

ASPECTS REGARDING SYNTHESIS AND APPLICATIONS OF ZnO NANOMATERIALS

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Abstract: Zinc oxide (ZnO) is a promising material which gained increasing interest in recent years owing to its preparation methods and remarkable performances. The paper presents the most common techniques for the synthesis of ZnO nanoparticles, such as mechanochemical process, precipitation, sol-gel method, solvothermal and hydrothermal processes. Due to their optical, mechanical, chemical and electrical properties, ZnO offers the possibility to be used in different technological domains, as well as the future outlooks for application of these materials.

Key words: zinc oxide, synthesis, applications.

1. Introduction

In the past decades, the field of nanomaterials and the adjacent researches was constantly in high expansion due to the experience and the capitalization of accumulated knowledge. A large variety of nanomaterials have attracted more attention due to their desirable properties and the possibility to use in innovative technology applications [22].

It is well known that the sizes, phases and morphologies of the nanomaterials have a great influence on their properties and technological applications. Therefore, many research efforts have focused on the control of phases size and dimensionality of nanomaterials [25]. Among different nanomaterials, zinc oxide (ZnO) is a versatile material with unique properties which are suitable for a wide range of technological applications such as solar

cells, transparent conducting electrodes, ultraviolet and blue light emitting diodes, laser diodes, thin film transistor, surface acoustic wave (SAW) devices, gas sensors, photocatalysts and so on [5], [9], [39].

In particular, ZnO is one of the most important binary II-VI semiconductor compounds with a natural n-type electrical conductivity, a direct energy wide band gap of 3.37 eV at room temperature, and a large exciton binding energy (60 meV) [4], [46], [48]. ZnO is a promising material due to its unique capacity to form different types of nanostructures such as nanowires [16], [41], [46], nanorods [12], nanotubes [44], nanobelts [41], nanorings [23], nanospheres [47], nanoflowers [11] and other complex morphologies [40].

Due to its vast industrial applications, ZnO powder has attracting considerable attention being used as additive in ceramics, glass, cement, paints, pigments,

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coatings, cosmetics and medicated creams [8], [21], [33].

Several novel and effective synthesis methods have been described in the literature for preparing of ZnO nanomaterial with various shapes and excellent properties, such as mechanochemical processing [1], precipitation [17], [18], [27], [39], sol-gel method [28], [31], [34], solvothermal method [30], [42], hydrothermal processing [2], [24] spray pyrolysis [16], thermal decomposition of organic precursors [26], chemical vapor deposition [6]. A selection of these methods and properties of the obtained ZnO nanoparticles is described in Table 1.

2. Synthesis of Zinc Oxide Nanomaterials

Synthesis of zinc oxide in the nanometric range for different applications has been a challenging domain during the last years.

The most important processes for the synthesis include careful choice of the concentration of the reactants, pH, temperature, environmental conditions.

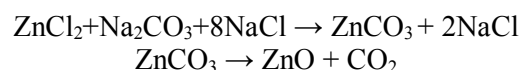
The following sections briefly review the most important synthesis techniques.

2.1. Mechanochemical Method

This method doesn't involve organic solvents for controlling the nucleation and growth of nanoparticles, being attractive from the environmental point of view. It involves high-energy dry milling which initiates a reaction through ball-powder impacts in a ball mill, at low temperature.

A solid "diluent" (NaCl), is added to the system, which acts as a reaction medium and separates the formed nanoparticles.

