ZINC OXIDE NANOPARTICLE SYNTHESIS WITH BANANA PEEL EXTRACT FROM JACKFRUIT BANANA: EFFECTS OF TEMPERATURE

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Abstract: ***Zinc oxide nanoparticles (ZnO NPs) play an important role in various industries, however methods in synthesizing it often lead to pollutions. Therefore, this study focuses on the green synthesis of ZnO NPs using banana peel extract (BPE) from Jackfruit Banana and to characterize the synthesized ZnO NPs. The ZnO NPs were synthesized with BPE using zinc acetate dehydrate ($Zn(CH_3CO_2)_2{\cdot}2H_2O$) as a precursor with a constant solution pH of 12 and temperature range from 50°C - 90°C. ZnO NPs were characterized using the Fourier-Transform Infrared (FTIR) Spectroscopy, X-Ray Diffraction (XRD), UV-Visible (UV-Vis) Spectroscopy and Brunauer-Emmett-Teller (BET) analysis. The FTIR analysis recorded peaks between 500 cm-1 700 cm-1 in the FTIR spectra as the presence of ZnO NPs. XRD analysis recorded peaks that corresponds to Bragg's reflection for ZnO crystals (JCPDS No. 36-1451) with average crystalline diameter ranging from 15 nm - 26 nm. The UV-Vis spectra recorded peaks between 366-372 nm with a band gap ranging from 3.30 eV - 3.40 eV. The BET surface area for the ZnO NPs ranged from 15 m2/g - 20 m2/g and mean particle size ranging from 55 nm - 69 nm. This work has successfully synthesized ZnO NPs with Jackfruit Banana peel extract and has identified that the temperature of 70°C provides the best condition for future synthesis of ZnO NPs. The combination of these unique characteristics offers endless application possibilities in medicine such as development of effective anti-fungal and antiseptic creams as well as to be used as semiconductors in electronics.***

Keywords: peel extract, metal oxide nanoparticles, green synthesis, zinc acetate dehydrate, biological synthesis

I. INTRODUCTION

Nanoparticles have peaked interests in many researches in these recent years due to their advantageous application in various industries such as medicine, manufacturing, electronics and so on. A great example of nanoparticles with a wide array of uses is zinc oxide nanoparticles (ZnO NPs). In the medical field, ZnO NPs are known for their antibacterial properties which allows it to be applied safely onto human skin in the form of powders, cream, surgical tapes and even shampoo in order to treat skin irritation, rashes as well as blisters[1]. In addition to that, ZnO NPs also posses high exciton binding energy as well as large bandwidth[2] which makes it an important semiconductor[3]. Conventional physical and chemical methods synthesize large quantities of nanoparticles in a short amount of time. These methods call for an abundant amount of toxic chemicals as capping agents that help maintain stability[4] and industrial scale production of nanoparticles has oriented a new kind of pollution into the environment[3]. Fortunately, various environmentally friendly alternatives have been introduced and are the subject of interest of many researchers. Biological synthesis of ZnO NPs is very advantageous because it is relatively simple, environmentally safe and also help widens their antimicrobial activity[5]. These methods utilize natural products, which are the key ingredients in green synthesis of nanoparticles[6] and by utilizing these readily available and renewable sources, the production of nanoparticles are no longer limited to costly and dangerous methods.

Green synthesis of metal oxide nanoparticles is a fascinating issue of the nanoscience and nanobiotechnology fields[8]. Conventional methods are fast and produce large amount of nanoparticles at one time, however they contribute to dangerous levels of toxicity in the environment as these methods require toxic chemicals as capping agents [9]. Both microorganisms and plants are capable in absorbing and amassing inorganic metallic ions from their surrounding environment which allows them to significantly reduce environmental pollution and reclaiming metals from industrial waste[10]. The nanoparticles prepared with plant extracts are relatively cheap, efficient and ecological catalysts that help reduce pollution[11]. Various fruits peel extracts are the subject of great interest as they posses similar properties to plant extracts such as being rich in bio-components that play a major role in the biological synthesis of nanoparticles and are also easily obtainable[14].

