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Research Article

Effect of Calcination Temperature on Crystalline phase and Grain size of ZnO Particles

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Abstract

In today's technology, ZnO as a semiconductor, has emerged as a leading candidate in green environmental management systems, owing to its strong oxidation ability, good photocatalytic properties, and large free-exciton binding energy. ZnO is a cost-effective, stable, and high photocatalytic material with good electrical properties and light transmittance, making it useful for various applications such as solar cells, photocatalysts, and electrical equipment. ZnO, being a photocatalyst, can be used for environmental clean-up efforts such as air purification, water purification, and deodorization. In this study, the zinc oxide (ZnO) was synthesised with a forced hydrolysis method and characterised by different characterization techniques. X-ray diffraction (XRD) was used to investigate the change in phase and crystal structure of ZnO particles at different calcination temperatures. Moreover, the average crystallite size of the particles was calculated at various calcination temperatures, using Scherrer equation. Also Scanning Electron Microscopy (SEM) used to image the surface morphology and size of the particles and it is found that the calcination temperature had a significant effect on the morphology of the particles. Additionally, differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) were used to observe the material transitions and changes in mass as the temperature increased.

Keywords

Calcination, ZnO, Forced Hydrolysis

1. Introduction

ZnO particles are fully attractive due to their unique characteristics including high binding energy, a wide band gap of approximately 3.35 eVis, strong oxidation ability, high photocatalytic, chemical stability, low material cost, and the ability to exhibit photocatalysis in the environment [1]. These promising characteristics of ZnO provide very helpful features in order to overcome the environmental issue. Due to its technological importance in various fields, the properties of ZnO have been the subject of many experimental and theoretical studies in recent years. ZnO, verified as a good candidate for different applications, including in piezoelectric devices [2], solar cells [3], transistors [4], textiles [5], light emitting diodes [6], gas sensors [7], photocatalysts [8], and as antibacterial and antifungal agents [9].

So far, various techniques have been utilised for the synthesis of metal oxide particles, including sol-gel, hydrolysis of inorganic salts, ultrasonic technique, microemulsion, and hydrothermal method, polar and polar solvent systems in the literature [10].

The present study investigates the impact of heating on particle size distribution, with the objective of achieving uniform particle sizes and controlling their dimensions

through controlled thermal processes. In this study, the forced hydrolysis method was chosen due to its simplicity and high yield. The subsequent calcination step, a common practice in the synthesis process, involves heating the precursor material to elevated temperatures to facilitate its transformation into the desired product. Herein, we reported the zinc oxide (ZnO) particles synthesised with a forced hydrolysis method followed by a calcination process under different temperatures at 500 °C, 700 °C, and 900 °C. The phase structure, size, morphology, thermal stability of samples studied by different characterization techniques; X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) Differential Thermal Analysis (DTA) of ZnO particles.

2. Materials and Methods

2.1. Materials

Zinc chloride ($ZnCl_2$), ammonium hydroxide (NH_4OH: ≥%25 NH_3 in H_2O) and distilled water (DI H_2O) were used as all the precursors were used directly without any pre-treatment and further purification.

2.2. Synthesis

The ZnO particles were produced using a forced hydrolysis method. First, 10 g of $ZnCl_2$ dissolved in 200mL distilled-water kept at room temperature while stirring for 5 minutes. In the next step, 10mL of ammonia (NH_4OH) is added dropwise to the solution at the same time pH controlled until achieving pH= 7.0 (The reactions that occur through the experiment have been listed). The white solution obtained as $Zn(OH)_2$ precipitated in the solutions. The result samples have been centrifuged for 10 minutes at 4000 rpm. The washing process repeated several times. To obtain ZnO powders, after the washing process was completed, particles were dried at 60 °C in the vacuum oven. Samples were calcined at different temperatures (rate of 11.3°C/min) 500°C, 700°C and 900°C for 30 minutes. Then, the samples were allowed to cool down to room temperature and grind to obtain the fine ZnO particles. The synthesis process depicted in detail at Figure 1.

