Review on The Gas Sensing Applications of Spinal Ferrie Nanoparticles

Binu P. Jacob, Associate Professor, Dept. of Physics, K.M.M. Govt. Women's College, Kannur

Abstract

The ferromagnetic spinel ferrite nanoparticles have become a promising material for gas sensors because of their porous structure and high sensitivity to a wide range of gases. High surface to volume ratio of ferrite nanoparticles improves the rate of gas adsorption and there by sensitivity to different toxic gases. This review focuses on crystalline structure, electronic and magnetic properties, and synthesis techniques of different spinel ferrite nanoparticles suitable for gas sensing applications. The processes involved in sensing gas namely adsorption-desorption and charge transfer are explained with highlight on their sensitivity and selectivity towards ammonia (NH_3), nitrogen dioxide (NO_2), hydrogen sulphide (H_2S), carbon monoxide (CO), and volatile organic compounds (VOCs). In addition, new methods to improve the sensitivity like metal doping, creation of composites with carbon-based matter, surface modification, the control of morphology, are investigated. Even after making a remarkable progress, issues related to selectivity, operational reliability, and environmental friendliness exist, which indicates that the improvement of such aspects through research must be aimed at the green synthesis, integration of the advanced sensors into the internet of things and designing of the smart and flexible gas sensors devoted to environmental monitoring, industrial safety, and medical diagnostics are needed in the future.

Keywords: Spinel ferrite nanoparticles, gas sensing, metal oxide sensors, ammonia sensing, nitrogen dioxide sensing, hydrogen sulphide detection, carbon monoxide sensing

1. INTRODUCTION

Over the past years, the research on gas sensing technology was a subject of great interest due to the wider usage in environmental monitoring, industrial process control, automotive emissions, and medical diagnostics [1, 2]. The quick sensing of hazardous or flammable gases at low concentration levels is highly essential in the aspect of human safety and environmental safety. However, some common disadvantages that are encountered in the use of traditional gas sensors include insensitivity, poor selectivity and high operating temperatures which demands improved sensing materials incorporating better performance parameters [3]. Of all the nanomaterials investigated as gas sensor, spinel ferrite nanoparticles have proved useful because of their peculiar properties like porous structure, high sensitivity, and compositional variability [2].

Spinel ferrites are a group of metal oxides with general formula MFe_2O_4 with M being a divalent metal ion, typically Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} or Cu^{2+}. They have a crystal structure, which has tetrahedral (A) and octahedral (B) sites, allowing cation distributions that affect electronic conductivity, surface reactivity and defect chemistry, all of which are important in their gas sensing mechanisms [4, 5]. High surface area to volume ratio of spinel ferrite nanoparticles offers more active sites to be filled with gas molecules and increases the rate of electron transfer between the states during the sensing mechanism. Also, their structural, morphological, and compositional properties can be tuned by different synthesis techniques like sol-gel, hydrothermal, co-precipitation and combustion techniques to optimise their sensitivity for certain gas target.

Some researchers have claimed that spinel ferrite nanoparticles can be used for detecting gases like ammonia (NH_3), hydrogen (H_2), nitrogen dioxide (NO_2), hydrogen sulphide (H_2S), carbon monoxide (CO) and volatile organic compounds (VOCs) with significant increase in sensor sensitivity, selectivity and response-recovery times at low operating temperatures compared with conventional metal oxide sensors [6,7,8,9]. Moreover, noble metals doping or ferrite compounding with other materials such as graphene or reduced graphene oxide further improves their sensing capability because of the beneficial synergetic effects.

