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**INVESTIGATION OF ENHANCED HEATING
PERFORMANCE IN MFe_2O_4 ($\text{M} = \text{Co}, \text{Fe}, \text{Mn}$)-BASED
MAGNETO-OPTICAL NANOCOMPOSITES FOR
BIOMEDICAL APPLICATIONS**

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INTRODUCTION

In recent decades, magnetic materials have played a crucial role in various technological fields, such as electric motors, sensors, data storage, and energy conversion. However, the reliance on rare-earth elements in many high-performance magnetic materials raises concerns regarding cost, supply, and environmental impact. Therefore, the development of high performance, environmentally friendly, and rare-earth-free magnetic materials represents a direction of both scientific and practical significance.

Spinel ferrites (MFe_2O_4 , where $\text{M} = \text{Co}, \text{Fe}, \text{Mn}, \text{etc.}$) are a promising class of materials due to their high chemical stability, low cost, and the ability to tune their properties through composition and structural modifications [1–3]. Upon scaling down to the nanoscale, these ferrite systems exhibit novel phenomena such as superparamagnetism, surface anisotropy, and interparticle interactions, which significantly alter their magnetic and optical properties. Consequently, ferrite nanoparticles have attracted considerable interest for applications including electromagnetic wave absorption, catalysis, energy storage, MRI contrast enhancement, magnetically guided drug delivery, and magnetic hyperthermia [4–6]. These applications require precise control over magnetic parameters such as saturation magnetization (M_s), coercivity (H_c), and magnetocrystalline anisotropy constant (K_1)—as well as optical parameters related to absorption and emission.

The properties of nanoferrites depend strongly on their crystal structure, particularly the distribution of cations between tetrahedral (A) and octahedral (B) sites. Alterations in cation distribution modify A–B superexchange interactions, thereby influencing saturation magnetization, coercivity, and magnetocrystalline anisotropy. Furthermore, defect states and localized levels within the bandgap play a significant role in optical properties [7–12]. However, current research largely examines these property groups in isolation, failing to systematically elucidate the interrelationships among synthesis conditions, structure, magnetic properties, and optical properties within a single material.

In addition, ferrite-based nanocomposites and materials capable of magneto-thermal and photothermal energy conversion are attracting significant

interest. In Vietnam, ferrite-metal hybrid materials, particularly those incorporating Ag and Au, have been investigated with a focus on exploiting surface plasmon resonance for biomedical applications [13, 14]. However, the relationship between the characteristics of the host material, the nature of the interface, and the efficiency of energy-to-heat conversion has not yet been systematically examined.

Based on this, the thesis establishes an integrated approach - linking fabrication conditions to structure and microstructure, then to magnetic and optical properties, and finally to energy conversion capabilities before developing ferrite-based magneto-optical composite material systems. In addition to ferrite-plasmon systems, the research extends to $\text{Fe}_3\text{O}_4@\text{TA-Fe}^{3+}$ nanoparticles, enabling a comparison of the energy conversion capabilities of two interfaces with distinct natures: the metal-oxide interface and the organic-metal coordination interface. This approach helps elucidate the role of the interface nature in energy conversion efficiency and provides a scientific basis for material design aimed at enhancing heat generation capacity. The thesis is defined as follows: **“Investigation of enhanced heating performance in MFe_2O_4 ($\text{M} = \text{Co, Fe, Mn}$)-based magneto-optical nanocomposites for biomedical applications”**.

To achieve the goal of enhancing heat generation capacity, the thesis focuses on the following key aspects:

- (i) Clarifying the influence of synthesis conditions on the crystal structure, microstructure, and cation distribution in MFe_2O_4 nanosystems.
- (ii) Establishing the relationship between microstructure and magnetic properties and clarifying the roles of particle size and inter-particle interactions.
- (iii) Analyzing optical characteristics and constructing a semi-empirical energy-level diagram based on UV-Vis and PL spectra.
- (iv) Investigating magneto-thermal and photothermal conversion characteristics in $\text{MFe}_2\text{O}_4\text{-Ag}$ and $\text{Fe}_3\text{O}_4@\text{TA-Fe}^{3+}$ magneto-optical nanocomposite systems.
- (v) Comparing energy conversion characteristics across material systems with different interfacial natures and clarifying the role of the interface.

(vi) Evaluating potential applications in biomedical heating based on the specific absorption rate (SAR), whereas intrinsic loss power (ILP), and thermal response parameters.

The thesis comprises an introduction, five main chapters, a conclusion, and appendices.

CHAPTER 1: OVERVIEW OF THE STRUCTURE AND MAGNETIC AND OPTICAL PROPERTIES OF MFe_2O_4 SPINEL FERRITE

Spinel ferrites (MFe_2O_4 , where $\text{M} = \text{Co}, \text{Fe}, \text{Mn}, \text{etc.}$) have a spinel crystal structure with the general formula $(\text{A})[\text{B}_2]\text{O}_4$, in which cations are distributed across A and octahedral B sublattices. Cation distribution is determined by various factors such as crystal field stabilization energy (CFSE), ionic size, and synthesis conditions and governs the magnetic, electrical, and optical properties of the material [1, 15–18].

For spinel ferrites, the inversion parameter x is a key factor reflecting the cation distribution at the A and B sites. This parameter can be determined using techniques such as Rietveld refinement of X-ray or neutron diffraction data, Mössbauer spectroscopy, Raman spectroscopy, and XPS [22–25]. Variations in the degree of inversion alter the A–O–B superexchange interaction, thereby directly influencing the physical properties of the materials.

The magnetic properties of spinel ferrites are mainly determined by superexchange interactions between magnetic ions at A and B sites. In addition to cation distribution, structural parameters such as the lattice parameter, oxygen parameter, bond lengths, and bond angles—significantly influence the strength of exchange interactions [30–33]. At the nanoscale, effects such as single-domain behavior, superparamagnetism, surface spin disorder, and interparticle dipole interactions become key factors governing the material’s saturation magnetization, coercivity, and effective magnetic anisotropy [36–55].

In addition to magnetic properties, the optical properties of spinel ferrites have also attracted great interest. Raman spectroscopy is used to investigate crystal structure and cation distribution [75–77], while UV–Vis absorption spectroscopy allows for the determination of electronic band structure, band gap energy, and Urbach energy – the latter being related to the degree of disorder in

the material [10, 78]. Photoluminescence spectroscopy provides information on defect levels and electron recombination mechanisms [81], whereas FTIR spectroscopy reflects metal–oxygen bonds and the local structure of the crystal lattice [89–92].

Although numerous studies have investigated the structural, magnetic, and optical properties of spinel ferrites, most research has focused on these properties in isolation. A systematic quantitative relationship linking cation distribution and structural parameters to both magnetic and optical properties has yet to be established. Furthermore, the use of optical data to construct semi-empirical energy-level diagrams and analyze energy-transition processes in ferrite nanosystems remains limited.

