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Biosynthesis of zinc oxide nanoparticles using *Ficus Auriculata* (elephant ear fig) leaf extract and their photocatalytic activity

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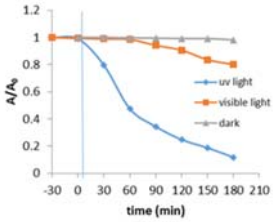
GRAPHICAL ABSTRACT



Comparison of MB photodecolourization in the dark, visible and UV light irraditation by ZnO-NPs

ABSTRACT

The synthesis of semiconductor metal oxide nanoparticles is an expanding research area due to their applications in photocatalysis. Recently, synthesis of metal oxide nanoparticles assisted by biomolecules have provide alternative to conventional methods due to its simplicity and eco-friendly. In the present study, an environmental friendly, low-cost and simple procedure for the biosynthesis of hexagonal zinc oxide nanoparticles (ZnO-NPs) using aqueous leaf extract of *Ficus auriculata* as capping agent is described. ZnO-NPs were synthesised via co-precipitation technique by treating zinc nitrate solution with sodium hydroxide in the presence of leaf extract. FESEM, EDX, XRD, FTIR, UV-Vis spectroscopy have been used for characterizing the ZnO-NPs. FTIR spectral data showed the presence of functional groups of both leaf extract powder and ZnO-NPs indicating the biomolecules have capped on the surface of the nanoparticles. XRD data showed the synthesised ZnO-NPs are wurtzite hexagonal structure with crystallite size of about 13.8 nm. FESEM micrograph image suggested the ZnO-NPs were mostly spherical shape while EDX analysis revealed the signals of Zn and O elements present in the sample. The synthesised ZnO-NPs were tested for the decolourization of methylene blue under visible and UV irradiation giving an efficiency of 19.8 and 88.2 % respectively.

Keywords: *ZnO-NPs, biosynthesis, photocatalytic activity, Ficus auriculata,*

1. INTRODUCTION

Controlled fabrication of ZnO-NPs without constrained by costs and hazardous chemicals is challenging. Previous researchers have successfully produced zinc nanostructure by employing methods such as sol-gel [1], solvothermal [2], hydrothermal [3], emulsion [4] and microemulsion [5]. However, these chemical methods are potentially hazardous and expensive due to the starting material and solvent used [6]. Recently, green syntheses of nanoparticles using plant material are extensively explored. Leaves contain biomolecules such as proteins, amino acid, alkaloids, phenols and terpenoids can act as capping agents for the nanoparticles. Biosynthesis assisted by plant is more advantages than other methods due to a variety of plants available and its cost effectiveness. Biosynthesis reduced the use of hazardous chemical including chemical reducing agent and toxic solvent [7].

Zinc oxide nanoparticles is a multifunctional metal oxide semiconductor. They have three crystalline structures which are wurtzite (hexagonal), rocksalt (cubic) and zinc blende (cubic) with wurtzite is the most stable. ZnO-NPs has wide direct band gap of 3.37eV which suitable for fabrication of nanoscale electronic and optoelectronic devices such as solar cells and UV detectors while their large binding energy (60 meV) makes ZnO-NPs can sustain high temperature in photovoltaic applications [8]. Meanwhile, ZnO-NPs are also effective as photocatalyst and have been investigated in degradation of pollutants such as methylene blue. ZnO-NP has become a leading nanomaterial as semiconductor, catalyst, antibacterial agents and gas sensor materials [9].

2. EXPERIMENTAL

2.1. Leaf extracts preparation

Ficus auriculata leaves were collected locally from UTM and the leaves were washed thoroughly using tap water and finally rinsed using deionized water. The leaves were air dried before ground into powder. 5 g of Ficus auriculata leaves powder in 100 mL deionized water were boiled for 30 min. After cooling, the extracted solution was vacuum filtered using Whatman filter paper no. 1 and centrifuged. The final extract was stored in refrigerator for further use.

