

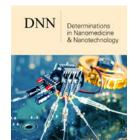


Mini Review: Synthesis and Applications of Spinel Ferrites (Mfe₂o₄)

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Abstract

Magnetic spinel ferrite materials have attracted considerable attention due to their diverse applications in biomedical, water treatment, and industrial electronic devices. This mini review focuses on the synthesis and applications of spinel ferrites across various fields, with a particular emphasis on doped spinel ferrite nanoparticles. These doped nanoparticles exhibit remarkable electrical and magnetic properties, making them highly suitable for various applications. For instance, in the biomedical field, spinel ferrite nanoparticles have shown promising potential in targeted drug delivery systems, magnetic hyperthermia for cancer treatment, and contrast agents for Magnetic Resonance Imaging (MRI). In water treatment, these nanoparticles have been utilized for the removal of heavy metals, organic pollutants, and dyes due to their excellent adsorption properties.

Additionally, in the realm of industrial electronic devices, spinel ferrite nanoparticles have been employed in high-frequency transformers, Electromagnetic Interference (EMI) shielding, and power inductors, showcasing their versatility and relevance in modern technological applications. Additionally, by substituting metallic atoms, the physical properties of spinel ferrites can be tailored, leading to enhanced performance. The review examines the latest and most significant developments in the utilization of magnetic ferrite nanoparticles and provides insights on choosing the appropriate magnetic ferrites for specific applications.

Keywords: Ferrites; Spinel ferrites; Nanoparticles; Applications

Introduction

Spinel ferrite materials are a class of metal oxides characterized by their spinel structures and can be denoted by the chemical formula AB204. Within this structure, metal cations occupy two types of positions: tetrahedral positions denoted by A and octahedral positions denoted by B. These metal cations' specific types, quantities, and arrangement within the crystal lattice play a crucial role in determining the physical and chemical properties of ferrites [1,2]. Nanocrystalline magnetic materials have captured the interest of researchers in multiple fields like physics, chemistry, biology, medicine, materials science, and engineering due to their exceptional and unique characteristics. These materials are considered nanomaterials, having particle sizes up to 100nm and a high surface-to-volume ratio. This distinctive feature leads to altered or improved reactivity, thermal, mechanical, optical, electrical, and magnetic properties when compared to their bulk counterparts [3-6]. While the chemical composition of bulk materials primarily determines their qualities, for nanomaterials, factors such as particle size and morphology, in addition to the chemical composition, play a significant role in shaping their characteristics.

Moreover, these properties can be finely adjusted depending on the specific particle size and chemical composition [3], [7-9]. Among the various nanomaterials, ferrites stand out as particularly intriguing materials from both practical and theoretical perspectives. Magnetic nanoparticles like CoFe₂O₄, MnFe₂O₄, CuFe₂O₄, ZnFe₂O₄, and NiFe₂O₄ have garnered

considerable attention due to their thermal and chemical stability, unique structural, magnetic, optical, electrical, and dielectric properties, and their wide range of technological applications. These applications span from photocatalysis, photoluminescence, biosensors, and humidity-sensors to catalysis, magnetic refrigeration, permanent magnets, magnetic drug delivery, and magnetic hyperthermia [10,11].

This study investigated the characteristics of spinel ferrites $(MFe_2O_4, M=Zn, Mn, Cu, and Co)$ and doped ferrites $(Cu^{+2}, Zn^{+2}, Mn^{+2}, Al^{+3}, Gd^{+3}, and Mg^{+2})$ using various transition metals. These materials were synthesized through multiple methods such as Sol-gel process, Co-precipitation, and Electrochemical Deposition. The research focused on exploring their thermal, structural, morphological, and magnetic properties.

Synthesis Process

The primary focus of this section is to introduce and evaluate some traditional methods used for synthesizing spinel ferrite nanoparticles (NPs) with the general formula MFe_2O_4 .

