

CHAPTER 1

INTRODUCTION

1.1 Magnetic nanoparticles

The development of new materials always leads to advances in technology and creates innovative solutions to old problems. Nanomaterials and nanotechnologies are the current key fields with the great challenges and possibilities. Nanomaterials also called nanostructure materials which are single phase or multiphase materials with size less than 100 nm at least in one of the dimension [1]. For example, ultrathin coatings have one nanoscale dimension, nanotubes and nanowires have nanoscale in two dimensions, whereas nanoparticles (NPs) have nanoscale in three dimensions.

Nanoparticles are ultrafine with sized between 1 and 100 nanometers. They may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures, therefore offer exciting opportunities for technologies at the interfaces between chemistry, physics and biology. Their appeal stems not only from their use as single particles, but also from their potential to form self-organized films and solids. Therefore nanoparticles are useful for a wide range of applications [2-6].

Magnetic Nanoparticles (MNPs) are a kind of nanoparticles with the unique feature of their response to magnetic force [7]. The interest in MNPs arises from the fact that the superparamagnetic or ferromagnetic properties of these particles allow the easy

fact that the superparamagnetic or ferromagnetic properties of these particles allow the easy isolation of products in solution by attracting them with the aid of an external magnetic field. Thus, suspended magnetic particles can be removed from large samples volume using a magnet and their isolation and purification are easier and faster than with other methods. In addition, the small size particle allows separation at a specific location that is relevant to a cellular biochemical process [4, 8]. Hence, superparamagnetic nanoparticles have a great potential for many applications in biomedical and catalysis areas [2, 9, 10].

In the last decade, increased investigations with several types of metal such as Nickel (Ni), Cobalt (Co), Iron (Fe), Magnetite (Fe_3O_4) and Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) have been carried out to synthesize magnetic particles capable of forming superparamagnetic dispersion in a carrier fluid of length scales from 1 to 100 nm. Among them, iron oxide particles such as Fe_3O_4 or its oxidized form $\gamma\text{-Fe}_2\text{O}_3$ are the best known material as magnetic carrier with excellent magnetic saturation due to the strong ferromagnetic behavior, less sensitivity to oxidation and relatively low toxicity compared to many other materials (e.g., nickel and cobalt which are toxic, susceptible to oxidation and hence are of little interest). Even though iron oxides have low initial magnetization, they are useful in oxygen rich environments because of their lower oxidation capacity, chemically stable, non cancerogen and biodegradable. However, the saturation magnetization of $\gamma\text{-Fe}_2\text{O}_3$ is lower than that of Fe_3O_4 . Because of these facts, Fe_3O_4 is also most commonly used for particle synthesis and employed in biomedical applications since their biocompatibility has already been proven [11].

1.2 Surface modification of MNPs

Uncoated magnetic nanoparticles have some limitations such as they have a large surface to volume ratio which possesses high surface energies leading to the aggregation to minimize the surface energies. The iron oxide nanoparticles have high chemical activity and get easily oxidized when exposed to air that result in loss of magnetic properties and dispersibility. Moreover, they undergo biodegradation with subsequent changes in magnetic properties. To overcome such limitations, the development of a proper surface coating to protect and keep the stability of MNPs is required.

The surface modification of MNPs by functional molecules/particles/polymers has many advantages. The growth process of the embryonic particles can be controlled and stabilized. It can provide functional groups at the MNPs surface for further derivatization or enhancement of the nanoparticle solubility in various solvents to extend their application capabilities. The mechanical and chemical performance of the nanoparticle can also be improved [12].

In general, surface modification can be accomplished by physical/chemical adsorption or surface coating of specific ligands. These strategies comprise grafting or coating with organic molecules, including small organic molecules, surfactants, polymers, biomolecules and inorganic layer. These general considerations are summarized in Fig. 1.1.

