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# ORGANIC SOL-GEL METHOD IN THE SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE NANOPARTICLES

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## ABSTRACT

Nanosized Zinc Oxide (ZnO) was synthesized using sol-gel method. The nanomaterials with structure were annealed at different temperatures ranging from 500 to 700°C which were chosen based on the Thermogravimetric (TGA) Analysis. The structure and morphology were characterized by Powder X-Ray Diffraction (PXRD) and Transmission Electron Microscope (TEM), respectively. The PXRD shows the increasing tendency in crystallite size when the annealing temperature increases and the hexagonal structure of ZnO. TEM further revealed the same tendency which the Zn NPs size increased with the annealing temperature.

**Keywords:** Nanoparticles, Sol-Gel Method, Crystallite Size

## 1. INTRODUCTION

Nanotechnology has become one of industry or field that developed rapidly. Research and Development (R and D) give more focus to this field since a lot of finding show that Nanotechnology can provide alternatives and solutions to various kinds of problems. Nanotechnology is the science of materials in range very close to molecular dimensions (1-100 nm) which has changed our viewpoint in many scientific aspects and has shown novel pathways for old problems remained unsolved through previous technologies (Ayatollahi and Zerafat, 2012). Nanotechnology offers great potential for benefit to humankind.

There are several ways that have been carried out by other researchers in order to change the nanoparticle sizes. The samples were sintered in muffle furnace (KSL 1600×MTI) in air at different heating rates i.e., from room temperature up to 900°C at the rate of 2°C per h and after that 4°C per h from 900 to 1250°C (Duhan *et al*., 2009). Other than that, a research by (Patil *et al*., 2011) showed that the surfactant-assisted sol-gel films were homogeneous, crack-free, contained anatase phase only with small grain size and showed an increase in Brunauer-Emmett-Teller (BET) surface area and wide range of pore size distribution compared to non-surfactant treated sample.

Different ligands, such as polymer and surfactants, are widely used to modify the surface of nanoparticles to stabilize and control the particle growth (Hou *et al*., 2005). In their experiments, a mixture of Trioctylphosphine Oxide (TOPO) and/or Hexadecylamine (HDA) was used to control the particle size, stabilize nanoparticle dispersion and limit further oxidation on the particle surface. A facile reduction approach with nickel acetylacetonate, $Ni(acac)_2$ and sodium borohydride or superhydride leads to monodisperse nickel nanoparticles in the presence of HDA and TOPO. The combination of HDA and TOPO used in the conventional synthesis of semiconductor nanocrystals also provides better control over particle growth in the metal nanoparticle synthesis. The size of Ni nanoparticles can be readily tuned from 3 to 11 nm, depending on the ratio of HDA to TOPO in the reaction system.

Highly concentrated ZnO sol has been successfully prepared by an improved sol-gel method (Vafaee *et al*.,

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2011). Water has been used as a modifier to control the sol-gel reaction and provide a way to increase the sol concentration and Zn intrinsic vacancies. The prepared ZnO sol has several times higher concentration than from other methods. It has a narrow size distribution and showed strong blue emission. It has been reported that by increase in both stirring velocity and temperature had resulted in faster particle formation (Yavarina *et al*., 2013). Although the nucleation time is not affected by stirring velocity, higher temperature causes faster reaction rate in all stages including nucleation. This method can be used for controlling the size of the nanoparticles. Yavarina *et al*. (2013) found that the average size of the nanoparticles changes with temperature, stirring velocity, capping and concentration of reactant. As temperature, stirring velocity and reactant concentration are increased the average size of the particles increase and capping the particle prevents/reduces larger nanoparticles.

Since there are quite a number of options to changing the parameters in order to control and change the particle size, with time and economic feasibility studies and considering to the technology available in the institution, we has consider to choose annealing temperature as the controlling factor.

## 2. MATERIALS AND METHODS

Zinc Oxide (ZnO) nanoparticles were synthesized using sol-gel method. Zinc acetate, $Zn(CH_3CO_2)_2$ with 99.99% purity, purchased from Sigma-Aldrich was dissolved in citric acid with 1 moL/dm$^3$ concentration and stirred for 2 days to obtainhomogeneous sol. The sol was then heated up to 80°C toobtain milky white gelatine which was then dried in an oven for 3 days to form dried powder. The as-synthesized powder was then crushed for at least 4 h to ensure homogeneousdispersion. Before being annealed at three different temperatures, TGA analysis was carried out to find the optimum annealing temperature based on the phase transition at TGA curve. 500, 600 and 700°C were chosen as annealing temperatures to obtain single phasecrystal and to study the effect of temperature on the crystal growth. Crystallography of the ZnO NPs e.g., crystallite size, phase and structure were determined by using XRD method and their morphology and the particle size were investigated using TEM.

