Chapter 1

Introduction and Review of Literature

This chapter includes:

- Introduction
- Surface to Volume Ratio
- Agglomeration of Nanomaterials
- Properties of Nanomaterials
- Various Applications of Nanomaterials
- Magnetic Phenomenon in Bulk Materials
- Iron Oxides
- Magnetic Domains
- Superparamagnetism
- Theoretical Formalism
- Review of Literature
- Motivation of Research in Iron Oxide Nanoparticles
- Reference
1.1 Introduction

Nanotechnology is commonly defined as the control, understanding and restructing of matter at nanometer scale as less than 100 nm to create materials with fundamentally new properties and functions. The prefix “nano” in the nanotechnology is solely related to the dimensions of the material. The “1-1000 nm rule” is based on the prefix “nano” that indicates one billionth of a meter and most simply comprehensible for users across diverse regulations. This definition has been improved to replicate the fact that the component nano brings some novel functionality to the current and future technologies. The “1-100 nm rule” says that engineered nanoparticles may be defined as any intentionally produced particle has characteristic dimension from 1 to 100 nm. These properties are not shared by non-nanoscale particles with the same chemical composition. However, the development of the nanotechnology could be limits the Moore’s law for electronic applications. Because, the quantum effects plays an important role to limits the classical applications of the materials [1]. The transition to nanotechnology can therefore be described as “step crossing this limit” and entering an area, in which new rules like the quantum size rules prevail.

Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing exponentially worldwide in the past few years. It has the potential to revolutionize the ways in which materials and products with the improved functionalities. It is already having a significant commercial impact, which will assuredly increase in the future as shown in Fig 1.1.

The decrease in particle size results in the increasing surface energy, which is then compensated by crystallographic changes such as lattice contraction, lattice deformation, defects, rearrangements and changes in morphology. Specific surface area (SSA) is defined as the surface area per unit of mass or volume. The SSA with volume exceeds 60 m² cm⁻³, then that material can be classified as nanomaterials. Those properties that arise due to the surface effects have this critical size range much smaller than 100 nm [1].
1.2 Surface to Volume Ratio

Nanomaterials have a relatively high surface area compared to the same volume or mass of the material produced in a bulk materials. If the given volume is divided into smaller pieces the surface area increases. So, the particle size decreases a greater proportion of atoms are found at the surface compared to core. Hence, nanoparticles have a much greater surface area per unit volume and makes more chemically reactive to enhance the functional properties [2,3].

1.3 Agglomeration of Nanomaterials

Agglomeration is the major problem during the synthesis of nanoparticles and it limits the technological applications. It is the collection of particles that are loosely bound with the following interactions such as van der Waals forces, electrostatic forces, physical entanglement, or surface tension. Aggregation is different from agglomeration where the
chemical or metallic bonds bring the particles to close contact, often resulting in the surface area slightly smaller than the sum of the individual surface areas of the participating particles. Agglomerates can be reversible, whereas aggregates are generally not reversible. Agglomeration or aggregation can alone significantly alter the behavior of the nanotherapeutics. These effects are mostly related to the toxic effects of nanotherapeutics during usage. The rate of agglomeration of nanoparticles is dependent on the concentration and the size of the nanoparticles. Agglomeration can be prevented by electrostatic or steric stabilizers or by using open flocks in the dispersion. Sometimes, excess surfactants could also cause the agglomeration in nano-dispersions.

1.4 Properties of Nanomaterials

Most of the nanostructured materials are crystalline in nature and they have unique properties. Filling polymers with nanoparticles or nanorods and nanotubes leads to significant improvements in their physicochemical properties.

1.4.1 Physical properties

Crystal structure of nanoparticles is same as bulk structure with different lattice parameters. It is known that the volume of an object decreases as the third power of its linear dimensions, but the surface area decreases only as its second power. This was especially strong when the sizes of nanomaterials are comparable to the Debye length. Simple calculations show that a particle of sizes of 30, 10, 3 nm have 5, 2 and 50 % of atoms residing on its surface.

