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Research Article

# Microwave-assisted Synthesis of ZnO Nanoparticles Stabilized with Gum Arabic: Effect of Microwave Irradiation Time on ZnO Nanoparticles Size and Morphology

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## Abstract

The conventional heating methods of nanoparticle synthesis regularly depend on the energy inputs from outer heat sources that resulted high energy intake and low reaction competences. In this paper ZnO nanoparticles stabilized with gum arabic are synthesized using precipitating method assisted by simple and cost effective microwave heating technique. The objective of this work is to investigate the effect of microwave irradiation time towards ZnO nanoparticles morphology and size. The effect of microwave irradiation time has been investigated at 2, 4, 6, and 10 minutes. Dynamic Light Scattering (DLS) was employed to measure the size of ZnO nanoparticles. Ultraviolet–Visible spectroscopy (UV-vis), Fourier-Transform Infrared Spectroscopy (FTIR) and X-Ray Diffraction (XRD) were used for the characterization of the ZnO nanoparticles. UV-vis absorption spectrum was found in the range of 350 nm indicating the absorption peak of ZnO nanoparticles. FTIR spectra showed peaks range from 424 to 475 $cm^{-1}$ which indicating standard of Zn–O stretching. The presence of (100), (002), and (101) planes were apparent in the XRD result, indicating the crystalline phase of ZnO nanoparticles. The increase in the microwave irradiation time affected the processes of nucleation and crystal growth promoted larger ZnO nanoparticles size. Microwave irradiation time at 2 minutes was selected as the best microwave irradiation time for smallest ZnO nanoparticles averaging about 168 nm sizes based on DLS analysis. 

***Keywords***: Microwave Heating; Irradiation Time; ZnO Nanoparticle; Gum Arabic

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## 1. Introduction

Zinc oxide (ZnO) is a promising wide band gap semiconductor ($E_g$ = 3.37 eV) and with a binding energy of 60 meV [1]. It has several favorable properties such as having a good thermal and mechanical stability, biodegradability, strong room temperature luminescence and antibacterial properties. ZnO nanoparticles are popular among scientists worldwide as they have unique chemical, physical and biological

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properties for wide industrial application. However, for industrial synthesis of ZnO nanoparticles repeatable properties faced difficult and troublesome issues. Normally the challenges are difficult to control the average particle size, particle size distribution, shape as well as phase purity.

There are several methods for the synthesis of ZnO nanoparticles including precipitation in solution [2], spray pyrolysis [3], hydrothermal synthesis [4], and sol-gel processes [5]. Hydrothermal growth methods are frequently correlated with long growth times, normally 10 h or greater using conventional hot-plate methods [7,8]. Microwave heating is able to reduce the growth length to minutes while maintaining good morphology and ZnO crystallinity. Publications on microwave-assisted synthesis as chemically green synthesis of chemical product has increased in order to eliminate the generation of hazardous substances and to reduce intensive energy consumption [8,9]. Several issued of different experimental variables over ZnO nanoparticles size, morphology, and physicochemical performances have been studied [10]. Microwave offers an adaptable heating mode to control the synthesis of nanoparticles. The wavelength of microwave has a strong effect on the penetration depths in the reaction solution, and thus can speed up the heating rate [11]. Consequently, the nucleation and the growth of nanoparticles are controllable [12]. Besides that, this method shows narrow particle size distribution, high purity materials and improved physicochemical properties [13].

In this present paper, ZnO nanoparticles stabilized with gum arabic were synthesized by using a microwave-assisted method. The current work emphasized on the green synthesis of ZnO nanoparticles using gum arabic (stabilizing agent). This stabilizing agent is a complex polysaccharide, which is extracted from the stems and branches of acacia trees [14]. Gum arabic is a hydrophilic, biocompatible, non-toxic and ecofriendly polymer [15]. When the gum arabic is adsorbed on the particle surface, steric hindrance, bridging or charge-patch are formed to stabilize the particles [16]. To the author's best knowledge, there appear to be no published studies on the microwave-assisted synthesis of ZnO nanoparticles using gum arabic as stabilizing agent.

