Chapter 1

ZnO Nanostructures Synthesized by Chemical Solutions

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Abstract

Nanomaterials have been synthesized using several different techniques. Some of these techniques are sophisticated, expensive and need certain training before use. However, there are other highly efficient methods for preparing nanomaterials that are easy to work with and require no specialized equipment, making them relatively inexpensive routes for synthesis. The least expensive routes are those that are classified as solution-based techniques such as colloidal, sol-gel and microwave-assisted synthesis. The focus of this chapter is on a general description of each technique with recent advances in synthesis, doping processes and applications. Specifically, these processes are discussed in connection with the synthesis of ZnO compounds and its related nanomaterials.

Keywords: ZnO, synthesis, chemical solutions, nanostructures

1. Introduction

An important II–VI semiconductor is ZnO which has been well-studied and applied in a variety of applications. It has a band gap of 3.6 eV and large exciton binding energy of 60 meV. Nowadays this material is considered as one of the most important large band gap semiconductors due to its easy synthesis, stability at room temperature, eco-friendly properties, being a direct band gap material and fast mobility. This material exists in three different crystal phases such as zinc blende, cubic or rock salt and wurtzite or hexagonal. The first two phases are obtained only in certain well-controlled conditions such as certain pressures and...
on specific substrates. However, the most common phase under ambient conditions is the wurtzite hexagonal crystal structure shown in Figure 1.

Another advantage of this compound is that it can be synthesized and deposited by employing different techniques. Slight variation in process conditions can result in different product morphologies and properties. Since the costs associated with research and industry is always an important consideration, it becomes necessary to use inexpensive and efficient methods to obtain the desired novel nanostructured materials with applications in different fields such as optoelectronics, solar cells, piezoelectric and sometimes in biological materials.

Sol-gel, colloidal solution and microwave-assisted synthesis are techniques that are still important in the synthesis of semiconductor nanomaterials. These techniques share some similar characteristics such as (i) they are relatively inexpensive; (ii) the efficiency of the synthesized materials is high; (iii) process parameters are easily controlled and (iv) these techniques are also well-studied. For these reasons, in this chapter we have focused on a review of these techniques, especially for the synthesis of ZnO, with emphasis on the recent advances in the synthesis of novel nanomaterials and its applications. A general overview of each process is also presented for ease of readability. The synthesized materials have been structurally characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Figure 2 shows a representative XRD pattern of ZnO. XRD patterns of synthesized material can be compared to reference patterns to determine phase purity or if there is preferential crystal orientation. Most of the time, ZnO is obtained as a polycrystalline film or powder which can be identified by its numerous diffraction peaks at relative intensities. Depending on the processing conditions, single crystal or preferential growth can occur.

Figure 1. Representation of ZnO wurtzite crystal structure (black and grey balls corresponds to Zn and Oxygen atoms).
in thin films that result in different relative peak intensities or missing peaks compared to the reference pattern. The 2-theta values of the (100), (002) and (101) lines in Figure 2 of the hexagonal crystal planes are located at 31.77°, 34.42° and 36.25° for wurtzite ZnO (Ref. JCPDS card # 36-1451).

Different processing parameters may result in different microscopic product morphologies of ZnO. From SEM, we can observe that this material could be obtained as nanoparticles.
(Figure 3), polycrystalline (Figure 4) and as a nanostructured thin film (Figure 5). All of these materials were synthesized under non-extreme conditions using colloidal synthesis to produce the source material. The crystal structure of these materials is the hexagonal wurtzite structure.

Figure 4. SEM image of polycrystalline ZnO thin film obtained through vacuum evaporation process, colloidal nanoparticles as source were used. The scale bar is 500 nm.

