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Synthesis of ZnO nano powder by a gel combustion method

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In this study, a gel combustion method was used to prepare ZnO nano powder. Zinc nitrate, nitric acid, and different fuels of glycine, urea, and citric acid were used with various ratios of fuel to salt and different primary pH values, followed by calcinations at temperatures of 400-600 °C. The results showed that using citric acid, fuel to raw material ratio of 0.5, a neutral pH, and a calcination temperature of 500 °C were the optimum conditions to prepare ZnO nano powder of about 30 nm.

Key words: Nano powder, Zinc oxide, Gel combustion, Glycine, Citric Acid.

Introduction

In the gel combustion method, the raw materials, which are usually a nitrate compound and a fuel, are dissolved in water. After controlling the pH, by a weak base such as ammonia, the mixed solution is heated to change the sol to a high viscosity gel. Increasing temperature, causes an exothermic combustion process and both organic materials as a reducing agent and nitrates as an oxidation agent change the gel to a very gray fine and intensively porous substance which later with the help of calcinations a final product will be prepared [1, 2]. There are different synthesis methods for ZnO nano powder preparation. Li [3] and Vaezi [4] performed some studies in the field of ZnO nano powder preparation via precipitation routes. They used a zinc salt and varied the pH and some other parameters. Chu et al. [5] by using zinc acetate, citric acid, and ammonia, succeeded in obtain his ZnO nano particles. Westin et al. [6] used a sol-gel method to produce ZnO nano particles and applied the prepared powder to a varistor application and observed very high electrical properties. Pillai et al. [7] used a sol-gel method as well. They tested some reaction modifier, dried the powder at 85 °C followed by calcinations at 500 °C, and got suitable results. In gel combustion, an oxidizing agent and a fuel as a reducing agent are used. Control of the oxidant to fuel ratio should create a high heat induced from the reactions. Therefore, in order to use an exothermic reaction, the selection of a suitable ratio of oxidant to fuel is very important. A non-suitable ratio of nitrate to fuel makes some unwanted intermediate phases or unreacted raw materials. Generally, the fuel should be reacted slowly and act as a complex maker of cations. Complexes increase the metallic cation solubility and hence prohibit preferred crystallization during evaporation of the primary water [2]. Gel combustion gives a homogenous, high purity, and high quality nano powders due to the possibility of stochiometric control [2]. Sousa et al. [8] used metallic nitrate plus urea and made ZnO nano powder with a size about 400-500 nm for varistor application. Hwang et al. [9] worked on ZnO nano powder made by a combustion method. They used glycine as a fuel and metallic nitrates with a stoichiometric ratio. In this research, a gel combustion method (a combination of sol-gel and combustion method) was used to prepare ZnO nano powder using citric acid as a fuel for the first time.

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Experimental Procedures

For all the experiments, the different materials were used such as zinc nitrate, urea, glycine, and citric acid. Table 1 shows the characteristic of the raw materials. The ratio of fuel to metallic nitrate was selected as 0.5, 1, and 2. The materials were weighed, dissolved in distilled water, and homogenized on a magnetic stirrer based on Table 2. After mixing and homogenizing metallic nitrate with fuel, while heating the solution, the gel combustion process was carried out and ZnO nano powder was prepared. The powders were calcined at 400-600 °C, then XRD and SEM were used and the results were analyzed.

Results and Discussion

XRD pattern of the above samples are shown in Figs. 1 to 3. Then, by the Scherer technique, the size of all crystallites was measured and the obtained results collected in Table 3. Also, the microstructures of samples with

Table 1. Raw material characteristics

Raw materials	Formulation	Molecular Weight (g/mol)	Purification (%)	Physical state	Manufacturer
Zinc Nitrate	$Zn(NO_3)_2 \cdot 6H_2O$	297.46	99	Solid	MERCK
Urea	NH_2CONH_2	60	99	Solid	MERCK
Glycine	$NH_2 \cdot CH_2 \cdot COOH$	75.05	99	Solid	BDH
Citric Acid	$C_6H_8O_7 \cdot H_2O$	210.14	60	Solid	MERCK

