



Study of Magnetic Spinel Ferrite (MFe₂O₄) Nanoparticles: From Synthesis to Application

Mr. G. D. Kale¹, Ms. P. P. Dhande² & Dr. S. S. Tathod³

¹Department of Physics,

Shri Vitthal Rukhmini Art's, Commerce & Science College, Sawana

²Department of Chemistry,

Babasaheb Naik College of Engineering, Pusad

³Department of Botany,

Shri Vitthal Rukhmini Art's, Commerce & Science College, Sawana

Corresponding Author – Mr. G. D. Kale

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Abstract:

This article has discussed the structural characteristics, electrical characteristics, magnetic behavior, synthesis techniques, and applications of the most important soft spinel ferrites. Magnetic ceramics are frequently called ferrites because of the Latin route ferrum. They are divided into two groups: hard (hexaferrites) and soft (garnets and spinels). Among soft ferrites, spinels have garnered special interest in recent decades. Chemically and thermally stable, spinels with the formula AB₂O₄ can be used in a wide range of applications. The cubic (isometric) crystal structure is where they crystallize. Examples of these applications include microelectronics, magnetic memory, water purification, absorber coatings, catalysis, biomedicine, antibiotic action, and the use of contrast agents in magnetic resonance imaging. The production, doping, and uses of several metal ferrite nanoparticle kinds are covered in this review, along with opinions on how to select the best spinel ferrites for a given application.

Introduction:

Due to their unique and remarkable properties, nanocrystalline magnetic materials have attracted attention from various fields, such as physics, chemistry, biology, medicine, materials science, and engineering. Nanomaterials have particle size up to 100 nm and high surface-to-volume ratio, which altered or enhanced reactivity, thermal, mechanical, optical, electrical, and magnetic properties as compared to their bulk counterparts [1–4]. While the chemical composition of bulk materials is the main determinant of their qualities, the particle size, and morphology of nanomaterials, in addition to the chemical composition, dictate the majority of their features. Furthermore, depending on the particle size and chemical composition,

these qualities can be fine-tuned [1, 5–7]. Ferrites are significant and fascinating materials from both a practical and theoretical standpoint. Magnetic CoFe₂O₄, MnFe₂O₄, CuFe₂O₄, ZnFe₂O₄, and NiFe₂O₄ nanoparticles have received a great deal of attention owing to their thermal and chemical stability, as well as their distinctive structural, magnetic, optical, electrical, and dielectric properties, and their broad range of technological applications including photo catalysis, photoluminescence, biosensors, humidity-sensors, catalysis, magnetic refrigeration, permanent magnets, magnetic drug delivery, magnetic (hyperthermia) [8,9]. This work described the thermal, structural, morphological, and magnetic properties of spinel ferrites (MFe₂O₄, M = Cu, Co, Mn, Zn, and Ni) and

doped ferrites (Zn^{+2} , Ni^{+2} , Al^{+3} , Mn^{+2} , Ag^{+} , Y^{+3} , Nd^{+3} , Ti^{+4} , Cd^{+2} , Dy^{+3} , Gd^{+3} , Cu^{+2} , Yb^{+3} , Eu^{+3} , Zr^{+4} , In^{+3} , Cr^{+2} , Pr^{+3} , Sm^{+3} , Ho^{+3} , Er^{+3} , Mg^{+2} , La^{+3} , and Ce^{+3}) with different transition metals, produced by Co-precipitation method, Hydrothermal and Solvothermal method, Microemulsion method, High-Temperature Thermal Decomposition method, Sol-gel method, Electrochemical Deposition method, Sonolysis or Sonochemical method, Microwave-Assisted method, and Biosynthesis methods [10,11]. Additionally, the purpose of this paper is to investigate and examine several subjects, including the numerous synthesis methods of MFe_2O_4 and their metal dopants, as well as their benefits and drawbacks, and the most relevant applications in conventional and current technologies. There are four main sections in the review paper. The classification of magnetic spinel ferrites and a brief overview of ferrites and their structures are all covered in the first section, "Magnetic spinel ferrites". The second section, "Magnetic properties," provides a brief overview of magnetic properties in spinel ferrites. The third section, "Synthesis methods," provides an overview of the main methods in the area of spinel ferrites. The impact of doping on the properties of magnetic spinel ferrites is discussed in the fourth section. The major applications of spinel ferrites are summarized in the final and fifth part, "Applications of spinel ferrites." [11]

Magnetic Spinel Ferrites:

Magnetic spinel ferrite materials have sparked a lot of attention recently because of the vital roles that play in improving scientific knowledge and understanding of magnetic materials in general, and ferrites in particular [12–14]. Ferrites are a class of ferrimagnetic ceramics that are used in a variety of electric and optoelectric devices due to their magnetic properties, high electrical resistance and

minimal eddy current losses [15–17]. Spinel ferrites have the typical formula MFe_2O_4 , where M is an ion of divalent metal and Fe is in the +3 oxidation state [18]. Ferrites are materials having a wide range of physical qualities, as well as low production costs and great chemical stability. Ferrites differ from garnet, hexagonal, and spinel in structure depending on their initial crystal lattice. There are 64 tetrahedral and 32 octahedral sites in a single unit cell, however, only 8 and 24 sites are filled by cations, respectively [19] (Fig. 1a) Based on the cations distribution in the octahedral and tetrahedral sites, there are three types of normal, inverse, and mixed spinel. As a result, the typical example for normal spinel (Fig. 1b) is $ZnFe_2O_4$ where the Fe^{3+} ions are found in the octahedral sites while Zn^{2+} ions are located in the tetrahedral sites. In addition, inverse spinel (Fig. 1c) is $NiFe_2O_4$ where Ni^{2+} ions and half of the Fe^{3+} ions are in the octahedral sites and the remaining half of the Fe^{3+} ions are in the tetrahedral sites [20]. This implies that the cation distribution between the two interstitial sites may have an impact on the magnetic properties of spinel ferrites [21–26]. Among spinel ferrites, cobalt ferrite ($CoFe_2O_4$) with high H_c , large cubic magneto crystalline anisotropy, and moderate saturation magnetization (M_s) is regarded as a hard-magnetic material. Due to these characteristics, it can be used for magnetic storage and a number of other applications [29]. In biomedical applications, it could be utilized for magnetic separation, magnetic resonance imaging, magnetically directed drug delivery, and hyperthermia for cancer treatment. It can be employed in industrial applications as bare nanoparticles for pollutant removal by adsorption or photocatalytic degradation. The essential features of $CoFe_2O_4$ NPs, such as their high M_s Value, visible light absorption capacity and low bandgap energy of 2.04 eV have attracted interest [30, 31]. Cation

distribution, M_s , and chemical and physical characteristics as well as crystallinity and surface area of CoFe_2O_4 have all been found to be influenced by synthesis procedures [12, 32, 33]. ZnFe_2O_4 NPs, one of the most important ceramic materials, have attracted attention in many applications due to their distinctive properties including high magnetic permeability, high Curie temperature, high electrical resistivity, low power loss [34, 35]. Due to their exceptional features, magnetic spinel material can be

used for numerous technical applications, such as transformer cores, read/write heads for high-speed digital cassettes, radio frequency circuits, and absorbers for electromagnetic waves. It's also a great addition to biomedical diagnostic and therapeutic applications. Because of the high surface area to volume ratio surface chemistry, and high density of defects, ferrite nanoparticle production has recently received greater attention [36,37].