Bananas are used for various purposes in Malaysia and this subsequently lead to large amount of wastes in the form of banana peels which are often discarded without further thought to its potential. Banana peels scientifically contain both antifungal and antibiotic components which have been successful in treating tomato fungus in the agriculture sector[12]. Furthermore, banana peel extract (BPE) has great potential to synthesize nanoparticles because it contains copious amounts of dopamine and L-DOPA among other bio-components that act as reducing agents and macromolecules such as lignins, petins and hemicellulose with stabilizing properties[13].

This research was conducted to synthesize ZnO NPs with BPE using zinc acetate dehydrate as a precursor. The

research focuses on the effects of varying precursor concentration and reaction temperature to produce the ZnO NPs as well as to characterize the synthesized material using Fourier-Transform Infrared (FTIR) Spectroscopy, X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET), Zeta Potential analysis and UV-Visible (UV-Vis) Spectroscopy.

II. METHODOLOGY

A. Material and Chemicals

The chemicals used in this study are zinc acetate dehydrate in powder form and sodium hydroxide in pellet form that were procured from R&M Chemicals. Thepeels of fresh Jackfruit Bananas were obtained from local food stall vendors located around Seksyen 7, Shah Alam, Selangor.

B. Preparation of Banana Peel Extract (BPE)

The steps taken to prepare the banana peel extract follows that of Agarwal (2017). Firstly, the peels were first washed clean with water and allowed to dry at room temperature overnight to remove excess moisture. Next, the peels were cut into small pieces and 50 g of the peels were added to 500 ml of ultra pure water in a 600 ml beaker. Then it was covered with aluminium foil and heated at a constant temperature of 70°C for 30 minutes and the stirred using a magnetic stirrer at 1000 rpm. The mixture was then filtered to remove the banana peels. The final extract was then stored at 4°C for further use.

C. Synthesis of Zinc Oxide Nanoparticles (ZnO NPs)

The method used for synthesis with different precursor concentrations and different reaction temperatures required a few parameters to kept constant when each parameter were manipulated are summarized in Table 1. Firstly, 0.1M solution of zinc acetate dehydrate was prepared in 1L bottom rounded flask bottle. Then, 20 ml of BPE was mixed with 180 ml of 0.2M zinc acetate solution following a ratio of 1:9. Next, 1M sodium hydroxide (NaOH) solution was added to reach a pH of 12. The mixture was then double boiled at constant temperature of 70°C for 1 hour with constant stirring at 1000 rpm using a magnetic stirrer until the mixture turned a pale yellow in colour and a white precipitate was formed at the bottom of the beaker. Next, a filter paper (Whatman No.1) was first weighed before being used to filter the mixture once heating was done. Finally, the residue was then dried at 40°C and was grounded into fine powder.

D. Fourier-Transform Infrared (FTIR) Spectroscopy

The FTIR analysis (Spectrum One FT-IR Spectrometer, Perkin Elmer) was carried out using scan range of 500-4000 cm-1 at room temperature. This analysis was used to determine the functional group of the synthesized ZnO NPs.

E. X-Ray Diffraction (XRD)

The X-Ray Diffraction (XRD) analysis (X'Pert Pro X-Ray Diffractometer, PANanalytical, Japan) with Cu-Kα radians at angle 2θ, a voltage of 40 kV, a current of 40 mA and speed angle of 5°/min. X-ray powder diffraction is a quick analytical technique primarily used to identify the phase of a crystalline material while also providing information on unit cell dimensions. Wong (2016) states that the size of the ZnONPs is determined using Debye Sherrer's equation:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where,

D = Crystalline size diameter
k = Sherrer constant (usually 0.9)
λ = Wavelength of X-Ray source, Cu Kα radiation (1.5406Å)
β = Full width at half-maximum (FWHM) of the diffraction peak
θ = Bragg's diffraction angle

