

Review

# New Perspectives on Iron-Based Nanostructures

Seyedeh-Masoumeh Taghizadeh <sup>1,2</sup>, Aydin Berenjian <sup>3,\*</sup>, Marziyeh Zare <sup>4</sup>  
and Alireza Ebrahimezhad <sup>5,\*</sup>

<sup>1</sup> Biotechnology Research Center, Shiraz University of Medical Sciences, Shiraz 71468-64685, Iran; taghizm@sums.ac.ir

<sup>2</sup> Department of Pharmaceutical Biotechnology, School of Pharmacy and Pharmaceutical Sciences Research Center, Shiraz University of Medical Sciences, Shiraz 71468-64685, Iran

<sup>3</sup> School of Engineering, Faculty of Science and Engineering, The University of Waikato, Hamilton 3240, New Zealand

<sup>4</sup> Department of Molecular Medicine, School of Advanced Medical Sciences and Technologies, Shiraz University of Medical Sciences, Shiraz 71336-54361, Iran; taghizm@yahoo.com

<sup>5</sup> Department of Medical Nanotechnology, School of Advanced Medical Sciences and Technologies, Shiraz University of Medical Sciences, Shiraz 71336-54361, Iran

\* Correspondence: aydin.berenjian@waikato.ac.nz (A.B.); a\_ebrahimi@sums.ac.ir (A.E.)

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**Abstract:** Among all minerals, iron is one of the elements identified early by human beings to take advantage of and be used. The role of iron in human life is so great that it made an era in the ages of humanity. Pure iron has a shiny grayish-silver color, but after combining with oxygen and water it can make a colorful set of materials with divergent properties. This diversity sometimes appears ambiguous but provides variety of applications. In fact, iron can come in different forms: zero-valent iron (pure iron), iron oxides, iron hydroxides, and iron oxide hydroxides. By taking these divergent materials into the nano realm, new properties are exhibited, providing us with even more applications. This review deals with iron as a magic element in the nano realm and provides comprehensive data about its structure, properties, synthesis techniques, and applications of various forms of iron-based nanostructures in the science, medicine, and technology sectors.

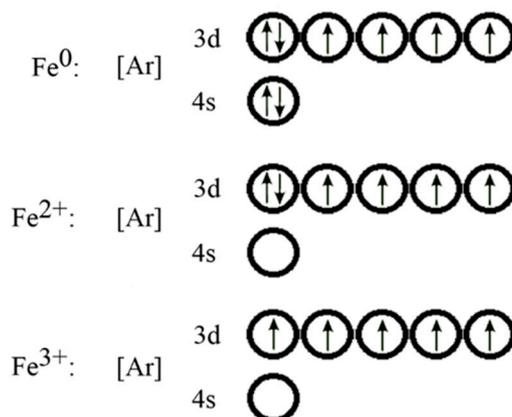
**Keywords:** Fe nanomaterials; Fe nanoparticles; ferric; ferrous; iron ores; synthesis methods

## 1. Introduction

Iron, in terms of mass, is the most abundant element on Earth. This element is an important constituent of the earth's outer and inner cores, and the fourth most important element in the earth's crust. Among all minerals, iron is one of the early elements identified by the human beings to be taken advantage of and used. It made an era in the ages of humanity; namely, the Iron Age is identified as the final epoch of the three-age division of the prehistoric ages. This came after the Bronze Age, when the human beings reached superior strength and hardness in tools and weapons by iron. In fact, the age of iron did not come to an end, but developed until the 21st century life. The United States of America alone produced ~49 million metric tons of iron ore in 2018. This number is larger for the world's largest iron ore mine producers, with Australia and Brazil, countries which produce 900 million and 490 million metric tons, respectively [1].

Pure metallic iron is rarely found on the lithosphere because, in the presence of oxygen and moisture, it will cause it to readily oxidize. In order to obtain metallic iron, oxygen must be removed from natural ores by reduction. From a chemical point of view, iron, with the chemical symbol "Fe" (from Latin: *ferrum*), is an element with an atomic number of 26, and is located in the first round of the transition metals. It is also the head of ferromagnetic materials. The D orbital of iron ([Ar] 3d<sup>6</sup> 4s<sup>2</sup>)

is not totally full (Figure 1) and can have different oxidation states. The most important states of iron oxidation are ferrous ( $\text{Fe}^{2+}$ ) and ferric ( $\text{Fe}^{3+}$ ). Ferrous iron links to sulfur and nitrogen ligands as well as oxygen ligands. Ferric iron tends to react to hard ligands, such as oxygenated ligands. The most common coordination number for iron (II) and iron (III) is six, which has an octagon spatial arrangement. Furthermore, for ferrous/ferric iron, there is also a tetrahedral arrangement (a coordination number of four), and also a square pyramid or a trigonal bipyramid (especially in a complex coordination of five).



**Figure 1.** Orbital diagram for iron and iron ions.

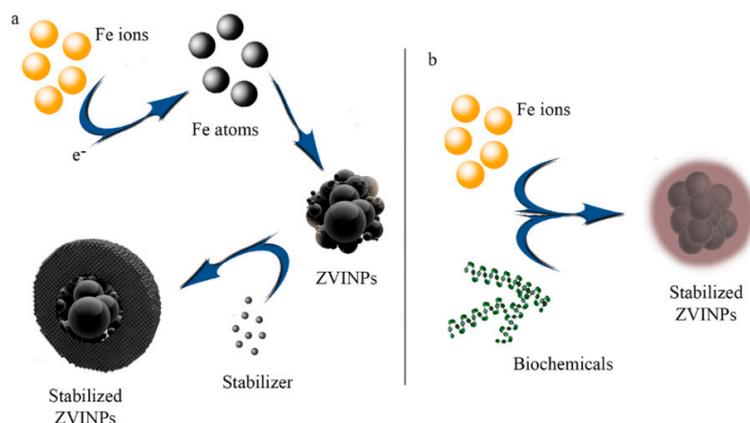
Iron has a shiny grayish-silver color but after combination with oxygen and water can make various forms of iron oxide, iron oxide hydroxide, and iron hydroxide. This diversity sometimes appears ambiguous but provides a colorful array of materials with divergent properties and applications. By taking this color pen set to the nano realm, it provides us with even more colors. The current review is dealing with this magic element and provides a wide view of iron, iron oxide, iron oxide hydroxide, and iron hydroxide in the nano realm.

## 2. Zero-Valent Iron

The appearance of pure iron ranges from silver to black or gray and has a metallic sheen with ferromagnetic properties. Pure iron is not used in the industry because of its softness and lack of sturdiness. Iron is usually used along with nonmetal elements (carbon, sulfur, phosphorus, and silicon), and sometimes with other metals (chromium, nickel, vanadium, and molybdenum) in alloy form, where the resultant product would be steel or cast iron. The cheap price and high strength of iron alloys have commoditized their use in the automotive industry, the hull of large ships, and buildings. Nanoparticles of pure iron are known as zero-valent iron nanoparticles (ZVINPs) and are usually synthesized by chemical reduction of iron ions [2]. In this manner, reducing agents, such as sodium borohydride or hydrazine, are used to reduce iron ions to iron atoms and subsequently iron atoms aggregate and form ZVINPs [3,4]. In addition to chemical reducing agents, some biochemical species are also able to reduce iron ions, and hence can be employed for the bio-reduction of iron ions to ZVINPs [5,6]. In comparison to chemical reduction reactions, in the bio-reduction reactions, no additional molecule is required to stabilize nanoparticles. Biologic molecules are sufficient for both the reduction and protection of the prepared particles [5,7–9]. However, when chemical reducing agents are employed, a second protective molecule is required to stabilize the particles (Figure 2).

