Synthesis and Characterization of Mn-doped ZnO Nanoparticles

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Declaration

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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List of Abbreviations

Nanometer	nm/ 10^{-9} m
Nickel	Ni
Iron	Fe
Cobalt	C_O
Chromium	Cr
Manganese	Mn
Zinc oxide	ZnO
Thiol	S-H
Zinc acetate dehydrate	$Zn(CH_3COO)_2.2H_2O$
Manganese acetate tetrahydrate	$Mn\ (CH_3COO)_2.4H_2O$
2-methoxy ethanol	$C_3H_8O_2$
Monoethanolamine	C_2H_7NO
Zinc sulphate	$Zn(SO)_4$
Sodium bicarbonate	$Na_2(CO)_3$
Potassium hydroxide	KOH
Sodium hydroxide	NaOH
Degree Celcius	°C
Hours	h
Megapascal	MPa
Milimoles	mmol
Mililitre	ml
Scanning Electron Microscopy	SEM
Transmission Electron Microscope	TEM
Fourier Transform Infrared Spectroscopy	FTIR
Scanning Electron Microscope-Energy Dispersive X-ray	SEM-EDX

Ultraviolet	UV
Photoluminescence	PL
Diluted Magnetic Semiconductors	DMS

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ABSTRACT

Mn-doped ZnO Nanoparticles has gained a lot of attention from the scientists and researchers to undergo this interest research due to its various applications in optoelectronic devices, chemical sensors, solar cells and photocatalyst. However, the doping efficiency was influenced by the strong tendency of the Mn dopant ions to segregate at the nanoparticles surfaces. Hence, many efforts have been made related to size, morphology and preparation on Mn-doped ZnO nanoparticles. In this project, co-precipitation method was used to synthesize Mn-doped ZnO nanoparticles. On the other hand, the effects of concentration of Mn dopant ions on the particle size, shape and optical properties of Mn-doped ZnO nanoparticles were investigated through Scanning Electron Microscope, Transmission Electron Microscope, Fourier Transform Infrared Spectroscopy, UV-Visible spectroscopy, Energy Dispersive X-rays and Fluorescence Spectrophotometer.

Keywords: Doping, manganese, zinc oxide nanoparticles, co-precipitation

ABSTRAK

Pendopan mangan ke atas zink oksida nanopartikel telah menarik perhatian ahli-ahli sains dan penyelidik dari seluruh dunia. Pelbagai penyelidikan telah dijalankan atas sebab pendopan mangan ke atas zink oksida nanopartikel boleh diaplikasikan dalam perlbagai bidang tertentu. Antaranya termasuklah sebagai peranti optoelektronik, kimia sensor, fotokatalis dan sebagainya. Tetapi, kecekapan pendopan akan dipengaruhi oleh kecenderungan yang kuat oleh Mn ion dalam proses pengasingan atas permukaan nanopartikel. Justeru, banyak usaha berkait rapat dengan saiz, morfologi serta sintesis pendopan mangan ke dalam zink oksida telah dijalankan. Dalam projek ini, cara ko-pemendakan telah digunakan untuk sintesis pendopan mangan ke atas zink oksida nanopartikel. Selain itu, kesan kepekatan pendopan mangan terhadap saiz zarah, bentuk dan ciri-ciri optic pada zink oksida partikel telah diselidik melalui Mikroskop Electron Pengimbas, Penghantaran Electron Mikroskop, Inframerah Transformasi Fourier, UV-Kelihatan Spectrometer, Serakan Tenaga Sinar-X dan Spektrofotometer Pendarfluor.

Kata kunci:Pendopan, mangan, zink oksida nanopartikel, ko-pemendakan

1.0 Introduction

In this fast paced world, nanotechnology has created a new industrial revolution globally and becomes a hot topic in recent material research fields. Many countries have invested in nanotechnology due to its small in size with huge immense potential. It is well-known and widely applied in many areas such as in nanofinishing of functional textiles, biomedical, electronics, batteries, solar cells, chemical coatings and so forth (Nanocompositech, 2005).

