A Review of Synthesis and Characterization of Zinc Oxide Nanoparticles with Small Particle Size Distribution

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Abstract:
Solvothermal synthesis has shown to have a great potential to synthesize Zinc Oxide nanoparticles (ZnO NPs) with less than 10 nm size. In this study, we present a rapid synthesis of ZnO NPs in which ZnO NPs with more uniform shape and highly dispersed were synthesized using zinc acetate dihydrate (Zn(CH3COO)2 2H2O) and potassium hydroxide (KOH) as a precursor and absolute ethanol as solvent via solvothermal method. Few techniques were exploited to characterize synthesized ZnO NPs including X-ray diffraction (XRD), transmission electron microscope (TEM), Brunauer-Emmett-Teller (BET), energy-dispersive X-ray spectroscopy (EDX), fourier transform infrared (FT-IR) spectroscopy, and ultraviolet visible (UV-Vis) spectroscopy. Synthesized ZnO NPs that were prepared via solvothermal synthesis method at 60 °C for 3 hours exhibited a wurtzite structure with a crystalline size of 10.08 nm and particle size of 7.4 ± 1.2 nm. The UV-vis absorption spectrum has shown peak at 357 nm indicate the presence of ZnO NPs. Hence, better quality with uniform size ZnO NPs can be easily synthesized with reduced amount of time via solvothermal synthesis method rather than using other complicated and lengthy synthesis methods.

Keywords: *Zinc Oxide nanoparticles; Solvothermal method; Small particle size; Spectroscopy*

1. Introduction

High demands of nanomaterials have produced enormous applications in global industries. Due to high demand as NPs based products, various types of engineered nanoparticles (ENPs) are synthesized for myriad of applications. These days, ZnO NPs have become a promising candidates and gained more attention especially in nanomedicine and nano semiconductors. ZnO NPs exhibit wurtzite crystal structure that has been widely used in industries due to its unique optoelectric properties. Besides, high optical absorption UVA and UVB in ZnO NPs are also beneficial in antimicrobial products in nanomedicine as nowadays various nanomaterials development have been applied to improve drugs and other medicine.Morphologically, ZnO NPs is an attractive compound that possess thermal and chemical stability. ZnO NPs are made into various shapes and sizes depending on the use of NPs in industries including textile, energy, food, cosmetics, and medicines and other characteristics that make them attractive for broad range of application. According to Li et al., solvothermal process is defined as performing chemical reactions in solvents under specific temperature. Matei et al. also stated that solvothermal synthesis can be easily performed under controlled condition as ZnO NPs can be synthesized into different morphologies depending on the reaction conditions.

Furthermore, NPs characterization using XRD, TEM, BET, EDX, FT-IR spectroscopy, and UV-Vis spectroscopy are fundamental steps especially for examining NPs surface properties and functionality. It is important to characterize NPs in order to determine the behaviour of NPs for further study such as toxicological studies. Ethanol was used for ZnO NPs synthesis as it has hydroxyl group that interact better with NPs as well as increase solubility to allow more interaction between parti. Particles and capping molecules.25 This method has utilized the organic solvent mainly ethanol which generally has low boiling point and generate high pressure that are conducive to obtain a better product crystallization. The aim of this research are to synthesize spherical ZnO NPs with less than 10 nm size

by using zinc acetate dehydrate and potassium hydroxide with a absolute ethanol as solvent via solvothermal method and to characterize synthesized ZnO NPs using few techniques including XRD, TEM, BET, EDX, FT-IR, and UV-Vis spectroscopy.

2. Experimental

2.1 Synthesis of Zinc Oxide Nanoparticles

Zinc oxide nanoparticles was synthesized using solvothermal synthesis process from modified published procedures. Briefly, 1.48 g of Zn(CH3COO)2 · 2H2O (Sigma- Aldrich, India) was dissolved in 63 ml of absolute ethanol (HmBG Chemicals) in a 250 ml Schott bottle and was heated under 60 °C with constant stirring. 0.74 g of KOH (VWR Amresco, US) was also dissolved separately in 33 ml of absolute ethanol in 100 ml Schott bottle under same condition of Zn(CH3COO)2 · 2H2O. After both solutions have dissolved completely, dropwise, KOH was added into Zn(CH3COO)2 · 2H2O slowly under 60 °C with vigorous stirring. The mixture solution was left for 3 hours until the reaction was completed. The obtained product was then dried at room temperature and ground to form powder.

