

## A Comprehensive Insight into Iron Oxide Nanoparticles: Synthesis and Applications

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### ABSTRACT

Iron oxide nanoparticles (IONPs) have grabbed much attention in the past years as they have different polymeric forms, including  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite),  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite), Fe<sub>3</sub>O<sub>4</sub> (magnetite),  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>, and  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub>. This review focuses on the various methods of synthesis of IONPs and their application. IONPs can be synthesized by variety of methods such as sol-gel, microemulsion, sonochemical, laser-assisted, microwave-assisted, and biosynthesis, of which green synthesis of nanoparticles is being promoted and paid attention to due to its eco-friendly, non-toxic, inexpensive, and less waste producing approach. The wide variety of applications of IONPs are attributed to its features such as magnetic properties, optimum particle size, high surface to volume ratio, biocompatibility, stability, and easy conjugation with other molecules. Some challenges in their synthesis and future perspective have also been discussed.

**Key words:** Applications, Green synthesis, Iron oxide nanoparticles, Iron oxides, Methods of synthesis.

### 1. INTRODUCTION

Nanoparticles have been a major area of interest for researchers for the past few decades and have revolutionized the world of nanotechnology due to their small sizes and high surface area to volume ratio [1]. However, there is much that remains undeciphered. Richard Feynman used the word "nanoparticles" for the 1<sup>st</sup> time in 1959 and laid the foundation of modern nanotechnology [2]. Production of nanoparticles involves manipulation at atomic levels involving chemical, biological, and engineering approaches to fabricate new materials of smaller size and has better properties as compared to the bulk materials. Transition to nanotechnology involves the increase in the surface atoms due to size reduction which results different characteristic of nanoparticles. There are innumerable application areas of nanoparticles ranging from catalysis [3], biomedical [4], electronics [5], imaging agents [6], and adsorbents [7] to food processing [8]. Application of nanoparticles is influenced by the factors such as precursors, temperature of the reaction, particle size, preparation pathway, cytotoxicity of the prepared nanoparticles, and side products.

Iron oxide is a common occurring natural mineral oxide found in nature. Preparation of homogenous iron oxide nanoparticles (IONPs) has grabbed much focus in recent era due to the simple preparation, better magnetic, and electrical properties. Iron oxide exists in eight forms of which main is hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), and magnetite (Fe<sub>3</sub>O<sub>4</sub>) [2]. Hematite is thermodynamically stable under ambient conditions, non-toxic, and resistive to corrosion and inexpensive. Therefore, can be effectively put to use in environmental related applications such waste water treatment. Maghemite and magnetite have wide industrial and biomedical applications.

IONPs are also used extensively as they have wide variety of applications. IONPs are known for their use in delivery of drugs [9], targeting agents [10], ferrofluids in hyperthermia [11], cancer therapy [12], gene therapy [13], cell proliferation [14], wastewater treatment [15], tissue engineering [16], photovoltaic devices [17], thermal ablation [18], pigments [19], catalysis [20], food related applications [21], etc.

Nowadays, scientists have shifted their focus toward developing sustainable methods of producing magnetic IONPs having improved properties. IONPs are being prepared through chemical methods and also through green synthesis. Green synthesis uses plants or microorganisms for the synthesis process of nanoparticles and has added advantages over the chemical synthesis as it is non-polluting, cheap, and non-toxic and requires minimum resources. After synthesis of IONPs, they can be functionalized and mounted with certain nanoparticles that may improve their pre-existing properties and increase their area of application. Therefore, functionalization and conjugation of IONPs become a crucial step for their targeted application. This review aims to highlight various methods of synthesis of IONPs through various methods and their applications to have better insight into its uses and thus improve their scope in today's era of nanotechnology.

### 2. OXIDES OF IRON

The main iron oxides, that is, hematite, maghemite, and magnetite exhibit polymorphism which involves temperature induces phase transitions. Each oxide of iron has their own unique magnetic, catalytic, structural, and biochemical properties which are responsible for their use for a particular application. Figure 1 represents crystal structure of different forms of iron oxide.

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### 2.1. Hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ )

It is the most commonly known form of iron oxide and is largely distributed in nature mainly in soils and rocks. The other names include as red ochre, iron sesquioxide, martite, and kidney ore. It is blood red in color in finally divided form and black or grey in granular or crystalline form. It can also be converted into maghemite ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). The energy band gap value for hematite is 2.3 eV. Conduction band originates from empty d-orbitals of  $\text{Fe}^{3+}$  and valence band originated from the mixture of 3d orbitals of  $\text{Fe}^{3+}$  which is occupied and non-bonding 2p orbitals of O [23]. It is weakly ferromagnetic or antiferromagnetic but becomes paramagnetic above 956 K (Curie temperature). It has corundum type of structure and crystallographic systems include rhombohedral.  $\text{Fe}^{3+}$  ions occupy two third of interstitial sites, while the  $\text{O}^{2-}$  is arranged in close packed hexagonal crystallographic system [24]. It has density of 5.26  $\text{g/cm}^3$  and melting point of 1350°C.