According to Kathirvelu, D'Souza, and Dhurai (2008), "Nanotechnology creates structures that have excellent properties by controlling atoms and molecules, functional materials, devices and systems on the nanometer scale by involving precise placement of individual atoms of the size around 1 nm to 100 nm."

Zinc oxide (ZnO) is an essential semiconductor with direct band gap of 3.3eV and a high excitant binding energy of 60meV. Due to its potential application in many areas such as in optoelectronic devices, solar cells, chemical sensor, photocatalyst and so forth, hence, it has attracted attention of more and more researchers and scientists to develop ZnO in the field of science and technology. In addition, ZnO is lower in cost and environmental friendly as compared to other metal oxides (Iqbal *et al*., 2011).

However, there is few studies show that undoped ZnO nanoparticles have certain limitation in their application. Thus, in order to enhance the optical, magnetic and electrical properties of ZnO, the transition metal-doped ZnO nanoparticles have been introduced. The modification of ZnO nanoparticles with impurity incorporation leads to possible application in UV optoelectronic and spin electronics (Wang *et al*., 2010).

Actually, the term "doped" is used to modify the optical or magnetic properties of the host by adding impurities ions against the host lattice (**Figure 1**). The doping with 3d metals such as Mn, Ni, Fe, C_O, Cr and the like will increase the surface area and reduce the particle size of ZnO nanoparticles (Yan & Xu, 2009). Mn is preferred for the doping of ZnO due to the d electron of Mn at t_{2g} level can easily overlap with the ZnO's valence bond as compared with other transition element. There are various studies shown that Mn-doped semiconductors have influenced the physical, chemical and structural properties of undoped ZnO nanoparticles. For example, the optical properties of undoped ZnO nanoparticles especially on the tuning of the band gap can be greatly improved at the nanoscale by Mn doping (Abdollahi *et al*., 2011).

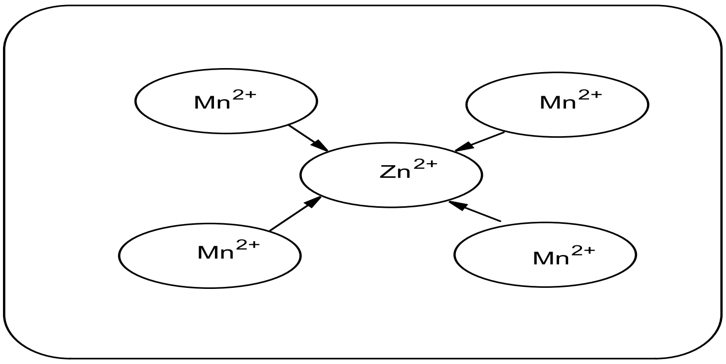


Figure 1: Mn-doped ZnO nanoparticles

There are few parameters that will definitely affect the particle size, shape and optical properties of Mn-doped ZnO nanoparticles such as the effect of concentration of manganese dopant ions, pH and surfactant (Abdollahi *et al*., 2011). In this project, we are only focus on the effect of Mn dopant concentrations (3 mol% to 20 mol%) on the composition, morphology and optical properties of Mn-doped ZnO nanoparticles.

Currently, the synthesis of Mn-doped ZnO nanoparticles can be through various types of methods such as wet-chemical, sol-gel, co-precipitate, solid-thermal, spray pyrolysis and the like. Most of the current studies synthetic methods for Mn-doped ZnO nanoparticles do not give doping efficiency and probably lack of physical, chemical and optical properties.

In order to enhance the optical properties and obtain a small particle size, hence, a search for alternative synthesis methods for efficiency Mn doping with ZnO nanoparticles has become the major interests of studies. Here, Mn-doped ZnO nanoparticles were synthesized through co-precipitate method. Zinc acetate ($Zn(ac)_2.2H_2O$) and manganese acetate ($Mn(ac)_2.4H_2O$) acts as precursors and absolute ethanol was used as a solvent to synthesis Mn-doped ZnO nanoparticles. Basically, the synthesis of electrostatically stable Mn-doped ZnO nanoparticles was performed in an alcoholic solution in order to avoid the formation of ZnOH (Jayakumar *et al.*, 2006).