Figure 5. SEM ZnO nanostructures using colloidal nanoparticles as source. The scale bar is 500 nm.
2. Some techniques for synthesizing ZnO nanostructures and nanoparticles

2.1. Sol-gel

The sol-gel process encompasses a variety of precursors, solvents and additives. But in general, the basis of the sol-gel process includes some form of hydrolysis and condensation reactions. In the case of ZnO, usually a zinc salt such as zinc acetate is used with water or an alcohol as the solvent. An example of possible hydrolysis and condensation reactions for ZnO are shown in Eqs. (1) and (2), where Zn(OR)₂ is a soluble salt.

\[ \text{Zn} (\text{OR})_2 \cdot \text{H} \text{₂O} \rightarrow \text{Zn(OH)}_2 + 2\text{R} \]

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

During the hydrolysis reaction, the soluble zinc precursor forms a zinc hydroxide intermediate that is able to condense with other intermediates to grow a zinc oxide inorganic polymer. The final product after drying has an amorphous structure and crystallization of ZnO particles require an annealing step. The morphology of the inorganic network can range from spherical nanoparticles to percolated gels and is highly dependent on the choice of precursors, water content, solute and solvent ratio, aging and additives. The sol-gel process has proven to be an inexpensive and relatively simple method of ZnO nanoparticle synthesis that is tailorable to produce unique nanostructures for different applications.

2.2. Colloidal solution

Colloidal synthesis is another well-known chemical solution method to obtain novel nanomaterials with different morphologies and sizes. All processing conditions involved in the system can be fixed to control nucleation and growth of the materials. The kind of interactions (physical and chemical) between particles include Vander Waals, electrostatic, Ostwald ripening and some other theoretical principles such as Derjaguin, Landau, Venvey and Overbeek theory (DLVO). These interactions can contribute to agglomeration and subsequently precipitation of the particles. Colloidal instability can be prevented through steric stabilization which usually requires a surfactant to maintain the colloidal suspension. Surfactants work in two ways: first, to prevent particulate interactions and second, to prevent the continuous nucleation and growth of particles.

2.3. Microwave-assisted synthesis

Microwave-assisted synthesis is a relatively recent technique that has been used for synthesis of nanomaterials. It has been considered as a promising approach to obtain novel nanomaterials in organic and inorganic fields. Additionally, microwave synthesis is considered as a green process and coheres perfectly to the principles formulated by Anastas et al. related to green chemistry [1].

Often a domestic microwave is used and the synthesis is carried out in solvent-free solutions. This technique allows for rapid and homogeneous heating of the system since energy is transmitted directly through molecular vibrations. The short heating ramp time of microwave synthesis allows for better control of particle size distribution compared to conventional
heating. On the contrary, the extremely high heating rate of microwave-assisted synthesis may cause the boiling point of the solution to increase by a few degree Celsius. Additionally, the microwave susceptibility will vary between different materials and temperatures.

The microwave energy is generated by a magnetron that transforms electrical energy into a strong magnetic field. The electromagnetic energy interacts with the solution, vibrating the molecules and giving sufficient activation energy to the system for chemical reactions to take place in seconds or minutes.

The reaction rate during microwave synthesis can be explained through the Arrhenius equation [Eq. (3)] as follows:

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

(3)

where \( K \) is the rate constant, \( T \) is the absolute temperature (in Kelvin), \( A \) is the pre-exponential factor, a constant for each chemical reaction that defines the rate due to frequency of collisions in the correct orientation, \( \Delta G \) is the activation energy for the reaction (in Joules) and \( R \) is the universal gas constant. Thus, the two parameters affecting the kinetics of a particular chemical reaction are temperature and activation energy.

Bilecka et al. reported that nanoparticle growth can be described using four thermodynamic parameters related to the Arrhenius equation through activation energy [2]. These variables are the activation energies for precursor solvation, monomer formation, nucleation and crystal growth. As with colloidal synthesis, nucleation and growth in microwave synthesis are governed by Ostwald ripening.

3. Synthesis of ZnO nanostructures and nanoparticles via chemical solutions: recent advances

Sol-gel, colloidal and microwave-assisted synthesis are effective techniques to efficiently obtain novel ZnO nanostructures. These techniques are relatively inexpensive and do not require sophisticated laboratory equipment. Additionally, slight variations in precursors or process parameters can produce different morphologies that can be applied in different technological fields.

3.1. Process, materials and precursors

The precursors used in these synthesis routes usually start with a basic salt of Zn, a solvent and a catalyser such as temperature. The Zn precursor must be soluble in the selected solvent such that it can provide the necessary Zn ions to produce ZnO particles. Other reagents may be added in order to substitutionally dope ZnO with metal cations such as Fe, Cu, Co and Ba. Additionally, surfactants may be added to maintain colloidal stability of the product or influence the morphology of the growing particles.

