SYNTHESIS AND CHARACTERIZATION OF Al_2O_3 ADDED Fe_3O_4 NANOPARTICLES VIA SOL GEL TECHNIQUE

This report submitted in accordance with the requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Hons.)

by

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Hons.). The members of the supervisory committee are as follow:

……………………………………

Dr. Mohd Shahadan Bin Mohd Suan – Signature & Stamp

ABSTRAK

Nanozarah magnetik (Fe_3O_4) yang ditambah dengan nanozarah aluminium oksida (Al_2O_3) telah disintesis dengan menggunakan kaedah sol-gel yang mudah dan tidak mahal. Kaedah ini telah menggunakan tenaga dan masa yang kurang daripada kaedah sintesis konvensional lain untuk menghasilkan nanozarah dengan kemurnian dan kawasan permukaan yang lebih tinggi. Oleh kerana kaedah sol-gel yang sangat bersih, pori-pori mikroskopik dan makroskopik dapat dihapuskan. Kesan komposisi nanozarah Al_2O_3 yang berbeza daripada 0,2,4,6,8,10 wt.% pada sifat nanozarah Fe_3O_4 telah diselidiki dan dinilai. Oleh itu, nanozarah yang disintesis telah dicirikan dengan X-ray difraksi (XRD), pengimbasan mikroskop elektron (SEM) dan ujian magnetik. Struktur nanozarah yang disintesis yang diperoleh dengan kaedah sol-gel telah dikaji menggunakan teknik difraksi sinar-X (XRD). Saiz zarah dan morfologi nanozarah yang disintesis telah diselidik dengan pengimbasan mikroskop elektron (SEM). Kemudiannya, sifat magnetik nanozarah yang disintesis telah diselidik dengan magnetometer kecerunan bergantian (AGM). Kerja-kerja ini menunjukkan bahawa reaksi sol-gel adalah kaedah yang berkesan untuk memperkenalkan Al_2O_3 sebagai nanozarah untuk diedarkan secara homogen di nanozarah Fe_3O_4 dan seterusnya mengurangkan sifat magnet Fe_3O_4.

ABSTRACT

The magnetite (Fe_3O_4) nanoparticles added with alumina (Al_2O_3) nanoparticles were synthesized by using a simple, non-expensive sol-gel method. This method consumed less energy and time than other conventional synthesis methods for processing of higher purity and higher surface area nanoparticles. Due to the very clean sol-gel method, microscopic and macroscopic pores could be eliminated. The effect of the difference compositions of Al_2O_3 nanoparticles which were 0,2,4,6,8,10 wt.% on the properties of Fe_3O_4 nanoparticles had been investigated and evaluated. Thus, the synthesized nanoparticles were characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and magnetic test. The structure of the synthesized nanoparticles obtained by sol-gel method were studied using an X-ray diffraction (XRD) technique. The particle size and morphology of synthesized nanoparticles were investigated by scanning electron microscopy (SEM). Subsequently, the magnetic properties of the synthesized nanoparticles were investigated by alternating gradient magnetometer (AGM). This work indicated that the sol-gel reaction is an effective method for introducing Al_2O_3 as nanoparticles to be homogeneously distributed in Fe_3O_4 nanoparticles hence reducing the magnetic properties of Fe_3O_4.

DEDICATION

This report is dedicated
to my beloved parents,
who educated me and enable me to reach this level
to my honoured supervisor,
Dr. Mohd Shahadan Bin Mohd Suan
for his advices, support and patience during completion of this project
and to all staffs & technicians,
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LIST OF ABBREVIATIONS

AGM	-	Alternating Gradient Magnetometer
$Al (NO_3)_3$	-	Aluminium Nitrate
Al_2O_3	-	Alumina / corundum
$Al_2O_3•3H_2O$	-	Gibbsite
$Al_2O_3•H_2O$	-	Diaspore
CH_3CHCH_2O	-	Propylene Oxide
EtOH	-	Ethanol
FCC	-	Face-Centred-Cubic
$Fe (NO_3)_3. 9H_2O$	-	Iron Nitrate Nonahydrate
Fe_3O_4	-	Magnetite
FYP	-	Final Year Project
h	-	Hour(s)
min	-	Minute(s)
MRI	-	Magnetic Resonance Imaging
SEM	-	Scanning Electron Microscopy
SPMR	-	Superparamagnetic Relaxometry
XRD	-	X-ray diffraction
α-Fe_2O_3	-	Hematite
γ-Fe_2O_3	-	Maghemite

LIST OF SYMBOLS

wt. %	-	Weight Percentage
%	-	Percentage
mm	-	Millimetre
nm	-	Nanometer
µm	-	Micrometer
GPa	-	Giga Pascal
MPa	-	Mega Pascal
° C	-	Degree Celsius
°	-	Degree
M	-	Molar
kV	-	Kilovolt
θ	-	Theta
N	-	Newton
ml	-	Millilitre
K	-	Kelvin
psi	-	Pounds per Square Inch

CHAPTER 1

INTRODUCTION

The research background, problem statement, objectives, scope and research significance of the project were introduced in this chapter. The background of the research, the materials and technique used to synthesize the materials were also described in this chapter.