Last but not least, the characterization of composition, morphology, and optical properties of Mn-doped ZnO nanoparticles were carried out through Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), UV-visible spectrophotometer, Scanning Electron Microscope-Energy Dispersive X-rays (SEM-EDX) and Fluorescence Spectrophotometer (Senthilkumaar *et al*., 2008).

1.1 Objectives

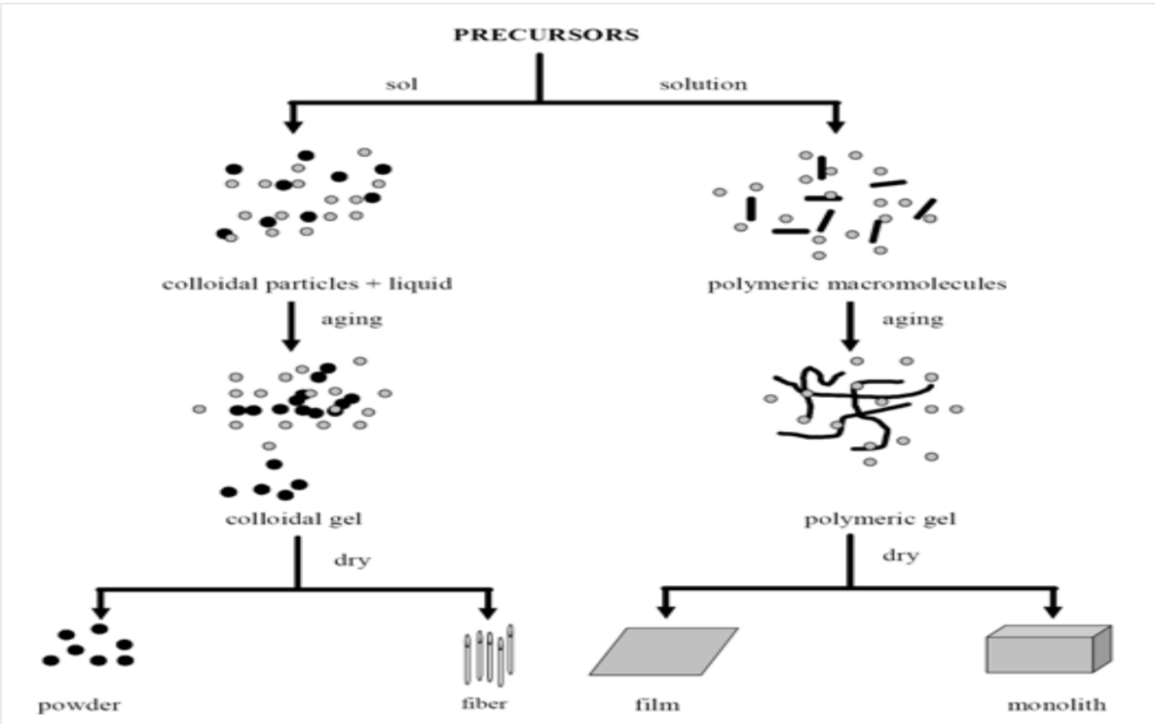
1. To synthesize Mn-doped ZnO nanoparticles.
2. To determine the effects of Mn dopant concentrations on the composition, morphology and optical properties of Mn-doped ZnO nanoparticles.

2.0 Literature Review

2.1 Synthesis of Mn-doped ZnO Nanoparticles

From the previous studies, there are generally five methods of synthesizing Mn-doped ZnO nanoparticles, namely sol-gel, solvothermal reaction with microwave heating, solid state reaction, hydrothermal and co-precipitation (Abdollahi, Abdullah, Zainal & Yusof, 2011).