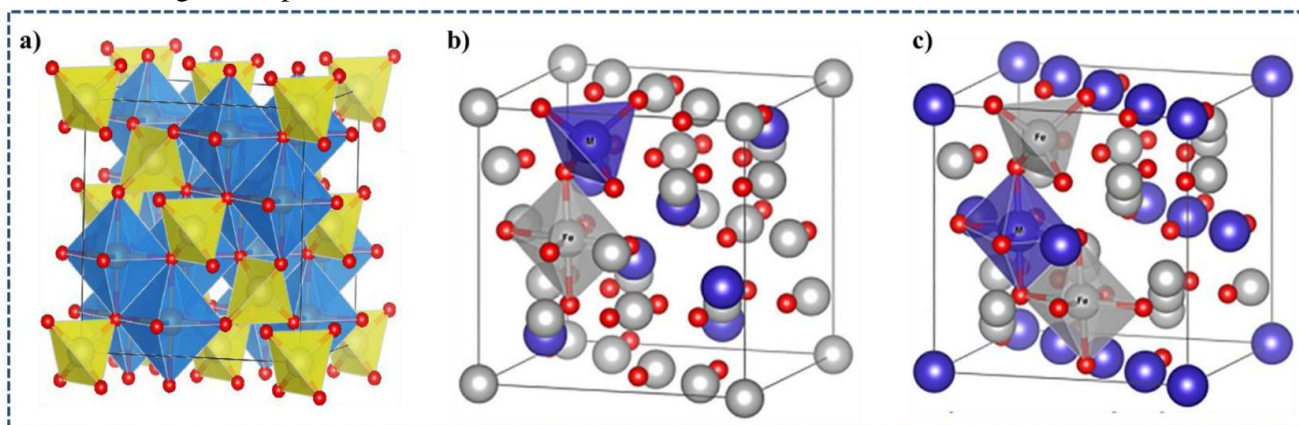


Fig. 1. a) Unit cell structure of magnetic spinel ferrite a) octahedral sites (blue), tetrahedral sites (yellow) and oxygen atoms (red) [30], b) normal spinel ferrite, and c) inverse spinel ferrite [31].

Spinel ferrite nanoparticles such as NiFe_2O_4 have received a lot of attention for various applications, including high-frequency circuits, the cores of radiofrequency transformers, antennas, inductors, and radar-absorbing materials, due to their high resistivity and low loss at high-frequency [38]. They also have a lot of potential as catalysts and/or catalytic supports for degrading organic and inorganic contaminants. By combining their magnetic properties, antimicrobial activity, and hyperthermia therapy of cancer, NiFe_2O_4 NPs are becoming increasingly relevant in biomedical applications such as magnetic resonance imaging (MRI), drug delivery systems, and hyperthermia treatment of cancer [39, 40]. Recently, research on NiFe_2O_4 NPs has attained considerable attention because of the differences in their physical and chemical properties from those

of free atoms or molecules as well as those of bulk solids, and have a wide range of potential applications [41, 42]. Ferrites play an important part in practically all electronic sectors due to their unique electromagnetic properties. Hard and soft ferrites are the two main types of ferrites. Manganese ferrite (MnFe_2O_4) is among the most fascinating soft ferrites. It has been extensively used in a range of applications over the past 50 years and has strong magnetic permeability and low losses. Magnetic resonance imaging (MRI), drug delivery, electronic devices, and several telecommunications divisions are among them. Compared to other spinel ferrites, manganese ferrite has a low resistance. The formula can be expressed as $[\text{Mn}_{1-i}\text{Fe}_i] (\text{Mn}_i\text{Fe}_{2-i}) \text{O}_4$, where brackets and parenthesis indicate the inclusion of a degree of inversion (i) [43]. However, it is well known that the method used to make ferrites

could change the degree of inversion of the crystal structure. It has shown that the preparation methods such as sol-gel can change the magnetic behaviour of zinc ferrite nanoparticles [44]. It implies that the cation distribution can affect the chemical and physical characteristics of spinel ferrite nanoparticles. Mixed spinel ferrites such as, $\text{CoMgFe}_2\text{O}_4$, $\text{CoZnFe}_2\text{O}_4$ and $\text{MgZnFe}_2\text{O}_4$ are another important family members of magnetic ferrites that are studied due to their outstanding properties like high electrical resistivity, chemical stability, and high Curie temperature [45–47].

Magnetic Properties:

Nano-sized magnetic materials, with great interest have received a lot of attention due to the increased demand for miniaturized technological devices. Understanding magnetic properties at the nanoscale is critical for improving permanent magnetic material performance. As is widely known, the shape, size, surface effects, magnetic anisotropy, and other parameters have a significant impact on the magnetic properties of nanoparticles [48]. Hysteresis is a dampening phenomenon in which two related quantities, such as strain and stress, magnetic field, and magnetic induction, lag behind or get out of phase. The word “hysteresis” is derived from the Greek language and means “to lag behind.” Lattice heating is a result of some properties, such as magnetic and mechanical ones, being energy dampened. Magnetic and mechanical hysteresis is the most well-known forms of dampening [48]. Any magnetic circuit with ferromagnetic material will typically exhibit the hysteresis phenomena. The delay between changes in the magnetic flux density in this material and changes in the magnetic field strength is what causes these phenomena. Although the hysteresis mechanism is well understood, creating an appropriate mathematical model based on an understanding of the phenomena

that explain the magnetization process is still a difficult issue. As a result, extensive research has been conducted over many decades to create a hysteresis model that is accurate and helpful in the field computations of ferromagnetic materials [49]. Measurements of hysteresis loops in technologically essential magnetic structures have revealed significant discrepancies from several fundamental and widely accepted ferromagnetism physics concepts [50]. In spinel ferrites, oxygen ions control the magnetic interactions between the spins of metallic cations in the octahedral and tetrahedral interstitial sites. Spin interactions with the exchanging of nearby atoms cause spinel ferrites to become magnetic. They are three different varieties of J_{AA} (A-O-A), J_{BB} (B-O-B), and J_{AB} (A-O-B) are governed by the super exchange process. The distance between the metallic ions and the oxygen affects the magnitude of these interactions. In comparison to A-O-A and B-O-B interactions, the A-O-B super exchange interaction is more significant. The dominant intra-lattice negative J_{AB} interaction induces an uncompensated antiferromagnetic order (i.e., ferrimagnetism) between the A and B sub-lattices. The magnetic moments of the divalent cations at the B sites are the only ones responsible for the net moment in an inverse spinel structure because the contribution of the iron cations at B sites cancels that of the iron cations at A sites. The magnetic moments of the iron ions at the B sites are located in an antiferromagnetic alignment in a normal spinel. The difference between the contributions of two average sub-lattice magnetic moments can be used to calculate the magnetization of spinel ferrite. Then the resultant saturation magnetization (M_S) of the ferrite at $T = 0$ can be expressed as follows:

where M_M refers the molar mass of ferrite, d is its density, N represents Avogadro's number, and $n_{B,i}$ denotes the

number of Bohr magnet, μ_B , associated with the i site of the unit cell. Magnetocrystalline anisotropy is a property of a magnetic material that defines the most energetically favourable crystallographic direction that spontaneous magnetization tends to align. For spinel ferrites, the magnetization axis direction is the stacking direction [111] of the close-packed arrangement but cobalt ferrite is not suitable for high permeability applications due to its significant magneto crystalline anisotropy and high Co concentration. The magnetic characteristics of spinel ferrites not only depend on the composition of the ferrites but also on the choice of dopants and synthesis conditions that can affect the magnetic structure of spinel ferrites. As a consequence, the physical properties of magnetic spinel ferrites like magnetic saturation, coercivity, magnetic anisotropy, and magnetostriction are mediated by intrinsic magnetic properties of elements of composition. The spinel ferrites with high magnetic saturation that the researchers showed are based on Ni, Mn, Mg, Co, Li, and Cu. Prasad et al. [51] synthesized nanocrystalline ferrites MFe_2O_4 ($M = Zn, Ni, Cu, \text{ and } Co$) using auto-combustion process. Among all prepared spinel ferrite, $CoFe_2O_4$ had the highest saturation magnetization of 41 emu/g, whereas $ZnFe_2O_4$ showed a low saturation magnetization value of 12.87 emu/g. Mohamed et al. [52] reported the saturation and coercivity values of $ZnFe_2O_4$ which rely on the cobalt doping ratio. By replacing Zn^{2+} ions with Co^{2+} the particle size of ferrite increased from 8.3 nm to 11.4 nm with an increase in the Co^{2+} doping content. The study revealed that the saturation magnetization value increased as the Co^{2+} content increased, from 40 emu/g when $x = 0.0$ –98 emu/g when $x = 0.4$. The magnetic anisotropy significantly changed when the Co^{2+} content of the $ZnFe_2O_4$ host lattice increased. The impact of Cu^{2+} , Ni^{2+} , and Co^{2+} substitution on the structural and

magnetic characteristics of $Li_{0.25}Mn_{0.5-x}M_xFe_{2.25}O_4$ spinel ferrites was reported by Mazen et al. [53]. The results showed the synergistic effect of replacing Mn^{2+} ions with Co^{2+} ions in enhancing the magnetic characteristics of Li–Mn ferrites.

Purnama et al. [54] studied the impact of calcination temperature on crystallite size magnetic properties of $CoFe_2O_4$ synthesized by co-precipitation process. It can be observed that as minor Co^{2+} and Fe^{3+} ions migrate between tetrahedral and octahedral sites, the saturation magnetization values increase. In addition, it was determined that the rise of the magnetic domain size, which promotes magnetization, was the explanation for how magnetization increased with particle size.

The magnetic properties, such as the inversion degree parameter, which are sensitive to the local structure, can be determined using a variety of element-specific techniques, such as Extended X-ray Absorption Fine Structure (EXAFS), X-ray Absorption near Edge Structure (XANES), Diffraction Anomalous Fine Structure (DAFS), and X-ray Magnetic Circular Dichroism (XMCD). Mossbauer spectroscopy is another important characterization technique used to characterize magnetic properties and determination of inversion degree of spinel ferrites. This characterization method is used to determine the hyperfine connection between the iron nucleus and the electronic charge of the nearby atoms. For this reason, the preparation methods, particle size, shape, and calcination temperature must be taken into consideration for the preparation and application of spinel ferrites.

Synthesis Methods:

Among the various methods available for the synthesis of spinel ferrite materials, the most popular include physical, chemical and biosynthesis methods that will be the focus of this section. Synthesis of magnetic nanoparticles, and second, the

modification of surface functionalities. Different processes can be utilized simultaneously to produce nanoparticles of various sizes. It is known that the synthesis process affects the physical and chemical behaviour of nanoparticles. The development of new preparation techniques and application scenarios has been a key area of research since the discovery of magnetic nanoparticles. The most widely utilized techniques for creating magnetic nanoparticles nowadays are physical and

chemical ones [55, 56]. On the controlled synthesis of various sizes, compositions, and morphologies of magnetic nanoparticles, numerous synthesis approaches have been explored in the literature [39,57]. Among the various methods available for the synthesis of spinel ferrite materials, the most popular include physical, chemical and biosynthesis methods that will be the focus of this section. Table 1 summarizes some preparation methods of spinel ferrite nanoparticles.

Table 1 preparation methods of spinel ferrites nanoparticles:

Methods	Iron source	Reaction Conditions	Solvent	Ferrite Nanoparticles	References
Sol gel	Fe(NO ₃) ₃ 9H ₂ O	150 ⁰ C	H ₂ O/Citric acid	ZnFe ₂ O ₄	[58]
Co-precipitation	FeCl ₃	75 ⁰ C	H ₂ O	COFe ₂ O ₄	[59]
Thermal Decomposition	Fe (acac) ₃	300 ⁰ C	Benzyl ether	COFe ₂ O ₄	[60]
Microemulsion	Iron (III) 2-ethylhexanoate (C ₂₄ H ₄₅ FeO ₆)	40 ⁰ C	Isooctane/H ₂ O	NiFe ₂ O ₄	[61]
Hydrothermal	Fe(NO ₃) ₃ 9H ₂ O	180 ⁰ C	H ₂ O	COFe ₂ O ₄	[62]
Sonochemical	Fe(NO ₃) ₃ 9H ₂ O	Room Temperature	H ₂ O	MnFe ₂ O ₄	[63]
Microwave assisted Synthesis	FeCl ₂	Room Temperature/800 W	H ₂ O	Titanium ferrite	[64]

Chemical Methods for Preparing Magnetic Nanoparticles:

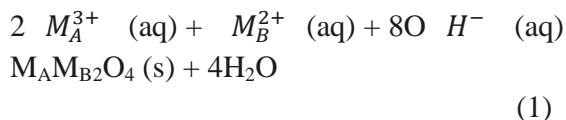
Chemical synthesis is the most common approach for preparing NPs since it has a high capacity for producing nanoparticles in a reasonable time and at a low cost. To date, several methods for preparing magnetic nanoparticles have been suggested and effectively used to fabricate a variety of magnetic nanoparticles. Based on the solvent used, all of these synthetic processes can be classified into two categories in terms of cost, size, and shape controllability: aqueous solvents and non-aqueous solvents. Aqueous-based magnetic nanoparticles are inexpensive, but it is difficult to control their shapes and sizes. Non-aqueous procedures are more expensive

than aqueous ones but have more control over size and shape [65,66]. The main focus of this section is to introduce and review the conventional methods that are used to synthesize the spinel ferrite NPs with the general formula MFe₂O₄.

