Recent Advances in Spinel Ferrite-Based Thin Films: Synthesis, Performances, Applications, and Beyond

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This review provides a comprehensive overview of the recent advances in the various typical spinel ferrite-based thin films with controlled synthesis, their performances, applications in multifunctional material fields, fundamental scientific challenges, and beyond. Firstly, the crystal structures of spinel ferrite-based thin films are introduced. Secondly, recent progress in traditional synthesizing and novel methods for preparation of spinel ferrite-based films are highlighted. Thirdly, their magnetism, electricity, optics performances, and applications in advanced information technology, energy storage and conversion, and environmental conservation fields are also summarized and discussed in-depth. Some effective strategies for optimizing performances and further applications are summarized. Finally, the present review work ends with a short discussion concerning the challenges, opportunities, and future prospects of spinel ferrite-based thin films.

Keywords: spinel ferrite-based thin films, controlled synthesis, performances, applications, future prospect

INTRODUCTION

Spinel materials are made of a general formulation of AB₂O₄, where the A and B are metal ions and comprise of A-O tetrahedron and B-O octahedron. On the basis of distribution of divalent metal ions and Fe³⁺ on the two cationic sites, spinel materials are mainly classified into three categories such as a normal spinel, inverse spinel, and complex spinel. The trend of interest in spinel materials has grown in recent significant representative research (Schloemann, 2000; Suzuki, 2001; Zhao et al., 2017). Among various spinel materials, spinel ferrites have drawn the attention of researchers owing to their interesting magnetic, electrical, and optical performances. These superior performances are due to high saturation magnetization, low coercivity, high Curie temperature, high electric resistivity, and so on. Spinel ferrites also exhibit intrinsic magnetic, electrical, optical, and catalytic properties originating from their diversiform composition, valence state, and electron configuration. Typical spinel ferrites, including those based on Fe, Ni, Co, Zn, and Mn, have multiple magnetic, electrical, and optical properties for practical applications (Zhao et al., 2017; Li et al., 2019; Du et al., 2020; Pham et al., 2020; Sun et al., 2020; Zhao et al., 2020; Narang and Pubby, 2021).

For spinel ferrite-based thin films, potential applications have been explored in information technology (magnetic sensing and data storage), the electronic industry (resistive switching devices, magnetization switching devices, and spintronic devices), and energy storage fields (supercapacitors, lithium-ion batteries as anodes and cathodes, catalysts, photoelectrodes, and so on) (Suzuki, 2001;
Lüders et al., 2006; Wang et al., 2017; Lei et al., 2019; Dongale et al., 2021). It is beneficial for spinel ferrite-based thin films to have manipulated composition, structure, and valence to make them suitable as multifunction materials in various fields. It is worth noting that these thin films have fascinating prospects in some energy conversion storage devices, such as batteries and

FIGURE 1 | (A) Illustration of the structures of spinel, (B) future development of spinel compounds, applications, preparations, and fundamental challenges. Reproduced from Zhao et al. (2017) with permission from the American Chemical Society.
water splitting, benefitting from their low prices and environmental friendliness (Vadiyar et al., 2016a; Han et al., 2016; Jiang et al., 2018; Nikam et al., 2020).

Given the rapid development of spinel materials, both the preparation and application of spinel ferrite-based thin films have achieved tremendous increasing progress with decades of research. Review articles that cover the most recent developments are urgently needed. However, there has been no comprehensive review of this hot topic. Herein, the recent significant representative preparation and application of spinel ferrite-based thin films are systematically summarized. This review article is divided into the following parts. Firstly, the basic compositions and crystal structural characteristics of spinel ferrite materials are introduced. With the overall understanding of spinel ferrite materials, the synthesis of typical spinel ferrite-based (Ni-based, Co-based, Zn-based, and Mn-based) thin films are systematically reviewed. The solid, solution, and vapor phase methods are discussed. Further, the traditional synthesis and novel methods of spinel ferrite-based thin films are also highlighted. Secondly, magnetic, electrical, and optical properties, and applications are summarized. In addition, some effective strategies for optimizing performance and application are summarized. Finally, fundamental scientific challenges and fascinating prospects are focused on. Some recommendations are put forward to address current challenges and future prospects. Future development will expect to concentrate on advanced electric information technology, energy storage and conversion, and environmental conservation fields, which are challenging issues. From this aspect, more research interests will concentrate upon the exploration of innovative multifunctional spinel ferrite-based thin films with insight into the effect between the structure and property relationship of spinel ferrite-based thin films and elevating the application in various fields.

