

EFFECT OF REACTION TIME OF ZINC OXIDE NANOPARTICLE SYNTHESIZED WITH BANANA PEEL EXTRACT

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Abstract—Zinc Oxide Nanoparticles was synthesized by green approach employing aqueous extract of banana peel. The objective of this study is to evaluate the potential of banana peel aqueous extracts for the synthesis of zinc oxide nanoparticles. Synthesize zinc oxide nanoparticles using banana peel aqueous extract at times 30mins, 1hrs, 1.30hrs, 2hrs and 2.30hrs. The effect of different time conditions (30mins–2.30hrs) is studied. The XRD suggested hexagonal wurtzite structure for these prepared zinc oxide nanoparticles. Synthesized zinc oxide nanoparticles were characterized using UV-Vis spectroscopy with maximum absorbance peak. The chemical group association and elemental composition of nanoparticles was analyzed using FTIR.

Keywords— *Green synthesized, zinc oxide nanoparticles, XRD, UV-Vis, FTIR, banana peel aqueous extract.*

I. INTRODUCTION

Nanoparticles has a wide variety of applications in various fields such as health, biomedicine, chemicals industries, food and feed, care products, environmental, drug and gene delivery, energy science, electronics mechanics and space industries [1-2].

A variety of synthetic methods are utilized to synthesis of zinc oxide nanoparticles. Three types in the synthesis of zinc oxide, that is, biological, physical and chemical methods. Design of processes that reduces or eliminates generation of hazardous substances is the key principle for sustainable chemistry. Synthesis of nanoparticles by developing green synthesis to produce greener and cleaner methods is a major focus of this research [3-6]. In this research, it is focused on the zinc oxide nanoparticle synthesis using banana peel aqueous extract. Because of biological methods employing either microorganisms or plant extracts are rapidly emerging as a simple alternative for nanoparticles synthesis [7]. Green routes are utilized for the production of zinc oxide nanoparticles because of the least possible number of chemicals utilized that produces least amount of pollutants and are energy efficient as well as cost-effective.

Zinc oxide is a semiconductor property that has a broad energy band (3.37eV), high bond energy (60meV) and high thermal and mechanical stability at room temperature make it attractive to have contributed to technology of electronics, optoelectronics and laser [8]. The piezo- and pyroelectric properties and its overwhelming properties of zinc oxide mean that it can be used as a sensor, optoelectronics, photonics, converter, energy generator, transducer, biomedical sciences and photocatalyst in hydrogen production [9].

Property of zinc oxide is good because able to produce blue-green luminescence and absorption in the ultraviolet (UV) region, which is used for textile industries, sensors, sunscreens photodetectors, catalyst and for obtaining solar energy [10-17].

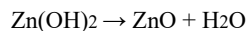
Banana peel is the one of the recommended method for green synthesis of zinc oxide nanoparticles. Banana peel parts have phytochemicals properties for synthesizing of zinc oxide nanoparticles. Banana peel is the natural extracts parts is a very friendly to the environment, cheap process because does not use costly equipment and takes less time for the process [22]. Banana peel is most preferred source because of allow to produce a stable production and several of sizes and shaped nanoparticle [23]. Banana peel as an extraction process is recommended because of more comparative techniques, to enhance the properties of production of zinc oxide nanoparticle, less hazardous to the environment and to maintaining the cost. Therefore, in this study synthesis of zinc oxide nanoparticles by using banana peel extract that is accessible in Malaysia. Banana peels have been chosen as the material in the extraction process through green synthesis to synthesized zinc oxide nanoparticles.

In the production of nanoparticles with specified properties, it has the problem that must be avoid by find the alternative way to get inexpensive, environmentally safe and efficient. Synthesis zinc oxide nanoparticles show that does not give negative affect to the environment. The most environmentally benign method uses plant extract as a reducing agent [24]. This biological approach to zinc nanoparticle synthesis is ideal in terms of green chemistry [25]. Green nanoparticles synthesis, using banana peel extracts has been conducted for many reasons, including eco-friendly ease of handling and cost effectiveness. The synthesis of nanoparticles using rich of phytochemicals in banana peel which allow efficient reduction of metal precursors for conversion into the nanoparticles. Therefore, plants have reducing agents as the chemicals which perform reduction reactions.