Different precursors used in sol-gel and colloidal techniques from recent publications have been summarized in Tables 1 and 2, respectively. The readers are asked to consult the relevant publications for details of these processes.
| Precursor                        | Solvent                  | Stabilizing agent          | Reference                        | Technique |
|---------------------------------|--------------------------|----------------------------|----------------------------------|-----------|
| Zn(CH$_3$OO)$_2$ 2H$_2$O        | CH$_3$OH, C$_2$H$_5$OH, C$_3$H$_7$OH, CH$_3$OH, C$_2$H$_5$OH | (CH$_3$CH$_2$OH)$_2$NH, N(CH$_3$CH$_2$OH)$_2$ | Pourshaban et al. [3] | Sol-gel   |
| Zn(CH$_3$COO)$_2$ 2H$_2$O/CuCl  | 2-methoxyethanol         | (CH$_2$(OH)CH$_2$-NH$_2$)  | Joshi et al. [4]                 | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, Ba(NO$_3$)$_2$ | 2-methoxyethanol     | (CH$_2$(OH)CH$_2$NH$_2$/DEA | Kasar et al. [5]                 | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, (NH$_2$)$_3$Fe(NO$_3$)$_2$ | Distilled water/ethylene glycol | –                           | Bahari et al. [7]                | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, Mn(CH$_3$COO)$_2$ 4H$_2$O | Isopropyl alcohol       | Urea                        | Kumar et al. [6]                 | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, C$_2$H$_5$LiO$_2$ | C$_2$H$_5$OH             | (CH$_2$(OH)CH$_2$-NH$_2$)  | Boudjouan et al. [8]             | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, CaCl$_2$ | CH$_3$OH, C$_2$H$_5$OH   | –                           | Slama et al. [9]                 | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, (CH$_3$COO)$_2$Co 4H$_2$O | CH$_3$OH     | Monoethanolamine (CH$_2$(OH)CH$_2$-NH$_2$) | Dhruvash et al. [10] | Sol-gel   |
| Zn(CH$_3$COO)$_2$ 2H$_2$O       | C$_2$H$_5$OH             | –                           | Singh et al. [21]                | Sol-gel   |
| Zn(CH$_3$COO)$_2$ 2H$_2$O/KOH   | CH$_3$OH                 | –                           | Kim et al. [22]                  | Sol-gel   |
| Zn(CH$_3$COO)$_2$ 2H$_2$O       | 2-methoxyethanol         | (CH$_2$(OH)CH$_2$-NH$_2$)  | Tabassum et al. [11]             | Sol-gel   |
| Zn(CH$_3$COO)$_2$ 2H$_2$O/Al(NO$_3$)$_3$ 9H$_2$O/AgNO$_3$ | C$_2$H$_5$OH | Diethanolamine (DEA)      | Khan et al [12]                  | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, NaCl  | CH$_3$OCH$_2$CH$_3$OH    | (CH$_2$(OH)CH$_2$-NH$_2$)  | Zhou et al. [30]                 | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O       | Isopropyl alcohol        | (CH$_2$(OH)CH$_2$-NH$_2$)  | Chebil et al. [23]               | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, Cu(CH$_3$COO)$_2$ | ...... | Diethanolamine (DEA)      | Agarwal et al. [14]              | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O       | 2-methoxyethanol         | (CH$_2$(OH)CH$_2$-NH$_2$)  | Haarindraprasad et al. [24]      | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O       | Dimethyl formamide       | Diethanolamine (DEA)      | Bhunia et al. [25]               | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, C$_2$H$_5$NO$_2$ | Distilled water/glacial acetic acid | –                           | Para et al. [26]                 | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, Ga(NO$_3$)$_3$ xH$_2$O | 2-methoxyethanol | (CH$_2$(OH)CH$_2$-NH$_2$)  | Wang et al [27]                  | Sol-gel   |
| [Zn(CH$_3$OO)$_2$ 2H$_2$O]      | 2-methoxyethanol         | (CH$_2$(OH)CH$_2$-NH$_2$)  | Alfaro et al. [28]               | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, LiOH, graphene | C$_2$H$_5$OH/EtOH       | –                           | Li et al. [29]                   | Sol-gel   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, Mg(CH$_3$COO)$_2$ 4H$_2$O, Al(NO$_3$)$_3$ | Isopropyl alcohol | Diethanolamine (DEA)      | Das et al. [13]                  | Sol-gel   |
| Precursor | Solvent | Stabilizing agent | Reference | Technique |
|-----------|---------|-------------------|-----------|-----------|
| Zn(CH₃OO)₂2H₂O | 1-butanol | (CH₂(OH)₂CH₂-NH₂) | Demes et al. [31] | Sol-gel |
| Zn(CH₃OO)₂2H₂O, SnCl₂2H₂O | Ethanol and chelating with glycerin | Acetic acid | Kose et al. [32] | Sol-gel |
| Zn(CH₃OO)₂2H₂O, Li(CH₃COO)₂2H₂O, Co(CH₃COO)₂2H₂O | (C₆H₅OH) | (C₆H₆O₂) | Bashir et al. [15] | Sol-gel |
| Zn(CH₃OO)₂2H₂O | Ethanol (C₂H₅OH) | (CH₂(OH)₂CH₂-NH₂) | Ayana et al. [33] | Sol-gel |
| Zn(CH₃OO)₂2H₂O, Li(CH₃COO)₂2H₂O, Co(CH₃COO)₂2H₂O | Ethanol (C₂H₅OH) | (CH₂(OH)₂CH₂-NH₂) | Wang et al. [16] | Sol-gel |
| Zn(CH₃OO)₂2H₂O, NaOH | 2-Propanol | – | Zimmermann et al. [34] | Sol-gel |
| Zn(CH₃OO)₂2H₂O | Acetone | TEA | Efafi et al. [35] | Sol-gel |
| Zinc nitrate hexa hydrate/Na-CMC | Deionized water | PEG-6000 | Liu et al. [37] | Sol-gel |
| Zn(NO₃)₂6H₂O/Bi(NO₃)₃5H₂O, NaOH | Deionized water | – | Rabbani et al. [39] | Sol-gel |
| Ti(OCH(CH₃)₃)₄, Zn(CH₃COO)₂2H₂O | Isopropyl alcohol | – | Boro et al. [38] | Sol-gel |
| Zn(CH₃COO)₂2H₂O, NH₄VO₃ | CH₃OH/MeOH | – | Slama et al. [17] | Sol-gel |
| ZnCl₂, FeCl₃, NH₄Ac, Zn(CH₃OO)₂2H₂O | C₂H₅O₂ | Isopropyl alcohol | Marimuthu et al. [40] | Sol-gel |
| (Zn(CH₃COO)₂2H₂O)/TiO₂ | Isopropyl alcohol | (CH₂(OH)₂CH₂-NH₂) | Birajdar et al. [18] | Sol-gel |
| Zn(CH₃OO)₂2H₂O, Co(NO₃)₂6H₂O | Double distilled water | [C₆H₅O₂, H₂O] | Sivakami et al. [41] | Sol-gel |
| Zn(NO₃)₂ citric acid and tetraethoxysilane | Ethanol (C₂H₅OH) | – | Moradi et al. [42] | Sol-gel |
| Isopropyl orthotitanate (TTIP), zinc nitrate tetrahydrate | Ethanol (C₂H₅OH) | Diethanolamine (DEA) | – | Sol-gel |
| Zn(CH₃OO)₂2H₂O | 2-Methoxyethanol | (CH₂(OH)₂CH₂-NH₂) | Ocaya et al. [43] | Sol-gel |
| Zn(CH₃OO)₂2H₂O, CoCl₂ | Polyvinyl alcohol | – | Verma et al. [19] | Sol-gel |
| [Zn(NO₃)₂6H₂O]/Ga(NO₃)₃ gelatin | Distilled water | – | Khorsand Zak et al. [20] | Sol-gel |
| Zn(CH₃OO)₂2H₂O | Distilled water/ethanol | (CH₂(OH)₂CH₂-NH₂) | Kiani et al. [44] | Sol-gel |