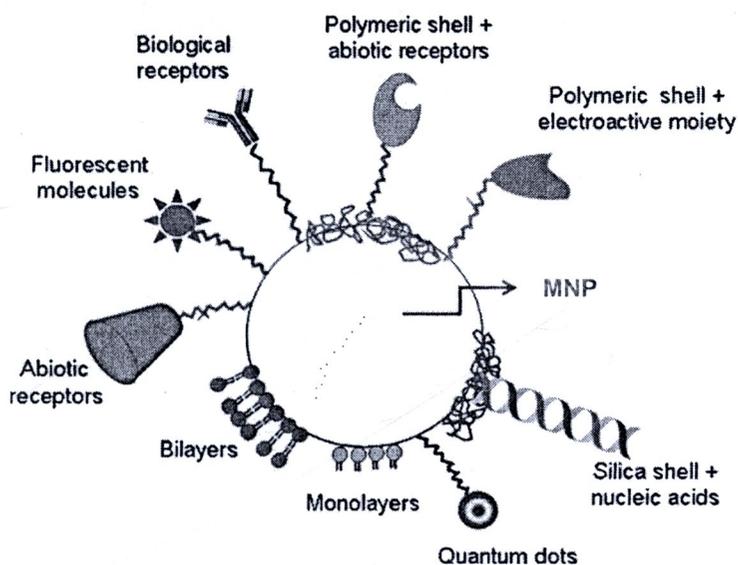


Figure 1.1 The possible approaches for surface modification of MNPs [12]

Table 1.1 provides a list of materials that could be used to modify the MNPs along with their applications. MNPs modified with various non-polymeric organic agents possess substantially high stability to MNPs. The ethylenediaminetetraacetic acid (EDTA) [13], Nitritriacetic acid [14], and dimercaptosuccinic acid (DMSA) [15] are the organic agents that have been used to modify MNPs. Various surfactants such as oleic acid [16, 17], stearic acid [18], decanoic acid [19], citric acid [20] and dodecyl amine [21] are usually used to enhance dispersibility in an aqueous medium.

Table 1.1 Different modifying materials which can be used for MNPs modification and their applications.

Modifying materials	Applications	References
PAA	Isolation of protein	[2, 22]
Phospholipids	Purification of rhamnolipid	[19]
PMAA	Separation of Tetracycline antibiotic	[23]
	Extraction of fluoroquinolones	[24]
Chitosan	Protein isolation	[25]
	Removal of Cu(II)	[26]
DMSA	Cell culture	[15]
Poly(vinyl pyridine)	Extraction of bisphenol A	[27]
APTES	Immobilization of protein	[28, 29]
Trimethoxysilyl propyl-methacrylate (TMSPM)	Enzyme mimic based on molecularly imprinted polymer	[30]
Dendimer	Gene delivery	[31]
Gelatin	Isolation of DNA	[32]
	Hyperthermic treatment of bone cancer cell	[5]
TEOS	Isolation of protein	[10]
	Biocatalyst carrier	[8]
	Removal of endocrine disrupting chemicals	[33]
Oligopeptide functionalized ionic liquid	Supported catalyst	[34]
Gold	Sensor	[3]

Polymeric materials including poly(methyl methacrylate) (PMAA) [35], polyacrylic acid (PAA) [22], polyvinyl alcohol (PVA) [9], gelatin [5], and chitosan [36, 37] have also been used for MNPs coating. Silica is the common inorganic compound for preparing the functionalized MNPs (Fig. 1.2). 3-Aminopropyl triethoxysilane (APTES) or *p*-aminophenyl trimethoxy silane (APTS) and mercaptopropyltriethoxysilane (MPTES) agents are also mostly employed for providing the amino and sulphhydryl groups, respectively [28, 29, 31].