Generally, ZVINPs are unstable and tend to oxidize and hydrate iron into oxides and iron hydroxides (4). In fact, ZVINPs usually exhibit the dual characteristics of iron ( $\text{Fe}^0$ ) and iron oxides or hydroxides. This feature is due to oxidation of exposed iron atoms on the surface of particles and the formation of an iron oxide/hydroxide shell around the zero-valent core (see Section 4.1.3) [2,7–9]. In order to prevent the oxidation reactions and maintain the properties of ZVINPs, coating with noble metals can be used. For instance, ZVINPs with gold or silver coating are effective in the treatment of cancer, and can

suppress the growth of cancer cells while possessing adequate biocompatibility with nonmalignant cells [10,11]. Minerals are the other applicable material to protect zero-valent iron nanoparticles. For instance, montmorillonite, which is a clay mineral, has been used as an effective protective agent and support [2]. In some investigations chelating agents, such as diethylenetriaminepentaacetic acid (DTPA), were used as a stabilizer for ZVINPs [7]. Biologic compounds were also shown to be effective for protection from oxidation. These compounds can make a thick coating around the particles and protect them from oxidation. It has been shown that by using biologic coatings any detectable iron oxides can be formed on the particles [5,12].



**Figure 2.** Chemical (a) and biological (b) reduction of iron ions to zero-valent iron nanoparticles (ZVINPs) and their stabilization.

ZVINPs gained diverse applications in environmental sciences and remediation proposes. These nanoparticles are used to remove arsenic from contaminated aquatic environments [13,14]. Extensive lab studies have shown the potency of these nanoparticles in the adsorption and degradation of halogenated hydrocarbons, such as trichloroethylene (TCE) [15]. These nanoparticles are also effective against pesticides, transition metals, organic dyes, and radioactive contaminations [7,16–18]. ZVINPs can also act as an antimicrobial agent which have a better performance in the absence of oxygen. The antimicrobial activity of these nanoparticles against *Escherichia coli* has been studied under anaerobic and aerobic conditions. In the absence of oxygen, when *E. coli* is exposed to 9 mg/L of iron nanoparticles for 10 min, bacterial cells were effectively disabled. In aerobic conditions, when the bacteria were exposed to 90 mg/L of iron nanoparticles for 90 min, the antimicrobial effects were negligible, since, in the presence of oxygen, ZVINPs are oxidized [19].

### 3. Iron Oxides

In the presence of oxygen and humidity, iron easily combines with oxygen and transforms to iron oxides. Iron oxides are widespread in nature and can be found in soil, rocks, lakes, rivers, seafloors, and even in living creatures [20]. Generally iron oxides receive much attention from scientists and researchers because of the variety in their physical and chemical properties. Iron reacts with oxygen in various states and therefore can be found in diverse chemical formulas with different properties as described in the following.

#### 3.1. Ferrous Oxide (FeO)

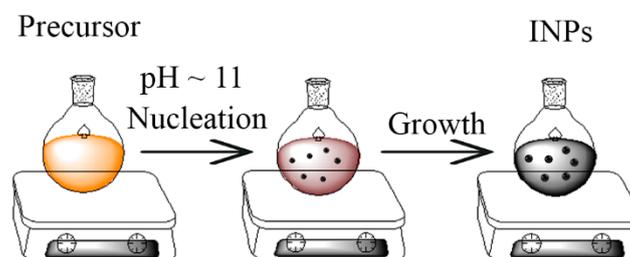
Fritz Wüst, a German metallurgist (1860–1938), named iron (II) oxide (ferrous oxide, Fe=O, Figure S1) as wüstite. It is a gray-black ore with a greenish shade. The FeO formula is not exactly correct because wüstite is a typical non-stoichiometric mineral. In this mineral the amount of iron is always less than the stoichiometric ratio, and there is no temperature at which a one-to-one ratio can be seen between iron and oxygen. In fact, there is deficient iron in the structure with compositions

ranging from  $\text{Fe}_{0.84}\text{O}$  to  $\text{Fe}_{0.95}\text{O}$  ( $\text{Fe}_{1-x}\text{O}$ ) [21]. It has an isometric (cubic) crystal system and has anti-ferromagnetic properties [22].

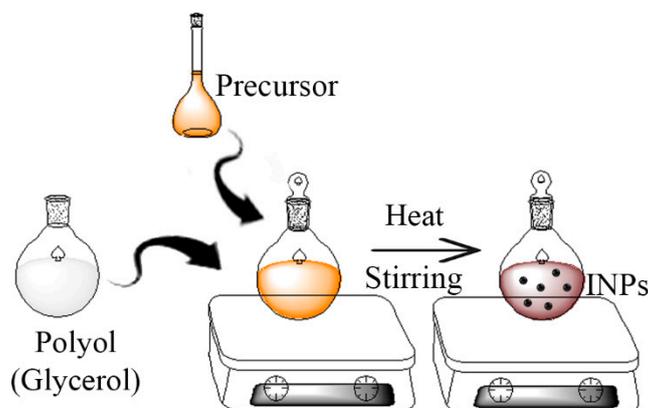
The most common methods for preparing wüstite nanoparticles are co-precipitation (Scheme 1), polyol method (Scheme 2), pyrolysis (thermal decomposition) of organometallic compounds (Scheme 3), micro emulsion, hydrothermal (Scheme 4), and sol-gel synthesis (Scheme 5) [23]. Among these methods, thermal decomposition of iron (II) or iron (III) complexes is the most employed technique [22,24,25]. wüstite nanoparticles can also be fabricated by physical approaches, such as ball milling, using a mixture powder of hematite and iron [26]. The main challenge in all the above-mentioned methods for preparing wüstite nanoparticles is to achieve nanoparticles with controlled size, shape, and composition [23].

Wüstite nanoparticles are semi-stable, and are therefore used in the creation of mixed phase nanoparticles [27]. Moreover, in order to create stability in wüstite nanoparticles, they are covered with organic ligands. In another approach, wüstite nanoparticles can be doped with other divalent metals (Dm), such as cobalt and magnesium, to fabricate  $\text{Dm}_{(x)}\text{Fe}_{(1-x)}\text{O}$ . These structures can be synthesized by the thermal decomposition of  $\text{DmFe}$  organometallic complexes or by solution-combustion methods [28,29]. The surface of the doped wüstite nanoparticles is oxidized to  $\text{DmFe}_2\text{O}_4$  and form a shell to protect the core from oxygen transmission. The thickness of the oxidized shell can be tuned through a controllable oxidation process and has significant effects on the core/shell ratio and exchange bias properties. For instance, it has been shown that a shell of  $\text{CoFe}_2\text{O}_4$  with 4 nm thickness is ideal for resistance to oxygen transmission [29].

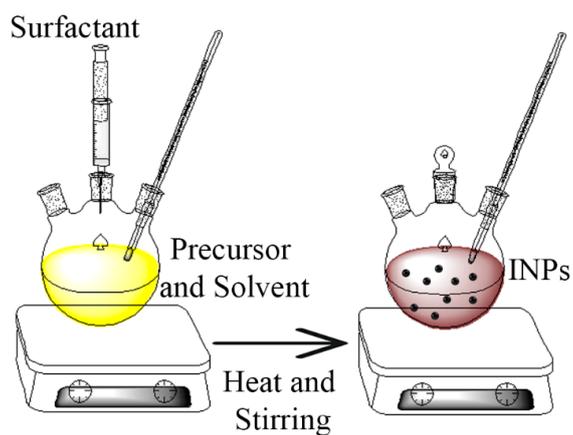
From application point of view, there are reports for the antimicrobial properties of wüstite nanostructures. It has been shown that the nanochains of carbon coated wüstite nanoparticles can kill bacterial cells within a short incubation time at minimal dosages [30]. Wüstite nanoparticles can be applied as radiation filters. Glasses with thin films of  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  nanoparticles are used as solar radiation filters. These filters are applicable on the building windows to prevent heat transmittance while visible light is passing through [31].



