Synthesis of Zinc Oxide from Oil Palm Leaves by Green Sol-Gel Method : Effect of Concentration Variation

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Abstract— **In this study, zinc oxide (ZnO) nanoparticle has been successfully synthesized using oil palm leaves extract (OPLE) as the stabilizing agent. ZnO currently has a great potential in food industry for example zinc oxide is used as a food additives due to its antioxidant properties. However, this study is focusing more on food packaging application as it is one of food safety requirement. Therefore, the structure of OPLE and ZnO nanoparticles synthesized from OPLE at different concentration of precursors has been characterized using Fourier Transform Infra-Red (FTIR) analysis and X-ray Diffraction (XRD) analysis by using green sol-gel method. The characterization of OPLE and the particle size of ZnO nanoparticles has been investigated and discussed.**

Keywords—Zinc oxide, ZnO, FTIR, XRD, Nanoparticles.

I. Introduction

Nanoparticle research is one of the science branch that have the most studied nowadays in various fields. There are great potential applications in biomedical, optical, electronic fields, food safety and many others. This is why nanoparticle based research have been conducted for food packaging application.

According to Ramesh et al. (2014), synthesis of zinc oxide nanoparticles recently has been a spot-light due to its antibacterial, wound healing and photochemical activity. There are various methods to synthesis ZnO. ZnO nanoparticles can be synthesized by using chemical synthesis, sol-gel method, precipitation method, green synthesis method and many other methods. In this research, green sol-gel method have been used as it is simple, easy, environmental friendly and also not expensive.

A review from Imoisi et al. (2015) stated that palm oil leaves has been used as the ruminant feed for decades until today. This proved that palm oil leaves is non- toxic. Their research on Oil Palm Leaves Extract (OPLE) has proven that it is beneficial to affect lipid profile, blood pressure, pressure, blood physical and biochemical cancer markers and is organ protective. Therefore it is suitable to use palm oil leaves in this synthesis of zinc oxide nanoparticles as it is safe from chemical and nontoxic as been proven from histological observations.

In this investigation, the OPLE will be characterized. This method will involve the extraction of palm oil leaves before we can synthesis the ZnO nanoparticles. Then, ZnO that was synthesized with different concentration will be characterize to investigate nanostructures of ZnO by using green synthesis method. Techniques that will be used are FTIR analysis and XRD analysis. This method of characterization will resulting in knowing the functional group and minerals contain in the OPLE and the ZnO nanoparticles. The average size also will be investigated and schematic results of zinc crystal will be prepared.

II. METHODOLOGY

A. *Materials*

Plant material

The palm oil leaves will be collected from UiTM Shah Alam nearest areas as the palm oil tree is easy to find at Shah Alam.

Chemical Materials

The precursor that will be used in this experiment is Zinc Nitrate Tetrahydrate ($ZnNO_3.4H_2O$) and Sodium hydroxide (NaOH).

B. *Experimental Procedure*

Extraction of Palm Oil Leaves

Before extraction the oil palm leaves is conducted, the oil palm leaves is collected and washed several times to remove dust particles. Then, clean oil palm leaves is left to dry in the oven at 100^oC. Then, dried leaves is cutted into pieces and grinded until it becomes powder. 20 g of oil palm leaves powder is placed it in the beaker together with 400 ml of distilled water. The mixture has been boiled for 1 hour at 80^oC until the colour change from watery. After that, the extract produce is cooled to room temperature and filtered using filter paper. The extract is stored in the refrigerator in order to be used in further experiment.

Figure 1: Sample Preparation

Synthesis of Zinc Nanoparticles

50 mL of 0.2 M Zinc Nitrate Tetrahydrate was prepared. 50 ml of OPLE is added into a beaker together with 0.2 M Zinc Nitrate tetrahydrate solution. The initial pH is determined using pH meter and NaOH is added until the pH reach 12. Then, the solution is boiled at 70ºC by using stirrer heater for 1 hour until the white colour paste produced. The white colour paste is filtered and heated in the oven for 5 to 6 h hours at 100ºC. Collect the paste into ceramic crucible to mash it and white colour of Zinc Oxide will be obtained. The procedure will be repeated with 0.3M, 0.4M, 0.5M, 0.6M, 0.8M and 1.0M of Zinc Nitrate Tetrahydrate Solution.