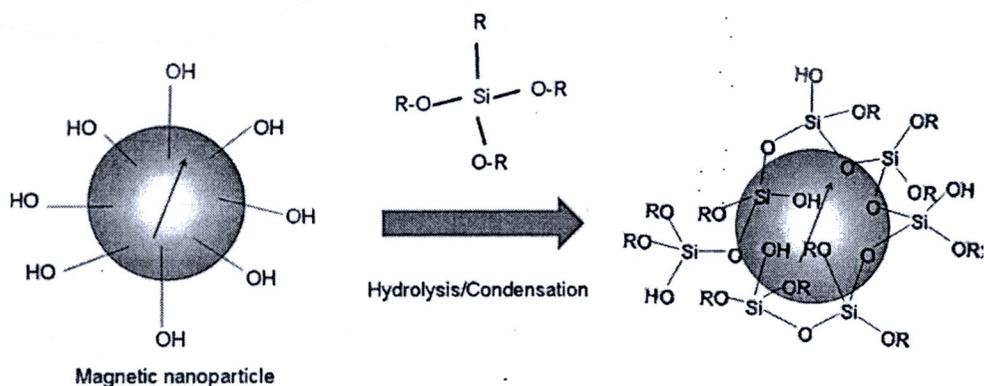


Figure 1.2 Silica surface coating of a magnetic nanoparticle [12]

Surface modified MNPs have been used in various applications such as in biomedicine, analytical chemistry, and catalysis. In biomedicine where MNPs are mainly adopted, MNPs have been successfully applied using magnetic separation technologies in cell manipulation, DNA sequencing, and drug delivery systems. In analytical application, MNPs modified with molecularly imprinted polymers were developed. These composite materials can provide the highly selective and more convenient separation for isolation of target analytes. For example, The synthesized

magnetic molecularly imprinted polymer (M-MIP) were used for the rapid extraction of bisphenol A from wastewater and milk samples [27], estrone detection [38], separation of tetracycline antibiotics from egg and tissue samples [23] and removal of endocrine disrupting chemicals from aqueous solutions [33]. Recently, Chen and co-workers [23] reported the synthesis of magnetic MIPs using oxytetracycline (OTC) as template molecule and applied for the direct extraction of tetracyclines (TCs) from egg and tissue samples. The extraction and clean-up procedures were carried out in a single step and the sample preparation procedure was simplified with significant reduction in both extraction time and solvent consumption.

In many cases, the modified shells can also be used for further functionalization and to promote the performance of the MNPs as an active functionalized material. This idea provides the modified MNPs for use as heterogeneous reagent or catalyst for organic synthesis which offer the ease of isolation from reaction mixture and also ability to reuse. However, only a few studies have been reported on modified MNPs as a supported catalyst and reagent. For instance, Jiang and co-workers [34] immobilized linear oligopeptide functionalized ionic liquid as asymmetric catalyst on the surface of MNPs and purposed to construct a combinative catalyst with high productivity and excellent enantioselectivity for aldol products. The results showed that magnetite-loaded oligopeptide functionalized ionic liquid served as a recyclable catalyst for aldol addition of ketone and aldehyde and its catalytic efficiency and selectivity can be finely designed by the characteristics of each part of the catalyst. In the same way, Che and co-workers [39] reported the

development of a novel type of Hoveyda–Grubbs catalyst by assembling magnetic nanoparticles with Grubbs I catalyst. This type of catalyst was found to be effective in the synthesis of a series of cyclic olefins, and found to be active with no loss of catalytic efficiency after repeated use.

In this study, the MNPs will be synthesized followed by surface modification. The modified MNPs will be then applied for two main uses as the magnetic-molecularly imprinted material and magnetic supported oxidizing agent for organic synthesis.

1.3 Aim of this research

1.3.1 To synthesize and characterize silica magnetic nanoparticles

1.3.2 To prepare magnetic-molecularly imprinted silica using silica magnetic nanoparticles and evaluate this binding characterization

1.3.3 To prepare magnetic supported oxidizing reagent using poly(allyl-morpholine *N*-oxide) modified silica magnetic nanoparticles and evaluate their effective loading in oxidation of benzyl halides compared to the activity of the pure standard NMO reagent. Solvent effect was also studied.