This chapter establishes the scientific foundation for investigating and selecting MFe_2O_4 base materials, focusing on three aspects directly related to the thesis objectives: (i) crystal structure and cation distribution, which determine microscopic interactions and magnetic properties; (ii) microstructure, nanoparticle size, and inter-particle interactions, which govern magnetic response and magnetocaloric conversion capability; and (iii) electronic structure and optical characteristics, which determine optical energy absorption and conversion capabilities. This serves as the basis for Chapter 4 to characterize and compare the structural, magnetic, and optical properties of MFe_2O_4 nanosystems, thereby enabling the selection of suitable host materials for developing composite materials and investigating the potential for enhanced heat generation in Chapter 5.

CHAPTER 2: OVERVIEW OF THE PHYSICAL MECHANISMS AND MAGNETOTHERMAL AND PHOTOTHERMAL HEATING OF MFe_2O_4 NANOFERRITES AND MAGNETO-OPTICAL NANOCOMPOSITES

When magnetic nanomaterials are under in an alternating magnetic field, electromagnetic energy can be converted into heat through magnetic loss mechanisms. For spinel ferrite nanoparticles, the contribution of eddy currents is typically negligible due to the material's low electrical conductivity [94]. The main heat generation mechanisms involve hysteresis loss for nanoparticles

exceeding the superparamagnetic limit, and Néel and Brown relaxation processes for superparamagnetic nanoparticles [97–100].

In the superparamagnetic regime, magnetic moments can relax via internal rotation within the nanoparticle (Néel relaxation) or rotation of the entire nanoparticle within the dispersion medium (Brownian relaxation). The effective relaxation time is determined by the combined contribution of these two mechanisms, with the mechanism possessing the shorter relaxation time dominating the heat generation [4,98–100].

To quantitatively describe the magneto-thermal process, Rosensweig's linear response theory has been widely used for superparamagnetic nanoparticles [103–105]. According to this model, heat generation power depends on magnetic susceptibility, magnetic field amplitude, excitation frequency, and effective relaxation time. Heat generation efficiency reaches a maximum when the material satisfies the condition of dynamic resonance between the relaxation time and the excitation frequency. However, in practice, ferrite nanoparticles, dipole interactions, size distribution, and structural heterogeneity can lead to significant deviations from theoretical predictions [107].

In addition to the magnetocaloric effect, ferrite nanomaterials and magneto-optical composites also possess the ability to convert light energy into heat. In systems containing noble metal nanoparticles, the localized surface plasmon resonance (LSPR) effect plays a crucial role in light absorption and heat generation [112–120]. According to Mie theory, photothermal conversion efficiency (η) depends directly on the material's optical absorption capacity and the ratio of absorption to total optical attenuation [82, 88, 116].

For spinel ferrites, light absorption primarily involves charge-transfer mechanisms, including ligand-to-metal charge transfer (LMCT) and intervalence charge transfer (IVCT) [130–138]. These mechanisms give rise to broad absorption bands in the ultraviolet–visible–near-infrared region and contribute significantly to the material's photothermal effect. In composite material systems containing organic components, π – π^* and n – π^* electronic transitions may also participate in photon absorption and energy conversion [141, 142].

Following light absorption, electronically excited states relax via non-radiative processes such as internal conversion, intersystem crossing, and electron–phonon interactions resulting in energy release as heat [130, 133, 141–144]. Consequently, η depends on both the optical absorption capability and the efficiency of these non-radiative relaxation processes.

The heat-generating performance of magnetic nanomaterials is typically evaluated via SAR, whereas ILP is used as a normalized parameter to minimize the influence of measurement conditions and enable comparisons across different studies [145–148].

In magneto-optical composite materials, simultaneous excitation using an alternating magnetic field and electromagnetic radiation can induce an energy resonance effect, thereby enhancing heat generation efficiency compared to either mechanism acting alone [6,153]. The temperature rise resulting from the photothermal effect can alter the magnetic relaxation time, bringing the material closer to dynamic resonance conditions. Simultaneously, the surface plasmon effect in composite material containing Ag or Au can enhance optical absorption and local electromagnetic interactions [154,155]. Numerous studies indicate that the SAR under simultaneous excitation exceeds the sum of the individual contributions from the magnetothermal and photothermal effects, demonstrating the existence of multi-field interactions within these magneto-optical composite materials [6,153].

This chapter presents the mechanisms of magneto-thermal and photo-thermal conversion in ferrite nanoparticles and composite materials. Regarding magneto-thermal conversion, Néel and Brown relaxations, as well as magnetic hysteresis losses, demonstrate that heat generation capability depends strongly on particle size, magnetic anisotropy, and excitation conditions; meanwhile, photo-thermal conversion can occur via plasmon absorption, charge transfer, and non-radiative relaxation. Consequently, combining magnetic and optical components can introduce additional energy-conversion channels, with magneto-plasmonic and magnetic–organometallic complex systems enabling the use of distinct optical absorption mechanisms. Based on this, the thesis selects and compares two systems $\text{MFe}_2\text{O}_4\text{--Ag}$ and $\text{Fe}_3\text{O}_4@\text{TA-Fe}^{3+}$ to evaluate

the role of interfacial nature in energy conversion efficiency and the enhancement of heat-generating power. Theoretical frameworks concerning SAR, ILP, η and thermal response serve as the basis for quantitative evaluation in subsequent chapters.

CHAPTER 3: EXPERIMENTAL

3.1. Sample preparation methods

3.1.1. Synthesis of MFe_2O_4 ferrite nanoparticles via the co-precipitation method

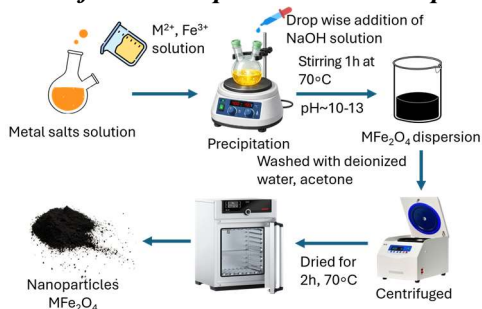


Figure 3.1. Schematic diagram illustrating the synthesis process of MFe_2O_4 ($M = Co, Fe, Mn$) nanoparticles via the co-precipitation method.

Chemicals: metal salts $MCl_2 \cdot xH_2O$, $FeCl_3 \cdot 6H_2O$, $C_6H_8O_7 \cdot H_2O$ và $NaOH$. HCl and acetone were used to adjust the reaction environment and purify the product. The synthesis procedure is illustrated in **Figure 3.1**.

Table 3.1. Codes of MFe_2O_4 ($M = Co, Fe, Mn$) under various pH and reaction temperature.

Sample	CoFe ₂ O ₄			Fe ₃ O ₄			MnFe ₂ O ₄		
	Reaction temperature	pH	Code	Reaction temperature	pH	Code	Reaction temperature	pH	Code
Series 1	70°C	12	CF1	70°C	13	Fe0	70°C	10	MF1
Series 2	40°C	11	CF2				70°C	11	MF2

3.1.2. Green synthesis of MFe_2O_4 ferrite nanoparticles via a microwave-assisted co-precipitation method

The chemicals are similar to those in **Section 3.1.1**, with the addition of coconut fiber extract. The preparation process is described in **Figure 3.3**. The resulting samples are designated as **CF3** and **MF3**.

