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Synthesis of ZnO Nanostructures via Gel-casting Method

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***Abstract*—**In this study, ZnO nano rods and ZnO ultrafine particles were synthesized by Gel-casting method. The synthesized ZnO powder has a hexagonal zincite structure. The ZnO aggregates with rod-like morphology are typically 1.4 μm in length and 120 nm in diameter, which consist of many small nanocrystals with diameters of 10 nm. Longer wires connected by many hexahedral ZnO nanocrystals were obtained after calcinations at the temperature over 600° C.The crystalline structures and morphologies of the powder have been characterized by X-ray diffraction(XRD) and Scaning electron microscopy (SEM).The result shows that the different preparation conditions such as concentration H2O, calcinations time and calcinations temperature have a lot of influences upon the properties of nano ZnO powders, an increase in the temperature of the calcinations results in an increase of the grain size and also the increase of the calcinations time in high temperature makes the size of the grains bigger. The existences of extra watter prevent nano grains from improving like rod morphology. We have obtained the smallest grain size of ZnO powder by controlling the process conditions. Finally In a suitable condition, a novel nanostructure, namely bi-rod-like ZnO nano rods was found which is different from known ZnO nanostructures.

***Keywords*—**morphology, nano particles, ZnO, gel-Casting method.

I. Introduction

NANO meter - size inorganic dots, tubes and wires exhibit a wide range of electrical and optical properties that depend sensitively on both size and shape [1,2]. Zno is an important electronic and photonic material because of its wids direct band gas of 3.37 eV. Because of the unique quantum confinement effects of nano particles, ZnO nano- particles, with different morphologies have potential wide applications in Varistors [3, 4], gas sensors [5, 6], ceramics [7], electrical and optical devices [8,9]. ZnO is one of the few oxides that show quantum confinement effects in an experimentally accessible size rang [10]. So the synthesis and morphology control of ZnO nano particles has received great attention recently [11, 12]. There are many studies on producing nano powder and there are many methods such as gel call, hydrothermal and chemical settling from the vapor phase [13]. Gel casting process is a new method of gel cell that is used in nano power production to decrease the problems of the previous methods such as the cost. In this method, there are more research possibilities with less cost because of the small number of the process steps and the low cost of the reactants. In this work, the synthesis of ZnO nano particles with rod-like shapes with the gel casting method is studied.

The phase composition, morphology and crystallite size of the obtained ZnO powder were characterize by XRD and SEM, respectively. The research shows that different conditions cause different results, also for the same conditions, using different a mount of the reactants causes a different powder size.

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II. Experimental

In this research, acryl amid monomers and two functional methyl base acryl amid monomers are used to make the pre-mixture. Both of these monomers are soluble in water and therefore the support solvent is not needed. In fact water is a good solvent in this case. The concentration ratio of AM to MBAM in the samples is 10 to 1 and 4 to 1, and the water concentration changes between 20% and 45% of the mixture. The added salt concentration is between 35% and 40% of the mixture. ((NH4)2S2O8) was used as the starter in the mixture. Without the starter, the mixture will not change to gel even at high temperatures. To make a better condition, before using the starter, N tetra methyl ethylene diamine was used 15% to 20% of the mixture, as the catalyst. Then by using 2% ((NH4)2S2O8) starter, with 18.5% to 29% concentration of the mixture, the gel was made in a short time at room temperature. In order to investigate the effect of the pH valve upon the grain size, hydrochloric acid or aqueous ammonia were dropped into the solution to get with different pH values. After that, gel was crushed by mortar and was calcinated at different temperatures in the oven. Finally, the crystallite size of the powder was evaluated from the peak broadening of XRD patterns based on Scherer's formula as follows [14].$D=0.9\lambda/B.\cos\theta$.

In which D in the crystallite size (nm), λ is the wavelength of the monochromatic X-ray beam (λ=0.154056 for Cu_{ka} radiation), B is the full width at half-maximum for the diffraction peak under consideration (rad), and θ is the diffraction angle (deg).

III. Results and Discussion

X-ray powder diffraction patterns of ZnO nano particles are illustrated in fig.1. All peaks can be well indexed to the Zincite phase of ZnO (2000 JCPDS- Inter. Cantu). No peaks from any else phase of ZnO and impurities were observed, which indicates the high purity of the obtained Zincite ZnO

nano particles. ZnO nano powder has a hexagonal zincite structure.