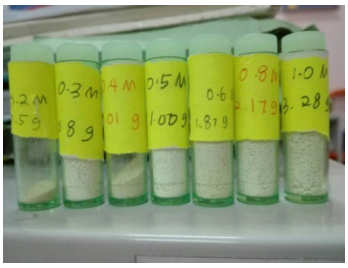

Figure 2: ZnO Powder

C. Characterization Techniques

Characterization of palm oil leaves extract

In order to get information about the functional group and also the composition of minerals in the POME, the following following techniques will be conducted.

- Fourier Transform Infrared Spectroscopy (FTIR)

Characterization of Zno Nanoparticles

Techniques that will be used to characterized ZnO nanoparticles that has been synthesized are as below in order to obtained the functional group and the size of the ZnO nanoparticle.

- Fourier Transform Infrared Spectroscopy (FTIR)
- X-ray Diffraction Analysis (XRD)

III. RESULTS AND DISCUSSION

A. Fourier Transform Infrared Spectroscopy (FTIR) Analysis on Oil Palm Leaves Exrtract (OPLE).

Figure 3 shows the FTIR spectrum of the OPLE. In the IR spectrum of Oil palm leaves, the band at 3296.12 cm^{-1} is due to stretching vibrations of O–H groups in water, alcohol and phenols and N–H stretching in amines. The C–H stretch in alkanes and O–H stretch in carboxylic acid appear at 2917.1 and 2849.69 cm^{-1} respectively. The strong band at 1736.43 cm^{-1} is attributed to the C=O stretch in aromatic group. The C=C stretch in aromatic ring appears at 1618.34 cm^{-1}. The C–O stretching in amino acid causes a band at 1029.21 cm^{-1}. Thus from the IR spectrum it can be observed that oil palm leaves sample is rich in phenols, carboxylic acid, amino acid and proteins. The presence of O-H group in OPLE indicates the suitability of the extract to be alcohol substituent in the synthesis. **Table 1** has summarized all the peak identification from FTIR spectrum of oil palm leaves.

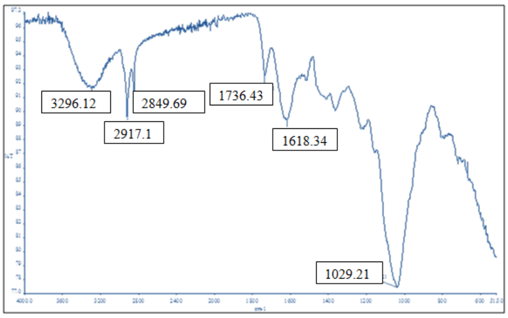

Figure 3: FTIR Analysis FTIR Spectrum for oil palm leaves

Table 1 : Peak Identificationof FTIR Spectrum of Oil Palm Leaves

No	Wave Number (cm^{-1})	Peak Assignments
1.	3296.12	O-H stretching of alcohol and phenols
2.	2917.1	C-H stretching of alkanes
3.	2849.69	O-H stretching of carboxylic acid
4.	1736.43	C=O stretching of aromatic group
5.	1618.34	C=C stretching of aromatic ring
6	1029.21	C-O stretching of amino acid

B. Fourier Transform Infrared Spectroscopy (FTIR) Analysis on Zinc Oxide

The presence of O-H groups the synthesis of ZnO nanoparticles in every concentration investigated is responsible by the extract as the phenolic group presence in the OPLE as well as the bending of alkane found in the ZnO is affected by the presence of it in the OPLE. From the FTIR spectrum observed, the strongest band of O-H groups present in 1.0M of pecursors as the band cover most of the y-axis.

