

SYNTHESIS AND CHARACTERIZATIONS OF MAGNETIC NANOPARTICLES

TAN CHING HONG

This project is submitted in partial fulfilment of the requirements for a
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DECLARATION

I hereby affirm that the work submitted is the result of my investigation except where otherwise stated.

It has not already been accepted by any application for another degree of qualification of this or any other university of institution of higher learning.

Tan Ching Hong

Resource Chemistry Program

Faculty Resource Science and Technology

University Malaysia Sarawak

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List of Abbreviations

Acetylacetone	acac
Area	cm ²
Atomic Absorption Spectroscopy	AAS
Blocking Temperature	T _B
Celsius	°C
Crystal Field Stabilization Energy	CFSE
Cyclic Voltammetry	CV
Deoxyribonucleic Acid	DNA
Face-Centered Cubic	fcc
Hematite	α-Fe ₂ O ₃
Hydroxide Ions	OH ⁻
Infrared	IR
Iron (II) Ions	Fe ²⁺ / Fe (II)
Iron (II) Oxide	FeO
Iron (III) Acetylacetonate	Fe(acac) ₃ / Fe(C ₅ H ₇ O ₂) ₃
Iron (III) Chloride	FeCl ₃ .6H ₂ O
Iron (III) Ions	Fe ³⁺ / Fe (III)
Iron Oxide	Fe ₂ O ₃
Iron Pentacarbonyl	Fe(CO) ₅
Jacobsite (Manganese Ferrite)	MnFe ₂ O ₄
Kilo Farad	kF / 10 ³ F
Kilo Hertz	kHz / 10 ³ Hz
Maghemite	γ-Fe ₂ O ₃
Magnetic Resonance Imaging	MRI
Magnetite (Iron Oxide)	Fe ₃ O ₄

Manganese (II) Ions	Mn^{2+}
Manganese (II) Chloride	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$
Manganese Oxide	MnO_2
Mass	g
Mili Current	$\text{mA} / 10^{-3} \text{ A}$
Mili Farad	$\text{mF} / 10^{-3} \text{ F}$
Mili Litre	$\text{mL} / 10^{-3} \text{ L}$
Mili Mole	$\text{mmol} / 10^{-3} \text{ mol}$
Molar / Molarity	M
Nanometer	$\text{nm} / 10^{-9} \text{ m}$
Nitrogen gas	N_2
Oxygen ions	O^{2-}
Percentage	%
Polyethylene Glycol	PEG
Polyvinylpyrrolidone	PVP
Potassium Chloride	KCl
Power of Hydrogen	pH
Ruthenium Oxide	RuO_2
Revolutions per Minute	rpm
Scanning Electron Microscopy	SEM
Silver Ions	Ag^+
Sodium Hydroxide	NaOH
Sodium Sulphate	Na_2SO_4
Transmission Electron Microscopy	TEM
Voltage	V
Zero Field Cooling	ZFC

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TAN CHING HONG

Resource Chemistry

Faculty of Resource Science and Technology

University Malaysia Sarawak

ABSTRACT

Magnetic nanoparticles can be applied in various applications such as drug targeting and delivery, magnetic resonance imaging, electrochemical cells, capacitors and etc. However, these applications require narrow size distribution and uniform shape magnetic nanoparticles and the synthesis of these magnetic nanoparticles often result in a broad size distribution. In present study, thermal decomposition method was adapted to obtain a monodispersed size and uniform shape of Fe_3O_4 nanoparticles while co-precipitation method was adapted to synthesize MnFe_2O_4 nanoparticles and the cyclic voltammetry was applied to examine the electrochemical properties of MnFe_2O_4 . The morphology, chemical composition and electrochemical properties of synthesized magnetic nanoparticles were characterized using SEM, TEM, AAS and CV respectively. It was found that by increasing concentration of $\text{Fe}(\text{acac})_3$, the Fe_3O_4 nanoparticles size increases, the addition of oleic acid created a more uniform nanoparticles and longer time duration of thermal decomposition had increased the size of Fe_3O_4 nanoparticles. MnFe_2O_4 nanoparticles size was affected by the heating temperature, the presence of surfactant PVP and the metal salt concentration with hydroxide ions. The highest specific capacitance of MnFe_2O_4 nanoparticles was found to be at 500 °C and the higher the mass of the MnFe_2O_4 nanoparticles, the higher the charge capacity.