2.2. Biosynthesis of ZnO-NPs using Ficus auriculata leaf extract.

The ZnO-NPs were biosynthesized by co-precipitation method describe by Singh et al., (2011) [10]. 20 mL of the leaf extract was heated to 60°C for 10 min, 50 ml 0.1 M of zinc nitrate solution and 50 mL 0.2 M sodium hydroxide solution were added drop wise under stirring. The mixture was continued stirred for 1 hour on magnetic stirrer resulting cream colored precipitate of zinc hydroxide formed. Then, the precipitate was collected by centrifugation at 4000 rpm for 15 min and washed with deionized water and ethanol. The ZnO-NPs were collected after dried in oven 24 hour at 80°C.

2.3. Characterization

All functional groups analyses were recorded using Fourier transform infrared (FTIR) Perkin Elmer Model 1600 using potassium bromide (KBr) pressed disc method. Optical absorption studies were carried out using ultraviolet-visible (UV-Vis) Shimadzu UV-160 1PC. The crystal phase information of sample was characterized from 20- 90°C by XRD with Cu Kα radiation (λ=0.15418 nm, 40 kV, 40 mA). The surface morphology of ZnO-NPs was analyzed using field emission scanning electron microscope JEOL JSM-6701F equipped with energy dispersive X-ray facility (FESEM/EDX). Samples were coated first with platinum (Pt) before analysis.

2.4. Photocatalytic decolourization of methylene blue(MB)

The photocatalytic activity of synthesized ZnO-NPs was tested by monitoring the decolouration of methylene blue in the dark, visible and UV light. A 2.24 μM methylene blue stock solution was prepared in 50 mL volumetric flask. 20 mg of ZnO-NPs were added into 20 ml of MB stock solution and the solution was stirred in the dark for 30 minutes to obtain adsorption equilibrium. The reaction was then continued by turning on the UV lamp (254 nm) and the decolourization of MB was monitored using UV-Vis spectrophotometer at wavelength 664 nm and 30 minutes time intervals for 3 hours.

3. RESULTS AND DISCUSSION

The formation of ZnO-NPs during the synthesis can be observed visually. Figure 1 is the UV-Vis absorption spectrum of ZnO-NPs dispersed in deionized water and the Figure shows excitonic absorption peak at 353 nm which lies below the absorption of bulk zinc oxide wavelength 380-388 nm [11-13]. Spectrum from previous study also shows similar UV absorption region of synthesized zinc oxide nanoparticles using *Ruta graveolens* aqueous stem extract [14]. Meanwhile, Figure 2 is the Tauc plot used in determination of ZnO-NPs band gap. From the graph, the band gap of ZnO-NPs is 3.25 eV which smaller than the band gap of bulk ZnO (3.30 eV) due to intrinsic defect.