F. UV-Visible (UV-Vis) Spectroscopy

Approximately 0.04 g of the samples were weighed and diluted with 10 ml distilled water. The prepared samples were shaken and allowed to settle before taking 3 ml for the UV-Vis analysis. The UV-Vis Spectroscopy(Lambda 750 UV/VIS Spectrometer, Perkin Elmer) was used to analyse the absorbance range of the synthesized ZnO NPs. The absorbance range was monitored within the wavelength range of 200-800 nm, a bandwidth of 2 nm and a scanning speed of 480 nm/min. The band gap energy (E_{bg}) is closely related to the electrical conductivity of ZnO NPs which can be calculated using the equation:

$$E_{bg} = \frac{hc}{\lambda} \quad (2)$$

Where,

E_{bg} = Band gap energy (eV)
h = Planck's constant (6.63×10^{-34} m^2 kg/s)
λ = Absorption wavelength in UV region
c = Speed of light (3.00×10^8 m/s)

G. Brunauer-Emmett-Teller(BET) Analysis

The BET (3FLEX Surface Characterization, Micromeritics) analysis was used to determine the surface area and particle size of 0.5g of the synthesized ZnO NPs with a pre-treatment temperature of 150°C and 300 min. The specific surface area (SBET) of the ZnO NPs can be determined from the nitrogen adsorption/desorption measurement by applying the Bruneauer-Emmett-Teller (BET) method and the diameter of the nanoparticles can be calculated using the equation[15]:

$$d_{BET} = \frac{6000}{\rho_{sample} \times S_{BET}} \quad (3)$$

Where,

d_{BET} = Mean crystalline size diameter
ρ_{sample} = Density of ZnO powder (ρ_{ZnO} = 5.60 g/cm^3)
S_{BET} = BET specific surface area (m^2/g)

III. RESULTS AND DISCUSSION

A. Functional Groups of Synthesized Zinc Oxide Nanoparticles (ZnO NPs)

The zinc oxide nanoparticles (ZnO NPs) synthesized with different temperatures recorded peaks at 628 cm^{-1}, 1182 cm^{-1}, 1373 cm^{-1} and 1698 cm^{-1} in the FTIR spectra (Fig. 1). From the data obtained, the peak recorded at 1182 cm^{-1} correspond to the C-O stretching of alcohols, ethers and esters which is within the range reported that is from 1000 cm^{-1} - 1300 cm^{-1} [7]. The peak recorded at 1373 cm^{-1} contribute to the possibility of the occurrence of C-C stretch (in-ring) aromatics as reported by Kumar (2017) that revealed the peak to be 1420 cm^{-1}. Next, the peak recorded at 1698 cm^{-1} correspond to C=O stretch of carboxylic acids which is close to the value reported at 1641 cm^{-1} [13].

The peak recorded for all samples at 628 cm^{-1} for ZnO NPs synthesized with different temperatures are within the range of the stretch for ZnO NPs as reported by Vishwakarma (2013) ranging from 400-800 cm^{-1} while Kumar (2017) reported a range from 527-664 cm^{-1} as the presence of ZnO NPs. From the data obtained, it an be concluded that when the reaction temperature was varied it does not significantly affect the intensity of the absorbance peak.

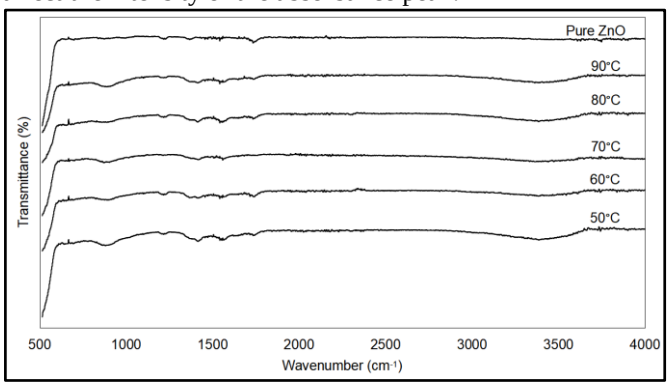

Fig. 1. FTIR range for varied temperatures of Synthesized ZnO NPs.