Keywords: magnetite, jacobsonite, nanoparticles, thermal decomposition, co-precipitation

ABSTRAK

Nanopartikel magnetik dapat diterapkan dalam berbagai aplikasi seperti ubat penargetan dan penghantaran, MRI, sel elektrokimia, kapasitor dan lain-lain. Namun, aplikasi ini memerlukan pengagihan saiz yang tinggi dan bentuk seragam nanopartikel magnetik dan sintesis nanopartikel magnetik ini sering mengakibatkan pengedaran dan saiz tidak seragam. Dalam kajian ini, kaedah dekomposisi terma telah diadaptasi untuk mendapatkan nanopartikel mono-bubaran saiz dan bentuk seragam Fe_3O_4 sedangkan co-precipitasi kaedah ini diadaptasi untuk mensintesis nanopartikel MnFe_2O_4 dan voltametri siklik diterapkan untuk menguji sifat elektrokimia dari MnFe_2O_4 . Morfologi, komposisi kimia dan elektrokimia sifat nanopartikel magnetik sintesis disifatkan dengan SEM, TEM, AAS dan CV masing-masing. Didapati bahawa dengan meningkatnya konsentrasi $\text{Fe}(\text{acac})_3$, saiz Fe_3O_4 nanopartikel meningkat, penambahan asid oleik mencipta lebih tinggi seragam nanopartikel dan tempoh yang lebih lama masa dekomposisi terma meningkat saiz nanopartikel Fe_3O_4 . MnFe_2O_4 nanopartikel saiz dipengaruhi oleh suhu pemanasan, kehadiran PVP surfaktan dan garam konsentrasi logam dengan ion hidroksida. Kapasitans khususnya tertinggi apabila MnFe_2O_4 nanopartikel dijumpai berada pada 500 °C dan semakin besar berat nanopartikel MnFe_2O_4 , semakin tinggi kapasiti muatan.

Kata kunci: magnetit, jacobsonit, nanopartikel, dekomposisi terma, co-presipitasi

1.0 Introduction

Nanoparticles are defined as small objects that behave as a whole unit of its transport and properties; it constitutes size range between 1 to 100 nanometers (“Standard Terminology Relating to Nanotechnology”). It is normally known as ultrafine particles, clusters, nanocrystals or quantum dots. In general, nanoparticles exhibit unique properties and are different from its bulk group properties (Basnet, 2010). Thus, nanoparticles field is becoming important day by day.

Magnetic nanoparticles are a class of nanoparticles which can be manipulated by using magnetic field. Such particles usually consist of magnetic elements such as transition metals iron, nickel and manganese in their chemical compounds. Due to its magnetic and unique properties, magnetic nanoparticles contribute in a variety of scientific and technological applications such as magnetic storage media, ferrofluids, magnetic refrigeration, magnetic resonance imaging (MRI), hyperthermic cancer treatment, cell sorting and targeted drug delivery (Ye *et al.*, 2006). However, the magnetic and chemical properties of magnetic nanoparticles are mainly depending on their particles size and their microstructures (Lu *et al.*, 2007).

The synthesis methods of magnetic nanoparticles are important as this will affect the particles size and morphology of the magnetic nanoparticles. There are three common methods for magnetic nanoparticles synthesis, namely co-precipitation, micro-emulsion and thermal decomposition (Lu *et al.*, 2007).