Co-precipitation Method:

Co-precipitation is a simple and cost-effective process for the synthesis of MFe₂O₄ NPs. The spinel ferrite NPs synthesized by this method is homogeneous in structure, highly pure, and of controllable size [67]. In this method, solution of stoichiometric quantities of metal salts (chlorides, nitrates or sulphates) is mixed at sufficient temperatures with a base, which acts as a precipitating agent. Multiple factors such as temperature, pH, reaction time, as

well as the type and the ratio of precursors play a significant role in controlling the size, shape, and properties of spinel ferrite NPs [68,69]. Equation (1) describes the mechanism involved in the co-precipitation method for the synthesis of ferrite NPs [70]:



The spinel ferrites prepared by this process are homogenous in structure, very pure, and of controlled size. Co-precipitation is a traditional way of producing MFe_2O_4 MNPs for chemical synthesis in this regard. This method can be used to disperse huge volumes of MNPs in aqueous media with ease. Using this method, the precursor elements co-precipitate in a solution at high or room temperature after the base addition in an inert atmosphere. The ability to scale up and achieve huge amounts of MFe_2O_4 MNPs is one of the most important advantages of the co-precipitation approach. Co-precipitation is therefore the most typical

chemical procedure used in industry to synthesize thousands of kilograms of MFe_2O_4 nanoparticles. However, the main challenges of the co-precipitation approach are morphological control, crystalline quality, and particle size distribution of MNPs [55,65]. The low crystallinity of NPs prepared with co-precipitation is the main difficulty associated with this method which can be improved with subsequent heat treatment [20].

CoFe_2O_4 nanoparticles with a typical co-precipitation process and a particle size range of 16–26 nm are presented in Fig. 2 [59]. In this procedure, polar solvents are utilized to dissolve inorganic salts such as nitrate and chloride to form a homogenous solution as the starting materials. It should be noted that factors like temperature, pH, and salt concentration that are detrimental to crystal growth and particle aggregation can control the size and shape of nanoparticles. The solid mass is collected and washed after precipitation. After that, the hydroxides are calcinated to produce crystalline oxides.

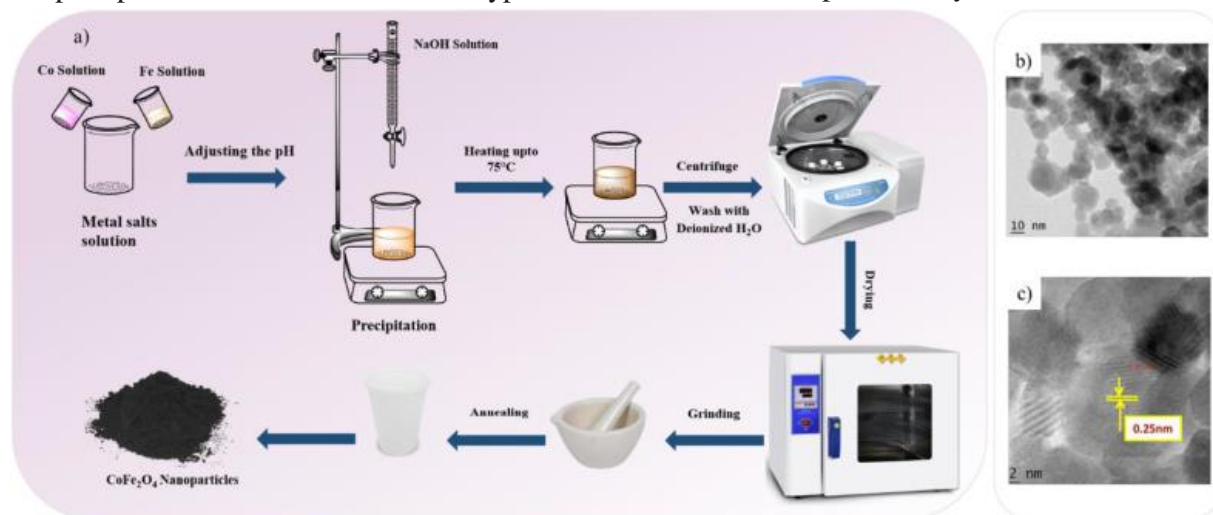


Fig. 2 a) Schematic diagram for the synthesis of CoFe_2O_4 NPs via co-precipitation technique, b) TEM image and c) HRTEM image of CoFe_2O_4 NPs [59].

Hydrothermal and Solvothermal Synthesis:

To create crystalline MFe_2O_4 magnetic nanoparticles, hydrothermal and solvothermal of MNPs can be produced by simple and effective

hydrothermal and solvothermal procedures. A nonaqueous solution, such as methanol, ethanol, or ethylene glycol, is used in solvothermal synthesis to dissolve the metal precursors under high pressure and at a moderate temperature. Hydrothermal

temperatures are more homogeneous. Additionally, more crystalline MFe_2O_4 MNPs can be synthesized by high-temperature decomposition. The thermal decomposition process of $CoFe_2O_4$ nanoparticles is schematically demonstrated in Fig. 4a. The fundamental advantage of this approach over co-precipitation is the separation of nucleation and growth phase of nanoparticles, resulting

in monodisperse magnetic nanoparticles with a narrow size distribution, uniform morphology and a high crystalline structure [80]. Without the use of size selection methods, monodisperse magnetic nanoparticles can be made. Fig. 4 b and c shows TEM images of the $CoFe_2O_4$ NPs with uniform size and average particle size of 13.2 nm and 9.3 nm derived via thermal decomposition process method [60].

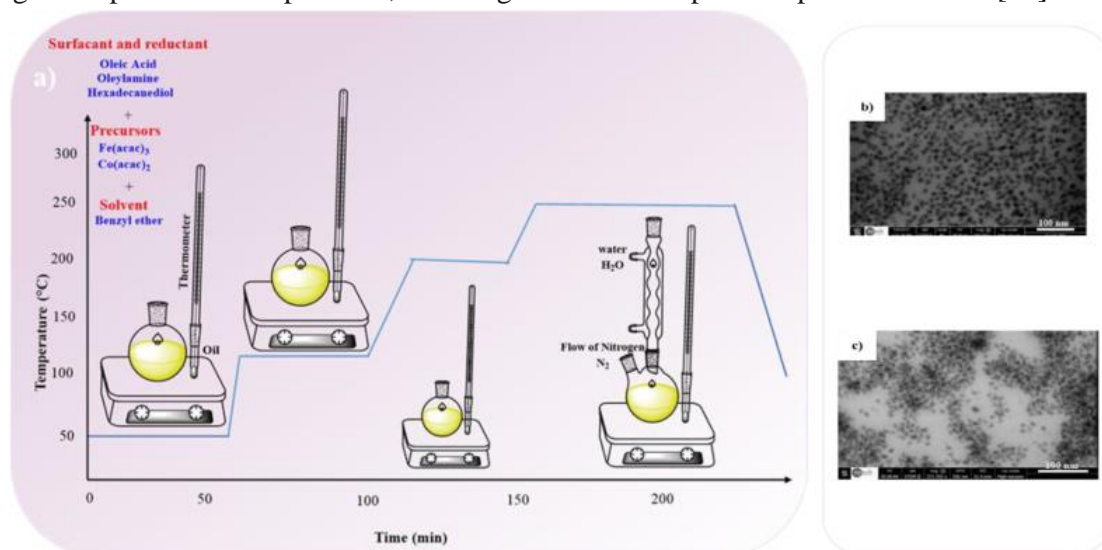


Fig 4.a) Illustration of thermal decomposition method, STEM images of $CoFe_2O_4$ NPs b) $d = 13.2$ nm and c) $d = 9.3$ nm [60].

