Scientific Research Publishing

Advances in Nanoparticles, 2025, 14(1), 1-11
https://www.scirp.org/journal/anp
ISSN Online: 2169-0529
ISSN Print: 2169-0510

Synthesis and Characterization of Fe_3O_4 Nanoparticles by Sol-Gel Method Using Water as a Solvent

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How to cite this paper: Mustafa, A., Ali, U., Mukarama, Iqbal, A., Qayyum, M., Haq, I.U. and Islam, F. (2025) Synthesis and Characterization of Fe_3O_4 Nanoparticles by Sol-Gel Method Using Water as a Solvent. *Advances in Nanoparticles*, **14**, 1-11.
https://doi.org/10.4236/anp.2025.141001

Received: December 13, 2024
Accepted: February 3, 2025
Published: February 6, 2025

Abstract

Ferromagnetic Fe_3O_4 nanoparticles were synthesized using water as the solvent through the sol-gel method, which was selected for its cost-effectiveness, simplicity, and eco-friendly nature. The synthesized nanoparticles were characterized using a variety of techniques, including Fourier Transform Infrared (FTIR) spectroscopy, X-ray powder diffraction (XRD), Scanning Electron Microscopy (SEM), Thermogravimetric Analysis (TGA), and Vibrating Sample Magnetometer (VSM). These characterizations confirmed the successful formation of Fe_3O_4 nanoparticles. The FTIR spectra identified characteristic peaks corresponding to the functional groups present, and XRD analysis, using Scherer's equation, determined an average crystalline size of 1.2 nm for the Fe_3O_4 nanoparticles. TGA results demonstrated the thermal stability of the nanoparticles, SEM imaging revealed distinct honeycomb-like structures for the nanoparticles synthesized with water as the solvent, while the VSM analysis was used to determine the magnetic behavior of the nanoparticles.

Keywords

Fe_3O_4 Nanoparticles, Sol-Gel Synthesis, Honeycomb Structures, FTIR, XRD, SEM, TGA, VSM

1. Introduction

Nanoscience and nanotechnology focus on materials and systems with dimensions typically in the range of 1 to 100 nanometers. At this scale, materials exhibit unique mechanical, thermal, and optical properties that are often significantly different from their bulk counterparts [1]. These properties make nanomaterials valuable for applications across various fields, including electronics, energy storage, biomedicine, and environmental science [2].

Magnetic nanoparticles, especially iron oxide nanoparticles like Fe_3O_4 (magnetite), have attracted significant interest due to their superparamagnetic properties, high surface area, and compatibility with biological systems [3]. These nanoparticles are utilized in a wide range of applications, including magnetic resonance imaging (MRI), drug delivery systems, cancer therapies utilizing hyperthermia, and various electrocatalytic processes [4]. They are also valuable in environmental applications, particularly for water purification and heavy metal removal, owing to their strong adsorption capabilities [5].

For example, German *et al.* (2006) introduced a flow-injection method for creating magnetite nanoparticles with a narrow size distribution of 2 - 7 nm. This approach, characterized by techniques such as X-ray diffraction and electron microscopy, enables precise control over particle size through continuous mixing under laminar flow conditions [6]. In another study, Ghandoor *et al.* (2012) employed a co-precipitation method to synthesize Fe_3O_4 nanoparticles with an average diameter of 10 nm, demonstrating superparamagnetic behavior confirmed through X-ray diffraction, TEM, and vibrating sample magnetometry [7]. Moreover, Yan *et al.* (2012) modified Fe_3O_4 nanoparticles with sodium citrate and oleic acid to enhance their dispersion, although this modification resulted in a reduction of saturation magnetization [8]. Zeynep *et al.* (2014) took a different approach by synthesizing $NiFe_2O_4$ nanoparticles using microwave-assisted combustion, noting that crystallite sizes increased with temperature and exhibited ferromagnetic behavior at room temperature [9].

All of these existing methods that are used for the synthesis of Fe_3O_4 nanoparticles have certain limitations [10] [11]. For instance, the flow-injection method allows for precise control over particle size but requires specialized equipment, making it complex and costly. The co-precipitation, while simpler, often leads to particle agglomeration and demands careful pH control, which can introduce impurities and affect morphology. The surface modifications can enhance stability but may reduce the magnetic strength of nanoparticles, limiting their applications. Additionally, the microwave-assisted combustion method requires strict temperature control to ensure consistency in size and morphology, leading to high energy demands and complicating scalability.