Basically, sol-gel techniques is a system involves the transition from a liquid 'sol' into a solid 'gel' phase. Solid particles with a diameter of few hundred-nanometers that are suspended in the liquid phase make up the sol. Sol-gel is one of the wet-chemical routes for synthesizing Mn-doped ZnO nanoparticles. The dispersion of oxides can be then altered to powders, thin films, fiber and monoliths for widely application (Ezema & Nwankwo, 2011) (**Scheme 1**).



Scheme1: Schematic representation of the Sol-gel process (Ezema & Nwankwo, 2011)

On this recent year, this technique is widely used by the most scientists and researchers due to its properties of being simple, inexpensive in production of a large number of samples, easier for controlling of composition, right-accurate control of mole ratio, good homogeneity, lower processing temperature which normally below glass transition (T_g) temperature, enabling mixing of dopant with precursors at molecular level and a general advantage of large area deposition (Yan & Xu, 2009). The precursors that used for the synthesis of Mn-doped ZnO nanoparticles are zinc acetate dehydrate [$Zn(CH_3COO)_2.2H_2O$] and manganese acetate tetrahydrate [$Mn(CH_3COO)_2.4H_2O$]. In addition, 2-methoxy ethanol [$C_3H_8O_2$] (**Figure 2**) or known as DME acts as a solvent for this technique whereby monoethanolamine (MEA) [C_2H_7NO] (**Figure 3**) act as a stabilizer respectively. Apart from that, the method has disadvantages which include the precursors need to be synthesized individually, dopants may segregate during gel formation, low density product may need annealing procedure and so forth (Jang *et al.*, 2010).

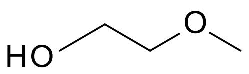


Figure 2: Structure of 2-methoxy ethanol

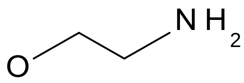


Figure 3: Structure of monoethanolamine

Besides, solvothermal reaction with microwave heating is also one of the methods for synthesis Mn-doped ZnO nanoparticles. This method relatively achieves higher level of doping among transition metal ions without any dopant clustering or oxide precipitation. Moreover, this reaction is efficiently simply and safely to be carried out. Furthermore, the reaction time consumed by solvothermal technique is less due to the energy is transmitted directly to the reacting fluids. Generally, the precursors used in this reaction are zinc acetate and manganese acetate which dissolved in ethylene glycol (**Figure 4**) at a pressure of 2MPa. Hence, the final product produced throughout dissolving in ethylene glycol has a clean surface. In case, higher pressure is pivotal in solvothermal reaction in order to prevent the formation of amorphous phases, hydroxides or unreacted organic salts. The synthesis parameters such as reactant concentration, pH value, reaction time and temperature are essential for the determination of morphology and composition of Mn-doped ZnO nanoparticles. However, this method is not favourable because higher pressure is needed for the process (Lojkowski *et al.*, 2009).

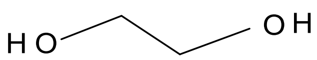


Figure 4: Structure of ethylene glycol

Besides the methods states as above, solid state reaction is also one of the techniques for synthesizing Mn-doped ZnO nanoparticles. Actually, solid state reaction is a chemical reaction without the use of solvent. It can produce more products than other method, environmentally friendly and inexpensive (Baruwati & Manorama, 2008). There are usually consisting of two steps for the synthesis of Mn-doped ZnO nanoparticles. Zinc sulphate, $Zn(SO)_4$ act as a precursor for this reaction. Next, sodium bicarbonate ($Na_2(CO)_3$) was mixed with zinc sulphate and heated under a temperature of 200 °C.