Table 1: Key Literature Summary

Reference	Focus Area	Key Findings	Relevance to Gas Sensing Applications
Andersen et al. (2018) [10]	Crystalline and magnetic structure–property relationships in spinel ferrite nanoparticles	Investigated the correlation between crystalline structure, cation distribution, and magnetic properties in various spinel ferrite nanoparticles using synchrotron X-ray diffraction and neutron scattering techniques.	Understanding cation distribution and magnetic ordering is crucial for tailoring electronic and surface properties for enhanced gas sensing performance.
da Silva et al. (2019) [11]	Structural and magnetic properties of spinel ferrite nanoparticles	Reported synthesis and detailed analysis of structural, morphological, and magnetic properties of spinel ferrites, highlighting the effect of particle size and synthesis conditions on their magnetic behaviour.	Provides insight into the influence of structural and magnetic tunability on charge transfer processes and adsorption capacities relevant for gas sensing.
Gardon & Guilemany (2013) [12]	Metal oxide gas sensors: fabrication, sensing mechanisms, and performance	Reviewed fabrication methods, gas sensing mechanisms, and performance characteristics of various metal oxide-based gas sensors, discussing factors affecting sensitivity and selectivity.	Offers fundamental understanding of metal oxide gas sensing mechanisms applicable to spinel ferrites for designing efficient sensors.
Gul et al. (2020) [13]	Al-substituted zinc spinel ferrite nanoparticles: structural, electrical, magnetic, and photocatalytic properties	Explored the synthesis of Al-doped $ZnFe_2O_4$ nanoparticles, analysing their structural, electrical, and magnetic properties along with photocatalytic activities under UV irradiation.	Highlights how dopant incorporation modifies electronic and surface properties, which can be leveraged for improving spinel ferrite-based gas sensor performance.

This review attempts at providing a systematic overview of the state-of-art of the gas sensing application of spinel ferrite nanoparticles in terms of method of synthesis, structural and morphological properties, gas sensing mechanisms, performance parameters and issues that are related to their real-life implementation. These aspects will enlighten the researchers and engineers to design new generation of spinel ferrite nanostructures-based gas sensors with various applications in daily life.

2. SPINEL FERRITE NANOPARTICLES: STRUCTURE, PROPERTIES, AND SYNTHESIS METHOD

Spinel ferrite nanoparticles are one important class of magnetic metal oxides with the general formula MFe_2O_4 where M is a divalent metal cation (Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Mg^{2+} or Cu^{2+}). Spinel ferrites adopt a cubic spinel structure of oxygen anions stacked in a close-packed structure with metals cations occupying tetrahedral (A) or octahedral (B) interstitial sites [5]. Divalent metal cations and their spatial distributions dictate their electronic, magnetic, and catalytic properties which can be utilized in sensing applications and gas sensing applications [14].

2.1. Structural Features

The spinel structure exhibits eight formula units in every unit cell, and the distribution of the divalent and trivalent cations (on the A and B sites) can be either normal or inverse spinel. In normal spinel, divalent cations will occupy the A site while trivalent cations occupy the B site, while in inverse spinel, the trivalent cations are equally distributed at A and B sites and divalent cations occupy the B sites [5]. The distribution affects the lattice parameters, crystallite size, energy surface, and the defect concentration, which all affect the gas adsorption and sensor performance.

2.2. Electronic and Magnetic Properties

Due to electron hopping between Fe^{2+} & Fe^{3+} ions that occupy the octahedral sites, spinel ferrite nanoparticles can exhibit some semiconductor properties. This electronic behaviour is crucial in their gas detection/sensing property. In the gas detection mechanism, the electron hopping process and thereby the charge transfer is affected by the adsorption of gas molecules on the surface of the ferrite nanoparticles, that changes their resistance. The magnetic properties of the spinel ferrite nanoparticles (soft / hard ferromagnetic) can offer easy recovery from the substrate and potential use for magnetic sensing or separation devices.

The dimension of spinel ferrite nanoparticles is nanoscale, which increases the surface area to volume ratio from a bulk material. More surface area provides more active sites available for target gas molecule adsorption, which increases the sensitivity and can reduce both response and recovery times. Other factors including oxygen vacancies, cation distribution, and surface defects can also play important roles toward enhancing reactivity and catalytic properties of spinel ferrite nanoparticles for certain gases [8,9,12,15].

2.3. Synthesis Methods

Several synthesis techniques are employed to fabricate spinel ferrite nanoparticles with controlled size, morphology, and crystallinity, which are essential for optimizing their gas sensing performance.

2.3.1. Co-precipitation Method

This method is relatively simple, inexpensive, and easy to scale up. In the co-precipitation method, metal cations dissolved in salt solutions are precipitated simultaneously by controlled addition of a suitable base to the solution, while maintaining constant pH and temperature conditions. After precipitation, the solid is washed, dried, and calcined, resulting in phase-pure spinel ferrite nanoparticles with the desired crystallinity and particle size [5,16].

