



Solution Phase Synthesis of Three-Dimensional ZnO Hierarchical Nanostructures

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Received: 25.09.2018; Revised: 02.10.2018; Accepted: 15.10.2018

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Abstract: Zinc oxide (ZnO) nanostructures have been studied extensively in the past 20 years for photocatalytic reaction because they determine their applications in various fields. Recently, more attention has been paid to assemble nanoscale building blocks into three-dimensional (3D) complex hierarchical structures, which not only inherit the excellent properties of the single building blocks but also provide potential applications in the bottom-up fabrication of functional devices. This review article focuses on 3D ZnO hierarchical nanostructures, and summarizes major advances in the solution phase synthesis.

Keywords: Zinc oxide • Hierarchical nanostructures • Solution phase synthesis

Introduction

ZnO nanostructures have been studied extensively in the past 20 years for photocatalytic reaction because they determine their applications in various fields. A suitable nanostructure of ZnO will enable higher efficiency of process and enhance the recovery of photocatalyst during post-treatment stage. Various previous studies have been aimed at the production of ZnO with different nanostructures (Meng et al., 2013, Jimenez-Cadena G et al., (2010), Manzoor U and Kim DK 2009). In the past decade, many different strategies have been employed to synthesize ZnO nanomaterials rich in morphologies. These has been varied from (i) zero dimensional quantum dots QDs, (ii) one dimensional nanowires/nanorods, (iii) two dimensional structures such as thin films or (IV) superstructures with complex 3D hierarchical morphology (Kriisa M et al., 2014, Ang JES et al., 2010). Many synthesis techniques are offered to prepare ZnO nanocomposite material which showed dissimilar morphologies: nano-rings,

nano-combs, nano-belts, nano-tubes, nano-rods and nano-sheets (Wei Q et al., 2005). Recently, more attention has been paid to assemble nanoscale building blocks into three-dimensional (3D) complex hierarchical structures, which not only inherit the excellent properties of an individual nanostructure but also generate new properties due to the interactions between the nano building blocks. So far, many synthesis strategies based on physical (physical and chemical vapor deposition, laser ablation, ball milling, lithographic, etc.), chemical (gas phase reaction, various solution phase synthesis), or biological methods have been used to obtain ZnO nanostructures and its nanocomposites. Comparing to other methods, solution phase route shows unique advantages, such as low cost (low in energy consumption and equipment costs), scalability, and ease of handling. Most of the solution phase reactions occur under mild condition with a relatively low temperature

(<200°C). Therefore, solution phase synthesis has attracted increasing interest. Typical solution phase synthesis includes sonochemical method, co-precipitation method, solvothermal and hydrothermal method, sol-gel, microemulsions, electrochemical and chemical bath deposition. This review article focuses on 3D ZnO hierarchical nanostructures and summarizes major advances in the solution phase synthesis.

Solution Phase Synthesis of 3D ZnO Hierarchical Nanostructures

A brief and concise description of solution phase synthesis of 3D ZnO hierarchical nanostructures is as follows:

Sonochemical method: In sonochemical methods, solution of the starting material (for e.g. metallic salts) is subjected to a stream of intensified ultrasonic vibrations which breaks the chemical bonds of the compounds. The ultrasound waves pass through the solution causing alternate compression and relaxation. This leads to acoustic cavitations i.e. formation, growth and implosive collapse of bubbles in the liquid. In addition, the change in pressure creates microscopic bubbles that implode violently leading to emergence of shock waves within the gas phase of the collapsing bubbles. Cumulatively, the effect of millions of bubbles collapsing produces an excessive amount of energy that is released in the solution. Transient temperatures of ~5000 K, pressure of ~1800 atm and cooling rates above 10¹⁰ K/s have been recorded at the localized cavitation implosion hotspots (Suslick KS 1990). The excessively high rate of cooling process is found to affect the formation and crystallization of the obtained products (Gendanken A 2003). This method has been used to synthesize a wide range of nanomaterials as metals, alloys, metal oxides, metal sulfides, metal nitrides, metal polymer composites, metal chalcogenides, metal carbides etc. (Bang JH and Suslick KS 2010). The advantages associated with sonochemical methods include uniform size distribution, a higher surface area, faster reaction

time and improved phase purity of the metal oxide nanoparticles.

