \tag{9}
\end{align*}
\]

Due to the effect of additives on the growth rate of different ZnO crystal sides, various ratios of water:EG can also cause different influences. It is reported that higher levels of EG results in growth inhibition along the [0001] direction, and due to the prevention of 1-D particles

---

**Figure 5.** Schematic representation of zinc oxide nanoparticles’ formation by hydrothermal method inside the autoclave.
from forming, the particle size is diminished. Similar to study of Pimentel et al.,⁶⁷ EG performance is reported as the adsorption on (0001) faces rich in Zn and prevention of the growth along the c-axis as a result of reducing the surface energy of these faces.

Another mechanism by Chen et al.,⁸² using zinc acetate dehydrate and sodium hydroxide as precursors is provided for the formation of ZnO by microwave-assisted hydrothermal methods according to reactions (10) to (14):

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (10)
\]

\[
\text{Zn(OH)}_2 \rightarrow \text{Zn}^{2+} + 2\text{OH}^- \quad (11)
\]

\[
\text{Zn}^{2+} + 2\text{OH}^- \xrightarrow{\text{MW}} \text{ZnO} + \text{H}_2\text{O} \quad (12)
\]

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-} \quad (13)
\]

\[
[Zn(OH)_4]^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (14)
\]

According to reaction (10), the dissolved Zn\(^{2+}\) and OH\(^-\) ions form the Zn(OH)\(_2\) colloids, and some produced Zn(OH)\(_2\) colloids are dissolved in the solution and reproduce the Zn\(^{2+}\) and OH\(^-\) ions according to reaction (11). When the concentration of Zn\(^{2+}\) and OH\(^-\) reach the supersaturation amounts, according to reaction (12), the formation of ZnO nuclei is facilitated in the presence of microwave. At the same time, similar to what has been reported by Pimentel et al.,⁴⁰ a number of Zn(OH)\(_2\) colloids in reaction (11), react with OH\(^-\) ions to form [Zn(OH)\(_4\)]\(^{2-}\) by undergoing reaction (13). [Zn(OH)\(_4\)]\(^{2-}\) acts as the growth unit for ZnO particles at high pH which can be decomposed by microwave heating based on reaction (14). Due to the presence of concentration gradient, the [Zn(OH)\(_4\)]\(^{2-}\) units can penetrate and adsorb to active regions of the ZnO nuclei surface, and produce particles with different morphologies.

Microwave radiation can affect the reactions and penetration, therefore enhancing crystallite growth rate, and resulting in the penetration and linking of the adjacent particles and primary particles to the outer layers of ZnO nanostructures that are the intermediate products of the reaction between primary nanoparticles and final nanostructures. Therefore, the role of the microwave is not only to accelerate the precursors’ reaction, but also to enable the growth and crystallization of ZnO nanoparticles with complex morphologies.¹⁸,⁸²

Another formation mechanism from zinc nitrate hexahydrate and sodium hydroxide is described by Huang et al.¹⁸ as reactions (15) and (16):

\[
\text{Zn(NO}_3\text{)}_2 + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2 \downarrow + 2\text{NaNO}_3 \quad (15)
\]

\[
\text{Zn(OH)}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{MW}} \text{Zn(OH)}_4^{2-} + 2\text{H}^+ \rightarrow \text{ZnO} + 3\text{H}_2\text{O} \quad (16)
\]

According to reactions (15) and (16), Zn\(^{2+}\) and OH\(^-\) ions react when exposed to microwave irradiation as a result of the reaction between zinc nitrate hexahydrate and sodium hydroxide, in order to form stable [Zn(OH)\(_4\)]\(^{2-}\) complex as the growth unit of ZnO nanostructure. Generally, the formation of ZnO complex nanostructures includes the formation of ZnO nanoparticles at first. Then, microwave radiation to these particles will lead to fusion of particles at the collision point, and more growth of primary particles to form complex structures. Accordingly, it seems that the growth of complex nanostructures does not occur only with the assistance of catalysts and surfactants, since the only materials used in the synthesis are Zn(NO\(_3\))\(_2\) and NaOH.

A similar mechanism is proposed by Majithia et al.⁵⁸ from zinc nitrate hexahydrate and hexamethylene tetramine (HMT) through reactions (17) to (20):

\[
\text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 6\text{H}_2\text{CO} + 4\text{NH}_3 \quad (17)
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \quad (18)
\]

\[
\text{Zn}^{2+} + 2\text{OH}^- \xrightarrow{\text{MW}} \text{Zn(OH)}_2 \downarrow \quad (19)
\]

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow 2\text{ZnO} \downarrow + 2\text{H}^+ \quad (20)
\]

\[
\text{Zn(OH)}_2 + \text{Si(OH)}_4 \rightarrow \text{Zn}_2\text{Si}_2\text{O}_7\cdot\text{H}_2\text{O} \downarrow \quad (21)
\]

By producing Zn\(^{2+}\) and OH\(^-\) ions from the hydrolysis of zinc nitrate hexahydrate and methylenetetramine, two competing reversible reactions of (19) and (20) take place. As the result of direct precipitation of ZnO (reaction 20), tetrapods and tripods are formed. The direct precipitation of ZnO from the solution leads to the linking and simultaneous growth of multiple lattices from common connection. In this case, each crystal grows along the c-axis and results in the formation of tetrapod and tripod morphologies. The single dimensional microtubes are formed as the result of the dissolution of Zn(OH)\(_2\) followed by its recrystallization as ZnO and the ripening phenomenon. Dissolution and recrystallization occur as the result of local heating by the microwave. The explanation given for the formation of a cap on tripods and rods, is that Si(OH)\(_4\) impurities in solution which are caused by glass test tubes, react.
with Zn(OH)$_2$ (reaction 21), which leads to the formation of silicate caps on the nanoparticles in solution, at prolonged periods of time along with high temperatures in the synthesis reaction.

The flower-like nanoparticles formation mechanism from zinc oxide and sodium hydroxide as precursors in the presence of ethylenediamine (EDA) is proposed by Rai et al.$^{86}$ through reactions (22) to (24):

$$[\text{Zn(OH)}]^{2-} \leftrightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (22)$$
$$\text{Zn}^{2+} + \text{EDA} \leftrightarrow [\text{Zn}-\text{EDA}]^{2+} \quad (23)$$
$$[\text{Zn}-\text{EDA}]^{2+} \xrightarrow{\text{MW}} \text{Zn}^{2+} + \text{EDA} \quad (24)$$

Given that the ZnO growth is influenced by nucleation and growth, on one hand, at high pH values according to reaction (22), rate of nucleation is slow, while growth happens at an accelerated speed, which is due to the presence of high concentration of [Zn(OH)$_4$]$^{2-}$ growth units and on the other hand, as a result of the acceleration of microwave heating, the growth rate is high. In terms of the particle growth, by adsorbing the [Zn(OH)$_4$]$^{2-}$ growth units to the preferred planes, the nuclei are formed and as the result of the merger, the particles grow. It is suggested that the formation of flower-like structures can be due to the aggregation of primary nuclei due to the high pH and the adsorption of the growth units on these masses. EDA by the formation of stable complexes (reaction 23) before the microwave radiation and release of Zn$^{2+}$ ions according to reaction (24), can control the composition of Zn$^{2+}$ with O$^{2-}$. Besides, EDA leads to the formation of microrods by adsorption to the formed crystals and the growth along the c-axis, along with the development of flower-like structure through the secondary nucleation on these particles and their growth. This structure is obtained as the result of the short time and rapid growth.

Another mechanism is proposed by Boudjadar et al.$^{87}$ from zinc acetate dehydrate and sodium hydroxide as precursors according to reactions (25) to (28) for producing nanosheets according to the alkalinity of the reaction medium:

$$\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \quad (25)$$
$$\text{Zn(CH}_3\text{OO)}_2 \rightarrow \text{Zn}^{2+} + 2(\text{CH}_3\text{OO})^- \quad (26)$$
$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (27)$$
$$\text{Zn(OH)}_2 \xrightarrow{\text{MW}} \text{ZnO} + \text{H}_2\text{O} \quad (28)$$

When the concentrations of Zn$^{2+}$ and OH$^-$ ions go beyond the saturation level, the ZnO nuclei are produced continuously based on reaction (28). However, it must be noted that the long particles are formed in the presence of OH$^-$ as a result of the ZnO crystallites polarity. Hence, the formation of ZnO nanosheets at high pH conditions occurs by preventing rapid growth in the c-axis direction because of adsorption of OH$^-$ ions to polar faces. The mechanism provided in this section is proven by electron microscopy and microstructural studies.

In another study by Guo et al.$^{88}$ the mechanism of ZnO particle formation from zinc acetate dehydrate and ammonia as precursors in the presence of triethanolamine (TEA) as the complexing agent, according to reactions (29) to (32), is discussed:

$$\text{Zn(CH}_3\text{COO)}_2 \rightarrow \text{Zn}^{2+} + 2(\text{CH}_3\text{COO})^- \quad (29)$$
$$\text{Zn}^{2+} + \text{N} (\text{CH}_2\text{CH}_2\text{OH})_3 \leftrightarrow [\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3]\text{Zn}^{2+} \quad (30)$$
$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \downarrow \quad (31)$$
$$\text{Zn(OH)}_2 + 2\text{OH}^- \xrightarrow{\text{MW}} [\text{Zn(OH)}_4]^{2-} \rightarrow \text{ZnO} + 2\text{H}_2\text{O} + 2\text{OH}^- \quad (32)$$

Initially, that the solution contains zinc acetate dehydrate and triethanolamine, plenty of Zn$^{2+}$ amino complexes are formed (reaction 30). When ammonia is added, Zn(OH)$_2$ precipitates (reaction 31) and re-dissolved, so homogeneous solution including [Zn(OH)$_4$]$^{2-}$ growth units are formed (reaction 32). The morphology of the particles is controlled by nucleation and growth rate which is influenced by the concentration of [Zn(OH)$_4$]$^{2-}$ ions. The effect of TEA on the morphology of particles is associated with the stability of the [Zn(OH)$_4$]$^{2-}$ ions affected by triethanolamine. As a result of the high content of [Zn(OH)$_4$]$^{2-}$ ions in the solution, the mean free path of the ions is reduced which results in the crystallite growth in certain directions and the formation of a different morphology.

The stages of ZnO formation by zinc chloride and urea precursors are proposed according to reactions (33) to (36) by Tseng et al.$^{91}$:

$$\text{CO(NH)}_2 + 3\text{H}_2\text{O} \rightarrow \text{CO}_2 \uparrow + 2\text{NH}_3\text{H}_2\text{O} \quad (33)$$
$$4\text{Zn}^{2+} + \text{CO}_3^{2-} + 6\text{OH}^- + \text{H}_2\text{O} \rightarrow 4\text{ZnCO}_3(\text{OH})_6 \cdot \text{H}_2\text{O} \downarrow \quad (34)$$
$$4\text{ZnCO}_3(\text{OH})_6 \cdot \text{H}_2\text{O} \xrightarrow{\text{MW}} 4\text{ZnO} + 4\text{H}_2\text{O} + \text{CO}_2 \uparrow \quad (35)$$
$$4\text{ZnCO}_3(\text{OH})_6 \cdot \text{H}_2\text{O} + 4\text{H}_2 \rightarrow 5\text{Zn} + 8\text{H}_2\text{O} + \text{CO}_2 \quad (36)$$

When the precursor solution is placed under microwave irradiation, the urea begins to decompose (reaction 33). Next, the hydrolyzed products (hydroxide and carbonate ions) react with Zn$^{2+}$ ions through reaction (34)
and produce zinc carbonate hydroxide hydrate. If the Zn\textsubscript{3}CO\textsubscript{3}(OH)\textsubscript{6}.H\textsubscript{2}O remain undecomposed, the resulting ZnO would be in a quasi-crystalline state, and not fully crystallized. This behavior highlights the need for calcination at the appropriate temperature for complete decomposition of Zn\textsubscript{4}CO\textsubscript{3}(OH)\textsubscript{6}.H\textsubscript{2}O and obtaining ZnO crystallite.

A mechanism was presented by Jianzhong et al.,\textsuperscript{112} for the production of ZnO from zinc nitrate hexahydrate and sodium hydroxide in the presence of the sodium dodecyl sulfate (SDS) surfactant, according to reactions (37) to (41):

\[
\begin{align*}
Zn^{2+} + OH^- &\rightarrow Zn(OH)\textsuperscript{+} \quad (37) \\
Zn(OH)\textsuperscript{+} + OH^- &\rightarrow Zn(OH)\textsubscript{2} \quad (38) \\
Zn(OH)\textsubscript{2} + OH^- &\rightarrow Zn(OH)\textsubscript{3}^- \quad (39) \\
Zn(OH)\textsubscript{3}^- + OH^- &\rightarrow [Zn(OH)\textsubscript{4}]^{2-} \xrightarrow{MW} ZnO \\
&\quad + 2H\textsubscript{2}O + 2OH^- \quad (40) \\
Zn^{2+} + SDS &\rightarrow Zn(SDS)^{2+} \quad (41)
\end{align*}
\]

OH\textsuperscript{-} ions and SDS molecules are competing ligands for Zn\textsuperscript{2+}. In small amounts of OH\textsuperscript{-}, the ZnO nuclei are coated with huge amounts of SDS molecules which prevent their further growth, and can lead to the formation of sheet shaped morphology. However, by increasing the OH\textsuperscript{-} amounts, both OH\textsuperscript{-} and SDS are competitively adsorbed by ZnO nuclei. As a result, the competition between SDS inhibition and OH\textsuperscript{-} promotion toward growth, leads to the formation of the rod morphology. In greater quantities of OH\textsuperscript{-}, this ion plays the main role in the growth of the different crystallite faces. Due to the presence of large amounts of Zn(OH)\textsubscript{n} complex in comparison to Zn-(SDS)n, which cause faster growth in line with c-axis, the needle-like morphology is produced. Due to the faster dissolution of ZnO nuclei in the strong alkaline environment, it is necessary to increase the critical size of the nuclei. Therefore, as a result of the aggregation of needle-like ZnO for stability, the flower-shaped morphology is synthesized.

The microwave-assisted solvothermal ZnO production mechanism from zinc acetate dehydrate as precursor in ethanol is proposed by Zhao et al.,\textsuperscript{94} as reaction (42):

\[
\begin{align*}
Zn(CH\textsubscript{3}COO)\textsubscript{2} + 2CH\textsubscript{3}CH\textsubscript{2}OH &\xrightarrow{MW} ZnO \downarrow \\
&\quad + 2CH\textsubscript{3}COOCH\textsubscript{2}CH\textsubscript{3} \quad (42)
\end{align*}
\]

In this case, it seems that esterification process between zinc acetate and ethanol is accelerated as a result of microwave irradiation. The rapid esterification process between zinc acetate and ethanol, which is derived from the rapid microwave heating, leads to the rapid formation of ZnO particles, and the resulting ethyl acetate dissolves in ethanol. Continuous production of ethyl acetate because of its low boiling point compared to ethanol results in the formation of large bubbles of ethyl acetate which is associated with the attachment of ZnO nanoparticles in the gas-liquid interface. The diameter of hollow spheres can be controlled by adjusting the concentration of ethyl acetate.

### 3.2. Microwave-assisted sol-gel method

#### 3.2.1. Principles

The sol-gel process includes the conversion of the precursors to an inorganic solid which by dissolving the desired metal ions as an inorganic metal salt (chloride, nitrate, sulfate, perchlorate, etc.) in an aqueous solution, or dissolving an organic metal salt (acetate, acetyl acetate, etc.) in a suitable organic solvent, forms a liquid sol that is converted to a semi-rigid solid, called gel, in the next step. Thus, the sol and gel are defined as follows: Sol is the suspension and distribution of discrete colloidal particles in the solution, whereas Gel is a colloidal or polymeric solid that has a liquid component, but in regards to the internal network structure, the solid and liquid components are widely distributed. By converting the sol to gel, if the precursor is made of the aqueous solution of inorganic salt, the process includes the formation of solid species of the solution and the formation of oxide or hydroxide colloids as the result of setting pH or increasing temperature, which the resulting gel is known as colloidal gel. In comparison, if the precursor is a combination of organic salts and a solvent, the process includes performing chemical reactions of hydrolysis, condensation, and polymerization, and the obtained gel is called polymeric, where the controlling factors of all processes are different from one another. After the formation of the gel and coagulation to form solid particles, the solvent is removed by heating.\textsuperscript{179–181} Thus, sol-gels are either colloidal or polymeric systems.