Table 2. Materials weighed in this research

Sample code	Fuel to Nitrate ratio (F/M)	Zinc Nitrate (g)	Fuel (g)
U1	0.5		0.5
U2	1	5	1
U3	2		2
G1	0.5		0.63
G2	1	5	1.26
G3	2		2.52
C1	0.5		1.76
C2	1	5	3.53
C3	2		7.06

different fuels are shown in Fig. 4. From the SEM microstructures and XRD patterns, it is possible to find out that citric acid to raw material ratios of 1 to 2, gave better results. Therefore, it is possible to suggest that using citric acid can bring down the formation temperature of the product due to the easier complex formation and homogeneous gel, thus the crystallite sizes are smaller in comparison to other fuels. When glycine was used, the heat released during combustion is more and as a result the combustion reaction enthalpy is more which yields both a growth of the crystallite size and a complete combustion reaction with more crystallize phase. Also, using citric acid fuel with a fuel to raw material ratio of 0.5, three primary solutions with three types of pH (acidic, basic, and neutral) were prepared and the gel combustion process

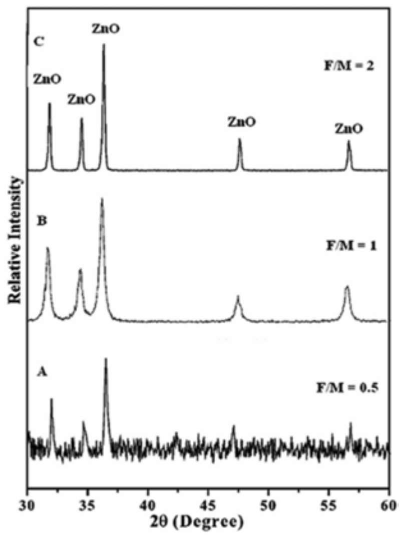

Fig. 1. XRD pattern of ZnO nano powders produced in three ratios of fuel (urea) to materials (F/M); (A) 0.5, (B) 1, (C) 2.

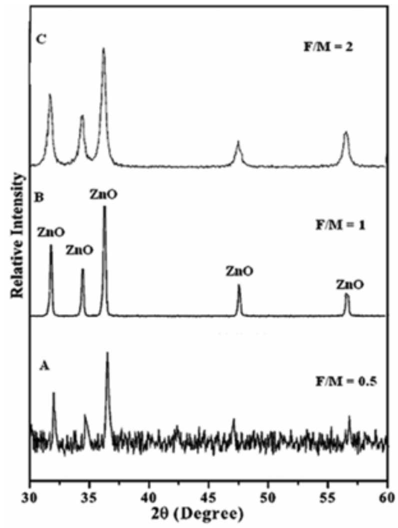

Fig. 2. XRD pattern of ZnO nano powders produced in three ratios of fuel (glycine) to materials (F/M); (A) 0.5, (B) 1, (C) 2.

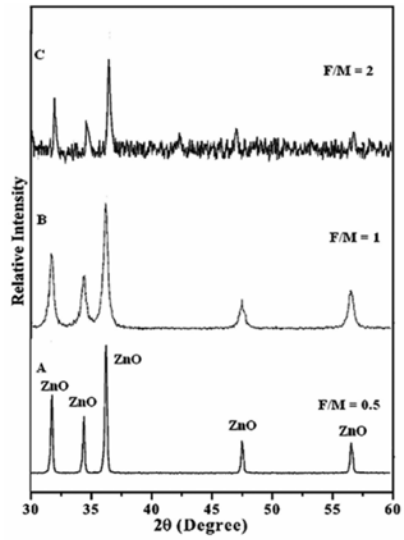

Fig. 3. XRD pattern of ZnO nano powders produced in three ratios of fuel (citric acid) to materials (F/M); (A) 0.5, (B) 1, (C) 2.