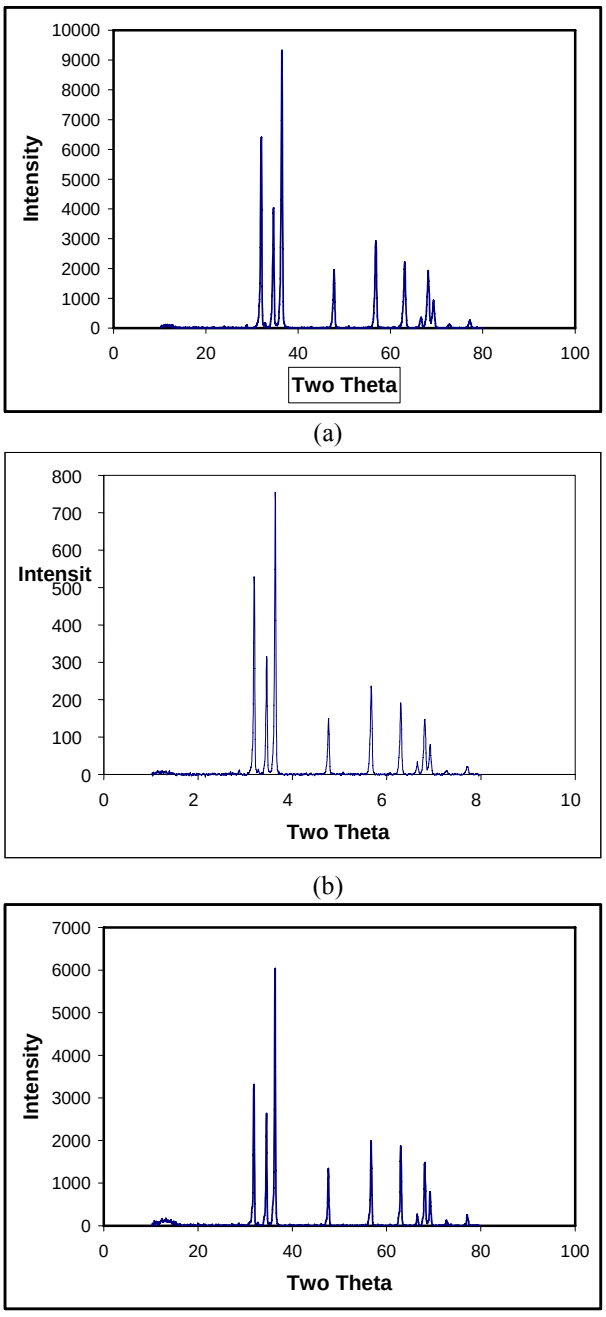


Fig. 1 XRD patterns of ZnO nano particles calcined at (a)400 °C, (b)500 °C, (c)600 °C for 3h.

A. Calcinations temperature

Fig.2. shows the ZnO particle size in term of temperature which was calculated based on the Scherrer equation. It can be seen that by increasing the temperature, the particle size will increase.

The Particles grow slightly at low temperatures and at high temperatures, the growth rate will increase. The diffraction peaks are sharper with the increase of the calcination temperature, which implies that the crystalline structure tends to more integrity and the average particle size increases with the increase of the calcination temperature.

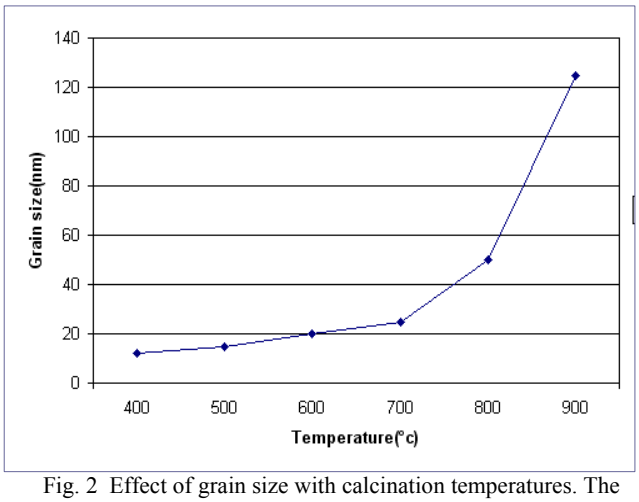


Fig. 2 Effect of grain size with calcination temperatures. The calcination time is 3h.

