Modified Combustion Synthesis of ZnO Nanoparticles Using Renewable Fuel

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Abstract. Zinc oxide nanoparticles were successfully synthesized using cost effective modified combustion synthesis route employing zinc nitrate hexahydrate as oxidant and palm oil derived C8 fatty alcohol as fuel in various ratios. The calcined zinc oxide exhibited hexagonal phase with wurtzite structure. The crystallite sizes of the samples were ranging from ca. 28 to 40 nm. Therefore, palm oil derived C8 fatty alcohol successfully played the role as low-cost and renewable fuel to synthesize zinc oxide nanoparticles.

1. Introduction

There are vast amount of studies conducted on zinc oxide (ZnO) nanoparticles. This is due to their unique physical, chemical and optical properties making it a potential material for a wide range of applications [1]. ZnO nanoparticles have been applied as electrode in solar cells, catalysts, varistor and in sun protection lotions [2-5]. Various morphology and size of ZnO nanoparticles makes them suitable for different applications. For example, ZnO nanoparticles with high specific surface area enhance photocatalytic ability in the visible light region [6].

ZnO nanoparticles with specific size and morphology can be tailored by choosing the suitable synthesis method to suit desired applications. Various methods have been reported to synthesize ZnO nanoparticles resulting in diverse morphology and particle size. Methods such as pulse laser ablations and thermal decomposition required the use of complicated and expensive equipments [7-8]. In addition, microemulsion and direct precipitation method required strict control of reaction condition such as pH of the precursor solution, temperature and time to obtain the desired nanoparticles [9-10]. Therefore, combustion synthesis is proposed as a simple, fast and economical approach to produce ZnO nanoparticles.

Combustion synthesis involves the redox reaction between an oxidizing reagent usually comprises of desired metal salts and a reducing reagent (organic compound acting as fuel) [4]. Previous studies used various fuels such as urea, glycine and citric acid to produce ZnO nanoparticles using combustion synthesis method resulting various morphologies, sizes and properties [1,4,11]. In this work, palm oil derived fatty alcohol was introduced as a new and renewable fuel to synthesize ZnO nanoparticles. Previously, palm oil derived fatty alcohol was used as organic template to produce mesoporous silica nanoparticles [12]. Palm oil derived fatty alcohol bearing eight carbon chain (C8) with various ratio were used to synthesize ZnO nanoparticles. Then, the morphologies and structural properties of the synthesized samples were investigated.

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2. Materials and Methods

2.1. Materials
All materials used in this study were of analytical grade and were used as received. The materials used were zinc nitrate hexahydrate, Zn(NO$_3$)$_2$.6H$_2$O, reagent grade 98% from Sigma-Aldrich and C8 fatty alcohol from Emery Oleochemicals (M) Sdn. Bhd.

2.2. Synthesis
Metal precursor was Zn(NO$_3$)$_2$.6H$_2$O while the fuel is palm oil derived C8 fatty alcohol. The Zn(NO$_3$)$_2$.6H$_2$O and C8 fatty alcohol formed almost homogeneous mixtures. The mixture was heated with an initial temperature of 50°C and was increased systematically until combustion occurred at around 200°C producing as-synthesized ZnO powder. The as-synthesized powder was subsequently subjected to calcination at 600°C to obtain the calcined ZnO powder. The calcined samples were named ZnO-1 (ratio 2), ZnO-2 (ratio 2.5), ZnO-3 (ratio 3) and ZnO-4 (ratio 3.5).

2.3. Characterizations
In order to identify the crystalline phase and crystal structure of calcined samples, X-ray diffraction (XRD) analyses were carried out using Shimadzu XRD-6000 diffractometer with CuKα radiation. The crystallite sizes of the samples were determined using Scherrer equation, 
\[ d = \frac{0.9\lambda}{\beta \cos \theta} \]
where \( d \) is the crystallite size in nm, \( \beta \) is the full width at half maximum (FWHM-in radian) and \( \theta \) is the Bragg diffraction angle. The crystallite sizes of the calcined ZnO were estimated based on diffraction plane with highest intensity. The morphology of the calcined samples were obtained using field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F) at an acceleration voltage of 5.0 kV. Prior to FE-SEM analyses, a small amount of the samples were dispersed in ethanol and sonicated to form a homogeneous mixture. Then, the homogeneous mixture was dropped onto an aluminium covered carbon taped sample holder and dried in air. The nitrogen adsorption-desorption analyses for specific surface area were completed using Quantachrome Autosorb iQ at liquid nitrogen temperature. Consequently, specific surface area of the samples were estimated by BET method using the adsorption branch of the isotherms.