In this method, the size and shape of spinel ferrite NPs can be adjusted by temperature, heating rate, the concentration of organic solids and type of organic solvent to make diverse shapes, such as cubic, and octahedral [81,82]. For biomedical applications of spinel ferrite NPs, thermal decomposition is preferable to the co-precipitation synthesis method due to high crystallite and narrow size distributions [83].

Sol-gel Auto Combustion Method:

The sol-gel method, illustrated schematically in Fig.6 a, has been widely used to create MFe_2O_4 MNPs with nanostructures for engineering applications due to the possibility of shape and size control [84]. Sol-gel procedure is a simple and low cost method, however, lack of

purity of final product is the main limitation of sol-gel method that thermal treatment is needed to achieve the high purity and crystalline nanomaterials [85,86]. The shape and crystallinity of the nanoparticles produced by this method are significantly influenced by the type of precursors that were present in the initial colloidal solution.

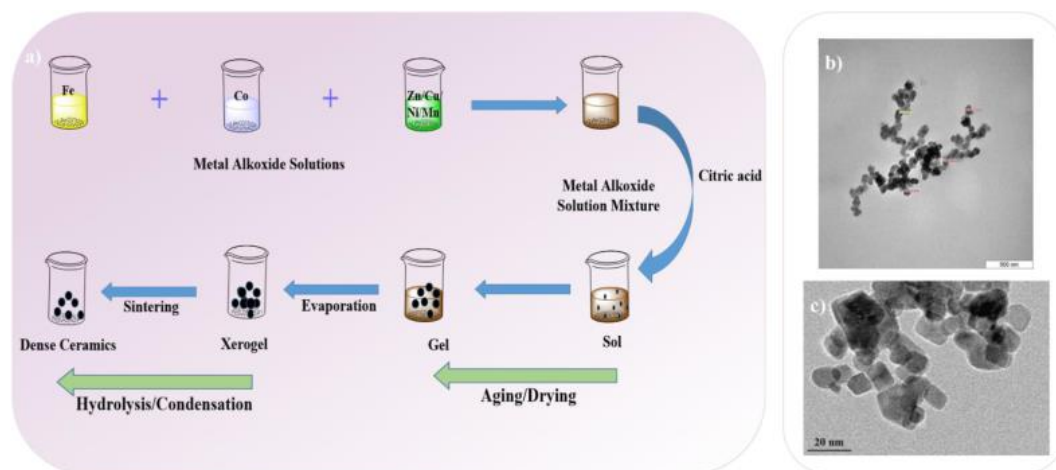


Fig. 5 The synthesis of spinel ferrite and transition metals-substituted spinel ferrite nanoparticles via sol-gel technique [84], b) CuFe_2O_4 via sol-gel combustion method [58], c) ZnFe_2O_4 NPs via sol-gel method [90].

In this method, the precursor solution is added to polymerization or hydrolysis reactions, which result in the production of sol. The gelation process makes use of polymer addition or sol condensation to gel then simple solvent evaporation is used to prepare MFe_2O_4 NPs. The main advantages of this method over alternative strategies include simple experiment setup, low temperature, and highly controlled synthesis [55,65]. Ferrite nanoparticles can be prepared using the sol-gel auto-combustion synthesis method, which combines chemical sol-gel and combustion processes [81]. This process uses an exothermic, self-sustaining, thermally-induced anionic redox reaction of xerogel, which is made from an aqueous solution containing the desired metal salts and an organic complexant such as urea, glycine, or citric acid. The temperature of the flame during combustion may range from 600 to 1350 °C [88,89]. The advantages of using sol-gel combustion are based on good chemical homogeneity, a highly pure and crystalline product, fine particle size, as well as easy control of stoichiometry of the final spinel. By adjusting the reactants ratio, pH, reaction conditions, and heat source, various shapes of ferrites such as nanospheres, hollow

nanocages, and nanorods can be synthesized [81]. Fig. 6 b and c shows TEM images of the Cu-ferrite with uniform size and average particle size of 56 nm and Zn-ferrite with average particle size in the range of 10–50 nm derived via sol-gel combustion and sol-gel methods, respectively [58,90].

Biosynthesis:

Biosynthesis of spinel ferrite nanoparticles using microbial enzyme or a plant phytochemical with stabilizing and/or reducing properties as an environmentally friendly method is an emerging research area and a suitable alternative to chemical and physical methods [91-94] (Fig.7a). Magnetotactic bacteria and iron-reducing bacteria have traditionally been utilized to synthesize metal ferrite magnetic nanoparticles. This method has shown potential in increasing the magnetization properties of metal ferrite NPs by doping them with cobalt. The phase of the produced magnetic nanoparticles is determined by the species of bacteria and the preparation circumstances (aerobic or anaerobic). *Actinobacter* bacteria, for example, can be used to synthesize maghemite nanoparticles with superparamagnetic properties in an aerobic

environment [95]. Since the mechanism of magnetic nanoparticle biogenesis is generally poorly understood, it is

challenging to pinpoint the variables that control shape and size while maintaining the proper saturation magnetization [65].

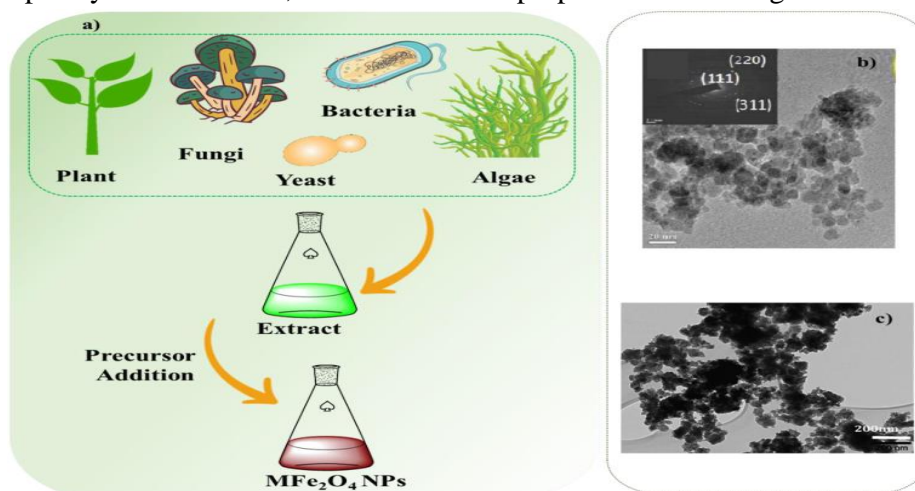


Fig. 6. a) Schematic biosynthesis of spinel ferrite nanoparticles, TEM images b) CuFe_2O_4 [96] and c) NiFe_2O_4 NPs [97].