## 3. RESULTS

**Figure 1** shows the TGA curve for Zn-O precursor powder prior the annealing process. The XRD patterns for the samples annealed at different temperature and typical one are depicted in **Fig. 2a and b**.

**Figure 3** illustrates the change in the crystallite size with increasing temperature. The annealed samples were further observed under the TEM to investigate the change in particle size with the change in temperature in **Fig. 4**.

## 4. DISCUSSION

TGA acts as a powerful tool to determine the suitable annealing temperature in material preparation by referring to the drastic drop in the weight percentage with the respective temperature on the TGA curve in **Fig. 1**. Here we can observe that the phase transition (Broido, 1969) takes place at temperature above 500°C. Therefore annealing temperature of 500, 600 and 700°C were chosen.

From XRD pattern shown in **Fig. 2**, all samples matched with the typical ZnO pattern with strong diffraction peaks occurred at 31.77° and 36.25° which suggest the favorable crystal grown at <100> and <101> direction, respectively (Pei *et al*., 2009). The XRD pattern further supports our TGA pattern which suggested the suitable annealing temperature must be above 500°C. All three samples show three major peaks which is at 31.77, 34.42 and 36.25° but only with increasing intensity when the annealing temperature increases. This also indicates that crystallization will be more complete when the temperature increases.

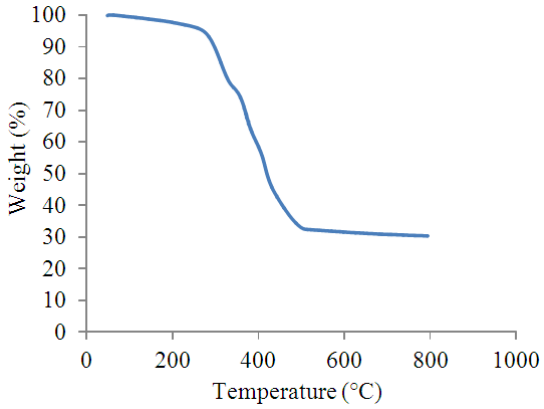



**Fig. 1.** TGA pattern for Zn-O precursor powder

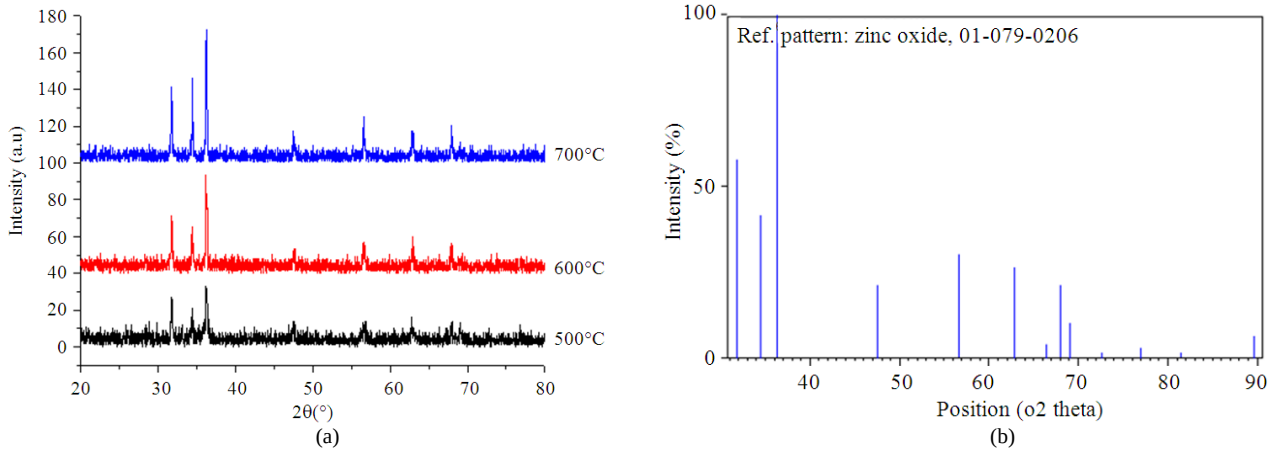



**Fig. 2.** (a) XRD of Zn-O precursor annealed at different temperatures (b) Typical XRD pattern for ZnO (Albertsson *et al*., 1989)