There are many reports on the production of ZnO nanoparticles by sol-gel method with conventional heating. Some of the reports include spherical,\textsuperscript{80,182–186} nanorods,\textsuperscript{183,185,187–189} nanoflowers,\textsuperscript{188} nanowires,\textsuperscript{190,191} nanodisks\textsuperscript{190} and chain-like\textsuperscript{137} morphologies. In this method, similar to the hydrothermal method, there have been reports on the synthesis of nanoparticles on the surface. Gao et al.\textsuperscript{192} and Beiraghdar et al.\textsuperscript{193} performed synthesis of nanoparticles and Oh et al.\textsuperscript{194} performed the combinatory synthesis of spherical and rod-shaped nanoparticles by sol-gel on the ITO glass surface successfully.

In the synthesis of ZnO nanoparticles by sol-gel method, chemical reactions play fundamental role. Along the
formation of the inorganic nanoparticles, the primary organic species (solvent and precursor) undergo chemical reactions that affect the particle size, shape, surface, assembling properties, chemical composition in specific cases, and crystallite structure. The high sensitivity of the chemical reactions to microwave radiation leads to the combination of sol-gel method with microwave chemistry, and affect the formation of inorganic nanoparticles by influencing the chemical reactions. Speeding the chemical reactions up under microwave irradiation is due to the improvement and acceleration of the dissolution of the precursor, faster kinetics of esterification reaction, faster formation of monomers, faster nucleation, and accelerated crystallite growth. An example of the microwave-assisted synthesis of ZnO nanoparticles is reported by Baghbanzadeh et al., Bilecka et al., and Xu et al. (see Table 3).

3.2.2. Formation mechanism

Most reported reactions on forming of ZnO nanoparticles take place through the benzyl route. In this case, nucleophilic attack of the hydroxy functional groups of the benzyl alcohol, on one carbonyl group of the acetylacetone ligand or carboxyl group of acetate ligand takes place. Consequently, alcoholysis leads to the formation of benzyl acetate and acetone in its enolate form in the case of acetylacetone, and the formation of benzyle acetate in the case of acetate, in the coordination sphere of the zinc atom. In the next step, formation of hydroxy species takes place by the release of benzyl acetate, acetone and H+ ion from the coordinated water molecule. Zn-OH species form the monomer for nanoparticle formation. Then, by releasing water, Zn-O-Zn units build up. The steps involved in the formation of zinc oxide nanoparticles by the sol-gel method through benzyl route are shown in Figure 6. The mechanism by which ZnO nanoparticles are formed during microwave-assisted sol-gel method was proposed by Bilecka et al. The formation of inorganic nanoparticles in a solution contains two processes of nucleation and growth. Both nucleation and growth processes have an impact on particle size, size distribution, and morphology. Nucleation begins through the supersaturation in the solution, which this supersaturation in the sol-gel process is provided by performing the reaction and as a result, the possibility of the monomers condensation on the nanoparticles or dissolution of them is provided by performing the reactions. Generally, the ZnO nanoparticles can be formed by the dissolution of precursor, formation of monomers through the esterification reactions, nucleation and crystallite growth. Therefore, in the formation of nanoparticles from zinc acetate precursors and benzyl alcohol, the first stage is the dissolution of zinc acetate in benzyl alcohol. Spanhel et al. justified the nucleation and growth through two Ostwald ripening and aggregation models. However, the test results were only consistent with Ostwald ripening model. According to Ostwald ripening model, as soon as the smallest molecular clusters (that can be even single cells) are formed, they combine to form another stable set. In fact, the formation of larger particles happens as a result of the dissolution of smaller particles and adsorption of their molecules on the surface of other particles. Aggregation model is justified based on reactions (43) and (44) and Ostwald ripening model based on reactions (45) and (46).

$$m_{n}Zn^{2+} + n_{0}O^{2-} \rightarrow (ZnO)_{m_0} \quad (43)$$

$$ZnO_{m_0} + (ZnO)_{m_0} \rightarrow (ZnO)_{2m_0} \quad (44)$$

$$ZnO_{m_0} \rightarrow (ZnO)_{m_0}+ Zn^{2+} + O^{2-} \quad (45)$$

$$Zn^{2+} + O^{2-} + (ZnO)_{m+n} \rightarrow (ZnO)_{m+n+1} \quad (46)$$

In the aggregation model, (ZnO)m0 clusters formed by reaction (43), in turn form the larger (ZnO)2m0 clusters due to the aggregation based on reaction (44). In comparison, in the Ostwald ripening model, the fine particles of the cluster formed by reaction (45) are dissolved, and the dissolved particles are adsorbed on the other clusters, and form the greater (ZnO)m+n+1 clusters through reaction (46).

3.3. Microwave-assisted combustion method

3.3.1. Principles

Synthesis by combustion method is a promising technique for the synthesis of high-temperature ceramics. The main advantage of this technique could be associated with the inherent characteristics of energy saving in this method because a large amount of energy required for the synthesis is obtained from carrying out the reaction itself. In this method, the exothermic reaction produces a powder. Depending on the nature of the reactants (solid, liquid or

<table>
<thead>
<tr>
<th>Table 3. The conditions of microwave-assisted sol-gel synthesis of ZnO nanoparticles.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Precursors</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Zinc acetylacetone hydrate; benzyl alcohol.</td>
</tr>
<tr>
<td>Zinc acetate; benzyl alcohol.</td>
</tr>
<tr>
<td>Zinc acetate dehydrate; lithium hydroxide; ethanol.</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
gas) and exothermal nature, synthesis by combustion method is divided into self-propagation high-temperature synthesis (SHS), low-temperature combustion synthesis (LCS), solution combustion synthesis (SCS), gel combustion, synthesis by sol-gel combustion (SSGC), emulsion combustion, and volume combustion synthesis (VCS). It is clear that SHS is more suitable in terms of energy savings. In this method, immediately after the ignition of exothermic reaction mixture by an external heat source (hot plate, microwave radiation and electric heating) a wave of rapid response with high temperature (0.1–10 cm/s and the temperature 1000–3000°C) is released in the reaction mixture. This wave, in turn, leads to the formation of the product without any additional energy consumption. In VCS method, all specimens are heated uniformly until the reaction is ignited in the entire volume. In the solution combustion synthesis (SCS), combustion occurs in a solution consisting of oxygen-containing species and fuel. Here, the condition for the rapid high-temperature reaction is provided by decomposition of oxygen-containing species. In this case, the solution also needs to be preheated. After heating up to 150–200°C, it is ignited spontaneously in the entire volume of the solution. It should be noted that in this mode, the ignition can occur locally as layered propagation or spontaneously in the entire of the volume. In this method, since the initial reaction takes place in a solution, there is the possibility of mixing the reactants at the molecular level. Therefore, it provides the precise and uniform composition of the nanoparticles. A high reaction temperature (>900°C) results in high purity and crystallization. Therefore, it makes the production of pure product, independent of the calcination stage. Short time of the reaction and the formation of various gasses during the SCS process prevent the growth of particles and leads to the production of particles with high specific surface area. In the synthesis by sol-gel combustion (SSGC) method, the solution containing oxygen and fuel is dried to form the quasi sol-gel medium. Finally, as the result of heating, the local ignition starts, and the product is produced as the process continues. After evaporation of the water and creating viscose sol-gel medium, the temperature increases quickly until reaching ignition temperature.

As mentioned in the combustion synthesis, the precursor is made of two components of the oxidizer and fuel. In some reported cases, the Banyan tree (BT) and Euphorbia Tirucalli (ET) Latexes plant, Citric acid, beetroot juice, pigeon pea, (Buchanania Lanza) leaves Chironji, fruit Artocarpus Gomezianusc, Xanthochymus Garcinia fruit, neem (Azadirachta indica) extract, Oxalyl di-hydrazide (ODH), L-Valine, L-Glutamine and Leucine, Tapioca starch pearls, acetic acid, glycine, Cassia fistula plant leaf extract, dextrose, urea, Nital solution (ethanol + nitric acid), glycine and
urea mix$^{211}$ are used as fuel for nanoparticles synthesis. Zinc nitrate plays two different roles in this procedure: as the source of zinc, and oxidizer. Given the dual role of zinc nitrate both in terms of oxidation capability and as the source of zinc, it is the most common oxidizer, and so in this case only the fuel is required. However, in some cases, the use of nitric acid$^{222}$ as an oxidizing agent is reported where in addition to the fuel, a third material such as zinc acetate is required as the source of zinc. In the case of fuel, urea and glycine are mainly used.

The ZnO particles synthesized by combustion method showed sponge-like,$^{206}$ spherical,$^{213,216,222}$ mushroom-like disks,$^{212}$ bullets,$^{212}$ buds,$^{212}$ cones,$^{212}$ bundles,$^{212}$ closed pine cone,$^{212}$ rose-like,$^{202}$ corncobs,$^{220}$ spongy cave-like,$^{211}$ bird nest,$^{222}$ nanocube,$^{222}$ and hexagonal-shaped$^{223}$ morphologies.

Microwave radiation, and its combination with combustion, is greatly focused upon because of its cheap, clean, safe, and short-term synthesis conditions with high yield. In microwave-assisted combustion synthesis, due to the mutual effect of matter and microwave, energy heats the matter at the molecular level and results in uniform heating of the material from the inside to the surface. Therefore, the heat distribution within the solution, and its transfer to the soluble substances, causes severe explosive reaction which results in the release of gasses and the formation of the nanostructure. Given that fact, this method of heating is capable of heating the solution in a matter of minutes therefore, the produced particles are smaller. It also has advantages such as simplicity of the process, creating uniform composition, low cost, energy saving, high product purity, and non-toxic products.$^{224}$ Reports based on microwave-assisted ZnO combustion synthesis method are cited in Table 4. The formation stages of zinc oxide nanoparticles in the combustion method are presented in Figure 7.

### 3.3.2. Formation mechanisms

A three-dimensional structure formation mechanism is proposed in microwave-assisted combustion synthesis method using zinc nitrate and urea by Cao et al.$^{100}$ based on reactions (47) and (48):

\[
\begin{align*}
CH_4N_2O + 2H_2O &\rightarrow (CH_2N_2O)_2^{2+} + 2OH^- \quad (47) \\
Zn^{2+} + 2OH^- &\leftrightarrow Zn(OH)_2 \leftrightarrow [Zn(OH)_4]^{2-} \\
&\rightarrow ZnO + H_2O \quad (48)
\end{align*}
\]

This three-dimensional structure formation includes nucleation and growth. Urea provides the grounds for nucleation and growth by adjusting the basicity and pH values within the precursor solution. As a result of the hydrolysis of urea based on reaction (47), OH$^-$ ions which play the vital role in nucleation are produced. ZnO is nucleated from [Zn(OH)$_4$]$^{2-}$ solution (Reaction 48) and with the aggregation of multiple nuclei, provides the possibility of ZnO nanostructure developing along the [0001] direction, which is the preferred direction for growth of ZnO.

Also, Manikandan et al.$^{102}$ justified nanoflakes formation mechanism by zinc nitrate and glycine in accordance with reaction (49):

\[
Zn(NO_3)_2 + 2C_2H_3NO_2 + 4O_2 \rightarrow ZnO + 5H_2O \\
+ 4CO_2 + N_2 + 2NO_2
\]  

However, the synthesis with the same conditions by combustion method with conventional heating leads to the formation of the agglomerated nanoparticles. The explanation for this behavior might be the extended reaction time and the possibility of particles’ sintering.

### 3.4. Other wet chemical microwave-assisted processes

#### 3.4.1. Principles

Details of other reports based on the ZnO synthesis with different solution methods are presented in Tables 5–7, and the mechanisms of nanoparticles produced under these conditions are investigated in the following sections. These proposed routes are different from hydrothermal and solvothermal methods. In hydrothermal and solvothermal procedures, reactions take place in a closed system which causes the pressure to increase, whereas the proposed solution routes take place under atmospheric pressure. Among these mechanisms, methods such as chemical deposition,$^{222}$ microwave radiation to wet mechanical powder of precursors,$^{84}$ and use of zinc scrap powder$^{229}$ and zinc sulfate heptahydrate$^{230}$ as the zinc sources are noticed. Through these methods, the simple morphologies such as nanorods,$^{36,97,104,106,231–235}$ spherical-like,$^{84,97,105,113,236–238}$ star-like,$^{105}$ flower-like,$^{72,97,105,113,235,239–242}$ peanut-like,$^{243}$ spinnous,$^{243}$ nanocubes,$^{234}$ needle-like,$^{72,106,237}$ leaf-like,$^{237}$ rice-like,$^{113}$ micro belts,$^{84}$ microtubes,$^{84}$ multi-linked,$^{244,245}$ wire,$^{246,247}$ dumbbell-shaped,$^{248}$ narcis-like,$^{249}$ straw bundle-like,$^{64}$ wide chrysanthemum-like$^{64}$, oat aristalike$^{64}$ nanosheet,$^{250,251}$ star-like$^{106,240}$ nanoflake$^{235}$ nanocandle,$^{106}$ nanodisc,$^{106}$ nanonut,$^{106}$ Ufo$^{106}$ and complex morphologies such as nanocake$^{106}$ and jellyfish$^{106}$ morphologies obtained by the reusing of nanoparticles in synthesis process.
<table>
<thead>
<tr>
<th>Precursors</th>
<th>Post treatments</th>
<th>Power</th>
<th>Holding time</th>
<th>pH Other effective parameters</th>
<th>Morphology &amp; size</th>
<th>Schematics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>zinc nitrate hexahydrate; urea.</td>
<td></td>
<td>800 W</td>
<td>20 min</td>
<td>nanoplatelets consisted of nanoparticles (20–40 nm)</td>
<td></td>
<td><img src="image" alt="schematics" /></td>
<td>224</td>
</tr>
<tr>
<td>zinc nitrate hexahydrate; urea.</td>
<td></td>
<td>170, 340, 680 W</td>
<td></td>
<td>flower-like (D: 2–5 μm)</td>
<td></td>
<td><img src="image" alt="schematics" /></td>
<td>100</td>
</tr>
<tr>
<td>zinc nitrate hexahydrate; urea.</td>
<td></td>
<td>340 W</td>
<td></td>
<td>flower-like nanostructures, agglomerated flakes, block-shaped particles (D: 100–300 nm)</td>
<td></td>
<td><img src="image" alt="schematics" /></td>
<td></td>
</tr>
<tr>
<td>zinc nitrate hexahydrate, glycine.</td>
<td></td>
<td>80%</td>
<td>2 min</td>
<td>nearly spherical (D: 20–25 nm) with a bit aggregation and with voids on the surface of particles</td>
<td></td>
<td><img src="image" alt="schematics" /></td>
<td>101</td>
</tr>
<tr>
<td>zinc nitrate hexahydrate, glycine; water.</td>
<td></td>
<td>750 W</td>
<td>10 min</td>
<td>nanoflakes (D: 16–21 nm)</td>
<td></td>
<td><img src="image" alt="schematics" /></td>
<td>102</td>
</tr>
<tr>
<td>zinc nitrate hexahydrate, urea; water.</td>
<td></td>
<td>700 W</td>
<td>10 min</td>
<td>spherical-shaped (10 nm)</td>
<td></td>
<td><img src="image" alt="schematics" /></td>
<td>225</td>
</tr>
<tr>
<td>zinc nitrate hexahydrate, ammonia; citric acid.</td>
<td>Calcination: 800°C, 2 h</td>
<td>900 W</td>
<td>10 min</td>
<td>nanorods</td>
<td></td>
<td><img src="image" alt="schematics" /></td>
<td>226</td>
</tr>
<tr>
<td>zinc nitrate hexahydrate, ethylene glycol (EG).</td>
<td></td>
<td>30 s</td>
<td></td>
<td>foamy structure (pore size: 2 μm)</td>
<td></td>
<td><img src="image" alt="schematics" /></td>
<td>227</td>
</tr>
</tbody>
</table>


3.4.2. Formation mechanisms

Bhatte et al.\textsuperscript{103} reported a mechanism for the formation of ZnO from zinc acetate and solvent 1–3, propane diol according to reaction (50):

\[
\begin{align*}
\text{H}_3\text{C} - \text{OC} - \text{O} - \text{Zn} - \text{O} - \text{CO} - \text{CH}_3 \\
+ \text{HO} - \text{H}_2\text{C} - \text{CH}_2 - \text{CH}_2 - \text{OH} \\
\rightarrow \text{H}_{3}\text{C} - \text{OC} - \text{O} - \text{H}_2\text{C} - \text{CH}_2 - \text{CH}_2 - \text{O} \\
- \text{CO} - \text{CH}_3 + \text{HO} - \text{Zn} - \text{OH} \rightarrow \text{ZnO}
\end{align*}
\]

(50)

By applying microwave heating, OH group of 1–3, propane diol reacts with an acetate ligand and produces zinc hydroxide and propyl ester. Consequently, as a result of zinc hydroxide dehydration under microwave irradiation, ZnO nanoparticles are produced.