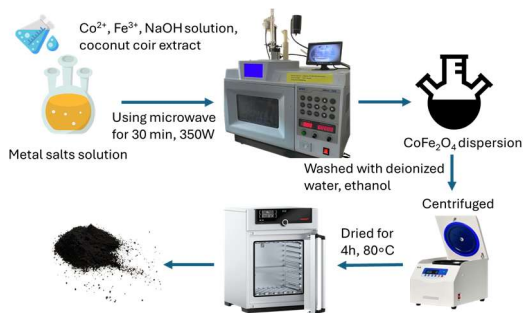


Figure 3.3. Schematic diagram illustrating the green synthesis of MFe_2O_4 ferrite nanoparticles via a microwave-assisted co-precipitation method.

3.1.3. Synthesis of MFe_2O_4 -Ag composite nanoparticles via the thermal decomposition method

Chemicals: $Co(acac)_2$, $Fe(acac)_3$, benzyl ether, OA, OLA, 1-octadecanol, n-hexan. The preparation process is described in **Figure 3.4**.

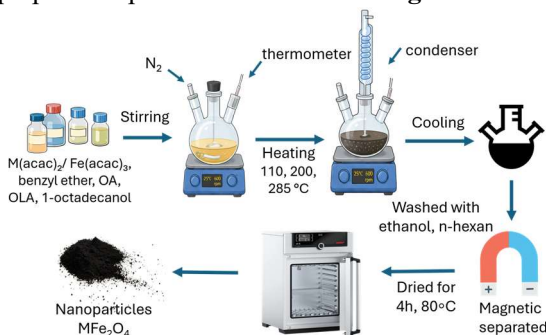


Figure 3.4. Schematic diagram illustrating the synthesis of MFe_2O_4 -Ag composite nanoparticles via the thermal decomposition method.

Table 3.2. Sample designation and synthesis parameters of MFe_2O_4 and MFe_2O_4 -Ag ($M = Co, Fe$) nanocomposites with different ferrite-to-Ag mass ratios.

Sample	Code	Mass ratio (MFe_2O_4 :Ag)	Mass of MFe_2O_4 (mg)	Concentration of $AgNO_3$ (mmol)
$CoFe_2O_4$	Co1	1:0	125	-
$CoFe_2O_4$ -Ag	CoA1	1:0,5	150	0,695
$CoFe_2O_4$ -Ag	CoA2	1:1	125	1,159
$CoFe_2O_4$ -Ag	CoA3	1:2	125	2,320

Sample	Code	Mass ratio (MFe ₂ O ₄ :Ag)	Mass of MFe ₂ O ₄ (mg)	Concentration of AgNO ₃ (mmol)
Fe ₃ O ₄	Fe1	1:0	120	-
Fe ₃ O ₄ -Ag	FeA1	1:0,5	160	0,742
Fe ₃ O ₄ -Ag	FeA2	1:1	120	1,112
Fe ₃ O ₄ -Ag	FeA3	1:2	120	2,225

3.1.4. Synthesis of Fe₃O₄@TA-Fe³⁺ composite nanoparticles via the co-precipitation method

Chemicals are similar to those in Section 3.1.1 and axit tanic. The obtained Fe₃O₄ is coded **FeTA0**. Fe₃O₄@TA-Fe³⁺ is prepared by the process, which is described in **Figure 3.5**.

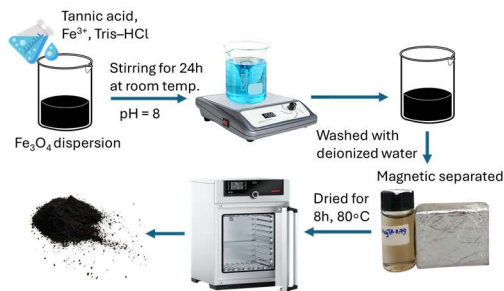


Figure 3.5. Schematic diagram illustrating the synthesis of Fe₃O₄@TA-Fe³⁺.

Table 3.3. Fe₃O₄@TA-Fe³⁺ sample and the corresponding precursor ratio.

Sample	Fe ₃ O ₄ (mg)	Tannic acid (40 mg/mL)	FeCl ₃ ·6H ₂ O (10 mg/mL)	Tris-HCl 0,01M
FeTA1	80 mg	2 ml	0,5 ml	-
FeTA2	80 mg	2 ml	1 ml	50 ml
FeTA3	80 mg	2 ml	2 ml	50 ml

3.2. Material characterization methods

Specific characterization techniques were employed, including structural (XRD, Raman, FTIR), morphological (SEM, TEM, HRTEM, EDX), optical (UV-Vis-NIR, PL), magnetic (VSM), and colloidal (DLS) analyses, as well as differential thermal analysis and thermogravimetric analysis. Additionally, experiments were conducted to investigate heat generation effects under

magnetic, optical, and combined stimuli, enabling quantitative assessment via the SAR parameter.

CHAPTER 4: STRUCTURE, OPTICAL, AND MAGNETIC PROPERTIES OF NANO FERRITES MFe_2O_4 ($\text{M} = \text{Co}, \text{Fe}, \text{Mn}$)

4.1. Crystal structure and physical properties of MFe_2O_4 spinel ferrite nanoparticles ($\text{M} = \text{Co}, \text{Fe}, \text{Mn}$) synthesized by the co-precipitation method

4.1.1. Effect of pH and reaction temperature on the structure, morphology, and particle size of MFe_2O_4 ($\text{M} = \text{Co}, \text{Fe}, \text{Mn}$) ferrite nanoparticles

4.1.1.1. X-ray diffraction analysis and structural parameters

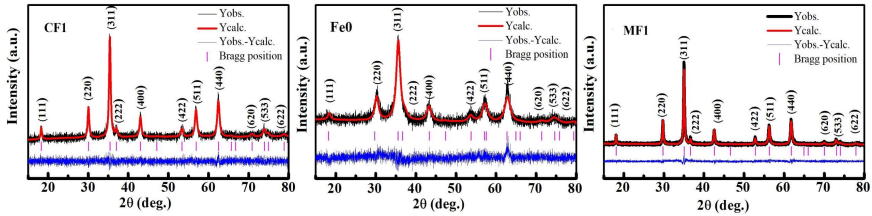


Figure 4.1. XRD patterns and Rietveld refinement results for CF1, Fe0, and MF1 samples (Series 1).

The XRD patterns (**Figure 4.1**) of the Series 1 samples show diffraction peaks that agree well with the JCPDS standard data of CoFe_2O_4 , Fe_3O_4 , and MnFe_2O_4 , characteristic of cubic spinel structures (space group $Fd\bar{3}m$).