B. Crystal Size of SynthesizedZnO NPs

The X-Ray Diffraction (XRD) analysis depicts specific patterns that are characteristically unique to each crystalline compounds that have regularly repeating atomic structures. By referring to Fig.2, the peaks at 2θ obtained from ZnO NPs synthesized under different temperatures recorded peaks at 32.06°, 34.60°, 36.44°, 47.87°, 56.90°, 63.19°, 67.34°, 68.36°, 69.70°, 73.29° and 77.43°. The data obtain corresponds to Bragg's reflection of (100), (002), (101), (102), (110), (103), (200), (112), (201) (004) and (202) respectively for ZnO crystals (JCPDS No. 36-1451). This indicates that the peaks belong to a hexagonal wurtzite structure[19] and it can be concluded that the synthesized ZnO NPs posses a good crystallite structure[16].

The sharp nature of the Bragg peaks recorded may result from the capping agent stabilizing process of the NPs while boarder peaks represent the small size of the particles and reflect the effects resulting from the experimental conditions[17]. However, at temperatures of 80°C and 90°C additional narrow peaks at 38.45°, 44.67°, 65.04° and 78.15° were recorded which maybe an indication that the synthesized ZnO NPs posses both cubic and hexagonal structures[18]. The minor peaks recorded at 78.15° reflect the impurities present in the synthesized ZnO NPs in the form of water soluble and water insoluble impurities that may be present on the surface of the synthesized nanoparticles[19]. Intense Bragg peaks obtained suggests that strong scattering of X-ray is focussed in the crystalline phase and may result from capping agents[17].

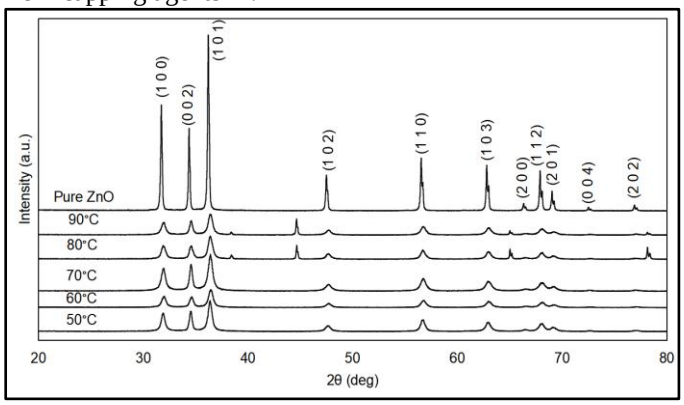

Fig. 2. XRD peaks for varied temperatures of Synthesized ZnO NPs.

The diameter for the crystalline size of the ZnO NPs can be determined using the Debye-Scherrer's equation (1) and the mean crystalline size obtained is tabulated in Table 1 for the ZnO NPs synthesized under different temperatures.

The crystalline size increases from 15.06 nm to 15.98 nm to 16.50 nm when temperatures increased from 50°C to 60°C and 70°C respectively. It then decreased to 14.46 nm when temperatures increased to 80°C before increasing to 26.03 nm when temperatures increased to 90°C. The calculated size was within range of the crystalline size reported from 15 nm - 26 nm [16]. It can be concluded that although the temperature 80°C recorded the smallest mean crystalline size diameter of 14.46 nm, the temperature of 70°C provides the optimum condition for the synthesis of ZnO NPs as it is free from additional peaks while recording a mean crystalline size of 16.50 nm.

Table1: Mean crystalline size for varied temperatures of Synthesized ZnO NPs

Temperature (°C)	Mean Crystalline Size Diameter (nm)
50	15.06
60	15.98
70	16.50
80	14.46
90	26.03

C. Particle Size of Synthesized ZnO NPs

Particle size of the synthesized ZnO NPs was analysed using theBrunauer-Emmett-Teller (BET) analysis. The results obtained from the BET analysis was used to calculate the mean particle size diameter using Equation 3 which were tabulated in Table 2 for ZnO NPs synthesized under varying

temperatures.