The formation mechanism using zinc chloride and sodium hydroxide is proposed by Al-Gaashani et al.\textsuperscript{237} and Li et al.\textsuperscript{109} according to reactions (51) to (57):

\[
\begin{align*}
\text{ZnCl}_2 + 2\text{NaOH} & \rightarrow \text{Zn(OH)}_2 \downarrow + 2\text{NaCl} \quad (51) \\
\text{Zn(OH)}_2 \downarrow + 2\text{H}_2\text{O} & \rightarrow \text{Zn}^{2+} + 2\text{OH}^- + 2\text{H}_2\text{O} \quad (52) \\
\text{Zn(OH)}_2 \downarrow + 2\text{OH}^- & \rightarrow [\text{Zn(OH)}_4]^{2-} \\
\text{OH}^- + \text{OH}^- & \text{MW} \rightarrow \text{O}^2- + \text{H}_2\text{O} \quad (54) \\
\alpha = 0; \quad \text{Zn(OH)}_2 + 2\text{H}_2\text{O} & \rightarrow \text{Zn}^{2+} + 2\text{OH}^- + 2\text{H}_2\text{O} \quad (55) \\
+ 2\text{H}_2\text{O} & \rightarrow [\text{Zn(OH)}_4]^{2-} \\
\text{Zn}_2\text{O(OH)}_6^{4-} + [\text{Zn(OH)}_4]^{2-} & \rightarrow [\text{Zn}_3\text{O}_2\text{(OH)}_6]^{6-} + \text{H}_2\text{O} \quad (56) \\
\text{Zn}_2\text{O(OH)}_6^{4-} + [\text{Zn(OH)}_4]^{2-} & \rightarrow [\text{Zn}_3\text{O}_2\text{(OH)}_6]^{6-} + \text{H}_2\text{O} \quad (57)
\end{align*}
\]
### Table 5. Conditions of solution route synthesis of ZnO nanoparticles using microwave from zinc nitrate precursor.

<table>
<thead>
<tr>
<th>Precurors</th>
<th>Post treatments</th>
<th>Power Holding time</th>
<th>Temperature pH</th>
<th>Other effective parameters</th>
<th>Morphology &amp; size</th>
<th>schematics</th>
<th>crystallographic properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc nitrate, ammonia;</td>
<td>water; polyvinyl</td>
<td>10 min</td>
<td>8</td>
<td></td>
<td>star-like (D: 19 nm)</td>
<td><img src="image1" alt="schematics" /></td>
<td>lattice constants: $a = b = 3.24$ $\text{Å}$, $c = 5.21$ $\text{Å}$</td>
<td>103</td>
</tr>
<tr>
<td>Pyrrolidone (PVP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate, hydrazine hydrate;</td>
<td>water</td>
<td>10 min</td>
<td>8</td>
<td></td>
<td>flower-like (D: 18 nm)</td>
<td><img src="image2" alt="schematics" /></td>
<td>lattice constants: $a = b = 3.24$ $\text{Å}$, $c = 5.21$ $\text{Å}$</td>
<td>105</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet mechanical mixture of</td>
<td></td>
<td>650 W</td>
<td></td>
<td></td>
<td>microbelts and microtubes (~ 0.5–10 μm)</td>
<td><img src="image3" alt="schematics" /></td>
<td></td>
<td>84</td>
</tr>
<tr>
<td>Zinc nitrate, sodium chloride</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate hexahydrate,</td>
<td>Reducing agent: pyridine</td>
<td>10 min</td>
<td>90°C</td>
<td>Concentration: 0.5, 1, 5, 10 mL</td>
<td>hexagonal nanoring (inner D: 130 nm, outer D: 250 nm), hollow structures, multi-linkedd chips</td>
<td><img src="image4" alt="schematics" /></td>
<td></td>
<td>244</td>
</tr>
<tr>
<td>Pyridine or aniline or triethanolamine; water.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate hexahydrate,</td>
<td>Reducing agent: pyridine</td>
<td>10 min</td>
<td>90°C</td>
<td></td>
<td>single hexagonal columns</td>
<td><img src="image5" alt="schematics" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium hydroxide; water.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate hexahydrate,</td>
<td>Reducing agent: aniline</td>
<td>10 min</td>
<td>90°C</td>
<td></td>
<td>nanosheets consist of nanoparticles</td>
<td><img src="image6" alt="schematics" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrazine hydrate or ammonia;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate hexahydrate,</td>
<td></td>
<td>4 h</td>
<td>120°C</td>
<td>12</td>
<td>wire-like (D: 80 nm, L: up to tens of micrometers)</td>
<td><img src="image7" alt="schematics" /></td>
<td>lattice constants: $a = 3.248$ $\text{Å}$, $c = 5.208$ $\text{Å}$</td>
<td>246</td>
</tr>
<tr>
<td>Sodium hydroxide; water.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate hexahydrate,</td>
<td>Reducing agent: hydrazine</td>
<td>10 min</td>
<td>8</td>
<td></td>
<td>flower-like structures consist of sharp nanorods as petals, spherical</td>
<td><img src="image8" alt="schematics" /></td>
<td>lattice constants: $a = b = 3.241$ $\text{Å}$, $c = 5.213$ $\text{Å}$</td>
<td>240</td>
</tr>
<tr>
<td>Hydrazine hydrate or ammonia;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate, ammonia;</td>
<td></td>
<td>1 kW</td>
<td>10 min</td>
<td>8</td>
<td>star-like structures (D: 0.5–15 μm)</td>
<td><img src="image9" alt="schematics" /></td>
<td>lattice constants: $a = 3.2532(4)$ $\text{Å}$, $c = 5.2037(3)$ $\text{Å}$</td>
<td>252</td>
</tr>
<tr>
<td>Water; polyvinyl pyrrolidone (PVP).</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc nitrate hexahydrate,</td>
<td></td>
<td>900 W 1, 3, 5 s (30s</td>
<td>13</td>
<td></td>
<td>(1, 3 s) microspheres consist of less amount of nanoplates, microsphere consist of more amount of nanoplates (t: ~20 nm)</td>
<td><img src="image10" alt="schematics" /></td>
<td></td>
<td>253</td>
</tr>
<tr>
<td>Sodium hydroxide; water.</td>
<td></td>
<td>on-off)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*References:*

103, 105, 84, 244, 246, 240, 252, 253
Table 6. Conditions of solution route synthesis of ZnO nanoparticles using microwave from zinc acetate precursor.

<table>
<thead>
<tr>
<th>Preursors</th>
<th>Post treatments</th>
<th>Power</th>
<th>Holding time</th>
<th>Temperature</th>
<th>Other effective parameters</th>
<th>Morphology &amp; size</th>
<th>schematics</th>
<th>crystallographic properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>zinc acetate dehydrate, sodium carbonate; polyethylene glycol (PEG400).</td>
<td></td>
<td>700 W</td>
<td>10 min</td>
<td></td>
<td></td>
<td>nanorod (D: 10–25 nm, L: 60–200 nm)</td>
<td></td>
<td></td>
<td>104</td>
</tr>
<tr>
<td>zinc acetate dehydrate, sodium hydroxide; 2-propanol.</td>
<td>Calcinations:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>236</td>
</tr>
<tr>
<td>zinc acetate dehydrate; ethylene glycol/ water.</td>
<td>1000, 800 W</td>
<td>10 h</td>
<td>100°C</td>
<td></td>
<td></td>
<td>peanut-like (L: 2.0–2.2 µm) consist of nanorods, multi-sphere aggregation (~2.5 µm) which consist of half microspheres (D: 1 µm) which consist of nanorod or nanoparticle aggregation (L: 300 nm)</td>
<td></td>
<td></td>
<td>243</td>
</tr>
<tr>
<td>zinc acetate dehydrate, potassium hydroxide; water.</td>
<td></td>
<td>800 W</td>
<td>3 min</td>
<td></td>
<td></td>
<td>nanorod (D: ~ 30–80 nm, L: ~ 1.5–3 µm)</td>
<td></td>
<td></td>
<td>233</td>
</tr>
<tr>
<td>zinc acetate dehydrate, ammonium hydroxide; water.</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td>239</td>
</tr>
<tr>
<td>zinc acetate dehydrate, sodium hydroxide; methanol; triethanolamine (TEA).</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>239</td>
</tr>
<tr>
<td>zinc acetate, ammonia; 1,4-butanediol.</td>
<td></td>
<td>200 W</td>
<td>2 min (30 s on – 30 s off)</td>
<td></td>
<td></td>
<td>polygonal shape (59 nm)</td>
<td></td>
<td></td>
<td>254</td>
</tr>
<tr>
<td>zinc acetate dehydrate, ammonium hydroxide; water.</td>
<td>Calcination:</td>
<td>400 W</td>
<td>5 min followed by 250 W for 10 min</td>
<td></td>
<td></td>
<td>dumbbell-shaped structures (D: 2 µm, L: 5 µm) consist of nanoparticles (100 nm)</td>
<td></td>
<td></td>
<td>248</td>
</tr>
</tbody>
</table>

(Continued on next page)
<table>
<thead>
<tr>
<th>Precursors</th>
<th>Post treatments</th>
<th>Power</th>
<th>Holding time</th>
<th>Temperature pH</th>
<th>Other effective parameters</th>
<th>Morphology &amp; size schematics</th>
<th>crystallographic properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>zinc acetate dehydrate,</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>ammonium hydroxide;</td>
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<tr>
<td>water.</td>
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<tr>
<td></td>
<td></td>
<td>90 s</td>
<td>9</td>
<td></td>
<td></td>
<td>narcis-like structures (D: 1–2.5 µm)</td>
<td>lattice constants: $a = 3.248 \text{ Å}$, $c = 5.206 \text{ Å}$</td>
<td></td>
</tr>
<tr>
<td>zinc acetate dehydrate,</td>
<td></td>
<td>900 W</td>
<td>150 s</td>
<td>9.5</td>
<td></td>
<td>wires with sword-like tips (D: 80–250 nm, L: 1–4 µm)</td>
<td></td>
<td>247</td>
</tr>
<tr>
<td>sodium hydroxide;</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>methanol, water; triethanolamine (TEA).</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Annealing: 400°C, 1 h, air</td>
<td></td>
<td>180 W</td>
<td>15 min</td>
<td>120°C</td>
<td></td>
<td>flower-like clusters consist of nanorods (D: 150–190 nm, sharp tips L: ~ 2 µm)</td>
<td>lattice constants: $a = 3.254 \text{ Å}$, $c = 5.197 \text{ Å}$</td>
<td>241</td>
</tr>
<tr>
<td>zinc acetate dehydrate,</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>potassium hydroxide;</td>
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<td></td>
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<tr>
<td>water.</td>
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<tr>
<td></td>
<td></td>
<td>10.3</td>
<td>85 s</td>
<td>85°C</td>
<td>10.3 Zn²⁺ Conc.: 0.025, 0.05, 0.12, 0.2 mole/L</td>
<td>spherical (2–8 µm), more rhombic type (5–6 µm) with very few flower type, rhombic (9 µm) and flowers (4 µm), flowers (3 µm) and lumps</td>
<td></td>
<td>228</td>
</tr>
<tr>
<td>zinc acetate dehydrate,</td>
<td></td>
<td>85 s</td>
<td></td>
<td></td>
<td></td>
<td>flowers (3–4 µm), flowers (1–2 µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ammonium hydroxide;</td>
<td></td>
<td></td>
<td></td>
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<td>waterpH adjusting agent:</td>
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<tr>
<td>sodium hydroxide.</td>
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<tr>
<td>Cooling: cooling in a water</td>
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<tr>
<td>bath, °C, 45 min</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Zn²⁺ Conc.: 0.087, 0.12 mole/L</td>
<td>rhombic (9 µm) and flowers (4 µm), rhombic (2–3 µm), sphere (2–3 µm) and lumps (10 µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>zinc acetate dehydrate,</td>
<td></td>
<td>10.3, 10.5, 11</td>
<td>85 s</td>
<td>85°C</td>
<td>10.3, 10.5, 11 Zn²⁺ Conc.: 0.12 mole/L</td>
<td>rhombic (9 µm) and flowers (4 µm), rhombic (2–3 µm), sphere (2–3 µm) and lumps (10 µm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7. Conditions of solution route synthesis of ZnO nanoparticles using microwave from other precursors.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Holding time</th>
<th>Power</th>
<th>Temperature</th>
<th>pH</th>
<th>Other effective parameters</th>
<th>Morphology &amp; size</th>
<th>schematics</th>
<th>crystallographic properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>zinc chloride, sodium hydroxide; water.</td>
<td>5 min</td>
<td>150, 450, 700, 1000 W</td>
<td>13.75</td>
<td></td>
<td></td>
<td>single shape nanoparticles (17 nm), spherical, needle-like, leaf-like (32 nm at 1000 W)</td>
<td></td>
<td></td>
<td>217</td>
</tr>
<tr>
<td>zinc sulfate, sodium hydroxide.</td>
<td>5 min</td>
<td>150°C</td>
<td>9</td>
<td></td>
<td></td>
<td>Nanosheet</td>
<td></td>
<td></td>
<td>250</td>
</tr>
<tr>
<td>Zn-dust powder (waste which has derived from hot dip galvanizing plant)</td>
<td>20 min</td>
<td>12</td>
<td>PEG amount: 0.25%</td>
<td></td>
<td></td>
<td>plate and rod-like BET: 21 m²/g</td>
<td></td>
<td></td>
<td>229</td>
</tr>
<tr>
<td>dissolved in nitric acid and filtered, sodium hydroxide; polyethylene glycol (PEG2000).</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>zinc chloride dehydrate, sodium hydroxide; water; gemini cationic surfactant (12–3-12, 2Br⁻).</td>
<td>5 h, 5 h, 10 h</td>
<td>300 W 100°C</td>
<td></td>
<td></td>
<td></td>
<td>flower-like consist of nanosheets</td>
<td></td>
<td></td>
<td>242</td>
</tr>
<tr>
<td></td>
<td>5 h</td>
<td>300 W 100, 140°C</td>
<td></td>
<td></td>
<td></td>
<td>flower-like</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 h</td>
<td>300, 400 W 100°C</td>
<td></td>
<td></td>
<td></td>
<td>flower-like, sphere and rod-like</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Continued on next page)
<table>
<thead>
<tr>
<th>Precursors</th>
<th>Holding time</th>
<th>Power</th>
<th>Temperature</th>
<th>pH</th>
<th>Other effective parameters</th>
<th>Morphology &amp; size</th>
<th>Schematics</th>
<th>Crystallographic properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>zinc oxide, graphite powder.</td>
<td>2 min</td>
<td>800 W</td>
<td></td>
<td></td>
<td></td>
<td>nanosheets (W: several to several tens of micrometers, t: 20–80 nm, L: several tens of micrometers or even millimeters, width/thickness ratio: &gt; 1000), raft-like</td>
<td></td>
<td>lattice constants: a = 0.325 nm, c = 0.521 nm</td>
<td>251</td>
</tr>
<tr>
<td>zinc chloride, ammonia; water.</td>
<td>20 min</td>
<td>240 W</td>
<td></td>
<td>7</td>
<td></td>
<td>flower-like (D: 5 µm) consist of nanorods</td>
<td></td>
<td>lattice constants: a = 0.3249 nm, c = 0.5206 nm</td>
<td>114</td>
</tr>
<tr>
<td>zinc oximate or zinc acetylacetonate monohydrate; alkoxyethanol (methoxyethanol, ethoxyethanol, or n-butoxyethanol)</td>
<td>4 min</td>
<td>800 W</td>
<td></td>
<td></td>
<td>precursor: zinc oximate, spherical, mandrel or pyramidal shape</td>
<td>zinc acetylacetonate monohydrate</td>
<td></td>
<td></td>
<td>255</td>
</tr>
</tbody>
</table>
\[ \text{[Zn}_{x-1}O_y(OH)_{z-2}]^{(2-n)-} + [\text{Zn(OH)}_4]^{2-} \rightarrow \text{Zn}_x\text{O}_y\text{(OH)}_z{n} = (z+2y-2x) - + \text{H}_2\text{O} \] (58)

\[ \text{Zn}^{2+} + \text{O}^{2-} \rightarrow \text{ZnO} \] (59)

