Preparing Magnetite Nanoparticles Ferro Fluid

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Abstract: *In this project, we synthesize magnetic Ferro fluid based on magnetite nanoparticles. Our goal was to develop cost-effective and affordable methods to synthesize stable form of Ferro fluid under aerobic conditions. Mixed of two bivalent and trivalent iron salts were mixed to synthesize the magnetite composite. The oleic acid based coating in an alkaline condition was employed as protective cover for the synthesized nanoparticles in order to prevent the undesired aggregation. The size of the particles was measured using a Scanning Tunneling Microscope (STM). The optimum conditions were studied by testing different mixing times and Fe(III)/Fe(II) stoichiometric ratios. The mixing ratio of 1.3:1 was found to be the optimum stoichiometric ratio for synthesizing the nano-magnetite in this study.*

Introduction

Magnetic nanospheres made of magnetite $(Fe(II)Fe(III)_2O_4)$ have many desirable properties for cleaning up water, such as being safe, compatible with living organisms, chemically stable, magnetic, and water-attracting. Scientists have used a solvothermal method to make hollow magnetic nanospheres, researchers have developed a hydrothermal method for making magnetite nanoparticles that dissolve well in water. These nanoparticles are highly soluble in water at room temperature, and they remain stable for at least a month [1,2]. Magnetite is a useful material in the coal processing industry due to its various benefits such as being easily available, having a high specific gravity, low viscosity, and being stable in suspension. In nanomagnetism research, there are several objectives, including developing strong magnets that are energy-efficient, spin-transistors with gain, spin-based qubits for quantum computing, bio-magnetic sensors, on-chip microwave oscillators, magnetic logic devices, and room temperature magnetic semiconductors that can be integrated with existing semiconductor technolog [3,4].

Ferrofluids are used in many important applications, such as bio sensing, medical imaging, medical therapy, magnetic impedance, water treatment, energy harvesting and transfer, and vibration control [5,6].

Ferro fluids are used in various practical applications, such as in vacuum chambers and computer disk drives to prevent dust particles from contaminating the hard disk [7,8].

Magnetic nanoparticles (MNPs) are attracting significant interest in the field of biomedicine due to their biocompatibility and their ability to interact with externally applied magnetic fields.. In recent years, there has been a surge in research focused on the synthesis, characterization, and application-specific modification of iron oxide and substitute ferrite nanoparticles, leading to emerging applications in various fields [9,10].

Different materials can be classified into five major groups, including diamagnetic, paramagnetic, ferromagnetic, ferrimagnetic, and antiferromagnetic, based on their magnetic behavior [11,12].

Diamagnetism is a type of magnetism that is present in all materials. In diamagnetic materials, all atoms have paired electrons and no unpaired electrons in their shells, which results in a net magnetic moment of zero, When exposed to an external magnetic field, diamagnetic materials become magnetized in the opposite direction of the field[13,14].

Paramagnetic materials are those that have partially filled orbitals containing unpaired electrons in their atoms or ions. This causes each atom to have a small net magnetic moment, When an external magnetic field is applied, the atomic magnetic moments partially align in the direction of the field.[15]

Superparamagnetism is an intriguing phenomenon that occurs in small ferromagnetic or ferrimagnetic particles. When these particles reach sizes of approximately 10 nanometers, they start exhibiting paramagnetic properties [16,17,18,19,20]

The amount of magnetism that remains in a ferromagnetic sample when the applied field is zero is referred to as retentivity, while the reverse magnetic field that must be applied to reduce the saturation magnetization to zero is known as coercivity. However, hysteresis parameters such as retentivity and coercivity are not purely intrinsic properties and depend on factors such as grain size, domain state, stress, and temperature. Therefore, these hysteresis parameters can be useful in magnetic grain sizing of natural samples.