The first objective of this study is to synthesize zinc oxide nanoparticle through a green synthetic pathway using banana peel extract. Second objective is to investigate the effect of reaction time on zinc oxide nanoparticles synthesized with banana peel extract. Third objective is to detect the presence of ZnONPs that were observed from absorption peak using Ultraviolet-Visible spectrophotometer (UV-Vis) analyzer. Next objective is to identify the structure of zinc oxide nanoparticles and identify crystallite size of ZnONPs using X-ray Powder Diffraction (XRD) analyzer and also to identify the functional group exists in the banana peel, the FTIR is used. Lastly, Brunauer, Emmett and Teller (BET) was used to identify the particle size.

This study is focusing on the synthesis of zinc oxide nanoparticles by using green synthesis to produce greener and cleaner methods

by using banana peel extract as the reducing agents. The parameter that is focused and set in this study is the time.



II. METHODOLOGY

A. Materials and Methods

A.1 Collection of sample

Banana peels were collected from Seksyen 7, Shah Alam, Selangor. The leaves were thoroughly washed for several times with distilled water and dried at room temperature to remove the moisture content effect by washing in the banana peel sample. Then, used for further studies.

A.2 Preparation of banana peel extract

Aqueous extract: Aqueous extract of banana peels was prepared. 20 grams of thoroughly washed peels were immersed in 200 ml of ultrapure water and heat the mixture until the solution was reached at temperature 70°C. After that, the extract was filtered using vacuum filter to remove insoluble fraction.

A.3 Green synthesis of zinc oxide nanoparticles

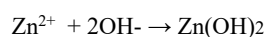
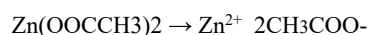
2 grams of zinc acetate dehydrate was added into 20 ml of prepared sample of banana peel extract. 2 Molar sodium hydroxide solutions were prepared by mixture of 1000 ml distilled water and 80 grams sodium hydroxide pellet. The 2 Molar Sodium Hydroxide solutions was added drop by drop using into the mixture of zinc acetate dehydrate with aqueous extract until the solution reached pH 12. Sample then divide into five for further studies which are into different time reaction at 30mins, 1hrs, 1.30hrs, 2hrs and 2.30hrs.

The solution was heated until solution was reached at temperature 70°C. After the solution was reach at temperature 70°C, the solution was heated for different time reaction at 30mins, 1hrs, 1.30hrs, 2hrs and 2.30hrs. A precipitate occurred in the solution. The solution was poured into distilled water until reached pH 7. The solution was filtered using vacuum filter and the precipitate was collected. The precipitate was dried at temperature 40°C in oven for overnight. Five dried white precipitate sample was form at different reaction times reaction and used for further analysis.

B. Characterization of zinc oxide nanoparticles

B.1 Reaction involved in the synthesized of ZnONPs

Redox process was involved in the synthesis of zinc oxide nanoparticles. Zinc acetate dihydrate aqueous solution was added into banana peel extract which was help in the reduction of Zn(II) to Zn(0) and maintains the size of particles formed in nanoscale by capping them from come into contact with each other. A cloudy solution was formed showed that the existence of reduction reaction. Sodium hydroxide (NaOH) was added as an accelerant to enhance the rate of reduction and nucleation process by direct precipitation of Zn^{2+} to Zn(OH)_2 in alkaline condition, pH12 followed by loss of water to form zinc oxide nanoparticles (Balavandy et al., 2015; Nishimura et al., 2011). The related chemical reactions are shown in the equation below:-



B.2 X-ray diffraction (XRD)