For Series 1, crystal size and microstrain vary significantly with pH. As the pH rises, supersaturation increases,

promoting nucleation and reducing crystal size. The extent of this effect depends on the nature of the M^{2+} cation- specifically regarding hydroxide solubility and CFSE with Mn^{2+} yielding the largest crystals, Co^{2+} producing intermediate sizes, and Fe_3O_4 resulting in the smallest crystals due to high nucleation density and superior resistance to agglomeration. (**Table 4.6**).

Table 4.6. Crystallite size (D) and lattice strain (ε) determined from the UDM

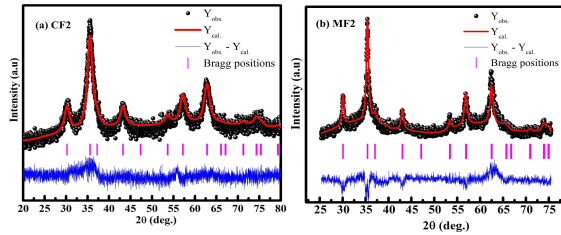


Figure 4.2. XRD patterns and Rietveld refinement result for (a) CF2 and (b) MF2 (Series 2).

model, and particle size (d) determined from FESEM images of the samples in two series.

Series	Sample	D (nm)	ε (10^{-3})	d (nm)
Series 1	CF1	14,00	1,48	14,65
	Fe0	9,21	0,33	9,02
	MF1	29,47	0,76	34,26
Series 2	CF2	7,23	2,27	7,5
	MF2	29,10	0,17	32,5

For Series 2, the results indicate that high temperatures promote diffusion, recrystallization, and crystal growth, while simultaneously reducing lattice stress.

4.1.2. Effect of pH and reaction temperature on the optical properties of MFe_2O_4 ($M = \text{Co}, \text{Fe}, \text{Mn}$) ferrite nanoparticles

4.1.2.1. Optical characteristics and semi-empirical energy level diagrams of CF1, Fe0, and MF1 samples.

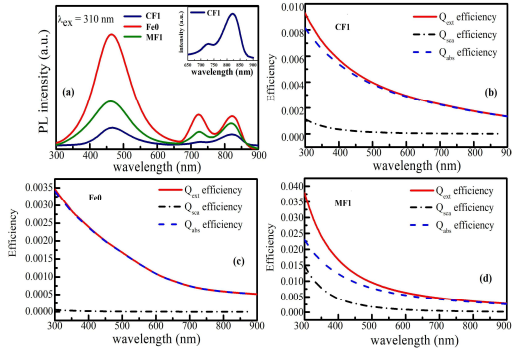


Figure 4.12. (a) PL spectra and (b–d) Mie coefficients of samples CF1, Fe0, and MF1 (Series 1).

By combining UV–Vis–NIR and PL data with theoretical studies by other authors [12, 83, 84], a semi-empirical energy level diagram for Series 1 is proposed in **Figure 4.11**. The optical band gap ($\sim 2.6 \text{ eV}$) is attributed to transitions between $\text{O}(2p)$ levels and e_g states at the octahedral site, whereas

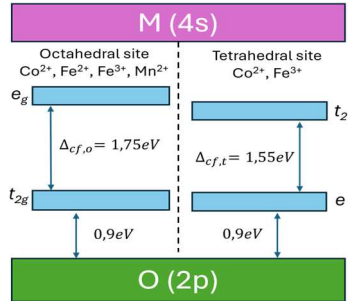


Figure 4.11. Semi-empirical energy-level diagram of CF1, Fe0, and MF1 nanoparticles (Series 1).

lower-energy absorption features ($\sim 1.7\text{--}1.8\text{ eV}$) may be associated with crystal-field splitting.

The calculation results (**Fig. 4.12b–d**) show that the Fe0 sample has a $Q_{abs}/Q_{ext} \approx 1$, indicating that absorption dominates and thus offers the potential for high photothermal conversion efficiency.

4.1.2.2. Optical characteristics and semi-empirical energy level diagrams of CF2 and MF2 samples

To evaluate the potential for photocatalytic application, band positions were estimated using the Mulliken method [149] - specifically, by constructing an energy band diagram referenced against the Normal Hydrogen Electrode (NHE).

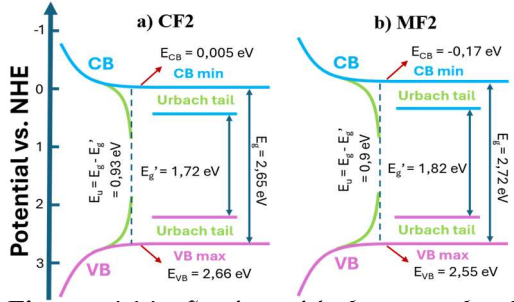


Figure 4.14. Semi-empirical energy-level diagrams of CF2 and MF2 (Series 2) referenced against NHE.

Figure 4.14 illustrates how the combination of the band gap, sub-band gap states, and favorable band positions facilitated efficient light absorption and charge transport.

4.1.3. Effect of pH and reaction temperature on the magnetic properties of $M\text{Fe}_2\text{O}_4$ ($M = \text{Co}, \text{Fe}, \text{Mn}$) ferrite nanoparticles

4.1.3.1. Magnetic properties of CF1, Fe0 and MF1 samples

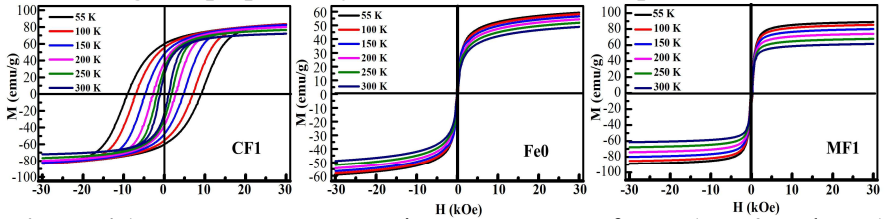


Figure 4.15. M - H curves at various temperature for CF1, Fe0 and MF1 samples (Series 1).

Figure 4.15 shows that CF1 and MF1 exhibit higher saturation magnetization M_s values than Fe0 due to cation distribution within the spinel structure, whereas Fe0 is strongly influenced by the nanosize effect and surface

spin disorder [27, 40, 181, 182]. The variation in coercivity H_c aligns with Kneller's law, while low R_{sq} values reflect the influence of surface spins, disordered spin layers, and inter-particle dipole interactions. The magnetic sizes of CF1 and MF1 are smaller than their geometric sizes, whereas Fe0 exhibits a larger magnetic size, highlighting the significant role of surface spin layers and dipole interactions in governing the magnetic properties of the ferrite nanoparticles.