Based on the calculated values, the particle size increased while BET surface area decreased as temperature increases. The condition might be caused by increased metal ions concentration that led to more nucleation and aggregation to occur during nanoparticles formations[16].At higher temperatures, more reactants are converted at a faster rate into ZnO NPs which may affect the capping capability of the banana peel extract (BPE) which works by maintaining the size of the particles formed[19].

It can be concluded based on the calculated mean particle size, the size of the ZnO NPs are slightly higher than the average diameter reported which is 49.7 nm[20] due to aggregatesduring nanoparticles formation. However, the temperature 80°C recorded the smallest mean particle size of 55.11 nm respectively.

Table 2: Mean particle size for variedtemperatures of Synthesized ZnO NPs

Temperature (°C)	BET Surface Area (m^2/g)	Mean Particle Size (nm)
50	15.34	68.98
60	15.95	66.34
70	18.68	56.65
80	19.20	55.11
90	15.51	68.23

D. Band Gap of the Synthesized ZnO NPs

The UV-Visible (UV-Vis) spectroscopy results obtained from ZnO NPs synthesized under different temperatures recorded peaks at 371.01 nm, 371.98 nm, 370.96 nm, 369.00 nm and 365.66 nm for 50°C, 60°C, 70°C, 80°C and 90°C respectively. The recorded peaks was within the range of 386-450 nm identified as "surface Plasmon resonance band" that was attributed to excitation of valence electrons of ZnO arranged in the nanostructure[17].

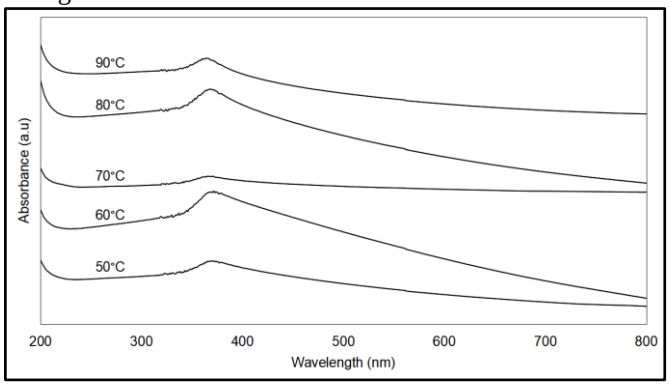

Fig. 3 : UV range for variedtemperatures of Synthesized ZnO NPs

The band gap energy (E_{bg}) of ZnO NPs were calculated using equation(2) and was tabulated in Table 3. The calculated band gap value for 80°C is 3.36 eV which are the closest to the theoretical band gap value of 3.37 eV[15] compared to other temperatures. It can be concluded that the temperature of 80°C provides the best condition for the synthesis of ZnO NPs.

Table 3: Band gap for variedtemperatures of Synthesized ZnO NPs

Temperature (°C)	Peak (nm)	Band Gap (eV)
50	371.01	3.34
60	371.98	3.33
70	370.96	3.34
80	369.00	3.36
90	365.66	3.39

IV. CONCLUSION

In conclusion, the peaks recorded for all samples at628 cm^{-1} in the FTIR spectra for zinc oxide nanoparticles (ZnO NPs) synthesized with different temperatures are within the range of the stretch for ZnO NPs as reported previous studies ranging from 400 cm^{-1} - 800 cm^{-1}[17]. Next, the peaks at 2θ in the XRD analysis obtainedcorresponded to Bragg's reflection for ZnO crystals (JCPDS No. 36-1451) which indicates that it is a wurtzite structure with average crystalline diameter ranging from 14 nm - 26 nm. The BET surface area for the ZnO NPs ranged from 15 m^2/g - 20 m^2/g and mean particle size ranging from 55 nm - 69 nm. Finally, the peaks obtained in the UV-Vis spectra recorded peaks ranging from 366 nm - 372 nm with a band gap ranging from 3.30 eV - 3.40 eV. Therefore, this work has successfully synthesized ZnO NPs with Jackfruit Banana peel and has identified that the temperature of 70°C provides the best condition for future synthesis of ZnO NPs.

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