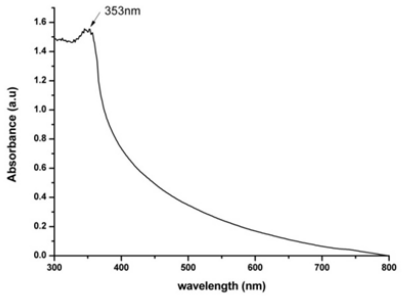


Figure 1 UV-Vis spectrum of ZnO-NPs

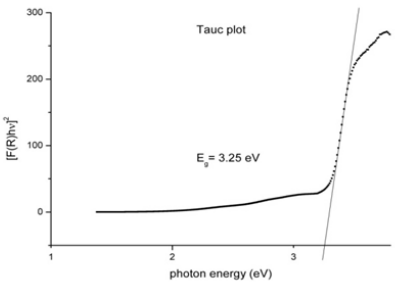


Figure 2 Plot of $(F(R)hv)^2$ vs hv

Overall structure of ZnO-NPs were determined in this study using a powder diffraction system with Cu-Ka x-ray tube (λ=1.54056 A°) was used. Figure 3 depicts the XRD pattern of the synthesized ZnO-NPs scanned at 2θ range from 10 to 90 degree. Diffraction peaks at 31.72°, 34.39°, 36.22°, 47.47°, 56.54°, 62.80°, 67.93°, 68.89°, 77.13° can be assigned to (110),(002), (101), (102), (110), (103), (112), (201) and (202) plane. All the corresponding peaks can be indexed to hexagonal phase (wurtzite structure) when compared with the Joint Comitee on Powder Diffraction Standard (JCPDS) card No. 36-1451. The broadening in the X-ray diffraction pattern indicates the nanosized of the material. There was no characteristic peak of impurities such as $Zn(OH)_2$ observed which means the sample was crystallized as pure ZnO form. The crystalline size of ZnO-NPs from Sherrer's equation is 13.8 nm.

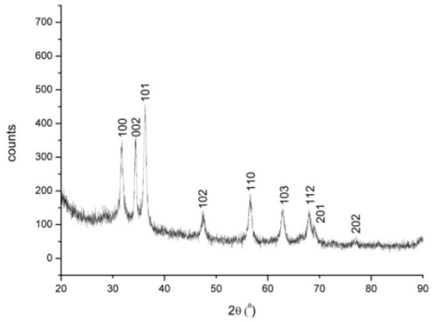


Figure 3 XRD pattern of hexagonal wurzite ZnO-NPs

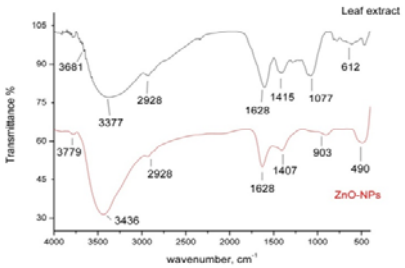


Figure 4 FTIR spectra of Ficus Auriculata leaf extract and ZnO-NPs

FTIR spectra for both *Ficus auriculata* leaf extract and synthesized ZnO-NPs were obtained in the range of wavenumbers 400-4000 cm-1 to identify of biomolecules functional groups that stabilize the ZnO-NPs. Figure 4 shows the spectra of *Ficus auriculata* leaf extract and the biosynthesized ZnO-NPs. FTIR spectra of *Ficus auriculata* leaf extract shows absorption band at 3800- 3200 cm^{-1} indicating the presence of several hydroxyl group (phenolic -OH). Peaks at 2928 cm^{-1} is due to C-H stretching vibrations of alkane group. A strong band at 1628 cm^{-1} is representing the C=O carbonyl group. The peak at 1415 cm^{-1} represents C-O-C while peak at 1077 cm^{-1} is correspond to in-plane bending O-H of alcohol group. Meanwhile, the ZnO-NPs FTIR spectrum reveal similar absorption band at 3436 cm^{-1}, 2928 cm^{-1}, 1628 cm^{-1}, 1407$cm^{-1}$and 903 cm^{-1} that attributed to same type of functional groups respectively. Most important peak observed at 490 cm^{-1} corresponds to standard peak of ZnO [15]. It may be concluded that biomolecules like myricetin and quercetin presents in the leaf have capped the ZnO-NPs and stabilize the nanostructure.

The study of surface morphology of the ZnO-NPs was demonstrated by FESEM/EDX. Figure 5 shows the micrograph of ZnO-NPs structure were mostly spherical with agglomeration formed larger cauliflower-like structure and this finding is supported by similar observation from previous study [16]. The size of the ZnO-NPs is starting minimum 15 nm to 63 nm with average size of 41 nm.

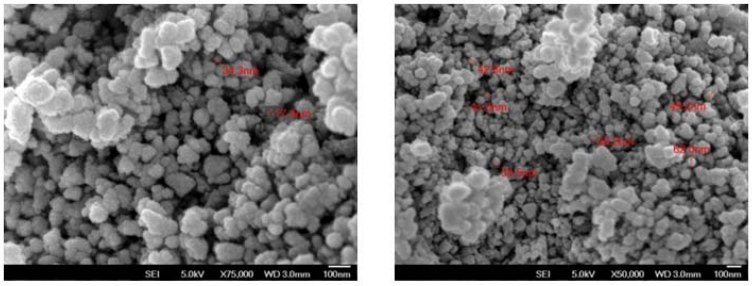


Figure 5 FESEM micrograph of ZnO-NPs (a) higher magnification (b) lower magnification

The EDX data show strong signal energy peaks for zinc (Zn) and weak signal energy peak for oxygen (O) confirmed the presence of ZnO-NPs. The spectrum also showed the signal energy peak for carbon (C) which indicates the presence of biomolecules originated from the leaf extract. The signal for platinum (Pt) was from the coating during sample preparation.