2.3.2. Sol-Gel Method

The sol-gel method provides excellent chemical homogeneity, with the added advantage of controlling the particle size. In the sol-gel method metal precursors are typically used in the form of nitrates or alkoxides and undergo hydrolysis and condensation reactions to produce a homogeneous gel network. Spinel ferrite nanoparticles in a consistent size range and controlled morphology can be made by drying the gel network and then calcining it [17]. For these reasons sol-gel methods are well suited for the synthesis of advanced functional materials.

2.3.3. Hydrothermal/Solvothermal Methods

These methods use high temperature and pressure (below the boiling point of water or organic solvent) in an aqueous or organic solvent medium to form crystalline spinel ferrite nanoparticles. Hydrothermal and solvothermal methods describe how nanoparticles form, while the reaction parameters lower or at high temperature (solvent-dependent), temperature (solvent-dependent), timing (hours to days), and solvent type define the particle morphology (defined morphologies include nanorods, nanospheres, and hollow particles).

2.3.4. Combustion Synthesis

In combustion synthesis, metal nitrates and organic fuels (urea, glycine) undergo an exothermic redox reaction that results in the fast formation of spinel ferrite nanoparticles. This method is superior because it allows for nanoparticles to have large surface areas and porous structure in a very short reaction time. It is also considered to be an energy efficient and cost-effective method to produce large amounts of nanoparticles.

2.3.5. Microwave-Assisted Synthesis

The use of microwave-assisted synthesis introduces uniform volumetric heating which can significantly reduce the time to perform the reaction and increase energy efficiency. Microwave-assisted synthesis can yield spinel ferrite nanoparticles that can control the nanoparticle size distribution and have better crystallinity due to the increased rates of nucleation and growth from the microwave irradiation process. Microwave-assisted synthesis has great potential for the efficient, low-cost synthesis of these nanoparticles in a scalable manner.

3. **Green Synthesis**

Green synthesis is the approach uses environmentally friendly approaches to synthesise spinel ferrite nanoparticles, that is, using plant extracts, biopolymer or biological materials as natural reducing agents and stabilisers, producing biocompatible and eco-sustaining nanoparticles for biomedical and environmental applications following the sustainable and green chemistry ethos. The selection of the synthesis route plays a key role in determining the particle size, morphology, crystallinity, surface defects, and cation distribution, which, together, determine the gas sensing performance parameters, with the sensitivity, selectivity, operating temperature, and stability.

4. GAS SENSING MECHANISMS AND PERFORMANCE APPLICATIONS

The mechanism for gas sensing with spinel ferrite nanoparticles relies on their electrical resistance change when they are exposed to target gas molecules [18]. Spinel ferrites are semiconducting metal oxide materials and interact with gas molecules on the surface of the material through adsorption-desorption processes.

In the ambient atmosphere, the oxygen molecules adsorb on the nanoparticle surface and take electrons from the conduction band to produce chemisorbed oxygen species (e.g., O_2^-, O^- and O^{2-}). Ideally, this creates a space charge layer of depleted electrons and increases electrical resistance.

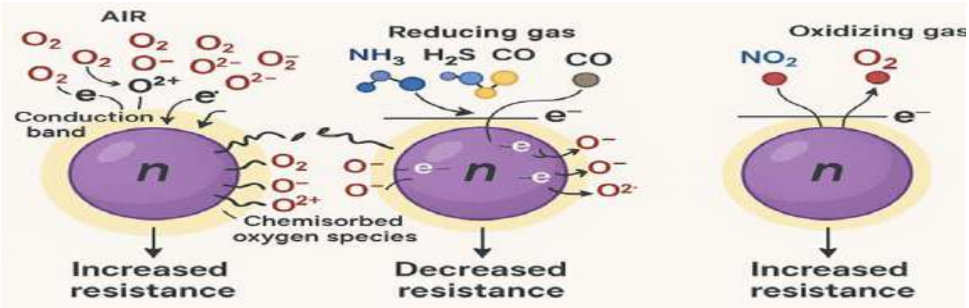

Figure 1: Gas Sensing Mechanisms [11]

When reducing gases such as ammonia (NH_3), hydrogen sulphide (H_2S), and carbon monoxide (CO) are introduced, the selected target gas reacts with the chemisorbed oxygen species and subsequently returns the captured electrons to the conduction band which results in decreased resistance. Conversely, oxidizing gases, particularly nitrogen dioxide (NO_2), first captures electrons from the conduction band upon adsorption, resulting in an increase in resistance.

