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SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE NANOPARTICLES

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ABSTRACT

Zinc oxide (ZnO) nanoparticles had been successfully synthesized via solution combustion method. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and glycine (NH_2CH_2COOH) was used as an oxidant and fuel, respectively. These reactants were mixed in different fuel-to-oxidant (F/O) ratios before undergoes different calcination temperatures (400, 500 and 600 ºC) for 2 hours in order to obtain desired product. The synthesized ZnO powders were characterized via XRD, FT-IR, SEM and TEM. The XRD and FT-IR data confirmed the formation of high purity of ZnO nanoparticles. SEM showed the morphology of ZnO was in spherical shape. The particle size of ZnO was found to increase from low F/O to high F/O ratio. Increment in calcination temperatures also tends to form the larger particle size due to the agglomeration of the particles. ZnO nanoparticles with different sizes were prepared by adjusting the molar ratio of zinc precursor to glycine and calcination temperatures.

Keywords: Zinc oxide; Nanoparticles; Solution combustion;

INTRODUCTION

Zinc oxide (ZnO) has attracts attention of various groups of researchers as being a wide band-gap-energy (3.37 eV) semiconductor with unique electronic, chemical and optical properties. Due to its unique properties, application of ZnO in the various fields of technology such as catalysis [1], sensors [2], varistors [3] and laser devices [4] are common nowadays. The unique properties of ZnO are highly related to the size and shape of the particles.The solution combustion method was selected to produce ZnO nanoparticles. The advantages of method were highlighted for its low cost and ability to produce high quality final product in short time. Herein, a facile solution combustion method had been developed which

produces well-controlled ZnO nanoparticles. It should be noted that this paper focused on the effect on the shape and size of ZnO nanoparticles by varying the parameters of synthesizing such ad calcination temperatures and fuel-to-oxidant ratio will be investigated.

EXPERIMENTAL METHOD

In this method, zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) (Hamburg Co.) was used as an oxidant and glycine (NH_2CH_2COOH) (Fisher Scientific) used as fuel for reaction. They are mixed together to form a clear solution and dried in the oven for 24 hours. After drying, the transparent precursor solution was obtained and placed in the furnace for combustion and followed by calcinations temperature ranging from 400 ºC to 600 ºC to remove residue organic compounds. The F/O ratios were ranging from 0.88 to 1.33 whereas the different ratio conditions, such as, fuel-rich, stoichiometric and fuel-deficient were investigated. The final products are characterized. Table 1 lists the sample numbers and conditions used for synthesizing ZnO nanoparticles. Powder X-ray diffractometer (PXRD) (Phillips X-Ray Diffractometer X'PERT PRO PW3040) was used to confirm the crystalline phases of the ZnO at ambient temperature and under normal condition. The stretching of the zinc- oxygen bonding was studied by Perkin-Elmer 1725X Fourier Transform Infrared Spectrophotometer. Scanning electron microscopy (SEM) (JEOL JSM-6400) was used to observe the surface morphology of the sample while transmission electron microscopy (TEM) (HITACHI 7100) was used to measure the particle size.

Table 1: Reaction conditions used for synthesizing ZnO nanoparticles

Sample ID	Molar ratio glycine-to-nitrate	Condition	Calcination temperature (º C)
G08400	0.88	Fuel-deficient	400
G08500	0.88	Fuel-deficient	500
G08600	0.88	Fuel-deficient	600
G11400	1.11	Stoichiometric	400
G11500	1.11	Stoichiometric	500
G11600	1.11	Stoichiometric	600
G13400	1.33	Fuel-rich	400
G13500	1.33	Fuel-rich	500
G13600	1.33	Fuel-rich	600

RESULTS AND DISCUSSION

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In the solution combustion process, thermochemical calculation on stoichiometric ratio between an oxidizer and fuel was calculated based on the principle of propellant chemistry[5]. It was noted that ratio of the total reducing valencies of fuel to the total oxidizing valencies of the metal nitrate should be unity. Zinc (Zn), hydrogen (H) and carbon (C) are considered as reducing elements with corresponding valencies of +2, +1 and +4, respectively while oxygen represents oxidizing element with corresponding valency of -2. Hence, the oxygen content of zinc nitrate is fully able to completely react with the fuel. The nitrogen is having corresponding valency of zero. Using the summation of chemical compound, the total calculated reducing valencies of fuel will be in positive and total calculated oxidizing valencies of metal nitrate will be in negative. The calculated valency for $Zn(NO3)2$ is 10-, while for $NH2CH2COOH$ is 9+. It is well known that glycine, one of the simplest amino acid can be used as fuel and chelating agent in chelating metal ions had been widely used in this method for synthesizing metal oxide.