1.1 Research Background

Scientific interest on nanomaterials has evolved due to its long-term disordered structure, high surface area, high boundary energy and porosity. These properties result in interesting structural, chemical, magnetic properties and so on that make nanomaterials attractive in countless applications in catalysis, materials science and others (Dura˜es. L *et al*, 2005). In recent years, studies have been conducted to change the properties of certain materials using nanoscale metal powders in their applications (U. Teipel, 2005 and G. Skandan *et al*., 1998). A research on the supply of oxide nanoparticles was reported by K. P. Jayadevan et al. Other authors have also studied and reported the synthesis of oxide nanoparticles (G. Skandan *et al*, 1999; G. F. Gaertner *et al*, 1994 and F. Ashrafi *et al*, 2012). The synthesis of Fe_3O_4 with Al_2O_3 nanoparticles by sol-gel method is the purpose of this study.

Alumina (Al_2O_3) is an important material widely used in the ceramics and electronics industries, composites and metallurgy. Generally, alumina has many interesting properties compared to other electrically insulating materials such as plastic, paper and glass, such as high insulation, high hardness, high stability and transparency. It is widely used in flame retardants, catalysts, insulators, surface protective coatings and composites. Therefore, the production of alumina nano-powder is very important. The most common methods are chemical vapor deposition, milling, combustion methods and hydrothermal. By milling, impurities easily contaminate the resulting powder. All these methods have disadvantages of impurity contamination, high temperature requirements, time for washing and aging or gelation, and the use of expensive materials.

Furthermore, magnetite (Fe_3O_4) nanoparticles have been extensively studied because of the novel applications of structural and functional elements. Recently, research regarding Fe_3O_4 has been received attention. Due to their potential uses such as not only in medical applications, but also in radiofrequency hyperthermia, pigment, cancer treatment, medical diagnostics, and magnetic resonance imaging (MRI) (Sun, J. *et al*, 2006; Pylypchuk, I. V. *et al*, 2016). However, the potential utilizations of the nanoscale particles are rigorously determined by their fundamental magnetic characteristics, for instances, hard magnets used for data storage as well as soft magnetic materials applied for magnetic switches.

There are various chemical-based methods for synthesizing nanoscale magnetite (Fe_3O_4) particles, such as solution combustion, coprecipitation or precipitation, hydrolysis and thermolysis of precursors, emulsion technology and sol-gel. The sol-gel process is advantageous over other techniques because it produces the large number of metal oxide nanoparticles with high purity and higher surface area. Moreover, other advantages can be considered for this synthesis technique, such as a general process with good uniformity and low processing temperatures.

The tiny particles in material chemistry can be obtained by sol-gel method. This method is mainly applied to synthesize metal oxides. The initial step of the process is to transform the feedstock to a colloidal solution. Then, the process is continued by forming a gel from the sol. There are polymers or distribute particles contain in the gel. However, chlorides or metal alkoxides are usually selected as precursors. Hydrolysation is undergone by these precursors and poly-condensed to form a colloid (Kumar *et al*., 2015). The sol-gel method is used to form a synthetic nano-powder. Sol-gel technology synthesized materials are commonly applied in dispersion processes, reactive materials, electronics, transducer and power supplies.

In continuing research on nanoparticles and new organic compounds, herein, a simple and efficient method for synthesizing Al_2O_3 and Fe_3O_4 nanoparticles is described. The effect of the difference compositions of Al_2O_3 nanoparticles on the properties of Fe_3O_4 nanoparticles will be investigated. The structure of the synthesized nanoparticles obtained by sol gel method will be investigated using an X-ray diffraction (XRD) technology. The magnitude of particle and morphology of synthesized nanoparticles will be studied using scanning electron microscopy (SEM), while magnetic characteristics of the synthesized nanoscale particles will be investigated by alternating gradient magnetometer (AGM).