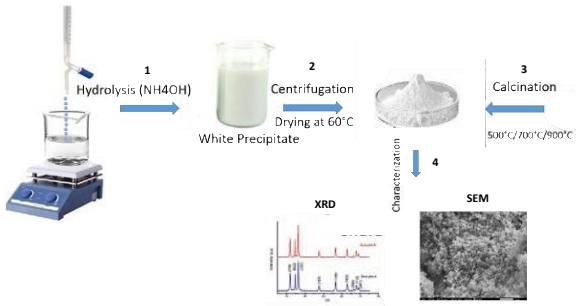

Figure 1. Synthesis and characterization steps of ZnO particles.

3. Measurement and Characterization

The XRD (Bruker D2-Phaser), SEM (Zeiss Evo 40, Leica EM ACE 200 vacuum coater, gold palladium coating), TGA (NETZSCH STA 409 C/CD), and DTA (NETZSCH STA 409 C/CD) techniques were used for the characterization and analysis in this study.

3.1. Characterization

Thermogravimetric analysis (TGA) was used to investigate the thermal stability of samples. The thermogravimetry (TG) curve was obtained in an air flow from 25 °C to 900 °C at a heating rate of 10°C/min. X-ray diffractometer (XRD) with Cu K (λ = 1.5418 Å) source was used to study the crystal structure and morphology of powders. Scanning electron microscope (SEM) characterization was performed under voltage of 15 kV.

4. Results and Discussion

4.1. TGA & DTA Analysis

Figure 2 depicted the TGA/ DTA curves of Simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$) precipitates which were obtained by hydrolysis of Zinc chloride aqueous solutions with NH_4OH. Significant mass loss steps accompanied by endothermic peaks were observed. The first mass loss (~11%) which was observed in the temperature range 25–135°C was attributed to the removal of adsorbed water. The second and third weight loss (7% and 6%) observed in the temperature range 135–195 °C and 195-250 °C which were assigned to the removal of the intercalated water. The fourth weight loss is assigned to the decomposition and dehydroxylation of hydroxides from Simonkolleite compound between 250-635 °C. The final product of thermal decomposition was found to be ZnO as confirmed by the XRD. The endothermic peaks observed at 135, 195 and 250 °C correspond to removal of water and dehydroxylation of hydroxides, the final endothermic peak can be attributed to the phase decomposition and phase transformation from Simonkolleite to ZnO structure.

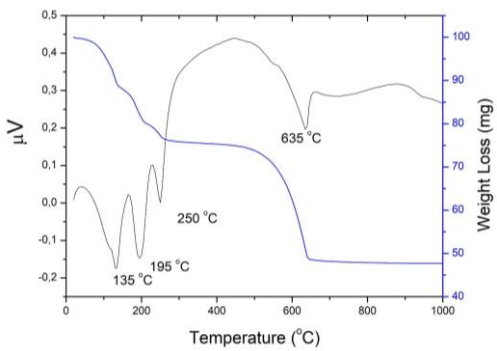

Figure 2. TGA/DTA analysis of simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$)

4.2. Structural Characterization:

XRD results of the ZnO samples before and after calcination at 500°C, 700°C and 900°C are shown in Figure 3. In order to control particle size and understand growth mechanisms three different firing temperatures (500 °C, 700 °C and 900 °C) were applied for calcination. All peaks before calcination are well matched with Simonkolleite ($Zn_5(OH)_8Cl_2 \cdot H_2O$) structure (JCPDS card no: 007-0155).

According to our synthesis method, when ammonia reacts with water it forms ammonia hydroxide and generates OH– ions as shown in equation (1). These Hydroxyl ions then interacted with Zn^{+4}, leading to the formation of Simonkolleite structures in the presence of chlorine ions as indicated in equation (2) and (3). Although the as-synthesised (white precipitate) samples were washed to remove the chlorine ions, it seems that the washing process was not successful due to the excess of chlorine ions in the system.