The Structures and Synthesis Methods of Spinel Ferrite-Based Thin Films

Typical spinel ferrite is briefly described as $\text{AFe}_2\text{O}_4$ (where $\text{A} = \text{Fe, Ni, Co, Mn, Zn, etc}.)$, these are composed of $32$ oxygen atoms with $32$ trivalent octahedral sites and $64$ divalent tetrahedral sites. Particularly, $\text{A}^{3+}$ and $\text{Fe}^{3+}$ normally take up $16$ octahedral sites and eight tetrahedral sites to maintain an electrically balanced state, respectively (Zhao et al., 2017; Narang and Pubby, 2021). Spinel ferrite can be classified into three different types depending on their situations of cation distribution: normal, inverse, and complex spinel as shown in Figure 1A, respectively. In the normal typical spinel ferrite structure, $\text{A}^{2+}$ cations occupy tetrahedral sites, whereas $\text{Fe}^{3+}$ cations occupy octahedral sites, as can be seen in $\text{ZnFe}_2\text{O}_4$ and $\text{CdFe}_2\text{O}_4$. For the inverse spinel ferrite structure, $\text{A}^{2+}$ cations only occupy octahedral sites, however, $\text{Fe}^{3+}$ cations are equally located at tetrahedral and octahedral sites, examples are $\text{Fe}_3\text{O}_4$, $\text{NiFe}_2\text{O}_4$, and $\text{CoFe}_2\text{O}_4$. For complex spinel ferrite structure, $\text{A}^{2+}$ and $\text{Fe}^{3+}$ cations are randomly located at tetrahedral and octahedral sites, i.e., $\text{MnFe}_2\text{O}_4$ or $\text{MgFe}_2\text{O}_4$ (Zhao et al., 2017; Pham et al., 2020).

In the preparation of spinel materials, the majority of methods involve chemical and physical transitions (Zhao et al., 2017). Herein, we summarize the traditional and innovative synthesis approaches of typical spinel ferrite-based thin films, including solid phase methods, solution phase methods, and vapor phase methods. The solid phase approaches consist of combustion, pulsed laser and decomposition methods, and so on (Suzuki, 2001; Hao et al., 2018a; Nikam et al., 2020). The solution phase approaches contain chemical solution deposition, sol-gel, solvothermal, and electro-chemical methods, etc. The vapor phase approaches involve magnetron sputtering, atomic layer deposition, and chemical vapor deposition, etc. The structure, morphology, defects, and loading substrate of spinel ferrite-based thin films have been designed on basis of the above controlled synthesis methods (Suzuki, 2001; Zhao et al., 2017). Among these synthesis approaches, sol-gel is a mild approach and has been widely employed in synthesizing spinel ferrite-based thin films. Generally speaking, metal salts are used to form precursors. Ethylene glycol, glacial acetic acid, or citric acid are adopted as a chelation agent. These reactants are mixed uniformly in the solvents. Then, hydrolysis, condensation, and other reactions occur to form transparent sol systems. The sol gradually turns into gel via the loss of fluid solvent during the aging process. Finally, the compounds are obtained through the calcination process (Ismail et al., 2018; Choueikani et al., 2021; Zhao et al., 2021).

During the development of spinel ferrite-based thin films synthesis, some other innovative technologies can be adopted such as ultrasound-assisted sol-gel, metallo-organic decomposition, and dip-coating methods, etc. Increasing numbers of methods have been found, and novel spinel ferrite-based materials have been synthesized. The structure, morphology, and loading substrates of spinel ferrite-based thin films could be rationally designed and applied in various fields. Table 1 summarizes the main methods reported to synthesize typical spinel ferrite-based thin films. Moreover, their performance (magnetism, electricity, and optics) and typical application examples are listed for comparison.

In addition, exploring facile methods to synthesize novel spinel ferrite-based thin films remains challenging. The representation methods will benefit the deep understanding of spinel ferrite materials’ performance and application. The fundamental scientific challenge will inspire the exploration of novel synthesis methods. At the same time, novel characterization methods and instruments need to be developed to further in-depth understanding of spinel ferrite-based thin films synthesis, performance, and applications in various fields.