When the fuel and metal nitrate reacts with each other completely, the theoretical stoichiometric equation for the formation o f ZnO can be represented by the following balanced equations:

$$Zn(NO_3)_2{\cdot}6H_2O(c) + 10/9NH_2CH_2COOH(c) = ZnO(c) + 14/9N_2(g) + 79/9H_2O(g) + 20/9CO_2(g)$$

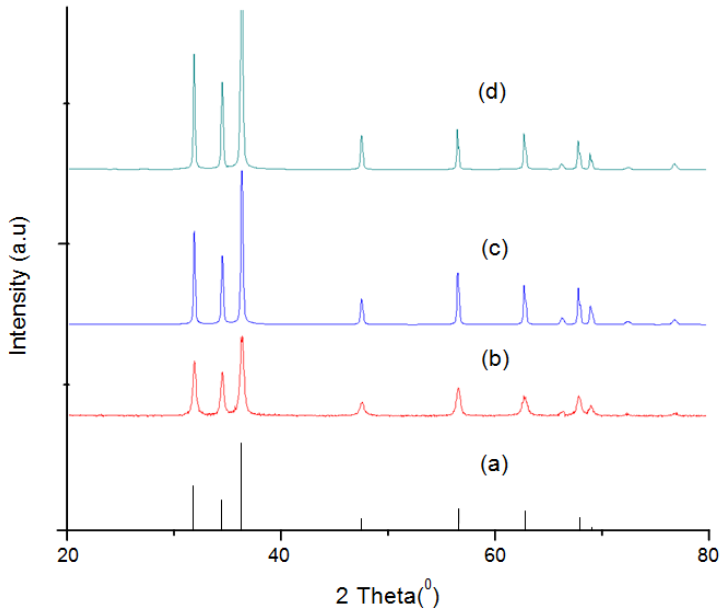

Figure 1: X-ray diffractogram of (a)standard ZnO and synthesized ZnO with (b) g08400, (c) g11400 and (d)g13400, respectively

X-ray diffraction of synthesized ZnO at various ratios is shown in Figure 1. Figure 1

shows the XRD patterns of the samples. This pattern shows that the crystalline phase of synthesized ZnO are fully matched with the hexagonal phase ZnO (wurtzite structure) reported in Joint Committee on Powder Diffraction Standards (JCPDS) card (No. 00-065-3411). With increasing calcination temperature in the reaction, the diffraction peaks of ZnO become highly intense and narrow. This indicates that ZnO is a highly crystalline sample when calcined at higher temperature with the increment of crystallite size as calculated from Debye-Scherrer equation and hence decreasing lattice strain [6].

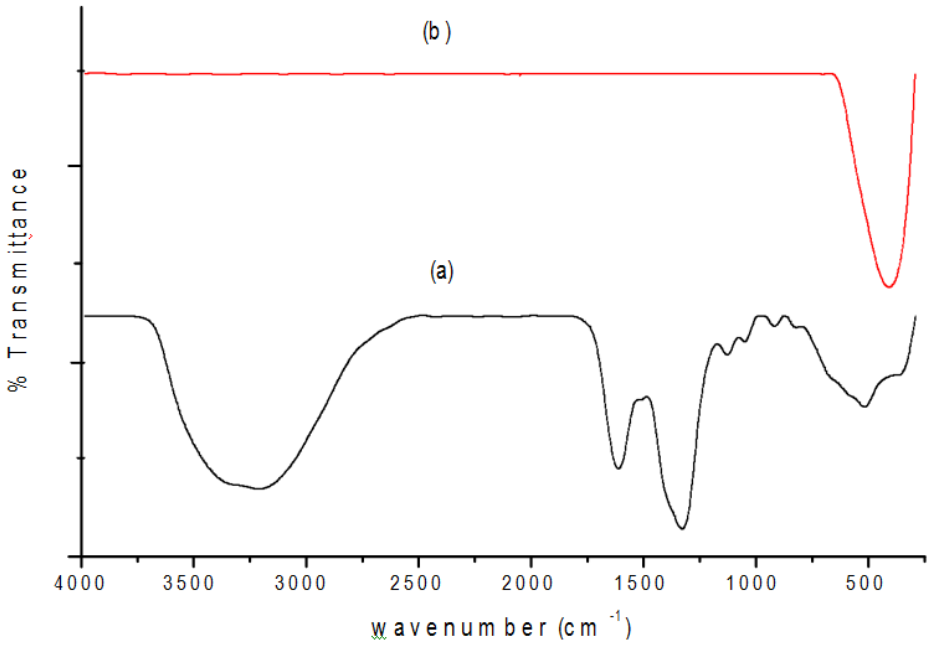

Figure 2: IR spectra for ZnO synthesized using glycine(a) before calcinations and (b) after calcinations