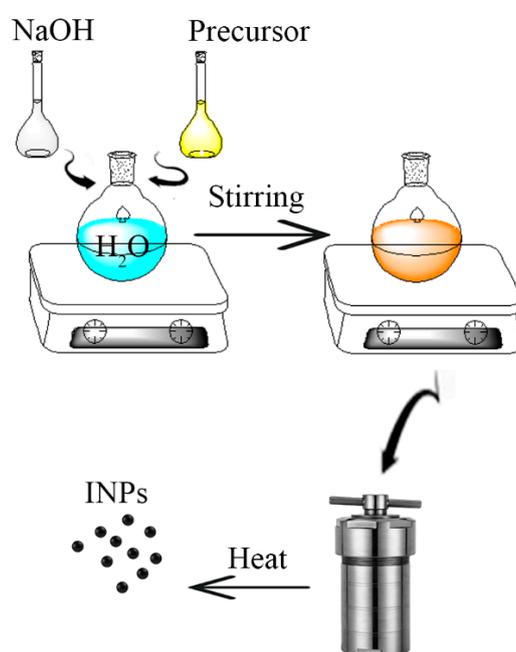
**Scheme 1.** Schematic illustration of a common precipitation reaction, INPs stands for iron nanoparticles.



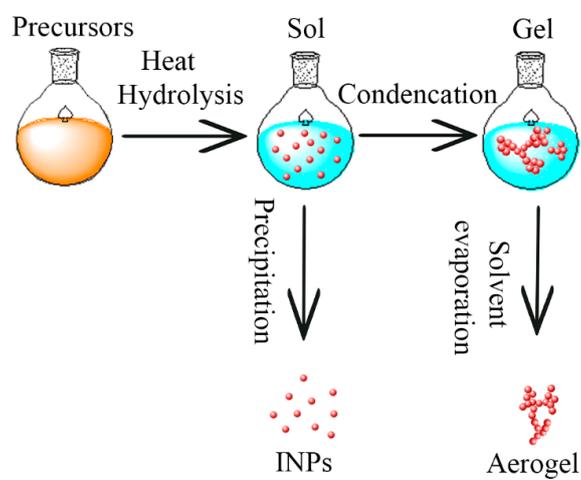
**Scheme 2.** Schematic illustration of a polyol reaction.



**Scheme 3.** Schematic illustration of a pyrolysis reaction.



**Scheme 4.** Schematic illustration of hydrothermal synthesis reaction.



**Scheme 5.** Schematic illustration of a sol-gel reaction.

### 3.2. Ferric Oxide (Fe<sub>2</sub>O<sub>3</sub>)

As its name indicates, ferric oxide is the oxide of iron (III) (O=Fe–O–Fe=O, Figure S1). This form of iron oxide is well-known as rust and can be found in red and brown. Ferric oxide is the result of dehydration reaction of FeO(OH) and Fe(OH)<sub>3</sub> at temperatures above 200 °C (Equations (1) and (2)). It can be found in its hydrated (see Section 3.2.2) or anhydrous forms. In the following we made a detailed reviews on the various phases of anhydrous ferric oxides.



#### 3.2.1. Anhydrous Ferric Oxides

Anhydrous forms of ferric oxide can be found in different polymorphs, such as alpha (α-Fe<sub>2</sub>O<sub>3</sub>), beta (β-Fe<sub>2</sub>O<sub>3</sub>), gamma (γ-Fe<sub>2</sub>O<sub>3</sub>), and epsilon (ε-Fe<sub>2</sub>O<sub>3</sub>). These minerals are the same in chemical structure but have differences in their crystal systems [32].

##### Hematite (α-Fe<sub>2</sub>O<sub>3</sub>)

The word hematite is taken from the Greek word hematicos, which means bloody. The chemical reaction to get hematite from magnetite is shown in Equation (3). Hematite is a widespread iron oxide and can be found in rocks and soil. It is the oldest known ore of iron that has ever formed on the Earth.



Hematite has a rhombohedral and hexagonal crystal system, and its crystal habit can be seen as either spindle, bar, oval, square, or spherical. It has a red metallic appearance. Hematite has different forms, but all forms have a red sheen. Hematite iron deposits are most significant in the steel industry and in the preparation of cast iron. This mineral is one of the precious rocks, and the fine cuts of its black crystals are used in making jewelry. Moreover, its powder is used in pigments, such as red pigment 22 and antirust [20].

The most common ways to produce hematite nanoparticles are chemical precipitation, the polyol process, pyrolysis of organometallic compounds, micro emulsion, hydrothermal synthesis, and sol-gel process [23,33,34]. These nanoparticles can also be obtained by calcination of mixtures of iron oxide nanoparticles at high temperatures (about 500 °C) [35]. Biosynthesis (plant mediated synthesis) is another route, in fact, a green route, for fabrication of hematite nanoparticles [36]. These particles can be fabricated by using various plants, such as root extract of *Arisaema amurense* [37], Tragacanth gel [38], *Citrus reticulum* peels extract [39], the extract of green tea leaves (*Camellia sinensis*) [40], *Ailanthus excelsa* [36], and guava (*Psidium guajava*) [41].

Hematite nanoparticles are the most stable iron nanostructure in the ambient conditions and have size and shape-dependent magnetic properties. The magnetic saturation is in direct relation to particle size, and by increasing the size, an increase in the magnetic saturation value can be observed. On the other hand, it has been shown that spherical nanoparticles have the highest magnetic saturation, while cubic and ellipsoidal nanoparticles are ranked in the next positions, respectively [42]. These nanoparticles can exhibit ferromagnetism or superparamagnetic behavior at room temperatures. However, in contrast to magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles, saturation magnetization values of hematite nanoparticles are very low [43]. These nanostructures have gained applications in the development of electrochemical devices, as cathode in lithium batteries, the fabrication of photo electrochemical systems to produce hydrogen from water using solar radiation, as photo reactive nanomaterial for the enhanced performance of photoelectrochemical cells, and as reusable catalysts [23,40,44]. These nanoparticles can be employed for the enhancement of the thermal conductivity of the base fluids in nanofluidic systems [41]. Hematite nanoparticles have a high capacity for metal ions' removal from aqueous

solutions. These particles can be employed for metal cations removal from acid mine drainage. It has been shown that hematite nanoparticles can completely remove aluminum, magnesium, manganese, and iron ions, while zinc and nickel ions remove over 80% and sodium and calcium ions remove up to 72% [35]. Hematite nanostructures are also able to decontaminate aqueous systems from different organic pollutants and can be used as an effective material in fertilizers fabrication [39]. The surface modification of hematite nanoparticles with the organic functional groups makes these particles more biocompatible and suitable to treat the chlorosis in plants, such as *Glycine max* [45].

#### Beta-Fe<sub>2</sub>O<sub>3</sub> ( $\beta$ -Fe<sub>2</sub>O<sub>3</sub>)

$\beta$ -Fe<sub>2</sub>O<sub>3</sub> is a scarce form of iron (III) oxides. This polymorph is a metastable phase and easily transformed into the more stable alpha ( $\alpha$ -) phase of ferric oxide. The transformation occurs at high temperatures, above 500 °C, but the mechanism of transformation and the changes which occur in crystal structure are, as yet, unclear. In fact, the exact crystal structure of the  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> is not defined, and this is due to difficulties in obtaining a  $\beta$  phase in pure monophasic crystals [46].  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> was discovered in 1958 and believed to have a cubic body centered crystal structure [47]. However, techniques for the fabrication of  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures have been developed and these structures can be obtained via simple chemical reactions. Solid state reaction is one of the most common techniques for the fabrication of  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, where NaFe(SO<sub>4</sub>)<sub>2</sub> is used as the precursor. In brief, a solution mixture of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> is evaporated in an oven at ambient atmosphere to obtain NaFe(SO<sub>4</sub>)<sub>2</sub>. The resulting powder is then fully grounded and mixed with NaCl, in a 1:2 ratio, and heated up to 400–500 °C in a muffle furnace. After cooling, the product should be dispersed in distilled water and washed to remove NaFe(SO<sub>4</sub>)<sub>2</sub> and Na<sub>3</sub>Fe(SO<sub>4</sub>)<sub>3</sub> [46,47]. In addition, colloidal  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures can be fabricated by hydrolysis of ferric ions in boiling water. The shape of prepared nanostructures can be controlled by the employing cobalt ions (Co<sup>2+</sup>). It has been shown that spherical and rod nanoparticles can be obtained in this order [48].