1.2 Problem Statement

Theoretically, magnetite (Fe_3O_4) existed with unique magnetic properties which applicable for many applications. However, the problem faced by current Fe_3O_4 which has the lower purity and the unavailability of Fe_3O_4 particles in nano-meter size which mostly synthesized from the conventional methods had reduced its theoretical efficiencies in electronic and medical applications. Hence, the Fe_3O_4 is needed to be reinforced with a material which can sustain the high purity of Fe_3O_4. Thus, alumina (Al_2O_3) nanoparticles which usually referred to as corundum is chosen to be added into Fe_3O_4. Nano-meter Al_2O_3 particles has been widely recognized as an efficient reinforce material because of its inert property at high temperature. Furthermore, Al_2O_3 has successfully been added into various materials and systems by using the sol-gel method. Hence it is assumed that this method can also be able to produce uniform or well distribution and high purity of Al_2O_3 nanoparticles throughout Fe_3O_4. Therefore, Fe_3O_4 added with Al_2O_3 nanoparticles will be simultaneously synthesized by using a single sol-gel reaction. The combination of Al_2O_3 added Fe_3O_4 nanoparticles through this method could contribute to better electronic and magnetic properties of Fe_3O_4 for electronic industries.

1.3 Research Objectives

The objectives of this research are summarized below:

i. To synthesize Fe_3O_4 added with Al_2O_3 nanoparticles via sol-gel technique.

ii. To characterize the structure and magnetic properties of Al_2O_3 added Fe_3O_4 nanoparticles.

iii. To investigate the effect of Al_2O_3 additions towards magnetic properties of Fe_3O_4 nanoparticles.

1.4 Scope of Research

This study work scope is synthesizing Fe_3O_4 added with Al_2O_3 nanoparticles by using sol-gel reaction. However, the 0,2,4,6,8,10wt.% ratio parameters of Al_2O_3 compositions have been added into Fe_3O_4 nanoparticles respectively during synthesizing. Thus, X-ray diffraction (XRD), scanning electron microscopy (SEM) and magnetic test were applied to characterize the synthesized nanoparticles. The synthesized nanoparticles structure obtained by sol gel method were investigated using an XRD technology. The magnitude of particle and morphology of synthesized nanoparticles were studied via SEM. However, magnetic properties of synthesized nanoparticles have been investigated by magnetic test.

1.5 Significant of Research

Upon the completion of this research, these issues contribute to propose a novel method to synthesize nanoscale particles. The sol gel reaction allows better distribution of Al_2O_3 nanoparticles with different compositions into Fe_3O_4 nanoparticles. The specific significance of this study is that the addition of the Al_2O_3 nanoparticles will affect the magnetic properties of Fe_3O_4 nanoparticles. This enhancement provides an opportunity to Fe_3O_4 nanoparticles to be applied in practical applications.

CHAPTER 2

LITERATURE REVIEW

The titles in the literature review are all included in the scope of the research in this chapter. It covers the materials will be used and the technique used to synthesis the materials.

2.1 Magnetite

In the 8th century, magnets were used in the navigation devices technology. This technology had been spread back to China. Since 200 BC, natural magnets, called loadstones are applied as fortune-telling devices (Mills, 2004). Magnetic nanoparticles have been applied by natural organisms, which known as magnetic bacteria, since old times to align and divert to favourable habitats along the geomagnetic areas (Blakemore, 1982). Chinese sailors and magnetic creatures are chemically made of Fe_3O_4 or magnetite. “Magnetite” is originated from the Magnesia region of Asia Minor, where there are a large amount of magnetite was found (Bellis, 2006).

Natural magnetite is found all over the world. It exists in a large amount of deposits. Magnets are applied to separate them from the beach. In fact, magnetite is naturally occurred, but may also be created through synthesis (Schwertmann & Cornell, 2000). Magnetite was first developed by LKAB Minerals for production of special fillers for plastics. It turns out that the natural magnetite in northern Sweden is very pure (MCuller *et al.*, 2003) and it can even be applied in food contact usages in plastics. However, synthetic magnetite is often advantageous. Especially for scientific research or special purpose, such as immunodiagnostics or protein separation, because of the need for nanoparticles. Nevertheless, synthetic nanoparticles generally tend to be unstable due to their high surface area making them susceptible to oxidation.

Magnetite is the mineral of iron oxide (Fe_3O_4) found in igneous, sedimentary and metamorphic rocks. It possesses the highest iron content about 72.4%. Besides, it is also the most commonly mined iron ore. In fact, Fe_3O_4 consists of both Fe^{2+} and Fe^{3+} ions. As the spinel group member, Fe_3O_4 have their standard formula $A(B)_2O_4$ where A represents Fe +2 and B represents Fe +3. A and B indicate varies metal ions occupying specific locations in the crystal structure. Therefore, the IUPAC name of Fe_3O_4 is called as ferrous-ferric oxide which can be built up from FeO and Fe_2O_3 (Figure 2.1).