Fig. .3 shows the SEM micrographs of ZnO nanoparticles calcined at 400, 500, 6oo ºC for 3h, respectively. It can be seen that the ZnO aggregates with rod – like shapes are formed by some small nano crystals assembled in one – dimensional order.

The average crystallite size of the sample after calcination at 400 ºC for 3h (Fig.3 (a)) is almost 10- 12 nm. The nanorods are almost 1.4 µm in length and 120 nm in diameter for these samples. The particle size of ZnO aggregates increases with the increase of the calcination temperature and it becomes regular hexahedron shape over 500 ºC. Some wires were connected by planes of the hexahedral nanocrystals with an average crystallite size almost 18 nm when the sample was calcined at 500 ºC for 3h (Fig. 3(b)). After being calcination at 600 ºC for 3h, the nano crystals connect more closely and form longer wires (Fig. 3 (c)). There are less nanorods in the sample calcined at 500 ºC that at 600 ºC. And the average particle size of the former is smaller than the letter while both are 1.4µm in length. It is found that the rod – like aggregates consist of small nanocrystals and micropores (Fig. 3(a)). All of below show that the rod – shapes of ZnO aggregates tend to more visible and the nano crystals tend to more integrate with the increasing of the calcinations temperature, which is consistent with the result indicated by XRD patterns.

B. Calcination time

The effect of the calcinations time upon the grain size of ZnO powder is shown in Fig.4. At low calcinations temperature the prolongation of calcination time has little influence upon the particle size. But when the calcination temperature increases to 700 ºC, the obvious influence upon grain size was found as shown in Fig. 4. At relatively high temperatures the calcination time seems to have greater effect upon the grain size.

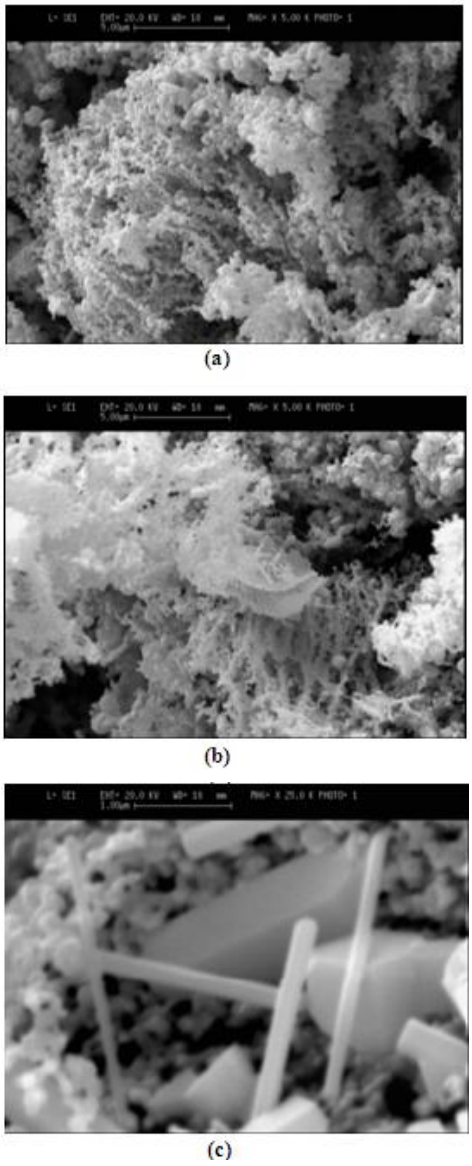


Fig. 3. SEM micrographs of ZnO powder calcined at (a) 400 °C, (b) 500 °C, (c) 600 °C for 3h.