1.4.2 Chemical properties

A large fraction of the atoms are located at the surface of the nanomaterial which increases the reactivity and catalytic activity of the materials. The large surface area to volume ratio, the variations in geometry and the electronic structure of nanoparticles have a strong effect on catalytic properties.

1.4.3 Electrical properties

The energy band structure and charge carrier density in the nanomaterials can be modified quite different from their bulk counterparts and in turn modifies the electronic properties of the materials. Nanoclusters of different sizes will have different electronic
structures and different energy level separations. So they show diverse electronic properties which depend on their size.

1.4.4 Magnetic properties

The magnetic moment of nanoparticles is found to be very less when compared with bulk. It is possible, that non-ferromagnetic materials ZnO, Au, Pt nanoparticles exhibit ferromagnetic or paramagnetic behavior at nanoscale. Therefore, the properties of nanoparticles depend strongly on their dimension. For example to size reduction, the structure of ferromagnetic particles changes from multi-domain to single-domain can exhibit superparamagnetism. Such magnetic nanoparticles have attracted considerable attention recently not only for fundamental research, but also for a broad range of applications, such as magnetic fluids [4], catalysis [5], ultra high-density magnetic storage media [6], biotechnology and biomedicine [7], magnetic resonance imaging [8], etc. Among these magnetic materials, iron oxides (Fe$_2$O$_3$ and Fe$_3$O$_4$) nanoparticles have been extensively investigated due to their excellent magnetic properties [9].

1.5 Various Applications of Nanomaterials

As of November 2009, in excess of 1000 nanotechnology products were on the market. Common applications include electronics, optics, textiles, medical devices, cosmetics, food packaging, water treatment technologies, fuel cells, catalysts, biosensors and components of environmental remediation [10]. Nanoscale iron oxide and zero valent irons are currently being used in different applications such as anodes in lithium ion battery, MRI, drug delivery, hyperthermia and groundwater to detoxify halogenated. Silver nanoparticles have well-known antimicrobial properties that have directly led to incorporation in the products ranging from bandages to socks to vacuum cleaners pollutants or reduce nitrates. Carbon-based nanomaterials such as single/multi-walled nanotubes are currently integrated into products such as plastics, orthopedic implants, electronics, catalysts, battery/fuel cell electrodes, water purification systems, and adhesives/composites. Other nanomaterial applications include drug delivery agents, components on DNA chips and composites to recognize and attach to disease/cancerous cells for targeted treatment and cell destruction.
1.6 Magnetic Phenomenon in Bulk Materials

The orbital motion of electrons in an orbit around the nucleus and the spin of the electrons were held responsible for magnetic moment for the magnetic materials. Thus, each electron has both spin and an orbital magnetic moment which acts as a weak magnet.

The magnetic materials can be classified according to their magnetic response with respect to applied magnetic field as shown in Fig 1.2(a-d). The magnetic moment per unit volume is called magnetization which changes by varying the strength of the magnetic field. The diamagnetic and paramagnetic materials have no magnetization without applying the magnetic field. Whereas, the ferro, anti-ferro and ferromagnetic have strong magnetization are called as magnetic materials. This material loses their magnetic properties at certain temperature and it is called as Curie or Neel temperature as shown in Fig 1.2e.

Diamagnetic materials have a weak, negative susceptibility to magnetic fields. These materials are slightly repelled by a magnetic field and the material does not retain the magnetic properties when the external field is removed. In diamagnetic materials all
the electrons are paired so there is no permanent net magnetic moment per atom. Diamagnetic properties arise from the realignment of electron paths under the influence of an external magnetic field. Most elements in the periodic table, including copper, silver, and gold are diamagnetic.

**Paramagnetic** materials have a small positive susceptibility to magnetic fields. These materials are slightly attracted by a magnetic field and the material does not retain the magnetic properties when the external magnetic field is removed. Paramagnetic properties are due to the presence of some unpaired electrons, and also from the realignment of the electron paths caused by the external magnetic field. Paramagnetic materials include magnesium, molybdenum, lithium, and tantalum.