The chemical equation shows as follow:

$$Zn(SO)_4.7H_2O + Na_2CO_3 \longrightarrow ZnO + Na_2SO_4 + CO_2 + 7H_2O$$

Then, manganese dioxide (MnO_2) was prepared by using the same method for the synthesis of ZnO nanoparticles. At last, ZnO nanoparticles was mixed with MnO_2 and forming Mn doping with ZnO nanoparticles. However, this method is not suitable for the reaction which requires solvent (Lakshmi & Ramachandran, 2006).

Besides the synthesis method stated as above, Mn-doped ZnO hierarchical microspheres can also be prepared by hydrothermal methods using zinc acetate and manganese acetate as precursors and ethylene glycol as solvent. Ethylene glocol besides acts as a solvent, it also serves as the reductant which reduces $Zn(A_C)_2$ / $Mn(A_C)_2$ to Mn-doped ZnO crystalline nanoparticles. Basically, the formation of Mn-doped ZnO hierarchical microspheres semiconductors can be illustrated through a growth mechanism shown in the equation below:

$$2HOCH_2CH_2OH \longrightarrow 2CH_3CHO \longrightarrow CH_3COOCH_3 + 2H \qquad (1)$$

$$Zn(Ac)_2 / Mn(Ac)_2 + 2H \longrightarrow Zn_{1-x}Mn_XO + CH_3COOH \qquad (2)$$

From equation 1 shown, dehydration of ethylene glycol produces acetaldehyde where acetaldehyde acts as reducing agent and donates a hydrogen atom. The reduction of Zn $(Ac)_2$ / $Mn(Ac)_2$ with the newly formed hydrogen atom will form Mn-doped ZnO nanoparticles which shown in equation 2.

The advantages of using this method for synthesis Mn-doped ZnO hierarchical microsphere through the self-assembly of nanocrystalline building blocks provide new opportunities for optimizing and enhancing the properties of the ZnO diluted magnetic semiconductors (DMS). However, a strong UV photoluminescence (PL) is hardly achieved due to the difficulty in controlling the interaction between the Mn dopant and intrinsic defects such as oxygen vacancies during the fabrication process (Hao *et al.*, 2012).

Last but not least, the synthesis of Mn-doped ZnO nanoparticles can be through co-precipitation method. There are numerous techniques for the preparation of Mn-doped ZnO nanoparticles, but the comparison of the properties of synthesized ZnO nanoparticles from others synthesis routes show that co-precipitation method is an efficient pre-concentration techniques for enhancing the optical properties of nanoparticles in terms of process simplicity, the times consumed are less, complex steps such as refluxing of alkoxides can be avoided, and is efficient. Apart from that, this technique eventually involves lower costs in which all the steps of synthesis are carried out at room temperature under ambient condition. Furthermore, it is environmental friendly too. In addition, the morphology and optical properties of the reaction is normally affected by the synthesis parameters like reaction time, surfactant, and reaction temperature (Rekha *et al.*, 2010). In the light of this, Mn-doped ZnO nanoparticles was synthesized by using this simple co-precipitation method in this study. The precursor used in this techniques are zinc acetate dehydrate ($Zn(OAc)_2.2H_2O$) (**Figure 5**) and manganese acetate tetrahydrate ($Mn(OAc)_2.4H_2O$) (**Figure 6**) in methanol (**Figure 7**). Potassium hydroxide (KOH) was added to the solution containing zinc acetate dehydrate and manganese acetate (Jayakumar *et al.*, 2006).

The materials will be used in this study are as follow:

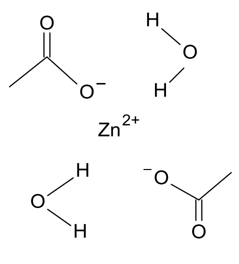


Figure 5: Structure of Zinc acetate dehydrate

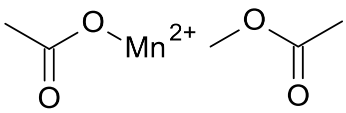


Figure 6: Structure of manganese acetate tetrahydrate

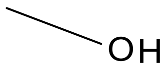


Figure 7: Structure of methanol

The introduction of donor impurities especially the transition elements into semiconductor provide an excess of electrons. There are generally two absorption mechanisms for the incorporation of donor impurities into semiconductors nanoparticles. It can be illustrated schematically in **Figure 8**. It will be possible to absorb photons by exciting electrons between the levels if the donor states are occupied. On the other hand, if the donor states are empty, then it will be possible to absorb light by exciting electron from the valence band to the donor states (Casiday & Frey, 2002).