$$2NH_4OH_{(s)} \rightarrow 2NH_4^+{}_{(aq)} + 2OH^-{}_{(aq)} \quad (1)$$

$$ZnCl_{2(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} \quad (2)$$

$$5Zn^{2+} + 8OH^- + 2Cl^- + H_2O = Zn_5(OH)_8Cl_2.H_2O \quad (3)$$

$$Zn_5(OH)_8Cl_2.H_2O_{(s)} \rightarrow ZnO_{(s)} + H_2O_{(g)} \quad (4)$$

The XRD peaks of samples before calcination and those calcined at 500 °C exhibited a polymorphic structure, in which the graph shows the presence of either Simonkolleite phase structure (marked with *) or ZnO. However, upon increasing the calcination temperature to 700 °C and 900 °C, the XRD peaks confirmed the appearance of pure ZnO crystal structure (JCPDS card no: 036-1451). Notably, significant XRD peaks were observed at angles (2θ) of 31.8°, 34.5°, 36.4°, 47.6°, 56.7°, 62.9°, 68.1°, and 69.3° when the samples were fired at 700 °C and 900 °C, which well matched with ZnO crystal structure. These angles correspond to (100), (002), (101), (102), (110), (103), (200), and (112) planes of ZnO respectively. However, additional peaks shown by stars when the samples were fired at 500°C may indicate the presence of impurities resulting from incomplete phase transformation of the Simonkolleite structure.

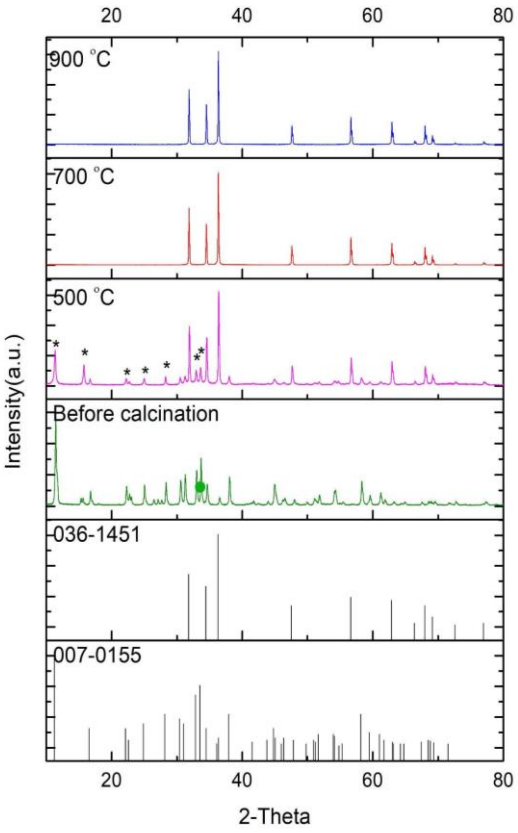

Figure 3. XRD graphs of the standard ZnO particles and as synthesised ZnO particles under different calcination temperatures (Before, 500 °C, 700 °C, 900 °C).

Moreover, average crystallite sizes were calculated, using the Scherrer equation for ZnO particles before and after calcination at 500°C, 700°C and 900°C. The calculation is done by taking FWHM and angle of the most intense peak which corresponds to (101). Average crystallite sizes for ZnO-500, ZnO-700, and ZnO-900 samples were measured as 42.7434 nm, 49.7306 nm, and 50.7144 nm respectively. As expected, the average crystallite size was increased with increasing the calcination temperature. This can be attributed to increased surface energy at high temperature, leading to agglomeration and grain growth.

4.3. Morphological Characterization

The morphology and ZnO particle sizes for all samples were characterised using the SEM (Figure 4). Results showed the shapeless non-uniform particles were obtained when the samples fired at 500 °C, and as the calcination temperature increased to 700 °C and 900 °C clear hexagonal facets started to appear that indicated the formation of ZnO crystal structure

