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# Modified iron oxide nanomaterials: Functionalization and application

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ABSTRACT

Iron oxide magnetic nanoparticles have aroused the interest of researchers of materials' chemistry due to its exceptional properties such as decent magnetic, electric, catalytic, biocompatibility, and low toxicity. However, these magnetic nanoparticles are predisposed towards aggregation and forming larger particles, due to its strong anisotropic dipolar interactions, particularly in the aqueous phase, consequently depriving them of dispersibility and particular properties, ultimately degrading their performance. Hence, this review focuses on modified magnetic nanoparticles that are stable, easily synthesized, possess a high surface area and could be facile-separated via magnetic forces, and are of low toxicity and costs for applications such as catalyst/catalyst support, food security, biomedical, and pollutant remediation.

## 1. Introduction

### 1.1. *Magnetic properties of $Fe_3O_4$ nanoparticles*

Magnetic nanoparticles (MN) is regarded as an engineered particulate material that measures less than 100 nm with an external magnetic field. It also exhibits a phenomenon called superparamagnetism, where it does not magnetize under the influence of magnetic field, which eliminates the risk of particle aggregation [1–3]. MN have been widely utilized in various applications, such as magnetic resonance imaging, protein immobilization, biotechnology, catalysis, microwave absorber, and cancer therapy (Fig. 1) [2,3]. The different synthesis process produces iron oxide with different external magnetic properties (Table 1).

Magnetite crystallizes in the inverse spinel structure $(Fe^{3+})(Fe^{2+}, Fe^{3+})$ to an FCC-close packed lattice of $O_2$, where 1/2 of the octahedral sites are occupied by equal amounts of randomly distributed $Fe^{2+}$ and $Fe^{3+}$, while 1/8 of the tetrahedral sites are occupied by the remaining $Fe^{3+}$. $Fe_3O_4$ is thermodynamically stable under common ambient laboratory environments, forming readily under most solvent-based nanoparticles synthesis conditions [1,4]. The bulk material is redox active, while the surface composition is easily varied by slight changes to $O_2$ partial pressure and substrate temperatures. Upon exposure to the ambient atmosphere, the surface of macro-scaled $Fe_3O_4$ crystallites are often covered with multilayer of $\alpha$-$Fe_2O_3$, and as is true with most oxides, with monolayer amounts of surface hydroxyl and physisorbed $H_2O$ [5–10].

## 2. Modification of MN

There is substantial attention to the progress of stable, well dispersed, reusable, and highly active MN [9,11–16]. There is mounting interest towards the modification of MN, where the nanoscale architecture of active centers influences the efficiency and selectivity.

### 2.1. *Chemical functionalization of MN*

#### 2.1.1. *Organic compound functionalized MN*

With the aid of an external magnet, chemically-functionalized MN could be separated recycled and purified from the products with minimum operational costs. Novel properties such as biocompatibility, water-dispersible, biodegradability, and fundamental magnetic properties could be meant for functional organic materials attached to MN.

*2.1.1.1. Acid-MN.* In most cases, acid functionalized MN are investigated due to their easy separation from the reaction mixture via an external magnet. A promising acid compounds in this case is sulfuric acid ($H_2SO_4$) [17]. The $H_2SO_4$ functionalized silica-coated MN is recyclable, non toxic, capable, mild, and harmless to the environment. The solid acid catalyst creates new opportunities to create a remarkable and effective system that assists catalyst recovery in various organic reactions [17,18].

Recently, sulfamic acid ($H_3NSO_3$) which is a dry non-hygroscopic, nonvolatile, and order less solid has been used as an efficient heterogeneous catalyst alternative for conventional acidic catalyst [19,20]. The combination of $H_3NSO_3$ on the surface of MN is used as a catalyst for several one pot synthesis with a water

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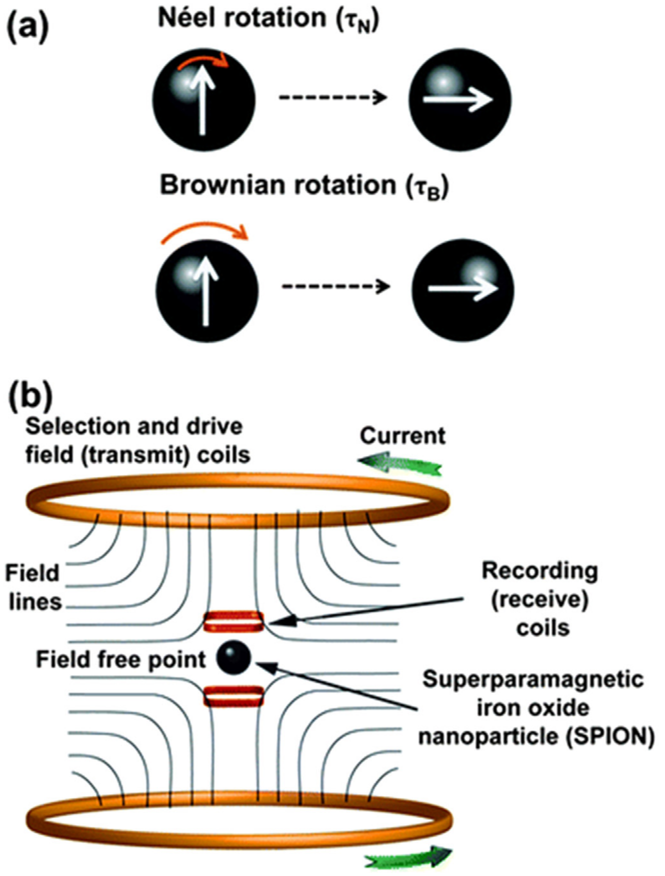

**Fig. 1.** Schematic representation of the magnetic relaxation mechanisms and the basic components of magnetic imaging system [3].