Co-precipitation method involves reaction between metal salts in basic condition. Oxidation of ferrous hydroxide in basic pH and adjusting molar ratio between ferric ions

and ferrous hydroxide both are used to form Fe_3O_4 nanoparticles by co-precipitation method. This method is lacking of size control, a wide range of magnetic nanoparticles size can be obtained. Furthermore, variations in the molar ratio of Fe^{3+} and Fe^{2+} lead to complicated change in the structure and the size distribution of iron oxides obtained but it is easy to operate and it can be used in a mass production of nanoparticles such as iron oxide nanoparticles (Li *et al.*, 2005). It is an economic, biocompatible and environmental friendly approach (Zhang *et al.*, 2010).

Apart from co-precipitation method, microemulsion method consists of dispersion of two immiscible liquids and both liquids are stabilized by the amphiphilic surfactant. Besides stabilizing both the liquids, it also lowers the surface tension between the two liquids hence making the solution transparent. Although microemulsion method produces narrowed size distribution magnetic nanoparticles and the size of magnetic nanoparticles is tailorable, it is difficult for scale up production as large amount of surfactants are needed (Ye *et al.*, 2006). Besides, extensively agglomerated magnetic nanoparticles are often obtained (Lee *et al.*, 2005). The magnetic nanoparticles generated are poorly crystalline due to low reaction temperature and the yield is low because of large amount of organic solvent is used to produce a little magnetic nanoparticles (Lee *et al.*, 2005).

Thermal decomposition is a process where metal precursor decomposes at high temperature to give magnetic nanoparticles. This method gives good size control, narrow size distribution, good crystallinity, and the dispersible magnetic nanoparticles. There are other methods such as sol-gel, reverse micelle, hydrothermal and etc. However, these methods produced magnetic nanoparticles sizes vary from 7 nm to 40 nm, give rise to particles agglomeration and poor particle size distribution (Baruwati & Manorama, 2008).

One of the major fields nanoparticles involved in is supercapacitors as the subject of energy is getting prominent with the utilization of limited fuel energy. Pang *et al.* (2010) have stressed on the importance of electrochemical capacitors or supercapacitors as the replacement of conventional capacitors and battery to provide high power capability and high energy density to modern devices. Cyclic voltammetry (CV) is one of the electrochemical properties used to acquire the information about redox potential of the electroactive species qualitatively. Its working potential is inclined linearly versus time like linear sweep potential with one exception. When the working potential reaches a set of potential, the working electrode's potential ramp is inverted. This can be done by countless time in an experiment and it is plotted with current of the working electrode versus the applied voltage (Bard & Faulkner, 2001). Li (2010) has stated that the morphology, structure, size, surface area, crystallinity and other parameters of nanoparticles affect the electrochemical behaviour of a material.

Magnetic nanoparticles should be smaller than 20 nm in size and give good uniformity and crystallinity for various applications (Ye *et al.*, 2006). On the contrary, most of the current synthetic methods for magnetic nanoparticles do not afford precise control of the particle size and their uniformity. Precise control of size distribution of magnetite nanoparticles synthesis was achieved by using iron pentacarbonyl $\text{Fe}(\text{CO})_5$ as a precursor, but $\text{Fe}(\text{CO})_5$ is very toxic and very expensive. Therefore, a search for alternative synthesis methods that control the size distribution of magnetic nanoparticles with low toxicity and cost are the major interests in many researches.

In this project, two types of magnetic nanoparticles namely, magnetite (Fe_3O_4) and jacobsite (MnFe_2O_4) were synthesized. Fe_3O_4 was synthesized using polyethylene glycol as

the solvent through thermal decomposition method while MnFe_2O_4 was synthesized by co-precipitation method. Some parameters and cyclic voltammetry electrochemical properties were investigated.