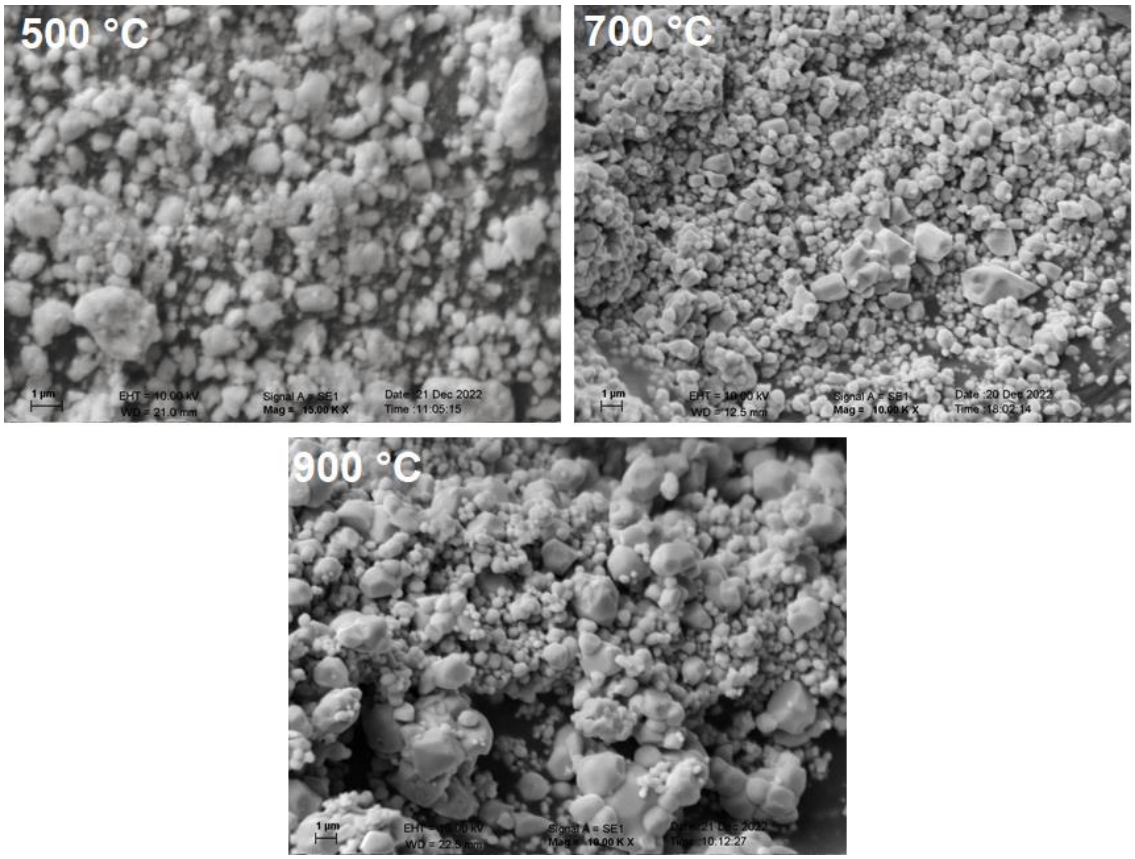

Figure 4. SEM images of the ZnO particles thermally decomposed at 500, 700 and 900 °C.