Applications of Spinel Ferrites:

The properties of ferrite, including its structure, particle size, and shape, can vary depending on the cation type and synthesis method employed, resulting in diverse applications.

Sensors:

Sensors are electronic devices that detect changes in a given material in a specific environment. Ferrite nanoparticle-based sensors possess exceptional sensitivity, low detection limits, and high signal-to-noise ratios. The detection of variations in humidity is one of the most common uses of sensors. The monitoring of humidity is a widespread practice in both industrial and residential settings, as it helps to maintain human comfort, regulate storage conditions for various items, and ensure optimal operating conditions for industrial processes and devices. Typically, humidity sensing is primarily attributed to the surface effects of the interaction between water vapor and solids. Ceramic-based humidity sensors that utilize metal oxides have shown superior performance in terms of physical stability, thermal capability, mechanical strength, and chemical resistance compared to polymer films, making them a suitable

choice for applications in electrochemical humidity sensors. The electrical properties of ceramic surfaces, such as resistance, capacitance, or electrolytic conduction, undergo changes due to the adsorption of water. In this case, when humidity rises, so does conductivity, resulting in a greater dielectric constant. The microstructural properties of a material that are related to the synthesis procedure determine its humidity-sensing efficiency. ZnFe_2O_4 nanoparticles exhibit high sensitivity for humidity sensing, which can be attributed to their small grain size, large surface area available for water vapor adsorption, and low barrier height. Similarly, CoFe_2O_4 , CuFe_2O_4 , and NiFe_2O_4 nanoparticles have demonstrated effectiveness in sensing oxidizing gases like chlorine. CoFe_2O_4 sensors and actuators are more durable and widely used due to their high HC values and stability. The combination of high magnetostriction, sensitivity to applied stress, chemical inertness, and low cost has sparked interest in the use of magnetostrictive CoFe_2O_4 composites for the development of magnetoelastic sensors. Additionally, due to its bifunctional nature in terms of stress sensing and actuation or contraction under

the influence of a magnetic field, CoFe_2O_4 has been identified as a smart material with numerous technological applications in position sensors [105]. For application in gas sensors, ferrites with a single metal ion dopant, mixed ferrite materials (multi-ion doping), composites of ferrite with other metal oxides, polymers, and carbon materials/ferrite-based core-shell structures were also studied and Ranga et al. [106] summarized the findings in these results.

Photo Luminescent Applications:

Mixed spinel nanostructures such as CoFe_2O_4 , NiFe_2O_4 , and ZnFe_2O_4 are known for their photoluminescence at room temperature, which is considered one of their most significant properties. The spectrum of photoluminescence offers insights into various characteristics such as surface oxygen vacancies, defects, charge carrier trapping, and transfer efficiency. The broad visible band emission in mixed spinel nanostructures such as CoFe_2O_4 , NiFe_2O_4 , and ZnFe_2O_4 is attributed to charge transfers among Fe^{3+} at octahedral sites, M^{2+} ($\text{M} = \text{Co}$, Ni , and Zn) at both tetrahedral and octahedral sites, and the surrounding O_2 ions. The blue emission peak at 460 nm is attributed to the Fe^{3+} transition at the ferrite sites, whereas the primary peak at 418 nm is attributed to the free electrons that are trapped at the oxygen vacancies. As the Ni content increased, the intensity of each peak decreased due to the rising bandgap, which reduced the electron-hole recombination ratio. Radiating flaws related to interface traps within grain boundaries caused the violet emissions. With increasing doping fraction, the luminescence intensity of Co^{3+} from CoFe_2O_4 decreases, implying a reduced electron-hole recombination ratio. The energy gap of nanocrystalline ZnFe_2O_4 was measured to be around 2.13 eV using photoluminescence [107].

Magnetic Applications:

The variation of exchange contact between tetrahedral and octahedral sites causes the magnetization to be dependent on grain size. To minimize media noise in high-density magnetic recording, the magnetic particles utilized should have a nanoscale size to limit the exchange interactions occurring between adjacent grains. To achieve great storage density, the particles must also have high HC values. The magnetic characteristics (MR, MS, and HC) of spinel ferrites are affected by their composition, particle size, crystal structure, and cationic distribution between octahedral and tetrahedral sites. Furthermore, they may exhibit antiferromagnetic, ferromagnetic, and paramagnetic behaviour [108]. A rise in HC values in spinel ferrites can be attributed to a combination of factors, such as spin disorder, spin canting effect, and an increase in surface barrier potential in surface layers. The fascinating and improved properties of magnetic nanoparticles compared to similar bulk materials can be attributed to the large surface-to-volume ratio of the nanoparticles, which leads to the presence of a significant number of atoms at the surface. Furthermore, the low number of coordination surface atoms in comparison to its interior atoms in nanoparticles results in different surface effects, such as spin canting, spin disorder, and the presence of a magnetically dead layer [109]. Materials possessing high coercivity are referred to as hard materials, whereas those with low coercivity are termed soft materials. Inductor cores, transformers, and microwave devices are made of soft materials, while permanent magnets are made of hard materials. In general, soft ferrites are characterized by a low coercivity value, and their magnetization can be adjusted, making them suitable for advanced electronic engineering purposes, such as transformer cores, high-frequency inductors, and microwave components [110].

Dielectric Applications:

The dielectric structure typically consists of grains that are good conductors separated by grain boundaries with low conductivity. The dielectric properties of spinel ferrites are influenced by factors such as structural homogeneity, cation distribution, particle size, density, and porosity. Additionally, the dielectric properties can be significantly affected by synthesis techniques and thermal treatment parameters such as temperature, time, and heating/cooling rates. The presence of a small Co^{2+} ion at the tetrahedral site in CoFe_2O_4 results in a lower lattice constant, facilitating electron hopping between Fe^{3+} and Fe^{2+} ions and acting as a source of charge carriers, leading to an increase in the dielectric behaviour of CoFe_2O_4 . The polarization in CoFe_2O_4 is determined by the low-frequency hopping of charge carriers, which accumulates and causes polarization when it reaches the grain boundaries, resulting in high dielectric constants. The synthesis method and thermal treatment factors such as temperature, time, or heating and cooling rate play a significant role in determining these properties. The hopping of charge carriers at higher frequencies, on the other hand, is unable to follow the alternating current-produced field and is thus incompletely polarized, resulting in low dielectric constants. The dielectric constant falls as grain size increases, resulting in a smaller grain boundary between the microscopic grains. Lower frequencies have a large dielectric constant, which lowers as frequency increases. At a certain frequency, the decrease in dielectric constant becomes stable since at higher frequencies, only the dielectric polarization is responsible for contributing to the dielectric constant. At low temperatures, the charge carriers have limited mobility and are unable to align themselves in the direction of the applied electric field, leading to weak polarization

and a low dielectric constant. However, with increasing temperature, the mobility of the charge carriers increases, resulting in enhanced polarization and a higher dielectric constant. The interaction between different valence states of elements found in nanosized ferrites heavily influences the polarization, leading to an increase in dielectric constant as the temperature rises due to a large number of charge carriers releasing and contributing to polarization. The high dielectric constants observed at high frequencies can be attributed to the presence of space charge polarization, which arises due to the inhomogeneous dielectric structure caused by variations in grain size and impurities [111]. NiFe_2O_4 has a dielectric structure consisting of conducting grains and grain boundaries. The transfer of electrons between Fe^{2+} and Fe^{3+} ions and holes between Ni^{3+} and Ni^{2+} ions enables electrical conduction and dielectric polarization. However, at higher frequencies, the electron/hole exchange frequency cannot keep up with the applied electric field, leading to lower polarization [112].