Aghababazadeh et al. [1] propose as reagents anhydrous ZnCl₂ and Na₂CO₃ powders and NaCl as a reaction medium and for separation of the nanoparticles. The zinc oxide precursor ZnCO₃ formed is calcined at the temperatures between 400 °C and 800 °C. The reactions involved in this process are:



Synthesis and properties of ZnO

Table 1

Method	Precursors	Properties	References
Mechanochemical	ZnCl ₂ , Na ₂ CO ₃ , NaCl	Hexagonal structures	[1]
Precipitation	ZnSO ₄ , NaOH	Hexagonal wurtzite structure	[18]
	Zn(NO ₃) ₂ , (NH ₄) ₂ CO ₃	Wurtzite structure	[27]
	Zn(CH ₃ COO) ₂ , NaOH	Hexagonal structure, flower shape	[17]
	ZnCl ₂ , NH ₄ OH, CTAB (cetyl trimethylammonium bromide)	Zincite structure; Particle size: 54-60 nm	[24]
Sol-gel	Zn(CH ₃ COO) ₂ , PVP, NaOH, PVP (polyvinylpyrrolidone)	Hexagonal wurtzite structure	[33]
	C ₁₆ H ₃₀ O ₄ Zn, TMAH (tetramethylammonium)	Particle size: 20-50 nm	[28]
	Zn(CH ₃ COO) ₂ , acid oxalic, ethanol	Hexagonal wurtzite structure	[31]
Hydrothermal	Zn(CH ₃ COO) ₂ , methanol, NaOH	Hexagonal wurtzite structure	[2]
	Zn(NO ₃) ₂ , HMT C ₆ H ₁₂ N ₄	Wurtzite structure	[24]
Solvothermal	Zn(CH ₃ COO) ₂ , PVP, ethanol, NaOH	Hexagonal structure	[42]
	ZnSO ₄ , NaOH, Na ₂ CO ₃ , stearic acid	Hexagonal wurtzite structure	[30]

Carrying out the process at a temperature of 400 °C ZnO nanoparticles with an average particle size of 51 nm and a surface area of 23.28 m²/g were obtained. ZnO with a hexagonal structure was obtained by others researchers [3], [36], working with the same reagents, but the calcination temperature varying between 400 °C and 800 °C. For the samples with heat treatment at 400 °C, the crystal size is about 18 nm, but with increasing the heat temperature the ZnO nanocrystalline size is higher, reaching 36 nm at 800 °C. The results show that the size of ZnO nanoparticles depends on milling time and calcination temperature [7], [36].

The advantages of this method are the low production costs, small particle sizes and limited tendency for particles to agglomerate, as well as the high homogeneity of the crystalline structure and morphology [37].

2.2. Precipitation Method

This method is widely used to obtain zinc oxide with repeatable properties. The method consists on a spontaneous reduction of an aqueous solution of a zinc salt (ZnSO₄, Zn(NO₃)₂, Zn(CH₃COO)₂) with a reducing agent, followed by precipitation of the precursor of ZnO from the solution and the thermal treatment [14]. This process is controlled by different parameters such as solution concentration, pH, reaction temperature, time of precipitation and washing medium [29].

A controlled precipitation method was used by Kumar et al. [16], having as reagents zinc sulphate (ZnSO₄) and NaOH. These solutions were mixed under vigorous stirring for 12 h. The precipitate obtained was filtered and washed with deionized water, then dried in oven at 100 °C and calcined in air at temperatures ranging from 300 to 900 °C for 2 h.

Raoufi et al. [26] used as raw materials in the experiments zinc nitrate Zn(NO₃)₂ and ammonium carbonate (NH₄)₂CO₃ in aqueous solutions. The precipitate obtained was collected by filtration and repeatedly washed with deionized water and ethanol, then dried in an oven at 100 °C for 6 h. The ZnO nanoparticles were synthesized by annealing of precursor at temperatures ranging from 250 to 550 °C for 4 h.

In the precipitation process also were used surfactants to control the growth of particles and to prevent coagulation and flocculation of the particles.

Microcrystals of ZnO with various shapes were synthesized from Zn(NO₃)₂·6H₂O and NaOH by Li et al. [20] in the presence of the surfactant sodium dodecyl sulfate (SDS). The presence of the surfactant influenced both the shape and size of the ZnO.