Different microwave irradiation times will synthesize different ZnO nanoparticles size and morphology [17]. Several studies had revealed the morphology changes with microwave irradiation time forming different types of complex nanostructures [15,16]. Although the synthesis process using stabilizing agent such as (sodium di-2-ethylhexyl-sulfosuccinate (AOT), it was difficult to control the growth under longer microwave irradiation time. In this present paper, research was conducted to investigate the effect of microwave irradiation time towards ZnO nanoparticles morphology and size using gum arabic as a stabilizing agent.

Previously, the size of ZnO nanoparticles was characterized using FESEM, TEM, and XRD [2,3]. Nevertheless, DLS was preferable in the current study as larger number of particles (in millions) could be measured via DLS [21]. The error in the size determination by dynamic light scattering method for spherical particles is rather low, not greater than 5-10% [22]. Therefore, in this study the more reliable size distribution can be obtained by using DLS.

## 2. Materials and Methods

### 2.1 Materials

Both zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ (98%, Aldrich) and sodium hydroxide (98.9%, Bendosen) of analytical grade were used without further chemical treatment and purification. The zinc salt used in this study was zinc nitrate so that the very pure phase of ZnO nanoparticles of high density could be obtained using microwave heating method [18]. Gum arabic was purchased from Texture Innovation Centre (TIC Gums), USA. Gum arabic solution was used straightaway after dissolving it in the de-ionized water in order to obtain reproducible results. De-ionized water was ob-

**Table 1.** PDI for ZnO nanoparticles synthesis at 2 min of microwave irradiation time

| Z-Average (nm) | PDI | PDI Width | Percent in Size Range | D(10) | D(50) | D(80) |
|---|---|---|---|---|---|---|
| 168 | 0.101 | 54.21 | 100 | 116 | 180 | 283 |

PDI=Polydispersity index
D=particle size distributions in 10%, 50% and 80%

tained from the Laboratory of Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang.

2.2 Method of ZnO Nanoparticles Synthesis

Firstly, 1% of gum arabic was dissolved in 100 mL of distilled water and heated at 350 Watt to dissolve the gum arabic. Amount of 2.974 g of solid $Zn(NO_3)_2.6H_2O$ zinc nitrate was added into 1% of gum arabic solution subjected to continuous stirring. Then the obtained solution was heated for 2 minutes in the microwave running at 350 W to fully dissolve the Zinc nitrate and gum arabic. 1 M NaOH solution was dripped into the zinc nitrate and gum arabic solution undergoing vigorous stirring until pH 10 achieved. Again, the mixture solution was exposed to microwave heating 350 watt at 2 minutes, 4 minutes, 6 minutes and 10 minutes. The white precipitate was cleaned using distilled water before the precipitate was dried in an oven at 80 °C.