**Ferromagnetic** materials have a large, positive susceptibility to an external magnetic field. They exhibit a spontaneous magnetic moment and are able to retain their magnetic properties after removing the external magnetic field. Ferromagnetic materials have unpaired electrons so their atoms have a net magnetic moment. They get their strong magnetic properties due to the presence of magnetic domains. In these domains, large numbers of atomic moments ($10^{12}$ to $10^{15}$) are aligned parallel. So that the magnetic force within the domain is strong. Iron, nickel, and cobalt are the examples of ferromagnetic material.

**Antiferromagnetic** materials are very similar to ferromagnetic materials but the exchange interaction between neighbouring atoms leads to the anti-parallel alignment of the spins. Therefore, the magnetic field cancels out and it was behave like paramagnetic material. The antiferromagnetic materials become paramagnetic at above transition temperature, known as the Neel temperature, $T_N$. (Cr: $T_N = 37^\circ$C).

**Ferrimagnetism** is only observed in compounds, which have more complex crystal structures than pure elements. Within these materials the exchange interactions lead to parallel alignment of atoms in some of the crystal sites and anti-parallel alignment in others. The material breaks down into magnetic domains, just like a ferromagnetic material and the magnetic behavior is also very similar, although ferrimagnetic materials usually have lower saturation magnetizations.
Fig 1.3. Crystal structure of inverse spinel structure (Fe₃O₄)

1.7 Iron Oxides

The most common iron oxide originates in nature with different forms such as maghemite (γ-Fe₂O₃), hematite (α-Fe₂O₃), wurtzite (FeO) and magnetite (Fe₃O₄). Generally, the divalent cations fully occupied at tetrahedral sites are called as normal spinel structure whereas the divalent cations are at the octahedral sites is called as inverse spinel structure. The divalent cations present on both A and B sublattices, then the structure is called as mixed spinel structure. Among them, the magnetite is a common iron oxide that have a cubic inverse spinel structure with oxygen forming an ‘fcc’ closed packing and Fe cations occupying tetrahedral sites and octahedral sites as shown in Fig 1.3.

Magnetite (Fe₃O₄) nanoparticles differ with their atoms and bulk counterparts in their physical and chemical properties. Each nanoparticles are considered as single magnetic domain, the quantum size effect and large surface areas lead to some dramatic change in magnetic properties resulting in superparamagnetic phenomena and quantum tunnelling of magnetization. Based on their unique physical, chemical, thermal and mechanical properties, superparamagnetic nanoparticles offer a high potential for different applications. These applications demand nanomaterials with specific size, shape, surface characteristics and magnetic properties. Based on these properties these materials
were used for separation (HGMS), high density data storage, ferrofluids, magnetic resonance imaging, wastewater treatment, bio-separations and biomedicines, catalysts and electrode materials and modified anti-corrosive coatings.

Typically the magnetic nanoparticle systems were based on iron or iron oxides. Iron has a higher magnetic susceptibility while its oxides have low susceptibility to find the advantage of easy magnetic nanoparticles. The oxidation reaction is a common reason for protecting the superparamagnetic $\text{Fe}_3\text{O}_4$ nanoparticles. The process can be done by the simple chemical methods.

$$\text{Fe}^{2+} (\text{aq}) + 2\text{Fe}^{3+} (\text{aq}) + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 (s) + 4\text{H}_2\text{O} \quad (1)$$

Generally, the fabrication of magnetic nanoparticles for biomedical application consists of three components: superparamagnetic core, protective biocompatible polymer coating and appropriate surface functionalization by drugs or proteins. A superparamagnetic core material is relatively safe, non-toxic and well tolerated for biological applications. The surface coating of magnetic nanoparticles is important to improve their stability, reduced toxicity or minimize protein absorption on the nanoparticles surface. Afterwards the surface functionalization of drugs was anchored via covalently bound functional groups (-OH, -NH$_2$, -COOH, etc..) to the surface of the magnetic nanoparticles that may be responsible for the superior interaction between particles and bio-molecules [11]. The structure of the interface and the orientation between two contiguous crystalline domains in the spheres are important parameters to understand the growth mechanism.