### 2.2. Maghemite ( $\gamma$ - $\text{Fe}_2\text{O}_3$ )

It is ferrimagnetic in nature and is a cubic system with defected spinel structure as vacancies are present in cationic sublattice.  $\text{Fe}^{3+}$  ions occupy tetrahedral sites and octahedral sites, while the oxygen anions form cubic closed packed array. Two-third of the sites are occupied by  $\text{Fe}^{3+}$  ions and one vacant site follows two filled sites. Its Curie temperature is 820-986 K and is n-type semiconductor. It is full oxidized form of magnetite. Maghemite is thermally unstable and transforms to hematite at higher range of temperature. It has a density of 4.87  $\text{g/cm}^3$ . Furthermore, it is easily magnetized in presence of external magnetic field. Energy band gap value for maghemite is 2.0 eV.

### 2.3. Magnetite ( $\text{Fe}_3\text{O}_4$ )

It is ferromagnetic in nature and is a face centered cubic system with inverse spinel structure with stacking plan as in polyhedral model. It has 32  $\text{O}^{2-}$  ions per unit cell and  $\text{Fe}^{2+}$  ions occupy half of octahedral sites and  $\text{Fe}^{3+}$  ions randomly distributed between tetrahedral and octahedral sites. Its Curie temperature is 850 K. The density of this type of oxide is 5.18  $\text{g/cm}^3$  and melting point lies in range of 1583-1597 K. It can behave as both p and n-type semiconductor as the divalent iron atoms can easily be replaced by  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and other divalent ions and has band gap of 0.1 eV.

### 2.4. $\beta$ - $\text{Fe}_2\text{O}_3$ and $\varepsilon$ - $\text{Fe}_2\text{O}_3$

$\beta$ - $\text{Fe}_2\text{O}_3$  has body centered cubic structure and is a rare iron oxide. It is anti-ferromagnetic nature and is thermodynamically unstable and is converted into either hematite or maghemite. The  $\text{Fe}^{3+}$  ions in occupy  $\beta$ - $\text{Fe}_2\text{O}_3$  the octahedral sites.

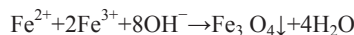
The  $\varepsilon$ - $\text{Fe}_2\text{O}_3$  form is a cubic system with orthorhombic crystal structure. It is a polymorphous intermediate posing structural similarity to both hematite and maghemite.

## 3. SYNTHESIS METHODS OF IONPS

IONPs can be synthesized by variety of ways such as coprecipitation, sol-gel synthesis, microwave irradiation, electrochemical methods, flow injection synthesis, spray or laser synthesis, thermal decomposition, microemulsion, ultrasound irradiation, and biosynthesis and are represented in Figure 2. The major problem that is encountered during the synthesis of nanoparticles is control over size, shape, porosity, polydispersity, morphology of nanoparticles, and reproducibility of method used for its synthesis.

### 3.1. Coprecipitation

This is the classical technique that is most commonly used for the synthesis of IONPs mainly  $\gamma$ - $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ . Its advantages include simplicity, large batch synthesis, and efficiency for the production of IONPs. In this method, a stoichiometric mixture of Ferric and Ferrous ion is used in molar 2:1 in absence of any oxidizing agent. To this mixture, aqueous solution of sodium and ammonium hydroxide is added to maintain pH between 8 and 14 which leads to precipitation of  $\text{Fe}_3\text{O}_4$  which can transform into  $\gamma$ - $\text{Fe}_2\text{O}_3$  in presence of oxygen. The chemical reactions for the process can be represented as below [25]:



The above transformation of magnetite to  $\gamma$ - $\text{Fe}_2\text{O}_3$  can also take place as a result of electron transfer reaction occurring in the suspension of nanoparticles depending on its pH. During oxidation, the migration of  $\text{Fe}^{2+}$  ions occur creating cationic vacancies in lattice framework to maintain balance of charges which also explain the defected spinel

