Modified Combustion Synthesis and Characterization of ZnO Nanoparticles Using Various Dispersants

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Abstract. Zinc oxide (ZnO) nanoparticles with hexagonal wurtzite structure were successfully synthesized via simple, cost-effective and environmental friendly modified combustion synthesis route. Three different type of dispersants namely glycerol, palm oil derived fatty alcohol (C8) and fatty ester (C12) were employed to produce the nanoparticles. X-ray diffraction patterns of calcined ZnO nanoparticles indicated the successful formation of ZnO. The crystallite sizes were at ca. 39.42 nm, 27.62 nm and 30.27 nm for ZnO produced using glycerol, fatty alcohol (C8) and fatty ester (C12). The morphology was of spindle-like shape for ZnO produced using glycerol and pseudo-spherical shape for ZnO produced using palm oil derived fatty alcohol (C8) and fatty ester (C12). Energy dispersive X-ray analyses showed the existence of zinc and oxygen peak suggesting successful formation of ZnO using various renewable dispersant.

1. Introduction
Metal oxide nanoparticles received immense interest in research due to their novel and difference in physical and chemical properties as compared to its bulk materials. There are several metal oxides nanoparticles produced for various applications such as copper oxide, nickel oxide and magnesium oxide [1-2]. Among these metal oxides, ZnO nanoparticles received increasing interest due to its various morphology, specific surface area and nanosize grain due to its exceptional properties such as wide band gap of 3.37 eV and a large exciton binding energy of 60 meV. These properties make ZnO nanoparticles a suitable candidate to be incorporated in dye-sensitized solar cells, semiconductor and other industrial applications [3-6]. For example, ZnO nanoparticles are considered as a suitable and cheaper alternative to titanium oxide in solar cells applications because it can replace the role of titanium as effectively [7].

In previous research, various techniques were developed to produce ZnO nanoparticles such as sol-gel method, direct precipitation method, vapour method and microwave-assisted combustion synthesis method [8-13]. However, these methods need to be performed under strict condition which is not favourable for low-cost production. Among them, combustion synthesis method is considerably simple, fast and cost-effective as compared to other methods. This is due to shortened reaction time to produce metal oxide powders and it does not require the used of catalysts to obtain the final product. In this paper, a simple method to prepare ZnO nanoparticles employing new and renewable palm oil derived fatty alcohols and fatty ester using modified combustion synthesis as fast, cost-effective and...
environmental friendly method is reported. Palm oil derived fatty alcohol was reported as a substitute for surfactant to generate carbon template for the formation of silica spheres [14].

2. Materials and methods

2.1. Materials
Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) (Sigma-Aldrich, Reagent grade, 98%) was used as the metal precursor and oxidant and three different dispersants which were glycerol (Sigma-Aldrich, 99%), palm oil derived fatty ester (12 carbon chains, 99.7%, Cognis) and palm oil derived fatty alcohol (8 carbon chains, 98%, Emery) were used as received.

2.2. Synthesis of ZnO Nanoparticles
Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) act as dual role as metal precursor and oxidant. The ratio of the metal precursor to the dispersant is 2.5:1 and was directly mixed on the heated plate for glycerol and fatty alcohol prior to combustion. The initial temperature was set at 50°C and was raised systematically until the mixture combusted to obtain as-synthesized material. The as-synthesized material is subjected to calcination at 600°C to obtain white ZnO powder. Dry fatty ester was heated using hot plate at initial temperature 50°C until it liquefies. (Zn(NO$_3$)$_2$·6H$_2$O) was added in the dissolved fatty ester at 100°C and raised gradually until combustion occurred. As-synthesized ZnO particles were calcined at 600°C to obtain ZnO nanoparticles.

2.3. Structural Characterizations
The calcined samples were subjected to characterization by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive x-ray (EDX). XRD patterns of the samples were obtained using Shimadzu XRD-6000 with CuKα radiation (30 kV and 20 mA) at 2θ range of 20° to 70°. The morphological feature and elemental analysis of the powder were investigated through FE-SEM using JEOL JSM-7600F field emission scanning electron microscope attached with EDX spectrometer at acceleration voltage of 5.0 kV for FE-SEM and acceleration voltage 20 kV for EDX. The powder being dispersed in ethanol before sonicated for 30 minutes. The homogenous solution was dropped on aluminium coated carbon tape and dried in air. Scherrer equation (1) was applied to the XRD patterns to estimate the crystallite sizes at the highest reflection peak (101) using FWHM method.

\[ D = \frac{0.9 \lambda}{B \cos \theta} \]  

Where D is crystalline size in nanometer (nm), \( \lambda \) is the wavelength of the radiation (1.54056 Å for CuKα radiation), B is the full width at half-maximum (FWHM-in radian) intensity and \( \theta \) is the diffraction angle.

3. Results and Discussion

3.1. Structural Characteristics of ZnO
The XRD patterns for ZnO nanoparticles using glycerol, fatty alcohol (C8) and fatty ester (C12) are shown in figure 1. All the samples exhibited three prominent peaks of (100), (002) and (101) reflection plane attributable to hexagonal wurtzite structure of ZnO. There are no other peaks observed in the XRD patterns suggesting no other phases formed during the combustion. The results shown in table 1 suggested that the crystallite size was significantly influenced by the type of dispersant used during combustion synthesis.
Table 1. The crystalline size of ZnO nanoparticles

| Dispersants         | D (nm) |
|---------------------|--------|
| Glycerol            | 39.42  |
| Fatty acid (C8)     | 27.62  |
| Fatty ester (C12)   | 30.27  |

3.2 Morphology and Elemental Analyses

The morphology of calcined samples was investigated using FESEM with acceleration voltage of 5 kV. Figure 2 shows the FESEM image of ZnO nanoparticles using glycerol as dispersant. As shown in figure 2, ZnO nanoparticles produced using glycerol as dispersant exhibited elongated spindle-like shape particles and the particles showed considerable necking due to high calcinations temperature. Figure 3 shows the FESEM image of ZnO nanoparticles using C8 fatty alcohol as dispersant. The particles exhibited agglomerated and pseudo-spherical in shape at ca. 100 nm. Figure 4 shows the FESEM image of ZnO nanoparticles using C12 fatty esters as dispersant. It can be observed that the particles were pseudo-spherical in shape at ca. 100 nm with considerable necking due to high temperature. Agglomerations and necking of particles observed in the images were due to the high calcinations temperature. The EDX spectra for all 3 samples exhibited zinc and oxygen peaks suggesting the formation of ZnO.

Figure 1. X-ray diffraction patterns of calcined samples of ZnO produced using glycerol, fatty alcohol (C8) and fatty ester (C12).

Figure 2. ZnO nanoparticles using glycerol.

Figure 3. ZnO nanoparticles using fatty alcohol (C8).

Figure 4. ZnO nanoparticles using fatty ester (C12).
4. Conclusions
ZnO nanoparticles with hexagonal wurtzite structures were successfully synthesized via combustion synthesis method. New and renewable palm oil derived fatty alcohol (C8), palm oil derived fatty ester (C12) and glycerol successfully played the role of dispersants to produce ZnO. No other phases formed during the combustion and the crystallite sizes were significantly influenced by the dispersants. Thus, it can be concluded that crystallite size produced by combustion synthesis can be reduced and controlled affectively in a simple, quick and cost-effective methods.

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Figure 4. ZnO nanoparticles using C12 fatty acid esters (C12).