The band of O-H group present showed up at 3374.05 cm^{-1}, 3445.47 cm^{-1}, 3406.44 cm^{-1}, 3398.7 cm^{-1}, 3400.04 cm^{-1}, 3402.56 cm^{-1} and 3349.32 cm^{-1} at concentration of 0.2M, 0.3M, 0.4M, 0.5M, 0.6M, 0.8M and 1.0M of precursor respectively.

The band correlated to ZnO from the spectrum are 871.43 cm^{-1}, 865.2 cm^{-1}, 834.72 cm^{-1}, 875.6 cm^{-1}, 834.91 cm^{-1}, 864.32 cm^{-1} and 679.05 cm^{-1} with at precursors with concentration of 0.2M, 0.3M, 0.4M, 0.5M, 0.6M, 0.8M and 1.0M respectively. The result obtained implied with experiments reported by Kumar et al. (2013) and Ochieng et al. (2015) with the agreement of several investigation reported similar cases, the band for metal oxide basically shown below 1000 cm^{-1}.

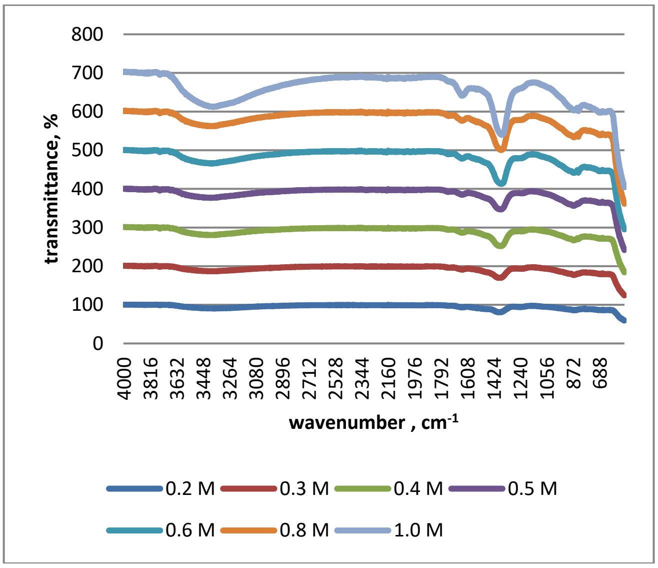

Figure 4: FTIR Analysis FTIR Spectrum for Zinc Oxide at Different Concentration.

Table 2 : Peak Identification of FTIR Spectrum for Zinc Oxide at Different Concentration.

Conc. (M)	Band of Adsoprtion (cm^{-1})				
	O-H	C≡C	C=O	C-H	Zn-O
0.2	3374.05	-	-	1383.07	871.43
0.3	3445.47	-	-	1378.72	865.2
0.4	3406.44	-	-	1360.72	834.72
0.5	3398.7	-	-	1372.97	875.6
0.6	3400.04	-	-	1356.26	834.91
0.8	3402.56	-	-	1371.98	864.32
1.0	3349.32	2171.41	1638.70	1359.94	679.05

C. X-ray Diffraction Analysis on Zinc Oxide

XRD pattern of the prepared Zinc oxide nanopowder is shown in **Figure 5(a)** until **Figure 5(g)**. The similar results were also reported by others. The (hkI) values are agreed well with the standard card of ZnO powder sample (JCPDS file No: 36-1451).

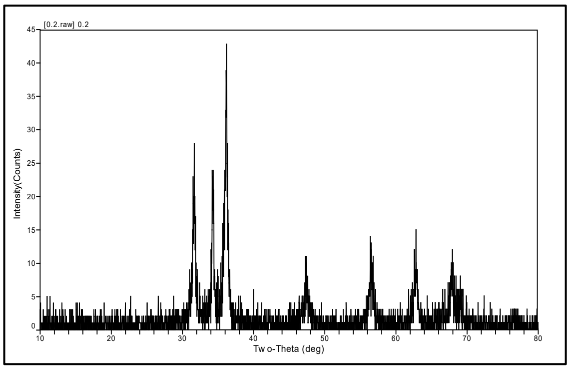

Figure 5(a): XRD Analysis on Zinc Oxide Produces from 0.2M Zinc Nitrate Tetrahydrate