The phases and crystallinity of the zinc oxide nanoparticles were characterized using an XRD analyzyer (D8 ADVANCE; Bruker AXS Inc, Madison, WI, USA) using a monochromatized X-ray beam with in the 2θ range of 20°–80° with a step size of 0.01° and a scanning rate of 5°/min. The X-rays used for this purposed were generate at 40 kV and 40 kA (J Mater Chem. 2012). The Debye–Scherrer equation was used to calculate the ZNPs crystallite size (D) from the highest diffraction peaks:

$$D = (k\lambda) / (\beta \cos \theta)$$

where k is the proportionality constant or shape factor and its value is 0.9, λ is the X-ray wavelength coming from Cu-K α , and its value is 1.54178 Å, β is the full width at half maxima of the diffraction peak in radians, θ is the Bragg's angle in degrees (Elements of X Ray Diffraction, 1956).

B.3 UV-Visible absorption spectroscopy (UV-Vis)

Double-beam UV-Vis spectrophotometer will help the absorbance spectra of zinc oxide nanoparticles were measured in the quartz cuvette with a 1 cm path length. The distilled water was used as a reference material for background correction [20]

B.4 Fourier transform infrared spectroscopy (FTIR)

Infrared absorption spectroscopy was used to determine the structures of molecules with characteristic of molecules by absorption of infrared radiation. The sample molecule exposed to infrared radiation in the range of Infrared region is 300 cm⁻¹ to 3900 cm⁻¹.

B.5 Brunauer, Emmett and Teller (BET)

The specific surface area of the samples was investigated by Brunauer, Emmett and Teller area analysis. The sample was operate at 150 °C for 300min.

III. RESULTS AND DISCUSSION

A. X-ray diffraction analysis (XRD)

The diffraction peaks in the XRD shown in Figure 1 indicated that the sample zinc oxide nanoparticles greatly showed the structure of hexagonal wurtzite, this confirmed that, almost all the samples that synthesized showed the XRD patterns of diffraction peaks at around 31.78°, 34.43°, 36.28°, 47.57°, 56.62°, 62.86°, 67.97° and 69.12°. By comparing all the five samples that synthesized at different reaction time with diffraction peaks of ZnONPs (Pure) greatly showed that diffraction peak for all five samples at around diffraction peaks for ZNPs (pure), respectively, Table 4.2. The diffraction peaks of the different samples of ZNPs formed at 30mins, 1hrs, 1.30hrs, 2hrs and 2.30hrs comparing and matched with the standard card of JCPDS Card No. 36-1451 (Zincite) and they proved to be characteristic structures of hexagonal wurtzite.

By applying the Debye–Scherrer equation to the full width at half maxima from the highest diffraction peaks, the average crystallite size of reaction time-induced ZNPs at 30mins, 1hrs, 1.30 hrs, 2hrs and 2.30hrs were found to be 38.33 nm, 51.97nm, 57.04nm, 73.07 nm and 1169.02 nm, respectively Table 1. By comparing crystallite size for all the samples that synthesized at different reaction time with ZNPs (Pure), the crystallite size of ZNPs (1.30hrs) are nearly the same with crystalline size of ZNPs (Pure).

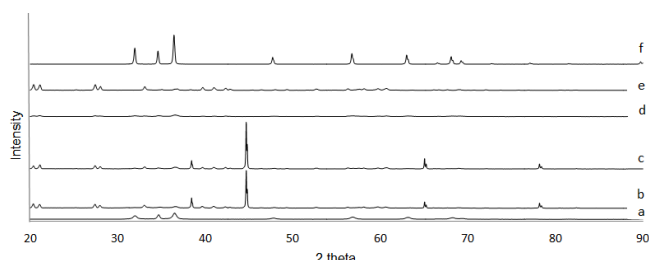


Figure 1: XRD of zinc oxide nanoparticles prepared at different time reaction conditions

Notes: a) 30mins b) 1hrs c) 1.30hrs d) 2hrs e) 2.30hrs f) Pure ZnO NPs

Sample	Crystallite size (nm)	Maximum absorbance (nm)
ZNPs (Pure)	64.06682	36.4114
ZNPs (30mins)	38.3300	36.4630
ZNPs (1hrs)	51.9700	44.6907
ZNPs (1.30hrs)	57.03783	44.6735
ZNPs (2hrs)	73.07468	36.6005
ZNPs (2.30hrs)	1169.02172	20.3972