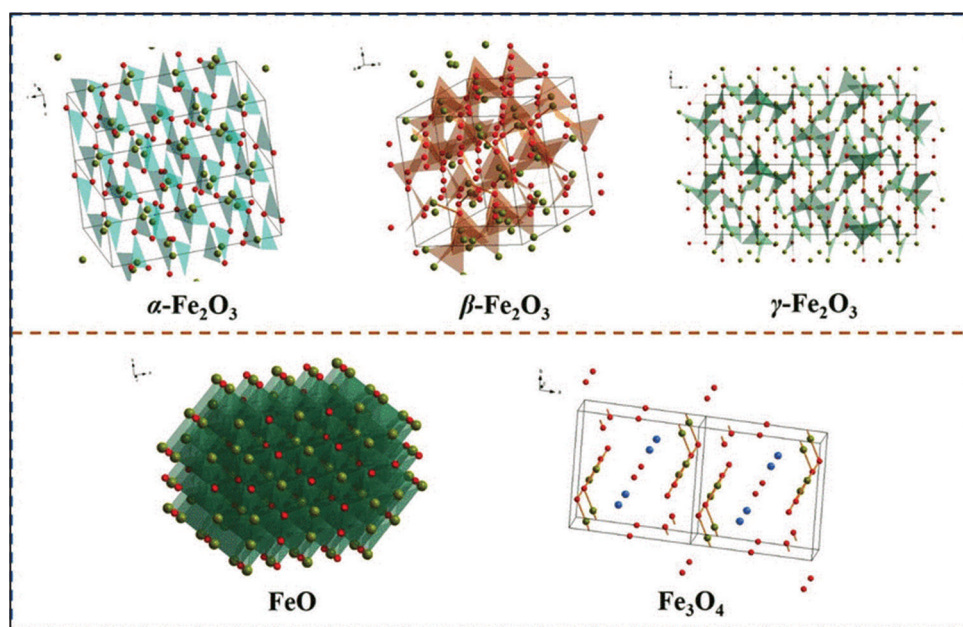
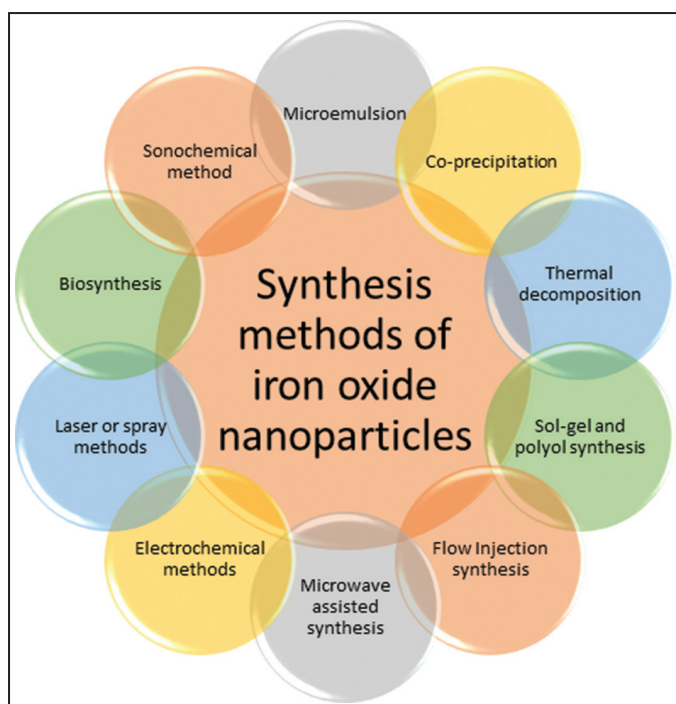


Figure 1: Crystal structure of the different forms of iron oxide (yellow globule:  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . Red globule:  $\text{Fe}^{3+}$ ) [22].



**Figure 2:** Schematic representation of various methods of synthesis of nanoparticles.

structure of  $\gamma$ - $\text{Fe}_2\text{O}_3$ . As only kinetic factors control the growth crystal, the control over size is limited.

The coprecipitation involves two stages, first nucleation occurs when the concentration of species reaches the super-saturation stage and then nuclei grow slowly by solute diffusion to the surface of formed crystal [26]. The size, magnetic characteristics, and surface properties of the nanoparticles can be tailored by adjusting pH, temperature, ionic strength, concentration of ferrous and ferric ions, type of ferrous and ferric salts, and addition of chelating agents.

Several modified coprecipitation methods have been developed, for example, Wu *et al.* reported magnetic  $\text{Fe}_3\text{O}_4$  nanopowder that was synthesized by chemical coprecipitation which was ultrasonically assisted [27].

### 3.2. Thermal Decomposition

The coprecipitation technique is kinetically controlled and the rate of particle formation is fast. Therefore, the size cannot be controlled. Furthermore, the reaction in coprecipitation is carried out at room temperature so the nanoparticles have low crystallinity. To tackle such situations, alternate methods have been proposed. One such method is thermal decomposition which can, further, divided into two approaches: Hot-injection approach where the reaction precursors are added to hot reaction mixture and conventional approach, in which the reaction mixture prepared at room temperature is further heated to high temperature in closed or open vessels. The thermal decomposition method of synthesis of nanoparticles has the advantage of better size control, higher crystallinity, and monodispersity. The method involves the decomposition of organometallic or higher coordinated iron compounds such as ferric (III) acetylacetonate [28], ferrocene [29], iron nitrosophenylhydroxylamine [30,31], iron-urea complex [32], and Prussian blue [33] dissolved in organic solvents. Organic molecules such as oleic acid, oleylamine, and 1-tetradecene are often added as stabilizer to obtain monodispersed IONPs. These stabilizer acts as inhibitor to the growth of the nanoparticles by affecting the adsorption of additives on the nuclei of growing nanocrystals and, hence, can be

used to tailor the shape and size of nanoparticles [34]. Recently, Hyeon *et al.* reported synthesis of IONPs from non-toxic iron chloride by thermal decomposition method [35].

This method can also be used to obtain different morphologies of nanoparticles such as nanocubes and nanospheres, for example, Amara *et al.* carried out thermal decomposition of various mixtures of ferrocene and polyvinylpyrrolidone to obtain magnetite nanospheres and nanocubes [36]. Chalsani *et al.* also synthesized cubic and spherical morphologies of IONPs from the thermal decomposition of  $\text{FeOOH}$  [37].