However, the sol-gel method, which uses water as a solvent, is preferred due to its simplicity, cost-effectiveness, and ability to control particle size and morphology [12]-[14]. This method also allows for the use of eco-friendly solvents, such as water, which aligns with the growing demand for green chemistry approaches

in nanoparticle synthesis [15].

In our study, Fe_3O_4 nanoparticles were synthesized using this sol-gel method, addressing several limitations of existing techniques. The use of water as a solvent not only eliminates the need for harsh chemicals but also ensures a safer, more environmentally friendly process. Moreover, this method allows for effective control over nanoparticle characteristics without relying on complex equipment or high temperatures, thereby reducing energy consumption and improving scalability. Unlike methods that require surface modifications, which can compromise magnetic properties, our approach produced stable nanoparticles with preserved superparamagnetic behavior. These unique advantages, combined with the simplicity, sustainability, and retention of functional properties, make the sol-gel method an innovative and advantageous alternative for nanoparticle synthesis [16].

2. Experiment

The synthesis of ferromagnetic nanoparticles was carried out using water as the solvent, with precise control of temperature and pH conditions to ensure consistency. The following is a detailed outline of the experimental procedures, chemicals, and analytical instruments used.

2.1. Chemicals

All chemicals used in the research had a purity of 99.9%. $FeSO_4{\cdot}7H_2O$ and $FeCl_3$ were sourced from Merck, while HNO_3 and NH_4OH were obtained from BDS. Distilled water was used from the laboratory. All chemicals were used without further purification. The pH paper was purchased from ChemCad (catalog number 5986-62).

2.2. Instruments

The analytical instruments used in this experiment were selected for their high precision and accuracy. These included an Analytical Balance (Shimadzu), Fourier Transform Infrared Spectroscopy (FTIR) (Shimadzu), X-Ray Diffraction Analysis (XRD) (Shimadzu), Field Emission Scanning Electron Microscope (FE-SEM) (JEOL 5910), and Thermo-Gravimetric Analysis (TGA/SDT) (G 600 V 8.3 Build 101). Additionally, various physical instruments were employed, including a magnetic stirrer, Liebig condenser, hot plate, furnace (Vulcane D 550), oven (EV 108AC-Kapa), centrifuge machine (Sigma 1-4), and centrifuge tubes, all sourced from the laboratory.

2.3. Synthesis Procedure

The ferromagnetic nanoparticles (Fe_3O_4) were synthesized using H2O as the solvent. The following outlines the procedure in detail, presented in different steps for synthesizing the nanoparticles with water as the solvent.

2.3.1. Preparation of 0.1 M $FeSO_4.7H_2O$ Solution

A 0.1 M $FeSO_4{\cdot}7H_2O$ solution was prepared by dissolving 0.716 g of powdered

$FeSO_4 \cdot 7H_2O$ in 20 mL of distilled water, providing a stable concentration suitable for use as a running solution in further analysis.

2.3.2. Preparation of 0.1 $FeCl_3$ Solution

A 0.1 M FeC_3 solution was prepared by dissolving 0.325 g of powdered $FeCl_3$ in 20 mL of distilled water, ensuring the solution's concentration was precise for use as a running solution in subsequent applications.

2.3.3. Preparation of Ferromagnetic Nanoparticles

Ferromagnetic nanoparticles were synthesized using the sol-gel synthesis method. For this purpose, pre-prepared solutions of $FeSO_4 \cdot 7H_2O$ and $FeCl_3$ were mixed in a condenser with the temperature precisely maintained at 70˚C using a digital water bath equipped with temperature sensors. The temperature was continuously monitored throughout the process to prevent deviations, ensuring consistent reaction conditions. The solution was stirred continuously with a magnetic stirrer to ensure uniform mixing and heat distribution. The pH was adjusted to 4 - 5 by the dropwise addition of 25% aqueous ammonia, and a calibrated pH meter was used to monitor and maintain the pH within the desired range. The pH was checked at regular intervals, and adjustments were made as necessary to keep it stable during the reaction. These conditions were critical to stabilizing the reaction environment, facilitating uniform nanoparticle growth, and minimizing agglomeration.

