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Supersaturation Control Growth of Nanoparticle ZnO and Size Distribution Control†

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Nanoparticle ZnO was synthesized in non-aqueous medium. UV adsorption spectra were measured and effective mass model was used to calculate particle size *in situ*. A technique method named as supersaturation control growth was developed, which dealt with addition of nanoparticle suspension with small size to another suspension with big size. As a result, those small particles completely dissolved and those big ones totally grew because of dissolution degree difference between small particles and the big ones. The particle number of big particle suspension kept being a constant and the growth rate was much higher than Ostwald ripening. Main characteristic of this technique is that size distribution of nanoparticles can be narrowed provided original size difference of two suspension is big enough and original size distribution is not too broad.

Key words: ZnO, Nanoparticle, Distribution, Growth kinetics, Adsorption edge, Band gap

I. INTRODUCTION

Semiconductor ZnO is widely applied in process of photo-electricity displayer, solar cell, photo catalysts [1-5]. Much attention has been paid to the preparation and properties of nanoparticle zinc oxide. When the size of a particle is less than a characteristic length scale of interest, such as the diameter of an exciton or the mean free path of an electron, then the properties of the particle can be significantly different from the bulk material. Such particles can be used as individual elements in a wide range of devices or can be assembled into larger scale structures. Band gap of nanoparticle ZnO increases with the decrease of its size. The average particle size in a nanoparticle ZnO can be obtained from the absorption onset using the effective mass model [6-11] where the band gap E^* (in eV) can be approximated by:

$$E^* = E_g^{\text{bulk}} + \frac{\hbar^2\pi^2}{2r^2}\left(\frac{1}{m_e^* m_0} + \frac{1}{m_\hbar^* m_0}\right) - \frac{1.8\text{e}^2}{4\pi \in\in_0 r} - \frac{0.124\text{e}^4}{\hbar^2(4\pi \in\in_0)^2}\left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0}\right)^{-1} \quad (1)$$

where E_g^{bulk} is the bulk band gap (eV), $\hbar$ is Plank's constant, r is the particle radius, m_e is the electron effective mass, $m_\hbar$ is the hole effective mass, m_0 is free electron mass, e is the charge on the electron, $\in$ is the relative permittivity, and $\in_0$ is the permittivity of free space. The validity of this approach was confirmed from analysis of high-resolution transmission electron microscopy (HRTEM) [12]. Ultraviolet adsorption and fluorescence wavelength of zinc oxide, when used as photo-electricity displayer, depends on ultraviolet absorption onset. Therefore, size and distribution of nanoparticle ZnO influence not only physical properties, such as surface area but also photo properties. Figure 1 shows the band gap and the corresponding absorbance onset plotted as a function of particle radius as predicted by Eq.(1) with m_e=0.26, $m_\hbar$=0.59, $\in$=8.5, and E_g^{bulk}=3.2 eV [6,12,13]. Strong dependence of band gap on particle size can only be found in small size region. Zhang [14] thought that quantum effect of ZnO nanoparticles was marked only in a diameter region less than 10 nm. Therefore, how to control size and distribution of nanoparticle ZnO is very important for its application.

Our previous researches [15-20] indicated that original size of nanoparticle, synthesized in alcohol solution could be as smaller as 3 nm in diameter. Then the size would continuously increase because of Ostwald ripening where small particle would continuously dissolve and the big ones would continuously grow. Much effort, in fact, has been paid to suppress Ostwald ripening. Seo and colleagues suppress Ostwald ripening of nanoparticle ZnO using adsorption of organic stabilizing agent [21]. In previous report we found that Ostwald ripening growth of nanoparticle ZnO could almost be stopped by adsorption of octanethiol [20]. During Ostwald ripening nanoparticles number will decrease so that the distribution of the nanoparticles will be influenced. The size distribution F of nanoparticles suspen-