### 3.3. Microemulsion

The concept of microemulsion was introduced by Hoar and Schulman and since then it is used for various applications. Microemulsions are transparent solution obtained on mixing oil phase with aqueous phase with small amount of ionic surfactant generally an alcohol of medium chain length [38]. The surfactant forms a layer between the oil phase and aqueous phase with the hydrophobic tails projecting into the oil phase while the hydrophilic heads projecting into the aqueous phase. The concentration of surfactant affects the shape, pore volume, surface area, crystallite size, and morphology of nanoparticles. A precipitating agent such as ammonia or tetrabutylammonium hydroxide is added to such microemulsions to produce magnetic nanoparticles. This method can be used to produce nanoparticles with size distribution range 4–15 nm with different methodologies and high surface area. Commonly used surfactants include sodium dodecyl sulfate, polyvinylpyrrolidone, and cetyltrimethylammonium bromide [39–41]. Recently, Okoli *et al.* synthesized IONPs using w/o (water dispersed in oil) and o/w (oil dispersed in water) emulsions for protein binding and separation. The specific area of nanoparticles produced with w/o microemulsions was  $147 \text{ m}^2/\text{g}$  and  $304 \text{ m}^2/\text{g}$  for o/w microemulsions [42]. Furthermore, Bumajdad produced IONPs with surface area of  $315 \text{ m}^2/\text{g}$  [43]. Laurent and Mahmoudi also encapsulated silica precursor with IONPs to reduce toxicity and increase stability of them [12].

### 3.4. Sol-gel and Polyol Method

It is a classical wet chemical synthesis primarily used for fabrication of material. It starts from a colloidal solution of metal oxides or alkoxide precursors referred to as “sol” which is then dried to obtained the nanoparticles in powder form.

Magnetic IONPs tend to agglomerate and form clusters due to high surface energies due to large surface to volume ratio and thus particle size increases. Another problem that is encountered in using sol-gel process is that the naked IONPs are easily oxidized in air losing their magnetic properties. To evade these limitations, the nanoparticles can be coated with polymers (polyvinyl alcohol [PVA], polyethylenimine, and polymethylmethacrylate), organic molecules (gelatin, chitosan, and dextran), or inorganic molecules (carbon, silica, and metals such as gold and silver). The solvent used in sol-gel method is generally water and the hydrolysis of precursors is brought by acid or base. Recently, Qi *et al.* reported the synthesis of magnetite nanoparticles of the average diameter 9–12 nm by sol-gel method using non-alkoxide precursor [44]. Furthermore, Lemine *et al.* reported sol-gel method for synthesis of  $\text{Fe}_3\text{O}_4$  nanoparticles of size 8 nm [45].

The polyol method is inverted sol-gel method and uses reduction reaction instead of oxidation reaction used in sol-gel process. In this method, the polyols serve as solvent, reducing agent as well as stabilizers to control particle growth and inhibit attraction between particles to prevent their aggregation of nanoparticles. Similar to sol-gel method, the iron precursor is suspended in polyol which is then



heated and stirred to reach boiling point of polyol. The reaction does not require as high temperature and pressure as in hydrothermal methods. Cai and Wan reported of Fe<sub>3</sub>O<sub>4</sub> nanoparticles of using ethylene glycol, diethylene glycol, triethylene glycol, and tetraethylene glycol of which only triethylene glycol resulted in nanoparticles without agglomeration [46].

### 3.5. Flow Injection Synthesis

Alvarez *et al.* reported synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles by flow injection synthesis method. In this, laminar flow of reactants takes place in a capillary reactor resulting in continuous or segmented mixing of reactants [47].

This method possesses high reproducibility and greater mixing homogeneity than other methods of synthesis of nanoparticles and also the reaction can be controlled precisely due to specific design of reactor for flow injection synthesis. However, the reaction conditions are more difficult to setup and require expensive equipment.

### 3.6. Sonochemical Method or Sonolysis

This method uses ultrasound waves to carry out reactions. This method has the advantage that it does not involve high temperature and pressure conditions and uses only alternative expansive and compressive ultrasound waves which carry out reaction in short time. The oscillating bubbles accumulate energy, grow, and then collapse releasing energy stored in it to carry out reaction in short period of time. This method can be used to prepare bare or functionalized nanoparticles. Recently, Theerdhala *et al.* employed this method to obtain L-arginine bonded to Fe<sub>3</sub>O<sub>4</sub> nanoparticles which could be used for drug-delivery [48]. Furthermore, Zhu *et al.* synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles that were dispersed on reduced graphene oxide sheets (Fe<sub>3</sub>O<sub>4</sub>-RGO) which when immobilized with hemoglobin can be used for the detection of hydrogen peroxide [49].

### 3.7. Microwave Assisted Synthesis

This method uses electromagnetic radiation of microwaves to carry out excitation of molecules. The excitation of molecule causes intense heating internally, thereby reducing time and energy consumption. Sreeja and Joy reported synthesis of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with particle size of 10 nm using microwave radiations at 150°C. The reactions occurred fast and heating was homogenous [50]. Similarly, Jiang *et al.* produce IONPs with cubic morphology and Hu *et al.* produced hematite, maghemite, and magnetite using microwave assisted methods [51,52].

The microwave-assisted method was also used to synthesize biocompatible IONPs such as dextran coated and polyacid conjugated IONPs [53,54]. This method has added advantage that the nanoparticles prepared can be easily prepared with this method can be easily dispersed in water as compared to those prepared with thermal decomposition.

### 3.8. Electrochemical Methods

Electrochemical method of synthesis of IONPs involves adjustment of the current density from an electrode generally of iron to tailor the particle size. Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles have been prepared under oxidizing conditions using electrochemical deposition by Kahn *et al.* [55]. Iron electrode dipped in aqueous solution of dimethyl formamide and a surfactant was used for synthesis of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles by Pascal *et al.* [56].

### 3.9. Laser or Spray Methods

These methods have recently gained attention as they allow for higher rate of production. In spray methods, solution of salts of Fe(II) and

Fe(III), along with a reducing agent, is sprayed on reactors, where the solvent evaporate leaving behind solute particles which consist of particle whose size depends on the initial size of the droplet landed on the reactor. Julian-Lopez *et al.* synthesized hybrid silica-iron oxide microspheres through spray drying method [57].