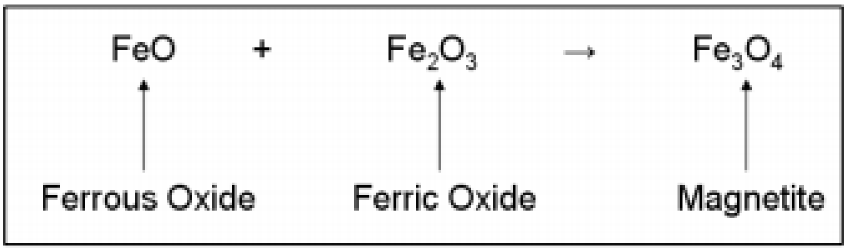

Figure 2.1: Over-magnetized magnetite synthesis reaction (Preserve & Blaney, 2007).

2.1.1 Properties and application of Fe_3O_4 nanoparticles

Fe_3O_4 is a hard, dark, non-transparent and metallic metalloid mineral. Its Mohs hardness is shown in the range of 5 to 6.5. It is easy to identify as it is one of the few minerals that attract ordinary magnets. Magnetite properties indicate that there is a relationship between existing and emergency uses (Table 2.1). Chemical and physical characteristics prove it to be a special material. It usually exists in an isometric crystal state. It is the mineral which performs the highest magnetic properties in nature (R. M. Cornell and U. Schwertmann, 2003).

Table 2.1: The nature of iron oxide (R. M. Cornell and U. Schwertmann, 2003).

Property	Magnetite
Colour	Black
Density	5.2 g cm^{-3}
Mohs hardness	5.5–6
Attraction to a magnet	Yes
Electrical conductivity	Semiconductor
Chemical composition	Fe_3O_4 (an oxide)
Volumetric heat capacity	3.8 kJ L^{-1} K^{-1}

Fe_3O_4 is naturally occurred. It may also be synthesized to obtain the desired nanoscale particles. Due to its unique electrical, thermal and magnetic properties and its extremely high density, it is utilized as a special filler. However, those properties will begin to modify as the diameter of the magnetite particles decreases to the nanometer scale. The Fe_3O_4 nanoparticles are composed of maghemite and magnetite particles ranging in diameter from 1 to 100 nm. Such nanoparticles can be applied for magnetic data storage, biosensing, and drug delivery. For nanoparticles, their surface area is proportional to volume. This allows the nanoparticles to have a relatively high binding ability and excellent dispersibility in solution. The size of between 2 and 20 nm, Fe_3O_4 nanoparticles are capable to exhibit superparamagnetic. For example, since there is no external magnetic field, the Fe_3O_4 nanoparticles will exhibit zero magnetization. However, external magnetic sources able to magnetize them. Due to this special property, magnetic nanoparticles have additional stability in solution.

Due to the Fe_3O_4 nanoparticles remarkable properties and many potential applications of technology, recent progress has been made in the development of nano-Fe_3O_4 particles. There are varies phases of Fe_3O_4. However, the magnetite phase able to display interesting features of superparamagnetic, biocompatibility, mild toxicity and greater surface area. These special features have been thoroughly studied. So far, magnetite Fe_3O_4 nanoparticles have been extensively investigated in various fields, for example magnetic storage, sensors, superparamagnetic relaxometry (SPMR), therapeutics ferrofluids and biomedicine.

In addition, Fe_3O_4 has several commercial applications. It is used as a catalyst in the industrial synthesis of ammonia, by the "Haber process". It has also been applied to prepare in dark pigment, which also called C.I pigment black 11 (C.I. No.77499). Fe_3O_4 nanoparticles has been applied as contrast agents in high-sensitivity biomolecular magnetic resonance imaging (MRI) scanning as well. Furthermore, Fe_3O_4 exhibits good adsorption in powder state which able to remove arsenic (III) and arsenic (V) from water.

Due to its nanoscale nature, bare iron oxide nanoparticles are easily to oxidize as well as are also susceptible to agglomeration in liquid state. Thus, surface modification is required to stabilize the iron oxide particles. These nanoparticles can be applied in various fields. There is a considerable difference between the magnetic structure of the surface layer and the magnetic structure in the nanoparticle core. These may have a significant impact on the magnetic properties of the nanoparticles. The magnitude of the nanoparticles has the effect on the nature of the nanocrystals. Therefore, controlling their size and polydispersity is quite