4.1.3.2. Magnetic properties of CF2 and MF2 samples

Figure 4.17 shows that MF2 sample is close to magnetic saturation, whereas CF2 sample is not fully saturated due to surface spin disorder associated with its small size. The

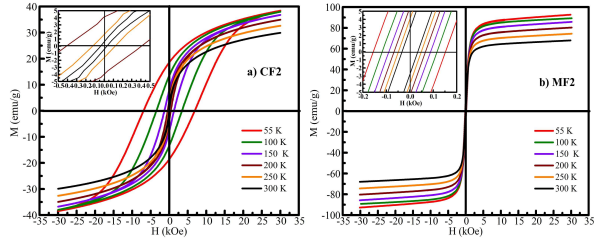


Figure 4.17. M - H curves at various temperature for CF2 and MF2 samples (Series 2).

values of H_c and M_r decrease with temperature and follow Kneller's law, reflecting the role of thermal fluctuations in the magnetization reversal process. Despite having a comparable K_1 at 55 K, CF2 exhibits significantly higher H_c and M_r values due to the strong magnetic anisotropy of Co^{2+} and a particle size near the single-domain limit, whereas MF2 tends to be magnetically softer due to the influence of thermal fluctuations. The temperature dependence of M_s and K_1 , along with the K_1 – M_s relationship, indicates that CF2 is primarily governed by cubic magnetocrystalline anisotropy, while MF2 is more strongly influenced by surface anisotropy and structural disorder. Overall, the magnetic behavior of the two samples is determined by the interplay between magnetocrystalline anisotropy, surface effects, and nanoparticle size.

4.2. Crystal structure and physical properties of MFe_2O_4 spinel ferrite nanoparticles (M = Co, Fe, Mn) green synthesis by a microwave-assisted co-precipitation method

4.2.1. Structure, morphology, and particle size

Cation distribution was determined via Rietveld refinement under $Fd\bar{3}m$ symmetry constraints. The results indicate that both systems possess a mixed spinel structure with a simultaneous distribution of M^{2+} and Fe^{3+} ions at A and B sites, closely matching the $x = 0.62$ value observed for sample MF2 in Series 2. The obtained inversion degree values are consistent with previous studies [178].

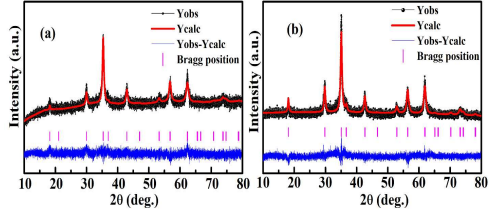


Figure 4.23. XRD patterns and Rietveld refinement result for (a) CF3 and (b) MF3 (Series 3).

4.2.3. Optical characteristics and semi-empirical energy-level diagrams

The PL spectrum (**Figure 4.29**) shows that the electron-hole recombination mechanism is strongly governed by defect states.

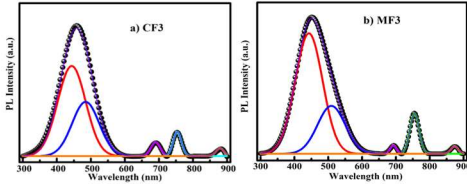


Figure 4.29. PL spectra and spectral analysis results for CF3 and MF3 samples (Series 3).

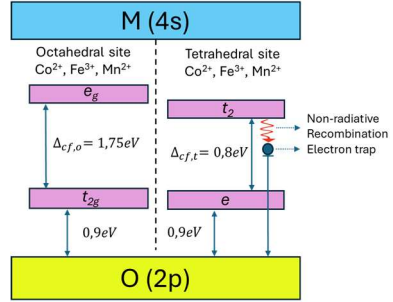


Figure 4.30. Semi-empirical energy level diagrams of CF3 and MF3.

Based on UV–Vis–NIR, Urbach, and PL results, the energy band diagram (**Figure 4.30**) reveals transitions primarily occurring between $O(2p)$ and the metal 3d states, with significant involvement of intermediate defect-induced levels, a feature distinguishing these samples from those of the same composition in Series 1. The effective crystal field splitting (~ 0.8 eV) reflects the modification of the coordination environment under microwave synthesis conditions.

4.2.4. Magnetic characteristics and interacting superparamagnetic models

4.2.4.1. Magnetic characteristics

Despite having comparable degrees of inversion, CF3 and MF3 samples exhibit markedly different magnetic properties. CF3 displays higher M_s , K_1 , M_r , and H_c values

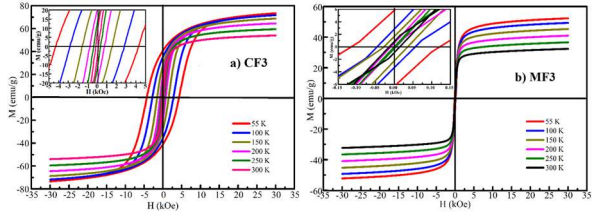


Figure 4.32. $M(H)$ curves of (a) CF3 and (b) MF3 samples (Series 3) at different temperatures. The insets show enlarged views of the low-field region.

due to effective A–B superexchange interactions and the strong spin-orbit coupling of Co^{2+} , whereas MF3 is more significantly influenced by surface spin disorder and dipole-dipole interactions [33,184]. The temperature dependence of M_s follows Bloch's law, while the H_c of CF3 sample aligns with the Kneller model, characteristic of a near-single-domain system. In contrast, MF3 sample shows signs of a surface spin-glass (SSG) state resulting from strong interparticle interactions.

4.2.4.2. Superparamagnetic interactions within the MnFe_2O_4 sample

Normalized magnetization results indicate that MnFe_2O_4 sample is not an ideal superparamagnetic material but rather an interacting superparamagnetic nanoparticles. Analysis using a modified Langevin model confirms the presence of weak-to-moderate interparticle dipole-dipole interactions, consistent with the magnetic hysteresis and ZFC/FC results [52].

This chapter elucidates the relationships among synthesis conditions, crystal structure, cation distribution, microstructure, and the magnetic and optical properties of MFe_2O_4 ($\text{M} = \text{Co}, \text{Fe}, \text{Mn}$) ferrite nanosystems, thereby establishing a physical basis for selecting host materials to enhance heat generation capacity in the subsequent chapter.

CHAPTER 5: MAGNETOTHERMAL AND PHOTOTHERMAL CONVERSION EFFECTS IN SPINEL FERRITE-BASED NANOCOMPOSITE SYSTEMS

5.1. Nanocomposite MFe_2O_4 –Ag ($\text{M} = \text{Fe}, \text{Co}$)

5.1.1. Crystal structure, morphology, and interface characteristics

The XRD patterns (Figure 5.1) show that the MFe₂O₄ samples crystallize in a cubic spinel structure ($Fd\bar{3}m$) with high phase purity. Upon combination with Ag, characteristic peaks of Ag (face-centered cubic, fcc, $Fd\bar{3}m$) appear distinctly, while the positions of the ferrite peaks remain virtually unchanged, indicating that Ag exists as a separate metallic phase rather than substituting into the crystal lattice.

Structural and spectroscopic results reveal two distinct interfacial interaction mechanisms: (i) in CoFe₂O₄-Ag, the plasmon effect primarily drives local electromagnetic field enhancement; (ii) in Fe₃O₄-Ag, plasmon-lattice interactions and charge transfer dominate, significantly altering lattice vibrations and the bonding environment. This distinction lays the foundation for the differing energy conversion characteristics to be analyzed in next sections.