Ferrimagnetism is a complex form of magnetic ordering observed in certain ionic compounds, such as oxides of iron. [21]

Antiferromagnetism is a type of magnetic ordering where the magnetic moments of atoms or ions in a crystal lattice are arranged in a way that their net magnetic moment is zero. [22]

Chemicals

1. Ferric Chloride Hydrate FeCl3

2. Ferrous sulphate heptahydrate FeSO4.7H2O

3. Oleic Acid

4. Concentrated Ammonia Solution

5. Kerosene

Procedures

Procedure 1 (1:1.3 ratio)

1. Dissolve 1 g of $FeCl_3$ in 150 ml of H_2O (solution A).

2. Dissolve 1.3 g of $FeSO_4.7H_2O$ in 150 ml of H_2O (solution B).
3. Mix solution A and solution B in a 1000 ml beaker and add 300 ml of H_2O.
4. Using a hand mixer, mix the mixture at the highest speed for 15 minutes while slowly adding concentrated ammonia drop by drop. Choosing the highest mixing speed and adding conc. ammonia slowly helps the particles form smaller.
5. During this time, the pH of the solution reaches 10, and at this pH, stop adding concentrated ammonia.
6. Prepare the soap (10 ml NH_3 + 15 ml oleic acid + 20 ml H_2O).
7. Prepare dilute hydrochloric acid (1 part HCl to 2 parts H_2O).
8. Put the solution on a hot plate (at 50°C) and add the soap, then add dilute hydrochloric acid drop by drop while continuously mixing. Stop the process when the pH becomes 7.
9. Put the solution on a magnetic ring to obtain a precipitate.
10. After a short time, two layers will appear, the top transparent layer and the bottom layer (black precipitate). decant the top layer and wash the precipitate with distilled water.
11. Dry the precipitate in an oven.
12. Dissolve the precipitate in kerosene.
    We have repeated the same procedure above to set the optimum conditions.

1. Different Fe(III):Fe(II) ratios
    a. 1.3:1
    b. 1.6:1
    c. 1.9:1
2. We set optimum mixing time:
    a. 15 min
    b. 30 min
    c. 40 min

Procedure 2 (ultrasonic method)

1. Dissolve 1 g of $FeCl_3$ in 150 mL of H_2O (Solution A).

2. Dissolve 1.3 g of FeSO$_4$.7H$_2$O in 150 mL of H$_2$O (Solution B).
3. Mix Solution A and Solution B in a 1000 mL beaker and add 300 mL of H$_2$O.
4. Use an ultrasonic device to mix the mixture at speed 7 for 15 minutes while adding conc. ammonia drop by drop slowly. (Choosing a high mixing speed and adding ammonia slowly helps the particles to form smaller.)
5. Stop adding ammonia when the pH becomes 10.
6. Prepare the soap solution by mixing 10 mL NH$_3$, 15 mL oleic acid, and 20 mL H$_2$O.
7. Prepare dilute hydrochloric acid (1 part HCl to 2 parts H$_2$O).
8. Add the soap solution to the beaker, then add dilute hydrochloric acid drop by drop while stirring continuously. Stop the process when the pH becomes
9. Place the solution on a magnetic ring to obtain a precipitate.
10. After a short time, two layers will appear: a top transparent layer and a bottom black precipitate layer. Remove the top layer and wash the precipitate with distilled water.
11. Dry the precipitate in an oven.