1.1 Problem Statement

Synthesis of controllable size distribution of magnetic nanoparticles for application such as capacitors is difficult as there are various synthesis parameters and synthesis methods which affect the formation of the uniform shape, desired size and monodispersed magnetic nanoparticles.

1.2 Objectives

- 1.) To determine the synthesis conditions that would affect the particles size and size distribution of magnetic nanoparticles Fe_3O_4 and MnFe_2O_4 .
- 2.) To optimize the synthesis conditions of magnetic nanoparticles.
- 3.) To obtain magnetic nanoparticles with controllable size.
- 4.) To examine the electrochemical properties of magnetic nanoparticles.

2.0 Literature Review

2.1 Magnetite Nanoparticles

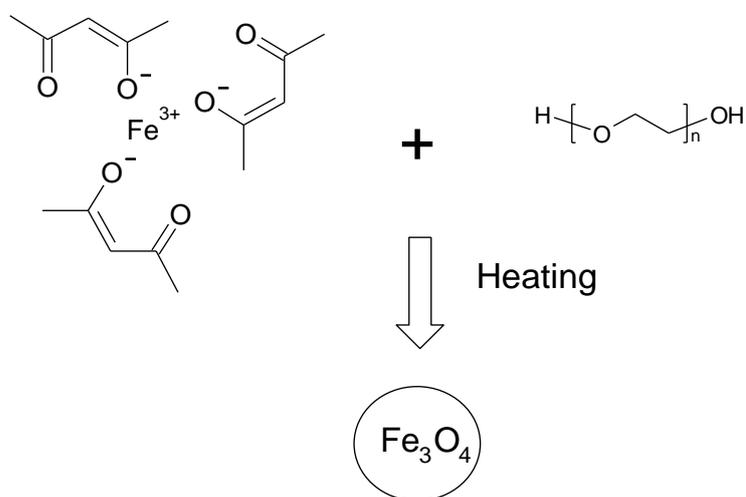
2.1.1 Synthesis Method and Mechanism

Sun and Zeng (2002) reported thermal decomposition method using metal acetylacetonate precursor in temperature 200 °C and 300 °C produced ranging from at least 4 nm monodispersed black-brown solution magnetic nanoparticles to large nanoparticles by decomposition of metal precursor and seed-mediated growth process which increased 2 nm diameter of nanoparticles. Although there was a great discussion about the feasibility of the magnetic nanoparticles obtained in organic solvent on biomedical applications (Li *et al.*, 2005), Sun *et al.* (2004) found that monodispersed iron oxide nanoparticles in organic solvent can be transferred to aqueous solvent which are suitable for biomedical applications.

The mechanisms of particles formation for thermal decomposition method have been discussed over the years. Basically, there are two mechanisms involved in obtaining monodispersed nanoparticles, which are nucleation and growth. Metal ions are created slowly by decomposition of the metal precursor or dissolution of the intermediate. Homogeneous nucleation occurs when the concentration of ions created overcome the supersaturation limit. This nucleation reduces the ion concentration thus forbidding secondary nucleation. In order to achieve a single kind of iron oxide (magnetite), Fe^{2+} and Fe^{3+} have to be prepared in this proportion $\text{FeO}:\text{Fe}_2\text{O}_3$, if excess Fe^{2+} or Fe^{3+} concentration exist in the solution than the proportion, oxidation or reduction process will occur. Roca *et al.* (2006) have stated that alcohol or polyol have the capabilities to induce reduction of Fe

(III) to Fe (II). The nucleation rate can be increased by increasing the heating rate which gives highly uniform particles as product (Roca *et al.*, 2006).

In the second mechanism, growth of the magnetic nanoparticles size is determined by the formation of surfactant-metal complexes. A diffusion mechanism which is known as Ostwald ripening decreases the growth rate of the larger particles and accelerates the smaller particles giving monodispersed nanoparticles. Nucleation of stable particles is slower than their growth, thus these two processes are separated and the reaction rate is determined by nucleation process. Seed-mediated reaction increases 2 nm or more particle diameter by additional growth of previously synthesized monodispersed nanoparticles (Roca *et al.*, 2006).