Before the microwave irradiation, while the precursor solution (PS) is being formed through reaction (51), Zn(OH)$_2$ is precipitated and dissolved (reaction 52). Next, after stirring, [Zn(OH)$_4$]$^{2-}$ is formed as a result of reaction (53), and acts as the growth unit. Due to microwave irradiation and because of the more extensive dissolution of Zn(OH)$_2$ in the solution based on reaction (52) in addition to formation of more OH$^-$ ions, reaction (54) takes place. Moreover, due to the penetration and the irregular movement of these ions, greater supersaturated condition is obtained. As a result of reaction (55) and the formation of [Zn(H$_2$O)$_{\alpha}(OH)_4$]$^{\alpha-2}$ complexes (in strong alkaline medium $\alpha = 0$), the growth units of nanoparticles are provided. Next, as a result of the aggregation and their reaction, the Zn$_{xO}_y$ (OH)$_z$$_n = (z+2y-2x)-$ clusters are formed based on the reaction (56) and (57). In order to form the first ZnO nuclei in the solution, the size of these clusters must reach their critical value. Therefore, depending on the conditions of solution, this reaction continues until the critical size is reached based on reaction (58). Considering the existence of O$^{2-}$ species obtained by reaction (54) and the presence of Zn$^{2+}$ in the solution, another reaction takes place (reaction 59). However, because of the strong alkaline conditions and the probable formation of [Zn(OH)$_4$]$^{2-}$ complexes, its likelihood is lowered.

The formation mechanism of ZnO from the zinc acetate and butanol/water solvent in the presence of triethanolamine (TEA) was proposed by Kajbafvala et al. using reactions (60) to (67):

\[
\text{[N(CH}_2\text{CH}_2\text{OH)}_3] + C_4\text{H}_10\text{O} + \text{H}_2\text{O} 
\rightarrow N - (\text{CH}_2\text{CH}_2\text{OH})_3 - C_4\text{H}_10\text{O} \] (60)

\[
N - (\text{CH}_2\text{CH}_2\text{OH})_3 - C_4\text{H}_10\text{O} + \text{Zn(CH}_3\text{COO)}_2\_2\text{H}_2\text{O} 
\rightarrow N - (\text{CH}_2\text{CH}_2\text{OH})_3 - C_4\text{H}_10\text{O} - (\text{OOCCCH}_3)\_2\text{Zn} 
+ \text{H}_2\text{O} \] (61)

\[
\text{Zn}^{2+} - \text{R} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 \downarrow + 2\text{H}^+ \] (62)

\[
\text{Zn}^{2+} - \text{R} + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2 \downarrow \] (63)

\[
\text{Zn(OH)}_2 \rightarrow \text{Zn}^{2+} + 2\text{OH}^- \] (64)

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} \] (65)

\[
\text{Zn(OH)}_2 + 2\text{NaOH} \xrightarrow{\text{MW}} [\text{Zn(OH)}_4]^{2-} \] (66)

\[
[\text{Zn(OH)}_4]^{2-} \rightarrow \text{ZnO} + 2\text{H}_2\text{O} + 2\text{OH}^- \] (67)

In the PS preparing step, TEA-butanol complex is formed as a result of TEA dissolution in butanol/water (reaction 60). Accordingly, by adding zinc acetate dehydrate, a new complex is formed as Zn$^{2+}-\text{R}$ (reaction 61) which forms Zn(OH)$_2$ colloid through reaction with water molecules (reaction 62). As a result of adding sodium hydroxide according to reaction (63), more Zn(OH)$_2$ is produced which dissolves according to reaction (64). By reaching the supersaturation situation, ZnO nucleation in solution takes place (reaction 65). As a result of microwave irradiation, and the reaction between Zn(OH)$_2$ and OH$^-$ (reaction 66), the [Zn(OH)$_4$]$^{2-}$ growth units are obtained. Here, reaction (67) leads to the growth of the particles as a result of reactions with ZnO nuclei.

The formation mechanism of rough microtubes was reported by Jiang et al. using reactions (68) to (70):

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \] (68)

\[
\text{Zn}^{2+} + 2\text{NH}_4^+ \rightarrow [\text{Zn(NH)}_4]^{2+} \] (69)

\[
[\text{Zn(NH)}_4]^{2+} + \text{OH}^- \xrightarrow{\text{MW}} \text{ZnO} + 2\text{NH}_4^+ + \text{H}_2\text{O} \] (70)

At first, the ammonia solution produces NH$_4^+$ and OH$^-$ based on reaction (68) and then in addition to adjusting the pH by adding precursor to it, the [Zn(NH)$_4$]$^{2+}$ growth unit is formed based on reaction (69). It is reported that ammonium (NH$_4^+$) may be adsorbed by ZnO nuclei and affect the growth direction of crystallites.

The formation of ZnO structures from the Hexamethylenetetramine (HMT) and ammonia solution alkaline agents is reported by Cho et al. using reactions (71) to (78):

\[
(\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 4\text{NH}_3 + 6\text{HCHO} \] (71)

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \] (72)

\[
\text{Zn}^{2+} + \text{OH}^- \xrightarrow{\text{MW}} \text{ZnO} + \text{H}_2\text{O} \] (73)

In the case that HMT is applied as the alkaline agent, [Zn(OH)$_4$]$^{2-}$ is unable to be formed due to its weak acid conditions (pH~ 6), and requirement of strong alkaline medium for the formation of [Zn(OH)$_4$]$^{2-}$. In addition, despite the production
of ammonium as a result of HMT hydrolysis (reaction 71), \([\text{Zn(OH)}_4]^{2-}\) is rarely formed in acidic conditions and the amount of growth units is low.

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \quad (74)
\]

\[
\text{Zn}^{2+} + 4\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-} \quad (75)
\]

\[
\text{Zn}^{2+} + 4\text{NH}_3 \rightarrow [\text{Zn(NH}_3)_4]^{2+} \quad (76)
\]

\[
[Zn(OH)_4]^{2-} \xrightarrow{\text{MW}} \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (77)
\]

\[
[Zn(NH_3)_4]^{2+} + 2\text{OH}^- \rightarrow \text{ZnO} + 4\text{NH}_3 + \text{H}_2\text{O} \quad (78)
\]

Nevertheless, when ammonia solution is used as alkaline agent, \([\text{Zn(OH)}_4]^{2-}\) is easily formed via reaction (75) and acts as the growth unit. It is also proposed that \([\text{Zn(NH}_3)_4]^{2+}\) complexes are produced as growth units through reaction (76).

Liu et al.\(^{114}\) proposed the following mechanism (reactions (79) to (84)) when the ammonia solution is used as an alkaline agent:

\[
\text{NH}_3\cdot\text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad (79)
\]

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \downarrow \quad (80)
\]

\[
\text{Zn}^{2+} + 4\text{NH}_3 \rightarrow [\text{Zn(NH}_3)_4]^{2+} \quad (81)
\]

\[
[Zn(NH_3)_4]^{2+} + 2\text{OH}^- \quad (82)
\]

\[
\leftrightarrow \text{Zn(OH)}_2 + 4\text{NH}_3 + \text{H}_2\text{O} \quad (82)
\]

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-} \quad (83)
\]

\[
[Zn(OH)_4]^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (84)
\]

Based on this mechanism, \([\text{Zn(OH)}_4]^{2-}\) is produced by reaction (82). Also, \([\text{Zn(NH}_3)_4]^{2+}\) complexes might be generated by reaction (81), and participate in the production of \(\text{Zn(OH)}_2\).

The formation mechanism of \(\text{ZnO}\), and the effect of sodium hydroxide is reported by Chaudhuri et al.\(^{228}\) as reactions (85) to (92):

\[
\text{Zn(CH}_3\text{COO)}_2 + 2\text{NH}_4\text{OH} \rightarrow \text{Zn(OH)}_2 + 2\text{NH}_4(\text{CH}_3\text{COO}) \quad (85)
\]

\[
\text{Zn(OH)}_2 + 4\text{NH}_4\text{OH} \rightarrow \text{Zn(NH}_3)_4(\text{OH})_2 + 4\text{H}_2\text{O} \quad (86)
\]

\[
\text{Zn(CH}_3\text{COO)}_2 + 6\text{NH}_4\text{OH} \rightarrow \text{Zn(NH}_3)_4(\text{OH})_2 + 2\text{NH}_4(\text{CH}_3\text{COO}) + 4\text{H}_2\text{O} \quad (87)
\]

\[
\text{Zn(NH}_3)_4(\text{OH})_2 \rightarrow [\text{Zn(NH)}_4]^{2+} + 2\text{OH}^- \quad (88)
\]

\[
[Zn(NH)_4]^{2+} + 2\text{OH}^- \xrightarrow{\text{MW}} \text{ZnO} + 4\text{NH}_3 + 2\text{H}_2\text{O} \quad (89)
\]

\[
[Zn(NH)_4]^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 + 4\text{NH} \quad (90)
\]

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow [\text{Zn(NH)}_4]^{2+} \quad (91)
\]

\[
[Zn(NH)_4]^{2+} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (92)
\]

By addition of ammonium hydroxide and zinc acetate, the \(\text{Zn(OH)}_2\) deposit is obtained (reaction 85). Besides, it redissolves as a result of addition of extra amounts of ammonium hydroxide (reaction 86) and ammonium. Thus, tetra ammonium zinc hydroxide is obtained through reactions (86) and (87) in the solution. As the result of its decomposition through reaction (88), the \([\text{Zn(NH)}_4]^{2+}\) growth unit is obtained which is able to form the \(\text{ZnO}\) nuclei and \(\text{Zn(OH)}_2\) sediments (reactions 89 and 90). Using the XRD analysis, two phases of \(\text{ZnO}\) and \(\text{Zn(OH)}_2\) with hexagonal and orthorhombic lattices, were observed. Through the addition of sodium hydroxide and adjustment of the pH, \(\text{Zn(OH)}_2\) can be decomposed to \(\text{ZnO}\) through reactions (91) and (92) and therefore increase the purity of the produced powder.

The formation mechanism of \(\text{ZnO}\) from zinc acetate dehydrate and ammonia precursors is explained via reversible reaction (93) by Tang et al.\(^{121}\):

\[
[Zn(NH)_4]^{2+} + \text{OH}^- \quad (93)
\]

\[
\leftrightarrow \text{ZnO} + \text{NH}_3 + \text{H}_2\text{O}
\]

This reaction leads to the precipitation and consecutive dissolution of \(\text{ZnO}\). First, the reaction between \([\text{Zn(NH)}_4]^{2+}\) and \(\text{OH}^-\) ions leads to the formation of \(\text{ZnO}\). At the end of growth, \([\text{Zn(NH)}_4]^{2+}\) concentration is reduced which leads to the reversal of the reaction, and causes the dissolution of \(\text{ZnO}\). This behavior may justify obtaining the flat top of the nanorods beside the small diameter.
4. Wurtzite structure

As mentioned earlier, in the microwave-assisted synthesis method, it is possible to control the morphology of ZnO nanostructures using various salts and modification of the controlling parameters. Before exploring the different morphologies and their formation mechanisms, it is necessary to analyze the properties of crystallite structure of ZnO.

The hexagonal ZnO Wurtzite structure is a polar crystallite with (0001) positive polar planes rich in Zn, (0001) negative polar planes rich in O, and a (10T0) nonpolar plane.67 (Figure 8)

Each Zn atom is adjacent to four O atoms as tetrahedral lattice. Zn$^{2+}$ and O$^{2-}$ ion layers are alternatively arranged in [0001] or the c-axis direction (Figure 8). As a result, the inherent asymmetry along the c-axis leads to the anisotropic crystallite growth. The polar face of the crystallite can also be the atomic layer of Zn or O which have different properties. Polarity is a property of crystal which is determined by the sequence of the attachments inside the crystallite while the termination of the plane is determined by the last atom on the plane. So, there are four types of (0001) plane structure in ZnO: Zn polar planes with the O or Zn terminal atom, and O polar planes with the O or Zn terminal atoms. For example, consider a nanoparticle with the Zn polar face and the Zn terminal atom, which is immersed in the solution. The most probable procedure for the growth of this particle is the formation of ZnO from Zn(OH)$_2$ based on reaction (94).

$$\equiv \text{Zn} - + \text{H} - \text{O} - \text{Zn} - \text{O} - \text{H}$$

$$\leftrightarrow \text{Zn} - \text{O} - \text{Zn} + \text{H}_2\text{O} \quad (94)$$

According to reaction (94), $\equiv\text{Zn}$ represents the terminal atom of the face that, at each stage of the growth, Zn will be the terminal atom again.257 In general, the crystallite growth is affected by the combination of structural parameters, such as the free energy of the surfaces, molecular attachments and dislocations, also external parameters such as solvent, additives, time, and temperature. Reducing the surface energy is the primary driving force of crystallite growth, which leads to formation of different morphologies.17 Unlike non-polar faces, polar faces have higher surface energy. According to Solis-Pomar et al.,117 the cleavage energy of the optimized {0001} planes is approximately 60% more than non-polar planes.67,69,96,106 Therefore, they can be configured in a way that the overall surface energy is reduced. Thus, the growth rate will be higher in the direction perpendicular to the (0001) polar faces in comparison to (10T0) non-polar faces. As a result, the rate of growth along different directions in this structure will be $V_{[0001]} > V_{[0110]} > V_{[0111]} > V_{[0001]}$. According to Al-Gaashani et al.,237 the reason for the enhanced growth along [0001] direction in comparison to [0001] direction, is the negative polarity of the [Zn(OH)$_4$]$^{2-}$ growth units, which along with the positive polarity of these faces, results in an elevated adsorption on the aforementioned planes. In some

Figure 8. Wurtzite structure and the polar and non-polar faces’ view.
cases, particle growth will be accompanied with their attachment for their stability in the system and energy reduction. The formation of the multi-linked morphologies as a single crystallite is justified based on the oriented attachment mechanism.\textsuperscript{17,68,244,245} In this case, the agglomerated particles are oriented in a way to reduce the energy, and the crystallites could be attached in a specific crystal direction. The reason for this behavior might be dehydration between coherent interfaces. It is reported that this oriented attachment is done by the macromolecules. Through this process, direct precipitation of ZnO from the solution, the twining phenomenon, the growth of multiple networks from the common attachment and the separate growth of each crystallite along the c-axis occurs (Figure 9).