In order to differentiate the bonding of the compounds before and after calcinations, FT-IR spectra (Figure 2) were studied for prediction the chemical bonding of the structure. Before calcinations of the product, IR spectrum clearly indicates the presence of the hydroxyl group, carboxyl group and nitrate groups. The bands at 3000-3750 cm^{-1} corresponded to stretching of O-H groups. The bands detected at 1620 cm^{-1} showed the existence of carbonyl group or C=O stretching vibration modes. The bands at 1390cm-1 is attributed to the vibration of the nitrate groups in $Zn(NO3)2$ and in the region from 700-300 cm^{-1} indicates to the C-O stretching and C-H bending vibration modes. After the samples undergo heat treatment, all these bands has been removed completely and new bands of ZnO stretching mode is found at the bands of 430 cm^{-1} [7]. This showed that transformation of the zinc-glycine complex to zinc oxide is completed and all impurities are successfully removed during calcinations. In the combustion synthesis, no doubt that many

intermediates products are formed during the reaction however they are not put into attention as the heat change involved depends only on the final and initial compound of the system.

SEM images of ZnO nanoparticles were clearly shown in Figure 3 (a and b) with 5,000 and 20,000 magnification are corresponding to the sample ID with G09400. The images show that the morphology of the particles was in spherical shape. The images show that the samples are porous and the particles were jointed to each together to reduce the high surface energy.

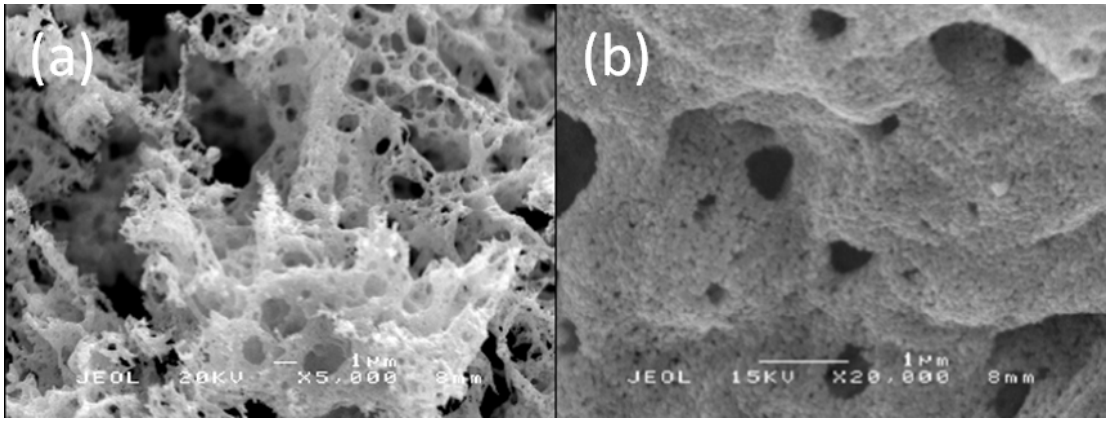

Figure 3: SEM images of the sample ID with G08400 in (a) 5000 magnification and (b) 20000 magnification

Figure 4 (a, b and c) present the TEM image which showed particle sizes of the synthesized ZnO nanoparticles in stoichiometric ratio (G08400, G08500, G09800). The images show the formation of nearly spherical particles which increase in size with increasing calcinations temperatures. The particle size also increase with the changing from fuel-deficient to fuel-rich, not show here because the amount of the fuel used in the reaction influences the agglomeration of the particle.

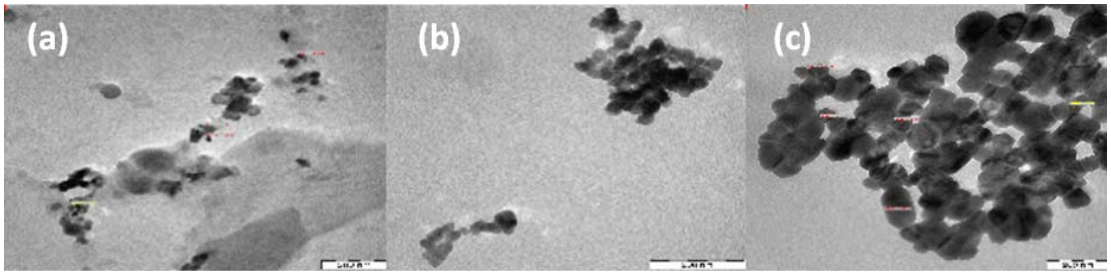

Figure 4: TEM images of sample ID with (a) G08400, (b) G08500 and (c) G08600

CONCLUSION

The properties of high purity ZnO nanoparticles synthesized via solution combustion method had been fully characterized. The calcination temperatures and fuel-to-oxidant ratio were found to play an important role in determining the size of the particles in the sample. Based on the results, it had been concluded that solution combustion method proved to be effective in producing ZnO nanoparticles with desired particle size by adjusting ratio or heating temperature.

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