Performances and Applications of Spinel Ferrite-Based Thin Films

Spinel ferrite is a class of magnetic materials, where its name results from its similarity with the naturally occurring $\text{MgAl}_2\text{O}_4$ mineral. Magnetic properties of spinel ferrite-based thin films contain ferro-, ferri-, para-, anti-ferro-, and diamagnetisms (Zhao et al., 2017). Most Fe, Co, and Ni-based compositions exhibit ferrimagnetism. The magnetic performance of typical spinel
### TABLE 1: Comparison of the synthesis methods, performance (magnetism, electricity, and optics), typical application examples, and performance metrics for typical spinel ferrite-based thin films.

| Spinel ferrite-based films | Synthesis methods | Performance | Applications | Performance metrics | References |
|----------------------------|-------------------|-------------|--------------|---------------------|------------|
| Fe₃O₄                     | Molecular beam epitaxy | Magnetism | Magnetization switching | Magnetic moment (3–5 µemu/f.u.) | Huang et al. (2015) |
|                           |                   |            |              | Saturation magnetization (250–500 emu/cc) | Cheng et al. (2012) |
|                           |                   |            |              | Specific capacity (1,100, 880 and 660 mA h/g at 0.1, 0.2, and 0.5 C) | Ishib e et al. (2020) |
|                           |                   |            |              | Cycling capability (100 cycles at 0.1 C) | Lüders et al. (2008) |
|                           |                   |            |              |                        | Hu et al. (2012b) |
|                           |                   |            |              |                        | Dongale et al. (2021) |
|                           |                   |            |              |                        | Yao et al. (2021) |
| NiFe₂O₄                   | RF sputtering     | Magnetism | Spintronics devices | Spin-polarization (42%) | Coll et al. (2014) |
|                           |                   |            |              |                        | Eskandari et al. (2019) |
|                           |                   |            |              |                        | Sagu et al. (2017) |
|                           |                   |            |              |                        | Lei et al. (2019) |
| NiFe₂O₄                   | Chemical solution deposition | Electricity | Resistive switching devices |                        |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| NiFe₂O₄                   | Co-precipitation   | Electricity | Aqueous battery | Specific capacity (18.56 mAh/g at 1 mA/cm²) |                        |
|                           |                   |            |              | Potential window (0.2–1 V) |                        |
| NiFe₂O₄/Co₃O₄             | Sol-gel           | Optics, magnetism | Functional material | Optical band gap (2.58–2.75 eV) |                        |
|                           |                   |            |              | Saturation magnetization (70.51–145.29 emu/cc) |                        |
|                           |                   |            |              | Coercive field (87.57–154.05 Oe) |                        |
| CoFe₂O₄                   | Atomic layer deposition | Magnetism | Advanced devices | Saturation magnetization (450 emu/cc at 10 nm, 230 emu/cc at 5 nm) |                        |
|                           |                   |            |              | Coercive fields (15 kOe at 10 nm, 11 kOe at 5 nm) |                        |
|                           |                   |            |              |                        | Coll et al. (2019) |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| CoFe₂O₄                   | Pulse laser-deposited | Magnetism | Spintronic devices | Saturation magnetization (457 kA/m, 474, and 697 kA/m at 30, 45, and 60 min) |                        |
|                           |                   |            |              | Anisotropy (290 kJ/m² with 1 0 O easy direction) |                        |
|                           |                   |            |              |                        | Sagu et al. (2017) |
|                           |                   |            |              |                        | Lei et al. (2019) |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| CoFe₂O₄                   | Chemical vapor deposition | Electricity | Supercapacitor | Capacitance (540 mF/cm²) |                        |
|                           |                   |            |              | capacitance retention (80% after 7,000 cycles) |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| CoFe₂O₄                   | Liquid phase epitaxy | Electricity | Electrocalyst | Overpotential (266 mV at 10 mA/cm²) |                        |
|                           |                   |            |              | Tafel slope (53 mV/dec) |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| CoFe₂O₄                   | Pulse laser-deposited | Electricity | Supercapacitor | Specific capacitance (774.4 F/g) |                        |
|                           |                   |            |              | Power density (3.277 W/kg) |                        |
|                           |                   |            |              | Energy density (17 W h/kg) |                        |
|                           |                   |            |              | Cyclic stability (125% after 1,500 cycles) |                        |
|                           |                   |            |              |                        | Choueikani et al. (2021) |
| CoFe₂O₄-silica            | Sol-gel           | Optics, magnetism | Magneto-optical | Specific Faraday rotation (310°/cm at 1,550 nm) |                        |