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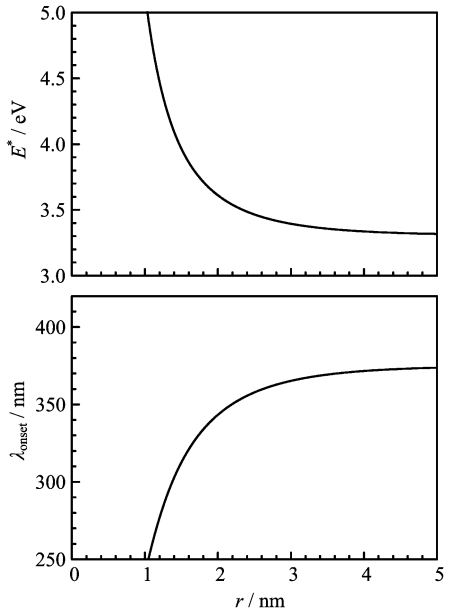

FIG. 1 Band gap, E^* and absorption onset wavelength λ of ZnO quantum particles versus particle radius.

sion can be calculated in terms of an equation below:

$$F = \frac{S_d}{\overline{r}} \tag{2}$$

where S_d is standard deviation of these nanoparticles, $\overline{r}$ is average radius. When F<5% the particles are called as mono-dispersion ones. It is well known that S_d can be calculated by:

$$S_d = \sqrt{\frac{\sum_{i=1}^{n}(r_i - \overline{r})^2}{n}} \tag{3}$$

For a suspension that total volume of ZnO is V_0, following equation can be obtained:

$$F = \sqrt{\frac{4}{3}\pi\overline{r}\frac{\sum_{i=0}^{n}(r_i - \overline{r})^2}{V_0}} \tag{4}$$

If $\sum_{i=0}^{n}(r_i - \overline{r})^2$ in Ostwald ripening is a constant, we can find that particle size distribution F will be proportional to square root of particle size. In other word, the size distribution will be widened due to Ostwald ripening. Therefore, Ostwald ripening generally is disadvantageous to the preparation of nanoparticle. In this research we designed a preparation procedure of nanoparticle ZnO, named as supersaturation control growth where Ostwald ripening was used to narrow the size distribution.

II. EXPERIMENTS

A. Preparation of nanoaprticle ZnO

Homogeneous solution synthesis of ZnO in water generally can not display quantum effect because that the particle size is not small enough. Non-aqueous synthesis of nanoparticle ZnO possesses some advantages, such as small size and controllable distribution to some extent [22-27]. Nanoparticle ZnO in this research was synthesized in 2-propanol (reagent grade). For a typical preparation, 1 mmol of a zinc acetate ($Zn(CH_3CO_2)_2{\cdot}2H_2O$; reagent grade) and 1 mmol of zinc perchlorate hexahydrate ($Zn(ClO_4)_2{\cdot}6H_2O$, reagent grade) was dissolved in 80 mL of 2-propanol in a covered flask under stirring at 50 °C respectively. A 0.02 mol/L NaOH (reagent grade) solution was prepared by adding sodium hydroxide to 2-propanol in a covered flask under vigorous stirring at 60 °C. After cooling to room temperature, 4 mL of the sodium hydroxide solution was added to 10 mL of 2-propanol and 4 mL zinc slat solution was added to 32 mL of 2-propanol. At room temperature (21 °C), the sodium hydroxide solution was then added to the zinc salt solution under stirring to give a total volume of 100 mL with 0.1 mmol zinc salt and 0.16 mmol NaOH. The overall nucleation reaction can be written as:

$$ZnX_2 + 2NaOH = ZnO + 2NaX + H_2O \tag{5}$$

where X refers to $CH_3CO_2^-$ or ClO_4^-. From the overall reaction it is seen that the synthesis is carried out with a 25% excess of Zn(II). Once the addition of the solution Ostwald ripening begins.

B. Supersaturation control growth of nanoparticle ZnO

100 mL of as-prepared nanoparticle ZnO suspension was aged for a given time so that the particle size was big enough. Then the suspension was divided into two parts. The first part was aged under the same conditions. New prepared nanoparticle ZnO (with smaller particle size) was added into the second part of the above suspension, which then was aged under the same conditions. A Shimadzu UV-2101PC was used to recorded ultraviolet adsorption spectra of the nanoparticle ZnO. Particle size of ZnO was calculated with effective mass model [6-11], details of which can be found from our previous works and other scholar's report [15-20,28,29].

