UNIVERSITI PUTRA MALAYSIA

MORPHOLOGY AND MAGNETIC PROPERTIES OF COBALT AND COBALT-PLATINUM MAGNETIC NANOPARTICLES PREPARED USING REVERSE MICROEMULSION

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By

GHAZALEH BAHMANROKH

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This thesis is focused on the preparation of cobalt and cobalt-platinum type magnetic nanoparticles by the reverse-micelle microemulsion method for the applications in ultra-high density magnetic recording media that could overcome the thermal stability limit of currently materials. Synthesizing nanoparticles (NPs) with a narrow size distribution and high uniformity is one of the prime goals of this research. To achieve that, nanoparticles were synthesized in aqueous cores of cetyltrimethylammonium bromide (CTAB) reverse micelles as a nano-reactor allowing nucleation and growth within a confined space and gaining the advantage of size restriction. A variation was introduced to the molar ratio of water to surfactant (ω) in preparing Co and $CoPt_3$ nanoparticles for four different ω:5, 10, 15 and 20. The as-prepared Co and $CoPt_3$ nanoparticles were annealed further under argon atmosphere at 400°C and 800°C respectively. Moreover since Co nanoparticles are rapidly oxidized upon exposure to air, coating of Co and $CoPt_3$ nanoparticles with a

gold shell was performed in the next step. Physical characteristics of as-prepared and annealed samples were studied as well.

XRD patterns of as-synthesized samples show the evidence that highly crystalline $CoPt_3$ NPs could form during precipitation in reverse-micelle microemulsion. However as-synthesized and annealed Co NPs showed very low crystallinity. Sintering of $CoPt_3$ caused an improvement in the crystallinity and disordered-ordered phase transition at 800°C, which subsequently changed the magnetic properties of $CoPt_3$. Coercivity increased with an increase of the ω ratio or particle size for both Co and $CoPt_3$ NPs. Annealing resulted in a significant increase in the coercivity which showed the highest values of 446.8Oe and 712.2Oe respectively for Co and $CoPt_3$ at room temperature which makes them good candidates for recording media. The TEM and FESEM results showed nanoparticles with spherical shape and narrow size distribution. The average size was in good agreement with the crystal size calculated by the Scherer formula and increased with an increased ω ratio. Hysteresis loops at room temperature for the as-synthesized Co and $CoPt_3$ show superparamgnetic-ferromagnetic behavior above the blocking temperature at 45K.

Core-shell Co-Au, $CoPt_3$-Au NPs were synthesised via a two step reduction process in reverse-micelle microemulsion solution. Gold coating increased the crystallinity of Co NPs but decreased that of $CoPt_3$. TEM results in high magnification show a core-shell structure with shell thickness around 2-3nm. After gold coating of Co NPs the coercivity decreased whereas the saturation magnetization increased due to oxidation protection. A typical high blocking temperature around 50 K was observed for $CoPt_3$-Au nanoparticles via a simple method.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SIFAT MORFOLOGI DAN SIFAT MAGNET KOBALT DAN NANOPARTIKEL MAGNET KOBALT-PLATINUM YANG DISEDIAKAN DENGAN MENGGUNAKAN BERBALIK MICROEMULSION

Oleh

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Tesis ini tertumpu kepada fabrikasi kobalt dan nanopartikel magnet kobalt-platinum dengan menggunakan teknik mikroemulsi berbalik untuk aplikasi media rakaman berketumpatan ultra-tinggi, yang akan mengatasi had kestabilan terma dalam bahan-bahan masa kini. Salah satu matlamat utama penyelidikan ini adalah untuk mensintesis nanopartikel-nanopartikel yang mempunyai taburan saiz yang kecil. Untuk mencapai matlamat tersebut, nanopartikel-nanopartikel telah disintesis di dalam teras akues micelles berbalik *cetyltrimethylammonium bromide* (CTAB) sebagai reactor-nano yang membenarkan nukleasi dan pertumbuhan dalam ruang yang terhad dan mendapat kelebihan daripada sekatan saiz. Kami telah mengubah nisbah molar air terhadap surfaktan (ω) kepada empat ω yang berbeza iaitu ω: 5, 10, 15, dan 20 dalam penyediaan nanopartikel-nanopartikel Co and $CoPt_3$. Nanopartikel-nanopartikel Co dan $CoPt_3$ yang disediakan kemudiannya telah disepuh lindap di dalam suasana argon dengan masing-masingnya pada suhu 400^{o}C dan 800^{o}C. Selain

itu, memandangkan nanopartikel-nanopartikel Co cepat teroksida apabila terdedah kepada udara, maka penyaduran petala emas pada Co dan $CoPt_3$ telah dilakukan pada peringkat seterusnya. Pencirian-pencirian fizikal sampel yang telah disediakan dan yang telah disepuh lindap turut dikaji.