FESEM, TEM, and EDX results indicate that the intrinsic structure of the ferrite is preserved, while Ag is primarily distributed on the surface. This spatial separation is crucial: the ferrite core governs magnetic properties and anisotropy, whereas Ag acts as a plasmonic center and forms the interface. Consequently, the magnetic and optical mechanisms can be controlled relatively independently, establishing the structural foundation for the magneto-thermal and photothermal effects discussed in subsequent sections.

5.1.2. Plasmonic characteristics and the influence of Ag on magnetic properties

Both CoFe₂O₄-Ag and Fe₃O₄-Ag samples exhibit the characteristic LSPR peak of Ag, with the resonance position depending on the electronic

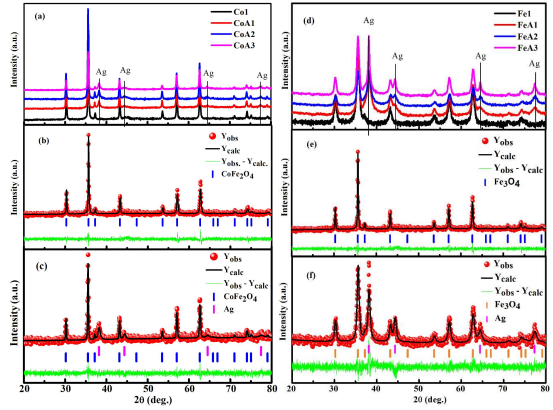


Figure 5.1. (a, d) XRD patterns; (b, e) Rietveld refinements of MFe₂O₄; and (c, f) Rietveld refinements of MFe₂O₄-Ag with the highest Ag content (M = Co, Fe).

environment of the ferrite matrix [201]. The presence of Ag reduces M_s in both systems but significantly increases H_c in $\text{CoFe}_2\text{O}_4\text{-Ag}$, while causing only a slight increase in $\text{Fe}_3\text{O}_4\text{-Ag}$, due to differing interface interaction mechanisms [202–204]. The results demonstrate

that the ferrite matrix plays a crucial role in simultaneously modulating the plasmonic response and magnetic properties of the composite materials.

5.1.3. Analysis of the magnetocaloric effect based on the H/H_c ratio and recovery kinetics

The magnetothermal effects of $\text{CoFe}_2\text{O}_4\text{-Ag}$ and $\text{Fe}_3\text{O}_4\text{-Ag}$ nanocomposites were analyzed based on the H/H_c ratio and the kinetic condition $\omega\tau_{\text{eff}}$. The results indicate that $\text{CoFe}_2\text{O}_4\text{-Ag}$ exhibits high magnetic anisotropy and a long relaxation time, resulting in a regime where $H \ll H_c$ and $\omega\tau_{\text{eff}} \gg 1$; this hinders magnetic reversal and reduces heat generation efficiency. In contrast, $\text{Fe}_3\text{O}_4\text{-Ag}$ possesses a shorter Néel relaxation time and satisfies the conditions $H \geq H_c$ and $\omega\tau_{\text{eff}} \ll 1$, allowing the magnetic moments to respond more effectively to the alternating magnetic field, thereby yielding higher SAR values [103, 105, 205, 206]. Thus, magnetothermal efficiency is determined by the compatibility between magnetic moment relaxation dynamics and excitation conditions, rather than relying solely on magnetic anisotropy.

5.1.4. Analysis of the photothermal conversion effect based on plasmon absorption, size, and electronic structure.

5.1.4.1. Optical absorption and analysis based on Mie theory

Mie analysis reveals that the optical response of the samples depends simultaneously on particle size and the plasmon effect of Ag. Incorporation of Ag significantly enhances optical extinction efficiency; however, the degree of enhancement varies between the two systems due to differences in particle size and the electronic environment of the ferrite matrix. The results indicate that the

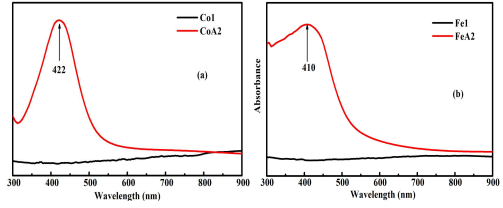


Figure 5.6. UV-Vis-NIR absorption spectra for Co1, Fe1 and Ag-containing composites CoA2, FeA2 in range of 300–900 nm.

photothermal effect depends not only on the presence of plasmons but is also strongly influenced by particle size.

5.1.4.2. Photothermal heating under laser irradiation ($\lambda = 532 \text{ nm}$)

All samples demonstrated photothermal conversion capabilities under 532 nm laser irradiation, with $\text{Fe}_3\text{O}_4\text{-Ag}$ exhibiting higher heat generation efficiency than $\text{CoFe}_2\text{O}_4\text{-Ag}$. Although Ag provides an additional plasmonic absorption channel, the results indicate that photothermal efficiency depends not only on absorption intensity but also on the ability to dissipate energy via non-radiative processes at the ferrite–Ag interface [6,120,155,207,208].

5.1.4.3. Photothermal conversion efficiency and related spectroscopic factors

Determinations of photothermal conversion efficiency reveal that Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{-Ag}$ consistently exhibit higher η values than samples based on CoFe_2O_4 (Table 5.2). This difference is attributed to the characteristic electronic absorption mechanisms of Fe_3O_4 , specifically $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge transfers combined with a more efficient non-radiative energy dissipation capability. In contrast, within the $\text{CoFe}_2\text{O}_4\text{-Ag}$ sample, the plasmonic effect is constrained by off-resonance absorption and a more significant contribution from scattering. Overall, the photothermal efficiency of $\text{MFe}_2\text{O}_4\text{-Ag}$ sample is governed by the interplay of plasmonic absorption, size effects, and the electronic structure of the ferrite host [153, 189, 209–211].

Table 5.2 The photothermal conversion efficiency (η) of samples Co1, CoA2, Fe1, and FeA2 was calculated from the cooling curves obtained after turning off the laser irradiation (532 nm; 0,3 W/cm²).

Sample	τ (s)	Q_0 (mW)	ΔT_{max} (°C)	A_λ	I (mW)	η (%)
Co1	259,36		6,48	0,36		4,61
CoA2	158,22	3,32	7,24	0,35	300	10,31
Fe1	134,89		9,98	0,99		8,14
FeA2	147,99		10,85	0,26		21,51

5.1.5. Heating effect under single and combined magnetic and optical excitation conditions

Under simultaneous magnetic field and laser excitation, samples Co1, CoA2, and Fe1 exhibit a combined efficiency coefficient $\eta_c < 1$, whereas FeA2 shows

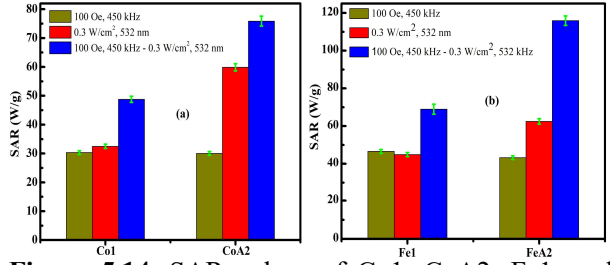


Figure 5.14. SAR values of Co1, CoA2, Fe1, and FeA2 suspensions under magnetic, photothermal, and combined excitation modes.

