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Controlled Synthesis of One Dimensional Zinc Oxide Nanostructures in terms of Modelling

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ABSTRACT

In the present work, a mathematical model is proposed for the control on the concentration of hydroxyl ion in the precursor solution to preserve low super saturation level, because in order to obtain the desired and high quality one dimensional Zinc oxide nanostructures it is important to control the super saturation of the reactants. It was observed that elevated super saturation amount support nucleation and moderate super saturation amount support crystal growth during the synthesis of one dimensional Zinc oxide nanostructures. The kinematic reactions in the precursor solution were observed with the help of Lengyel-Epistein theory. Experimentally, the synthesis of ZnO nanostructures was also performed through Aqueous chemical growth method.

1. INTRODUCTION

Nanotechnology has brought the new insights of the materials. Nanomaterials are divided into three classes such as 0, 1 and 2-dimensional nanostructures. 0-dimensional nanostructure, are generally known as quantum dots or nanoparticles (1nm–100nm) having an aspect ratio close to unity. These are utilized very heavily in variety of industrial/biological applications [1,2]. 1-dimensional semiconductor nanostructures such as nanowires, nanofibers, nanotubes and nanorods have also been utilized in variety of applications [3,4]. The nanotubes have also been investigated not only in academic research

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but in industrial applications too due to their enormous capability as building blocks for other structures. 2-dimensional nano materials also showed their promise in different applications like optical coatings, corrosion protection, and semiconductor thin films devices [3,5].

Zinc oxide (ZnO) is regarded as most commonly studied material in last four to five decades. More importantly since the start of nano era it is in the spotlight of every researcher due to its magnificent structures, properties and applications. ZnO has numerous applications due to its unique properties. It has produced tremendous results in the fields such as optoelectronics, sensors, biomedical sciences, electronics and photonic crystals. Recently, photo catalytic ability of ZnO nanowires has gained lot of interest in environment protection applications. Among all materials ZnO no doubt holds the huge variety of nanostructures in terms of structure and properties. The vast application is based on the large number of morphologies that this material adopts by means of different fabrication condition into nanowire, nanotubes, nanorods, nanoribbons, nanoneedles, nanocable etc. ZnO is a semi-conductor material having direct wide band gap (3.37eV), high refractive index which is higher than 2 and a sizeable exciton binding energy (60eV) at room temperature [3]. In past few years several growth techniques have been used for the synthesis of ZnO and variety of ZnO nanostructures were synthesized by utilizing various approaches [3]. These methods include sol-gel [6] electrochemical deposition [7-8] chemical vapor transport and condensation [9-10] Metal organic chemical vapor deposition [11] thermal evaporation [12] ion beam-assisted deposition [13-14] laser ablation [15] sputter deposition [16] and hydrothermal method [17]. All these methods produce good quality nanostructure with different morphology. Hydrothermal synthesis is a robust and economical method and has an edge on other methods, because it is less time consuming, low growth temperature (<100˚C), environment friendly, simple equipment unlike the other method mention. Due to these properties of hydrothermal method was used for large scale production of ZnO [18]. The salts include Zinc nitrate hexahydrate$(ZnNO_3)_2.6H_2O$, Zinc acetate $Zn(CH_3COO)_2.2H_2O$ and Zinc chloride $Zncl_2$ that are generally used for the synthesis. Among these, three salts Zinc nitrate hexahydrate is considered as the most commonly used salt. Zinc chloride is normally favored in electrodeposition technique. Zinc acetate dihydrate, which is a preferred salt for the synthesis of ZnO nanowires is very rarely utilized as a Zinc source as far as hydrothermal method is concerned [17,19]. In this work Zinc nitrate hexahydrate $(ZnNO_3)_2.6H_2O$ salt is considered as a source of Zinc ion (Zn^{+2}) and Hexamethylenetetramine ($C_6H_{12}N_4$) as the source of hydroxyl ions (OH^-) to show the growth of one dimensional ZnO nanostructures that is nanowires in this case [20].