Water splitting and hydrogen production is one of the most promising approaches to overcoming the global energy crisis. Water splitting can be performed via photoelectrochemical reactions which employ ferric oxide nanoparticles as the photoanode material. Due to availability, photochemical stability, and high efficiency for light absorption, in the past decades, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) has been envisioned as a strong semiconductor photocatalyst. However, there are some obstacles with hematite. For instance, its low conductivity reduces the photoelectrochemical activity and there are also some other defects, such as large over potential and short hole transport distance. Recent studies introduced  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> as a more promising phase for light assisted water splitting.  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> has a smaller band gap than hematite and therefore is more efficacious in light absorption and photoelectrochemical reactions [47].

#### Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>)

Maghemite is the second most abundant form of ferric oxide. It has a cubic and tetragonal crystal system and its crystal habit is cube, plate, or spindle in shape. The color of maghemite is brown or reddish brown. Its combination is metastable and at high temperatures (about 500 °C), it turns into the alpha phase. Maghemite has ferrimagnetic properties and its nanoparticles show superparamagnetic properties [49,50]. The most common techniques for maghemite nanoparticles production are co-precipitation, polyol process, micro emulsion, hydrothermal synthesis, sol-gel process, and the pyrolysis of organometallic compounds [23]. These particles can also be obtained by the oxidation of magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles via thermic treatments [50–52]. The conversion of magnetite to maghemite can also be seen on the surface of magnetite nanoparticles that forms a core-shell structure of magnetite-maghemite [53]. To improve the properties of the prepared nanostructure, the surface of the maghemite, nanoparticles can be functionalized using divergent biocompatible compounds, such as amino acids, fatty acids, silica, and hydroxyapatite [52]. Surface modifications were also done by multiwall carbon nanotubes (MWCNTs) and ethylenediaminetetraacetic acid (EDTA) [52].

Even polymeric materials have been used [54–56]. Doping is another approach to improve the properties and functionalities of maghemite nanoparticles. For instance, these nanoparticles can be doped with rare-earth elements, such as yttrium [57]. On the other hand, maghemite nanoparticles themselves can be used for the decoration of other nanostructures, such as carbon nanotubes. Maghemite nanoparticles decorated on carbon nanotubes have been used for the fabrication of oxygen evolution reaction (OER) electrocatalysts [58]. Also, maghemite nanoparticles are used in magnetic recording media, biocompatible magnetic fluid production, and electrochromic devices [23].

The other well studied application of maghemite nanoparticles is in the environmental sciences. These nanoparticles are efficient to remove heavy metals, such as uranium [56], hexavalent chromium ions [59,60], copper(II), and lead(II) ions [52], from aqueous systems. Maghemite nanoparticles are so promising in this field that they can clean up contaminated water to drinking water standards [60].

Like hematite nanoparticles, maghemite nanoparticles can also be used in fertilizer formulations. In contrast to chelated irons, employment of maghemite nanoparticles in plant fertilizers resulted in more improved agronomic properties such as growth rate of leaves and chlorophyll content [57]. Also, maghemite nanoparticles can improve plants' abiotic stress tolerance. Delivery of maghemite nanoparticles by irrigation in a nutrient solution to plants resulted in a significant reduction of hydrogen peroxide and malondialdehyde formation. These effects were discussed as nanozyme properties of maghemite nanoparticles [57].

Maghemite nanoparticles have been approved by the FDA to be employed in medical and pharmaceutical sciences [61,62]. These nanoparticles can be used for theranostic applications [63]. Nanostructures of maghemite can illustrate the high values of magnetic saturation (near or equal to magnetite nanoparticles) that makes them ideal for biomedical magnetic applications, such as magnetic labeling, magnetically guided deliveries, and hyperthermia therapies [51,63–65]. For instance, it has been shown that by using 10 nm maghemite nanoparticles an increase in the temperature of up to ~50 °C is possible [51]. Maghemite nanoparticles are also a promising candidate for the fabrication of dual functional nanostructures. Fluorescent magnetic nanoparticles are one of them. In an experiment rhodamine isothiocyanate (RITC) is covalently encapsulated within maghemite nanoparticles and used for cell labeling. These nanostructures were found to be pH sensitive and introduced as a pH sensor for animal tissues and cell compartments [66]. In another experiment rhodamine was used for labeling a maghemite–albumin nanohybrid to combine targeting by the iron-acquisition pathway and photothermal therapies [67].

Maghemite nanoparticles can be employed in magnetofection techniques. Nanoparticles with efficient coatings, such as dendrimers, can couple fragments of DNA and take them into the cell under magnetic stimulus [68].

Drugs can also be delivered by these nanoparticles. In an attempt to fabricate a potential drug carrier, maghemite nanoparticles were functionalized with divergent molecules, such as human serum albumin (HSA), aminobenzoic acid, poly (ethylene imine) (PEI), and poly (ethylene oxide)-block-poly(glutamic acid) (PEO–PGA) [69–71]. Maghemite nanoparticles were also employed for the fabrication of multi stimuli-responsive smart nanogels. By combining thermo-responsive polymers, such as poly (vinyl alcohol)-*b*-poly(*N*-vinylcaprolactam) copolymers with maghemite nanoparticles, an innovative drug delivery system was obtained that is glucose-, pH-, thermo-, and magnetic-responsive. In addition, the magnetic properties of the maghemite nanoparticles make nanogel effective for magnetically-induced heating and magnetic resonance imaging (MRI) performance [72].

Maghemite nanoparticles can be used as a high sensitivity magnetic biosensor. In an experiment, it has been shown that, based on the giant magneto-impedance (GMI) effect, MAT-LyLu cells that grow in the presence of 0.1 mg/mL nanoparticles for 24 h make detectable modifications in the magnetic field at 1 MHz frequency [65].

Beside all the mentioned applications, maghemite nanoparticles have gained applications in tissue engineering and biologic scaffolds preparation. The inclusion of these nanoparticles in the scaffolds'

polymer network resulted in the significant improvement in physical and chemical characteristics of the prepared scaffolds. It has been shown that gradual increase of nanoparticle concentration in the polymer network significantly increases the polymer's hydrophilicity, water swelling, Young modulus (mechanical stiffness), effective viscosity, and negative value of electrical potential [73,74]. Maghemite nanoparticles also improve biologic properties of the scaffolds. Polymers imbedded with maghemite nanoparticles pose increased biocompatibility and cell adhesion index [73]. It has been shown that addition of maghemite nanoparticles to the scaffolds can increase initial cell adhesion by 1.4-fold, enabling earlier cellular proliferation confluence [74]. In some cases, doping with maghemite nanoparticles provides scaffolds with specific advantages for particular tissues. For instance, the application of these nanoparticles in scaffolds for bone repair and regeneration resulted in higher mineral induction [74]. In regard to skin repair, nanoparticle-doped scaffolds provide a higher cell proliferation rate for human skin fibroblast cells [75]. Maghemite nanoparticles were also used for tissue engineering a heart valve to obtain the required properties of an aortic heart valve. Fabricated materials using this technology are desirable scaffolds for human aortic smooth muscle cells migration and proliferation. In addition, these scaffolds provide a mutual adaption in terms of clotting time and hemolysis percent [76].