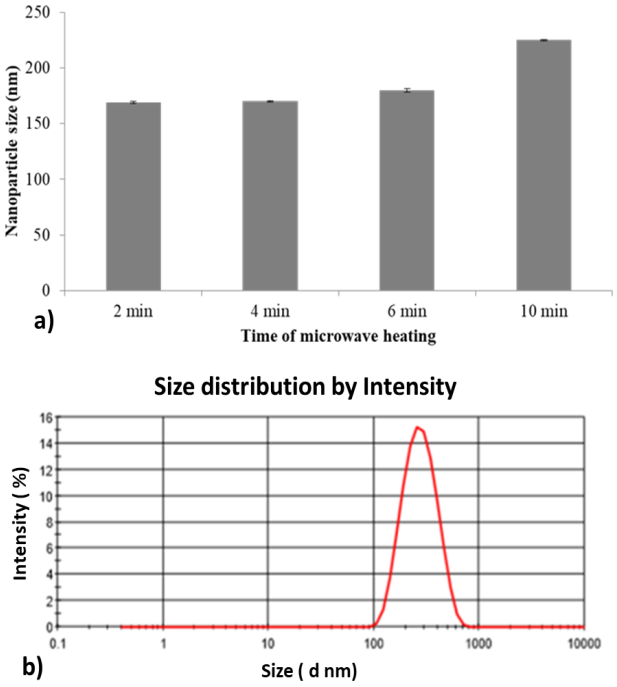



**Figure 1.** a) Aggregates ZnO nanoparticles hydrodynamic size at different irradiation time of microwave heating (watt) based on DLS analysis. b) Size distribution by intensity of aggregates ZnO nanoparticles synthesized at 2 min of microwave irradiation time

2.3 Characterization

30 µL of ZnO solution was diluted in 2 mL of de-ionized water. The nanoparticle sizes based on DLS analysis were measured using Zetasizer Nano ZS (Malvern Instruments). The optical properties of ZnO nanoparticles was analysed using the UV-vis spectrophotometer in the range of 250 nm to 800 nm. The chemical composition of the synthesized nanoparticles was studied using the by a Shimadzu Fourier Transform Infrared (FTIR) spectrophotometer in the range of 400-4000 $cm^{-1}$. The crystal structures of the prepared ZnO nanoparticles were analyzed using the Philips X'Pert MPD (Multi-Purpose Diffractometer) XRD using Cu-Kα1 radiation ($\lambda$ = 1.5406 nm). The X-ray powder diffraction patterns were recorded at every 0.01° in the angular range of 20°-80° using monochromatic X-rays. The size and the morphology of the ZnO nanoparticle were examined using the field emission scanning electron microscope (FESEM). The ZnO nanoparticles were disperse in ethanol and sonicated for 15 minutes. Next the disperse solution of ZnO nanoparticles were dried on the carbon tape. The sample was coated with platinum in order to avoid charging during the observation.

## 3. Results and Discussion

DLS is a characterization technique which is commonly used for calculating the hydrodynamic diameters of suspended nanoparticles based on their Brownian movements [23]. DLS produces absolute values for an ensemble of particles. As shown in Figure 1(a), the calculated average hydrodynamic diameter based on DLS analysis shows aggregates ZnO nanoparticles size that are approximately similar value which are 168 nm, 170 nm, and 180 nm at 2 minutes, 4 minutes and 6 minutes respectively. The slight increase in the aggregates nanopar-

**Table 2**. Average crystallite size of ZnO nanoparticles synthesis 2 minutes of microwave irradiation obtained from (101) plane

| 2θ | FHWM | Average crystallite size (D) (nm) | Inter planner distance (d) (nm) | Cell parameter *a=b* | Cell parameter *c* |
|---|---|---|---|---|---|
| 36.26 | 0.330 | 25 | 2.48839 | 3.24940 | 5.20540 |

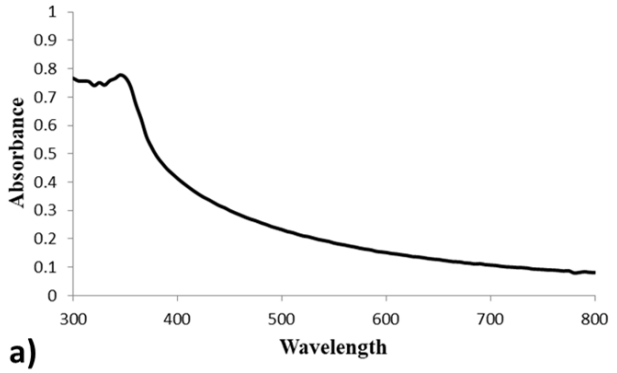
ticles size within 6 minutes of microwave irradiation might be cause of the protective role of gum arabic, as it retards the growth and agglomeration of nanoparticles by steric effect [16].