After stirring for 2 hours under these controlled conditions, the solution was allowed to cool and then centrifuged at a speed of 10,000 rpm for 20 minutes. The nanoparticles settled at the bottom of the centrifuge. The solution was filtered, and the nanoparticles were collected on filter paper and washed thoroughly with distilled water to remove any residual impurities. The nanoparticles were then dried in an oven set at 70˚C with temperature control to ensure uniform drying. A small portion of the nanoparticles was reserved for Thermogravimetric Analysis (TGA), while the remaining nanoparticles were calcined in a furnace at 900˚C, with careful temperature to achieve the desired crystallinity.

3. Results and Discussion

The following characterization was carried out to confirm the synthesis of Fe_3O_4 nanoparticles.

3.1. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy is a powerful characterization technique used to study the vibrational motions of atoms or molecules and to analyze the characteristic peaks associated with different functional groups present in a sample. Figure 1 illustrates the FTIR spectra of Fe_3O_4 nanoparticles synthesized using the sol-gel method with water as the solvent. The analysis covers the absorption band range of 4000 - 650 cm^{-1}.

In the higher wavenumber range, from 3700 cm^{-1} to 3000 cm^{-1}, a broad, shallow

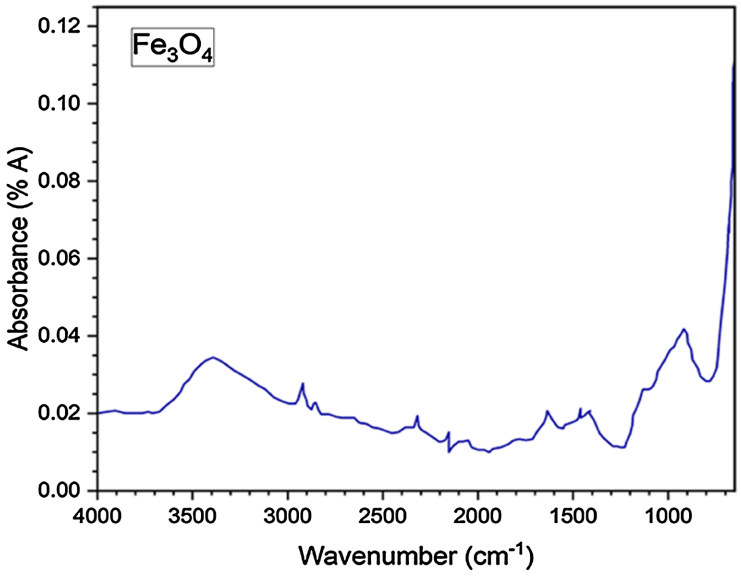

Figure 1. FTIR Spectroscopy of Fe_3O_4 Nanoparticles.

peak indicates the presence of O-H or C-H bonds, likely due to moisture or residual organic compounds. This observation is further supported by distinct peaks at 1630 cm^{-1} (O-H bending) and 3390 cm^{-1} (O-H stretching), which suggest the presence of absorbed water or hydroxyl groups in the sample [17]. Peaks around 2200 cm^{-1} are associated with water de-ionization.

A key feature of the spectrum is the sharp peak at 1100 cm^{-1}, corresponding to Fe-O stretching vibrations, which serve as a clear indicator of iron oxide [18]. This strong peak is characteristic of Fe_3O_4 and points to a well-defined crystalline structure. Additionally, the noticeable increase in absorbance below 1000 cm^{-1}, particularly within the 650 - 900 cm^{-1} range, further confirms the presence of Fe-O vibrations, indicating the presence of iron oxide [19]. While, some minor fluctuations in the spectrum may be attributed to residual agents from the sample preparation process, the overall analysis underscores the dominant presence of Fe_3O_4 with good crystallinity and a well-defined structure.

3.2. XRD Analysis

Use X-ray Diffraction (XRD) is commonly used to identify the crystal phase and determine the crystallite size of Fe_3O_4 nanoparticles. XRD reveals the hexagonal structure of Fe_3O_4 and provides insights into the structural properties of nanoparticles, including crystalline size, lattice strain, chemical composition, and crystalline orientation.