1.8 Magnetic Domains

The ferromagnetic materials contain a number of small regions with different size and shapes are called domains. Weiss was first proposed the mechanism of magnetic domains. The directions of magnetization in various domains are different, so that the net magnetization is zero in absence of an external magnetic field. Each domains are uniformly magnetized region, where the local magnetization reaches the saturation value. The multi domain structure was observed in ferri and anti-ferromagnetic materials which lead to minimize the total energy of a magnetic body. Two adjacent domains are separated by transition regions in which the spins gradually rotate from a domain to the
other domain, such transition region is called domain wall. The domain walls can be classified according to the angle between the magnetization in adjacent domains.

1.9 Superparamagnetism

The superparamagnetic behavior can be described as a combination of paramagnetic and ferromagnetic properties. Therefore, the particles behave as magnetic in applied field and do not manifest magnetic properties when the applied magnetic field is removed. This is due to the fact that there are physically fewer spins in the particle that need to be rotated, thereby it requires less energy. These types of particles have been uniformly distributed in the dispersed medium without being aggregated when the applied field is removed. Therefore, superparamagnetic nanoparticles have gained growing interest and the magnetic properties can be well controlled by an external applied magnetic field, which can be potentially used for various applications. Below a critical size, mono domain nanoparticles become superparamagnetic at room temperature and the orientation of their magnetic moment becomes unblocked against the thermal fluctuations.

The average time for the switching of magnetization direction between the easy directions of magnetization is called the superparamagnetic relaxation time (τ). For a mono domain magnetic particle with uniaxial anisotropy, the reversal of the magnetization occurs only through coherent rotation, also it is found that τ follows an Arrhenius Law:

\[
\tau = \tau_0 \exp \left( \frac{KV}{k_B T} \right)
\]  

(2)

If the bulk material is made smaller, its coercivity increases when the domains not being able to subdivide into as many smaller units and continues until a critical size is reached. At this critical size the particle can be single domain because the energy rate of forming a domain wall exceeds the reduction in magnetostatic energy. This is known as the single domain limit. For spherical particles this radius is:

\[
R_{sd} = \frac{9E_a}{\mu_0 M_s^2}
\]  

(3)
Where $E_{\sigma}$ represents the total domain wall energy per unit area and $M_s$ is the saturation magnetization at absolute temperature.

### 1.10 Theoretical Formalism

Superparamagnetic nanoparticles are unstable due to thermal fluctuation when the ambient thermal energy exceeds the magnetic anisotropy energy [12]. If the temperature ($T$) decreases, the transition from kinetically responsive magnetic moment to the kinetically unresponsive magnetic moment which acquire thermal blocking temperature $T_B$. For $T<T_B$, thermal fluctuations in the orientation of the moment of each particle are slower than the measuring times, so the particle moment remains fixed and coercive. For $T>T_B$ thermal fluctuations allow the moments to align with a small measuring field, where they exhibit large-moment paramagnetism with a $1/T$ behavior given by [13]

$$M(T) = \frac{HM_s^2}{3k_B T}$$  \hspace{1cm} (4)

Where, $k_B$ is the Boltzmann constant, $H$ is the applied magnetic field, $M_s$ is the saturation magnetization and $M(T)$ is the magnetic moment and it is zero for $T<T_B$, but thermally unblocked for $T>T_B$. This phenomenon results in a peak in $M_{ZFC}(T)$ near $T_B$. The ratio of the anisotropic energy to the thermal energy is

$$\frac{KV}{k_B T_B} = 25$$  \hspace{1cm} (5)

Where, $K$ is the effective uniaxial anisotropy and $V$ is the particle volume.