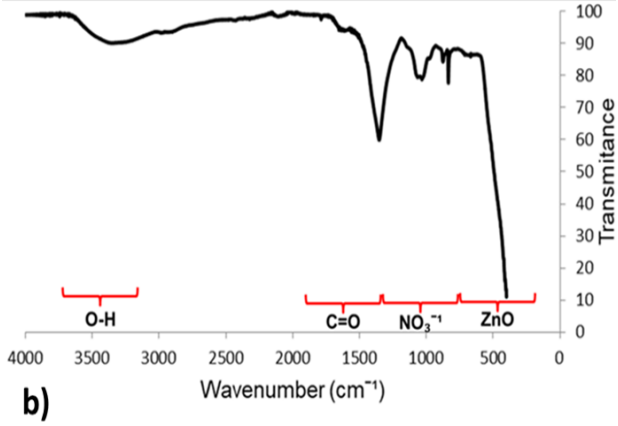
At 10 minutes of microwave irradiation time, the aggregates nanoparticles size increased to 225 nm almost 34 % from the size at 2 minutes of microwave irradiation time. It was found that by increasing irradiation time to 10 minutes, the aggregates nanoparticle size of ZnO nanoparticles increased. This was mainly due to the fact that both processes of nucleation as well as crystal growth were affected by microwave irradiation time which indirectly promoted the larger particles. In addition, longer microwave irradiation times will directly increase the heating rate that will effected the gum arabic coating to stabilized the resulted nanoparticle increase in the aggregates nanoparticles size.

This result is similar with other report finding that by increasing microwave irradiation time from 10 to 15 minutes, aggregates ZnO nanoparticles size increased from 50 to 150 [24]. Due to its penetration characteristics, microwave irradiation can speed up the reaction rate homogeneously resulted uniform nucleation and quick crystal growth for development of crystallites with narrow size distribution [25]. As shown in Figure 1(b), besides small particle size, microwave assisted synthesis resulted a unimodal narrow particle size distribution of ZnO nanoparticles. A unimodal narrow particle size distribution directly demonstrated monodisperse condition of the ZnO nanoparticles solution. The polydispersity index (PDI) of this ZnO nanoparticle synthesis at 2 min of microwave irradiation time was 0.101 as shown in Table 1. A sample with PD < 20% are considered to be monodisperse [26]. As the aim to obtain the smaller size of ZnO nanoparticle, microwave irradiation time at 2 minutes was selected as the best microwave irradiation time for ZnO nanoparticles synthesis. Figure 2(a) shows the optical properties of ZnO nanoparticles synthesized at 2 minutes of irradiation time. A sharp peak was formed at 355 nm, representing the hexagonal phase of ZnO nanoparticle [27].

In order to understand the mechanism of the formation of ZnO nanoparticles, the FTIR measurement was conducted at room temperature for wavenumber ranging from 4000 $cm^{-1}$ to 400 $cm^{-1}$. Figure 2(b) shows the compositional analysis of ZnO nanoparticles synthesized at 350 watt. The broad band at 3447 $cm^{-1}$ corresponded to the O–H mode of vibration within the hydroxyl groups. A peak at 1352 $cm^{-1}$ might be due to carboxylic acid. A peak near 1033-835 $cm^{-1}$ is due to $NO_3$ bonding which might be due to the absorption of nitric acid group on the ZnO surface. The peak in the region between 424 to 475 $cm^{-1}$ is allotted to Zn–O stretching [28].

XRD diffraction patterns of the ZnO nanoparticles synthesized at 2 minutes of irradiation time is shown in Figure 2(c). There are



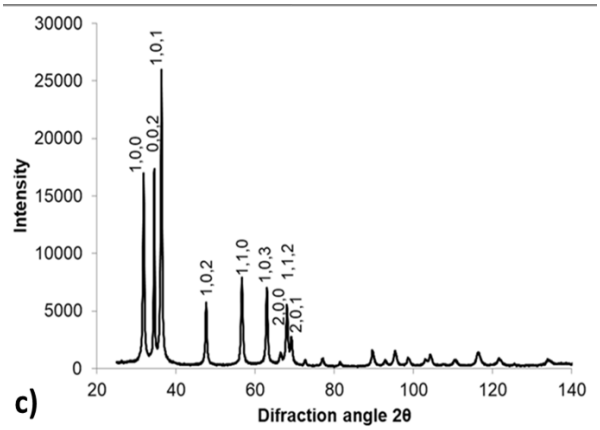




**Figure 2.** a) UV-vis spectra of ZnO nanoparticles b) FTIR spectra of ZnO nanoparticles c) XRD spectra of ZnO nanoparticles synthesized at 2 min of microwave irradiation time