Waste water treatment Industrial wastewater management has become one of the most pressing issues in developed countries in recent years. Textile wastewaters contain a variety of non-biodegradable organic dyes, as well as other pollutants in varying concentrations. Untreated effluents harm not only humans and animals but also plants. RhB is a synthetic, highly poisonous, water-soluble organic dye that is commonly found in the wastewaters and is widely employed as a colorant in various industries. For the treatment of RhB-containing water, various procedures have been used, including ozonation, the electrochemical method, and the Fenton process. In recent years, magnetic NPs have attracted considerable attention due to their special magnetic properties, high adsorption capacities and surface area to

volume ratio. The extensive applications of spinel ferrite NPs in water and wastewater-related treatments have been shown in many studies. The roles of spinel ferrite nanoparticles include their potential use as an adsorbent for pollutants and their ability to catalyse the degradation of organic pollutants under photocatalytic conditions. These applications have been widely studied. CoFe_2O_4 is used in wastewater treatment due to its several useful properties. First, it has a high capacity for adsorbing pollutants from water. Second, the material's magnetic properties enable the separation of nanoparticles using an external magnetic field, making it easy to remove them from the water. Finally, CoFe_2O_4 has a low energy bandgap, which means it can be used for photocatalytic degradation of RhB when exposed to visible light [113]. Moreover, CuFe_2O_4 is also being explored as a potential material for various fields of water purification such as adsorption of toxic metals, degradation of organic dyes and photocatalysis [114]. CuFe_2O_4 can be used as cost-effective adsorption for removing MB from water and wastewater when combined with a suitable adsorbent. In addition, ZnFe_2O_4 can be utilized as a magnetically recyclable material to remove chemical impurities (such as colors) and biological contaminants from water/industrial wastewater treatment [115]. Kefeni et al. [116] conducted a review on the various applications of spinel ferrite nanoparticles, including their use for disinfecting pathogens, modifying membranes, extracting analytes, and sensing and detecting different types of metal ions in water and wastewater treatment.

Catalytic Applications:

Spinel ferrites are commonly used as heterogeneous catalysts due to their ease of recovery from reaction mixtures by filtering or using an external magnetic field, making the process cost-effective and environmentally friendly through their

multiple recyclings. To be economically valuable and ecologically friendly, heterogeneous catalytic nanoparticles play a key role in the selective protection of functional groups. The catalytic characteristics of various spinel ferrites (MFe_2O_4 , where M is Cu, Ni, Co, or Zn) were evaluated, and the CoFe_2O_4 catalyst showed the most excellent performance with benzaldehyde, achieving 63% conversion and 93% selectivity, while the CuFe_2O_4 catalyst demonstrated the best performance with H_2O_2 oxidant, attaining 57.3% conversion and 89.5% selectivity. The catalytic activity of materials is greatly influenced by particle size, surface area, morphology, and chemical composition. The catalytic activity of nanocrystalline spinel ferrites is also influenced by the distribution of cations between tetrahedral (A) and octahedral (B) sites. CoFe_2O_4 has been found to exhibit superior catalytic performance compared to other ferrites [117].

Photocatalytic applications
Photocatalysts are important materials that facilitate the use of solar energy in oxidation and reduction reactions, with numerous applications including removing water and air pollution, managing odors, deactivating bacteria, splitting water to generate hydrogen, inactivating cancer cells, and other areas. Currently, photocatalysis is a preferred method for removing dyes, as irradiation of light on a semiconductor can generate electron-hole pairs that can be utilized for oxidation and reduction processes. Dye degradation is caused by the generation of active radicals during the photocatalytic reaction. There are only a limited number of materials that can perform both photo-oxidation and photo-reduction, meaning they can effectively remove harmful organic compounds while also efficiently absorbing visible light. Ferrites have a wide surface area and many reaction sites due to their small crystallite size, which

increases photocatalytic activity. The effectiveness of photocatalysis depends on various factors such as the choice of photocatalyst, size of the nanoparticles, level of crystallinity, accessibility of the active surface to pollutants, and resistance to diffusion of organic pollutants. These parameters can significantly impact the photocatalytic properties of the material. Small particle size and high crystallinity are important factors that enhance the specific surface area and active sites, leading to improved photocatalytic activity. Ferrites are excellent candidates for photocatalysis due to their spinel crystal structure and bandgap that can absorb visible light. They are capable of degrading a wide range of contaminants [118]. Spinel ferrites such as NiFe_2O_4 , ZnFe_2O_4 , CuFe_2O_4 , and SnFe_2O_4 have shown light activity, magnetic recyclability, low cost and eco-friendly. These spinel ferrites can be coupled to commonly used photocatalysts to add magnetic properties into it, to help easy separation by an external magnetic field as well as enhance photocatalytic degradation of contaminants and stability. Fe_2O_3 considered as stable semiconductor for photocatalyst reactions due to low band gap (2.3 eV), recyclability earth abundant high harvesting light and excellent stability, and ease of surface modification relative to other spinel ferrites. Heterojunction construction can be an effective strategy to simultaneously utilize high redox potential and broad absorption range which is merely not possible in either bare or doped photocatalysts. Cai et al. [119] showed in photocatalytic mechanism of Zn ferrites based heterojunction, the photon-illuminated electron is migrated to the conduction band reducing Fe^{3+} to Fe^{2+} also generating. SO_4^{2-} Radical on conduction band. OH at valence band. Removal efficiencies for chemical oxygen demand and organic carbon at 300 min were 50.5% and 78.6%, respectively. Due to the rapid recombination

of charge carrier and small hole dispersion distance, ferrites as the single component doesn't have acceptable performance. Therefore, doping in ferrites suppresses the recombination rate of charges and lower luminescence intensity. Different support materials were utilized to magnify adsorptional ability by increasing surface area and improving thermal and chemical stability. The various support such as SiO_2 , g- C_3N_4 , carbon nanotubes grapheme, and metal organic framework were used.