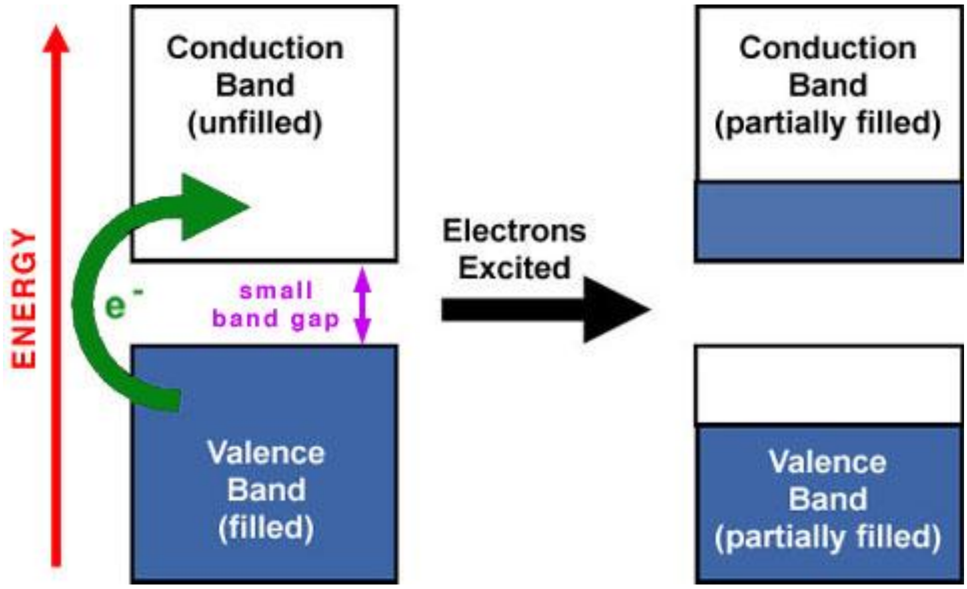


Figure 8: Impurities absorption mechanism (Casiday & Frey, 2002)

Generally, there are few synthesis parameters that can be used to determine the composition, morphology and optical properties of Mn-doped ZnO nanoparticles. Here, there are consisting of reaction temperature, reaction time, pH, surfactant and the concentration of manganese dopant ions.

Reaction temperature is undoubtedly plays a fundamental role on indicating the relationship between the reaction temperature with the composition, morphology and optical properties of Mn-doped ZnO nanoparticles. From the previous studies, it shows that with the increasing of temperature from 300 °C to 600 °C, the average grain size of ZnO also increases. Undeniably, the crystallization of Mn-doped ZnO nanoparticles also improved. However, the increase of average grain size of ZnO nanoparticles not only depends on the factors of higher reaction temperature but it also closely related to the doping of Mn onto ZnO nanoparticles. Furthermore, the surface morphology of ZnO becomes smoother with the descending of annealing temperature. Upon Mn doping at higher temperature, the characteristic of optical properties show that the band gap energy exhibit red shift with the indication of lower in band gap (Zhang *et al.*, 2010). The optical band gap can be calculated through the formula as shown below:

$$(\alpha hv)^2 = A(hv - Eg)$$

A = Constant

hv = The photon energy

Eg = The energy gap

α = The absorption coefficient

Next, the reaction time is also one of the paramount key on determining the effect of particle size, shape and optical properties of Mn-doped ZnO nanoparticles. From the studies, the ratio of Mn / ZnO needs to fix and the duration time is varied between 4 h to 12 h. The morphology of Mn-doped ZnO nanoparticles is characterized through Scanning Electron Microscope (SEM). Through the SEM images, it can be seen that at 4 h, 6 h and 8 h, the Mn doping ZnO nanoparticles shows no obvious change on the growth of ZnO nanoparticles. On the other hand, the growth time for 10 h and 12 h, the Mn-doped ZnO nanoparticles shows extremely well-distributed with high homogeneity. At the end, the study investigate that 12 h is the most suitable time for the synthesis of Mn-doped ZnO nanoparticles (Yang *et al.*, 2010).