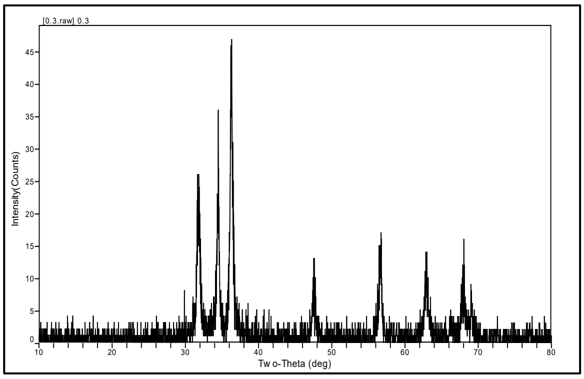

Figure 5(b): XRD Analysis on Zinc Oxide Produces from 0.3M Zinc Nitrate Tetrahydrate

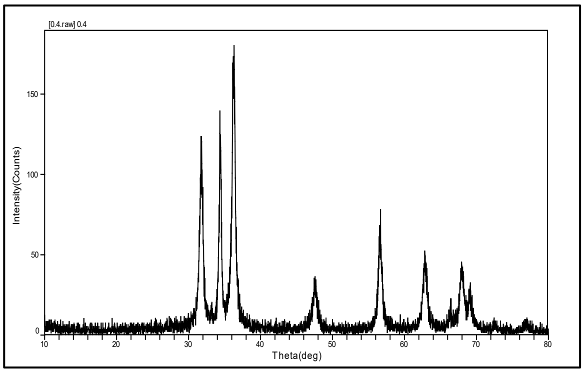

Figure 5(c): XRD Analysis on Zinc Oxide Produces from 0.4M Zinc Nitrate Tetrahydrate

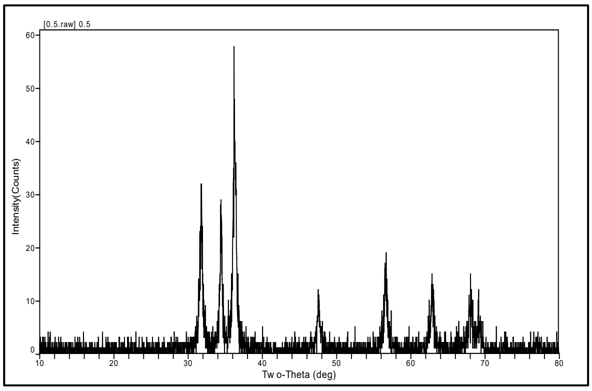

Figure 5(d): XRD Analysis on Zinc Oxide Produces from 0.5M Zinc Nitrate Tetrahydrate

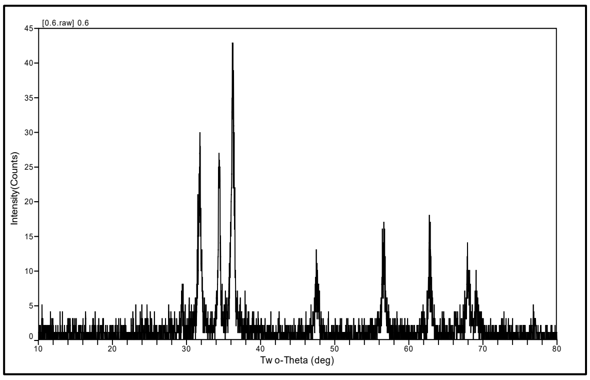

Figure 5(e): XRD Analysis on Zinc Oxide Produces from 0.6M Zinc Nitrate Tetrahydrate