**Table 1.** Precursors and solvents used in the synthesis of ZnO by the sol-gel process.
| Precursor                                      | Solvent                  | Stabilizing agent                                      | Reference                | Technique   |
|-----------------------------------------------|--------------------------|--------------------------------------------------------|--------------------------|-------------|
| Zn(CH$_3$OO)$_2$ 2H$_2$O, sulfo propyl methacrylate, potassium | Ethylene glycol          | –                                                      | Liu et al. [45]          | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O                       | Distilled water          | Poly(vinyl alcohol) (PVA)                              | Nagvenkar et al. [46]    | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, LiOH·H$_2$O           | Ethanol (C$_2$H$_5$OH)   | –                                                      | Yuan et al. [47]         | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, tetraalkylammonium hydroxide | DMSO                     | NEt4OH                                                 | Panasiuk et al. [48]     | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O                       | Ethanol                  | Triethyamine, diethylamine                            | Gupta et al. [49]        | Colloidal   |
| (Zn(NO)$_3$)$_2$·6H$_2$O, NaOH                  | Distilled water          | 1-Thioglycerol (TG) and 2 mercaptoethanol (ME)         | Hodlur et al. [50]       | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O                       | Deionized water          | Hexamethylenetetramine                                | Guo et al. [56]          | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, KOH                  | Methanol                 | –                                                      | Rahman [51]              | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, KOH                  | Methanol                 | PVP                                                   | Gutul et al. [52]        | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, KOH                  | Ethanol                  | 3-aminopropyltriethoxysilane                          | Moghaddam et al. [53]    | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, NaOH                  | Ethyl alcohol            | –                                                      | Liu et al. [54]          | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O                        | Diethylene glycol.       | –                                                      | Xie et al. [60]          | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O                        | Ethanol                  | LiOH                                                   | Verma et al. [61]        | Colloidal   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, NaOH                  | 2-propanol               | –                                                      | Moghaddam et al. [64]    | Microwave   |
| GO, Zn(NO)$_3$·3NaOH                           | Deionized water          | –                                                      | Tian et al. [65]         | Microwave   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, NaOH                  | Distilled water          | Guanidinium carbonate, acetyl acetone,                | Hamedani et al. [66]     | Microwave   |
| Zinc hydroxide                                 | Distilled water          | Cetyltrimethylammonium bromide                         | Rai et al. [67]          | Microwave   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O, NaOH, NH$_2$OH        | Deionized water          | –                                                      | Yanga et al. [69]        | Microwave   |
| (Zn(NO)$_3$)$_2$·6H$_2$O, hydrazine hydrate     | Distilled water          | –                                                      | Krishnakumar et al. [70] | Microwave   |
| ZnSO$_4$·7H$_2$O, GO, NaOH                     | Distilled water          | –                                                      | Lua et al. [71]          | Microwave   |
| Zn(CH$_3$OO)$_2$ 2H$_2$O                        | Deionized water          | –                                                      | Zhu et al. [72]          | Microwave   |
| Precursor                                | Solvent                  | Stabilizing agent | Reference          | Technique |
|-----------------------------------------|--------------------------|-------------------|--------------------|-----------|
| ZnSO₄, NaOH                              | Deionized water          | –                 | Liu et al. [73]    | Microwave |
| Zn(NO₃)₂                                 | Deionized water          | –                 | Rassaeia et al. [74] | Microwave |
| Zinc oxide, ammonium hydroxide          | Deionized water          | –                 | Lu et al. [75]     | Microwave |
| ZnSO₄, NaOH                              | Deionized water          | –                 | Limaye et al. [76] | Microwave |
| Zinc acetylacetonate monohydrate        | Water                    | Ethoxyethanol, ethoxyethanol, and n-butoxyethanol | Schneider et al. [77] | Microwave |