2.2 Characterization of ZnO Nanoparticles

Different techniques were used to characterize the synthesized ZnO NPs. Crystal structure and primary crystal size was characterized using XRD (Xpert Pro Diffractometer, Netherlands). The XRD pattern was obtained using X-ray diffractometer with Cu-Kα radiation of 40 kV and 30 mA with step size of 0.017°. Basically, copper grid was prepared by applying fomvar coating on the copper grid. ZnO NPs were diluted with ethanol and sonicated with ultrasonic cleaner (Elma, Germany) for 30 minutes. Then, 4 µl of ZnO NPs sample was loaded onto the coated copper grid before being observed under TEM. Besides, Brunauer-Emmett-Teller (BET) (Quantachrome, US) was used to analyse the surface area of the synthesized ZnO NPs. About 0.3 g of ZnO NPs powder were placed in the tube and was allowed to degas at 175 °C for 2 hours as referred to Zhou et al.27 in flowing nitrogen. The sample was then placed in the metal hole, pressed until the sample compressed inside the hole, and analysed using FT-IR (Thermo scientific Nicolet iS10, US). Ultraviolet visible spectroscopy (UV-vis) (Perkin Elmer Lamda 25) was also used in order to determine the optical absorption spectra of ZnO NPs that was dispersed in water.

3. Results and discussion

3.1 X-Ray Diffraction (XRD)

XRD pattern of synthesized ZnO NPs is shown in Figure 1. Based on the XRD pattern, synthesized ZnO NPs has high purity of wurtzite crystalline structure as the diffraction peak is seen to be intense and narrower. This result was also being compared with the given standard XRD pattern of ZnO (JCPDS 36-1451) for confirmation purpose. Apart from that, as mentioned by Tagreed et al.29 the average crystalline structure (D) was calculated according to Debye-Scherrer's formula:

$$\text{Scherrer's Equation:}$$
$$\text{Particle size } (D_p) = \frac{0.89\,\lambda}{d\cos\theta}$$

Where 0.89 refers to Scherrer's constant, is λ a wavelength of X-rays, θ refers to Bragg diffraction angle, and d is full width at half maximum (FWHM) of diffraction peak. The most intense diffraction was chosen which is <010> and the crystalline size of synthesized ZnO NPs was determined to be 10.08 nm. Besides, the percentage of zinc content from the synthesized ZnO NPs via the XRD analysis, which revealed that there is 99% of zinc without any other elements being detected as shown in Table 1. From his obtained data, it shows that synthesized ZnO NPs were determined to be of high purity.

Table 1: Pattern list of ZnO NPs obtained from XRD

Chemical Formula	Reference code	Compound name	Score (%)
Zn	98-000-9346	Zincite	99

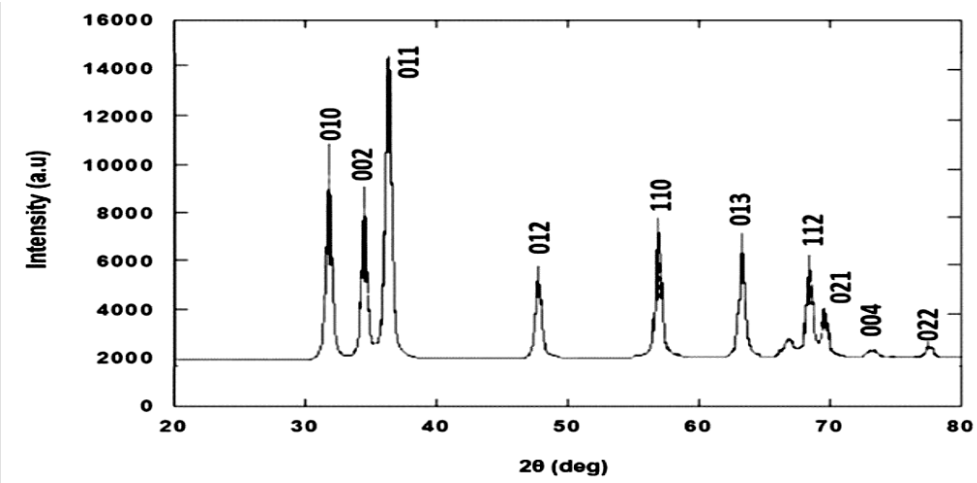

Figure1. XRD pattern of synthesized ZnO nanoparticles

3.2 Transmission Electron Microscope (TEM)

Physical characterization of NPs is commonly characterized using transmission electron microscope (TEM). Phoohinkong et al. stated that TEM was carried out in order to obtain high accuracy of the actual particle size and shape pattern. This shows that TEM is one of the reliable tools for NPs characterization. The calculated mean size of synthesized ZnO NPs was determined to be 7.4 ± 1.2 nm. TEM particle distribution result in Figure 2 also confirmed that a narrow size distribution of ZnO NPs can be obtained via solvothermal synthesis method.

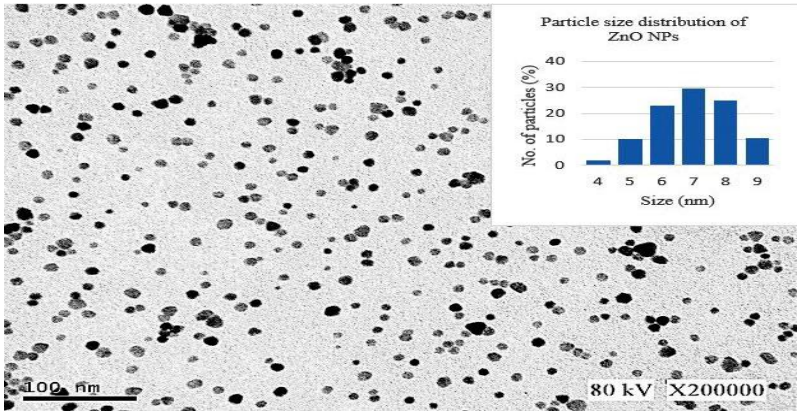

Figure 2. ZnO NPs image under transmission electron microscope (TEM) and particle size distribution of ZnO NPs

The synthesized ZnO NPs observed under TEM also correlates with the XRD patterns that reveal high purity of wurtzite crystalline structure of ZnO NPs. Therefore, this shows that solvothermal synthesis can be used to obtain a better image that proves the presence of less than 10 nm of synthesized ZnO NPs with high dispersity.