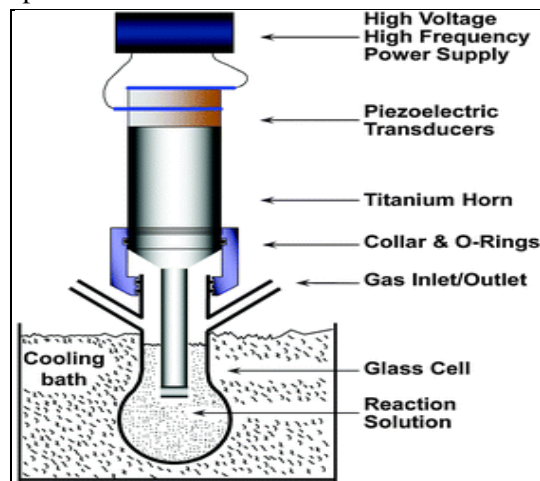


Figure 1 A typical laboratory rig for sonochemical reactions (Hangxun et al., 2013).

Co-precipitation Method: Co-precipitation method involves precipitating the oxo-hydroxide form from a solution of a salt precursor (metal salts like nitrates or chlorides) in a solvent (like water) by using a precipitating medium. Once a critical concentration of species in solution is reached, a short burst of nucleation occurs followed by growth phase. The size and shape of particles is greatly influenced by solution pH, temperature and concentration of salt. After precipitation, filtration and washing is done followed by calcination to convert hydroxide into oxides with a definite crystalline structure. Zinc oxide has also been precipitated from aqueous solutions of zinc chloride, zinc sulphate and zinc acetate (Kołodziejczak-Radzimska A et al., 2010). Controlled parameters in this process included the concentration of the reagents, the rate of addition of substrates, and the reaction temperature. The precipitating medium usually employed includes NaOH, NH₃ or NH₄OH, Na₂CO₃ etc. (Jadhav AP et al., 2009). In process of synthesis of nanopowders based on precipitation, it is increasingly important for surfactants to be used to control the growth of particles. The presence of these compounds affects not only nucleation and particle growth, but also coagulation and flocculation of the particles. The surfactant method involves chelation of the metal



cations of the precursor by surfactants in an aqueous environment. The advantages of this method are low cost, mild reaction conditions like low synthesis temperature, the possibility to perform direct synthesis in water, simplicity of processing, the ease of scale-up, flexibility in modulation of core and surface properties (Mukhtar M et al., 2012, Mascolo MC et al., 2013, Kalantari K et al., 2013, Sadegh H et al., 2014).

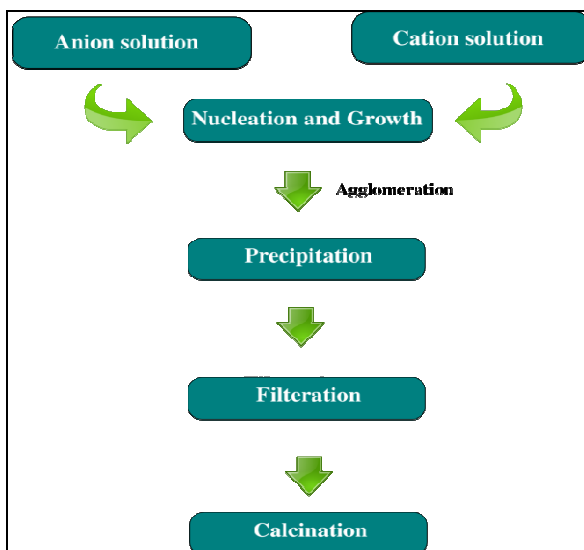


Figure 2 Flow chart of co-precipitation method (adapted from Wikipedia).