C. PH value

Effect of pH value upon the grain size is shown in Fig. 5. It is found that when the pH value in below 7 the value of grain size is almost constant, which means acid solution could restrain grain growth. When the pH value is beyond 7, however, the line goes up very quickly which indicates that a total alkali environment would enhance grain growth. In this paper nano –ZnO powders were obtained mainly by controlling hydrolysis. It is well known that acid is usually -

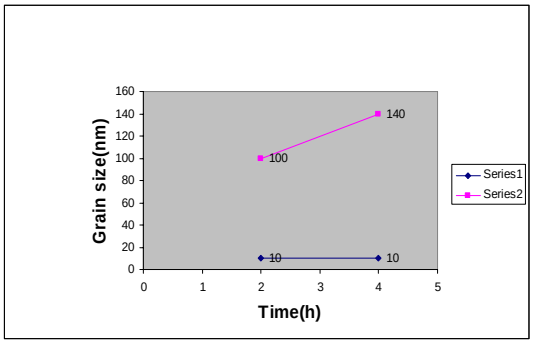


Fig. 4. Grain size change as a function of the calcination time at different temperature, series1 (300oC), series2 (700oC)

used to restrain hydrolysis while alkali can accelerate hydrolysis during reaction. When pH is beyond 7 which means environment do benefit to accelerate hydrolysis, the large aggregated particles are formed and grain tend to grow quickly.

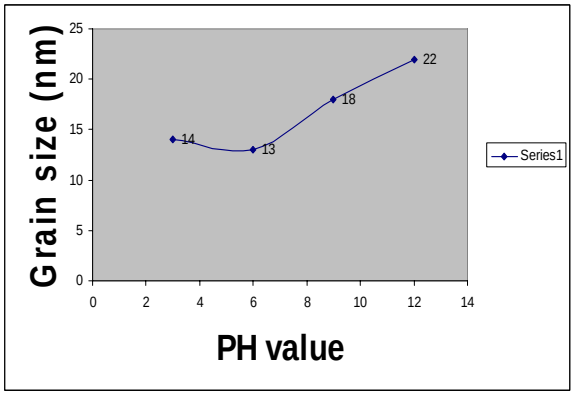
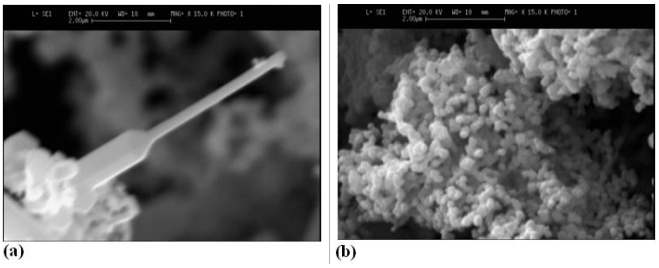


Fig. 5. Relationship between the size of ZnO particle and the pH value, while the calcined at 600 oC.

D. Concentration

Some experimental parameters, such as the concentrations of reactants, the molar ratio were considered during the synthesis of the rod – shaped ZnO nano particles. Fig.6 shows the SEM micrographs of ZnO nano particles obtained under different experimental conditions. Fig.6 (a) shows the SEM micrograph of the ZnO nano-particles obtained in the condition of concentrations of Zn (No3)2 and water were a molar ratio 1:1. It can be found a nanostructure, namely bi-rod – like ZnO nano rods, which is different from known ZnO nanostructures. When the concentrations of Zn (No3)2 and water were a molar ratio 1:2, regular hexahedral nano particles with a particle size of 100 nm (Fig. 6(b)) were obtained while no rod – shaped particles was found in the SEM micrograph. All results form SEM micrographs show that the existence of excess water is important to the formation of rod – shaped Zno nano particles and excessive existence of water prevents the growth of Zno particles in forms of rod – shape.



(a) (b)

Fig. 6. SEM micrographs of ZnO nanoparticles synthesized under different conditions, (a)bi-rod-like ZnO nanorods, (b)hexagonal ZnO nanoparticles.

IV. Conclusions

In conclusion, the unusual rod – shaped aggregates of ZnO nano crystals in hexagonal phase were synthesized by gel-casting method. Results of x-ray patterns show that all peaks can be well indexed to the Zincite phase of ZnO. SEM micrographs show that the ZnO nano particles assembled in one – dimensional order to form the rod – like shapes and there are many micropores among the nano crystals for the samples calcinated at 400- 500 ºC for 3h. While the nano-crystals are closely connected together one by one for the sample calcined at over 600 ºC. By controlling the conditions, nano scale powder can be made. Among all parameters, temperature, calcinations time, concentration and pH value have the most effect on the particle size.

Also at higher temperatures, the time of calcination has more influence on the particle size. The crystal size is less than 100 nm. This result shows that the particle size of the ZnO is about 12 nm. Finally, the gel – casting method guarantees the production of ZnO for different application especially reins for cement materials in nano composites.

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