|                           |                   |            |              | Modal birefringence (order of 10⁶) |                        |
|                           |                   |            |              | Figure of merit (2.02° at 1,550 nm) |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| ZnFe₂O₄                   | RF sputtering     | Magnetism | Functional material | Saturation magnetization (13–18 emu/cc) |                        |
|                           |                   |            |              |                        | Coll et al. (2014) |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| ZnFe₂O₄                   | Mechanochemical   | Electricity | Supercapacitor | Specific capacitance (433 F/g) |                        |
|                           |                   |            |              | Energy density (86 W h/kg) |                        |
|                           |                   |            |              | Cycling stability (91% retention up to 4,000 cycles) |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| CdS/ZnFe₂O₄/Zn₁₋ₓSnₓO₄   | Solvothermal processes, ionic layer adsorption reaction | Optics, electricity | Photocatalytic |                        |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| ZnFe₂O₄                   | Auto-combustion   | Electricity | Lithium-ion battery | Specific capacity (560 mA h/g at 0.5 A/g and 330 mA h/g at 3.5 A/g after 100 cycles) |                        |
|                           |                   |            |              | Coulombic efficiency (98%) |                        |
|                           |                   |            |              |                        | Das et al. (2018) |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| ZnFe₂O₄                   | Sol-gel method   | Electricity | Resistive switching | Set voltages (0.9–2.8 V) |                        |
|                           |                   |            |              | Retention time (10⁴ s) Endurance (~200 cycles) |                        |
|                           |                   |            |              | Activation energies (170–210 meV) |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| ZnFe₂O₄                   | Pulsed laser deposition | Optics, electricity | Photocathodes |                        |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| ZnFe₂O₄                   | Hydrothermal reaction | Optics, electricity | Photocatholytic |                        |                        |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| MnFe₂O₄                   | Sol-gel, metallo-organic decomposition | Magnetism | Functional material | Saturation magnetization (5.4 emu/cc) |                        |
|                           |                   |            |              | Remanent magnetization (1.1 emu/cc) |                        |
|                           |                   |            |              | Coercive fields (113.3 Oe) |                        |
|                           |                   |            |              |                        | Chand Verma et al. (2011) |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| MnFe₂O₄                   | Pulsed laser-deposited | Magnetism | Functional material | Magnetic moment (4.8 µemu/f.u.) |                        |
|                           |                   |            |              | Exchange stiffness constant 106–168 e effective saturation magnetization (1.1–4.2 kg) |                        |
|                           |                   |            |              |                        | Rajagiri et al. (2018) |
|                           |                   |            |              |                        |                        |
|                           |                   |            |              |                        |                        |
| MnFe₂O₄/ (Pb₁₋ₓSrₓ)TiO₃   | Metal-organic reaction | Electricity, magnetism | Magnetoelectric material | Saturation magnetization (109–119 emu/cc) |                        |
|                           |                   |            |              | Remanent magnetization (3.6–4 emu/cc) |                        |
|                           |                   |            |              | Coercive fields (101–102 Oe) |                        |
|                           |                   |            |              | Magnetoelectric coefficient (2.82–4.29 V/Oe cm) |                        |
ferrimagnetic NiFe$_2$O$_4$ thin films were prepared using RF sputtering on SrTiO$_3$-based substrates. It is reported that these films present remarkable enhanced magnetic moments in comparison with bulk substrates, and the electronic performance has been modulated from conducting to insulating by changing the growth conditions, which has meant that these films have been proposed for potential application in spintronics devices (Lüders et al., 2006). In addition, pulse laser-deposited CoFe$_2$O$_4$ thin films also exhibited a change in the saturation magnetization, coercivity, and magnetic anisotropy for magnetic oxide-based spintronic devices application (Eskandari et al., 2019). Moreover, the magnetism of typical ZnFe$_2$O$_4$ and MnFe$_2$O$_4$-based thin films have also been investigated for tuning the saturation magnetization, coercivity, magnetic moment, Curie temperature, and magnetic anisotropy properties (Chand Verma et al., 2011; Raghavan et al., 2015; Bala et al., 2017; Rajagiri et al., 2018). These favorable magnetic properties of spinel ferrite-based thin films have made them an eye-catcher for material science researchers. Therefore, these ferrite materials are desired to further widen their application range in magnetoelectric and magneto-optical fields.