Solvothermal and Hydrothermal Method:

Solvothermal method: These methods are employed to prepare a variety of nanomaterials by dispersing the starting material in a suitable solvent and subjecting it to moderately high temperature and pressure conditions which lead to product formation. The synthesis takes place in an autoclave, where the mixture of substrates is heated gradually to a temperature of 100–300°C and left for several days. As a result of heating followed by cooling, crystal nuclei are formed, which then grow. When the reaction is performed using water as the solvent, the method is called hydrothermal synthesis. Chemical parameters (type, composition and concentration of the reactants, ratio-solvent/reducing agent) and thermodynamic parameters (temperature, pressure and reaction time) affect the final particle formation. It was also observed that basicity and hydrolysis ratio of the reacting medium together with the steric

or electrostatic stabilization of the reactive molecules affect the nucleation and growth steps, which in turn control the particle size, shape, composition and crystal structure of particles.

Hydrothermal method: The hydrothermal method does not require the use of organic solvents or additional processing of the product (grinding and calcination), which makes it a simple and environmentally friendly technique. This process has many advantages, including the possibility of carrying out the synthesis at low temperatures, the diverse shapes and dimensions of the resulting crystals depending on the composition of the starting mixture and the process temperature and pressure, the high degree of crystallinity of the product, and the high purity of the material obtained (Djurišić AB 2012, Tsuzuki T 2002). Another advantage of this technique is the use of suitable surfactants that can tune the particle characteristics and limit their agglomeration. Solvothermal methods have successfully been employed to prepare various nanocomposites displaying a combination of the properties of their parent nanoparticles.

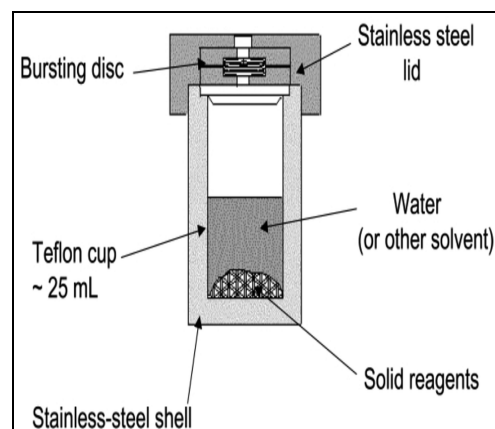


Figure 3 Experimental set up for hydrothermal synthesis (Khan. Latif Ullah ., Khan, Zahid Ullah. 2017).

Sol-gel Method: Sol-gel method gained attention as a promising method for the synthesis of nanomaterials owing to their mild reaction conditions and building up the materials from molecular precursors leading to variation in

materials and properties (Guglielmi M et al., 2014). The resulting product of sol-gel method is either films (Jeon HJ et al., 2003, Lee JH and Park BO 2003) or colloidal powder (Zhang H and Chen G 2009, Chen DH and He XR 2001, Ennas G 1998). The sol-gel method has capability of producing micro and nanostructures. The size, shape and structure of final product are greatly influenced by the reaction parameters (Chiang CL and Ma C.C.M, 2002, Nazir R 2008).

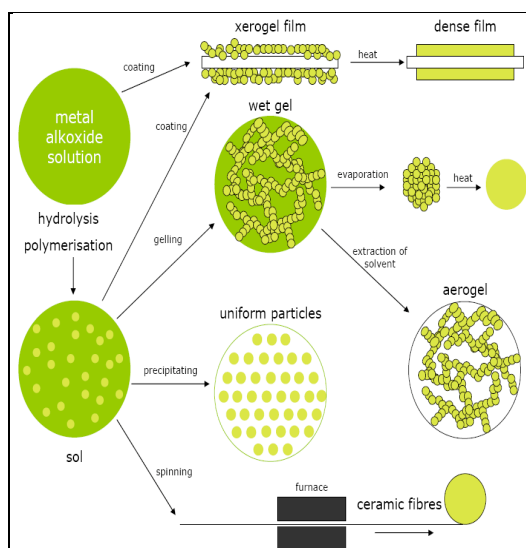


Figure 4 Flow chart of sol-gel synthesis (Cannavale, et al., 2010).