5. Effective parameters

5.1. pH

In relation to the effect of pH, several studies are conducted which show that, Zn(OH)\textsubscript{2} is not formed at pH < 12, therefore, the pH = 12 is found to be the critical value to form ZnO nanoparticles. By reducing the pH, crystallization is also reduced, suggesting that the higher pH exhibits more grain growth. So change in pH leads to considerable changes in the shape and size of the particles\textsuperscript{81} (Figure 10). In fact particle morphology is controlled through nucleation and growth and these two processes depend on the concentration of [Zn(OH)\textsubscript{4}]\textsuperscript{2−} ions and the pH value.\textsuperscript{88} The importance of pH in the formation of ZnO nanoparticles is related to the stability of complexes. In fact Zn\textsuperscript{2+} is solvated by water molecules in aqueous solutions and could appear as several hydroxyl monomeric species such as Zn(OH)\textsuperscript{+} (aq), Zn(OH)\textsubscript{2} (aq), Zn(OH)\textsubscript{3} (aq), Zn(OH)\textsubscript{3} (s), Zn(OH)\textsubscript{3} (aq) and Zn(OH)\textsubscript{4}\textsuperscript{2−} (aq) that at certain concentration of Zn\textsuperscript{2+} ions, the stability of the complexes depends on pH and temperature of the solution.\textsuperscript{231} In fact the alkaline environment is among the requirements of this process because the bivalent metal ions cannot be hydrolyzed under acidic conditions.\textsuperscript{116} Due to the dehydration of the hydroxyl species, the growth of the newly formed ZnO nuclei is mainly subject to the reactions between zinc and hydroxyl complexes on the crystallite surface of ZnO nuclei. Generally, the suitable pH conditions for the growth of nanoparticles with wire/rod morphology is reported to be 5 < pH < 12 without the intervention of any additives.\textsuperscript{231} On the other hand at low pH values, Zn(OH)\textsubscript{2} is formed while at high or average pH, both [Zn(NH\textsubscript{4})\textsubscript{2}]\textsuperscript{2+} and Zn(OH)\textsubscript{2} are present in the solution. Therefore, at lower pH values, the particles are less likely to grow because of the presence of lower growth unit. By increasing the pH and the amount of OH\textsuperscript{−} ions, nucleation rate is enhanced while the speed of growth is limited. Moreover, in the case that OH\textsuperscript{−} exceeds the saturation point, the

Figure 9. Formation of Tripod and Tetrapod morphologies as a result of the growth of linked nuclei from a common junction. Top row: Schematic representation. Bottom row: SEM image of the related nanoparticles. (© MDPI. Reprinted with permission from Majithia et al.\textsuperscript{68} Permission to reuse must be obtained from the rightsholder.)
growth units are surrounded by the extra OH$^-$ ions before settling on the crystallite. Therefore, the speed of growth is limited and the length-to-diameter ratio will be a small value. So an optimum pH value is essential to obtain desirable particle size. The optimum pH which yielded the higher length-to-diameter ratio is reported as pH = 11 \(25^{\text{a}}\) (Figure 11). It is reported by Komarneni et al.\(25^{\text{b}}\) that the high efficiency of ZnO production at higher pH is obtained due to complete precipitation and decomposition in comparison to lower pH. According to Tang et al.\(12^{\text{c}}\) at higher pH values, the solubility of Zn in aqueous solutions increases, which could affect the growth, morphology, and inherent defects of the crystal. By increasing the solubility of Zn, the degree of supersaturation decreases which results in a decreased initial nucleation rate and less accessible nucleation sites that results in longer particles with higher diameters. On the other hand pH can have a crucial role on the competition between suppression role of surfactant molecules and promotion role of OH$^-$ ions. According to Jianzhong et al.,\(11^{\text{d}}\) the needles formed as the result of the competition between the SDS molecules and OH$^-$ ions, form flower-like morphology at higher pH values. This happens due to the lack of stability of nuclei in strong alkaline conditions and tendency to form agglomerations in order to reach the critical size. Also elongation of each sub unit related to domination of OH$^-$ ions. Also it is reported that high pH leads to nuclei agglomeration and adsorption of growth units on these nuclei, which leads to the establishment of flower-like morphology\(86^{\text{e}}\) (Figure 12).

5.2. Duration

Baghbanzadeh et al.\(79^{\text{f}}\) and Pimentel et al.\(40^{\text{g}}\) have been investigated the effect of duration time in microwave-assisted synthesis of ZnO nanoparticles. Its increase leads to increase in length-to-diameter ratio of the nanorods.

![Figure 10](image1.jpg)

**Figure 10.** SEM images related to the morphology of the particles obtained as a result of varying pH as (a) 13.00 and (b) 13.96, indicating the influence of low pH changes on particle morphology. (© Elsevier. Reprinted with permission from Caglar et al.\(81^{\text{h}}\) Permission to reuse must be obtained from the rightsholder.)

![Figure 11](image2.jpg)

**Figure 11.** SEM images related to the particle size (length to diameter ratio) as \(A_1 < A_3 < A_2\) obtained through changing pH as (a) 12, (b) 11 and (c) 9, indicating the need for suitable pH to obtain particles with a maximum length to diameter ratio. (© Elsevier. Reprinted with permission from Uma Sangari et al.\(25^{\text{i}}\) Permission to reuse must be obtained from the rightsholder.)
and elongation of them. It is mentioned that for time periods shorter than 10 minutes, no effect is observed on this ratio and on the other hand, the surface defects are observed on the nanoparticles.\textsuperscript{79} However, time increase is responsible for obtaining smoother surfaces in addition to change in size of nanoparticles.\textsuperscript{256} So very short times results in irregular morphologies and is a morphology damaging factor.\textsuperscript{260} It can be concluded from these statements that time does not change the morphology and particle shape. It is also considered the possibility of controlling the rod-shaped nanoparticles through timing as one of the advantages of microwave heating (Figure 13). It is also stated by Caglar et al.\textsuperscript{81} that in the synthesis durations less than 10 minutes, no trace of ZnO sediments can be found. When synthesis duration is in the range of 10–30 minutes, the largest and best crystallite size is associated with the 20 minutes period. By varying the exposure time, only the particle size (especially in diameter) is affected while the orientation and shape remains unchanged. Also same result is reported by Jianzhong et al.\textsuperscript{112} On the other hand, the morphology change is reported by Chen et al.\textsuperscript{82} as sheet-rod-tube stages. In fact, these changes are related to the growth of nanoparticles and their elongation too (Figure 14). Unlike nanorods, the time increase is reported by Liu et al.\textsuperscript{250} as a factor of reducing the size of nanosheets. According to Majithia et al.\textsuperscript{68} increasing microwave heating time leads to reduction in the diversity of morphologies, and result in single-shape morphology (Figure 15). The increased efficiency of ZnO

Figure 12. Morphology change stages by altering pH and agglomeration of particles formed in higher pH to achieve stability. Top row: Schematic representation of the formation process. Bottom row: Related SEM images. (© Springer. Reprinted with permission from Jianzhong et al.\textsuperscript{112} Permission to reuse must be obtained from the rightsholder.)

Figure 13. SEM images related to the obtained particle size (length to diameter ratio) through changing time as (a) 1, (b) 2, (c) 3, (d) 5, (e) 10 and (f) 30 minutes, indicating the effect of time on the particle size. (© John Wiley and Sons. Reprinted with permission from Baghbanzadeh et al.\textsuperscript{79} Permission to reuse must be obtained from the rightsholder.)
production as the result of increase in heating time to a certain extent is also considered by Guo et al. In relation with production efficiency it is stated by Bilecka et al. that, in conjunction with increase in size, increasing the efficiency of ZnO production has an ascending-descending rate over time. The agglomeration along with growth of the particles as a result of increase in time is reported by Zhao et al. and Shinde et al. So, increasing the time has similar effect to increasing pH and, as the result of the agglomeration and growth of particles, the flower-like morphology can be obtained.

5.3. Calcination

According to Andrade Gomes et al. and Lee et al., before calcination, there are some unknown phases which decompose after calcination, and pure ZnO can be obtained after post treatment (Figure 16). Also, the migration of the particles’ boundaries occurs, and the coagulation of small particles leads to the formation of larger ones (Figure 17). Presence of the unwanted zinc carbonate hydroxide hydrate compound \( \text{Zn}_4\text{CO}_3\text{(OH)}_6\cdot\text{H}_2\text{O} \) is referred by Tseng et al. which prevents the full crystallization of ZnO. The removal of this phase is possible through calcination. About the influence of this post-treatment on nanoparticles’ morphology, it is considered by Cakir et al. as a factor to increase the length of nanoparticles.

5.4. Surfactant/modifying agent

The morphology of nanoparticles could be controlled by the inhibitory or incentive performance of a number of
additive species in a solution containing amines, acids, and alkalis. The effect of different additives used in the synthesis has been studied in this work. Considering different polarity of ZnO hexagonal crystal planes, small molecules can be adsorbed by different crystallite surfaces during the growth. The adsorption of these agents prevents (or even promote in some cases) the rapid growth of crystallites in the direction perpendicular to the coated surface. Thus, the organic additives or auxiliary products are added to adjust the shape.20

1. Ethylenediamine (EDA)
It has been reported by Rai et al.86 that using EDA leads to the fabrication of flower-like structure via the formation of stable complex with Zn\(^{2+}\) ions. Then, EDA entraps the ions in its structure and also releases them

Figure 17. SEM images related to the effect of calcination on particle aggregation, size and removing unknown phases remained after synthesis by changing the calcination conditions as (a) without calcination, (b) 400, (c) 600 and (d) 800°C. (© Elsevier. Reprinted with permission from Lee et al.261 Permission to reuse must be obtained from the rightsholder.)

Figure 18. EDA performance and its effect on particle growth as a result of (a) suppressing the growth perpendicular to the non-polar faces and (b) preparing secondary nucleation conditions through molecular adsorption on the non-polar faces. Left: Schematic representation of the formation process. Right: Related SEM images. (© ACS. Reprinted with permission from Rai et al.86 Permission to reuse must be obtained from the rightsholder.)
with microwave irradiation. Adsorption on micro-rods, and also secondary nucleation on the particles through etching the six faces of \{0110\} crystal, will lead to the formation of flower-like morphology and micro-rods branching from all six sides of the primary micro-rod. On the other hand, adsorption of growth units on the (0001) faces of agglomerated nuclei at high pH, due to faster growth along [0001] direction, leads to the formation of flower-like morphology (Figure 18)\(^{106}\). Moreover, the formation of needle-like morphology is reported by Cho et al.\(^{106}\) as a result of using EDA. According to the tendency for higher adsorption of the growth unit in comparison with EDA molecules on the (0001) faces of the crystal, the crystallite growth rate in the [0001] direction is higher than the direction perpendicular to the lateral faces and thus such morphology is obtained.

2. Triethanolamine (TEA)
In a report by Guo et al.\(^{88}\) the role of TEA on the morphology and growth has been associated with the formation of stable complex with Zn\(^{2+}\), controlling its usage, and reducing the free path way of the ions by producing large amounts of [Zn(OH)\(_4\)]\(^{2-}\). In addition, the effect of TEA on the growth of the particles has been stated by Kajbafvala et al.\(^{113,239}\) that its adsorption on the ZnO nuclei will lead to steady growth in all directions. (Figure 19 and 20).

3. Sodium dodecyl sulfate (SDS)
In the case of SDS molecules (anionic surfactant), It is stated by Jianzhong et al.\(^{112}\) that SDS plays an inhibitory role in the growth of crystallites due to the formation of a stable complex of Zn(SDS)\(_n\), which leads to the formation of a sheet-like morphology. In fact, due to the tendency of SDS to be adsorbed by (0001) polar faces,\(^{262}\) it prevents the growth in these directions but its influence will be dominant on morphology only if it is able to compete with the role of OH\(^-\) ions as growth stimulants (Figure 21).

4. Cetyl triethyl ammonium bromide (CTAB)
Yu et al.\(^{96}\) and De Moura et al.\(^{263}\) reported that CTAB (cationic surfactant) is completely ionized in water and thus, sharing of ions occurs between [Zn(OH)\(_4\)]\(^{2-}\) growth unit and CTA\(^{+}\), where CTAB acts as an ion carrier. As shown in Figure 22, in small amounts, it forms the spherical micelles. Micelles are the molecular agglomeration of the surface active material which has agglomerated as the

\[\text{Figure 19.} \text{ Schematic representation of the performance of TEA and suppressing the growth of particles along the c-axis.}\]

\[\text{Figure 20.} \text{ SEM images related to the effect of TEA on particles' morphology by preventing the growth along the c-axis. (a) without TEA and (b) with TEA. (© Springer. Reprinted with permission from Guo et al.\(^{88}\) Permission to reuse must be obtained from the rightsholder.)}\]
rods at high amounts of CTAB. These agglomerations are in fact, the fat molecules which are configured in the liquid solution in spherical or rod shape, and this matter originates from the amphipathic nature of the fatty acids which have two hydrophilic and hydrophobic heads. In the following, the spherical micelles cause the formation of flower-like microstructures and rod micelles cause the formation of rod-like microstructures. At high temperatures, CTAB capsules can be destroyed, and so individual CTAB molecule can be adsorbed on a growth unit and carry them toward ZnO nuclei, leading to the formation of a needle-like morphology. The effects of CTAB have been attributed to its influence on kinetics of reaction by Shen et al. According to Liu et al., CTAB surfactant molecules which are able to be adsorbed on the crystal surface due to the electrostatic forces between CTAB and the growth unit, play a double role of structural orientation and prevention of particles from agglomerating. Additional roles such as dispersion and inhibition of agglomeration in the synthesis of other nano-particles have also been reported for CTAB. In fact, when the amount of CTAB is not sufficient to form micelles, it acts as dispersing

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**Figure 21.** Representation of the SDS molecules and the competition of its inhibitory role with the promotive role of OH\(^-\) toward growth through changing pH. Left: Schematic representation of the formation process. Right: Related SEM images. (© Springer. Reprinted with permission from Jianzhong et al. Permission to reuse must be obtained from the rightsholder.)

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**Figure 22.** Schematic representation of CTAB performance in low and high doses and its effects on morphology through changes in the formed micelles.
Moreover, CTAB may act as transitional environment or correcting agent for the small crystallite nuclei in the initial solution. The surfactant molecules adsorbed on the surfaces of the crystallite nuclei act as the communication platforms for small nuclei to join the cluster. Indeed, CTAB has a limiting role on the scope of adsorption on the planes. Since the adsorption of CTAH on (0001) faces is easier (due to attachment to growth units), the preferred direction of growth is the c-axis, and crystallite sheets present relatively uniform growth rate (Figure 23). A comparison between Figures 24a and 24c shows that in the presence of CTAB, the particles have more uniform growth and larger diameters.

5. Polyethylene glycol 400 (PEG400)

PEG surfactant which is an organic polymer material with non-polar carbon chains, is usually used for controlling the growth of nanocrystallites. As a result of PEG400 adsorption on the crystallites and reduction in the activity of the crystal, rod-like morphology is obtained. Indeed, the reduction of growth rate in some directions, leading to the creation of such morphologies. The role of PEG400 is attributed to its regular chain structure by Shen et al.235 and Liu.

![Figure 23](image1.png)

**Figure 23.** Schematic representation of regular crystal growth as a result of different amounts of CTAH adsorption on different crystal faces.

![Figure 24](image2.png)

**Figure 24.** TEM images related to the morphology changes through varying CTAB amounts as (a) 0 mol, (b) 8 mmol and (c) 20 mmol. (© Elsevier. Reprinted with permission from Fan et al.96 Permission to reuse must be obtained from the rightsholder.)

![Figure 25](image3.png)

**Figure 25.** Changing the particle size resulting from the use of PEG400 as a surfactant. (a) with PEG400, (b) without PEG400. (© Elsevier. Reprinted with permission from Erten-Ela et al.232 Permission to reuse must be obtained from the rightsholder.)

![Figure 26](image4.png)

**Figure 26.** Schematic representation of regular crystal growth as a result of different amounts of PEG400 adsorption on different crystal faces.
et al.\textsuperscript{265} In fact, the oxygen atoms in the entire PEG400 can be attached to Zn\textsuperscript{2+} species and form chain-like precursors. As a result of its decomposition, the rod-like nanostructure is formed under the microwave irradiation. Moreover, the effect of PEG has been clarified on size reduction of the nanoparticles in the work conducted by Erten-Ela et al.\textsuperscript{232} (Figure 25). PEG400 has a performance similar to CTAB except that due to the differences in molecular structure, it has different adsorption behavior (Figure 26).

6. Acetyl acetate (ACAC)

In regards to ACAC, the role of this substance on the formation of nanorods is described by Hamedani et al.,\textsuperscript{97} as creation of growth conditions along the [0001] direction. In fact, this complexing factor could be adsorbed on (0001) face with positive polarity and form this morphology by accelerating the growth in c-axis, and inhibiting growth in the direction perpendicular to c-axis (Figure 27).