Electrical performance and application of spinel ferrite-based thin films, especially in emerging random access memories and energy storage devices, have recently achieved great attention owing to the shortcomings of Flash memories and increasing fossil energy consumption. The spinel ferrite-based thin films have also been applied in many storage fields, such as resistive random access memory, supercapacitors, Li-ion batteries, electrocatalysts, and so on (Hu et al., 2012a; Wang et al., 2013; Hu et al., 2014; Hwang et al., 2017; Sagu et al., 2017; Jiang et al., 2018; Nikam et al., 2020; Dongale et al., 2021). Spinel ferrite-based resistive switching materials are one of a few promising resistive random access memory candidates. Large fluctuating resistance states, degradation of endurance and retention time, and the controversial physical mechanism in practical applications are challenging reliability issues that need to be solved. Many efforts have been made to enhance the performance of resistive switching devices to satisfy the requirements of commercial applications, such as impurity doping, introduction of metal nanoparticles, interface engineering, and bilayer structure (Pan et al., 2014). Recently, Fe$_2$O$_4$, NiFe$_2$O$_4$, CoFe$_2$O$_4$, and MnFe$_2$O$_4$-based films, un-doped or doped with various valence elements (Ce, Gd, Cr, Cu etc.), have demonstrated remarkable improvements in their resistive switching characteristics (Hu et al., 2012a; Hu et al., 2012b; Hu et al., 2014; Hao et al., 2017a; Hao et al., 2018b; Hao et al., 2019a; Hao et al., 2019b; Ishibe et al., 2020). For example, NiFe$_2$O$_4$-based memory devices presented enhancement for resistive switching characteristics, such as a reduction of set/reset voltage, favorable endurance and data retention time via partial substitution of Fe$^{3+}$ with trivalent Gd$^{3+}$, Ce$^{3+}$, or Cr$^{3+}$ doping, or partial substitution of Ni$^{2+}$ with divalent Cu$^{2+}$ doping (Hao et al., 2017a; Hao et al., 2018b; Hao et al., 2019a). Moreover, related magnetism of NiFe$_2$O$_4$ thin films has been modulating by impurity doping and introducing metal nanoparticles (Ag or Au). It is worth noting that Bao’s group made significant contributions in the spinel ferrite-based resistive switching materials research. They effectively improved the resistive switching performances and clarified the switching mechanism by various modification methods (Hao et al., 2017b; Hao et al., 2018a; Hao et al., 2018c). In addition, coexistence behavior of resistive and magnetization switching with ferrite-based thin films have inspired much attention in the scientific world and the business community for promoting data storage density. The resistive and magnetization switching has been achieved in devices through the manipulation of applied electric fields in which a Cr-doped NiFe$_2$O$_4$ switching layer was prepared via a facile chemical solution deposition approach (Hao et al., 2019a). The above devices presented stable operating voltage, prominent endurance (>10$^5$ cycles), large on/off memory window (>10$^3$), and superior retention time (>10$^8$ at 25°C). Moreover, the saturation magnetization of the devices exhibited reversible switching in different resistance states for promising application in resistive and magnetization switching devices. This behavior provides a deeper insight into the potential applications in nonvolatile memory and magneto-electric coupling devices. Moreover, the challenges of further boosting property and application in memory, energy storage devices, and outlook for future innovative research directions are also anticipated.