Scheme 1: Chemical Reaction of Magnetite Nanoparticles Synthesis through Thermal Decomposition Method

$\text{Fe}(\text{acac})_3$ and PEG were used to form magnetite nanoparticles in present study as shown in Scheme 1 and these materials are discussed in the following section to understand its feasibility.

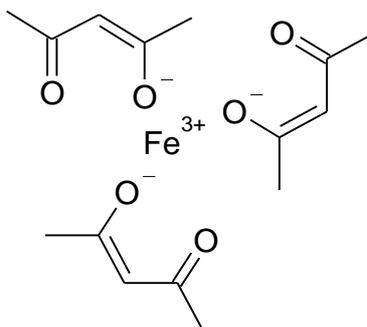


Figure 1: Structure of Iron (III) Acetylacetonate

Iron (III) acetylacetonate ($\text{Fe}(\text{acac})_3$) in Figure 1 is the precursor used in synthesizing magnetite nanoparticles (Sun & Zeng, 2002). $\text{Fe}(\text{acac})_3$ has the chemical formula of $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$ with dark red colour appearance (Long *et al.*, 2008). $\text{Fe}(\text{acac})_3$ is widely used due to its inexpensive characteristics compared to $\text{Fe}(\text{acac})_2$ or Fe (II) acetate and it produces the same result as the later precursors (Sun *et al.*, 2004). $\text{Fe}(\text{acac})_3$ has lower moisture sensitivity, less favour hydrolysis compared to metal alkoxides and halides (Willis *et al.*, 2007). Other than that, this metal acetylacetonate is relatively environmental friendly, can be used to give metal oxide nanoparticles in a simple and direct route by heating a polar and oxygen-containing solvent (Willis *et al.*, 2007). Spivey (2005) has stated that IR spectrum analysis showed that acac from metal acetylacetonate was removed one by one at different temperature. Roca and co-workers (2006) have shown that a higher

concentration of $\text{Fe}(\text{acac})_3$ will also result in a smaller nanoparticles due to a larger supersaturation during the nucleation process.

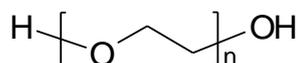


Figure 2: Structure of Polyethylene glycol (PEG)

Polyethylene glycol (PEG) in Figure 2 is a protein-resistant polymer that is non-toxic, non-immunogenic and non-antigenic. It is suitable to be used in bio-application and is environmental friendly (Li *et al.*, 2005). Besides, PEG has been identified as a green solvent having promising properties in medicinal chemistry (Smith *et al.*, 2005). PEG has high boiling point, high polarity and high coordinating capacity with the particle surfaces (Theppaleak *et al.*, 2009). PEG has been used as a solvent, stabilizer and reducing agent for the preparation of nano-silver colloids (Su *et al.*, 2010). Luo *et al.* (2005) have found out that both ethylene glycol and PEG are suitable reducing agents which had reduced Ag^+ ion to silver nanoparticles. Nanoparticles with PEG were successfully experimented in DNA delivery *in vitro* (Gengler *et al.*, 2007). PEG was modified with different terminals to replace hydroxyl group to become a better stabilizer (Theppaleak *et al.*, 2009).

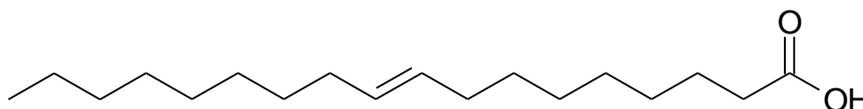


Figure 3: Structure of Oleic Acid

Oleic acid is used as surfactant as shown in Figure 3 in magnetic nanoparticles synthesis.