3. Results and Discussion

3.1. Structural properties
The XRD patterns for the samples are shown in figure 1a). All samples exhibited nine diffraction peaks assigned to the formation of ZnO with hexagonal wurtzite structure. The peaks were at ca. 20 = 31.9°, 34.6°, 36.4°, 47.7°, 56.7°, 63.0°, 66.2°, 68.0° and 69.1° corresponding to (100), (002), (101), (102), (110), (103), (200), (112) and (201) diffraction planes. The narrow and high intensity of diffraction peaks in the XRD patterns suggested high crystallinity of calcined ZnO powder. No other peaks were observed in the XRD patterns, suggesting that no other phases were formed during the synthesis. The crystallite size for ZnO-1 was ca. 28.5 nm while for ZnO-2 was ca. 27.6 nm. ZnO-3 has the highest crystallite size of ca. 40 nm while ZnO-4 was 39.4 nm. However, the crystallite size did not exhibit an increasing or decreasing trend with increased of oxidant-to-fuel ratio. Figure 1b) shows the variation of crystallite size as a function of oxidant-to-fuel ratio. The crystallite size suddenly increased for the ratio of ZnO-2 and ZnO-3 suggesting that it can be further adjusted between these ratios.
3.2. Morphology analysis
The FE-SEM images showed that the particles were agglomerated with irregular shapes and sizes. The agglomeration of particles can be classified as hard (strong bonding) or soft (weak bonds by Van de Waals forces) as reported [12]. However, some particles were observed to be less than ca. 100nm. Particles that are less than 1μm tend to agglomerate due to high energy and surface area [13].

3.3. Nitrogen adsorption-desorption analysis
Figure 3 and figure 4 show the nitrogen adsorption-desorption isotherms for calcined ZnO-2 and ZnO-3, respectively. The samples showed similar isotherm patterns exhibiting Type II normally obtained for non-porous materials. At relative pressure above 0.95, the amount adsorbed was high suggesting
that the adsorption occurred on the external surface area of the samples. The inset in figure 3 shows the adsorption branches considered to estimate the specific surface area using BET method. Lower crystallite size for ZnO-2 resulted in higher specific surface area of 3.5 m$^2$/g. On the other hand, ZnO-3 with highest crystallite size of 40 nm has a specific surface area of 1.8 m$^2$/g. The low value of specific surface area was probably due to agglomeration of particles as observed in SEM images.

![Figure 3. ZnO-2 adsorption-desorption isotherm.](image3.png)

![Figure 4. ZnO-3 adsorption-desorption isotherm.](image4.png)

4. Conclusion

ZnO nanoparticles were successfully synthesized via modified combustion synthesis employing a new and renewable fuel, palm oil derived C8 fatty alcohol. The calcined samples exhibited ZnO with hexagonal wurtzite structure and the crystallite size range was between 28 to 40 nm. The low value specific surface area of the samples which were 3.5m$^2$/g and 1.8m$^2$/g were probably due to agglomeration of particles. Therefore, palm oil derived C8 fatty alcohol successfully played the role as new, renewable and low-cost fuel in producing ZnO nanoparticles.

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References

[1] Kumar V R, Kavitha V T, Wariar P R S, Nair S U K and Koshy J 2011 J. Physics & Chem. Solids 72 290
[2] Rani S, Suri P, Shishodi P K and Mehra R M 2008 Solar Energy Mat. & Solar Cells 92 1639
[3] Jang Y J, Simer C and Ohm T 2006 Mat. Research Bulletin 41 67
[4] Sousa V C, Segadaes A M, Morelli M R and Kiminami R H G A 1999 Intl. J. Inorganic Mat. 1 235
[5] Strunk J, Kahler K, Xia X and Muhler M 2009 Surf. Science 603 1776
[6] Ahmad M, Hong Z, Ahmed E, Khalid N R, Elhissi A and Ahmad W Ceramics International
[7] He C, Sasaki T, Shimizu Y and Koshizaki N 2008 Appl. Surf. Science 254 2196
[8] Bigdeli F, Morsali A and Retailleau P 2010 Polyhedron 29 801
[9] Sui X, Liu Y, Shao C, Liu Y and Xu C 2006 Chemical Physics Lett. 424 340
[10] Chen C C, Liu P and Lu C H 2008 Chemical Engr. Journal 144 509
[11] Tarwail N L, Jadhav P R, Vanalakr S A, Kalagi S S, Pawar R C, Shaikh J S, Mali S S, Dalavi D S, Shinde P S, Patil P S 2011 Powder Tech. 208 185
[12] Misran H, Singh R and Ambar Yarmo M 2008 Microporous & Mesoporous Mat. 112 243
[13] Trommer R, Alves A K and Bergmann C P 2010 J. Alloys & Compounds 491 296