**Table 1**
Effect of external magnetic properties based on the synthesis process applied.

| No | Synthesis process | Specific saturation magnetization (emu $g^{-1}$) | References |
|---|---|---|---|
| 1 | Chemical precipitation methods | 4.62 | [1] |
| 2 | Modified Stöber method combined with the layer-by-layer (LbL) assembly technique | 54 | [2] |
| 3 | Coprecipitation of $Fe^{3+}$ and $Fe^{2+}$ with an aqueous NaOH solution | 65.53 | [3] |
| 4 | On the surface of halloysite nanotube | 27.91 | [4] |
| 5 | Hydrothermal method | 21.5 | [5] |

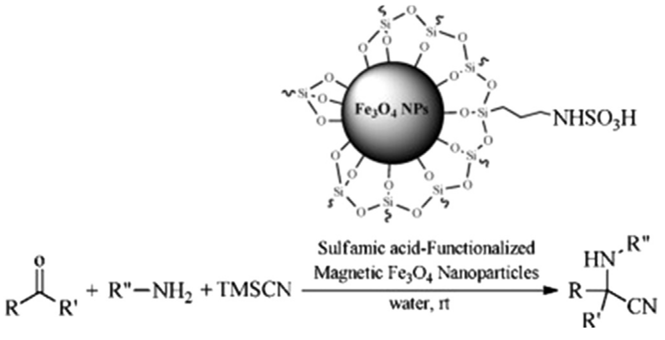

**Fig. 2.** Synthesis of $H_3NSO_3$-MN [22].

medium at room temperature of acetalization, esterification, nitrile formation, tetrahydropyrnylation of alcohols, michael addition, and transesterification of β-ketoesters (Fig. 2) [21,22]. For example, for the past few years, chlorosulfuric acid has been used to produce N-propylsulfamic acid-functionalized magnetite $Fe_3O_4$ nanoparticles. It is a dry non-volatile and odourless solid, and has been demonstrated as a competent heterogeneous catalyst [22,23]. Furthermore, certain studies have focused on a combination of $H_3NSO_3$ and MN as catalysts for the synthesis of quinolone derivative treatment of 2-amino bensophenone with various carbonyl compounds, reporting a high yield (72–98%) under solvent-free conditions [24].

The functionalization oleic acid ($C_{18}H_{34}O_2$) onto the surface of MN is normally done to reduce agglomeration. The functionalization of $C_{18}H_{34}O_2$-MN normally began by re-dispersing MN in aqueous solution of sodium dodecylbenzene sulfonate, poly-(oxyethylene)nonylphenyl ether, or di(2-ethyhexy) adipate [25,26]. The second surfactant could coat the primary surfactant to form a structured surfactant bilayers. Several studies have prepared a bilayer surfactant-stabilized magnetic fluid with the initial fatty acid layer and a secondary layer of other surfactants [27]. MN synthesis has been also performed in aqueous solution coated with bilayer $C_{18}H_{34}O_2$. Moreover, the synthesis of bilayer $C_{18}H_{34}O_2$ stabilized MN was accomplished using $C_{18}H_{34}O_2$ as the primary and secondary layer surfactant [25]. The procedure reliably generates colloidal systems that are stable for more than 3 months, which is verified when no precipitate was formed after that time [28,29].

For extensive biological application, the amount of unbound or free $C_{18}H_{34}O_2$ needs to be decreased for further reduction in the cytotoxicity of the formulation. For biomedical application, the ratio of the bound-to-free $C_{18}H_{34}O_2$ can have significant impacts on the interaction of MN with oleic acid with regards to the mode of internalization and toxicity [27–29].

*2.1.1.2. Silane-MN.* The silane (SiH4) agents, including mercaptopropyltriethoxysilane, 3-aminopropyltriethyloxysilane, and p-aminophenyl trimethoxysilane are frequently deliberated as prospective candidates in order to manipulate the surface of MN [30–32]. This surface manipulation improves the biocompatibility, highly stable under fluorescent, and arrange for moderately high density surface functional end groups, which helps connect it to other metals, polymers, and biomolecules. After salinization, the core shell MN was treated with ammonia to create a bond with active COOH. The presence of many OH groups on the MN surface leads to reactions with alkoxysilane reagents, brought about by the construction of Si-O bonds, which supports the terminal functional groups available for immobilization of other substances [30,32].

Some studies have employed magnetic support to increase the affinity of MN towards $SiH_4$ derivatives [33,34]. For example, tetraethyl orthosilate has been employed to present a highly reactive silanols (Si-OH) on the surface of MN to develop its interactions with γ-aminopropyltriethoxysilane an organosilane, which is a bifunctional molecule having a trialkoxy group (which can bind covalently to the free OH groups on the surface of particles) and an organic head group functionality that defines the final chemical character of the modified surface [35,36].

*2.1.1.3. Amino-MN.* Amino ($C_2NH_4O_2R$) functionalized magnetic nanopartciles are universally employed for conjugation with biomolecules and drugs [37]. As conductive molecules, $C_2NH_4O_2R$ has been extensively incorporated with MN for enzyme immobilization application. MN functionalized with 3-aminopropylthriethoxysilane as an $C_2NH_4O_2R$ derivative has been prepared using the chemical co-precipitation method [38,39]. The synthesized material has been used as a substrate for lipase immobilization. Indeed, the amino-MN found a special application of well dispersed DNA biosensor. It is noted that the naked MN has the capacity to adsorb DNA, but aggregates due to attractive forces