Figure 2 shows the XRD pattern of Fe_3O_4 nanoparticles prepared using water as the solvent exhibit essential peaks corresponding to Fe_3O_4 at $2\theta = 30.54^\circ$, 35.90°, 43.45°, 53.80°, 57.40°, and 62.90°, which indicate the crystal phase of the ferromagnetic nanoparticles [11]. The XRD spectra indicate that the synthesized powders are in the nano-scale range and confirm the specific structure of Fe_3O_4.

The average crystallite size of the ferromagnetic nanoparticles was determined

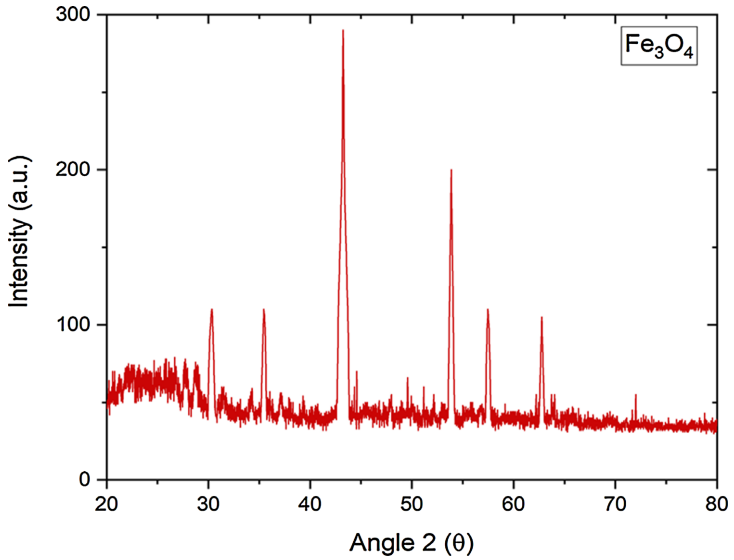

Figure 2. XRD Analysis of Fe_3O_4 nanoparticles.

from the broadening of the XRD peaks using Scherrer's formula:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where D is the crystallite size, λ is the wavelength of the incident X-ray radiation in nm, K is a shape-dependent constant typically taken as 0.94, θ is the diffraction angle, and β is the full width at half maximum (FWHM). The average crystallite size of the Fe_3O_4 nanoparticles prepared in this study was found to be 1.2 nm. The nanoscale crystallite size determined from XRD (1.2 nm) indicates the high degree of control achieved in the synthesis process. The use of water as a solvent also ensured minimal impurities, as indicated by the FTIR spectra, which show characteristic Fe-O vibrations without significant interference from residual organic compounds.

3.3. SEM Analysis

The Scanning Electron Microscopy (SEM) analysis offers comprehensive insights into the microstructure and morphology of the powdered nanoparticles. The SEM images reveal the primary structural characteristics of the nanoparticles synthesized via the sol-gel method, indicating a predominantly spherical morphology with notable self-assembly behavior. The iron oxide (Fe_3O_4) nanoparticles exhibit a distinctive cubic inverse spinel structure [3], which is critical to their magnetic properties. Notably, the SEM image was captured at a magnification of ×10,000, showing the unique honeycomb-like arrangement of the Fe_3O_4 nanoparticles prepared with water as the solvent, as illustrated in **Figure 3**. The use of water as a solvent in the sol-gel synthesis process played a significant role in determining the morphological and structural characteristics of Fe_3O_4 nanoparticles. Water, being an eco-friendly solvent with a high dielectric constant and polarity, facilitates the uniform distribution of precursor ions, promoting controlled nucleation and growth

during the synthesis process. This uniformity is evident in the predominantly spherical morphology observed in SEM images, with a honeycomb-like arrangement that suggests effective self-assembly.