III. RESULTS AND DISCUSSION

A. Supersaturation control growth of nanoparticle ZnO

Before and after adding new prepared ZnO particles, UV adsorption spectra of ZnO nanoparticle were recorded and are given in Fig.2. In a short time after

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the addition, original big particles rapidly grew. After that their growth behavior was similar to those particles without adding new prepared ZnO. In Fig.3, new prepared ZnO was added at an aging time of 666, 2271, and 3755 min respectively. It can be seen that total growth rate of the nanoparticles ZnO was much higher than that without adding new prepared ZnO. If new prepared ZnO particle is continuously added, the growth of ZnO particles will be much more rapid than Ostwald repining. We call this method as supersaturation control growth. UV adsorption spectra of nanoparticle ZnO at very beginning of the addition are given in Fig.4. After 2 min of the addition, the spectra displayed features of both big particles and new prepared small particles. Then the characteristic of small ones disappeared. These results mean that all of those new prepared smaller particles dissolved, which promoted the growth of those original big ones. Therefore, the number of those original big particles will not change because that completed dissolution of those small particles will not increase total particle number and total growth of those original big particles will not decrease particle number. A potential application of this technique method is cultivation of single crystal where crystals can grow at a high speed without nucleation of new crystal seeds.

B. The influence of supersaturation control growth on size distribution of nanoparticles

In Ostwald ripening the cost of big particles growth is dissolution of small particles because of their difference of dissolution degree. In other words, particle number will decrease due to Ostwald ripening. In the above supersaturation control growth of nanoparticles, particle number is a constant provided the size difference between added small particles and original big particles is big enough. In this case growth rate of each big particle will be proportional to its surface area:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = CS \tag{6}$$

where V is particle volume, C is a constant related to some factors such as temperature, S is surface area of a particle. It is well known $V=(4/3)\pi r^3$, $S=4\pi r^2$. r is particle radius. So we have:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = 4\pi r^2 \frac{\mathrm{d}r}{\mathrm{d}t} \tag{7}$$

Combination of Eq.(6) and Eq.(7) give:

$$\frac{\mathrm{d}r}{\mathrm{d}t} = C \tag{8}$$

Eq.(8) means that growth rate of particle radius is a constant in supersaturation control growth, which is independent on size of the particles. In other words, original size difference of big particle and so that $\sum_{i=1}^{n}(r_i-\overline{r})^2$ is a constant in supersaturaiton control growth. The distribution of particles size can be calculated as:

$$F = \frac{1}{\overline{r}}\sqrt{\frac{\sum_{i=1}^{n}(r_i-\overline{r})^2}{n}} \tag{9}$$

where particle number n is a constant. The size distribution of nanoparticles can be found to be reversely proportional to particle size while the size distribution in Ostwald ripening growth is proportional to square root of particle size (Eq.(4)). Eq.(9) suggests that the bigger the particle size in supersaturation control growth is, the more narrow the size distribution is. 50 mL of r_1=1.47 nm new prepared ZnO particles was added to 50 mL of r_2=2.23 nm (aged for 2271 min) particles. After aging for another 5 h the other 50 mL of new prepared ZnO was added again. UV adsorption spectrum of as-prepared nanoparticle ZnO after a total aging time of 2888 min is given in Fig.5. The spectrum of nanoparticle ZnO after aging 4965 min and without supersaturation control growth is also given in Fig.5. It can be

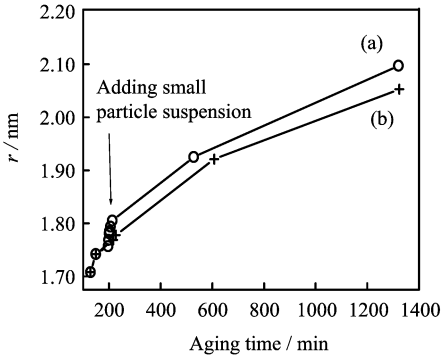

FIG. 2 Influence of supersatuation control growth on ZnO nanoparticle growth speed. ZnO was prepared from $Zn(OAc)_2$ and NaOH at 21 °C, r_1=1.49 nm, r_2=1.96 nm. Addition time: 196 min. (a) With supersatuation control, (b) Without supersatuation control.