The sol-gel process contains the formation of solid material from a solution by using a sol or a gel as an intermediate step. The synthesis of metal oxide materials often involves controlled hydrolysis and condensation of the alkoxide precursors or salts. The main steps of preparation of metal oxides powder by the sol-gel process: (i) preparation of the precursor solution; (ii) hydrolysis of the molecular precursor and polymerization via successive bimolecular additions of ions, forming oxo-, hydroxyl, or aquabridges; (iii) condensation by dehydration; (iv) solvent evaporation and organic compounds removal to form xerogel; and (v) heat treatment of the xerogel to form powders. Properties of the final products, including the particle size, surface area, crystallinity, and agglomeration, are highly dependent on the reaction parameters, especially the

precursors, solvents, additives, evaporation, drying, and post-treatment conditions. A sol-gel material before the final consolidating treatment is typically amorphous. Its transformation into a crystalline, glassy or nanostructured system depends not only on the nature of the initial system, but also on the conditions chosen for the annealing process (i.e. temperature, heating and cooling rates and reaction atmosphere). It is interesting, cheap, facile and low-temperature technique that allows for the fine control on the product chemical composition, as even small quantities of dopants, such as organic dyes and rare earth metals can be introduced in the sol and end up in the final product finely dispersed. Advantages of this method are low cost, mild reaction conditions like low synthesis temperature, the possibility to perform direct synthesis in water, simplicity of processing, the ease of scale-up, flexibility in modulation of core and surface properties, simplicity of equipment, the ability to accurately control stoichiometry and high homogeneity.

Electrochemical and Chemical Bath Deposition:

Electrochemical deposition (ECD) and chemical bath deposition (CBD) methods are facile and can produce materials or nanostructures that cannot be obtained by other deposition methods. The CBD process only requires suitable solution containers and substrate mounting devices while for the ECD method, additional power supplies, electrodes (counter electrode/CE, reference electrode/RE) are necessary, and the substrate (working electrode/WE) must be conductive

Electrochemical deposition: It is a liquid based deposition process where an electrical current is passed through a polar liquid by applying an electric potential between electrodes. Due to this electrical energy injection, the liquid breaks into ions and other charged compounds and depending on the charge on the ions/compounds and the potential of electrodes these charged material deposit on electrode. Electro deposition offers rigid control of film thickness, uniformity and deposition rate with low equipment cost and starting materials. The material deposition in this process follows Faraday's

law. More importantly, the morphology and orientation of the deposited samples can be tuned by controlling the reaction thermodynamics and kinetics, including solution properties, additives, substrate, temperature, and electrochemical parameters (applied potential, current density, etc.) (Skompska M and Zarebska K 2014, Kumar M and Sasikumar C 2014, Switzer JA and Hodes G 2010, Choi KS et al., 2010, Lincot D (2010), Bhattacharya R 2008). The synthesis of ZnO nanostructures via the ECD process includes the reduction of precursor at the electrode, the super saturation at the vicinity of the electrode, and subsequent precipitation. By carefully controlling the number of charged particles transferred the amount of deposited materials can be controlled. Electro-deposition process is especially very useful in nano fabrication in nanotechnology.