Now it is an established fact that experimental study is always costly and time consuming as well. Therefore, Mathematical modeling and simulations can pave a smart way in this regard. Mathematical modeling is regarded as a process or a way of representation to observe the nature or behavior of the system with the help of mathematical formulas. Mathematical model also plays a crucial part in the analysis of the system which other models

like physical, chemical, linguistics etc. can't do. They can help us to understand the physical behavior of the system. Simulations on models rather experiments on actual system is an economical way for measurements in saving time and cost. Beside this the control on parameters also allows us to predict the future natures which haven't been possible in experiments. The belief that the results obtained through mathematical model and simulations can be verified by experiments is the base of such kind of studies. As far as author's knowledge is concerned no study based on Mathematical modeling and simulations has yet to publish to see the control on concentration of OH^- ions in the precursor solution during the synthesis of ZnO nanowires in the super saturation level. The results obtained through experiment and through simulation were compared for validation of study.

2. EXPERIMENTAL METHODOLOGY

The synthesis process was performed in clean room environment in order to avoid any contamination and influence of impurities. For the quality synthesis of ZnO nanostructures the use of smooth and contamination free substrate is very important. In current work gold coated glass substrate was utilized. The Aqueous Chemical Growth (ACG) method was employed to synthesize ZnO nanostructures. Initially, the substrate was immersed into a beaker containing the solution of low concentrated hydrofluoric acid. After few minutes, it was washed with acetone and dried under the flow of nitrogen gas at room temperature. As seed solution Zinc acetate dihydrate was spin coated on the gold coated glass substrate three times at 3800 rpm. Then the substrate was lightly heated at around 95°C for 3-4 minutes in order to obtain good adhesion of the seed particles on substrate's surface.

The preparation of precursor solution was performed by taking equi-molar concentration (1:1) of hexamethylenetetramine and Zinc nitrate hexahydrate and both were dissolved in 275 ml deionized (DI) water with the help of magnetic stirrer.

Afterwards the substrate was dipped into the precursor solution contained beaker. Finally, the beaker was placed into a pre-heated oven at 95°C. After 6 hours the oven was turned off and left for 30-40 minutes to cool down. Then the sample was washed with DI-water and dried through flow of nitrogen [21-22].

The main reason for constructing models is to make predictions, which leads to scientific understanding of the chemical reaction and physical approach. To make more accurate predictions, more of the reactions would have to be integrate to this model. Since this model is based on Lengyel-Epstein [23] model therefore assumed that certain chemical concentration does not change. For this purpose, several assumptions have been made. MATLAB was used for the simulation of the Lengyel-Epstein model to obtain results. The obtained result has a close consistency with the previous published report.

In order to obtain the control on the synthesis of one dimensional ZnO nanowires, it is very important to understand the process of decomposition of Hexamethylenetetramine

and Zinc nitrate during the synthesis process of ZnO nanowires. Synthesis process of ZnO nanowires can be represented by the following chemical reaction. All the reactions are in equilibrium state and can be controlled by balancing the reaction parameter, such as synthesis temperature, synthesis time, and precursor concentration in the saturation level. In general, the precursor concentration determines forward and backward equilibrium reaction [24].

Hydrothermal decomposition of hexamethylenetetramine for obtaining $(\boldsymbol{OH^-})$.

$$\frac{1}{4}(CH_2)_6N_4 + \frac{3}{2}H_2O \longrightarrow \frac{3}{2}HCHO + NH_3$$

Hydroxyl (OH^-) supply reaction.

$$\frac{1}{2}NH_3 + \frac{1}{2}H_2O \longrightarrow \frac{1}{2}NH_4{}^+ + \frac{1}{2}OH^-$$

Decomposition of Zinc nitrate for obtaining Zn^{+2} from metal salt.

$$\frac{1}{4}(ZnNO_3)_2 \,.\, 6H_2O + \frac{3}{2}H_2O \rightarrow \frac{1}{4}Zn^{+2} + \frac{1}{2}NO_3{}^-$$

Supersaturation reaction.

$$\frac{1}{4}OH^- + \frac{1}{4}Zn^{+2} \longrightarrow \frac{1}{4}Zn(OH)_2$$

Synthesis reaction of ZnO nanowires.