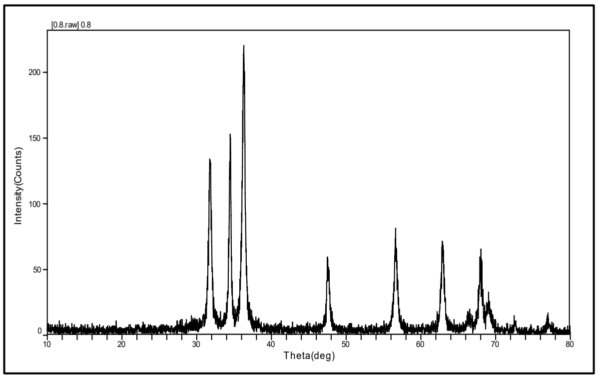

Figure 5(f): XRD Analysis on Zinc Oxide Produces from 0.8M Zinc Nitrate Tetrahydrate

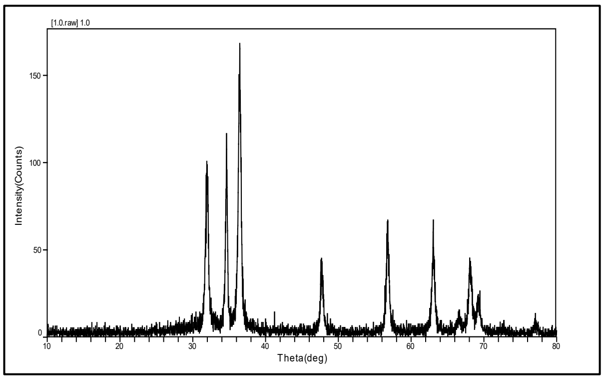

Figure 5(g): XRD Analysis on Zinc Oxide Produces from 1.0M Zinc Nitrate Tetrahydrate

Ochieng et.al. (2015) state that, the appearance of sharp diffraction patterns confirms the small size as well as high crystalline of the synthesized nanoparticles. The XRD patterns obtained in this study were also similar to XRD patterns obtained in literatures. The Bragg's reflection obtained also similar to a literature from Kolekar et.al. (2011), Kumar et. Al (2013) and several other literatures. The indices imply with the ZnO wurtzite structure (standard JCPDS card 36-1451). **Figure 6** shows the standard JCPDS card of bulk ZnO with hexagonal structure (JCPDS - 36-1451).

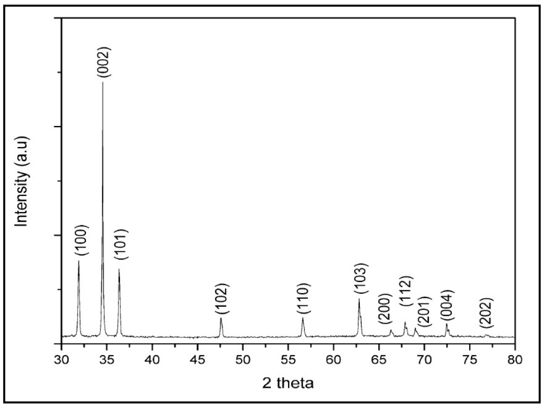

Figure 6: The standard JCPDS Card of Bulk ZnO with Hexagonal Structure (JCPDS - 36-1451)

The crystallite average size, Dp, of the prepared nanopowder can be calculated by using Scherrer's formula.

$$D = \frac{K\lambda}{B\cos\theta}$$

Where λ is the wavelength of X rays used (1.54060 Å), β is the full width at half maximum (FWHM) and θ is the angle of diffraction. In this case, to obtained the average particle size , the maximum peak in every spectrum need to be considered. The Scherrer's constant, K= 0.9, X-ray wavelength, λ= 1.5406 Å. The average particle size obtained from concentration of 0.2M, 0.3M, 0.4M, 0.5M, 0.6M, 0.8M and 1.0M of precursors are 17.46 nm, 18.47 nm, 18.91 nm, 19.64 nm, 20.73 nm, 21.32 nm and 22.04 nm respectively. From the result obtained, the particle size of ZnO is increased as the concentration increase. The crystallite average sizes of prepared nano powder are summarized in **Table 3**.