Sol-gel method

The sol-gel method and the sol-gel auto-combustion synthesis are two techniques commonly used to produce MFe2O4 magnetic nanoparticles with precise nanostructures for engineering applications. The sol-gel method involves adding a precursor solution to undergo polymerization or hydrolysis reactions, leading to the formation of a sol. By using polymer addition or sol condensation to gel and simple solvent evaporation, MFe204 nanoparticles are obtained. This method allows for easy control over the shape and size of the nanoparticles, but it has a drawback of low purity, requiring thermal treatment to achieve high purity and crystallinity. On the other hand, the sol-gel auto-combustion synthesis combines the sol-gel and combustion processes. It utilizes an exothermic anionic redox reaction of xerogel, which is derived from an aqueous solution containing metal salts and an organic complexant like urea, glycine, or citric acid. The combustion reaction takes place at a high temperature range of 600 to 1350 °C, resulting in ferrite nanoparticles with excellent chemical homogeneity, high purity, crystallinity, and fine particle size. Moreover, adjusting the reactants ratio, pH, reaction conditions, and heat source allows for the synthesis of various shapes of ferrite nanoparticles, including nanospheres, hollow nanocages, and nanorods. In summary, the sol-gel method is a simple and low-cost approach for producing MFe₂O₄ nanoparticles with control over shape and size, but it requires additional thermal treatment for higher purity. On the other hand, the sol-gel auto-combustion synthesis offers the advantage of producing highly pure and crystalline nanoparticles with fine particle size and allows for the synthesis of different shapes through parameter adjustments [1,2].

Co-precipitation method

Co-precipitation is the method which is a straightforward and cost-effective process for producing MFe_2O_4 NPs. The NPs obtained

through this method possess a homogeneous structure, high purity, and controllable size. The process involves mixing a solution containing stoichiometric amounts of metal salts (such as nitrates, chlorides, or sulfates) with a base at sufficient temperatures, which acts as a precipitating agent. Several factors, including temperature, pH, reaction time, and the type and ratio of precursors, significantly influence the size, shape, and properties of the spinel ferrite NPs. This method allows for the production of homogeneous and pure spinel ferrites of controlled sizes. Co-precipitation is a conventional approach used in chemical synthesis, particularly for dispersing large volumes of MNPs in aqueous media. In this method, precursor elements co-precipitate in a solution at high or room temperature under an inert atmosphere.

The ability to scale up and produce significant quantities of MFe2O4 MNPs is one of the most important advantages of the co-precipitation approach. Therefore, it is commonly employed in industrial settings to synthesize large quantities of MFe_2O_4 nanoparticles. However, challenges associated with the co-precipitation method include achieving precise control over morphology, crystalline quality, and particle size distribution of the MNPs. The low crystallinity of NPs produced by co-precipitation is the primary drawback, which can be improved through subsequent heat treatment [12].

Electrochemical deposition

In electrochemical synthesis, the fundamental idea revolves around transferring an electric current between two or more electrodes (referred to as the anode and cathode), which are immersed in an electrolyte. Through this process, the anode generates metal ion species within the electrolyte. These metal ions are then reduced at the cathode with the aid of stabilizers to form the corresponding metal. It's worth noting that altering the deposition potential and electrolyte composition has a substantial impact on the film-forming characteristics of magnetic nanoparticles, as supported by existing literature [13].

Applications

Spinel ferrites, denoted as MFe_2O_4 , find various practical uses. The unique characteristics of these ferrites, such as their structure, particle size, and shape, can be tailored based on the cation type and synthesis technique used, leading to a wide range of applications in different fields.

Sensors

Sensors are electronic devices designed to identify alterations in specific materials within a given environment. Among these sensors, those incorporating ferrite nanoparticles demonstrate remarkable sensitivity, low detection limits, and high signal-tonoise ratios. One prominent application of sensors is the detection of humidity variations, a common practice in both industrial and residential settings. This is crucial for maintaining human comfort, regulating storage conditions for various items, and ensuring optimal operation of industrial processes and devices. The interaction between water vapor and solids at the surface level is primarily responsible for humidity sensing. Ceramic-based humidity sensors that employ metal oxides have proven to be highly effective due to their physical stability, thermal capability, mechanical strength, and chemical resistance, outperforming polymer films. Consequently, they are particularly suitable for use in electrochemical humidity sensors. The electrical properties of ceramic surfaces, such as resistance, capacitance, or electrolytic conduction, undergo changes as they adsorb water. With rising humidity levels, conductivity increases, leading to a higher dielectric constant [14].