#### $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub>

$\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> has an orthorhombic crystal system and shows properties between the alpha and gamma phases [32,77]. The  $\epsilon$ -polymorph of Fe<sub>2</sub>O<sub>3</sub> is unique due to its significant ferromagnetic resonance and coupled magnetoelectric features that cannot be found in any other phases [78]. This compound is metastable and at temperatures from 500 °C to 750 °C it turns into hematite (alpha phase). The preparation of the pure epsilon phase is also very challenging due to the contamination with alpha and gamma phases. There are some techniques to achieve a high proportion of epsilon phase [79]. However, the optimal reaction condition to achieve single-phase  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> remains as a challenge for the future [78]. Recent studies have shown that this compound was used in the glazing of ceramics in ancient China [20]. Rod-shaped  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> with a large coercive field were used in a mesoscopic ferrite bar magnet which can be used as a probe in magnetic force microscopes [80].

#### Zeta-Fe<sub>2</sub>O<sub>3</sub> ( $\zeta$ -Fe<sub>2</sub>O<sub>3</sub>)

As mentioned in detail previously, there are four well-known polymorphs for ferric oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub>), which are similar in chemical structure but differ in crystal structures and, hence, physical properties. However, in 2015, via synchrotron X-ray diffraction experiments, a new phase was introduced for ferric oxide. It evolved from cubic  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> during a high pressure (above 30 GPa) treatment and was termed zeta-Fe<sub>2</sub>O<sub>3</sub> ( $\zeta$ -Fe<sub>2</sub>O<sub>3</sub>). After pressure release the structure was retained and was stable at an ambient atmosphere. The structure was also stable at high pressures up to 70 GPa, which is above the pressures that induced phase transfer in other ferric oxide phases. This structure shows antiferromagnetic properties with ~69° K Neel transition temperature. The discoverers claimed that this novel phase may have unique physicochemical properties that would lend it particular applications [81].

#### 3.2.2. Hydrous Ferric Oxide (Ferrihydrite)

Hydrous ferric oxide or ferrihydrite is one of the well-known iron compounds with a 5Fe<sub>2</sub>O<sub>3</sub>·9H<sub>2</sub>O chemical formula. However, there are also other reported formulas such as Fe<sub>5</sub>HO<sub>8</sub>·4H<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub>·2FeO(OH)·2.6H<sub>2</sub>O [82,83]. The indeterminate chemical formula of ferrihydrite is due to the variability of the content of combined water. Ferrihydrite has a hexagonal crystal system (hcp) and a spherical habit crystal. Based on the constitutive crystallites, ferrihydrite can be considered between two diffraction end-crystalline structures which are described as two- or six-line ferrihydrite. This nomination is based on the number of scattering bands in their X-ray diffraction patterns.

It is interesting that ferrihydrite can just be found in the nature as nanocrystals in a dark brown or reddish brown color [20,83]. It is a widespread mineral on the Earth and can be found in soil and sediments of hot springs, marine environments, and fresh waters. In these environments ferrihydrite nanostructures precipitate by the oxidation of aqueous Fe(II) solutions that contain dissolved organic matter. The oxidation occurs at neutral pH and it is obvious that presence of organic compounds significantly affects the crystallinity of the resulted nanostructures [84,85]. Ferrihydrite can be mineralized as nanoparticles in the ferritin protein of animals, plants, and microorganisms, where it is utilized in intracellular iron storage [86]. It has been shown that crystalline and amorphous ferrihydrite nanoparticles in the size range of 3–6 nm can be assembled within ferritin [87]. Some microbial cells are also able to mineralize ferrihydrite nanostructures on the cell surface. The structure is mostly nanostructured polysaccharide-iron hydrogel and produced under microaerophilic conditions. Nanostructures which are produced by the bacterium *Klebsiella oxytoca* are one of the well-known and studied mineralize ferrihydrite nanostructures. This iron reducing bacterium (FeRB) is able to ferment ferric citrate under microaerophilic or anaerobic conditions and produces a Fe(III)-hydrogel [88–91]. Other bacterial cells, such as *Staphylococcus warneri*, *Xanthomonas campestris*, and *Ralstonia* sp., were also reported to be able to fabricate an Fe(III)-binding exopolysaccharide and develop polysaccharide-iron nanostructures [92–94]. Synthetic ferrihydrite nanoparticles can also be prepared chemically. The reaction can be performed at ambient atmosphere by adding an alkaline solution (NaOH) to the solution of ferric ions (e.g., ferric nitrate,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , or ferric chloride,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) under constant stirring [95,96].

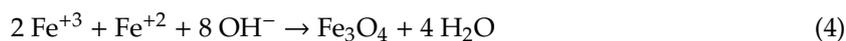
Both synthetic and biologic ferrihydrite nanostructures exhibit weak magnetic (paramagnetic) behavior. Low magnetic response beside good contrasting properties and biostability make the ferrihydrite a valuable contrasting agent for MRI imaging [97]. However, there are some techniques to improve the magnetic moment of ferrihydrite nanoparticles. It has been shown that the heat treatment of ferrihydrite nanoparticles at low temperatures (about 160 °C) enhances the average magnetic moment of biosynthesized nanoparticles. It is claimed that an enhanced in magnetic moment can be due to the partial agglomeration of nanoparticles throughout heat treatment process [98].

Ferrihydrite nanoparticles have gained applications in environmental remediation activities. These particles can be employed to remove mineral contaminants such as Pb(II), Cd(II), Cu(II), Zn(II), phosphate, and arsenate from aqueous solutions [99,100]. In the case of organic contaminants, ferrihydrite nanoparticles are known to effectively improve the bioremediation activities. Microorganisms play the main role in this regard and ferrihydrite nanoparticles can enhance microbial degradation of a wide range of contaminants [101]. In recent attempts scientists tried to inject a colloidal ferrihydrite in the subsurface to create reactive zones and promote biodegradation reactions [101]. There are also some attempts to enhance particles' mobility in the soil column via polymer coatings as a surface engineering strategy or post flushing with particle-free electrolyte solutions [101,102]. The injection of ferrihydrite nanoparticles in the soil column is not just profitable for the soil microorganisms; the soil that is treated with ferrihydrite nanoparticles is even more beneficial for plants. It has been shown that soil enrichment with ferrihydrite nanoparticles enhances the growth and chlorophyll content in the maize seedlings [103].

### 3.3. Ferrous Ferric Oxide ( $\text{Fe}_3\text{O}_4$ )

Ferrous ferric oxide is well known as magnetite and its name is taken from the Greek word “magnet”. Its IUPAC (International Union of Pure and Applied Chemistry) name is iron (II, III) oxide, and its common chemical name is ferrous-ferric oxide. It has two iron (III) and one iron (II) in combination with four oxygen. The structural formula of  $\text{Fe}_3\text{O}_4$  is shown in Figure S1. Magnetite has a crystal cubic-hexoctahedral system with an octahedral habit crystal. It has a black appearance with a metallic opaque sheen. This combination is fragile and has caught the attention of researchers because of its outstanding properties and has therefore has been thoroughly studied. Magnetite is ferrimagnetic and can be employed as a permanent magnet [20,32].

It is interesting that magnetite shows superparamagnetic qualities in the nanometer range (1 to 100 nanometers). This means that nanoscale magnetite fails to maintain magnetization after removal of the external magnetic field. This unique property makes magnetite nanoparticles one of the most employed nanostructures in technology, science, and especially in medicine. Wide applications of magnetite nanoparticles have led to the development of various methods for their synthesis. Some of the common methods of magnetite nanoparticle synthesis are pyrolysis of organometallic compounds, polyol process, micro emulsion, hydrothermal synthesis, sol-gel, and coprecipitation [104]. Coprecipitation is the most commonly employed technique. In this method, magnetite nanoparticles are produced using bivalent and trivalent hydrated salt ions in the presence of a strong base under controlled atmosphere. The chemical reaction is as provided in Equation (4).