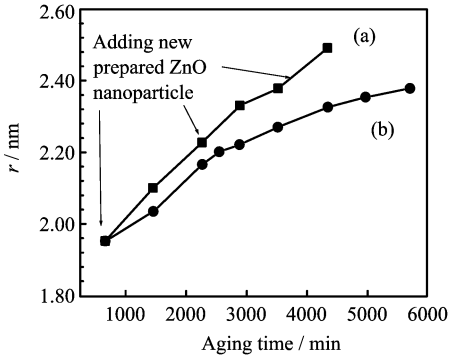

FIG. 3 Effect of mutilple supersatuation control growth on growth rate of ZnO nanoparticle ZnO prepared from $Zn(OAc)_2$ and NaOH at 21 °C, addition time: 666, 2271, and 3755 min. (a) With supersatuation control, (b) Without supersatuation control.

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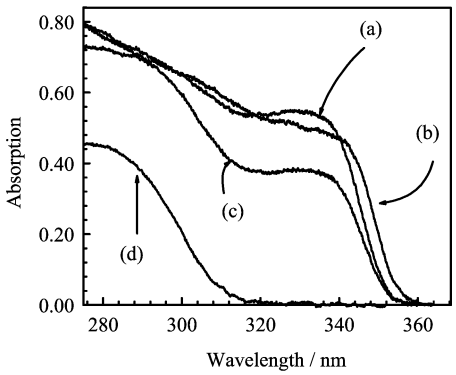

FIG. 4 UV spectra of ZnO suspention in supersatuation control growth. ZnO was prepared form $Zn(OAc)_2$ and NaOH at 21 °C. (a) Original ZnO particle, r_2=2.23 nm, (b) After aging another 624 min, (c) After adding new prepared ZnO for 2 min, (d) New prepared ZnO particle r_1=1.47 nm.

found that both spectra possess closed adsorption edge. In terms of effective mass model, their average particle size is closed. This result means that supersaturation control growth can promote particle grow. Moreover, it can be found from Fig.5 that supersaturation control growth resulted in a steeper spectrum near adsorption edge than Ostwald ripening. Our previous research indicated that the narrower the particle size distribution is, the steeper its UV spectrum near adsorption edge is [29]. Therefore, supersaturation control growth can narrow size distribution of nanoparticles.

C. Condition of supersaturation control growth

50 mL of r_1=1.49 nm and 50 mL of r_2=1.76 nm (aged for 196 min) nanoparticle ZnO was mixed. After aging for another 331.5 min (527.5 min total aging time), UV spectrum was recorded. The spectrum is given in

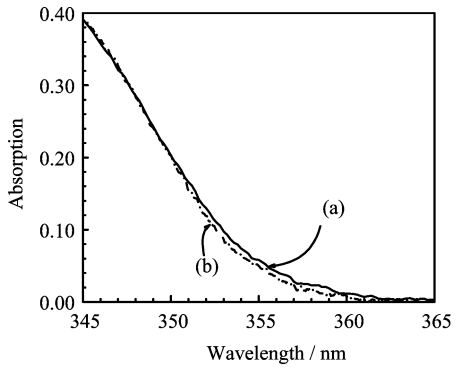

FIG. 5 Effect of supersatuation control growth on ZnO particle distribution prepared form $Zn(OAc)_2$ and NaOH at 21 °C, r_1=1.47 nm, r_2=2.23 nm. (a) Aging for 4965 min without supersaturaiton control, (b) Aging for 2888 min after twice supersaturaiton control.

Fig.6. UV spectrum of nanoparticle ZnO after aging for 608 min and without adding new prepared ZnO is also given in Fig.6. Their wavelength of adsorption edge and the slope of the spectra are almost the same. These results mean that their particle size and size distribution are almost the same. This result suggests that marked size difference is necessary for obtaining distribution narrowing effect. Nanoparticle ZnO was also prepared from zinc perchlorate. The UV adsorption spectra are given in Fig.7. Compared with that of ZnO, prepared from zinc acetate, the spectrum of zinc perchlorate is gentler, which means that the size distribution of the latter is broader. ZnO particles of r_1=1.48 nm and the same amount of ZnO of r_2=1.88 nm was mixed. The UV spectrum after aging for 186 min (392 min total aging time) is given in Fig.8. The UV spectrum after aging for 395 min and without adding new prepared ZnO is also given in Fig.8. Two suspensions give almost the same average particle size. However, the ZnO coming from Ostwald ripening gave a steeper spectrum than the one from supersaturation control growth. This result means that the size distribution of nanoparticle ZnO prepared from supersaturation control growth is broader than that of Ostwald ripening. These results