**Table 2.** Precursors and solvents used in the synthesis of ZnO by colloidal/microwave synthesis.
3.2. Recent studies and applications

Various morphologies of ZnO can be obtained from the sol-gel process including nanorods [3], inhomogeneous films [4, 5], inhomogeneous nanoparticles [6] and nanocomposites [7].

The structural effects of cation doping on ZnO nanoparticles was investigated in several studies. When doped with lithium, it was found that the concentration of Li+ ion substitution for Zn2+ directly affected the XRD intensity of the (002) plane, but did not affect the grain size or crystallinity of the nanoparticles [8]. When ZnO was doped with Ca2+ ions, the average particle size was increased to 40–90 nm which could be attributed to the larger ionic radius of Ca2+ that substituted for Zn2+ ion sites [9]. Likewise, the average grain size reduced when a small radius ion is substituted for Zn2+ (0.74 Å) in the hexagonal wurtzite structure such as Co2+ (0.58 Å) [10]. Doping with Al3+ ions also showed the same tendency in reducing particle size, however, impurity phases such as Al2O3 and ZnAl2O4 were also observed [11]. Additionally, co-doping of ZnO with Ag+ and Al3+ ions showed the formation of crystal defects due to the difference in ionic radius between Ag+, Al3+ and Zn2+. Crystallinity improved proportionally with increased Ag+ doping concentration, however, lattice defects and dislocations increased with Al3+ substitution [12]. Further dopant studies also demonstrated that limited dopant precursor solubility provoked a random distribution of dopant throughout the product [13]. Most research about doping ZnO has resulted in improved optical and electrical properties due to improved morphology or intrinsic material properties [14–20].

Synthesis of ZnO of different morphologies without doping is also important to consider since product morphology alone can affect device properties. Without any dopant ZnO can be obtained under normal laboratory conditions with well-aligned nanorods, agglomerated nanoparticles and inhomogeneous thin films composed of nanoparticles, quantum dots, nano-wires, spheres or nano-cubes [21–44].

Colloidal synthesis technique can be utilized to obtain nanocomposites of ZnO and other materials. Nano-sheets of poly (styrene-methyl methacrylate-sulfopropyl methacrylate potassium)/ZnO nanocomposites were obtained by Liua et al. [45]. Dissolving ZnO in other materials can result in a great combination and co-application of materials such as ZnO/PVA (Polyvinyl alcohol) [46]. The same process was done to produce ZnO/TiO2 multilayer thin films [47]. This technique allows obtaining well size-controlled nanoparticles such as those reported with use of dimethyl sulfoxide, but the author reports that the solvent and post-annealing treatment are also important factors in the crystallization process and average particle size [48].

Several authors have reported that the product morphology can be altered between flakes, hexagons, particles and flower-like morphologies by adding different surfactant material [49]. Agglomeration of ZnO nanoparticles was reduced by adding capping agents to different thiol molecules during synthesis [50]. It was demonstrated that the colloidal stability of nanoparticles can be maintained after dispersion in monoethanolamine (MEA). Also, hybrid structures can be obtained through this method like ZnO-Au reported recently [51]. Dispersion of nanomaterials could also be maintained through an additive such as poly (N-vinylpyrrolidone) which has been shown to maintain colloidal stability for more than a couple of months [52]. In the same way agglomeration of ZnO quantum dots can be prevented through a capping
agent such as 3-aminopropyltriethoxysilane in order to maintain their quantum properties [53]. Stabilization of the colloidal particles ensures that particle size and shape does not change with time allowing for more repetitive results for each batch of material. Stable colloidal solutions have also been used to grow novel nanostructures on several kinds of unique substrates such as wood that can allow for new ecological applications in future [54–63].

Colloidal and sol-gel processing are both chemical techniques that can be used to easily obtain different nanomaterials; similarly, microwave-assisted synthesis can obtain similar products but has been explored very little. In microwave-assisted synthesis, most reactions take place in a short amount of time and have resulted in the synthesis of good ZnO nanostructures. The technique has obtained spherical nanoparticles that are stable in solution for up to 50 days, and can be deposited several times on a substrate without any change in its morphology. Similarly, it is possible to obtain composites such as ZnO-nanoparticles on reduced graphene oxide. Also, the morphology is highly dependent on the complexing agent where the reaction takes place or if a dopant is added, such as that reported for obtaining ZnO nanoflowers, nanorods and nanoparticles. Additionally, a research group has confirmed the formation of flower-like to rod-like nanostructures by changing the system temperature. Other works have also reported about dumbbell-shaped nanoparticles, nano-flowers, graphene-ZnO nanocomposites, straw-bundle, chrysanthemum and nanorod-based microspheres obtained under certain temperature conditions. [2, 64–78].

4. Conclusions and future directions

The techniques listed in the above paragraphs remain as the most important chemical solution-based routes to synthesize ZnO. Within the same processing method, a variety of material morphologies and properties can be obtained by subtle changes in temperature, additives, dopants or other parameters. There has been a wide range of organic and inorganic particles that have been synthesized and applied in different fields through these techniques. Investigating the effects of processing conditions on ZnO nanoparticles is still a hot topic in current research for their applications in optoelectronic and solar cell devices.

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