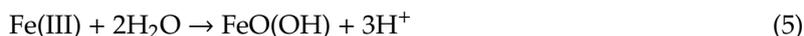


It is fair to mention that magnetite nanoparticles are the most studied and employed iron-based nanostructures. These particles have gained myriad divergent applications in engineering, such as data storage and transfer [105], the rising up and the aggregation of activated sludge [106], heavy metal absorbents [107,108], nanocatalysts [109], and various others. In addition to the various engineering applications of magnetite nanoparticles, plenty of studies were also performed for the medical application of magnetite nanoparticles in drug delivery, magnetic resonance imaging (MRI), hyperthermia therapy, and immunoassay [110,111]. In order to employ magnetic iron oxide nanoparticles in medical applications, they are usually coated with biocompatible organic or inorganic molecules, such as silica, amino acids, lipoamino acids, carbohydrates, proteins, and polymers [112–122]. Biocompatible magnetite nanoparticles have also been widely used in biological sciences for magnetic labeling and the magnetic separation of the cells and biomolecules (e.g., nucleic acids, enzymes, and antibodies) [123–136]. These nanoparticles gained some applications to increase the performance and addressing the defects of fermentation industries. Magnetite nanoparticles can increase the performance of microbial cells and make high performance cells. It showed that magnetite nanoparticles can increase the permeability of the cell membrane toward improvement in mass transfer and increasing the cell functions [123,137,138]. On the other hand, certain concentrations of magnetite nanoparticles can affect biofilm formation by microbial cells which is a major problem of the fermenters [139,140]. A recent study showed that by using magnetite nanoparticles in a fermentation period, valuable industrial strains can be protected from potential phage infections [141].

It is interesting that living creatures employ magnetite nanoparticles for navigation. Magnetotactic bacteria are Gram-negative bacteria that are able to build specialized magnetite nanostructures. Members of this bacterial family are able to fabricate magnetosome nanostructures that are biogenerated magnetite nanocrystals engulfed by a phospholipid bilayer. Magnetosomes are arranged in a line in the cytoplasm of bacteria and act as a compass needle to provide the ability of magnetotaxis for the cell [142]. Magnetosomes can be in diverse morphologies and it has been shown that environmental conditions have an immense effect on their morphology [143]. Biogenic magnetite nanoparticles are not restricted to the bacterial realm and there are obvious reports for the presence of these nanostructures in migratory and non-migratory animals. It has been shown that, like arrangement of magnetosome in the bacterial cytoplasm, magnetic nanoparticles are arranged in short or long chains in the ethmoid and lateral ethmoid bones of migratory and non-migratory fishes [144]. The chains of magnetic nanoparticles were also reported in the plants. Magnetic nanoparticles are located in the form of chains in the wall of the phloem sieve tubes (i.e., the vascular tissue of plants) [145]. Interestingly, magnetite nanoparticles have been identified in human tissues (e.g., brain, meninges, heart, liver, spleen, and cervical skin) [146]. In addition, human stem cells are able to degrade and synthesize magnetic nanoparticles [147].

#### 4. Ferric Oxide-Hydroxide (Ferric Oxyhydroxide)

Ferric oxyhydroxide is composed of iron, oxygen, and hydrogen with the  $\text{FeO}(\text{OH})$  chemical formula ( $\text{O}=\text{Fe}-\text{OH}$ , Figure S1). In aqueous matrixes, ferric ions can hydrolyze to some extent and produce ferric oxyhydroxide. As shown in Equation (5), this hydrolysis reaction produces protons and, to some extent, makes the environment acidic. Ferric oxyhydroxide is usually encountered as hydrated forms with the  $\text{FeO}(\text{OH})\cdot n\text{H}_2\text{O}$  general formula (see the Section 4.2) and anhydrous ferric oxyhydroxide. These two forms are discussed in the following sections.



##### 4.1. Anhydrous Ferric Oxyhydroxides

Like ferric oxide, anhydrous ferric oxyhydroxide can be found in four different polymorphs, denoted as the  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  phases. Different phases are distinguished by their distinct crystalline structure [20].

###### 4.1.1. Goethite ( $\alpha$ - $\text{FeOOH}$ )

Goethite is the main component of iron rust and is also the main compound of bog iron ores. In recent years, this mineral has been used as iron ore and known as brown iron ore. Goethite is an antiferromagnetic mineral [148]. It has an orthorhombic crystal system and its crystal habit is usually either needle, star, or hexagonal [20,148]. Its color in the crystalline state is dark brown or black and yellow. When powder, it is semi-transparent to opaque.

Recent investigations revealed that nanostructures of goethite can be formed in nature. By cryogenic Fe Mössbauer spectroscopy studies it was discovered that in the marine and lacustrine environments the ferric oxyhydroxide phase is the nanogoethite [149]. The laboratory synthesis of goethite nanoparticles is usually performed by using ferric nitrate ( $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ) or ferric chloride hexahydrate ( $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ ) as an iron precursor. In this order a basic solution, mostly sodium hydroxide ( $\text{NaOH}$ ), is added to the iron solution with continuous stirring until a clear solution of yellowish-brown color is formed. This yellowish-brown precipitate is ferrihydrite and needs to age to goethite [96,150]. The aging process is done at high temperatures, about 60–100 °C [96,151,152]. The speed of the base addition is a critical point in the process and is inversely proportional to the resulting particles' specific surface area. It is shown that by varying the rate of base addition from 1 mL/min to 10 mL/min the obtained specific surface area is reduced from  $101 \pm 5 \text{ m}^2/\text{g}$  to  $64 \pm 2 \text{ m}^2/\text{g}$  [96]. The major problem with these techniques is that the produced nanoparticles are not uniform in shape and size. Recent experiments indicated that this problem can be solved by controlled synthesis reactions. These reactions are based on the fact that presence of additional molecules, such as carbohydrates, can control the crystals' growth pattern. It has been shown that such compounds can drive the reaction to induce isotropic growth of goethite nanocrystals [150].

High quality goethite is rare and usually polished to be used in making jewelry [20]. From an industrial standpoint, goethite is among the main pigments (brown ochre; a yellowish-brown pigment) which has been used since ancient times. Goethite nanoparticles have gained some environmental applications and are used to remove metallic cation pollutants, such as arsenic and chromium [152–154]. These nanoparticles are also used as an absorbent for the removal of fluoride from contaminated waters [83]. Surface modification studies were also performed to enhance the nanostructures' stability and mobility in porous media. Humic acid is reported to be efficient in this regard. However, the major drawback is aggregation in the presence of divalent cations, e.g., calcium and magnesium ions, which is due to complexation phenomena related to the interaction of divalent cations with humic acid [155].

Goethite nanoparticles are able to quench free radicals. This property can be used to improve the oxidative stability of commercial products to enhance the storage time. For instance, gasoline oxidation is a factor that significantly decreases the gasoline storage time. A study on the gasoline

induction period indicated that goethite nanoparticles can inhibit gasoline oxidation and significantly elongate the induction period of the commercial gasoline [156].

#### 4.1.2. Akaganeite ( $\beta$ -FeOOH)

The name of this compound has been taken from the Akagan mine in Japan. It is an antiferromagnetic mineral and has a monoclinic crystal system with hexagonal, bar-like, star-shaped, and prismatic crystals [157]. Its appearance has a tan-brown color with a metallic sheen. This mineral has been found in different parts of Earth as well as in the rocks from the Moon. This mineral can be found in corrosion of iron and hot springs that contain chloride [158]. Although akaganeite is known as one of the anhydrous forms of FeOOH, in chloride-containing environments. In such conditions, chloride takes part in the structure and so the exact structure would be  $\text{FeO}_{0.833}(\text{OH})_{1.167}\text{Cl}_{0.167}$  [158]. In fact, it is composed of an iron oxyhydroxide framework with tunnels, hollandite channels, that is filled with chloride ions [157,158].

The nanostructure of akaganeite is mostly formed in nanorods and can be synthesized by hydrolysis of an iron chloride solution. The reaction is performed at high temperatures, about 80 °C, and usually in the presence of surfactants, e.g., poly (ethylene oxide) (PEO) or polymers (e.g., polyethyleneimine) as a capping agent and structure director to control the particle size distribution and particles shape [159–161]. Control over the particles' size is possible by varying the concentration of the capping agent. In fact, smaller nanorods can be obtained by increasing the concentration of capping agent [159].