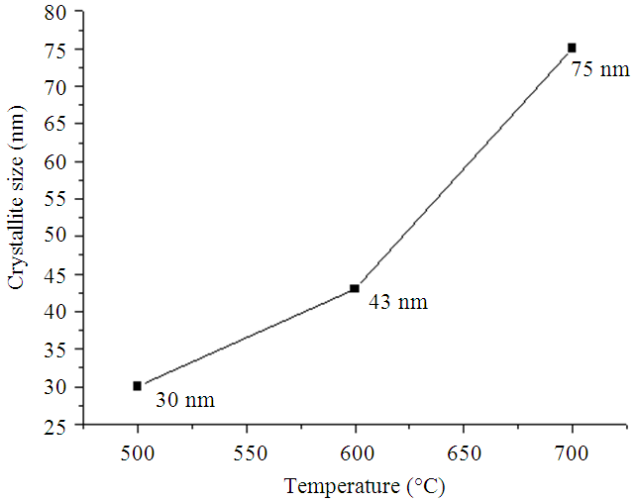
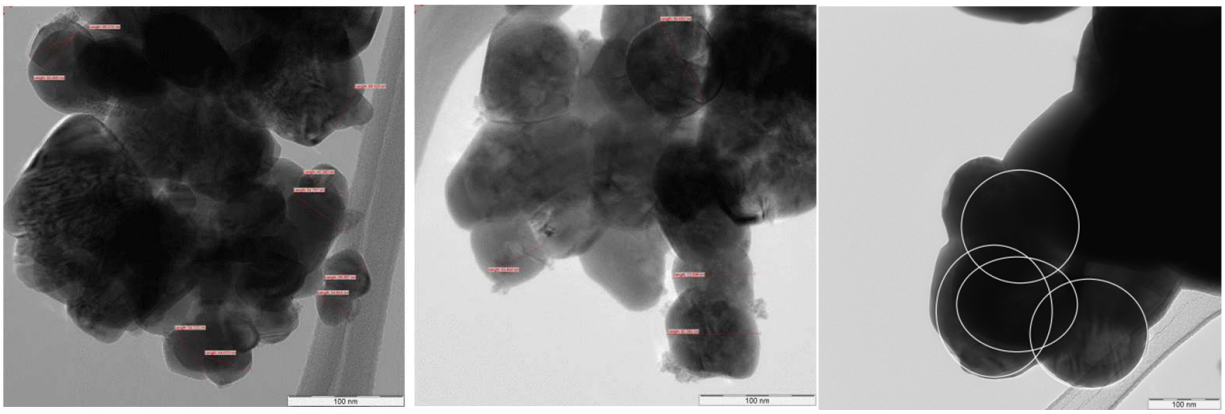



**Fig. 3.** Change of crystallite size with the annealing temperature



(a) (b) (c)

**Fig. 4.** TEM images for samples annealed at (a) 500 (b) 600 and (c) 700 °C

We can conclude that temperature of 500°C and above is sufficient enough to remove all the organic residues during the sol-gel process and to form a single hexagonal phase (Pierre, 2002). The crystal direction of the hexagonal crystal structure of ZnO are found in all three samples. However we would also like to investigate how the other crystallography parameter such as crystallite size changes when the annealing temperature increases. The crystallite size is estimated by using the Scherrer equation:

$$t = \frac{k\lambda}{\beta cos\theta}$$

Where:

k = The Scherrer constant, which was chosen to be 0.9 in this analysis
β = The integral breadth of the reflection at 2θ and
λ = The wavelength of the X-ray used in the diffracto meter

We can observe that crystallite size increases almost linearly when the annealing temperature. This serves as a powerful tool for us to control the crystallite size by choosing the suitable annealing temperature.

From the TEM images depicted in **Fig. 4** we can roughly estimate the size of the particles is about in the range of 40, 70 and 100 nm, respectively. This agrees well with the crystallite size calculated from XRD data which is 30, 43 and 75 nm, respectively. We can further confirm that by increasing the annealing temperature we can increase the size of the nanoparticles and the size is controllable depending on the annealing temperature.

## 3. CONCLUSION

The sol-gel method using citric acid and zinc citrate has been demonstrated. The XRD pattern shows that the ZnO with hexagonal phase is formed at 500°C and above. Increasing of the annealing temperature suggested the increase of crystallite size and TEM images further showed the size of the NPs also increase concurrently with hte annealing temperature. Variation of annealing temperature has proved to be a powerful tool to control the particle size.

## 4. ACKNOWLEDGMENT

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