Corak-corak XRD untuk sampel yang disediakan menunjukkan nanopartikel-nanopartikel $CoPt_3$ yang berkristaliniti tinggi boleh dibentuk semasa pemendakan micelle berbalik. Walaubagaimanapun, nanopartikel-nanopartikel Co yang telah disediakan dan yang telah disepuh lindap mempunyai kristaliniti yang sangat rendah. Pensinteran pada suhu 800^{o}C $CoPt_3$ menunjukkan peningkatan dalam kristaliniti dan fasa transisi tidak tertib kepada tertib yang kemudiannya mengubah sifat-sifat magnet $CoPt_3$. Daya paksa meningkat dengan peningkatan nisbah ω bagi kedua-dua nanopartikel-nanopartikel Co dan $CoPt_3$. Sepuh lindap telah meningkatkan daya paksa dan menunjukkan nilai tertinggi pada 446.76 Oe untuk Co dan 712.16 Oe untuk $CoPt_3$ pada suhu bilik yang membuatkan bahan-bahan ini sesuai untuk digunakan sebagai media rakaman. Hasil kajian melalui TEM dan FESEM menunjukkan bentuk sfera, taburan saiz yang kecil, dan saiz purata selari dengan saiz kristal yang dikira melalui formula Scherer dan meningkat dengan peningkatan nisbah ω. Gelung histerisis pada suhu bilik untuk sampel yang disediakan bagi Co dan $CoPt_3$ menunjukkan sifat superparamagnet kepada ferromagnet di atas suhu pemblokan pada 45K.

Teras-petala nanopartikel-nanopartikel Co-Au dan $CoPt_3$-Au telah disediakan dengan proses dua peringkat penurunan dalam larutan micelle berbalik. Penyaduran emas meningkatkan kristaliniti nanopartikel-nanopartikel Co tetapi walaubagaimanapun telah mengurangkan kristaliniti $CoPt_3$. Keputusan-keputusan TEM pada pembesaran tinggi menunjukkan struktur teras-petala dengan ketebalan petala sekitar 2-3nm. Selepas penyaduran emas pada nanopartikel-nanopartikel Co, daya paksa berkurangan tetapi kemagnetan tepu meningkat disebabkan perlindungan oksidasi. Suhu pemblokan yang tinggi sekitar 50 K telah diperhatikan bagi nanopartikel$CoPt_3$-Au melalui teknik yang ringkas.

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I certify that a Thesis Examination Committee has met on 15th February 2012 to conduct the final examination of Ghazaleh Bahmanrokh on her thesis entitled "**Morphology and Magnetic Properties of Cobalt and Cobalt-Platinum Magnetic Nanoparticles Prepared Using Reverse-Micelle Microemulsion**" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Uiversiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master Degree.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

GHAZALEH BAHMANROKH

Date: 15 February 2012

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LIST OF ABBREVIATIONS

Å	angstroms
AFM	Antiferromagnet
AOT	Sodium bis(2-ethylhexyl) sulfosuccinate
Co	Cobalt
$CoPt_3$	Cobalt-platinum
CTAB	Cetyltrimethylammonium bromide
D	Diameter
DDAB	Diodecyldimethylammonium bromide
DL	Double layer
emu/g	Electromagnetic unit per gram
EDX	Energy dispersive x-ray spectroscopy
FC	Field-cooled
fcc	face-centered cubic
fct	face-centered tetragonal
FM	Ferromagnet
hcp	hexagonal closed packed
g	gram
Gb/in^2	Gigabits (10^9 bits) per square inch
H	Magnetic field strength
H_C	Coercivity
H_E	Exchange bias filed
nm	nanometer
NPs	nanoparticles
M_r	Remanent magnetization
M_S	Saturation magnetization

Oe	orsted
V	Volume
χ	Magnetic susceptibility
XRD	X-ray diffraction
ZFC	Zero field-cooled

CHAPTER 1

INTRODUCTION

1.1 Back ground of the study

Through the past several decades, amorphous and more recently nano-crystalline materials have been investigated for application in magnetic devices. An example is the high density magnetic random access memory technology which has grown over the past decades due to its potential to store more data, access that data faster and also to use less power than current memory and technologies. Demands for continues increase in the data storage density bring the challenge to overcome physical limits for currently used magnetic recording media. Benefits were found in the nano-crystalline alloys because of their chemical and structural variations on the nano-scale which are important for developing optimal magnetic devices with high properties.

Magnetic nanoparticles are attracting much attention because they offer the opportunity to study magnetism in between the atomic and bulk limits and because ordered arrays of ferromagnetic properties are of potential interest for applications such as ultra-high-density magnetic recording devices. Recently magnetism recognized as a nanoscle phenomenon (Aharoni, 2000). The atomic exchange interaction that defines ferromagnetism is typically on the length scale of 10nm for most materials (Skomski, 2003).