Treatment of waste water

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 nonbiodegradable 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, watersoluble 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.

Applications in biomedical

In biomedical applications, magnetic nanoparticles must possess certain characteristics to be effective. They need to have high magnetic saturation values and be biocompatible, while also remaining stable and non-agglomerated when dispersed in water. These nanoparticles find utility in various cellular functions, such as magnetic fluid hyperthermia, drug delivery, and stimulation of metabolic pathways through thermal excitation. Among the magnetic nanoparticles, $MnFe_2O_4$ nanoparticles have gained significant attention in the field of biomedicine.

This is due to their desirable properties, including straightforward synthesis, controllable size, high magnetization value, superparamagnetic nature, ability to be monitored by an external magnetic field, and high biocompatibility. Scientists have found that by modifying the surface of $MnFe_2O_4$ nanoparticles, like incorporating them into mesoporous SiO₂ nanospheres or coating them with mesoporous SiO₂, their stability in water can be enhanced, along with improved biocompatibility, and prevention of agglomeration and degradation. Magnetic hyperthermia is an emerging supplemental treatment for malignant tumors that involves the use of suitable magnetic nanoparticles in a magnetic field to generate heat, aiding in the elimination of damaged tissues. This process is carried out within a temperature range of 41 to 46 °C. Ferromagnetic materials exhibit hysteretic characteristics under a time-varying magnetic field, leading to magnetically induced heating. Magnetic nanoparticles have the advantage of being low in toxicity, biocompatible, and well-tolerated by living organisms, making it easier to evaluate their specific absorption rates quickly. Some studies propose using magnetophoresis, which involves a magnetic field gradient acting on the magnetically induced magnetic moment of a particle, as an effective method for delivering ferrimagnetic nanoparticles to a tumor site. Additionally, magnetophoresis is utilized in various commercial and industrial procedures to separate magnetic nanoparticles suspended in fluids. Despite these promising applications, a fundamental challenge of hyperthermia is to minimize harm to neighboring normal tissues during the treatment process.

Challenges and Future Prospects

In recent decades, there has been considerable interest in nanoscale spinel ferrites due to their unique characteristics, including stability in chemical and thermal environments, strong coercivity, high anisotropy constant and Curie temperature, moderate saturation magnetization, high electrical resistance, and minimal eddy current loss. These properties make them promising candidates for various applications in biomedicine, catalysts, water treatment, and energy fields. To fully utilize the potential of magnetic spinel ferrites, researchers are focusing on refining their properties through modifications in synthesis methods, allowing control over particle size, shape, and crystallinity. Doping is also recognized as an effective approach in preparing nonaggregated and uniform nanosized spinel ferrites.

One of the notable applications of magnetic spinel ferrites is in magnetic hyperthermia, although this field is still in its early stages. Addressing challenges related to fine-tuning the size, shape, and magnetic properties of nanoparticles is essential for advancing this area. Furthermore, exploring efficient surface modification methods for spinel ferrites is crucial, particularly for biomedical applications where optimal performance is desired. Regarding waste water treatment, magnetic spinel ferrites have shown potential in degrading organic pollutants through photocatalysis. However, there are still challenges that require further investigation to fully develop the photocatalytic properties of spinel ferrite nanoparticles for this purpose.

Conclusion

In recent times, there has been significant interest in MFe2O4 materials due to their distinct characteristics, which include their ability to remain stable under various mechanical, chemical, and thermal conditions. They exhibit high coercivity, elevated anisotropy constant and Curie temperature, along with high electrical resistance, moderate saturation magnetization, and minimal eddy current loss. The synthesis methods used to create MFe_2O_4 play a crucial role in determining their utility in various applications; efficient synthesis processes result in MFe_2O_4 that performs better and withstands the conditions during their creation. However, when considering biomedical applications, it is essential to explore cost-effective methods for synthesizing large quantities of MFe_2O_4 with uniform size and shape. Additionally, a comprehensive assessment of the toxicity of specific MFe_2O_4 nanoparticles is imperative.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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