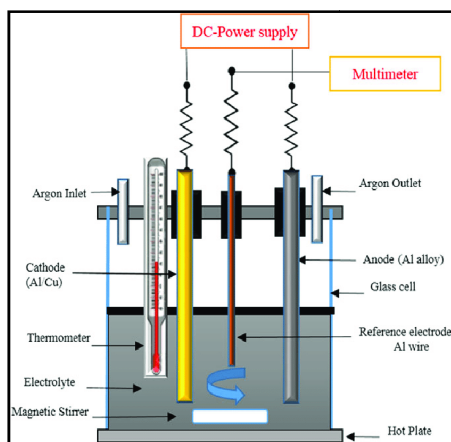


Figure 5 Experimental setup of electro-deposition (Prabu and Wang, 2017).

Chemical Bath Deposition: Synthesis of ZnO nanostructures via chemical bath deposition (CBD) is based on a direct chemical reaction involving dissolved zinc ions and oxygen precursors in the solution. Different from ECD where the deposition only occurs on the conductive substrate, the growth of ZnO in CBD process can take place either in the solution or on the substrate surface. The morphology and assembly of ZnO products can also be controlled by the solution, additives, and so on (Shi Z and Walker AV 2015) Moreover, patterned or flexible ZnO hierarchical nanostructures can be

obtained by applying corresponding substrates (Hodes G 2007).

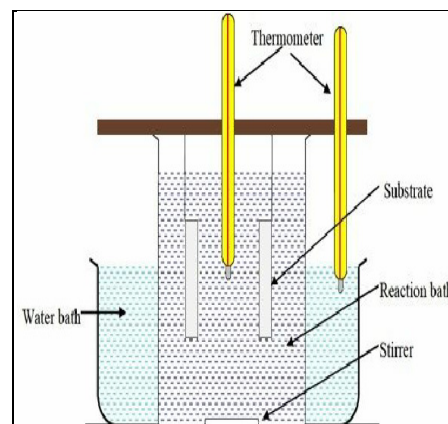


Figure 6 Experimental setup for chemical bath deposition (Zein and Alghoraibi, 2014).

Microwave synthesis: Microwave synthesis is relatively new and an interesting technique for the synthesis of oxide materials. Microwave techniques eliminate the use of high temperature calcination for extended periods of time and allow for fast, reproducible synthesis of crystalline metal oxide nanomaterials. This method has been of increasing interest as it is relatively low energy and time consuming (Baghbanzadeh M et al., 2011). The reaction times are reduced from a few hours to several minutes without compromising the particle purity or size. Faster reaction rates can be achieved by employing high heating rates which favor rapid nucleation and formation of small, highly monodisperse particles. Microwave-assisted methods involve quick and uniform heating of the reaction medium with no temperature gradients through two mechanisms: dipolar polarization and ionic conduction. Utilizing microwave energy for the thermal treatment generally leads to a very fine particle in the nanocrystalline regime because of the shorter synthesis time and a highly focused local heating. Highly crystalline nanoparticles of ZnO have been successfully synthesized using microwave-assisted routes. Automation allows control over the reaction conditions and hence facilitates manipulation of particle size, morphology and crystallinity (Bilecka I et al., 2010). The choice

of starting metal oxides precursors (as acetates, chlorides, isopropyls) and solvents (as ethylene glycol, benzene) can govern reaction success, particle size and crystal structure (Bilecka I et al., 2008).

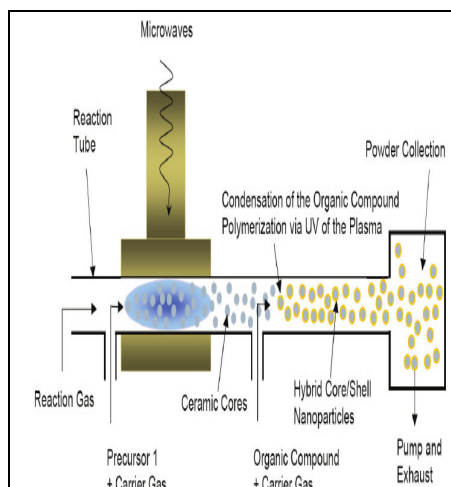


Figure 7 Set-up scheme for the microwave plasma synthesis of hybrid core/shell nanoparticles (Hanemann and Szabó, 2010).