Table 1: The effect of various reaction conditions at time (30mins, 1hrs, 1.30hrs, 2hrs and 2.30hrs) on the synthesis by comparing with pure ZNPs

B. UV-Visible absorption spectroscopy (UV-Vis)

The Figure 2 showed the UV-Vis absorption of zinc nanoparticles obtained from banana peel extract. Ultraviolet-Visible spectroscopy used to detect the presence of ZnO NPs in samples. Intense absorption peak in the samples were observed by UV-Vis spectrum (300nm to 500nm).

It was observed that the samples at different reaction time 1hrs, 1.30hrs, 2hrs and 2.30hrs for synthesized ZnO NPs shows 360nm corresponds to the optical absorption of the synthesized ZnO NPs, respectively Figure 2. ZnO NPs exhibit a characteristics broad absorption peak at 360nm.

Increasing the reaction time of the sample was heated to synthesize ZnO NPs were used to investigate the effective one reaction time to synthesize ZnO NPs. By comparing and matched diffraction pattern of ZnO NPs (Pure) with all the five samples at different reaction time was observed when increasing the reaction time of the sample heated at constant temperature 70°C from 30mins to 2.30hrs accompanied by the sharpening of peak at 360nm. Hence, it was concluded that increasing the reaction time will increase the matched with diffraction pattern of ZnO NPs (Pure). In this study, it was noted that at ZnO NPs (1.30hrs) and ZnO NPs (2.30hrs) are more nearly matched with diffraction pattern of ZnO NPs (Pure).

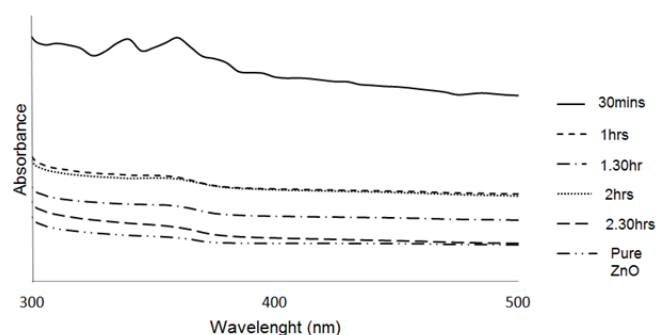


Figure 2: UV-Vis of zinc oxide nanoparticles prepared at different time reaction conditions.

C. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra comparison at different reaction time from 30mins, 1hrs, 1.30hrs, 2hrs and 2.30hrs in synthesized ZNPs using banana peel extract in Figure 4.4. Bands shown in between 3500cm⁻¹ to 3200cm⁻¹ belongs to O-H stretches from alcohol, phenol or maybe some water residues remain on the nanoparticles, 1580cm⁻¹ to 1640cm⁻¹ are -NH₃ deformation of NH₃ in amino acids or carboxylic acid salt (COO⁻) anti-symmetric. There is a significant band appeared at 515cm⁻¹ which is owned by Zn-O vibrational stretching that further confirmed the formation of ZNPs.

Peak position frequency (range cm⁻¹) shows that the confirmation of the formation of zinc oxide nanoparticles for all time reaction from 30mins, 1hrs, 1.30hrs, 2hrs and 2.30 hrs. Table 3 shows peak position frequency range for bond observed [21].