The change in resistance is directly proportional to the concentration of the target gas, allowing for quantification. Further, factors such as particle size, surface area, porosity, number of oxygen vacancies, and distribution of cations, determine the ultimate performance of the semiconductor gas sensor by affecting adsorption capabilities and charge transfer.

4.1. Performance Applications for Various Gases

4.1.1. Ammonia (NH_3) Sensing

The spinel ferrite nanoparticles like $NiFe_2O_4$, $CoFe_2O_4$, and $ZnFe_2O_4$ have shown high sensitivity to ammonia due to their strong surface adsorption abilities and quick electron exchange. Ammonia sensing is an important criterion in agricultural storage facilities, food industries and environmental monitoring to maintain safety and quality. They have high sensitivity at low ppm values, very fast response and recovery rates, high selectivity against distracting gases like ethanol and acetone. They have moderate operating temperatures and can be used at room temperature when doped or combined with compatible composites. Enhanced response to NH_3 gas is reported for Cu doped $MnFe_2O_4$ nanoparticles prepared by coprecipitation technique [19]. Deivatamil D. et al have reported very high efficiency in sensing NH3 by 5wt% Ni- doped $MnFe_2O_4$ [20].

4.1.2. Nitrogen Dioxide (NO_2) Sensing

Nitrogen dioxide (NO_2) is a harmful pollutant that comes from car emissions and industrial activities. Spinel ferrites like $CoFe_2O_4$ and $MnFe_2O_4$ utilize electrical resistance to detect NO_2, and can achieve a significant increase in resistance when the gas is absorbed. These materials have excellent performance characteristics. They have low concentration detection capabilities from sub-ppm to a few ppm, high selectivity due to the strong oxidising properties of NO_2, moderate operating temperature with improved stability, and excellent reproducibility over multiple cycles of sensing, indicating their suitability for environmental monitoring. A. A. Bagade et al. [21] have reported high sensor response at moderately low temperature (150 °C) for cobalt substituted $MnFe_2O_4$.

4.1.3. Hydrogen Sulphide (H_2S) Sensing

Hydrogen sulphide (H_2S), a toxic and corrosive substance, can be efficiently detected using spinel ferrite nanoparticles such as $CuFe_2O_4$, $MgFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$ and $CoFe_2O_4$, as the strong catalytic activity of spinel ferrite nanoparticles significantly promote redox reactions by supporting adsorbed oxygen species [22,23]. The spinel ferrite materials are demonstrated as high sensitivity materials with high detection limits in the ppm and ppb range; they have rapid response and recovery time, with a fast reaction kinetics; and with proper structural optimising they can operate at low temperatures; they also have very stable performance when exposed for extended periods without significant baseline drift, enable them to be used in industrial safety applications, and environmental monitoring scenarios.

4.1.4. Carbon Monoxide (CO) Sensing

Carbon monoxide (CO) is a toxic gas that is colourless and odourless and hence its reliable detection is necessary in domestic and industrial environments. Spinel ferrite nanoparticles such as $MgFe_2O_4$, $BiFe_2O_4$, $NiFe_2O_4$ and $CoFe_2O_4$ (which have been doped) have been studied for many decades for CO sensing due to their enhanced sensing properties [24,25]. In CO sensing, these materials show moderate sensitivity and selectivity, which can be improved through noble metal doping (e.g. Pt, Pd). The materials can operate at lower temperatures than traditional metal oxide sensors and has good repeatability and species response linearity, which make them good for the practical sensing of carbon monoxide.

4.1.5. Volatile Organic Compounds (VOCs) Sensing

Since the Spinel ferrite nanoparticles have high surface reactivity, they are useful for sensing volatile organic compounds (VOCs) such as ethanol, acetone, and formaldehyde. The high surface reactivity of these materials allows the gas to be adsorbed and detected very effectively [9]. Especially, ferrite-graphene composites are promising candidates to sense VOCs at room temperature due to the higher number of adsorption sites and better electrical conductivity with the addition of graphene. Overall, spinel ferrites and ferrite-graphene composites have stronger sensitivity, rapid response and recovery times, good selectivity from morphological and compositional tuning, and can easily be adapted towards the values needed to suit the sensing requirements for applications such as breath analysis or clinical diagnostics of humans, indoor air monitoring for air quality and industrial safety systems.