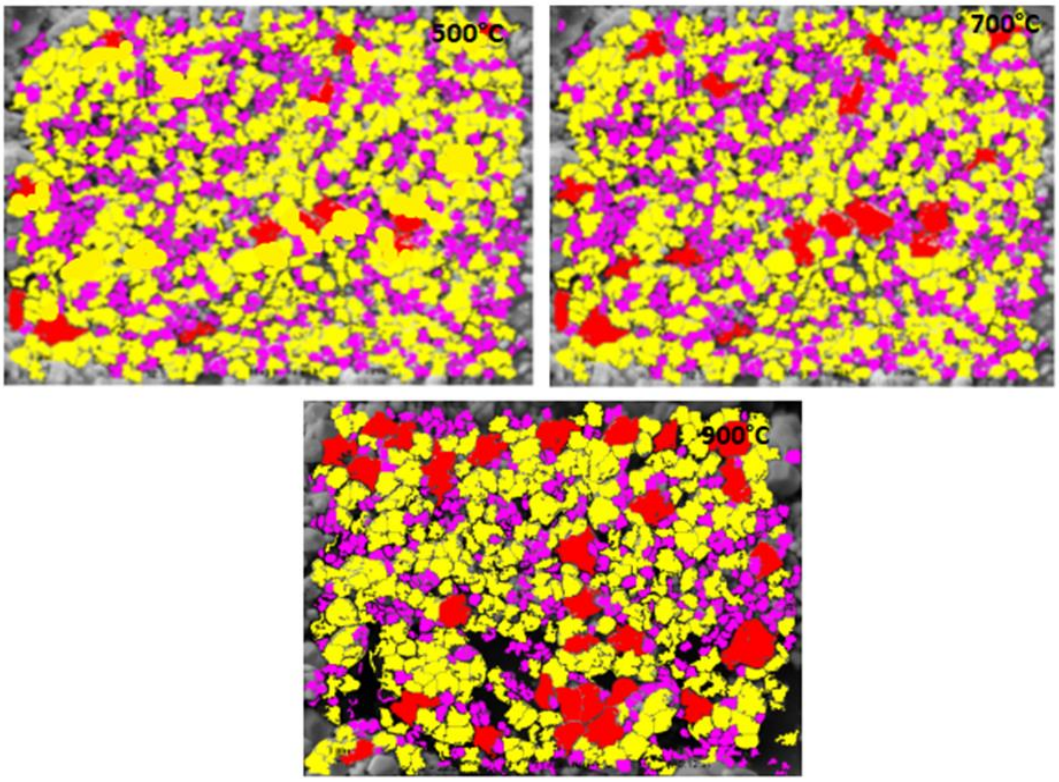

Figure 5. Average particle size in the ranked area of the ZnO particles thermally decomposed at 500, 700 and 900 °C. (Red>Yellow>Purple).

The particle size distribution of the sample was determined by electron microscopy imaging software (Clemex vision lite). The results showed that the sample that measured at 500 °C the small particle size of ZnO was observed and by increasing the temperature to 700 °C and 900 °C the growth takes place in the samples. The average particle size for all samples, in detail, presented in table 1.

Table 1. Estimated structure parameters and average particle size of ZnO particles

Samples	Average particle size (nm)	Maximum (nm)	Minimum (nm)
ZnO- 500	2298 nm	2804.6547	502.8645
ZnO- 700	2308 nm	3203.9472	503.2040
ZnO- 900	2311 nm	3644.2309	503.2051

5. Conclusion

The study concludes that the calcination temperature has a significant effect on the morphology of ZnO particles synthesised using a simple precipitation technique. X-ray diffraction (XRD) was used to analyse the peaks corresponding to different planes of ZnO, and. Using the Scherrer equation, the average crystallite sizes of the particles were calculated at different calcination temperatures, for ZnO particles at 500°C, 700 °C, and 900°C. By using Scherrer Equation, the average sizes of ZnO-500, ZnO-700, and ZnO-900 were found to be 42.7434 nm, 49.7306 nm, and 50.7144 nm respectively. The average sizes of particles increase at elevated temperatures, which might be caused by increasing surface energies that lead to agglomeration of the particles. The study was also characterised by scanning electron microscopy (SEM) to image the surface morphology and particle size distribution. The size of particles was found to approximately range from 2298 nm to 2311 nm with increasing calcination temperature, indicating that the calcination temperature had a significant effect on the morphology and particle size. Additionally, TGA/DTA analysis was performed to deduce the phase transition temperature and thermal stability of samples. The findings indicated that the temperature for the formation of pure ZnO crystalline structure obtained at least 635 °C.

Authors' Contributions

Conceptualization Mahla Shahsavar Gocmen, Ayşe Dulda; methodology Yiğit Gül, Mithat Emre Şahbazoğlu; investigation Gabriel Uğurgel, Enes Barış Bilge, Umut Doğan Gürkan; resources Gökçe Çiçek Kaya, Ömer Faruk Uslu, Batuhan Yıldız, Gurur Unan, Kris Terzioğlu; data curation Mahla Shahvar Gocmen; writing Mahla Shahsavar Gocmen; writing-review and editing Mahla Shahsavar Gocmen, Ayse Dulda; supervision Ayse Dulda.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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