Wang Y., et al. [39] obtained ZnO nanoparticles from ZnCl₂ and NH₄OH in the presence of cationic surfactant CTAB (cetyltrimethyl-ammonium bromide). The resulting ZnO powder was annealed at 500 °C to remove residues of surfactants. Highly crystalline ZnO with a wurtzite structure and spherical nanoparticles of 50 nm was obtained.

The precipitation method is an unsophisticated, high quality, relatively low cost method with high manufacture yield.

2.3. Sol-Gel Method

The obtaining of ZnO nanoparticles by sol-gel method is interesting due to its simplicity and relatively mild conditions of synthesis. This method also enables to modify the surface of ZnO by using some organic compounds and, as consequence, changing the properties and extending its domain of applications. Suwanboon et al. [34] prepared nanocrystalline ZnO powder by sol-gel method from zinc acetate dihydrate Zn(CH₃COO)₂·2H₂O, polyvinyl

pyrrolidone (PVP) and NaOH. The precipitate obtained was dried at 60 °C and calcined at 600 °C in air for 1 h.

The XRD characterization indicates a wurtzite or hexagonal structure with small average crystallites of about 45 nm. The morphology was modified from platelet-like to rod shape when adding PVP into solution.

The sol-gel method was also used by Sharma to obtain zinc oxide nanoparticles with good antibacterial activity [31]. The raw materials used for the synthesis were zinc acetate, oxalic acid and water. The white gel precipitate obtained was heated first at 87 °C for 5 h, and then at 600 °C for 2 h.

Ristic et al. [28] obtained nanocrystalline ZnO powders, using zinc 2-ethylhexanoate dissolved in 2-propanol and an aqueous strong alkaline solution of tetramethylammonium (TMAH). The colloidal suspension was aged for 30 min and washed with ethanol and distilled water, then dried at 60 °C. ZnO particles with sizes of the order of 20-50 nm have been obtained.

Sol-gel method offers several advantages comparing to the previous mentioned methods, e.g. low cost of the apparatus and raw materials, reproducibility and flexibility of forming nanoparticles [32].

2.4. Hydrothermal Method

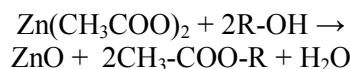
The hydrothermal method is a simple and environmentally friendly technique, which takes place in an autoclave at a programmable temperature and reaction time. A hydrothermal process was proposed by Aneesh et al. [2], using as reagents $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, NaOH and methanol. The reagents were heated gradually at 100-300 °C for several days, followed by cooling, when crystal nuclei were formed. The resulting solid product was washed with methanol, filtered and dried at 60 °C. The process is followed by the formation of nanoparticles with hexagonal wurtzite structure. The particles

size increases with increasing temperature and concentration of the precursors.

The hydrothermal method has many advantages over other processes: it is free of organic solvents and did not need any additional grinding and calcination of the products. This process assures an easy control of the particle size, high degree of crystallinity, different morphologies by adjusting the reaction conditions and high purity of the obtained material [2], [24].

2.5. Solvothermal Method

The solvothermal technique was applied for the synthesis of different nanosized metal oxides with large surface area, high crystallinity and high thermal stability [35], [42]. The method is based on thermal decomposition of an organometallic compound in organic solvent. A solvothermal method was proposed by Yiamsawas et al. [34], using as solvent ethanol and as precursors $\text{Zn}(\text{CH}_3\text{COO})_2$, PVP poly(vinylpyrrolidone), and NaOH. The reaction mixture was stirred for several minutes and heated in autoclave at 80 °C for 24 h. The white powder was precipitated, washed with alcohol and dried at 60 °C overnight. The process involved the following reaction:



Segovia et al. [30] obtained different morphologies of ZnO nanostructures (nanoneedles, nanorods and nanowires) by controlling the solvothermal reaction conditions. The chemicals reagents used were ZnSO_4 , NaOH, Na_2CO_3 , stearic acid and ethanol-water as solvents. The precursor ZnO was synthesized by mixing the solutions of ZnSO_4 , Na_2CO_3 and NaOH at 60 °C under stirring. The white suspension obtained was separated and washed with distilled water.