The temperature dependence of the saturation magnetization $M_s$ may be neglected for sample with Curie temperature $T_C>>T_B$, the distribution of the blocking temperature $f(T_B)$ may be evaluated as

$$f(T_B) = \frac{3k_B}{HM_s^2} \frac{dT}{dT} (TM_{ZFC}(T))$$  \hspace{1cm} (6)

The distribution of the blocking temperature $f(T_B)$ is converted into particle volume distribution function $f(V)$ via anisotropic energy to the thermal energy

$$f(T_B) = 1/(T_B)^2 d/dT[TM(T)]$$  \hspace{1cm} (7)
Therefore, the ZFC thermomagnetic data \( M_{ZFC}(T) \) may be directly mapped to a size distribution function that represents both the average magnetic diameter of the particles and the distribution in the particle size.

1.11 Review of Literature

Reviews play an important role in keeping important and interesting information up to date with the current state of the research in any areas. This review aims to focuses on development of the monodispersed \( \text{Fe}_3\text{O}_4 \) nanoparticles for multifunctional applications. It is attempted to classify the importance of materials, preparation, physicochemical characterization and various biological/technological applications of the \( \text{Fe}_3\text{O}_4 \) nanoparticles.

1.11.1 Synthesis of magnetite nanoparticles

In almost all applications, various chemistry based processing routes have been developed to produce the monodispersed shape and size based on surface chemistry and consequently changes their physicochemical properties [14]. The size and shape of the magnetic nanoparticles was altered by using appropriate temperature and solvent based experiments. Because, all the solvents are depends on various temperature conditions for taking reaction kinetics. Generally, aqueous solvent are used in precipitation method to attain different particle size in the range of \(< 30 \) nm which is suitable for efficient biological applications and large scale production with low coast [15]. The limitation of magnetic nanoparticles using aqueous solvent have low stability that tends to highly aggregated and flocculates due to high surface area which limits the uniform shape of the final particles [16]. So, it is necessary to acquire monodispersed shape and increase the stability of magnetic nanoparticles by using high boiling point of organic solvents. The organic solvents in thermal decomposition methods such as benzyl ether, phenyl ether were used in the reaction at the temperature range of above 350 °C. Ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol were used as a solvent in the range of below 250 °C for solvothermal reactions [17]. In solvothermal synthesis, the progressions of nucleation might be quicker than grain growth at higher temperature and result in a reduction in particle size which would favour the monodispersed morphology of magnetic nanoparticles [9]. For example the solvothermal method was used to produce the different morphologies of the \( \text{Fe}_3\text{O}_4 \) nanoparticles.
The morphologies such as nanospheres, nanorods, nanoflowers, nanowhiskers, nanotubes, nanorings, nanowire, core-shell, octahedral etc were used to improve the technological applications [18-28].

1.11.2 Antiviral activity

The antibacterial property of metals or metal oxide nanoparticles has been extensively explored. But the antiviral properties remain an undeveloped area and many pathogens are still questionable [29]. The diseases caused by viruses present challenging problems with worldwide social and economic implications. Developing antiviral drugs which can target the virus and maintaining host cell viability is challenging [30]. So, the metal or metal oxide nanoparticles have been proposed as antiviral systems taking advantage of the core material and/or the ligands shell [31]. Among many nanostructures particles, superparamagnetic iron oxide nanoparticles (SPIONs) were used in gene therapy and clinical development as imaging agents and preclinical studies for theranosis applications. Recently, magnetite nanoparticles with polymeric microfiltration membranes were used for removing virus from polysulfone water [32]. Streptavidin coated Fe₃O₄ nanoparticles enhanced adeno-associated viral vector delivery for human neural stem cell infection [33]. Also, chitosan/Fe₃O₄ composites make a sensor for electrochemical detection of HIV sequences [34]. Therefore, the superparamagnetic nanoparticles play a vital role for antiviral treatment to improve clinical applications.