Supercapacitors, such as typical electrochemical capacitors, have been regarded as one of the most promising candidates in energy storage fields resulting from their superior advantages (high power density, lower cost, and long life, etc.) (Li et al., 2019). Electrode materials have a vital role in the performance of supercapacitors. Therefore, many studies concentrated on exploring novel electrode materials for high performance supercapacitors. For the past few years, spinel ferrite-based thin films as supercapacitors electrode materials have gained much attention owing to their outstanding advantages, such as ease of synthesis, low cost, and high theoretical capacity (Li et al., 2012; Jiang et al., 2018; Nikam et al., 2020). The pulsed laser-deposited CoFe$_2$O$_4$ films exhibited enhanced electrochemical property and supercapacitor electrode performance, such as superior power density (3,277 W kg$^{-1}$), energy density (17 W h kg$^{-1}$), and cyclic stability (125% after 1,500 cycles) (Nikam et al., 2020). Additionally, the comparative research of individual and mixed aqueous electrolytes with ZnFe$_2$O$_4$ nanoflake film electrodes in a supercapacitors application has also been investigated (Vadiyar et al., 2016b). Although the spinel ferrite-based thin film supercapacitors show high performance, there are still some challenges to be addressed before commercialization.

In comparison with supercapacitors, batteries generally possess higher energy density and operating voltage (Pham et al., 2020). However, some challenges such low capacity, poor cycling stability, and limited low-temperature performances impose restrictions on their commercial applications in hybrid vehicles and energy storage devices. Recent efforts have been focused on investigating the
electrochemical performance of spinel ferrite-based thin films as both anodes and cathodes for rechargeable lithium-ion and aqueous batteries (Cheng et al., 2012; Wang et al., 2013; Wang et al., 2015; Hwang et al., 2017; Choi et al., 2018; Das et al., 2018; Huang et al., 2020; Dongale et al., 2021). For example, rugated porous Fe$_2$O$_3$ films as high-performance anode materials presented a specific capacity of 1,100, 880, and 660 mA h g$^{-1}$ at 0.1, 0.2, and 0.5 C, respectively, a stable charge/discharge platform, and high cycling stability (Cheng et al., 2012). Moreover, ZnFe$_2$O$_4$-carbon black porous film-derived negative electrodes for a lithium-ion battery have been investigated, which delivered a steadily reversible specific capacity of 560 mA h g$^{-1}$ at 0.5 A g$^{-1}$, which maintained for approximately 100 cycles. The above electrodes also presented a 330 mA h g$^{-1}$ specific capacity at 3.5 A g$^{-1}$ (Das et al., 2018). For future work on spinel ferrite-based thin film batteries, effective strategies, such as doping, carbon coating, and multi-electrode designing, is suggested to further boost electrochemical performance and insight into advanced mechanism of spinel ferrite-based thin films. Moreover, some perspectives and critical challenges for future spinel ferrite-based thin films research also deserve to be explored and addressed.

In addition, spinel compounds have been widely investigated as catalysts in various fields. Hydrogen and oxygen evolution reactions are major reactions in water splitting, which were mentioned as a major approach to generate H$_2$ for clean energy (Zhao et al., 2017). Spinel ferrite-based thin films can be used as electrocatalysts in water splitting and energy conversion/storage (Kumbhar et al., 2015; Han et al., 2016; Sagu et al., 2018; Lei et al., 2019; Lan et al., 2020). For example, well-aligned mesoporous CoFe$_2$O$_4$ films have been developed by surface epitaxial growth for an efficient electrocatalytic oxygen evolution reaction. It is interesting that the self-support CoFe$_2$O$_4$ film electrodes delivered an overpotential of 266 mV in oxygen evolution at a 10 mA cm$^{-2}$ current density and exhibited good stability. The obvious and steady catalytic property of CoFe$_2$O$_4$ films was ascribed mainly to the mesoporous structures, the numerous exposed active sites, and efficient charge/electron transfer (Lei et al., 2019). Electrospray technique-derived ZnFe$_2$O$_4$ thin films with photo-absorber material for photoelectrochemical water splitting were fabricated and were found to increase discharge potential, induce more active sites, and enhance the photocurrent of 53 $\mu$Acm$^{-2}$ at 1.23 V versus RHE (Wang et al., 2017). In addition, innovative p-type Co-doping ZnFe$_2$O$_4$ films, as prospective cathodes for photoelectrochemical water splitting, were prepared via hydrothermal reaction and sintering treatment, in which the photocurrent density was 0.22 mA cm$^{-2}$ at 0 V vs. RHE with improvement by about 7.33-fold compared with that of the n-type ZnFe$_2$O$_4$ (0.03 mA cm$^{-2}$ at 0 V vs. RHE) (Lan et al., 2020). Given the advantages of spinel ferrite-based thin films, further optimization and development in electrocatalytic performance is highly desired. Some effective strategies including electronic structure regulation, micro-structure engineering, and phase and composition modulation need to be further explored and adopted to regulate the electrocatalytic performance of spinel ferrite-based thin films.