nine diffraction peaks position at 2θ of 31.8, 34.4, 36.2, 47.5, 56.6, 62.8, 66.4, 67.9, and 69.1 which corresponded to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) crystal planes of hexagonal wurtzite ZnO, respectively [29].

X'Pert High Score version 2.0 was used to measure the x-ray wavelength, the full width at half-maximum (FWHM) of the diffraction line and the diffraction angle. On the other hand, the crystallite size was calculated using the Scherrer equation Equation (1) for the broadening of diffraction peaks [30].

$$LC = \frac{180}{\pi} \cdot \frac{K \cdot \lambda}{\cos\theta \sqrt{FWHM^2 - s^2}} \quad (1)$$

Here, $K$ is the wavelength of Cu (1.5406 Å), s is the instrumental broadening (0), $\lambda$ is the Scherrer constant (0.89), FWHM is the full-width at half-maximum of the (101) plane attained from the EVA software, and $\theta$ is the angle of (101) plane. Table 2 shows the calculated average crystallite size of ZnO nanoparticles synthesis in 2 minutes of irradiation time was 25 nm.

FESEM image as shown in Figure 3 showed spherical morphology controlled growth of aggregates ZnO nanoparticles at 2 minutes of microwave irradiation time. Despite size increasing, microwave irradiation time not result in a significant morphological change when microwave irradiation time exceeds 10 minutes (Figure not included). This may be due to the steric effect of gum arabic as stabilizing and capping agent that control the polarization of $[Zn(OH)_4]^{2-}$ as growth species. Some researchers reported incompatible result, which is the morphology of ZnO nanoparticles change with irradiation time forming including ZnO star-shaped, needle-shaped, and flower-shaped [13,19].

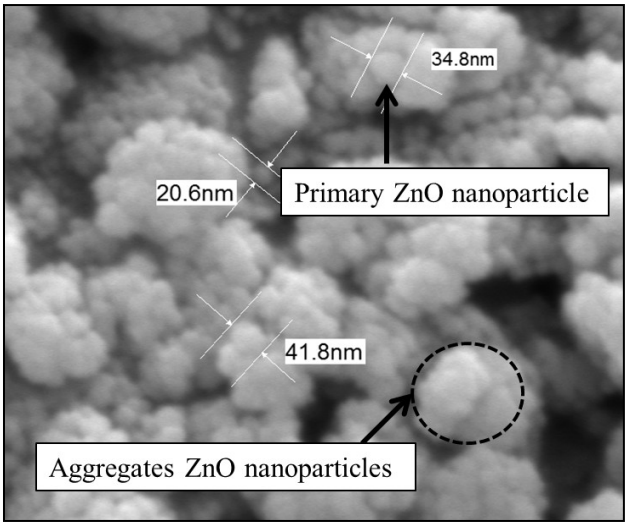



**Figure 3.** FESEM image of aggregates ZnO nanoparticles at 2 min of microwave irradiation time. The primary size of ZnO nanoparticle was calculated 20-40 nm, and the aggregates size was 150-200 nm

## 4. Conclusions

Microwave-assisted heating is a low cost, simple and greener approach to synthesize ZnO nanoparticles by using gum arabic as stabilizing agent. In this study, size and morphology-controlled growth of ZnO nanoparticles was achieved within range of investigated microwave irradiation time. ZnO nanoparticles size increase with the increase of microwave irradiation time. Two minutes of microwave irradiation time is sufficient in order to obtain small size of ZnO nanoparticles at 350 watt.

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