1.11.3 Anti-cancer activity

Breast cancer is a leading cause of cancer death in North America and European Union. One in eight lifetime risk of this disease happens every year. An advance stage of this breast cancer may not be cured by surgery alone and it is typically treated with adjunct chemotherapy. Paclitaxel, cisplatin, carboplatinum, doxorubicin, decitabine or their combinations are considered as first line chemotherapeutic agents (CTAs) for various cancer treatments. But it has shown limited efficacy as second and third-line chemotherapy agents [35,36]. However, chemotherapeutic drugs can cause secondary malignancies and have additional detrimental side effects due to their inability to discriminate between rapidly proliferating cancer cells and healthy dividing cells [37]. This is due to lack of specificity and poor pharmaco-bioavailability, leading to incidence
of normal organ toxicity and major side effects. So, the urgent need to develop therapeutic modalities with no or minimal side effects to normal organs. In order to address this issue, the use of magnetic nanoparticles with natural dietary phytochemicals in cancer therapeutics is being explored. The use of an external magnetic field for drug targeting could be considered as precise advantages [38]. The majority of the magnetic nanoparticle research is focused on below 100 nm size of the particles. The engineered nanoparticles with less than 100nm can passively or actively target the diseased sites, avoiding unwanted adverse effects of the drugs at non-target site. Recent reports shows that 50 nm sized particles shows 34 % and 100 nm sized particles shows 26 % of cellular uptake whereas above 100 nm particles are absent in the blood and other organs [39]. For example, the thymoquinone does not substantially affect the viability of normal human lung fibroblasts, and intestinal cells but induce cytotoxicity to cancer cells at the same concentrations [40]. The magnetic nanoparticles produce free radicals by Fenton reaction and attack cancerous cells by destroying lipids, proteins, and enzymes, often resulting in cell death. Tumour cells contain low levels of free radical scavengers, and free radicals have recently been shown to contribute to the mechanism of anticancer therapeutic agents. Therefore, the generation of a large amount of free radicals in tumor tissues may have potential as a future anticancer therapy [41].

1.1.1.4 Environmental remediation

Arsenic contamination of drinking water sources is estimated to affect over 144 million peoples around the world. Spurring the development of numerous water treatment technologies to limit negative health impacts associated with exposure to arsenic contaminated water including skin lesions and cancers [42]. The greater surface area per unit mass of Fe₃O₄ nanoparticles leads to a higher rate of adsorption than bulk iron and promising materials for remediation of arsenic contaminated source water [43]. Compared to γ-Fe₂O₃ nanoparticles, the Fe₃O₄ chestnut like hierarchical structure with strong ferromagnetic properties remove 74 % of As(V) ions and robust with Freundlich isotherm model due to multi-layer adsorption [44]. The saturation magnetization of the Fe₃O₄ (55.4 emu/g) is higher than γ-Fe₂O₃ (44.2 emu/g) which leads to the strong adsorption and easy magnetic separation from aqueous solution [45]. The flower like α-Fe₂O₃ nanostructures with high surface area of 130 m²/g has attractive adsorption of
both As(V) and Cr(VI) ions from aqueous solution [46]. The dimercaptosuccinic acid functionalized Fe₃O₄ nanoparticles have multifunctional adsorption process to remove toxic soft materials such as Hg, Pb, Ag, Cd, and As ions respectively [47]. Other than ferrite nanoparticles, the cotton-candy-like CuO 3D hierarchical microstructures were used as an adsorbent for removing As(III) ions from drinking water [48]. Similarly, the chromium (VI) ions were removed within 30 minutes using magnetic chitosan iron (III) hydrogel [49]. The high density of toxic metals adsorbed in lattice position at the surface can be related to size and crystal growth [50]. In summary, different mechanisms of toxic metals adsorption appear to dominate as a function of the surface coverage in magnetic nanoparticles.