1.1.1 Magnetic recording media for extremely high density data storage

Magnetic recording media is one of the most important components in any magnetic recording systems. The state of the art and research into hard disk media is approaching nano-scale and sub-nanoscale engineering. Nano-scale means the dimensions smaller than one billionth of a meter. In magnetic media, information is stored in a group of tiny magnets (Yasui *et al.*, 2008). The desire for higher density data storage involves materials with high coercivity. Being able to store data in an ever decreasing amount of space to continue device miniaturization leads one correctly to conclude that the smaller the magnetic bit, the higher the density of data can be stored within a given amount of space. To that end it would seem that magnetic nanoparticles would be an obvious choice for the next generation of magnetic data storage. In a digital recording scheme, if similar poles of two groups of magnets force each other, it is considered as 1, whereas opposite poles force each other, it is considered as 0.

Recently researches achieve small grains with size below 6nm, which will enable a 2.5 inch diameter hard disk to have 500-600 trillion small magnets (Piramanayagam *et al.*, 2007). However when the grain size is reduced down to this scale, a phenomenon called superparamagnetism poses a limit on magnetic properties. This is one of the key challenges in development of recording media.

1.2 Importance of nanomaterials and magnetic nanomaterials

Nanoscale particles research has recently become an important field in the materials science. Nanoscience and nanothechnology deal with the synthesis, characterization, and exploration of nanostructured materials (McHenry *et al.*, 2000). The nanoparticles are ultrafine particles in the size of nanometer order (1nm=10^{-9}). Nanostructure is between atomic and finite bulk systems. The vast interest in nanostructured particles mainly arises from the fact that these structures possess novel physical and magnetic properties that differ from those of bulk materials. This is significant in the case of nanoparticles that have a large surface to volume ratio with a high percentage of surface atoms, resulting in unexpected properties. Individual nanostructures include clusters, quantumdots, nanocrystals, nanowires, and nanotubes. Some nanostructure materials and assemblies are summarized in Table 1.1. Suitable control of the properties of nanomaterials brings new devices and technologies. Nanoscience and nanotechnology have two approaches: one is the bottom-up, that is, the miniaturization of the components, as articulated by Feynman, who stated in the 1959 lecture that "*there is plenty of room at the bottom*" (Feynman, 1959); and the other ones is the approach of the self-assembly of molecular components, where each nano-structured component becomes part of the supra-structure. Compared with the top-down lithographic techniques, bottom-up chemical synthesis and self-assembly approaches offer much more flexibilities in creating nanostructures and especially magnetic nanostructures with controlled size, shape, composition and so many physical properties.

Table 1.1 Nanostructures and their assemblies.

Nanostructure	Size	Materials
Clusters, nanocrystals Quantum dots	Radius, 1-100nm	Insulators, semiconductors, metals, magnetic materials
Other nanoparticles	Radius, 1-100nm	Ceramic oxides
Nanobiomaterials, photosynthetic reaction centre	Radius, 5-10nm	Membrane protein
Nanowires	Diameter, 1-100nm	Metals, semiconductors, oxides, sulphides, nitrides
Nanotubes	Diameter, 1-100nm	Carbon, layered chalcogenides, BN, GaN
Nanobiorods	Diameter, 5nm	DNA
Two-dimensional arrays of nanoparticles	Area, several nm^2-μm^2	Metals, semiconductors, magnetic materials
Surfaces and thin films	Thickness, 1-100nm	Insulators, semiconductors, metals, DNA
Three-dimensional superlattices of nanoparticles	Several nm in three dimensions	Metals, semiconductors, magnetic materials

Cobalt and cobalt-platinum alloys are employed primarily for magnetic purposes and numerous applications such as patterned recording media, memory shape devices, magnetoresistive nanosensors and magnetic nanodevices (MEMS). The novelty of these alloys means that it can be advantageously employed in flow meters for handling corrosive liquids and for the magnetic jigs used in electropolishing baths.

1.3 Classification of magnetic materials

The term magnet is typically taken for only certain classes of materials that produce their persistent magnetic field even in the absence of an applied magnetic field. The response of materials to applied magnetic field is a phenomenon known as magnetism. The overall magnetic behavior of a material can vary widely, depending on the structure of the materials, and particularly on its electron configuration. Several forms of magnetic behavior have been observed in different materials, including: ferromagnetic, paramagnetic, diamagnetic, antiferromagnetic, ferrimagnetic and superparamagnetic materials.