From the previous studies, it has shown that pH is also one of the fundamental keys for determining the physical, chemical and optical properties of Mn-doped ZnO nanoparticles. It has shown that the change in pH will significantly cause the change in particle size too. At higher pH, the luminescent intensity increases whereby at lower pH, the luminescent intensity decreases (Zhuang *et al.*, 2003).

There have studies show that to prevent Mn-doped nanoparticles aggregation, oleic acid in **Figure 9** act as a capping surfactant has been introduced. Oleic acids with the carboxylic acid group are covalently bonded to the surface of Mn-doped ZnO nanoparticles in order to stabilize the dispersion in the formation of Mn doping with ZnO nanoparticles. Furthermore, oleic acid coating on the surface of nanoparticles reduces surface oxidation, surface anisotropy and particle interaction. More importantly, the enhancement of polarity of the solvent is achieved. Nevertheless, oleic acid surfactant affects the morphology and shape of Mn-doped ZnO nanoparticles. Besides that, according to Le Chatelier’s principle, the oleate anions will bind more easily on the surfaces of nanoparticles with the increasing amount of oleic acid (Liu *et al.*, 2008).

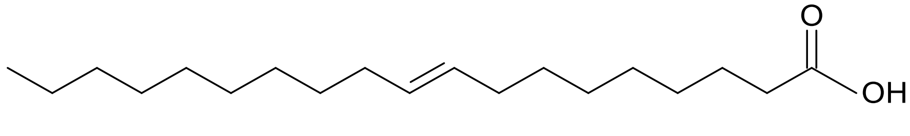


Figure 9: Structure of oleic acid

The effect of concentration of manganese dopant ions on the composition, morphology and optical properties has also been determined from the previous studies. Actually, the ratio of Mn / ZnO is closely depending on the concentration of dopant ion, manganese. The reaction time need to fix and the concentration of manganese dopant ions is varied from 2 %, 5 % and 10 %. The effect of manganese dopant concentration on the chemical composition can be carried out through Scanning Electron Microscope-Energy Dispersive X-rays (SEM-EDX). The mass% of each element which included Zn, O and Mn can be known through the SEM-EDX analysis. From the previous studies, it can be seen that the amount of Mn element in the sample increased depending on the increasing Mn incorporation in the solution. Therefore, the SEM-EDX analysis confirmed the presence of Mn in the samples (Viswanatha *et al*., 2004).

The influence of Mn dopant concentration on the surface morphologies of Mn-doped ZnO nanoparticles was studied by Scanning Electron Microscope (SEM). It has been shown that with the increasing of manganese concentration, the grain size of ZnO nanoparticles also increases and the particles tends to agglomerate and clumped together. It is due to the incorporation of Mn^{2+} ions into the ZnO crystal lattice and the growth of the ZnO nanoparticles. Furthermore, the incorporation of Mn^{2+} ions into ZnO lattice is by substitution rather than by precipitation (Yang *et al.*, 2010).

The influence of manganese dopant concentration on the optical properties of Mn-doped ZnO nanoparticles were investigated through UV-visible Spectroscopy and Fluorescence Spectrophotometer. For UV-visible spectroscopy, the band gap energy shows the decreasing trends upon the increasing of Mn concentration. Basically, it is due to the sp-d exchange interactions between the band electron and the localized d electron of manganese ion substituting the zinc cation (Ezema & Nwankwo, 2011).