### 1.11.5 Anode for lithium ion battery

The rechargeable and relatively long cycle times of Lithium-ion batteries (LIBs) are widely used today in portable electronics, telecommunication and medical devices [51,52]. The current generation of LIBs is based on electrode materials in which Li⁺ is stored by insertion between structural layers during charging and extracted from the layers during discharging without significant structural change to show excellent cycling performance [53]. The use of nanoparticles in LIBs is still largely hampered by their poor long-term cycling stability, energy density and charge/ discharge rate capability [54]. Generally, the nanostructured materials face two major challenges for practical applications. First, it suffers from poor capacity retention, which is attributed to their huge volume expansion during lithiation/delithiation processes. Second, the solid-electrolyte inter-phase (SEI) layer formed by electrolyte decomposition on the surface of anode materials can degrade the battery performance tremendously [55]. So, the effective way to mitigate the above problems is to fabricate the magnetic nanostructured active materials with high surface areas and short diffusion paths. Considerable research is therefore being directed to the study of emerging alternative anode materials with higher theoretical capacities such as graphite carbon (372 mAh g⁻¹), SnO (876 mAh g⁻¹), SnO₂ (780 mAh g⁻¹), FeO (744 mAh g⁻¹), Fe₂O₃ (1005 mAh g⁻¹) and Fe₃O₄ (926 mAh g⁻¹) respectively [56-58]. Compared to other nanomaterials, the magnetite nanoparticles are one of the most promising candidates as anode materials for LIBs due to high theoretical capacities, low cost, ease of fabrication and low toxicity [59]. Porous hollow Fe₃O₄ beads
constructed with rod-shaped Fe₃O₄ nanoparticles have specific capacitance of > 700 mAh g⁻¹ and stability was decreased (100 mAh g⁻¹) after 50 cycles [60]. Similarly, the nanocubes deliver a capacity of 418 mAh g⁻¹ and have a high Coulombic efficiency of 94-100% upto 60 cycles [61]. The Fe₃O₄ nanoparticles can be homogeneously incorporated into a carbon matrix to form mesoporous composite exhibits excellent cyclic and rate performance as anode material. The stable specific capacity of 1010 mAh g⁻¹ was obtained and reaches at equilibrium of 800 mAh g⁻¹ for 50 cycles [62]. The discharge/charge capacities of graphene magnetic composite improve the Coulombic efficiency of > 95% during the subsequent cycles, indicating an excellent cycling performance [63]. However, the porous nanosheet and ternary magnetic nanocomposite as an anode in Li ion batteries is significantly improved nearly 100% discharge-charge efficiency and maintained stability during the subsequent 100 cycles with a specific capacity above 700 mAh g⁻¹ [64,65]. This outstanding electrochemical behavior of magnetite nanoparticles can be attributed to the unique micro/nanostructures, texture, surface properties and combinative effects from the different chemical composition in the nanocomposites.

1.1.6 Other applications

The ultra-small superparamagnetic Fe₃O₄ nanoparticles are useful as contrast agents in magnetic resonance imaging (MRI) to evaluate: areas of blood brain barrier (BBB) dysfunction related to tumors and other neuro inflammatory pathologies, the cerebro vasculature using perfusion weighted MRI sequences, and in-vivo cellular tracking in central nervous system disease or injury [66]. In clinical applications, magnetic nanoparticle hyperthermia for cancer treatment is very important to ensure a maximum damage to the tumor while protecting the normal tissue [67]. Recently, the hyperthermia treatment using the PVP coated magnetite nanoparticles were increases the specific absorption rate (SAR) value increases from 28 to 50 W g⁻¹ and the obtained value is higher than uncoated nanoparticles (20 to 45 W g⁻¹) with an increase in the field from 167.6 - 335.2 Oe [68]. The SAR is defined as a measure of the rate at which energy is absorbed by the body when exposed to a radio frequency (RF) by electromagnetic field. For protein purification, the successful synthesis of NTA-terminated magnetite nanoparticles offers a simple and versatile platform for separating six histidine-tagged protein using dopamine anchors [69]. The oleic acid stabilized Fe₃O₄ colloidal fluids
were improve the multifunctional applications such as fluorescent, ionic conduction and rheological behavior at room temperature [70]. The Fe$_3$O$_4$@ZIF-8 microspheres as catalysts could be easily filled into a capillary micro reactor and have excellent catalytic activity at a shorter residence time for Knoevenagel condensation reaction of benzaldehyde and ethyl cyano acetate [71]. The excellent SERS activity of the Fe$_3$O$_4$@C@Ag composite microspheres was used for the detection of trace persistent organic pollutants such as aromatic pentachlorophenol (PCP), diethylhexyl phthalate (DEHP) and trinitrotoluene (TNT) [72]. Therefore, the magnetite nanoparticles have been extensively used for various biological and technological applications.