1.4 Synthesis and characterization of nanoparticles

In the past few years, nanoparticle production by a size-controlled or shape-controlled procedure (Lim *et al*., 2006) has been a new and interesting research focus. Increasing the storage density requires more strict control over the morphology of the magnetic material and strong reduction of its dimensions, down to the sizes of the single domain. Generally, the shape, size and size distribution of nanoparticles can be controlled by employing different synthetic methods. During the last decades, many methods have been employed to prepare magnetic cobalt and cobalt-platinum nanoparticles. The most important key is to avoid agglomeration of nanoparticles during the synthesis because the coalescence of the nanoparticles may loss their characteristic properties. Usually special organic compound such as surfactants, polymers and stabilizing ligands are used to passivate the particles to prevent them from aggregation. Nanocrystalline materials were manufactured passed on physical and chemical processes. It is often difficult to say which technique is better for synthesis nanoparticles but chemical methods are used frequently for their convenience and rapidity. The basic principle of chemical synthesis of nano-structured materials is to initiate chemical reactions and control the nucleation and growth of the reaction products. Among various chemical syntheses, microemulsion based method is creating stable colloids with good size dispersion and are typically carried out at low temperature. Also reverse-micelle microemulsion method is introduced to obtain the un-agglomerated, uniform and size controllable nanoparticles. They are easy to develop to an industrial level, but they suffer from the disadvantage that the particles are sometimes less crystalline and more polydispersed because of low nucleation rate at low reaction temperature. Restricted reverse-micelle microemulsion (water-in-oil) environment was allowed synthesis of materials in tiny droplets of water encapsulated into oil as the main phase in reverse-micelle conditions. Water pools of these reverse-micelles act as nano-reactors for performing simple reaction of synthesis, and the size of the nano-crystals is determined by size of these pools. The size of the water pools are controlled by the molar ratio of water to surfactant in the system. We apply the reverse-micelle microemulsion method for the synthesis of magnetic cobalt and alloy cobalt-platinum nanoparticles. XRD, EDX, TEM, FESEM, VSM and in other studies SQUID was used for analysis and investigate characterization of magnetic nanomaterials.

1.5 Significant of the study

Metal and alloy nanoparticles exhibit very interesting electronic, magnetic, optical, and chemical properties. Their unique features depend on their size, shape, surface composition, and surface atomic arrangement. The advance in storage capacity of magnetic recording media is due to combination of increasing coercivity and magnetization of particles, lowering system noise and improving head design. Providing high coercivity to prevent demagnetization requires that the grains of materials to be as small and uniform in size and shape.

Microemulsions have been the subject of extensive research over the last two decades because of their scientific and technological importance. Microemulsions can have characteristic properties such as ultra-low interfacial tension, large interfacial area and capacity to solubilise both aqueous and oil-soluble compounds.

1.6 Problem statements

One of the issues afflicting memory is the fact that it is difficult to store information for as long as 10 years (Schiller, 2009). In order to overcome this problem, scientists and engineers have been looking for a way to increase the density of magnetic grains used for storage, as well as use materials with high magnetic anisotropy energy (MAE). The future of extremely high density recording media beyond 1 $Tbits/in^2$ require further reduction of magnetic grain size and thus materials with ultra-high magnetocrystalline anisotropy are needed to overcome the superparamagnetic limit (Wang *et al.*, 2006). The other problem is retaining the magnetization of the medium despite thermal fluctuations that is happened in superparamagnetic edge.

1.7 Objectives of the study

In this thesis, we are aiming at developing tailored magnetic materials at the nanoscale by chemical method for the application in ultra-high density recording media. Cobalt-platinum alloys are high coercivity materials used as permanent magnets. The objectives of this work are:

1. To prepare mono-dispersed, uniform and sized-controllable Co and $CoPt_3$ nanoparticles using reverse-micelle microemulsion method.

2. To study in detail the influence of molar ratio of water to surfactant on the size and character of Co, $CoPt_3$ and Co-Au, $CoPt_3$-Au core-shell nanoparticles, employing the experimental ω ratio (ω=[water]/[surfactant]: 5,10,15 and 20).
3. To investigate the morphology, crystal structure and magnetic properties of Co, $CoPt_3$, Co-Au and $CoPt_3$-Au nanoparticles for four different ω ratios before and after annealing.
4. To attempt measuring blocking temperature with a new simple method.

1.8 Outline of the thesis

Given the importance of detailed understanding of the structural, morphology and magnetic properties of nanostructures materials for the applications described above, this study will focus on the general introduction about the research background, scope, problem statement and objectives of the study. Chapter 2 concerns with the background and synthesis of magnetic nanoparticles and core-shell nanoparticles. Preparation of nanomaterials with microemulsion method and related literatures in view of preparation techniques together with characterization of magnetic nanoparticles were discussed as well. Chapter 3 focused on theoretical background which includes brief introduction to magnetism and the chemistry of metals and alloys. Chapter 4 highlights the methodology of the study; including materials, sample preparation and characterization methods applied. Chapter 5 deals with the results and discussion on characterization of as-prepared and annealed nanoparticles before and after gold coating. Chapter 6 summarizes the results and gives some suggestions for future work.

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