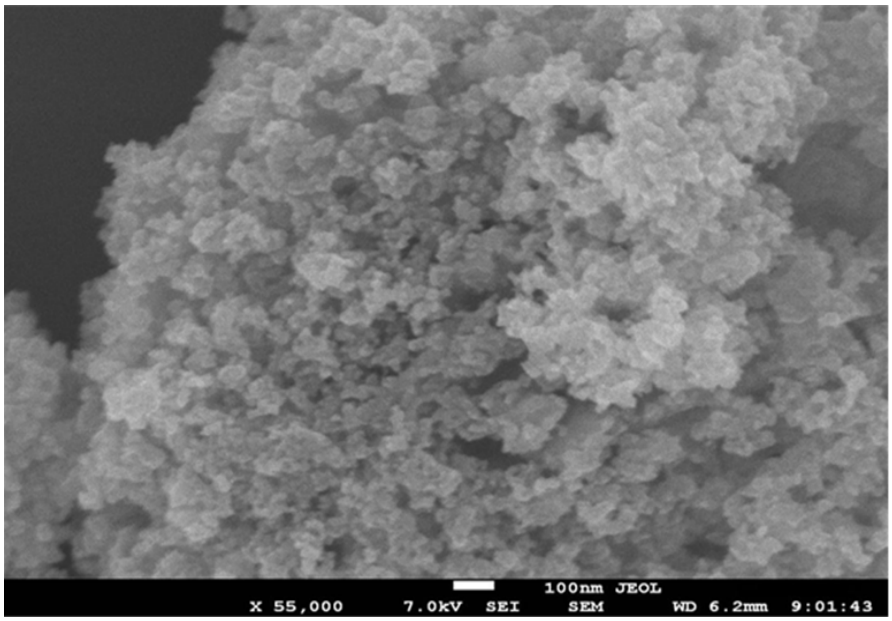

Figure 3. SEM picture of Fe_3O_4 nanoparticles showing its morphology.

3.4. TGA Analysis

Thermogravimetric Analysis (TGA) was conducted on the samples before calcination. TGA provides insights into the thermal decomposition behavior of nanoparticles by monitoring weight changes as the temperature increases. This analysis reveals the thermal stability of the samples by recording weight loss associated with thermal events.

Thermogravimetric analysis measures changes in physical and chemical properties of materials as a function of temperature, with either a constant heating rate or constant temperature, or by monitoring mass loss over time. It can identify various physical phenomena, such as phase transitions, vaporization, sublimation, absorption, and desorption.

Additionally, TGA provides information on chemical phenomena, including chemisorption, desolvation (especially dehydration), decomposition, and solid-gas reactions such as oxidation or reduction. The TGA analysis was performed within the temperature range of 40˚C to 1000˚C. Figure 4 illustrates the thermal decomposition of Fe_3O_4 nanoparticles prepared using water as the solvent. The first weight loss, occurring between 50˚C and 200˚C, is attributed to the removal of moisture from the sample, with a weight loss of approximately 0.35 mg. A second weight loss, around 1.65 mg, was observed between 200˚C and 400˚C, which is associated with the loss of organic content, including solvent residues [20]. Once the compound reaches thermal stability, the weight of the sample remains nearly constant, indicating that the Fe_3O_4 nanoparticles are thermally stable. The

thermal stability observed in TGA analysis further underscores the structural integrity of the nanoparticles, which is attributed to the controlled synthesis environment facilitated by water as the solvent.

3.5. VSM Analysis

The A Vibrating Sample Magnetometer (VSM) was used to evaluate the magnetic behavior of Fe_3O_4 nanoparticles by measuring magnetization (M) in unit of "emu/g" as a function of the applied magnetic field (H) in unit of "Oe". The M-H curve obtained from this analysis shows how the sample's magnetization responds to varying magnetic field strengths, providing insight into its magnetic properties as shown in Figure 5. The saturation magnetization (M) was determined to be