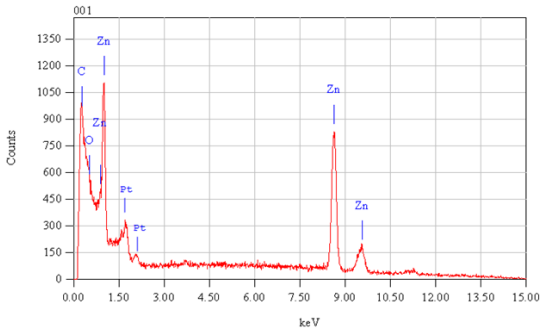


Figure 6 EDX spectrum for ZnO-NPs

The photocatalytic activity of ZnO-NPs was investigated by decolourization of MB under visible and UV light illumination. 20 mg ZnO-NPs sample was added into 20 mL MB solution and the solution was stirred in the dark for 30 minute to achieved adsorption-desorption equilibrium. At given time interval, 3 mL suspension was sampled for absorption analysis on UV-Vis spectroscopy. The wavelength monitored at 664 nm for MB absorption. Figure 7 is the photodecolourization time profiles of A/A_0 are shown.

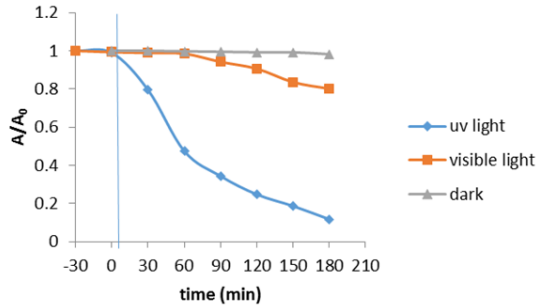


Figure 7 Comparison of MB photodecolourization in the dark, visible and UV light irraditation by ZnO-NPs

Based on the photodecolourization of MB (Figure 7), ZnO-NPs photocatalyst can perform better under UV light than visible light irradiation. After 180 min, 19.8 percent and 88.2 percent of MB have been decolourized under visible and UV irradiation respectively. ZnO-NPs have poor decolourization efficiency under visible light probably due to its wide band gap. For large scale application requires artificial sources of UV light since sunlight composed only 5% of UV and they are expensive and affect negatively on general human health in case of long term duration of UV exposure. Thus the most favourable condition is under sunlight. In order for photocatalyst to be effectively photoexcited under sunlight is by reducing the band gap. Different methods are available for surface modification such as doping [17].

4. CONCLUSION

In the present study, zinc oxide nanoparticles with hexagonal wurzite structure have been successfully fabricated via a green, simple and inexpensive method using the leaf extract of *Ficus auriculata* which act as an effective capping agent. The zinc oxide nanoparticles were crystalline, spherical with an average size of 41 nm and having a direct band gap of 3.25 eV. UV-Vis absorption spectrum of the zinc oxide nanoparticles shows characteristics absorption peak at 353 nm due to its surface plasmon resonance. FTIR spectra of the leaf extract powder and synthesized zinc oxide nanoparticles shows similarity of functional groups presents. EDX of the samples present the only existence of zinc (Zn), oxygen (O) and carbon (C) indicating the zinc oxide nanoparticles is pure. The use of synthesized zinc oxide nanoparticles as photocatalyst was studied for the decolourization of methylene blue dye in the dark, under visible and UV light sources. The results showed that the synthesized zinc oxide nanoparticles were able to decolourize the methylene blue effectively under UV than visible light.

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