A surfactant is required to withstand high temperature condition where it is able to perform in temperature at least 200 °C and provides a desired surface chemistry with functions. Many surfactants have low volatility and create covalent or ionic bonding with nanoparticles surface, but only a few, such as oleic acid can deliver narrow size distribution and uniform nanoparticles (Willis *et al.*, 2007).

Oleic acid is often involved in synthesis of magnetic nanoparticles with metal precursor because oleic acid is known to stabilize dispersion in formation of nanoparticles in nonpolar solvent due to covalent bonding between the carboxylic acid group and the surface of nanoparticles. The oleic acid aliphatic carbon chain extends out to the nonpolar solvent to prevent aggregation of the nanoparticles by a steric or entropic mechanism (Roca *et al.*, 2006; Wilson *et al.*, 2002). All the oleic acid molecules are covalently bonded to the surface of magnetic nanoparticles, thus there is no free oleic acid in the solution when synthesizing magnetic nanoparticles (Roca *et al.*, 2006). The carboxylic acid functional groups present in the magnetite nanoparticles synthesis inhibit formation of cubic inverse spinel structure that is usually formed in magnetite (Wilson *et al.*, 2002). The surfactants have the capabilities to influence nucleation and growth process of nanoparticles in a reaction solution depending on the way the surfactant adhere to the surface of the nanoparticles (Roca *et al.*, 2006). Oleic acid provides a dense monolayer on the surface of nanoparticles which helps control the particles growth and protects the body from toxicity (Willis *et al.*, 2007; Wilson *et al.*, 2002). Besides, Oleic acid surfactant not only shows dynamic salvation but also prevents particles aggregation. Furthermore, Oleic

acid coating on surface of nanoparticles reduces surface oxidation, particles interaction and surface anisotropy (Roca *et al.*, 2006). Oleic acid provides higher solubility in nonpolar organic solvent than other surfactants to give solubility in more polar and aqueous solvents and it has carbonyl groups which are known to bond strongly with the metal oxide surface. Oleic acid has the potential to modify the nanoparticles surface for applications purposes in future (Willis *et al.*, 2007).

One of the parameters affecting the size of nanoparticles is the heating temperature. The temperature to synthesize monodispersed magnetic nanoparticles should be high (Sun *et al.*, 2004). Sun *et al.* (2004) have suggested that the nucleation and growth processes are not fast reactions; hence the temperature is needed to increase to a certain level and remain it for sometimes before raising it up to a higher temperature which holds up that different temperature is required for the removal of acac. Secondly, particles aggregation resulting in a larger group of magnetic nanoparticles will be avoided by applying temperature condition from not more than 600 °C (Sun *et al.*, 2004; Willis *et al.*, 2007; Wilson *et al.*, 2002). Other than that, inert atmosphere by providing nitrogen gas (N₂) throughout the reaction should be applied to prevent oxidation from Fe₃O₄ to γ-Fe₂O₃ dark brown materials further to α-Fe₂O₃ at high temperature (Dixit & Jeevanandam, 2009; Sun *et al.*, 2004; Wilson *et al.*, 2002).

Furthermore, studies have introduced that longer reaction time will generate larger nanoparticles which can be attributed to particles growth by Ostwald ripening (Baruwati & Manorama, 2008). After 24 hours, the spherical nanoparticles will lose its identity and form cubic particles (Li *et al.*, 2005). The reaction time should not be more than 2 hours to prevent agglomeration. (Baruwati & Manorama, 2008).

Moreover, as mentioned, seed-mediated growth is a process where the synthesized nanoparticles are sent into growth by same precursor. It adds a layer on the synthesized nanoparticles and increases the size of the nanoparticles. Park *et al.* (2005) have initiated a highly reproducible method similar to seed-mediated growth which highly size distribution of nanoparticles was obtained without size-selection process. They have also successfully controlled the size of nanoparticles with the deviation of 1 nm. The synthesis involves different concentration and variety sizes of seeds (Park *et al.*, 2005).