$$\frac{1}{4}Zn(OH)_2 \longrightarrow \frac{1}{4}ZnO_{(s)} + \frac{1}{4}H_2O$$

During the synthesis of ZnO nanowires, the concentration of Zinc ion and hydroxyl ion can be determined through mathematical model by using Lengyel-Epstein reaction [23]. In the presented work Lengyel-Epstein reaction was used to form the new model equation. During the growth of ZnO nanowires one of the important parameters is to control the super saturation of the reactants. It is observed that elevated super saturation amount support nucleation and moderate super saturation amount support crystal growth during the synthesis of Zinc oxide nanowires [5]. Because of high pH environment if plenty of OH^- is generated in a very short interval of time, then Zn^{+2} would come up with little amount to the ZnO nanowires synthesis. Due to the very fast utilization of the nutrient further synthesis of ZnO nanowires will stopped [24]. It is therefore the concentration of OH^- that should be controlled in the super saturation level in order to obtain the better synthesis of ZnO nanowires. Ordinary differential equation (ODE) was used for the analysis of the concentration of OH^-.

$$\frac{1}{2}NH_3 + \frac{1}{2}H_2O \longrightarrow \frac{1}{2}NH_4{}^+ + \frac{1}{2}OH^-$$

$$\frac{1}{4}Zn(OH)_2 \longrightarrow \frac{1}{4}ZnO_{(s)} + \frac{1}{4}H_2O$$

In the present mathematical model, the concentration of OH^- and Zn^{+2} can be represented by X and Y respectively. In this mathematical model two ODE's were used to determine the rate of change of OH^- and Zn^{+2} as equation of concentration. The rate of

change of the concentration was determined from the experiment of the growth process of ZnO nanowires.

The ODE's based on the method proposed by Chicone [25] are given as equations (1) and (9).

$$\frac{dX}{dt} = \frac{4m_1[(CH_2)_6N_4]}{m_2+[NH_3]} - 4m_3[Zn^{+2}]X - 2m_4[OH]\frac{XY}{\rho+X^2} \quad (1)$$

$$\frac{dX}{dt} = C_1 - C_2X - 2C_3\frac{XY}{\rho+X^2} \quad (2)$$

Where C_1, C_2 and C_3 are the positive parameters.

To obtain a comprehensive mathematical model it is mandatory to make the variable dimensionless as shown below in equation (3).

$$X = \sqrt{\rho}x \qquad Y = \frac{\rho c_2}{c_3}y \qquad t = \frac{\tau}{c_2} \quad (3)$$

where τ is the parameter that is denoting the time of the concentration of $(CH_2)_6N_4)$ and $Zn(NO_3)_2$

$$v_1 = \frac{C_1}{\sqrt{\rho}\,C_2} \qquad v_2 = \frac{C_3}{\sqrt{\rho}\,C_2} \qquad C_1 = v_1\sqrt{\rho}C_2 \quad (4)$$

v_1 and v_2 are the two lumped (dimensionless) parameters.

Substituting equation (3) and equation (4) in equation (2)

$$\frac{d\sqrt{\rho}x}{d\frac{\tau}{C_2}} = v_1\sqrt{\rho}\,C_2 - C_2\sqrt{\rho}x - \frac{2C_3\left(\sqrt{\rho}x\frac{\rho C_2}{C_3}y\right)}{\rho+\left(\sqrt{\rho}x\right)^2} \quad (5)$$

$$C_2\sqrt{\rho}\frac{dx}{d\tau} = v_1\sqrt{\rho}\,C_2 - C_2\sqrt{\rho}x - \frac{2C_3\left(\sqrt{\rho}x\frac{\rho C_2}{C_3}y\right)}{\rho(1+x^2)} \quad (6)$$

Taking out $\sqrt{\rho}\,C_2$ as common

$$C_2\rho\frac{dx}{d\tau} = C_2\sqrt{\rho}\left(v_1 - x - \frac{xy}{1+x^2}\right). \quad (7)$$