Figure 27. ACAC adsorption on (0001) crystal faces and exciting the growth in the direction perpendicular to the faces. Left: Schematic representation of the formation process. Right: Related SEM image. (© Elsevier. Reprinted with permission from Hamedani et al.\textsuperscript{97} Permission to reuse must be obtained from the rightsholder.)

Figure 28. Guanidinium carbonate adsorption on (0001) crystal faces and exciting the growth in the direction perpendicular to the faces and attaching the particles under microwave radiation. Left: Schematic representation of the formation process. Right: related SEM image. (© Elsevier. Reprinted with permission from Hamedani et al.\textsuperscript{97} Permission to reuse must be obtained from the rightsholder.)

Figure 29. PVA2000 adsorption on (0001) crystal faces and suppressing the growth in the direction perpendicular to the faces and exciting the growth in the direction perpendicular to the non-polar faces. Left: Schematic representation of the formation process. Right: Related SEM image. (© Springer. Reprinted with permission from Shen et al.\textsuperscript{235} Permission to reuse must be obtained from the rightsholder.)

Hamedani et al. also consider adsorption of guanidinium carbonates on (0001) faces of the formed nuclei, with negative polarity. This material is also reported to form nanorod morphology, which form flower-like morphology due to the agglomeration of these nanorods (Figure 28). The effect of PVA2000 on the flake-like morphology is attributed to the adsorption of this material on crystallite (0001) faces, and prevention of the growth along the direction perpendicular to these faces by Shen et al. (Figure 29). Moreover, the role of PVP as CTAB has been attributed to its effect on the kinetics of the reaction.

8. Triethyl citrate – tripotassium citrate

The effect of these chemicals depends on the performance of citrate ions. It is reported that by adsorption of citrate ions on the (0001) faces of the crystallite, the contact between growth units and these planes is lost, and their growth is suppressed along c-axis. In the case that the citrate ions are not present in the solution, star-like morphology is obtained due to the aggregation of the particles and their subsequent growth. Also, with the addition of citrate ions to the solution, the crystallite grows in six directions perpendicular to the non-polar faces at low concentrations of growth units, and wide hexagonal nanodisk morphology is obtained. At average and high concentrations of the growth units, the UFO and ball morphologies are obtained, respectively due to the further and uniform growth in all directions (Figure 30).

9. o- (m- or p-) nitrobenzoic acid

This organic acid is introduced by Su et al. as selective adsorption agent which controls the growth of ZnO crystallite faces by adsorption on different faces in different directions. Nitro groups are resided in different positions of benzoic acid and, thus, various space steric hindrances can affect crystallite growth. The space steric hindrance is great in order of ortho, meta, and para, respectively. Thus similar morphologies are obtained in all three cases. However, the size and the amount of components in the microstructure will be different as p-ZnO > m-ZnO > o-ZnO (Figure 31).

Figure 30. Formation of (a) star-like, (b) disk, (c) UFO and (d) ball morphologies as a result of nuclei aggregation and different growth rates in different directions. Left: Schematic representation of the formation process. Right: Related SEM images. (© ACS. Reprinted with permission from Cho et al. Permission to reuse must be obtained from the rightsholder.)
10. Triton X-100

In a report by Pimental et al., it has been stated that this substance plays a role in preventing the aggregation of the particles. This chemical also prevents the growth of particles in a direction perpendicular to non-polar faces by adsorbing on them which leads to the formation of nanorod morphology (Figure 32).

5.5. Solvent

Effect of the solvent will be largely focused on the duration of the synthesis process while some solvents play the role of morphology modifier in addition to the role of polarity. It has been stated by Baghbanzadeh et al. that EG, as a solvent with high loss tangent, leads to the reduction of the heating time to less than 1 minute in order to achieve the desired temperature. Also, EG inhibits the growth of particles and even its incredibly high dosages prevent the formation of nanoparticles (Figure 33). The effects of water, ET and EG solvents have been compared by Pimentel et al. and it has been stated that more polar solvents lead to the formation of smaller crystallites. Thus, according to this theory, and considering the polarity of the above solvents as water > ET > EG, the size of the crystallites obtained from the synthesis of the above solvents should be as $D_{\text{water}} < D_{\text{ET}} < D_{\text{EG}}$. However, the proposed theory is not true about EG and the size of crystallite is obtained as $D_{\text{EG}} < D_{\text{water}} < D_{\text{ET}}$. In fact, growth along [0001] direction...
in the presence of EG, as a solvent with a lower polarity, is reduced and therefore smaller ZnO crystallites are achieved. This result may be due to the high viscosity of the polymer material which affects the mobility of primary particles, and thus limits the process and affect the growth of crystallites. This severe impact is due to high tendency of EG to be adsorbed by the particles. Furthermore, due to the high polarity and high EG interaction with microwave, the aggregation and integration of nanoparticles by local heating is possible. Similarly, it has been reported by Zhang et al.\textsuperscript{17} that based on the presence of OH groups in the EG solvent, Zn\textsuperscript{2+} ions have a tendency to react with EG molecules. Thus, depending on the concentration of EG, various [Zn(EG)]\textsuperscript{2+} or [Zn(EG)\textsubscript{3}]\textsuperscript{2+} complexes can be formed. Here, the EG molecules tend to be adsorbed on (0001) planes which are rich in Zn. Besides, by forming the mentioned complexes and reducing the surface energy of these planes, the growth along [0001] direction will be prevented.

In this report, the reduced particle size due to increased concentrations of EG is justified by the reduced penetration of the ions in the solution due to the increase in the viscosity of the solution as the result of the increase in EG amount. On the other hand, EG affects the morphology by forming nanorods with flat surface, while synthesis using water leads to the formation of pencil-like nanoparticles. The main explanation for this observation is the higher growth rates along [0001] direction in the synthesis with water. As a result, the surface area of the (0001) planes is quickly reduced and (10\text{10}) planes with lower growth rates determine the morphology. In fact, as a result of this growth, the length is increased but area of the top section is reduced. The faster the growth rate of (0001) planes is, the higher the reduction rate of top area would be and more sharpness is obtained. Thus, nanoparticles have pencil-like morphology. In comparison, at slow growth rate, the nanoparticles will have flat end (Figure 34) also it has been

Figure 34. Formation of nanorod with flat top and nanorod with pencil-like tip morphologies as a result of using various EG and water solvents. Left: Schematic representation of the production process Right: related SEM images. (© Springer. Reprinted with permission from Pimentel et al.\textsuperscript{67} Permission to reuse must be obtained from the rightsholder.)

Figure 35. SEM images related to morphology changes from rod to semi-spherical particles and hollow sphere by changing the type of solvent as (a) water, (b) benzyl alcohol and (C) ethanol. (© IOP Publishing. Reprinted with permission from Zhao et al.\textsuperscript{94} Permission to reuse must be obtained from the rightsholder.)
explained by Cho et al., that the reduced concentration of the growth units over the process can be the reason of the formation of flat surfaces. In addition, the effect of solvent on the morphology is justified by Zhao et al., where solvothermal synthesis with ethanol results in the formation of hollow spherical morphology. The synthesis under same conditions with benzyl alcohol leads to the absence of the said morphologies. This phenomenon is explained by the theory of bubble pattern in which as a result of low ethyl acetate boiling point in comparison to benzyl acetate, the formation of hollow sphere morphology is possible by ethanol solvent (Figure 35). According to this theory, the mechanism of particle formation for hollow spheres is explained by the formation of bubbles due to boiling of the solvent, and formation of ZnO shell on the outer surface of the bubbles due to the aggregation of particles (Figure 36). Authors also suggest that the effect of solvents on the morphology could be as a result of the interaction between solvent and particle surface that affects the preferred growth direction. Hollow sphere morphology formation is reported by Zhang et al., through using ethylene alcohol solvent, too. The effect of 1-butyl-3-ethyl imidazolium tetrafluoroborate ([Beim]BF₄) or 1-butyl-3-ethylimidazolium chloride ([Beim]Cl) ionic liquids have been described by Zheng et al. as facilitating the formation of caltrop-like sphere morphology, in addition to absorbing microwave radiations that results in high nucleation and growth rates. In order to reduce the surface energy of the crystal planes, ZnO crystals which obtained through Zn(OH)$_2$, are grown along the c-axis to reduce the energy of the (0001) planes and form nanorods. [Beim]$^+$ with imidazole rings are adsorbed on the crystal faces of the ZnO nuclei that have formed on the aggregation center. Also, considering the slow growth rate of (0001) polar faces, caltrop-like spheres are obtained. The

![Figure 36. Hollow sphere morphology obtained as a result of solvent boiling and joining the particles on the resulting bubbles. Top row: Schematic representation of the formation process. Bottom row: Related SEM images. (© IOP Publishing. Reprinted with permission from Zhao et al.94 Permission to reuse must be obtained from the rightsholder.)](image)

![Figure 37. SEM images related to morphology changes through changing the type of solvent from EDA to water under the same conditions as (a) EDA and (b) water. (© Springer. Reprinted with permission from Shen et al.235 Permission to reuse must be obtained from the rightsholder.)](image)
roles of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), glutamic tetrafluoroborate ([HGlu]BF₄) and 1-n-butyl-3-methyl imidazolium tetrafluoroborate ([Bmim]BF₄) ionic liquid solvents are reported by Rabieh et al., Tong et al. and Wang et al. as the inhibitors from agglomeration. The determining role of ethylenediamine (EDA) solvent in fabricating the flower-like morphology is referred by Shen et al. This non-aqueous solvent reduces the concentration of precursor by forming [Zn(en)₂]²⁺, leading to declination in the rate of ZnO formation. As a result, the concentration of precursor and the formation of ZnO are controlled, and result in the oriented growth of ZnO crystallites, and obtaining regular morphology. However, in the synthesis by water solvent under the same conditions, due to the high growth rate, clusters of nanoparticles are obtained (Figure 37). By comparing 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF₄), and ethanol solvents, it is suggested by Wang et al., that the higher polarity of Bmim⁻ leads to shorter reaction times. It is reported by Komarneni et al. that particles have more surface area in the presence of ethanol, compared to the particles synthesized in absence of ethanol. According to the work conducted by Schneider et al., the solvent selection has stronger effect on particle size, so that solvents with the higher boiling point lead to formation of particles with larger sizes.

### 5.6. Temperature

Regarding the effects of temperature, Baghbanzadeh et al. stated that high temperatures lead to faster crystallization, and can affect the final product. It has been explained by Ivanov et al. that the increase in temperature leads to reduction in the average particle size. It is believed that an increase in heating temperature leads to increased ZnO production efficiency to certain degree. It is reported that temperature can affect the growth rate. Indeed, nucleation occurs at low temperatures, and the morphology of particles approaches the rod-like state with increasing temperature due to the accelerated growth along c-axis. Since this effect is similar to that of the concentration of the reducing agent, these two factors can reinforce each other, and rod morphology is synthesized by increasing both of them. Also it is stated that an increase in temperature leads to corresponding rise in the particle growth rate and this increase, presents the ascending-descending trend along with the increased crystallite size. According to Jianzhong et al., sensitivity of the ZnO nanostructures’ growth rate to temperature along the [001] (c-axis) is greater than [100] and [101] ones. According to these authors, temperature has more prominent role than time in the synthesis of nanostructures. According to Huang et al., formation of ZnO nuclei is followed by obtaining the dandelion morphologies at lower temperatures as a result of the attachment of the nanorods in polar (0001) faces, in-line with their growth along c-axis direction. At slightly higher temperatures, due to suppression of growth along c-axis, there is the possibility of nanosheets formation. Next, as a result of their growth, a new thruster vane structure is obtained. As the result of the preferred growth along c-axis, newly formed nuclei are converted to nanorods. With further increase in temperature, nanowires will be produced as a result of the growth of nanorods in the same direction. Another possible condition in the case of increasing pressure due to temperature rise and decreasing Zn²⁺ concentration due to particle precipitation from solution is the increase in the diameter and localized dissolution of nanorods along with their attachment to each other, which results in spindle morphology. The growth of such attached nanoparticles is justified by the theory of oriented attachment. According to this theory, the ZnO nuclei are obtained as a result of supersaturation of the solution. These nuclei will react in the preferred direction to attach to the primary rod or slice particles and form complex morphologies. Based on this theory, the adjacent nanoparticles are spontaneously assembled via sharing their usual crystallite side, and attaching at the face intersection (Figure 38). According to Lu et al., microwave heating at low temperatures leads to ZnO nucleation and with increasing temperatures, ZnO particles grow. Moreover, as the result of the aggregation of small particles, flower-like morphology is synthesized. With further rise of temperature and pressure, the flower-like structure is decomposed and converted into the shuttle-like and column/rod-like structures (Figure 39). It is noted by Jianzhong et al. that at high temperatures, especially in the hydrothermal method, the particles tend to dissolve due to the rise in pressure. Therefore, the sharp petals are synthesized as the result of this action. In addition, at lower temperatures, as the result of the nuclei aggregation, microsphere morphology consisting of sheets is obtained. By rising the temperature, this morphology changes to the flower-like morphology consisting of nanorods. Eventually, through further increase in the temperature, the resulting morphology will be sharper and thinner (Figure 40).

### 5.7. Power

Microwave power is directly related to the solution heating rate. It is reported that the excessive increase in power can have negative effects as it reduces the specific surface area. Also, it is pointed out by Cao et al. that in the combustion synthesis method, a high level of power leads to the high speed and therefore short combustion reaction times which do not favor nucleation and particle growth. Increased power is considered by Promnopas et al. as
Figure 38. Formation of (a) dandelion, (b) thruster vane, (c) wire and (d) spindle morphologies as a result of temperature changes. Left: Schematic representation of the formation process. Right: Related SEM images. (© Elsevier. Reprinted with permission from Huang et al.18 Permission to reuse must be obtained from the rightsholder.)

Figure 39. Formation of shuttle-like and rod-like morphologies obtained through increasing temperature and decomposition of flower-like structure. Top row: Schematic representation of the formation process. Bottom row: Related SEM images. (© Cambridge University Press. Reprinted with permission from Lu et al.47 Permission to reuse must be obtained from the rightsholder.)
growth factor of particles, since it reduces the number of smaller particles or dissolves them. However, it is reported an increase in particle size by decreasing power.\textsuperscript{70} According to Al-Gaashani et al.\textsuperscript{237} the increased power leads to variation of the morphologies along with an increase in their size. They consider the aggregation phenomenon at high powers, as the result of sudden temperature rise of the solution due to microwave irradiation, and formation of hot spots in the solution that have higher temperatures than the bulk solution. These hot spots lead to the overheating phenomenon through which the solution temperature gets higher than its value in conventional heating, therefore viscosity is reduced. As a result of decreased viscosity, the opportunity for impact increases which results in the increased tendency of the ZnO nuclei for aggregation and increase in size. Due to the changes in temperature and viscosity at each moment, the obtained morphology will not be uniform. The leaf-like morphology at higher power values which is obtained as the result of the agglomeration of particles at specific conditions of temperature and viscosity of the solution, are also discussed (Figure 41). The formation of needle-like morphology is reported to be caused by the increase in power. According to Zhu et al.\textsuperscript{260} at very high or very low power values, damaging effects on the morphology are widely seen and consequently, an irregular morphology is achieved. The particle size reduction as a result of increased power is also reported by Pimentel et al.\textsuperscript{40} They have also noted that at very low powers and times, ZnO structure cannot be formed due to the lack of sufficient temperature. Moreover, at very high powers and times, the particles melt and reactions stop because of the evaporation and increasing pressure, probably due to the temperature increase over melting point of ZnO nanoparticles ($\sim750^\circ$C). The power increase leads to the reduced particle size and formation of thinner nanorods due to an increase in the amount of formed nuclei. In addition, at higher power values (600 W), aggregation of small particles and formation of flower-like morphology is reported.