Akaganeite has aroused widespread interest as a new generation of adsorbent material owing to its outstanding uptake capacity for toxic anions and cations [157,158,162]. Akaganeite ion exchange capability strongly depends on the hydroxyl groups located outside of the hollandite channels [163]. Formation of oriented aggregations is a key feature of the akaganeite nanorods [161,164]. New synthesis techniques have been developed to fabricate mesoporous akaganeite nanorods with increased specific surface area and hierarchical scaffold structure which is formed through the nano-rods' aggregation [161]. These structures can provide even more uptake capability for akaganeite nanorods. Akaganeite nanorods can also be used as catalyst material. Among various iron oxide and iron oxide hydroxide nanostructures, akaganeite nanorods are the most effective catalysts for the reduction of 4-nitrotoluene using hydrazine hydrate as a reducing agent [83]. One of the promising applications of akaganeite nanorods is in the fabrication of magnetite nanorods. Converting akaganeite nanorods into magnetite is a common approach for the synthesis of ellipsoidal magnetite nanoparticles. This conversion can be performed through a reduction reaction by using a chemical reducing agent, such as hydrazine (Equation (6)) [160].



#### 4.1.3. Lepidocrocite ( $\gamma$ -FeOOH)

Lepidocrocite is also called esmeraldite or hydrohematite. It is thermodynamically metastable and based on the aqueous condition, undergoes a phase transition to a more stable iron oxide structure [165,166]. This iron combination has anti-ferromagnetic properties. It can be formed in crystalline or amorphous structures from iron oxidation phenomena, such as atmospheric oxidation or sea corrosion [167]. Its crystal system and structure are orthorhombic, and its crystal habit is normally string-shaped [168]. Its appearance has a ruby red to orange-brown color, has a semi-metallic sheen, and is found in rocks, soil, and rust. It has transparent crystals that form thin sheet-like structures [169]. This fine appearance captures attention of jewelry designers and takes lepidocrocite to the jewelry industry.

Nanoscale lepidocrocite can be formed by the oxidation of zero-valent iron nanostructures (ZVINS) in oxygenated aqueous matrixes [170]. By the oxidation of ZVINS, ferrous ions diffuse out of the structure and an oxidized layer will form on the zero-valent core. The complete oxidation of zero-valent core resulted in the collapse of the core-shell structure and complete variations in the structure and

composition. The resulting structure was a reddish-brown powder of nanosheets and nanoneedles which are characteristic morphology of iron oxide nanostructures [170,171]. In another approach, lepidocrocite nanoparticles can be fabricated by adding sodium hydroxide (NaOH) to a solution of ferric ions to reach a pH of ~6 [167,168,172].

Like other iron-based nanostructures, nanoscale lepidocrocite has gained applications as adsorbent and catalyst. It can be employed to remove heavy metals (e.g., chromium and uranium) and metal complex dyes (e.g., Lanacron brown S-GL which is known as Acid Brown 298, LBS-GL) [167,172,173]. These nanostructures are able to catalyze degradation reactions. For instance, lepidocrocite nanoparticles were employed for the degradation of carbon tetrachloride (CCl<sub>4</sub>) and it showed that the compound was degraded in a second-order reaction [171]. From a microbiological point of view, it has been shown that iron reducing bacteria (IRB) can employ nanoscale lepidocrocite as an electron acceptor when special compounds (e.g., hydrogen, formate, pyruvate, serine, lactate, or N-acetylglucosamine) are utilized as electron donors [174].

#### 4.1.4. Feroxyhyte ( $\delta$ -FeOOH)

Feroxyhyte has a hexagonal closed-packed crystal system and is essentially a planar antiferromagnet [175,176]. It can be found naturally as yellowish-brown deposits in iron-manganese nodules at high pressure environments, such as a very deep ocean and gleysol. However, by exposure to surface environment or aerated conditions, it converts to goethite [177]. It is the only phase of anhydrous ferric oxide-hydroxide that has significant magnetic properties at room temperature [178,179]. Feroxyhyte nanoparticles are usually synthesized by the rapid oxidation of ferric hydroxide (Fe(OH)<sub>2</sub>), whereas hydrogen peroxide and the resulting nanostructures can be in plate, needle, or sphere morphologies [176,178,180–182]. In addition, magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles can be used as a precursor to fabricate feroxyhyte nanoparticles. In this technique, magnetite nanoparticles are rapidly oxidized in the air [178]. Irradiation-based techniques were also developed to fabricate these nanoparticles [180]. In these approaches  $\gamma$ -irradiation is used to reduce ferric ions to ferrous and then a white suspension of ferric hydroxide is resulted. The resulting ferric hydroxide can be oxidized rapidly while coming into contact with atmospheric oxygen [180].

Nanostructures of feroxyhyte have a promising potential in environmental sciences and wastewater treatment. These particles can activate hydrogen peroxide to generate reactive oxygen species (ROS) which are effective in degradation of organic molecules [181]. Feroxyhyte nanoparticles can also eliminate inorganic pollutants. It has been shown that mesoporous feroxyhyte nanoparticles and ferrous ions have a synergistic action for phosphate immobilization. Hydroxyl groups on the nanoparticles and in-situ generated ferric ions were found to promote phosphate immobilization. This  $\delta$ -FeOOH/Fe(II) synergistic system can reach about 94% removal efficiency at acidic pH [183]. Doping of nanostructures with foreign metal ions, such as copper and manganese, is another approach to enhance the catalytic and adsorbent properties of feroxyhyte nanoparticles [178,179,184]. These nanostructures are applicable in batch and continuous flow models to remove heavy metal (e.g., arsenic, cadmium, mercury, and nickel) pollutants from drinking water [185,186]. Feroxyhyte can be used as a coating for other nano-adsorbents, such as maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles, to improve their stability and recovery capacity. It has been shown that maghemite nanoparticles with various ratios of feroxyhyte coating have different potentials for chromate (VI) removal, and the optimal mass ratio of coating to core is 1.0 [187].

Feroxyhyte nanoparticles can be used as a photocatalyst for water splitting and hydrogen generation. Besides common nano size features such as the small particle size and high surface area, these nanoparticles have a small band gap energy and mesoporous structure that make feroxyhyte nanoparticles a suitable photocatalyst [188]. Like what we have in the remediation activities, foreign metal doping can also increase the photocatalytic activity of feroxyhyte nanoparticles. Nickel ions (Ni<sup>2+</sup>) can be used to increase the conductivity and charge transfer in the particles. By loading Ni(OH)<sub>2</sub>

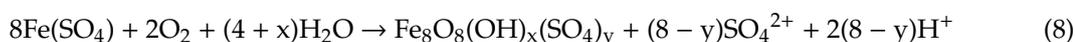
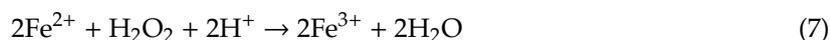
on the surface of the resulting structure, charge separation will also improve. These modifications significantly enhance the photocatalytic activity of ferroxhyte nanoparticles [189].

Ferroxhyte nanoparticles behave superparamagnetically or ferromagnetically at ambient temperature [176,182]. Therefore, these particles can be considered in technical, medical, and biomedical practices as an alternative for previously employed magnetic nanoparticles. Experimental evidences showed that ferroxhyte nanoparticles can release heat under an alternative magnetic field and the heat production can be controlled by changing the mass of nanoparticles [182].

#### 4.1.5. Schwertmannite

In 1994 schwertmannite was introduced as a novel iron oxyhydroxysulphate from the Pyhäisalmi sulphide mine, Province of Oulu, Finland. It was found in ochreous precipitates from acid, sulphate-rich waters [190]. Schwertmannite has a structure similar to akaganeite, the only difference being that schwertmannite has sulfate ions instead of chloride ions so it is called iron oxyhydroxysulfate mineral with the chemical formula of  $\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x \cdot n\text{H}_2\text{O}$  ( $1 \leq x \leq 1.75$ ) [191,192]. It is poorly crystalline nanometric material with tetragonal crystal system and paramagnetic behavior [193]. It appears as an opaque yellowish-brown and has a fibrous morphology under the electron microscope [190,191].