Laser can also be used for heating the gaseous mixture of iron precursors to produce small and non-aggregated nanoparticles. Laser radiation is used for gas phase synthesis of nanoparticles. IONPs were obtained when Fe(CO)<sub>5</sub> and ethylene mixture were irradiated with laser and air was used as an oxidant [58].

### 3.10. Biosynthesis

The use of plant and microorganisms for the synthesis of nanoparticles has been the most attention seeking topic of the decade as they are non-toxic, easy, pollution free, and inexpensive alternative for the synthesis of nanoparticles in comparison to other techniques. The microbial enzymes in microorganisms and the phytochemicals present in the plants are responsible for the reduction and oxidation reaction involved in the formation of nanoparticles. IONPs can be prepared with the help of sucrose [59], *Ficus carica* (common fig) dried fruit extract [60], aloe vera and flaxseed extract [61], *Eucalyptus globulus* [62], *Eichhornia crassipes* [63], *Ruellia tuberosa* [64], *Avicennia marina* flower extract [65], *Hylocereus undantus* [1], and many more. Bharde *et al.* also reported the synthesis of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> using bacteria *Actinobacter* sp. and iron (III) chloride under aerobic conditions [66]. Recently, Sunadaram *et al.* also synthesized magnetite nanoparticles capped with biomolecules from rhizosphere soil bacteria *Bacillus subtilis* sp. and the process shows applicability for bulk synthesis [67].

The advantages and disadvantages of the above-mentioned methods are summarized in Table 1.

## 4. APPLICATION OF IONPS

The advantages of IONPs include high surface to volume ratio, superparamagnetic biocompatibility, better colloidal stability, better size control, and reproducibility. Moreover, they can easily be used for targeted applications using their magnetic properties. Some of the areas of applications of IONPs are mentioned below:

### 4.1. Catalysis

Catalysis is dependent on the number of active sites present on the surface area of catalyst. Surface of a catalyst must contain greater number of sites so that the reactants may easily undergo adsorption, reaction, and then desorption. In modern era, catalysts are generally in nanometric scale as they are more effective than conventional catalysts as they have higher surface area to volume ratio. The iron oxides have been used in number of catalytic reactions such as in the oxidation of styrene [68], thermal decomposition of ammonium perchlorate [69], hydrogenation of carbon dioxide to aromatic compounds [70], catalytic decomposition of hydrogen peroxide [71], production of biodiesel from castor oil [72], and production of hydrogen and oxygen, removal of carbon dioxide.

Iron oxides nanoparticles may have crystal defects which may be associated with a plane defect, line defect, or point defect. These defects attribute to different surface properties and play important role in chemical reaction as they help in electron transfer process [73].

### 4.2. Thermal Combustion

Iron oxides are added to propellants to increase combustion rate and its thrust-time curve. Therefore, playing an important role in tailoring

**Table 1:** Advantages and disadvantages of various methods of synthesis of iron oxide nanoparticles

Method of synthesis of iron oxide nanoparticles	Advantages	Disadvantages
Coprecipitation method	Simple and effective	Inappropriate for the synthesis of high untainted, precise stoichiometric phase
Thermal decomposition method	Uniformity particle size	Formation of side products and requirement of high amount of energy
Microemulsion method	No organic solvents involved and efficient control of the particle size	Requires high temperatures and critical pressure
Sol-gel or polyol method	Aspect ratio, precisely controlled in size, and internal structure	High permeability, weak bonding, low wear resistance
Flow Injection method	Homogeneity with high mixing with a accurate control of the procedure and good reproducibility	Under a laminar flow regime in a capillary reactor, it requires continuous or segmented mixing of reagents
Sonochemical method or sonolysis	Size distribution in narrow particle	Mechanism is not well understood
Microwave assisted synthesis	Narrow size distribution and uniform size	Ferrite colloids of small size
Electrochemical method	Controllable particle size	Inability to reproduce
Laser or spray method	Large-scale products	Requires very high temperatures
Biosynthesis	Good reproducibility and scalability, high yield, and low cost	Slow and laborious

the burn rate of propellants. Fujimura *et al.* studied the effect of particle size and surface is of iron (III) oxide catalyst on burning rate of hydroxyl-terminated polybutadiene (HTPB) containing ammonium perchlorate as an oxidizer and concluded that catalytic efficiency increases with increase in specific area of nanosized iron (III) oxide catalyst [74].

Ammonium perchlorate is the mostly commonly used oxidizer used in propellants. However, the decomposition mechanism is not fully understood as it is a complex mechanism and occurs in two decomposition stage. First, endothermic reactions occur between perchloric acid and ammonium forming products such as nitrogen monoxide, dinitrogen oxide, oxygen, and chlorine at a temperature below 623 K. Second, exothermic reactions occur with release of volatile products which take place above 623 K. The presence of hematite nanocatalyst alters the exothermic positions of higher temperature decomposition stage showing its catalytic effect [75]. The catalytic effect of IONPs on decomposition of ammonium perchlorate is due to proton transfer mechanism. However, iron oxide is subjective to aggregation and leads to decrease in active sites during exothermic reactions of ammonium perchlorate [76].