Table 3 : Average Particle Sizes Obtained from Different Concentrations.

Concentration, M	2θ, deg	FWHM, deg	Average Particle Size, D, ang	Average Particle Size, D, nm
0.2	36.16	0.4998	174.62	17.46
0.3	36.26	0.4094	184.71	18.47
0.4	36.28	0.4726	189.14	18.91
0.5	36.26	0.4615	196.47	19.64
0.6	36.22	0.4443	207.29	20.73
0.8	36.34	0.3962	213.23	21.32
1.0	36.46	0.4214	220.43	22.04

IV. CONCLUSION

In conclusion, the objective of this study have been completed and discussed. ZnO nanoparticle has been successfully synthesized through green synthesis method from oil palm leaves considering different concentrations of precursor which is Zinc Nitrate Tetrahydrate as a zinc source.

Before characterization ZnO is conducted, the extract of palm oil leaves had been characterized first by using FTIR analysis. From the result obtained, it can be concluded that , OPLE was rich in phenols, carboxylic acid and amino acid as there are the presence of O-H group of alcohol and phenol and also carboxylic acid. Besides, the presence of amino acid was detected as the spectrum showed the stretching of C-O band from the analysis. The O-H group presence indicates the suitability of OPLE to be alcohol subtituent in green synthesis method.

FTIR analysis of ZnO powder shows the presence of phenol group and alkane group in the ZnO. This may be responsible by OPLE that rich with phenol and alkane group. The band showed up at 3374.05 cm^{-1}, 3445.47 cm^{-1}, 3406.44 cm^{-1}, 3398.7 cm^{-1}, 3400.04 cm^{-1}, 3402.56 cm^{-1} and 3349.32 cm^{-1} at concentration of 0.2M, 0.3M, 0.4M, 0.5M, 0.6M, 0.8M and 1.0M of precursor respectively. This concluded that the OPLE extract is suitable to be alcohol subtituent.

The band correlated to ZnO from the spectrum are 871.43 cm^{-1}, 865.2 cm^{-1}, 834.72 cm^{-1}, 875.6 cm^{-1}, 834.91 cm^{-1}, 864.32 cm^{-1} and 679.05 cm^{-1} with at precursors with concentration of 0.2M, 0.3M, 0.4M, 0.5M, 0.6M, 0.8M and 1.0M respectively. The result obtained implied with experiments reported by Kumar et al. (2013) and Ochieng et al. (2015) with the agreement of several investigation reported similar cases, the band for metal oxide basically shown below 1000 cm^{-1}.

Characterization of ZnO powder using XRD analysis resulted that with the increases of concentration lead to the increasing of particle size. This is proven by a report from Wirunmongkol et.al (2013). The particle size obtained are 17.46 nm, 18.47nm, 18.91 nm, 19.64 nm, 20.73 nm and 21.32 nm at different concentration of precursor which are 0.2M, 0.3M, 0.4M, 0.5M, 0.6M, 0.8M and 1.0M respectively. The particle sizes resulted from XRD analysis in this investigation are implied with the sizes reported by Sagar et al. (2013), Sivakumar et al. (2014), Ramesh et al. (2014), Ochieng et al. (2015) which is less than 50 nm.

Besides, the XRD spectrums showed the sharp peaks at all the concentration. According to Ochieng et.al (2015) these appearances showed up because the ZnO has a small size of nanoparticles and also has high crytallinity.

Although this investigation studies has been carried out systematically, there are still issues that need to be improved. In order to confirm the result obtained in this investigation, it is suggested to repeat on the similar case by using other synthesis method. As this investigation is designed for food packaging application, it is suggested to do research on the antimicrobial activity to study the effect of concentration on the growth of bacteria. Thus, the use of plant extracts has proven that it is a green method for the synthesis of zinc oxide nanoparticles and presents adverse area for further studies.

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