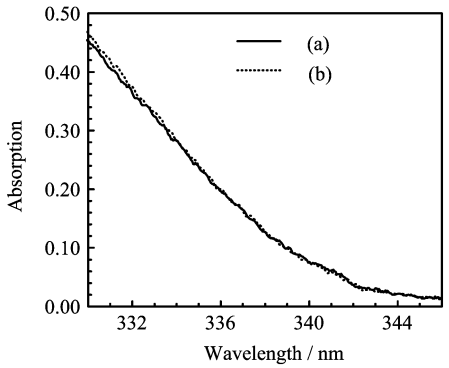

FIG. 6 Effect of supersatuation control growth on distribution of ZnO particle size r_1=1.49 nm, r_2=1.76 nm. (a) With supersatuation control aging for 527.5 min, (b) Without supersatuation control aging for 608 min.

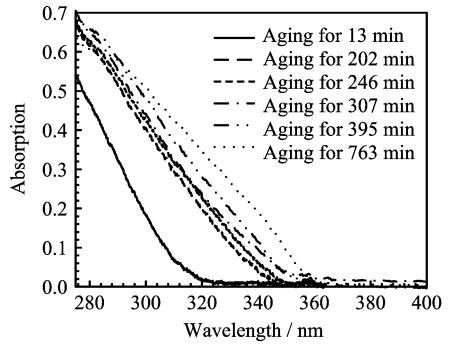

FIG. 7 UV absorbence of nanoparticle ZnO prepared from $Zn(ClO_4)_2$ and NaOH at 21 °C with 1 mmol/L $Zn(ClO_4)_2$ 25% excess.

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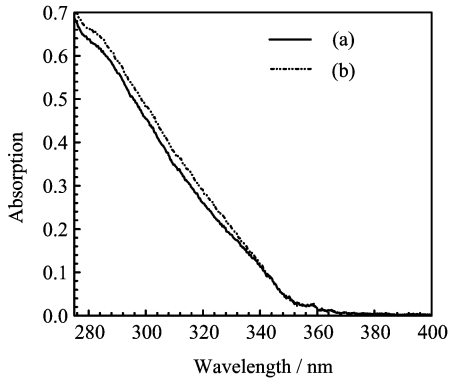

FIG. 8 Comparison of nanoparticle ZnO UV absorbence with and without supersatuation control growth. ZnO was prepared from $Zn(ClO_4)_2$ and NaOH at 21 °C. (a) With supersatuation control aging for 392 min, (b) Without supersatuation control aging for 395 min.

mean that too broad distribution of nanoparticles is disadvantageous to supersaturation control growth. In this case, particle size in two suspensions will partly overlap each other. Those particles, coming from small average size will not completely dissolve and some particles belong to big particle suspension will dissolve too. As a result, total distribution of nanoparticles will be broadened. All of the above results indicate that there exist two basic conditions for supersaturation control growth. The first is that particle size difference of two suspensions should be big enough. The second is that original distributions of two nanoparticle suspension should not be too broad.

IV. CONCLUSION

In solution homogeneous preparation of nanoparticles, supersaturation control growth is used to narrow particle size distribution, which is dealt with addition of small particle suspension to big one suspension. In this case, those small particles will completely dissolve. Those big particles will totally grow with a constant particle number. Main characteristic of this technique method is that size distribution of nanoparticle can be narrowed provided original size difference of two suspension is big enough and original size distribution is not too broad. Therefore, supersaturation control growth can be used to prepare mono-dispersion nanoparticles. The other two advantages of supersaturation control growth are that growth rate of nanoparticle can be much higher than that of Ostwald ripening and particle number will not increase. Therefore, this technique can be used to prepare single crystals.

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