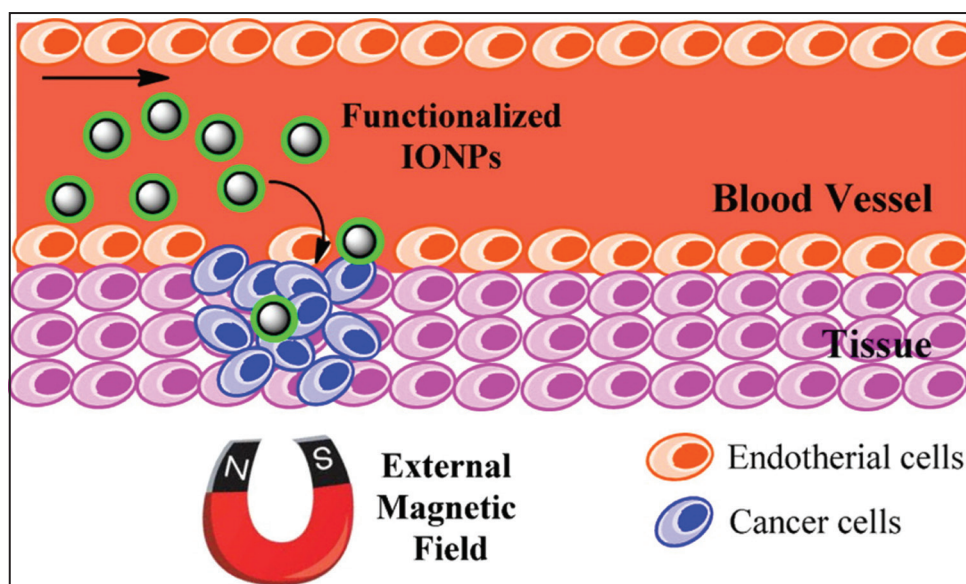
#### 4.3. Labeling and Imaging Agents

The use of IONPs as labeling and imaging agents may be attributed to the magnetic properties which are responsible for its targeted applications. Montet *et al.* used arginine -glycine-aspartic acid bind with IONPs for targeting BT-20 tumor and showed that nanoparticles can be targeted to cell surface in tumor cells [77]. Imaging studies were also performed with bare IONPs for labeling lymphocytes and leukocytes. MRI can be used for imaging at a resolution approaching the size of cell if the cell can be loaded with magnetic IONPs [78]. To increase the cell capacity, the IONPs are often combined with peptides, dendrimers, fragments of protein, folic acid, etc. A nanoparticle conjugate developed by binding methotrexate (MTX), a chemotherapeutic drug to IONPs, is a potential MRI contrast agent and a drug carrier for controlled drug delivery in cancer, as represented in Figure 3. The MTX-conjugated nanoparticles release drug under low pH conditions similar to the lysosome [79].

Similarly, IONPs functionalized with PVA were used for detection of neurodegenerative diseases. Amino-PVA functionalized IONPs were taken up by brain-derived microglial and endothelial cells and may be used of MRI detection of active lesions responsible for neurodegenerative diseases [80]. Hadjipanayis *et al.* developed IONPs binding with an antibody to detect mutant responsible for deletion of epidermal growth factor receptor present on glioblastoma multiforme cells. The results revealed that the survival of glioblastoma cell significantly decreases when conjugated nanoparticles bind to it and poses no toxicity to human astrocytes [81].

#### 4.4. Thermal Ablation and Hyperthermia

Hyperthermia is the preferential death of tumor cells by heating cells in the range of 41–47°C [82]. IONPs generate heat when an alternating magnetic field is applied in combination of internal magnetic moment fluctuations in the particle which is used in hyperthermia. On contrast, thermal ablation uses higher temperature than hyperthermia which is above 47°C. Thermal ablation causes rapid death of tumor cells. The problem faced in using these methods is the maintenance of lower temperature for normal tissues while heating the tumor part to higher temperature. For cancer therapy, localized hyperthermia is used, in which a small area is heated with the help of radio waves, ultrasonic waves, and microwaves [83]. A major challenge faced during thermal ablation and hyperthermia is the dosage of IONPs needed to maintain the heating rate required to obtain therapeutic temperature. To minimize the dosage and increase the heating rate, anisotropy or the monodispersity of the nanoparticles sample should be increased. Gonzales-Weimuller *et al.* showed the dependence of heating rate on the particle size of IONPs for magnetic hyperthermia [84]. The results showed that on increasing particle size, higher heating rates can be achieved. The hyperthermic effect can be increased by surface functionalization and decreasing thickness of surface coating. Inorganic coating such as gold coating used by Mohammed *et al.* increases the hyperthermic effect [85]. The gold coating on the IONPs increased the retention of superparamagnetism better than uncoated IONPs. Furthermore, the low-frequency magnetization field could possibly be used for hyperthermia if gold coated nanoparticles were used.



**Figure 3:** Schematic representation of magnetic nanoparticle-based drug delivery system. It shows how with the help of external magnetic field, magnetic carriers concentrate at the targeted site. After accumulation of magnetic carrier drugs are released from them which are effectively taken up by the tumor cells [34].

Therefore, IONPs can be used a promising hyperthermia agent but with further improvement by improving particle size, morphology, and reproducibility.