After cancelling out the common factor equation (7) will becomes

$$\frac{dx}{d\tau} = v_1 - x - \frac{xy}{1+x^2} \quad (8)$$

$$\frac{dY}{dt} = m_3[Zn^{+2}]X - m_4[OH^{-1}]\frac{XY}{\rho+X^2} \quad (9)$$

$$\frac{dY}{dt} = C_2X - C_3\frac{XY}{\rho+X^2} \quad (10)$$

$$\frac{d\left(\rho\frac{C_2}{C_3}y\right)}{d\left(\frac{\tau}{C_2}\right)} = C_2\sqrt{\rho}\,x - C_3\frac{\sqrt{\rho}x\frac{C_2}{C_3}y}{\rho(1+x^2)} \quad (11)$$

$$\left(\frac{\rho{C_2}^2}{C_3}\right)\frac{dy}{d\tau} = C_2\sqrt{\rho}\left(x - \frac{xy}{1+x^2}\right) \quad (12)$$

$$\frac{dy}{d\tau} = \frac{C_3C_2\sqrt{\rho}}{\rho\,{C_2}^2}x\left(1 - \frac{y}{1+x^2}\right) \quad (13)$$

After cancelling out the common factor equation (13) becomes

$$\frac{dy}{d\tau} = v_2 x\left(1 - \frac{y}{1+x^2}\right) \tag{14}$$

According to Lengyel-Epstein model [8] the dimensionless equations are represented by equation (15)

$$\frac{dx}{d\tau} = v_1 - x - \frac{xy}{1+x^2} \quad ; \quad \frac{dy}{d\tau} = v_2 x\left(1 - \frac{y}{1+x^2}\right) \tag{15}$$

Considering the first order differential equation of the form

$$\frac{dx}{dt} = vx \tag{16}$$

which we know has a solution of the form $x(t) = c_1 e^{vt}$

By using first principle (ab-initio differentiation) method

$$x'(t) = \lim_{h\to 0} \frac{x(t+h)-x(t)}{h}, \tag{17}$$

$$x'(t) = \frac{dx(t)}{dt},$$

$$\frac{d}{dt}x(t) = \lim_{h\to 0} \frac{x(t+h)-x(t)}{h}. \tag{18}$$

To approximate differential equation (16) at some fixed value of h, equation (18) can be represented as $vx(t) \cong \frac{x(t+h)-x(t)}{h}$. It can be written as

$$x(t+h) \cong x(t) + hvx(t). \tag{19}$$

If we know the solution of the dependent variable x at any time 't', it is possible to imprecise the value of x at any time t + h using equation (19).

To start we have fixed the time step size h and we know the value of the unknown (dependent variable) solution x of our differential equation initially at time t = 0 that is $x(0) = x_0$ for some number x_0 the approximation of x at time t + h is

$$x(h) \cong x(0) + hvx(0).$$

The approximate value is obtained by performing the successive iteration of the equation after n steps at $t_n = t_{n-1} + h$ we get

$$x_{n+1} = x_n + h\left(v_1 - x_n - \frac{4x_n y_n}{1+{x_n}^2}\right), \tag{20}$$

$$y_{n+1} = y_n + hv_2 x_n \left(1 - \frac{y_n}{1+{x_n}^2}\right). \tag{21}$$

This equation also depends on the parameter v_1 and v_2. Due to which at least two possible behaviors predicted by Lengyel-Epstein model [23] that is oscillating concentration and steady-state concentration. If the variation of a parameter changes the qualitative behavior of the steady-states, then it is called Hopf bifurcation [26]. By qualitative mean number of steady-state and stability of the steady-states. Changes in either of these two will portrait both the phases. Therefore, bifurcation in a sense is change in phase portrait of the system with change in a parameter if $v_2 = \frac{3v_1}{5} - \frac{25}{v_1}$. The steady-state concentration is obtained if $v_2 > \frac{3v_1}{5} - \frac{25}{v_1}$ whereas oscillating concentrations will arise if $v_2 < \frac{3v_1}{5} - \frac{25}{v_1}$.

From the experiment it was observed that the concentration of OH^- *and* Zn^{+2} showed steady-state nature which shows that the concentration OH^- does not change after a certain period of time which indicates that no further reaction occurs after this time period.