$\eta_c \approx 1$. The results indicate that the dual heating effect is not a linear summation of the two individual mechanisms but depends on the modulation of magnetic relaxation dynamics via the parameter $\omega\tau_{\text{eff}}$. Notably, $\text{Fe}_3\text{O}_4\text{-Ag}$ achieves a state closer to the optimum than $\text{CoFe}_2\text{O}_4\text{-Ag}$, enabling the maintenance of heat generation efficiency under combined excitation [212,213].

5.2. Nanocomposite $\text{Fe}_3\text{O}_4\text{@TA-Fe}^{3+}$

5.2.1. Core-shell structure and Fe^{3+} -polyphenol coordination interactions

TGA-DTA results indicate that Fe_3O_4 possesses high thermal stability, whereas $\text{Fe}_3\text{O}_4\text{@TA-Fe}^{3+}$ samples exhibit decomposition stages characteristic of an organic coating. The variation in thermal behavior with Fe^{3+} content confirms the formation of a TA-Fe^{3+} coordination network and suggests that the coating exists as an organic-inorganic hybrid structure, the nature of which depends on the strength of the Fe^{3+} -polyphenol coordination [214–216].

5.2.2. Crystal structure and lattice distortion

XRD results and Rietveld refinement (Figure 5.16) indicate that all samples crystallize in a cubic spinel structure with high

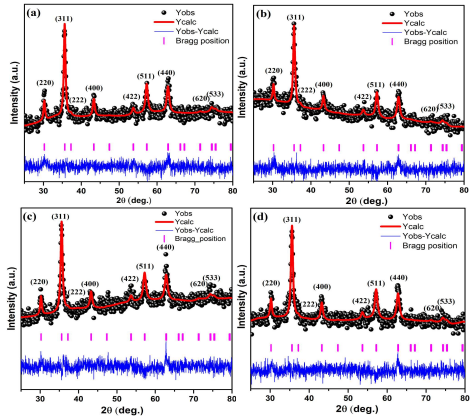


Figure 5.16. XRD patterns and Rietveld refinements of (a) FeTA0, (b) FeTA1, (c) FeTA2, and (d) FeTA3.

phase purity. The TA-Fe³⁺ coating does not alter the phase or crystallite size but increases lattice microstrain. These results suggest that the TA-Fe³⁺ layer resides primarily on the surface and induces local stress at the interface without affecting the Fe₃O₄ core structure.

5.2.3. Core-shell morphology and structure

TEM and HR-TEM images reveal particles with sizes in the range of 14–16 nm, consistent with XRD results. Direct observation confirms the presence of an amorphous TA-Fe³⁺ shell, approximately 1–2 nm thick, encapsulating a highly crystalline Fe₃O₄ core. These findings substantiate the core-shell structure of the Fe₃O₄@TA-Fe³⁺ sample and the formation of an organic–inorganic interface, which plays a crucial role in modulating the material's functional properties.

5.2.4. Spectroscopic characteristics and Fe³⁺–polyphenol coordination interactions at the interface

FTIR and Raman analyses confirm the formation of a TA-Fe³⁺ coating on the Fe₃O₄ surface, evidenced by characteristic changes in polyphenol groups and the appearance of vibrations associated with Fe–O–C bonds. Furthermore, the results indicate the formation of an interface characterized by strong chemical interaction and local structural distortion, consistent with XRD analysis.

5.2.5. Magnetic properties and the role of the interface region

Following the TA-Fe³⁺ coating, saturation magnetization decreased due to magnetic dilution effects and surface spin disorder. Some samples exhibited hysteresis loop asymmetry and exchange bias, indicating the formation of exchange interactions between the Fe₃O₄ core and the disordered spin layer at the interface. The results demonstrate that the TA-Fe³⁺ layer serves not only as a protective coating but also modulates the system's magnetic properties through interfacial interactions.

5.2.6. Colloidal properties and surface stability

The TA-Fe³⁺ coating significantly reduces hydrodynamic size and increases the negative magnitude of the zeta potential, demonstrating a substantial improvement in the dispersion stability of the Fe₃O₄ sample. This is

attributed to an electro-steric stabilization mechanism, wherein the TA-Fe³⁺ coordination layer acts as a functional interface that controls interparticle interactions and inhibits aggregation.

5.2.7. Photothermal heating effect and SAR optimization

5.2.7.1. Photothermal heating and selection of a representative material

The TA-Fe³⁺ coating significantly enhances the photothermal heating capability of Fe₃O₄ under NIR laser irradiation. The efficiency increases with the coating content, peaking at the FeTA2 sample, and subsequently decreases when the shell becomes excessively thick. The results indicate that the photothermal effect is governed by the electronic structure of the coordination layer, energy transfer efficiency across the shell, and the colloidal dispersion state. Due to its superior performance, FeTA2 was selected as the representative sample for further studies.

5.2.7.2. Dependence of SAR on concentration and excitation power

For the FeTA2 sample, the SAR increases with laser power but exhibits a non-monotonic dependence on concentration. The maximum value is reached at 1.0 mg/mL, whereas at higher concentrations, scattering effects and interparticle interactions reduce the specific heat generation efficiency. The results indicate that simultaneous optimization of material concentration and excitation conditions is necessary to achieve maximum photothermal efficiency.

5.2.7.3. Analysis of optical absorption characteristics across the entire wavelength range.

UV-Vis-NIR spectra reveal that the TA-Fe³⁺ coating does not significantly alter the absorption characteristics of the Fe₃O₄ core. However, Mie theory analysis indicates a shift in the dominant optical attenuation mechanism from scattering to absorption. This transition promotes non-radiative dissipation and is the primary factor driving the enhanced photothermal effect of the Fe₃O₄@TA-Fe³⁺ samples.

5.2.7.4. Photothermal conversion efficiency and experimental limits

Repeated heating-cooling cycles (**Figure 5.27**) show that the maximum temperature remains virtually unchanged, demonstrating the high photothermal stability of the FeTA2 sample. The photothermal conversion efficiency (η),

determined from the heating–cooling curves, ranges from 19.7% to 30.6%, with an average value of approximately 25%. This result is significantly higher than that of conventional inert coatings but lower than that of certain pure polyphenol systems. It should be noted that η depends significantly on optical absorbance and measurement conditions; therefore, it must be evaluated in conjunction with ΔT and SAR_{pho} . Overall, the $Fe_3O_4@TA-Fe^{3+}$ samples exhibits stable and efficient photothermal conversion capabilities under NIR excitation.