#### 4.5. Drug Delivery

The conventional way of drug delivery is based on taking the drug orally or intravascularly, and then, the drug is distributed throughout the human body. However, the affected organ takes up only small amount of drug due to distribution of drug throughout the body and reduced drug diffusion. Targeted drug delivery is essential to bring about the necessary therapeutic effect of the drug and for this magnetic iron nanoparticles are a promising agent. Functionalized magnetic IONPs can be used to carry the required drug to the affected organ. In general, the functionalization of nanoparticles is done with components that are biocompatible and can cross the biological barriers. For drug delivery, stability and surface properties are important for the drug to be efficient. The size of the functionalized nanoparticles so as to penetrate through cells without being removed by the renal activity. In addition, charge on the functionalized IONPs is also important as positively charged nanoparticle has a better uptake by human breast cancer cells than negatively charge nanoparticle. Adsorption of IONPs with a hydrophobic surface is easy [86]. S. Correia Carreira *et al.* reported the uptake of IONPs by human placenta and demonstrated the effect of size on toxicity and transport through placental barrier model [87]. Kebede *et al.* reported conjugated IONPs with chitosan functionalized with insulin and 51% reduction was seen in blood glucose level for different levels of diabetes [88]. Veisheh *et al.* showed that the external magnetic field hampers the response of drug functionalized magnetic IONPs [89]. Drug delivery by nanoparticles is also affected by factors such as temperature, pH, osmolality, type of target cell, functionalization group, and route of drug delivery. Different types of polymers and copolymers that can be used to functionalize nanoparticles used in drug delivery are represented in Figure 4.

#### 4.6. Biosensors

IONPs can be effectively used to sense biomolecules with high sensitivity and thus can diagnose diseases at an early stage. IONPs can act as magnetic relaxation switches (MRS) due to superparamagnetic core of individual nanoparticle. Perez *et al.* reported that mRNA,

pathogens, enzymes, and proteins can be detected with the help of MRS nanosensor with high sensitivity [90]. Functionalized IONPs bead-based nanoparticle can be used as detector or generator of signal and used for diagnosis of lactate, cholesterol, glucose, creatinine, and urea [91] and is represented in Figure 5.

IONPs with Glucose oxidase, gold, and carbon nanotube chitosan composite sensors have been developed with high accuracy, more sensitivity, and high stability. Recently, lysine modified monomer with 10, 12-pentacosadiyonic acid (Lys-PCDA) on IONPs was used to detect and capture serum proteins [92]. There are still challenges in use of magnetic IONPs as biosensors.

#### 4.7. Other Application

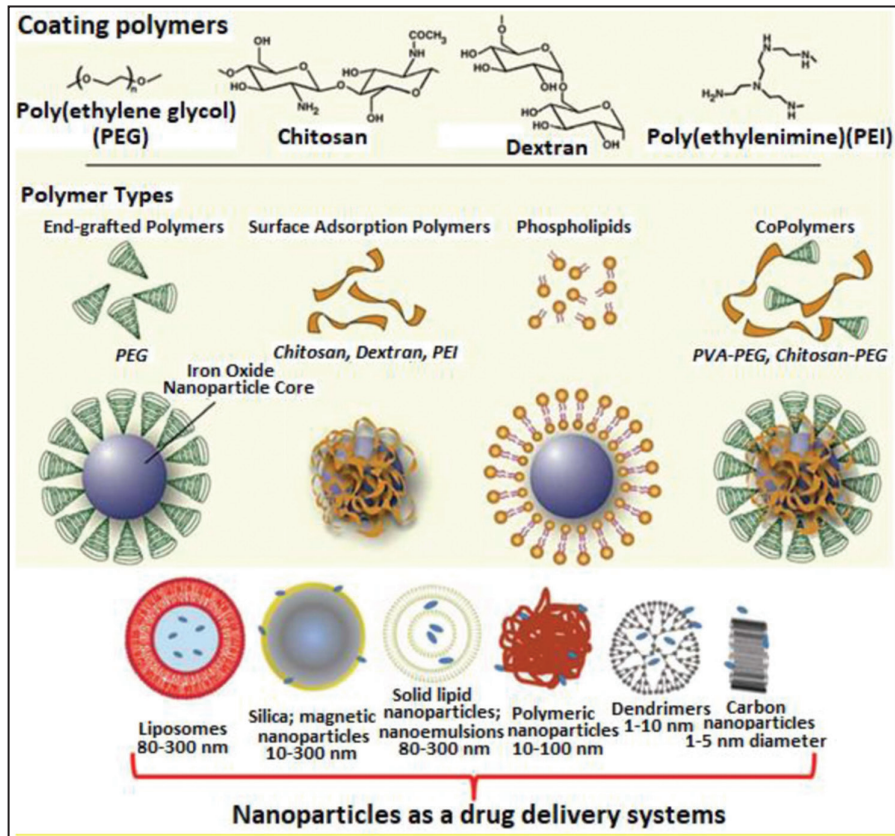
IONPs have also been used in fertilizers and pesticides. Furthermore, they have been used to increase crop yields in combination with carbon nanotubes [93]. IONPs have been used for seed treatment before seed sowing. They are known to increase breakdown of starch and produce larger number of leaves, more biomass, and changes in the leaf morphology. Precision farming with the help of magnetic farming has also been reported.