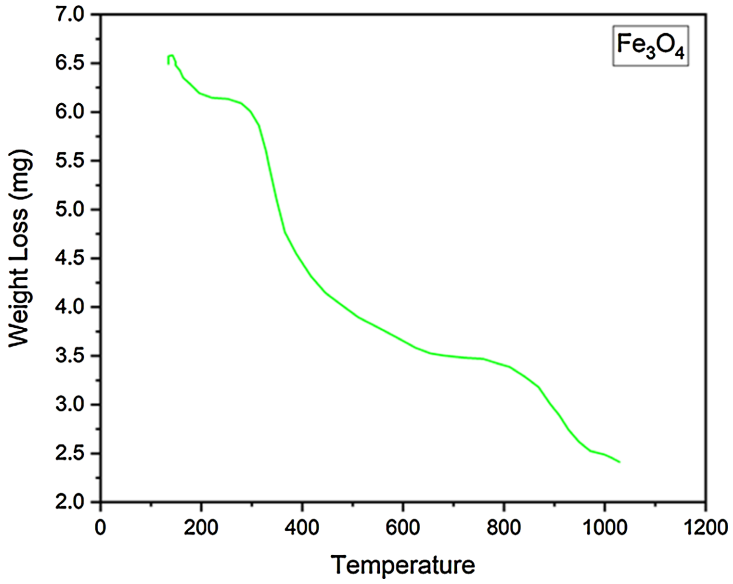

Figure 4. TGA Analysis of Fe_3O_4 nanoparticles.

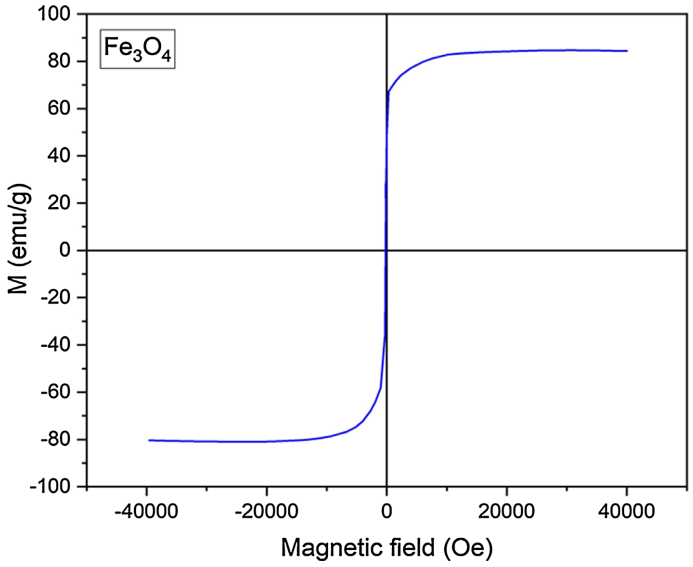

Figure 5. VSM graph of Fe_3O_4 nanoparticles.

approximately 80 emu/g, slightly lower than the bulk value of 92 emu/g, likely due to surface spin canting and finite size effects.

The coercivity (Hc) was measured as 50 Oe, indicating low resistance to magnetization reversal, consistent with superparamagnetic behavior. The remanence (Mr) was approximately 5 emu/g, further supporting the superparamagnetic nature of the nanoparticles, where thermal energy at room temperature overcomes magnetic anisotropy barriers. The observed magnetic behavior strongly correlates with the nanoparticle size and morphology. Smaller particles (<20 nm), as suggested by SEM/XRD results, are expected to exhibit single-domain structures and superparamagnetic properties, which is consistent with the low Hc and Mr values. These properties make Fe_3O_4 nanoparticles suitable for applications such as magnetic hyperthermia, drug delivery, and magnetic separation.

4. Conclusion

Ferromagnetic nanoparticles (Fe_3O_4) have been successfully synthesized using water as a solvent via the sol-gel method. The resulting nanoparticles were thoroughly characterized using various techniques, including FTIR, SEM, XRD, and TGA. The FTIR spectra displayed characteristic peaks in the 400 - 900 cm^{-1} regions, corresponding to Fe-O bonding vibrations. XRD results identified the characteristic planes of the nanoparticles, with the average crystallite size determined using Scherer's equation being 1.2 nm. SEM analysis confirmed that the Fe_3O_4 nanoparticles exhibit a self-assembled, spherical morphology. TGA analysis indicated that the Fe_3O_4 nanoparticles are thermally stable to a certain extent. The VSM analysis determined the magnetic behavior of these nanoparticles. This suggests that the Fe_3O_4 nanoparticles prepared using water as the solvent have a consistent average size of 1.2 nm and show good magnetic behavior.

Acknowledgements

We would like to thank Chairman Department of Physics, UET Lahore, Pakistan, for their support and assistance during this study. Special thanks to Dr. Inam ul Haq for their valuable contributions.

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