was repeated. The nano powders obtained were calcined at 500 °C and a microscopic evaluation was performed. The results are shown in Fig. 5. According to the above Figs, it may be concluded that using a neutral medium in the gel combustion method, gives a more homogeneous and finer microstructure. When the pH is increased from 2 to 10, in addition to a color change of the primary

Table 3. Crystallite sizes of ZnO nano powder by the Scherer technique

Sample code	nm
U	53
G	34
C	22

solution, both the combustion reaction and volume of external gases will be dramatically extremely increased. This is due to this fact that the nitrate ions make an oxidizing medium around metallic ions, which is useful for burning off the organic part of a gel, so increasing the pH (adding ammonia) causes an increase in NO_3^- ion content and thus the combustion reaction rate will be increased. The reaction, which happens during ionization of citric acid at different pH values, is as follows:

$$H_3Cit \leftrightarrow H_2Cit^- + H^+ \quad pH < 3 \tag{1}$$

$$H_2Cit^- \leftrightarrow HCit^{2-} + 2H^+ \quad 3 < pH < 6.5 \tag{2}$$

$$HCit^{2-} \leftrightarrow Cit^{3-} + 3H^+ \quad pH > 6.5 \tag{3}$$

These reactions show when the pH is acidic, citric ionization is very low, so the role of complexation by the citric acid becomes weak. Also, when the pH is increased to 7 (neutral), citric anions are as cit^{3-}, so the role of complexation by the citric acid is the highest at pH = 7 because the number of bonding between citrate anions and metallic cations are increased. Therefore, a more homogenized gel will be prepared. When the pH is higher than 7, an ionization disorder of citric acid will be created and finally, the role of complexation by the citric acid will become weak or disappear which causes a precipitation of some materials in the form of a hydroxide material. In order to achieve a suitable temperature for calcination, three temperatures of 400, 500, 600 °C were tested on prepared gel combustion nano powders and XRD patterns were assessed. Figure 6 shows XRD patterns of powders calcined at different temperatures.

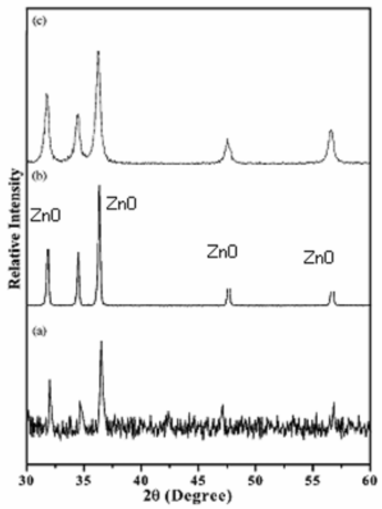

Fig. 6. XRD patterns of ZnO nano powders prepared by gel combustion method at different temperatures of (a) 400 °C, (b) 500 °C, (c) 600 °C.

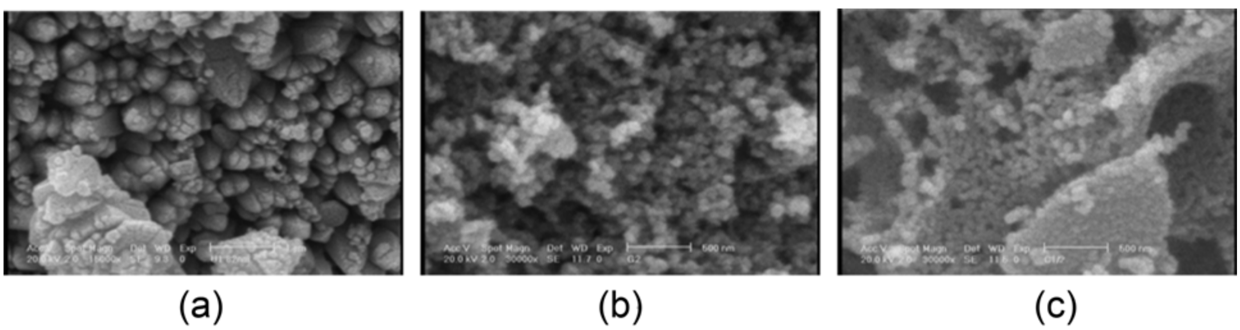

Fig. 4. SEM pictures of ZnO nano powders using different fuels (a) Urea, (b) Glycine, (c) Citric acid.