IONPs are also used in food related applications, where they are used in nanocoatings, packaging materials, nanofood [21], etc. They are also used in environmental related applications where they enhance waste water treatment, soil remediation, adsorption of gaseous pollutants and their decomposition, reducing wastes in manufacturing processes, energy saving by improving fuel efficiency, improvising fuel cells and batteries, solar panels, aerogels, thermoelectric materials [94,95], etc. IONPs are used in coatings of photovoltaic devices [17], construction materials, automobile additives, textile industries, defense and aerospace engineering, etc.

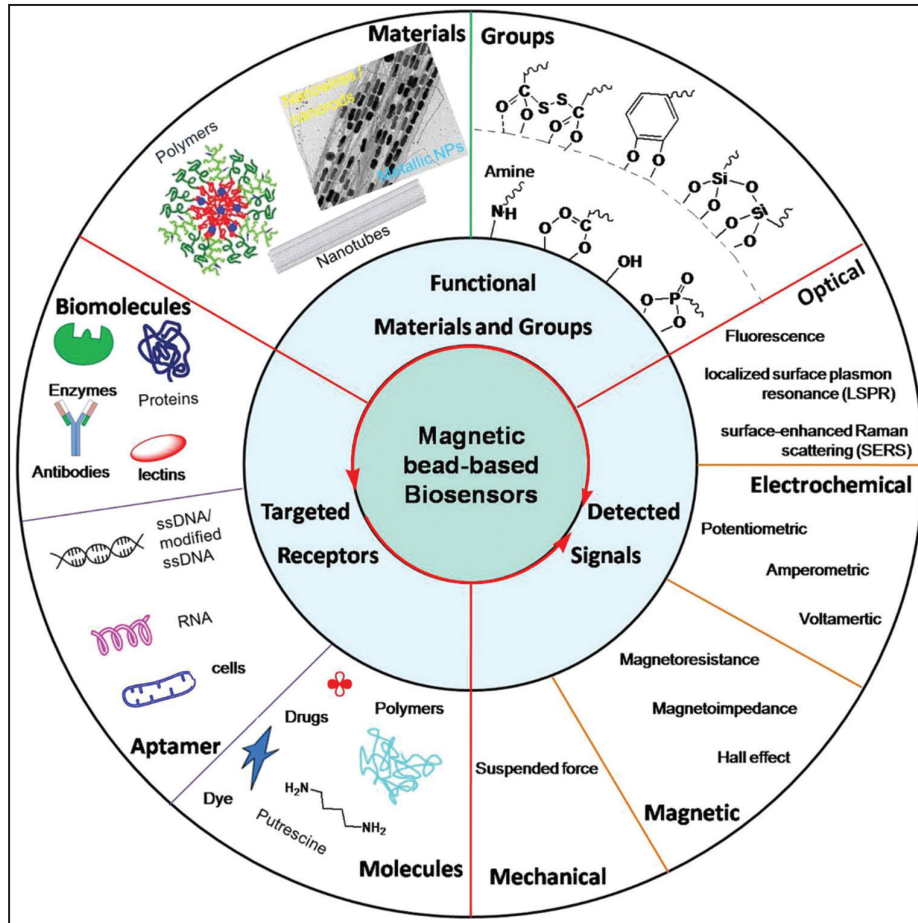
### 5. FACTORS CONTRIBUTING TO THE EFFICACY OF IRON OXIDE NANOPARTICLES OVER OTHER NANOPARTICLES

- The ways to obtain IONPs are simple, easy, and non-hazardous
- The preparation of IONPs is cost-effective and only involves higher cost of production when high end use is required as in drug delivery, imaging agents, and contrasting agents





**Figure 4:** Schematic representation of various types of polymers and copolymers that can be used for surface functionalization of nanoparticles in drug delivery system [89].



**Figure 5:** Type of magnetic bead-based biosensors and related information [34].

- IONPs have high surface to volume ratio that allows greater interaction with reactants or the group to be functionalized on the nanoparticle surface
- Shape, durability, scalability, reproducibility, growth, and nucleation of IONP can be controlled proving to be an added advantage in its application
- By tailoring the surface functionalization of IONPs, it can be used for selective adsorption of metals. Thus, can be used for remediation of metal ions from the environment
- High magnetic susceptibility makes IONPs an efficient material for the use in targeted applications
- These IONPs can easily be removed from the body by renal clearance, thereby an effective drug delivery system can be established using these nanoparticles
- The ability of IONP suspension to absorb oscillating magnetic field and convert it into thermal energy finds applications in hyperthermia and thermal ablation
- High coactivity, low Curie temperature, and excellent catalytic properties make IONPs first choice for the reaction, where a cheap catalyst is required.

## 6. CONCLUSION AND SUMMARY

To conclude, great progress has been achieved in the areas related to synthesis and applications of IONPs in various fields, of which some are enlisted above. However, much remains to be deciphered so as to achieve better control over size, morphology, nature, solubility, magnetic properties, compositions, monodispersity, and surface to volume ratio. A major challenge that is encountered during the synthesis is the variation in particle size distribution and dispersity in solvents as IONPs are hydrophobic in nature. These problems can be dealt by better synthesis methods and conjugation with other materials mainly of organic origin so that the nanoparticles can be used for applications related to diagnosing, imaging, labeling, and other medical applications which are the need of the hour. The future perspective related to IONPs is to develop greener methods of synthesis that should have more greener applications as the toxicity related to nanoparticles is the concern.

## 7. CONFLICTS OF INTEREST

No conflicts of interest were present between the authors.

## 8. ACKNOWLEDGMENTS

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