Colouring:

Ceramic dyes are composed of metal transition oxides and possess exceptional chemical and thermal stability, as well as a high tinting strength when dispersed and fired with glazes or ceramic matrices. They also exhibit a high refractive index, resistance to acid and alkali, and low abrasive strength when dispersed and fired with glazes or ceramic matrices. Each pigment's color is achieved by combining chromophore agents (often transition metals) with an inert oxide matrix. CoFe_2O_4 is a black pigment that is frequently used in the ceramic industry. The performance of the pigment is affected by the coating crystallization, with a higher number of crystals in the glass leading to a brighter color. ZnFe_2O_4 NPs have a high covering power and a low cost and are thermally stable, insoluble, and resistant to aggressive media. ZnFe_2O_4 spinel pigments react with the corrosive environment, producing cationic soaps that enhance the binder's mechanical strength and reduce solubility. During the process of annealing, the color of ZnFe_2O_4 may be affected by both the particle size and the annealing temperature. This is because annealing can result in a reduction in the total reflecting surface of the powder, which can have an impact on the overall color. The system undergoes a significant change at high annealing temperatures due to the removal of defects (such as oxygen vacancies), leading to less

distorted tetrahedral and octahedral sites and, as a consequence, better-defined color. By selectively choosing cations to occupy specific sites within the spinel lattice (for example, Zn^{2+} in A sites and Fe^{3+} in B sites for $ZnFe_2O_4$), it is possible to modify or create new properties of pigments when dispersed in an organic binder [120].

Corrosion Protection:

Metal corrosion is typically caused by an electrochemical reaction in which metal ions dissolve due to the presence of certain factors, such as moisture, oxygen, and chemicals like chloride ions, which can dissolve protective layers of oxides on the metal surface and accelerate the corrosion process. The electrochemical process of metal corrosion can be limited by converting ferrous (Fe^{2+}) ions to ferric (Fe^{3+}) ions, which operate as inorganic corrosion inhibitors. This process can result in the production of a passivation layer that prevents both cathodic and anodic reactions, thus limiting the corrosion of the metallic substrate. Organic coatings protect against corrosive conditions by acting as a barrier or mechanical protection. Nanocontainers can be incorporated into an organic coating and used to release corrosion inhibitors, thereby protecting the metal substrate from corrosion. Coating with $CoFe_2O_4SiO_2$ nanoparticles can enhance the corrosion protection performance of coatings by filling and covering free cavities and electrolyte pathways more effectively than using $CoFe_2O_4$ alone. The inclusion of $CoFe_2O_4SiO_2$ Nano pigment into epoxy coatings improves the coating corrosion resistance noticeably. Moreover, applying a $ZnFe_2O_4$ coating on the surface of particles like diatomite, talc, wollastonite, and kaolin has been found to greatly enhance their corrosion resistance. Surface treatment with low levels of $ZnFe_2O_4$ (16–20 wt %) improves corrosion resistance [121].

Antimicrobial Applications:

Iron plays a significant role in the development of microbial infections, as many organisms use iron sequestration as a defense mechanism. Microorganisms resistant to Fe^{+2} and Fe^{+3} also display unexpected resistance to several antibiotics. MFe_2O_4 nanoparticles have been shown to possess excellent antibacterial properties against various bacteria and fungi. *Escherichia coli* has been found to develop resistance to excess iron primarily by changing the way it absorbs iron. $CoFe_2O_4$ nanoparticles (NPs) are commonly used for biomedical purposes because of their ability to combat various human infections. Their high surface area-to-volume ratio and nanoscale size make them effective against harmful microorganisms. A nanocomposite called $CoFe_2O_4@SiO_2@Ag$, when combined with Streptomycin, has demonstrated significant antibacterial properties against both Gram-positive and Gram-negative microorganisms. The inclusion of Ag NPs on $CoFe_2O_4@SiO_2$ prevents aggregation and enables easy retrieval from the solution after disinfection through an external magnetic field, owing to the presence of a magnetic core in the composite. $CoFe_2O_4$ attaches to microorganism membranes, lengthening the lag stage of the bacterial growth phase, widening microorganism production time, and enhancing bacterial cell division. The antibacterial activity of $CoFe_2O_4$ nanoparticles is attributed to the generation of superoxide (O^{2-}) and hydrogen peroxide (H_2O_2) that exhibit antibacterial properties. The migration of these effective oxides over the cell membrane of bacteria leads to the antibacterial activity of the ferrite nanoparticles against unicellular fungi. $ZnFe_2O_4$ nanoparticles have been found to possess effective antibacterial activity against different strains of bacteria, including *Lactobacillus*, *Escherichia coli*, *Bacillus cereus* (which are Gram-positive), and *Aeromonas hydrophila* and *Vibrio*

harveyi (which are Gram-negative). The antibacterial activity of the nanoparticles was observed to be dependent on their small crystallite size and surface area [122,123].

Biomedical Applications:

For use in biomedical applications, magnetic nanoparticles need to have high magnetic saturation values and be biocompatible, while also being stable and non-agglomerated when dispersed in water. These nanoparticles can be used within individual cells to facilitate magnetic fluid hyperthermia, drug delivery, and stimulation of metabolic pathways through thermal excitation. MnFe_2O_4 nanoparticles have attracted significant interest in the field of biomedicine due to their desirable properties, including simple synthesis, controllable size, high magnetization value, superparamagnetic nature, ability to be monitored by an external magnetic field, and high biocompatibility. The surface modification of MnFe_2O_4 NPs by incorporating them into mesoporous SiO_2 nanospheres or coating them with mesoporous SiO_2 can enhance the stability of the nanoparticles in water, improve their biocompatibility, and prevent their agglomeration and degradation. The physical properties of CoFe_2O_4 , particularly its great stability, have sparked a lot of interest in possible biomedical applications. CoFe_2O_4 has been utilized for medication administration, imaging, and brain tumor therapy in general. At high concentrations of CoFe_2O_4 NPs, metal ions are released, and a portion of these ions can enter cells and lead to cytotoxicity. One possible reason for this could be that the inhibition of cell transcription and protein synthesis leads to changes in cellular function. The adverse effects can be eliminated or reduced by applying a biocompatible SiO_2 coating. The coating of CoFe_2O_4 NPs caused a decrease in their adhesion as the SiO_2 matrix possessed a negative charge. The NPs exhibited superparamagnetic properties with low MS

values, increased compatibility, and became well-suited for medical applications, including drug delivery to cancer cells and the use of a contrast agent for cancer diagnosis in magnetic resonance imaging. Hyperthermia is a therapeutic procedure used to treat oncological diseases, whereby living tissues containing both healthy and carcinoma cells are exposed to constant overheating (above 43 °C), leading to necrosis. However, hyperthermia induced by magnetic nanoparticles through magnetic induction may provide a promising solution by selectively heating and destroying tumor tissue while minimizing damage to healthy tissue. Magnetic hyperthermia is a recently developed supplementary treatment for malignant tumours that involves the use of appropriate magnetic nanoparticles in a magnetic field, generating heat that aids in the elimination of damaged tissues at a temperature ranging [123].

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