5.8. Washing solvent

It has been reported by Chen et al.\textsuperscript{82} that in the case of tubular structures, the best washing solvent is water since the particles’ wall thickness is thin with weak bonds.
5.9. Precursor concentration

Regarding the effect of precursor (\(\text{Zn}^{2+}\) source), it has been stated by Boudjadar et al.\(^87\) that at low concentrations of precursor, the reaction is not completed and therefore, pure \(\text{ZnO}\) cannot be obtained. It is even possible that at low concentrations, there would be no \(\text{ZnO}\) powder produced. It is also reported that microwave irradiation increases the size of the crystallites over time but the coarser crystallites are achieved through solutions with higher concentrations of precursors.\(^77\) According to Liang et al.,\(^20\) \(\text{Zn}^{2+}\) species play a decisive role in the making of flower-like and rod-like morphology. In the case of adding alkaline agent, zinc hydroxide complexes including \(\text{Zn(OH)}^+\), \(\text{Zn(OH)}_2\), \(\text{Zn(OH)}_3\) and \([\text{Zn(OH)}_4]^{2-}\) are formed depending on the alkaline agent. At \([\text{OH}^-]:[\text{Zn}^{2+}]=2:1\), the reaction product is \(\text{Zn(OH)}_2\) which has low solubility in water and so a turbid solution is obtained. In greater quantities of \(\text{OH}^-\) ions, the \(\text{Zn(OH)}_3\) and \([\text{Zn(OH)}_4]^{2-}\) complexes with higher solubility are formed and a transparent solution is obtained. If the \([\text{Zn(OH)}_4]^{2-}\) species are present in the solution, these growth units are directly attached to the nucleation sites and as the result of growing the twin crystallites in the preferred planes, flower-like morphology is achieved. If the \(\text{Zn(OH)}_2\) species are present in the solution, they will be attached to the amorphous deposits of the suspension. Moreover, at higher temperatures, as a result of the dissolution of \(\text{Zn(OH)}_2\) and formation of \([\text{Zn(OH)}_4]^{2-}\), growth rate of the \(\text{ZnO}\) nuclei which resulted from \(\text{Zn(OH)}_2\) increases and rod-like morphology is obtained. Zhang et al.\(^75\) discussed the role of the type of precursor on the morphology. It is reported that in synthesis using the same solvent, by changing the precursor type from zinc acetate to zinc nitrate, particle morphology is converted from the hollow to the full sphere.

5.10. Reducing agent (concentration or type)

Since the amount of reducing agent (\(\text{OH}^-\) source) has direct correlation with \(\text{pH}\) value, the results of this factor can be attributed to the results of the \(\text{pH}\) effect. In general, in aqueous solution, \(\text{OH}^-\) ions are formed as a result of hydrolysis of the alkaline agents, and based on the presence of the \(\text{Zn}^{2+}\) ions resulting from the precursor solution, \(\text{Zn(OH)}_2\) will be formed as the result of the reaction between \(\text{OH}^-\) and \(\text{Zn}^{2+}\). Microwave heating will lead to the formation of \(\text{ZnO}\) nuclei from the decomposition of \(\text{Zn(OH)}_2\).\(^244\) According to Lu et al.,\(^47\) the increased amount of \(\text{NH}_4\text{OH}\) leads to the formation of rod-like morphology and increased in length-to-diameter ratio; i.e., elongation due to higher growth tendency along \(c\)-axis. Similar to the process in Figure 39, by increasing the \(\text{NH}_4\text{OH}\) concentration, the nanoparticles will have flower-shuttle-rod morphologies. The effect of \(\text{NaOH}\) on the morphology is attributed to its impact on the growth rate of different sides of the crystallites by Jianzhong et al.\(^112\) This substance also increases the tendency of growth along \(c\)-axis. Also the importance of this substance is attributed to its effect on the formation of \([\text{Zn(OH)}_4]^{2-}\) growth unit by Hamedani et al.\(^97\) The effects of urea on the morphology during combustion synthesis is attributed to its role on adjusting the alkalinity of the solution.\(^100\) It is reported by Kajbafvala et al.\(^113\) that addition of \(\text{NaOH}\) to the PS results in the increased concentrations of the produced \(\text{Zn(OH)}_2\), and it influences the growth rate and the morphology. According to Ma et al.,\(^244\) the value of the pyridine alkaline agent has
significant impact on the morphology of the obtained nanoparticles. On the other hand, different alkaline additives have different alkalinity and adsorbency on different sides of the crystallites, thus they lead to various growth rate and morphologies, which justify diversity of morphologies with changing the type of alkaline agent from pyridine to aniline and triethanolamine (TEA). The resulting morphologies are nanoring and multi-attached needles at different concentrations of pyridine, while the hexagonal column and nanosheet morphologies are reported in the synthesis by aniline and TEA. It has been reported by Krishnakumar et al. that obtaining different flower-like and spherical morphologies are due to the usage of hydrazine hydrate and ammonia, as the alkaline agents. Also difference in ammonia concentration is considered to be responsible for the growth and morphology changes of the nanoparticles. According to Kajbafvala et al., ammonia solution alkaline agent plays a role in the production of the [Zn(NH)₄]²⁺ growth unit through the NH₄⁺ ion and adjusting the pH of the solution through the production of OH⁻ ions as the result of reaction with water. Also, the ammonium ions (NH₄⁺) may affect the preferred growth sides and the final morphology as a result of adsorption on different crystallite surfaces by increasing the surface energy. The effect of hexamethylenetetramine (HMT) and ammonia solution alkaline agents are compared by Cho et al. It has been reported that, based on the stability of [Zn(OH)₄]²⁻ in strong alkaline conditions, this unit hardly is formed due to the poor acidic conditions by HMT; but in the case of ammonia solution, the [Zn(OH)₄]²⁻ and probably [Zn(NH₃)₄]²⁺ growth units are mentioned. Accordingly, due to the higher concentration of the growth units around the ZnO crystallite, the growth rate will be increased. It has been reported that in the presence of ammonium hydroxide, even at high Zn²⁺ concentrations, the highest ZnO yield is 50% while with the addition of sodium hydroxide to PS and changes in pH, production efficiency can be optimized up to 100% at an optimal pH value. This is related to the dissolution of the remaining Zn(OH)₂ via sodium hydroxide. In fact, the remaining Zn(OH)₂ leads to the reduced production efficiency of ZnO. The triethanolamine (TEA), sodium hydroxide and hexamethylenetetramine (HMT) alkaline agents are compared by Ma et al. It is pointed out that different morphologies can be achieved due to the different pHs of solution as NaOH (>14) > TEA (9.74) > HMT (6.74), as a result of using various alkaline agents. It is worth noting that OH⁻ certainly determines the final morphology through the formation of Zn(OH)₄ complexes and controlling the growth rate of crystallite faces. The greater pH values mean higher amounts of OH⁻ and thus, as a result of using sodium hydroxide as the alkaline agent, the high amount of OH⁻ stimulates growth in c-axis. On the other hand, due to the strong alkaline medium, the formed nuclei are unstable and tend to dissolve. Hence, for the sake of the particles stability in this medium, the critical size of nuclei increases and the particles are agglomerated. As a result, particle size will be larger in the case of sodium hydroxide and HMT. However, in the case of TEA, this factor not only plays the role of OH⁻ source but also serves as an organic template. In this case, the poor alkaline conditions lead to the formation of ZnO nuclei, but at the same time the nuclei are adsorbed by some chains of TEA, due to the ion-dipolar interaction between polymer hydrogen atom and ZnO oxygen atom, and form (ZnO-TEA)ₙ. It is noteworthy that these ligands tend to be adsorbed selectively on specific crystal faces and prevent anisotropic growth. On the other hand, there is the possibility of agglomeration of ZnO particles due to the attraction force of TEA chains.

Figure 43. Formation of narcis-like morphology as a result of nucleation and growth of the petals on the six side of prismatic nucleus and growth of each one along the c-axis. Top row: Schematic representation of the formation process. Bottom row: Related SEM image. (© Elsevier. Reprinted with permission from Kajbafvala et al. Permission to reuse must be obtained from the rightsholder.)
The effects of sodium hydroxide and ammonia as the alkaline agent are compared by Thangaraj et al.\textsuperscript{53} According to this report, using ammonia leads to deposition of dried Zn(OH)\textsubscript{2} while using sodium hydroxide leads to the formation of ZnO nanoparticles that are obtained directly with no need for the post-treatment. Therefore, it can be concluded that the achievement of pure ZnO might be associated with the alkaline agents rather than a surfactant. However, the size of the particles depends on both of these factors. In the case of the narciss-like morphology, it is suggested by Kajbafvala et al.\textsuperscript{249} that the adsorption of agents such as ammonium ions on the nuclei might affect the growth direction. Also it is noted that every nano-petal is nucleated from six \{10\textsuperscript{1}0\} faces and grow along c-axis. Intermolecular forces such as van der Waals forces can cause the formation of the obtained morphology (Figure 43).

5.11. Irradiation cycling mode

The effect of irradiation cycling on the synthesis of nanoparticles is studied by Zhu et al.\textsuperscript{64} It is reported that different morphologies cause by different heating modes. As a result of different rates of heating, ZnO nucleation occurs at different periods in the solution. For example, at radiation modes of continuous (H), 12 s on + 10 s off (M) and 4 s on + 12 s off (L), ZnO nucleation in solution occurs within 1 minute, 2 minutes and 20 minutes, respectively, which could influence the final morphology. Therefore, nucleation stage can have an influence on the final morphology. According to this report, the straw-bundle like, chrysanthemum-like and nanorod-based microsphere morphologies are achieved under different modes of heating. In the average heating speed, the concave sphere is formed, whereas at the high rates of heating the two spheres are attracted to each other and attached to reduce the surface energy and form a twin crystal. At low heating rates, the nuclei are more aggregated and form larger particles as a result of the growth. In fact, different heating rates will cause obtaining primary particles with different morphologies. The reason for the formation of the concave sphere could be due to various energies of the crystal faces or the adjacency of EG and Zn\textsuperscript{2+} molecules. As heating continues under the

![Figure 44](https://example.com/figure44.png)

Figure 44. Changes in nanoparticles' morphology by changing the heating cycle as (a) H: continuous, (b) M: 12s- 10s on off and (c) L: 4s off on-12s. Left: Schematic representation of the formation process. Right: Related SEM images. (© ACS. Reprinted with permission from Zhu et al.\textsuperscript{64} Permission to reuse must be obtained from the rightsholder.)
same conditions, due to the re-dissolution of the initially unstable particles, new nuclei are formed on the primary particles and grow. The growth of these nuclei occurs only due to the re-dissolution of primary particles and Ostwald ripening phenomenon along the c-axis (Figure 44).

Figure 45. Formation of cavity through re-dissolution caused by aging. Left: Schematic representation of the formation process. Right: Related SEM images. (© ACS. Reprinted with permission from Cho et al.106 Permission to reuse must be obtained from the rightsholder.)

Figure 46. Formation of nanocake morphology as a result of nanorods’ growth on the surface exposed to the synthesis solution due to the use of pre-synthesized nanodisk particles in the precursor solution. Left: Schematic representation of the formation process. Right: Related SEM image. (© ACS. Reprinted with permission from Cho et al.106 Permission to reuse must be obtained from the rightsholder.)

Figure 47. Formation of jelly fish morphology as a result of nanorods’ growth on the surface exposed to the synthesis solution due to the use of pre-synthesized UFO particles in the precursor solution. Left: Schematic representation of the formation process. Right: Related SEM image. (© ACS. Reprinted with permission from Cho et al.106 Permission to reuse must be obtained from the rightsholder.)
5.12. Aging treatment

Aging treatment conserves the formed nanoparticles in PS after microwave heating operations for specified time at room temperature. The operation generally leads to the dissolution of nanoparticles from the preferred faces in the preferred directions. This operation is applied in the production of nut and candle-like morphologies by Cho et al. The proposed mechanism is that after the formation of disk and rod-like morphologies during the synthesis operations, aging largely happens on (0001) faces because of their higher energies compared to (10T0) faces. Thus, due to the higher rate of dissolution along the c-axis, porous morphology is formed.

5.13. As-synthesized nanoparticles

In a report by Cho et al., structures such as bulky microstar, nano-cake, and micro-jellyfish are obtained using as-synthesized nanoparticles. If the star-like particles are used, the morphology will have thicker cluster because of more growth. When the nanodisk particles are used in the synthesis of nanorods, as a result of twinning nanorods or nanoneedles on (000T) crystal faces and their growth along the [0001] direction, nanocake morphology is obtained. Besides, the micro-jellyfish morphology is formed by using UFOs and growth of nanoneedles on the UFO particles.

6. Effect of zinc oxide nanoparticles’ morphology on particle properties

Particle morphology and method of fabrication have a great influence on designing structures with optimal properties. According to the importance of crystallite defects on the properties of zinc oxide nanoparticles, the microwave heating method gains prominence. The formation of lattice defects, due to the rapid formation of crystals, is dominant. Some morphological-related properties of ZnO nanoparticles which are synthesized by microwave-assisted method are discussed below.

6.1. Catalytic performance

The morphology of zinc oxide catalysts has a great influence on their catalytic activity due to the differences in polar faces area, oxygen vacancies, surface area, and particle size. Indeed, what determines the influence of particle morphology and the amount of oxygen vacancies on the ZnO crystal, is the surface area of the crystal polar faces. Each morphology has a different portion of the (000T) and (0001) polar faces. The amount of oxygen vacancies is also affected by the surface area of the polar faces, because polar faces are able to produce oxygen vacancies. In fact, oxygen vacancies act as active catalytic sites and prevent the recombination of the electrons and holes by capturing the photo-generated electrons. The basis of the photocatalytic activity of zinc oxide against compounds is that, by absorbing light energy, zinc oxide is excited to a higher energy level. If the absorbed energy is greater than the band gap, then the valance electrons are transmitted to the conduction layer and therefore create an electron-hole pair (EHP). The basic role of oxygen vacancies is preventing the recombination of the EHPs. Holes oxidize the hydroxyl groups and water which adsorbed on the ZnO surface, and leave OH radicals. Also by adsorption of electrons on the electron receiver species such as O2, which are in turn adsorbed on the zinc oxide surface, O2• radicals would be produced which in follow can lead to the oxidation of adsorbed organic compounds to harmless compounds. On the other hand, some researchers believe that depending on the adsorption desire of various compounds on different Zinc oxide faces and their optical degradation, the type of exposed faces and thus the type of morphology will be important. Another effective parameter on the catalytic activity of particles is the surface area of nanoparticles. Since photocatalytic reactions take place on the surface of nanoparticles, special surface area of nanoparticles determines the amount of organic molecules adsorbed on their surfaces. Hence, despite the almost same band gap and particle size, the spherical morphology has shown better performance against the methylene blue degradation, in comparison to the flower-like morphology, which is due to the higher amounts of pores and surface area. Also, the microtube morphology, due to its hollow tubular structure, has a greater surface area than sheet and rod morphologies and thus has better catalytic activity against methyl orange degradation. Comparison of catalytic activity of nanoparticles with different morphologies has proven that flower, sheet, needle and rod morphologies has higher photocatalytic docolorization efficiency for Rhodamine B (RB) solution, respectively. In fact, flower morphology has a higher UV absorption than other morphologies. This type of morphology has higher surface area and more tip, steps and kink sites, which is due to the porous and branched structure. Due to the existence of this type of structure, the amount of single Zn atoms on the defects to join the pollutant molecules, is higher and the penetration of pollutants also happens quicker. Comparison of the catalytic activity of nanoparticles with rod, hexagonal prism, peanut-like, butterfly-like and spherical morphologies against methyl
orange degradation indicates that spherical particles, which are composed of smaller particles with higher surface area, have better performance. In fact, the produced EHPs are transmitted to the surface more effectively.\(^2\) Another factor that can affect catalytic activity of particles and optical properties through influencing the band gap energy is the crystallite size. The larger crystallite size results in lower band gap energy and thus leads to a lower catalytic activity.\(^2\) Due to its surface defects and special morphology, rod-assembled microsphere morphology has a good catalytic activity against methylene blue degradation, and has shown good stability which can be utilized for removing organic pollutants.\(^3\) Also synthesized semi-spherical nanoparticles have shown good catalytic activity against O-acylation of alcohol and phenol.\(^4\)

### 6.2. Gas sensing performance

If zinc oxide nanoparticles expose to air, oxygen molecules can be adsorbed on the defects of the particles surface, and form $O_2^-$, $O_2^{2-}$, and $O^2-$ ions by capturing electrons from the conduction band, which creates an electron depletion layer on the surface of the particle and the resistance enhances. Since gas sensors generally operate at 573K and higher temperatures, $O_2$ and other species are more important than the others.\(^2\)\(^3\) When the sensor is exposed to the reducing gas atmosphere, oxygen ions react with gas molecules and the trapped electrons at the surface are again taken back by the valance band of zinc oxide, and the resistance of sensor decreases.\(^5\)\(^6\)\(^7\) In the oxidizing atmosphere, the gas molecules capture electrons and increase the width of the depletion layer, thus resistance of the sensor increases. In fact, sensor response is defined as a proportion of sensor resistance in the presence of gas and air.\(^8\)\(^9\)\(^10\) Despite the provided mechanisms, there are still unknown factors which affect the sensing performance of the gas sensor. It should be noted that ZnO crystal has zinc interstitial defects (Zni), oxygen vacancy ($V_o$), zinc vacancy ($V_{Zn}$), intermediate oxygen ($O_i$), and antisite oxygen ($O_{Zn}$), which Zn, and $V_o$ release electron, but $V_{Zn}$, $O_i$ and $O_{Zn}$ consume free electrons, which are respectively labeled as donors and acceptors.\(^11\)\(^12\)\(^13\) Detection of these defects by photoluminescence (PL) spectroscopic method has shown that the percentage of donor defects is directly related to the sensor performance. In comparison to the surface area of the nanoparticles, percentage of surface defects plays a decisive role in improving the performance of sensor,\(^14\) so that the flower-like nanostructures consisting of needle, rod and semi-spherical particles have shown better performance against NO$_2$ gas, respectively. The same order is true for the donor defects in these structures.\(^15\)\(^16\)\(^17\) Engineering of these defects can also results in the enhancement of sensor performance. Annealing of particles at different temperatures and atmospheres has a great effect on sensor performance. Through annealing, the nanoparticles will be exited the structure, and numerous cavities will be created on the surface of the petals which can affect the penetration pathway of gas molecules. Among the temperatures of 400, 500 and 600°C and atmospheres of O$_2$, N$_2$, H$_2$ and air, the annealed flower-like nanoparticles have the highest amount of donor defects at 500°C and N$_2$ atmosphere, and subsequently have a better performance in detecting ethanol (at optimum temperature).\(^18\)\(^19\) Morphology of the nanoparticles affects their gas sensing performance by influencing the pathways of gas molecules and amount of the exposed faces.