Lattice plane	Diffraction peaks					
	ZNPs (Pure)	ZNPs (30mins)	ZNPs (1hrs)	ZNPs (1.30hrs)	ZNPs (2hrs)	ZNPs (2.30hrs)
100	31.924	31.958	32.961	32.961	31.771	33.114
002	34.593	34.644	34.542	34.372	34.678	35.001
101	36.412	36.463	36.327	36.225	36.559	36.548
110	56.727	56.727	57.543	56.047	56.965	56.302
Table 2: The effect of various reaction conditions at time (30mins, 1hrs, 1.30hrs, 2hrs and 2.30hrs) on the synthesized by comparing with pure ZnO NPs using XRD analyzer						
201	68.355	68.083	68.304	78.164	68.151	68.865

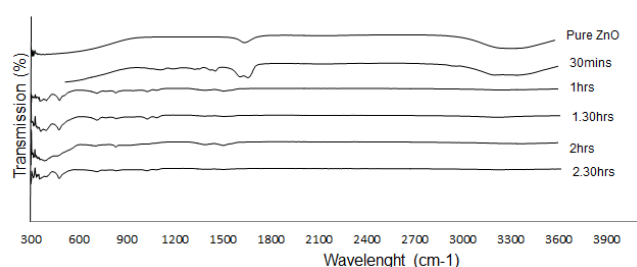


Figure 3: FTIR of zinc oxide nanoparticles prepared at different time reaction conditions.

Sample	ZNPs (0.5hr)	ZNPs (1hr)	ZNPs (1.5hr)	ZNPs (2hr)	ZNPs (2.5hr)
Functional group	Absorption band (cm-1)				
O-H stretching	3407.98	3229.45	3229.97	3359.50	3229.92
C-OH stretching	1503.71	1503.81	1507.40	1506.70	1506.34
Zn-O	479.10	479.10	475.31	384.01	478.50

Table 3: Absorption band observed in the FTIR spectra

D. Brunauer, Emmett and Teller (BET)

The Brunauer, Emmett and Teller (BET) data showed that varying the reaction time sample, significantly affected the BET surface area and total area in pores obtained from ZnONPs as shown in Table 4.

Samples	BET surface area (m ² /g)
ZnONPs (0.5hr)	17.1310
ZnONPs (1hr)	38.7498
ZnONPs (1.5hr)	31.7947
ZnONPs (2hr)	25.7270
ZnONPs (2.5hr)	36.2485

Table 4: BET surface area and total area in pores of different ZnONPs samples prepare

The BET surface area values of ZnO NPs synthesized at different reaction time of sample that synthesized ZnONPs are illustrated in Figure 4. Based on surface area values, it can be derived that increase the reaction time of the sample was heated to synthesized ZnO NPs can be used to increase the surface area of the ZnO NPs nanostructures. Therefore, as the diameter of the nanoparticle decreases, the surface area increases, as expected.

IV. CONCLUSION

In this study, ZnONPs has been successfully synthesized through a green synthetic pathway with the aid of banana peel extract as reducing agent as well as stabilizing agent. Different reaction time 30mins, 1hrs, 1.30hrs, 2hrs and 2.30hrs of the sample heated at constant temperature 70°C to synthesize ZnONPs were

used to investigate the effective one reaction time which compared among the five sample that with ZnONPs (Pure) sample. The synthesized ZnONPs were characterized using XRD, UV-Vis and FTIR. XRD analysis revealed that the particles were hexagonal wurtzite which was comparing and matched between diffraction peaks with the standard card of JCPDS Card No. 36-1451 (Zincite) and comparing crystallite size for all the samples that synthesized at different reaction time with ZNPs (Pure), the crystallite size of ZNPs (1.30hrs) are nearly the same with crystalline size of ZNPs (Pure). ZnONPs synthesized were characterized using UV-Vis spectroscopy with maximum absorbance peak at 360nm and it was noted that at ZNPs (1.30hrs) and ZNPs (2.30hrs) are more nearly matched with diffraction pattern of ZNPs (Pure). Besides, FTIR spectroscopy show that there is a significant band appeared at 515cm⁻¹ to all the five samples at different time reactions that which is owned by Zn-O vibrational stretching that further confirmed the formation of ZnONPs. As a conclusion, ZnONPs (1.5hr) was investigate the effective one reaction time because more nearly matched with ZnONPs (Pure) by characterized accordingly using UV-Visible absorption spectroscopy (UV-Vis), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Brunauer, Emmett and Teller (BET).

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