In nature, schwertmannite nanocrystals were formed through the oxidation of ferrous ions and subsequently ferric ions precipitation. Synthetic schwertmannite nanoparticles can also be fabricated by the chemical oxidation of ferrous ions. Usually ferrous ions are provided from an  $\text{FeSO}_4$  solution and hydrogen peroxide is used as an oxidizing agent (Equation (7)). Precipitation occurred by hydrolysis of the resulting ferric ions. Ferric ions first form a complex intermediate with water molecules and then, at high concentrations of sulfate ions ( $\text{SO}_4^{2+}$ ), transform into schwertmannite. The total reaction is illustrated in Equation (8) [192].



Biosynthesis (biogenic fabrication) is another technique for the fabrication of schwertmannite nanostructures. It is dependent on the biological ferrooxidation of ferrous ions by iron oxidizing microorganisms that are able to oxidize ferrous ions or elemental sulfur as a source of energy. These organisms can precipitate nano-sized schwertmannite at ambient temperature and acidic pH (~2–3) [194]. *Acidithiobacillus ferrooxidans* is the most known and studied bacteria in this family [195].

Schwertmannite was found to have considerable potential as an absorbent material, which is applicable for water treatment and soil remediation purposes. It has a promising potential to remove both mineral (e.g., arsenic, chromium, antimony, and fluoride) and organic contaminants [192]. Song et al. (2018) compared the characteristic features of chemically synthesized and biogenic schwertmannite nanostructures that are important for remediation purposes [196]. They show that chemical synthesis can fabricate more schwertmannite than biogenic methods. But biogenic methods provide larger nanoparticles with larger specific surface area. From a surface morphology point of view, chemically synthesized particles have a smooth surface, while the surface of the biogenic particles is chestnut shell-like with higher saturated adsorption capacity [196]. In addition, biogenic schwertmannite has a higher chemical stability. Synthetic schwertmannite is more sensitive to the aging process and conversion to the goethite [197]. Key features of the biogenic nanoparticles can even be improved by a simple heating. Heating up to 250 °C resulted in the significant increase in the particles' porosity, specific surface area, and efficiency for contaminants removal [198]. Biofabrication of schwertmannite has a critical point; adherence of prepared nanostructures to the reactor wall during the biosynthesis process resulted in deterioration of particles' structural characteristics. To eliminate the adhered schwertmannite, Zhang et al. introduced additional schwertmannite into the reactor

system prior to schwertmannite biosynthesis. They show that by doing so, all biogenic schwertmannite nanostructures are in a suspended form [199].

#### 4.2. Hydrated Ferric Oxyhydroxides

Ferric oxyhydroxide is usually encountered as hydrated forms with a  $\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$  general formula. The monohydrate form of this compound is the most common form and is known as ferric hydroxide and its simplified formula is  $\text{Fe}(\text{OH})_3$  (Figure S1f). For the first time it was reported from the Proprietary Mine at Broken Hill, New South Wales, Australia and called bernalite in homage to the British crystallographer J. D. Bernal (1901–1971) [200]. Bernalite is structurally related to perovskites (a calcium titanium oxide mineral,  $\text{CaTiO}_3$ ) and its small crystals, up to 3 mm, occurs as flattened pyramidal to pseudo-octahedral with slightly concave faces. Due to goethite inclusions, the crystals can be transparent to opaque with pale green (bottle-green) color [200,201].

Bernalite nanoparticles can be transformed from goethite nanorods at alkaline pH (~10) and in the presence of arsenate. Arsenate has a key role in the formation of bernalite and the abundance of bernalite is in direct relation with the arsenate concentration [202]. In the laboratorial experiments, ferric hydroxide can be easily obtained by increasing the pH of a ferric ions solution up to about 8 as in Equation (9) shows [203].



It can be a basic reaction to prepare a precursor for other iron-based nanoparticles. For instance, ferric hydroxide was used as a precursor for the generation of monodisperse ferromagnetic and superparamagnetic iron oxide nanoparticles [204]. In a similar manner, controlled dehydration of ferric hydroxide resulted in  $\text{Fe}_2\text{O}_3$  [205]. In a novel approach, Thuy et al. (2014) employed the reaction for the fabrication of colloidal ferric hydroxide to remove heavy metals from water. They combined the coprecipitation of ferric hydroxide and flotation technique using gamma poly-glutamic acid ( $\gamma$ -PGA) for collecting Au, Bi, Co, Cd, Cu, In, Ir, Mn, Ni, Pb, Pd, Pt, Te, Sb, Rh, Ru, and Zn. To perform the precipitation reaction, they added a solution of sodium hydroxide to heavy metals contaminated water containing ferrous ions [206]. Coprecipitation of ferric hydroxide can also be performed in the presence of other nanoparticles, such as magnetite nanoparticles, and form a core-shell structure. Arefi et al. showed that the resulting core-shell nanostructure is applicable as a heterogeneous catalyst for the direct oxidative amidation of alcohols with amine hydrochloride salts [207].

### 5. Iron Hydroxides

Iron hydroxides can be found in two different structures as ferrous hydroxide and ferric hydroxide. Molecular structure of ferrous hydroxide is provided in Figure 1, and it can be denoted as  $\text{Fe}(\text{OH})_2$  or  $\text{FeH}_2\text{O}_2$ . Basically, it is a nearly white substance, but by exposure to oxygen, ferrous ions are oxidized to ferric and provide a greenish to reddish-brown color of ferric hydroxide. Chemically, ferrous hydroxide is produced as a gelatinous precipitate when ferrous ions are exposed to an alkali, such as hydroxide salts or ammonium (Equation (10)). In the synthesis of ferrous hydroxide nanoparticles, the employed alkali has a significant effect on the shape and surface features of the resulted nanostructure. It was shown that ammonium derived the reaction to make nanospheres with a porous surface, while hydroxide salts (e.g., NaOH) make smooth nanorods. It is obvious that the product is sensitive to the oxygen, and hence the reaction should be performed under an inert atmosphere [208].



Nanostructures of ferrous hydroxide are great activators for hydrogen peroxide to produce hydroxyl radicals. This potential provides the particles a Fenton-like catalyst property that can be employed to degrade organic pollutants as a Fenton-like activator of hydrogen peroxide [208]. The molecular structure of ferric hydroxide is provided in Figure 1. Ferric hydroxide was discussed in detail in Section 4.2.

The content of this review was summarized in tabular format as Supplementary Material and provided in Table S1 for a quick overview.

## 6. Conclusions

Iron as a well-known element from the ancient time, retaining an outstanding position in the human life and culture. Due to its different valency and combining power with oxygen atoms and water molecules, it comes in a colorful variety of compounds with diverse chemical structures and physical appearances. In the recent years, by taking iron compounds to the nano realm, we can improve the iron to achieve unrepresented properties and applications. In this review 19 different compounds of iron, from pure iron to combined forms of iron with oxygen and water, were investigated for their structures, properties, synthesis routes, and applications as nanomaterials. Nanostructures of iron can be prepared by simple chemical reactions and even in some cases these structures are achievable via biologic pathways or biochemical reactions. Provided data demonstrate that iron-based nanomaterials can be employed in medical, biomedical, industrial, engineering, environmental, and agricultural sceneries. The discovery of the potential applications of iron-based nanomaterials only in its emerging phase and there will be a huge amount of investigations in this regard in the future.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2227-9717/8/9/1128/s1>, Figure S1: Molecular structures of iron compounds, FeO (a), Fe<sub>2</sub>O<sub>3</sub> (b), Fe<sub>3</sub>O<sub>4</sub> (c), FeOOH (d), Fe(OH)<sub>2</sub> (e), and Fe(OH)<sub>3</sub> (f), Table S1: A tabular summary of the data that provided in the main manuscript.

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