In this regard, flower-like, star-like and spherical morphologies have displayed better performance when it comes to CO gas detection, respectively.\(^20\) The flower-like structure which is composed of many constituent units, due to the provision of nanocavities for gas transition, displays a better performance.\(^21\) This statement is also true in the comparison of flower-like and urchin-like morphologies.\(^22\) In another comparison, the seven-spine structure has even better behavior than the flower-like structure against ethanol.\(^23\) In an investigation, hollow microsphere structure showed faster response and recovery against the ethanol than wire, tube, plate and semi-spherical structures.\(^24\)

Another structure that shows a good performance for the gas sensor application is the oriented nanorod arrays growing on different substrates. These arrays, due to the high surface-to-volume ratio of the rods and their vertical orientation, which results in more communication channels between oxygen anions and gas molecules than the interconnected state, have improved performance. This type of structure has enhanced performance against the H$_2$, NH$_3$ and CO gases.\(^25\) Comparison of arrays obtained from the microwave and conventional heating methods has shown that microwave heating, due to the creation of faster growth conditions, creates more regular and more vertical arrays with hexagonal rough ends which have more uniform distribution. The surface defects of nanoparticles also increase due to the collision of Zn$^{2+}$ and O$^{2-}$ ions during the polarity alignment process occurring during microwave heating. The result of this good orientation and exposure of faces with high energy is the improved performance of the sensor against CO gas.\(^26\) Despite the aforementioned statements, the detailed understanding of the nanoparticle morphologies’ effect on sensor performance is complicated due to the interaction of several factors, such as size, shape and electronic properties of the particle. In this case,
determinant role of the polar faces on the sensor performance is worthy of note. If Zn terminated (0001) faces with positive polarity are in contact with the oxygen atmosphere, they can easily adsorb oxygen species.\textsuperscript{291} Therefore, optimizing the interaction between surface and gas is possible by designing the appropriate morphology and adjusting the exposed faces. The sequence of active faces on photocatalytic property and gas sensor has been reported as (0001)\textgreater\{10\textbar T0\}\textgreater\{10 T1\} and\textgreater(00\textbar T0), which can be useful in designing the appropriate morphology with the most exposed faces.\textsuperscript{292} The selective performance of the gas sensor against different gases is another feature of nanoparticles with different morphologies that can be related to the interaction of different molecules with different crystallite faces. Flower-like, rod and semi-spherical structures have displayed good sensing performance against CO, CH\textsubscript{4} and ethanol, respectively. The sensing performance of rod and nanoparticle morphologies is independent of temperature, which is important from a technological point of view.\textsuperscript{97} The infrared spectra have shown that synthesized nanoparticles with semi-spherical, needle, and leaf-like morphologies can be utilized as infrared gas sensors to detect CO\textsubscript{2} and CO.\textsuperscript{237}

### 6.3. Antibacterial performance

The mechanisms proposed for the antibacterial activity of ZnO are mainly comprised of direct contact of ZnO nanoparticles with cell walls and destruction of its integrity, release of antimicrobial ions, which are mainly consist of Zn\textsuperscript{2+} and formation of reactive oxygen species (ROS) including H\textsubscript{2}O\textsubscript{2} and O\textsubscript{2}-. The features that create such properties in ZnO nanoparticles are related to its good response to the UV light, which leads to increase in conductivity that is preserved a long time after turning off the UV light. This is related to the electron depletion region and the production of free radicals as a result of exposure to UV light. Here, the morphology of nanoparticles affects the antibacterial properties of zinc oxide nanoparticles through the amount of polar faces. Highest antibacterial activity is obtained from morphologies with the highest amount of the exposed (0001) faces, because of having a high density of oxygen vacancies, which play a decisive role in the production of ROS.\textsuperscript{293} Antibacterial properties of various zinc oxide morphologies have shown that microspheres composed of nanobelts represent an effective performance against Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli) microorganisms.\textsuperscript{253} In a comparison, mulberry-like nanoparticles had stronger antibacterial effect than leaf-like and flower-like nanoparticles on Candida albicans.\textsuperscript{270}

Therefore, nanostructure surface defects and crystal orientation generally play a decisive role on the properties of nanoparticles, which leads to the importance of designing and engineering of nanostructures to achieve the highest functional efficiency.

### 7. Advances in ZnO hierarchical structures

Recent advances in the use of zinc oxide nanoparticles and microwave-assisted synthesis lead to the designing and engineering of hierarchical structures composed of different nanoparticles that result in the detection of extraordinary properties of these structures in comparison to blank state of them, due to their synergistic effects.

These hierarchical structures include the composition of nanoparticles in the form of hybrid composites or decorated surfaces of nanoparticles, doped nanoparticles and the creation of core-shell structures, or even a combination of them. As examples of the mentioned hierarchical structures, the structure of multi-walled carbon nanotube decorated with ZnO nanoparticles has shown enhanced performance against alcohol sensing, which is a function of microwave power, and hence represents better behavior at higher powers.\textsuperscript{294} A large integral area of the cyclic voltammetry loop in electrochemical measurements has shown that ZnO layer on graphene can be used in supercapacitors.\textsuperscript{295} The core-shell structure of Cu\textsubscript{2}O nanocube/ZnO nanoparticle composite, due to its specific structure, reduces the recombination tendency of the hole and photo-generated electron and has significant effect on photocatalytic performance.\textsuperscript{296} The rGO/ZnO composites composed of ZnO nanoparticles, which are attached to the graphene sheets, have shown enhanced performance as glucose sensors, supercapacitors and photocatalysts. Morphology of ZnO nanoparticles attached to the graphene surface as nanoparticle,\textsuperscript{297–301} nanorod,\textsuperscript{302} nanowire,\textsuperscript{303} microcube,\textsuperscript{304} nanoflake,\textsuperscript{304} nanoneedle,\textsuperscript{304} and flower\textsuperscript{305,306} will also play a major role in nanostructure performance.\textsuperscript{304} In fact, the presence of graphene sheets, because of their unique electrical properties, affects the transfer of electrons. Like the graphene, TiO\textsubscript{2} reduces the tendency of EHPs to recombination and affects its optical properties.\textsuperscript{307} However, ternary nanostructure of ZnO/TiO\textsubscript{2}/rGO has represented enhanced photocatalytic performance than single and binary structures of ZnO and ZnO/\textit{rGO}.\textsuperscript{308} In the ZnO nanorod structure decorated with Cu nanotip, the strong interaction of metal-support creates defects and micro strain in Cu nanoparticles which extremely affects the catalyst behavior.\textsuperscript{309} The
ternary structure of ZnO/ZnS/γ-Fe2O3 with hollow sphere morphology, consisting of several crystals of ZnO, ZnS and γ-Fe2O3, can adsorb and even trap the bovine serum albumin (BSA) protein in their cavity.310 The core-shell structure of ZnO/ZnS consisting of ZnS nanoparticles attached to ZnO nanorods has photocatalytic activity two times higher than ZnO nanorods.311 The Au/ZnO structure, consisting of a gold nanoparticle on the center of the hexagonal basal plane of a zinc oxide nanoparamid, has an enhanced photocatalytic performance and solar energy conversion.312 Other structures of Au/ZnO have also been reported which affect the ZnO photocatalytic performance.313,314 Hierarchical nanostructure of ZnO/CdS in the form of nanocables composed of CdS nanoparticles on the core-shell structure of ZnO nanorod/CdS have much higher photocatalytic activity against the degradation of rhodamine-B and methylene blue than pure ZnO nanorods, CdS nanoparticles and even core-shell nanostructure of ZnO/Cd.315 Carbon coated ZnO nanorods are able to decrease the cellular toxicity of ZnO nanorods in addition to the improvement of ZnO photocatalytic performance against degradation of methylene blue.316 Also antibacterial and photocatalytic properties of Ag/ZnO nanostructures are significantly improved.317,318

8. Summary and Future Trends

Microwave heating in combination with methods such as hydrothermal, sol-gel and combustion methods are used to synthesize the zinc oxide nanoparticles, and its various aspects are discussed in the present work. The most important issue about the microwave-assisted synthesis of ZnO nanostructures is its mechanism and influential factors. Thus, these issues are fully examined and different mechanisms, as well as the different associated factors discussed in the studies, are explained. Also, all different morphologies and zinc oxide nanostructures synthesized using this method were examined. Different morphologies obtained via this synthesis method indicate the fact that microwave has high potential for the synthesis of different zinc oxide nanostructures.

However, the microwave-assisted synthesis of zinc oxide nanostructures is extremely extensive field of study and many works have been conducted in this regard. However, there are still various vague aspects that could be a basis for future researches; determining a certain mechanism for the synthesis of zinc oxide nanoparticles using the microwave is one of these areas. In different microwave-assisted synthesis methods, various mechanisms are set for synthesis, that in some cases the proposed mechanisms are in conflict with one another.67,106,256 Determining the correct mechanism in the microwave-assisted synthesis of ZnO nanoparticles with different morphologies, size and desired structures can be useful. Moreover, the factors affecting the synthesis of zinc oxide nanoparticles (pH, time, the effect of calcination, and temperature) are among the other issues to be considered. Although these factors are studied in various articles, the effective factors on zinc oxide nanoparticles synthesis are not completely investigated yet. The importance of these investigations lies in the recognition of these factors during the synthesis of the nanoparticles. They can be controlled, and thus nanoparticles with desired morphology, size, and structure can be achieved. Another topic that is proper to conduct extensive researches in the synthesis of zinc oxide nanoparticles is to use the microwave with ultrasonic waves. There are some articles in this regard in which the microwave and ultrasonic waves are used for the synthesis of nanoparticles.319,320 Applying this method in the synthesis of zinc oxide nanoparticles can improve the properties of the synthesized nanoparticles and enhance their performance.57 Another method for the synthesis of zinc oxide nanoparticles is microwave plasma. This method, which is used in limited articles is for the controlled synthesis of ZnO nanostructures.321–323 In this method synthesis methods in the gas phase, microwave, and plasma technologies are combined to synthesize the desired nanoparticles.57

Another point considered in the synthesis of ZnO nanostructures with microwave is the mass production using this method. To produce large quantities of materials at the nanoscale using microwave, usually the microwave-assisted continuous synthesis is used. In this method, the obtained nanopowder has high purity and it is also consistent in terms of structure. Applying batch reactors is the most widely used method for the microwave-assisted synthesis of nanoparticles; however, this method has some disadvantages including heterogeneous distribution of reactants and temperature inside the reactor, inadequate mixing, differences in physical and chemical properties of the obtained products from different batches, inherent discontinuity, difficulty of mass production and the frequent need for purification after synthesis.57

Zinc oxide nanoparticles have wide and various applications. Some of the applications of zinc oxide nanoparticles include field effect transistor,324 UV detector,325,326 gas sensors,327,328 biosensors,329,330 LEDs,331,332 solar cells,333,334 field emission,335,336 and food applications.337,338

Upon the applications of zinc oxide nanoparticles, it should be noted that these nanoparticles are not only
used in single forms. These nanoparticles are synthesized as nanocomposites, core-shell or doped ZnO and are applied in many applications including photocatalysts, supercapacitors, water treatment, gas sensors and Li-ion battery anodes. For example, many studies are conducted on zinc oxide nanocomposites synthesis with graphene. More research on the synthesis of nanocomposites using the microwave and the analysis of its affecting factors can help the development of these functional nanocomposites. Among other nanocomposites synthesized by microwave method is the zinc oxide-CNT nanocomposites and nano ZnO-TiO2. Further research on the synthesis of these nanocomposites could be beneficial in the use of these nanocomposites.

Synthesis of core-shell ZnO nanoparticles, is among the other subjects that should be considered; and there is only a single report in this regard. In this paper, hollow ZnO nanoparticles are synthesized by microwave and hydrothermal methods. Zinc oxide nanoparticles can be synthesized with other materials such as graphene, CuO, Au, Cu, NiO, Co, CeO2 and B2O3, with the aid of microwave. Zinc oxide nanoparticles, which doped other nanoparticles, have numerous applications. These nanoparticles, which are also synthesized by microwave-assisted method, are among other research areas with high potentials in the microwave-assisted synthesis of zinc oxide nanoparticles.

The synthesis of zinc oxide nanoparticles with hierarchical structures using microwave method is another research field. Previously, the ZnO nanoparticles with this structure were synthesized by microwave. Since the zinc oxide nanoparticles with this structure are used in lithium batteries, gas sensors, and also are applied to the superhydrophobic surfaces and electrohydrodynamically deposited coatings, it seems that more attention to microwave-assisted synthesis of zinc oxide nanoparticles is worthy of attention.

Zinc oxide single crystallites have applications such as light-induced water splitting and gas sensors. So far, Ni-doped ZnO single crystallites have not been synthesized using microwave and, thus, this could be new field of research regarding the possibility of the research on the microwave-assisted synthesis of single crystallites.

Synthesis of Amorphous zinc oxide nanostructures is among the other cases considered in the microwave-assisted synthesis. According to some articles, the nanostructures obtained during microwave-assisted synthesis are partially amorphous. However, the objective of these studies is the synthesis of crystallite zinc oxide and there is no determined method for the microwave-assisted synthesis of amorphous zinc oxide nanostructure. Finally, it

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**Figure 48.** Conceptual diagram related to the possible areas for development and expansion of future research in the field of microwave heating.
should be noted that the microwave is also used for growth of nanoparticle arrays on seed layers. Previously, microwave-assisted synthesis of nanoparticle arrays on seed layers was mentioned as one of the appropriate fields of research using microwave synthesis.

The proposed areas used in the microwave-assisted synthesis of zinc oxide nanoparticles are summarized in

**References**


183. J. Ungula, and B. F. Dejene. Effect of solvent medium on the structural, morphological and optical properties of...


268. A. Cifuentes, J. L. Bernal, and J. C. Diez-Masa. Determination of critical micelle concentration values using


353. M. M. Ismail, W. Q. Cao, and M. D. Humadi. Synthesis and optical properties of Au/ZnO core–shell nanorods