3.3 Brunauer-Emmett-Teller (BET)

BET was carried out in order to determine the specific surface area for three different sized of ZnO NPs by N2 adsorption temperature of 77 K. Figure 3 shows nitrogen (N2) adsorption-desorption isotherms of ZnO NPs obtained from BET analysis (Quantachrome, US). Figure 3 also shows a typical

type IV adsorption obtained from synthesized ZnO NPs. The isotherm relative was observed to be relative flat and similar result was also obtained by Zhou et al.

Table 2 BET results of synthesized ZnO NPs in comparison with other analytical techniques

Constant C	BET Surface area	Average Particle size DBET	Average Size via TEM	Crystal Size via XRD
28.904	101.32 m^2/g	9.7 nm	7.4 nm	10.8 nm

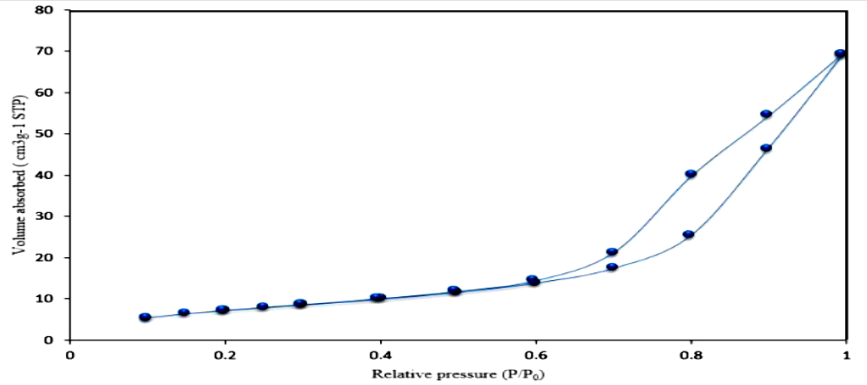

Figure3: N2 adsorption- desorption isotherms of ZnO NPs

This shows that smaller NPs attribute to high surface area. Furthermore, the average particle can also be calculated from BET data. Since the shape of ZnO NPs was determined to be in spherical shape, average particle size can be calculated based on the equation $D_{BET} = 6000/ \rho \cdot Sw$ in which D_{BET} is the average particle size, ρ is the theoretical density of the sample which was 6.11 g cm^{-3}, and Sw is the obtained surface area as referred to Zhou et al. and Ghasemzadeh et al. Table-2 summarised the BET results of ZnO NPs. Thus, this confirms that the particle size of synthesized ZnO NPs was in nanoscale which is approximately 10 nm.

3.4 Absolute Ethanol as a Solvent

From the obtained TEM result as shown in Figure 2, it shows that solvent also plays an important role for ZnO NPs synthesis. This includes the physico-chemical properties of ZnO NPs in terms of size and shape. The utilization of absolute ethanol as a solvent has formed a highly dispersed small ZnO NPs with uniform shape and size that was determined to be less than 10 nm as expected. Similar finding also described the formation of spherical shape of ZnO when ethanol was being used as a solvent. Therefore, eminent production of ZnO NPs with uniform spherical shape with high dispersity can be easily obtained by utilizing ethanol as a solvent for solvothermal synthesis method. Other benefit of using absolute ethanol would be the short period of synthesis process needed to produce less than 10 nm of ZnO NPs with uniform size.

4. Conclusion

ZnO NPs with less than 10 nm (7.4 nm) was successfully prepared by using zinc acetate dihydrate and potassium hydroxide via the solvothermal synthesis process. The utilization of absolute ethanol as a solvent was able to produce uniform shape and better dispersity of ZnO NPs. Synthesized ZnO NPs were also able to be confirmed by various characterization techniques including XRD, TEM, FT-IR, and UV-vis spectroscopy. XRD has revealed awurtzite crystalline structure of ZnO NPs where by physical characterization of ZnO NPs was determined by using TEM and size less than 10 nm of ZnO NPs was obtained. BET revealed that the synthesized ZnO NPs has high surface area that correlate with the particle size obtained from TEM. EDX has proven the purity of synthesized ZnO NPs which contain high Zn and O element composition. FT-IR and UV-vis spectroscopy also showed the absorbance spectrum that indicates the presence of ZnO NPs. This study also presents a potential effective method to prepare ZnO NPs within shorter time with smaller particle size distribution.

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