For obtaining various nanostructures, the precursor ZnO in ethanol-water was autoclaved at the same temperature (180 °C) for 72-186 h, varying some reaction conditions. Nanoneedles were obtained when ZnO in water-ethanol was heated in absence of stearic acid; nanorods formed by autoclaving ZnO with additive stearic acid and nanowires were obtained from layered nanocomposite ZnO/stearic acid.

Some major advantages of the solvo-thermal synthesis method are: reactions performed under determined conditions; ZnO nanopowders with various morphologies were obtained by controlling the reaction conditions.

3. Potential Applications

Zinc oxide is considered a special material, due to its chemical and physical properties. The wide range of properties offers to ZnO the possibility to be used in different technological domains, such as opto-electronics, solar cells and piezo-electric sensors. ZnO also attracted great interest as raw material in pharmaceutical and cosmetic industry, as pigment in paints, concrete and rubber industry, UV filter in products, textile industry and so on.

3.1. Selection of Potential Applications

Opto-electronic industry. ZnO is considered as a potentially attractive material for light-emitting devices in the ultraviolet (UV) region, because of its large exciton binding energy (60 meV).

Due to its direct, wide bandgap of 3.37 eV, ZnO can be used as light-emitting diodes, photodetectors, in sensors, in solar cells and devices emitting a surface acoustic wave [19], [38].

Cosmetic industry. Due to its antibacterial and good antifungal activity, zinc oxide is widely used in production of various raw materials used in medicine

such as disinfectant agents and for dermatological applications [8].

ZnO nanoparticles absorb UV radiation and can be used in sun protective creams [33].

Concrete and rubber industry. Zinc oxide is also used for concrete manufacturing, because by addition of ZnO powder, the processing time and resistance of concrete against water can be improved.

Zinc oxide is known as additive in rubber industry, acting as activator for sulphur vulcanization, by increasing the efficiency of the cross-linking system. Incorporation of zinc oxide filler in silicone rubber improves the mechanical and thermal properties.

Due to the high surface energy, ZnO nanoparticles have tendency to agglomerate and to form particles of large size in the polymer matrix of the coatings [21]. Thus, surface modification of ZnO is necessary to prevent the agglomeration of ZnO nanoparticles and also to ensure the perfect dispersion within rubber matrix [15].

Textile industry. The applications of nanoparticles in textile industry become attractive because provide high durability for treated fabrics due to large surface area and high surface energy that ensure better affinity for fabrics and leads to an increase of the desired textile functions [45].

Many researches shows that the ZnO nanoparticles used in finishing processes improve UV absorption characteristics to the treated materials but also add two functions: an antibacterial activity and self cleaning property [13].

Research regarding the use of zinc oxide in matrix of films of chitosan showed a better antibacterial activity since the decrease of molecular weight of chitosan increases the antibacterial activity. This phenomenon was explained as the decrease of chitosan molecular weight in the composite, which improves the movement of the chains in the solution by decreasing the viscosity [10].

4. Conclusions

Zinc oxide is a multifunctional material, which has the capacity to be obtained in a variety of structures which allow to be used as new material in different domains.

This review presents recent advances on synthesis and potential applications of zinc oxide nanomaterials.

Techniques for preparation of ZnO nanoparticles can be divided into physical and chemical methods depending on properties and desired applications. By using these techniques, the oxide powders can be mixed with other materials (organic or inorganic), improving their chemical, mechanical, electrical and optical properties.

The effectiveness of the surface modification of ZnO nanoparticles is checked by the preparation of nanocomposites containing modified nanoparticles in various polymeric matrix.

Until now, ZnO material covers a wide spectrum of areas of applications in science and industry and still presents greater potential for new applications in sustainable development of human activities.

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