3. RESULT AND DISCUSSION

The experimental results of ZnO nanostructures shown in Figure 1 were obtained through ACG method. Figure 1(a) is revealing the synthesized ZnO nanorods, whereas Figure 1(b) is showing the image of grown ZnO nanowires which were obtained by changing pH of the precursor solution. 25% ammonia solution was added drop by drop in order to obtain the desired change. It is clear from the images that grown ZnO nanostructures have hexagonal face and perpendicular to c-axis direction as well. This indicates that the experimental work has been performed with lot of care and all the parameters were in precise control.

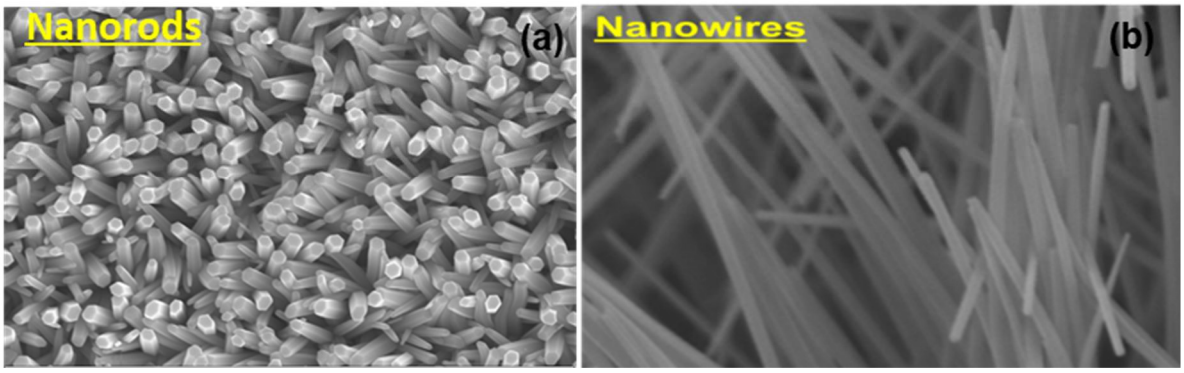

Figure 1. FESEM images of synthesized ZnO nanostructures.

The Figure 2 is revealing the concentration of Zn^{+2} and OH^- ions obtained through experiment. It can be seen from Figure 2(a) that at first the Zn^{+2} ions concentration increased briskly which could be associated to change in temperature that is from room temperature to 95°C as discussed in detail in experimental set up. Once the oven has been shut off after six-hours precursor solution starts to cool down gradually and that initiates the exponential decay in Zn^{+2} ions concentration. Finally, the concentration of Zn^{+2} ions became saturated. This shows that no further chemical reaction took place between positive and negative ions. The exponential decay in the concentration of Zn^{+2} ions reveals that Zn^{+2} ions were reduced due to its chemical reaction with OH^- ions in order to form solid ZnO. Figure 2(b) is highlighting the identical kind of concentration behavior for the OH^- ions. Exponential rise in the concentration of OH ions is a result of chemical reaction among the OH^- ions. Whereas during the synthesis of ZnO nanowires chemical reaction of OH^- ions with Zn^{+2} ions caused the exponential decay in the OH concentration. The linearity of the curve in the end indicates that no further chemical reaction takes place after about 5 hrs.

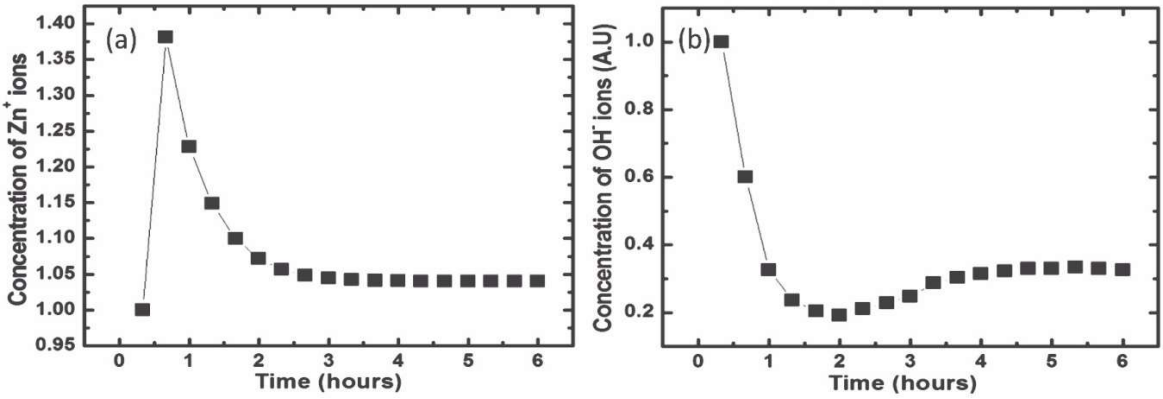

Figure 2. Experimental results of the concentration of Zn^{+2} and OH^{-} ions.