Microemulsion method: This method comprises two immiscible phases (oil and water) which are separated by a monolayer of surfactant molecules forming two binary systems-water/surfactant and oil/surfactant-such that the hydrophobic tails of the surfactant molecules are dissolved in the oil phase and the hydrophilic head groups in the aqueous phase. Broadly the method comprises of mixing appropriate amounts of the surfactant, oil, water and the metallic precursor (for instance, organometallic precursor can be added as a solution in the oily phase) by stirring at room temperature to prepare a homogenized phase (Sanchez-Dominguez M et al., 2009). Reducing/oxidizing/precipitating agents are then added, under vigorous stirring, to enable sedimentation of the nanoparticles. The microemulsions act as nanoreactors for synthesis of the nanoparticles. This is then followed by centrifugation, wash cycles and drying/ calcination. Shape and size can be manipulated in these methods by affecting the various self-assembled structures formed in the binary systems (Solans C et al., 2005). The ability to control the formation of different

kinds of core-shell structures with sub-nanometric resolution is seen as a major benefit of this technique (Stankic S et al., 2005). Additionally, the method also provides the possibility to manipulate size and morphology of nanoparticles by adjusting parameters such as concentration and type of surfactant, the type of continuous phase, the concentration of precursors and molar ratio of water to surfactant. The disadvantage associated with this method involves the necessity of several washing processes and further stabilization treatment due to aggregation of the produced nanoparticles (Wu W et al., 2008). Modifications have been incorporated to overcome these disadvantages. For instance, reverse microemulsion technique has been used to produce monodisperse spherical ZnO nanoparticles. The modification was that ZnO nanoparticles were not directly produced in the microemulsion but by the thermal decomposition of zinc glycerolate microemulsion product during subsequent calcination process (Yildirim OA and Durucan C 2010). The modified technique prevented agglomeration whereas the calcinations temperature and concentration of surfactant could be varied in order to tune the particle size and morphology of the ZnO nanoparticles, respectively.

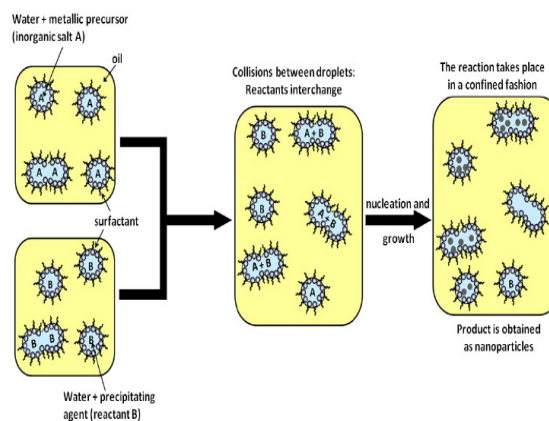


Figure 8 Scheme of the w/o microemulsion reaction method for the synthesis of inorganic nanoparticles.(Sanchez-Dominguez, 2009).

Conclusions

3D ZnO hierarchical nanomaterials possess a high surface area with porous structures, and facilitate



multiple physical and chemical processes. In addition, the hierarchical materials not only inherit the excellent properties of an individual nanostructure but also generate new properties due to the interactions between the nano building blocks. Therefore, 3D ZnO hierarchical nanostructures provide a wide range of applications. This review article summarized the main progress in the synthesis of 3D ZnO hierarchical nanostructures via different solution phase methods, such as sonochemical method, co-precipitation method, solvothermal and hydrothermal method, sol-gel, microemulsions, electrochemical and chemical bath deposition. Although great success has been made on the controllable synthesis of 3D ZnO hierarchical architectures, there is still room for improvement in terms of quality and scale of the products. Moreover, new synthesis methods also provide opportunities to explore novel morphology and to understand the formation mechanism of the nanostructures.

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