5. STRATEGIES FOR PERFORMANCE ENHANCEMENT AND FUTURE PERSPECTIVES

In order to enhance the gas sensing capabilities of spinel ferrite nanoparticles, a significant number of engineering and modification methods have been developed with the goal of improving important metrics including sensitivity, selectivity, response-recovery time, and stability to perform well in real-world sensing applications [26,27].

5.1. **Metal Doping**: Doping spinel ferrites with noble metals (e.g., Pt, Pd, Ag, Au) or transition metals (e.g., Cr, Cu, Mn) is a popular solution to optimize gas sensors. The introduction of metal dopants creates more active sites, modifies the electronic structure, increases catalytic activity, and increases the number of oxygen vacancies that allow better gas adsorption and charge transfer processes. For example, Pd-doped $NiFe_2O_4$ has exhibited greater sensitivity towards NH_3 at lower operating temperatures than undoped samples.

5.2. **Composite Formation with Carbon-Based Materials**: Composites of spinel ferrite nanoparticles with carbonaceous materials including graphene, reduced graphene oxide (rGO), or carbon nanotubes (CNTs) exhibit superior sensing properties. The carbon materials provide excellent electrical conductivity and a high surface area while the ferrites contribute catalytical/semiconducting aspects to the composite, forming a nanohybrid material that has better sensitivity, faster response-recovery times, and does not require elevated temperatures to operate.

5.3. **Surface Modification and Functionalization**: Surface engineering strategies, like coating ferrite nanoparticles with functional polymers, metal oxides or molecular layers, can help improve gas selectivity and stability. Functionalization with specific ligands can also enhance the efficiency of the sensor towards target gases through selective adsorption or catalytic conversion.

5.4. **Morphological and Structural Control** The behavior of gas sensing can be significantly influenced by tailoring the morphology (nanorods, nanosheets, hollow spheres, porous structures, etc.) and controlling the crystallite size. The nanostructures with greater porosity and surface area provide more active sites for gas interaction, thereby improving sensitivity and lowering the temperature to achieve optimal performance.

5.5. **Optimizing Operating Parameters:** Adjusting factors such as sensor film thickness, operating temperature, humidity conditions, and applied bias voltage also contribute to performance optimization in practical applications.

5.6. Future Perspective

Although significant strides have been made in the investigation of spinel ferrite nanoparticles as gas sensing materials, there are still many barriers for commercialization and widespread applications. First, selectivity toward one specific gas amidst competing gases remains a challenge, though this may become less of an issue with the design of molecularly imprinted ferrite-based sensors, or designed sensor unit arrays employing algorithms for pattern recognition. Additionally, operational stability and repeatability over time under varying environmental conditions (such as humidity or temperature) must be improved for commercial applications. Some aspects of room temperature sensing have been achieved, but optimizing these types of sensors to remove the requirement of heating in most ferrites will allow for deployment in portable and wearable devices, something that requires more development and optimization. A major concern in moving forward is the potential toxic effects and environmental consequences of ferrites containing heavy metals, which warrants attention to green synthesis methods and biodegradable composite designs. Future studies should focus on the integration of spinel ferrite or ferrite composites with flexible substrates, and integration with wireless and Internet of Things developmental paths to further enhance the ability of spinel ferrite-based gas sensors to advance into smart sensors for environmental monitoring, safety in industry, and diagnostic healthcare applications.

6. CONCLUSION

In conclusion, spinel ferrite nanoparticles present considerable potential as active gas sensing materials due to their semiconductive nature, catalytic activity, and structural diversity. They can demonstrate high sensitivity and selectivity toward various toxic and hazardous gases, and can be used in conjunction with dopants, composites, and surface treatments to improve sensing performance further. However, challenges around selectivity in mixed gas environments, long-term durability, operational stability at room temperature, and environmental toxicity remain as barriers in realising the full potential of spinel ferrite nanoparticles for commercial gas sensing application. Future work should be focused on developing eco-friendly synthesis processes; incorporating spinel ferrites into flexible and wearable gas sensing platforms; and applying machine learning techniques to improve efficiency of gas detection. These efforts can lead to the development of successful next generation gas sensors that could operate in competent, reliable manner across diverse applications for either environmental remediation, industrial process safety, and/or monitoring our health care systems.

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