The values v_1 = 1, v_2 = 20 and h = 1/80 for the steady-state concentration zone were given by Chicone [26]. Considering these values along with x(0) = 1, y(0) = 1 as initial values the simulation of Lengyel Epstein model [24] was performed utilizing MATLAB. The results of simulations are shown in Figure 3 for the Zn^{+2} and OH^{-} concentrations. Figure 3 is clearly showing that the simulated behaviors of Zn^{+2} and OH^{-} ions are almost identical in comparison with experimental results of Figure 2. It was also derived from Figure 3 that initially Zn^{+2} ions participated heavily in the chemical reaction because of the rapid variation in the solution. This produced a quick rise in Zn^{+2} ions concentration. On the other hand, the decay in the concentration showed in Figure 3 is highlighting the saturation in the chemical process. The reason for this saturation was the stability of chemical reaction and involvement of Zn^{+2} and OH^{-}ions in the chemical process of synthesis of nanostructures. Finally, it is also important to point out that the more iterations will affect the forecast built by the growth model. The obtained results found to be in good agreement of experimental data with analytical method.

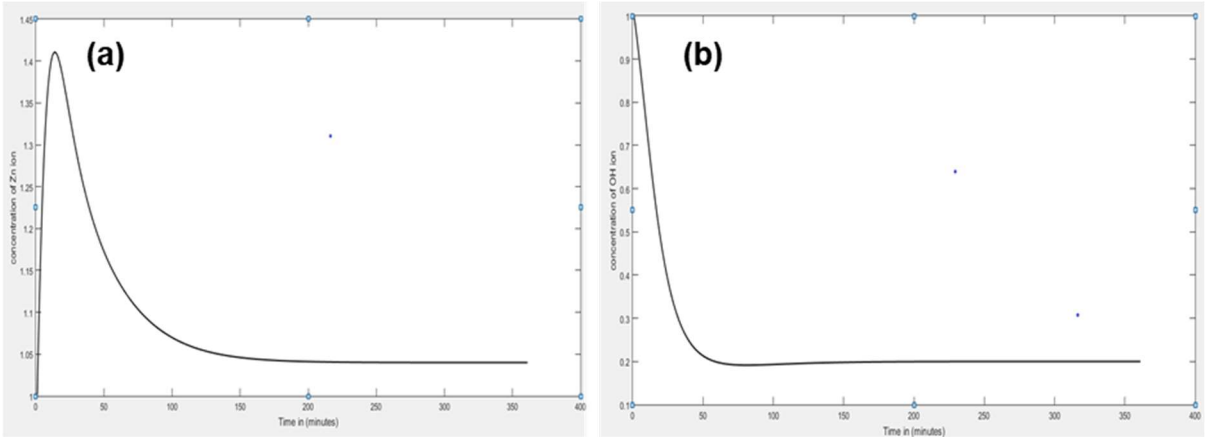

Figure 3. Simulation results showing the concentration of Zn^{+2} and OH^{-} ions.

4. CONCLUSION

This investigation has been performed to propose a mathematical model to predict the controlled synthesis of one dimensional ZnO nanostructures. In this model the used chemical equations were derived from the aqueous chemical growth method and used for the determination of the concentrations of Zn^{+2} and OH^{-} ions. The obtained results of proposed mathematical model were showed good agreement with the results achieved from the experimental investigations. The mathematical model proposed in this study can become a bench mark for achieving the one dimensional ZnO nanostructures of required diameter and length. Beside this by optimizing the simulation of growth parameters, this model will also help to get high quality ZnO nanostructures. Moreover, this study enables the researchers to use this model for achieving the controlled synthesis of other nanostructures as well.

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