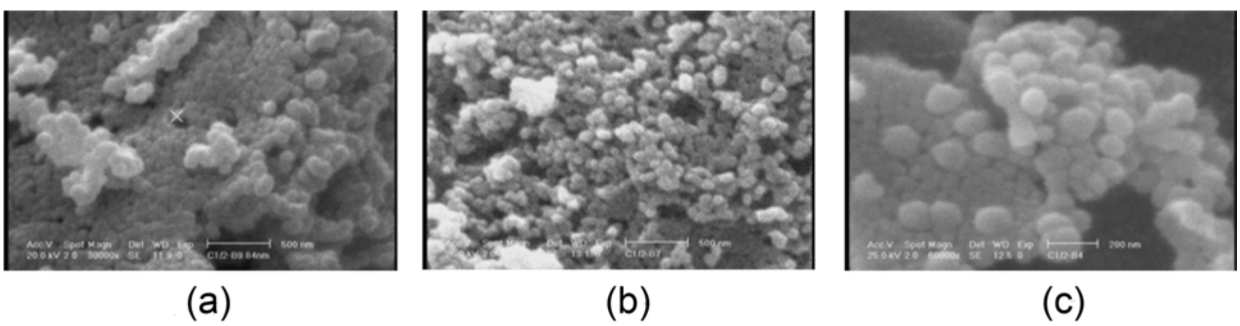

Fig. 5. Microstructure of ZnO nano powders in three different media of (a) pH = 4, (b) pH = 7, (c) pH = 10.

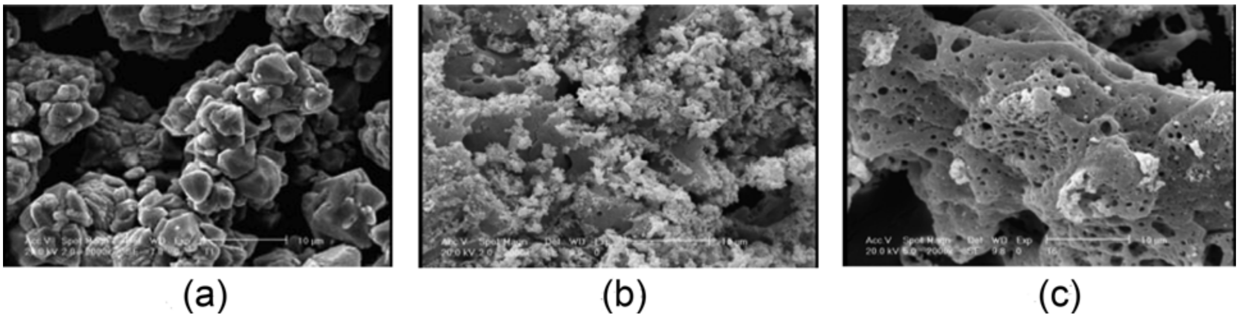

Fig. 7. Microstructural images of nano powders produced by the gel combustion method and calcined at different temperatures of (a) 400 °C, (b) 500 °C, (c) 600 °C.

As Fig. 6. shows, with low temperature calcination, no peaks are apparent for ZnO nano powders and an amorphous phase is completely seen in the XRD patterns, while at temperatures of 500 and 600 °C, ZnO peaks are observed. Scanning electron microscopy (SEM) from calcined nano powders at different temperatures are shown in Fig. 7.

Conclusions

The following results were obtained:

1. It is possible to prepare nano powder using a gel combustion method.
2. Using citric acid in a gel combustion method acts both as a gel agent and a fuel, which makes a homogeneous suitable nano powder.
3. The most desired fuel to raw materials ratio is 0.5 when citric acid is used.
4. A neutral pH, in the gel combustion process creates a fine and homogeneous ZnO nano powder.
5. A calcination temperature of 500 °C is desired to change amorphous particles to a crystalline phase.

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