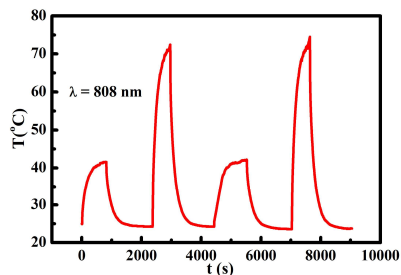


Figure 5.27. Photothermal stability of FeTA2 nanoparticles evaluated through repeated laser irradiation on/off cycles ($\lambda = 808$ nm) over 9000 s at power densities of 0.3 and 1.0 W/cm².

5.2.8. Magnetic heating effect and recovery kinetics

Under AMF ($H = 12$ kA/m; $f = 340$ kHz), the SAR_{mag} value increased from 125.8 W/g for FeTA0 to 154.2 W/g for FeTA2. This increase indicates that the $TA-Fe^{3+}$ coating contributes to enhancing the magnetothermal performance of the system. For Fe_3O_4 particles approximately 14 nm in size, the Néel relaxation mechanism dominates. The $TA-Fe^{3+}$ coordination layer creates a region of disordered spins at the surface and reduces interparticle interactions, thereby modulating relaxation dynamics in a manner favorable for magnetic energy dissipation. The results demonstrate that the system's magnetothermal performance depends not only on saturation magnetization but is also strongly influenced by interfacial effects.

5.2.9. Heating characteristics under magnetic, optical, and combined excitation

Calculation results indicate that FeTA2 exhibits higher SAR_{pho} , SAR_{mag} , and SAR_{com} values than the pristine Fe_3O_4 sample. Notably, under simultaneous excitation, SAR_{com} reaches 579.6 W/g, reflecting the enhanced energy conversion efficiency of the system following $TA-Fe^{3+}$ coating (**Figure 5.33**).

This effect is attributed to the synergy between two photothermal mechanisms: photothermal heating alters recovery kinetics, while the TA-Fe³⁺ layer simultaneously enhances optical absorption and modulates surface spin states. Consequently, the Fe₃O₄@TA-Fe³⁺ sample achieves high combined heating efficiency under bio-safe excitation conditions, demonstrating potential for application in multimode photothermal systems.

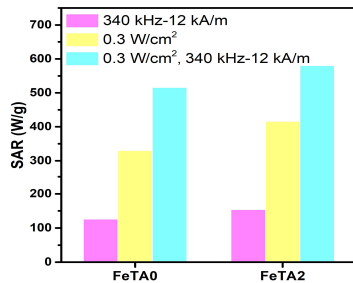


Figure 5.33. Comparison of the SAR values of FeTA0 and FeTA2 (1.5 mg/mL) under different excitation modes.

5.3. Comparison of energy conversion in MFe₂O₄-Ag and Fe₃O₄@TA-Fe³⁺ nanocomposite

While the MFe₂O₄-Ag optimizes energy conversion through distinct physical mechanisms, namely plasmonic and magnetic effects, the Fe₃O₄@TA-Fe³⁺ achieves high efficiency through the close coupling of photonic, thermal, and spin-dynamic processes at the interface. In other words, the former system relies on electronic resonance, whereas the latter is based on the modulation of spin dynamics and surface chemistry.

This chapter investigated and compared the energy conversion capabilities of two ferrite-based composite systems, MFe₂O₄-Ag and Fe₃O₄@TA-Fe³⁺, thereby clarifying the roles of the optical material component and interfacial region in heat generation. For the MFe₂O₄-Ag system, the presence of Ag significantly enhanced heat generation under simultaneous magnetic-photothermal excitation, with the plasmonic effect contributing to enhanced optical absorption. However, the degree of enhancement depended on the nature of the ferrite and the characteristics of the composite system.

A. CONCLUSIONS

Based on the research results, the dissertation has achieved its objective of elucidating the structure-property relationships of MFe₂O₄ (M = Co, Fe, Mn) ferrite nanoparticles, thereby enabling the selection and design of magneto-optical composite systems for enhanced heat generation with potential

biomedical applications. The main findings are as follows:

1. Elucidation of the structural characteristics and synthesis conditions for the selection of the ferrite host material.
2. Establishment of the relationships among the structure, magnetic properties, and optical properties of the ferrite host material.
3. Selection of a suitable ferrite host material for enhancing heat generation.
4. Enhancement of heat generation using a ferrite–plasmonic system.
5. Development of the non-plasmonic $\text{Fe}_3\text{O}_4@\text{TA-Fe}^{3+}$ system to expand the approaches for enhancing heat generation.
6. Proposal of a materials-design framework for enhancing heat generation.

B. RECOMMENDATIONS AND FUTURE RESEARCH DIRECTIONS

- Further optimize the particle size, magnetic anisotropy, and dispersion state to bring the system closer to the optimal dynamic condition ($\omega\tau_{\text{eff}} \approx 1$), thereby improving magnetic-to-thermal conversion efficiency.
- Extending research into new interfacial hybrid systems (metals, polymers, and two-dimensional materials), while elucidating the charge-transfer mechanisms and electronic nature of the interfaces to control energy-dissipation mechanisms and enhance photothermal effects.
- Combine experiments with theoretical simulations, including micromagnetic simulations, Monte Carlo methods, and DFT, to quantitatively describe magnetic-moment dynamics and energy-conversion mechanisms.
- Investigate biomedical applications, including assessments of stability, toxicity, and heating efficiency under in vitro and in vivo conditions.

LIST OF THE PUBLICATIONS RELATED TO THE DISSERTATION

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3. **Tran Thi Ngoc Nha**, Dang Ngoc Toan, Dinh Thanh Khan, Le Thi Tuyet Ngan, Le Viet Bau, Tran Dang Thanh, Do Hung Manh, Pham Thanh Phong, Nguyen Xuan Phuc, Structure-property relationships of CoFe_2O_4 and MnFe_2O_4 nanoferrites: Deep insights into optical and magnetic properties, *Ceram. Int.*, 2025, 51, 50091-50102.
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7. **Trần Thị Ngọc Nhã**, Phạm Hồng Nam, Đỗ Hùng Mạnh, Trần Đăng Thành, Phạm Thanh Phong, Xác định các thông số đàn hồi và kích thước tinh thể của nano MFe_2O_4 từ nhiễu xạ tia X và phổ FTIR, SPMS 2023.

8. **Tran Thi Ngoc Nha**, Dang Ngoc Toan, Pham Hong Nam, Do Hung Manh, Tran Dang Thanh, Dinh Thanh Khan, Pham Thanh Phong, Structural and optical properties of MFe_2O_4 ($M = Co, Fe, Mn$) nanoferrites prepared by co-precipitation technique, IWAMSN 2024.

9. **Trần Thị Ngọc Nhã**, Đặng Ngọc Toàn, Trần Đăng Thành, Đỗ Hùng Mạnh, Phạm Thanh Phong, Optical and Magnetic Properties of $CoFe_2O_4$ Nanoparticles Synthesized via Green Method, SPMS 2025.

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