1.12 Motivation of Research in Iron Oxide Nanoparticles

The iron oxide nanoparticles have been shown great potential in biological and technological applications due to their superior functional properties and it was strongly related to the monodispersed size and shape. Also, it has been extensively investigated due to variety of interesting properties such as superparamagnetism, water soluble, high colloidal stability, reproducible, biocompatibility, coast effective and environment friendly.

1.12.1 Objective and scope of the present work

The aim of the present work was to achieve large scale synthesis of monodispersed pristine and surface functionalized Fe$_3$O$_4$ nanoparticles using simple chemical methods (Co-precipitation, polyol and solvothermal). The different chemical methods were used to produce the different morphologies with controlled size (monodispersed). The structural, morphological, magnetic, biological, and electrical properties were studied for multifunctional applications such as antiviral, anticancer, environmental remediation and anodes as Li-ion battery. To accomplish these aims, the following objectives were set.

1.12.2 Preparation of pristine and surface functionalized Fe$_3$O$_4$ nanoparticles

The monodispersed shape and size of the Fe$_3$O$_4$ nanoparticles were prepared by facile and environmental friendly chemical process with the proper choice of precursor and growth conditions. The following procedures were used for the synthesis of different morphologies of the Fe$_3$O$_4$ nanostructures.
The monodispersed nanoprism shaped Fe₃O₄ nanoparticles were prepared by simple co-precipitation method and it was used as a nanocarrier for quercetin molecule. This particle was used to study the anticancer activity of breast cancer cells.

The polyol method was employed to produce the monodispersed spherical, flower like cluster and nanoprism shaped particles with the size range of < 50 nm using different surfactants including PEG and PVP. These magnetite nanoparticles were used to study the antiviral activity of swine flu (H1N1) virus.

The different morphologies such as aggregation, spherical, spherical balls, hollow sphere, cube, root-like, chain-like, whiskers, 3D hierarchical and cabbages were prepared in the size range of 20 nm to 3 μm using solvothermal method. These different shaped particles were used to study the various applications including anticancer, arsenate removal and anode in Li-ion batteries.

After getting different morphologies of pristine Fe₃O₄ nanoparticles, the nanoprecipitation method was employed to load the drugs or yeast cells.

**1.12.3 Characterization techniques**

The prepared pristine and surface functionalized Fe₃O₄ nanoparticles were characterized by using various techniques to investigate their structure (XRD and FTIR), composition (EDS), morphology (FESEM, TEM, HRTEM and FFT), surface charge (zeta potential), magnetic properties (VSM), electrical properties (impedance analysis) and biological properties (UV-vis spectroscopy, RT-PCR, flow cytometry, optical and fluorescence microscope).

**1.12.4 Multifunctional Applications**

The present works focuses the three different applications such as targeted drug delivery, environmental remediation and energy storage devices by using different surface functionalized Fe₃O₄ nanoparticles. The pristine and different polymers (PEG and PVP) coated Fe₃O₄ nanoparticles were used to study the antiviral activity of swine flu virus. The in-vitro analysis was used to study the anticancer activity of breast cancer cells (MCF-7) by using quercetin and thymoquinone loaded Fe₃O₄ nanoparticles. The diethylamine functionalized (cabbage shape) and yeast cross-linked Fe₃O₄
nanoparticles were used for complete removal of arsenate from aqueous solution. Finally, the Fe$_3$O$_4$@graphene sheet nanocomposite nanostructures were used to improve the electrochemical performance of anode for Li-ion batteries.

The present research on Fe$_3$O$_4$ nanoparticles provides significant improvement in the functional properties to overcome the problems in biological, environmental and technological applications.
Reference