It is worth noting that some spinel ferrite-based thin films exhibited unique optical characteristics, such as absorption, optical bands, birefringence, and Faraday rotation, which have been adopted for magneto-optical recording devices and photocatalysts (Li et al., 2010; Bharathi et al., 2011; Chen et al., 2017; Chavan et al., 2019; Henning et al., 2019; Yu et al., 2019; Labchir et al., 2020; Lan et al., 2020; Choueikani et al., 2021). For example, low index magneto-optical CoFe$_2$O$_4$-silica nanocomposite thin films were fabricated using the composite method and presented an intrinsic Faraday rotation of 310°/cm at 1,550 nm for an NP 1.5% volume fraction, and the modal birefringence was the order of 10$^{-4}$ (Choueikani et al., 2021). Moreover, the ZnFe$_2$O$_4$ samples showed the best photocatalytic performance for degradation of Orange II dye (100% after 180 min) (Yu et al., 2019). Although the ferrite-based thin films have potential and cost-effective advantages as adsorbent photocatalysts to remove environmental contaminants, the related research is still lacking and limited. Furthermore, the large-scale application and long-term sustainability remain challenging issues. As a result, it encourages more investigations to solve these challenging issues by designing novel spinel ferrite-based thin film materials and improve treatment technology in water remediation technology and environmental conservation areas.

**Fundamental Scientific Challenges and Beyond**

In recent decades, the compositions, synthesis, performance, and application of spinel ferrite-based thin films have seen rapid development (Table 1). Future research would continue to enrich spinel ferrite systems, developing novel synthesis methods and expanding the application fields. The future applications of spinel ferrite materials are shown in Figure 1B (Zhao et al., 2017). Over the past decades, the progress of research in this field has been extremely noteworthy and significant. However, at present, investigations into spinel ferrite-based thin films are limited. Other spinel ferrite-based thin films will deserve investigation in the future. Meanwhile, exploring innovative inorganic-organic hybrid spinel ferrite-based thin films is also a novel path to widen the spinel ferrite-based thin film systems.

Moreover, the majority of novel synthesis methods can be adopted to fabricate spinel ferrite-based thin films, whereas the preparation is still limited. To explore a facile path to prepare spinel ferrite-based thin films beyond traditional methods remains challenging. The in-situ technique to investigate the relationship of structure, property, mechanism, and application of spinel ferrite-based thin films is still less understood. At the same time, novel characterization methods and instruments need to be introduced for better understanding of spinel ferrite-based thin film performance. The future application development of spinel ferrite-based thin films is also challenging. Consequently, future breakthroughs to overcome the aforementioned challenging issues are highly desirable. These fundamental scientific challenges will offer impetus in exploring novel synthesis methods, optimizing performances, and development
application of spinel ferrite-based thin films. Further efforts are supposed to concentrate on advanced electric information technology, energy storage and conversion, and environmental conservation fields (Zhao et al., 2017; Chandrasekaran et al., 2018; Pham et al., 2020; Sun et al., 2020; Carlos et al., 2021; Liu et al., 2021). Therefore, this fundamental scientific challenge deserves more attention and stimulates research activity in these research fields. It is believed that this review will lay the path for development of spinel ferrite-based films in future technology.

CONCLUSION

In summary, the developments of controlled synthesis, magnetic, electrical, and optical properties, applications in multifunctional material fields, and beyond for various typical spinel ferrite-based thin films were summarized. The composition and structures of spinel ferrite-based thin films were introduced. Recent advances in the synthesis of spinel ferrite-based films methods were highlighted. The performances of magnetism, electricity, and optics were also summarized. The magnetism, electricity, and optics applications in advanced information technology, energy storage and conversion, and environmental conservation fields were also reviewed. We also presented discussion concerning the challenges and future prospects of spinel ferrite-based films. Some recommendations were put forward to address the current challenges and future prospects.

AUTHOR CONTRIBUTIONS

AH and XN wrote the manuscript. AH supervised and edited the manuscript.

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