Results and discussion

There are many factors that could be determining the success of the magnetite preparation, but the main indicator to successful preparation is the magnetite behavior of the produce toward the external magnetite field. In the first step, we have tested our procedure by preparing the magnetite by mixing 2 equivalents of Fe(III) salt with 1 equivalent of Fe(II) salt. In the atmosphere of concentrated ammonia added drop-by-drop until the pH of the solution reached 10. A black precipitate start forming as the acidity exceeded 7 on the pH scale. The final product is black precipitate of the iron oxide could easily be detected as magnetite by waving piece of magnet close by the solution. However, since the Fe(II) could easily oxidize to Fe(III) a brown solution may appear to indicate the forming of Fe(III) oxides, maghemite (Fe2O3, γ-Fe2O3) as shown in Figure 1.
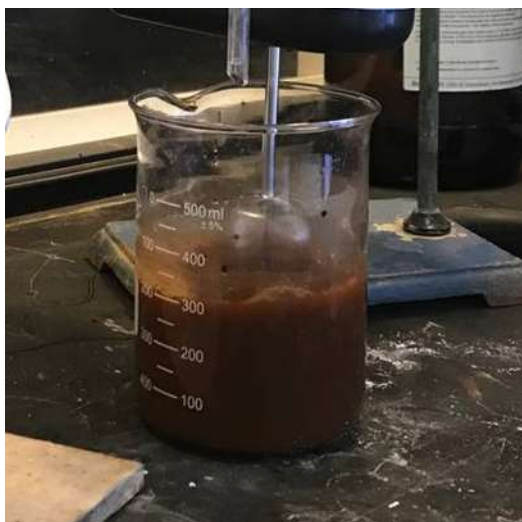

Figure 1 : oxidation of magnetite to maghemite

To overcome the undesirable oxidation, the ratio Fe(III)/Fe(II) were adjusted to be 1.3:1 instead of 2:1. Such modification in the mole ratio ensure to maintain the ratio between two oxidation states even after the aerobic oxidation of Fe(II). Especially when preparation procedure requires a vigorous mixing. The magnetite solution we have obtained was black as it shown in Figure 2
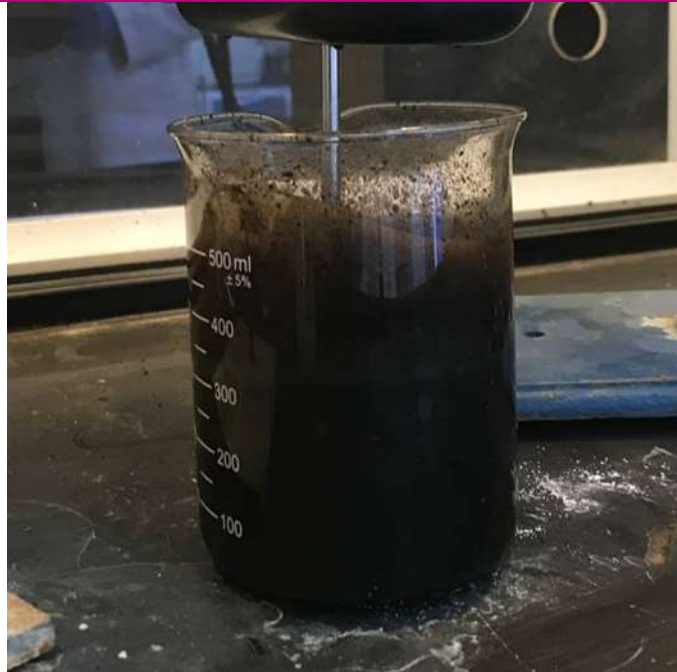
Figure 2: formation of magnetite

the confirmation of the magnetite formation is easily detected directly after monitor the attraction of the precipitate toward the approaching piece of magnet. To ensure that we only filter magnetite. We have washed and decant the solution while a strong piece of magnet was hold against the bottom of the beaker. After several washing steps, the black precipitate was dried in 70 ^{o}C oven. The forming crystal showed a clear attraction toward magnets even after months in the sealed containers, indicating of the stability of the forming magnetite over time.

In this study, we aimed to prepare the magnetite ferrofluid. Therefore, the procedure shifted toward preparing an isolated particles that could behave independently as a magnet. Isolation of the particle is the most sensitive task in preparing the magnetite nanoparticles. Not only one need to ensure forming nanoscale particle but formally distributed sizes of the particle are crucial. In our first attempt, we have mixed the solution to ensure that all the forming particles are scattered in the solution by vigorous continuous mixing following consecutive addition of the coating soap (oleic acid surfactant). The coating will ensure that the forming hydrophobic surfactant will prevent undesired aggregation of the magnetite particle. After 30 min mixing, the sample were left to dry in the room temperature overnight. The final product was measured using scanning tunneling microscope (STM) as shown in the Figure 3
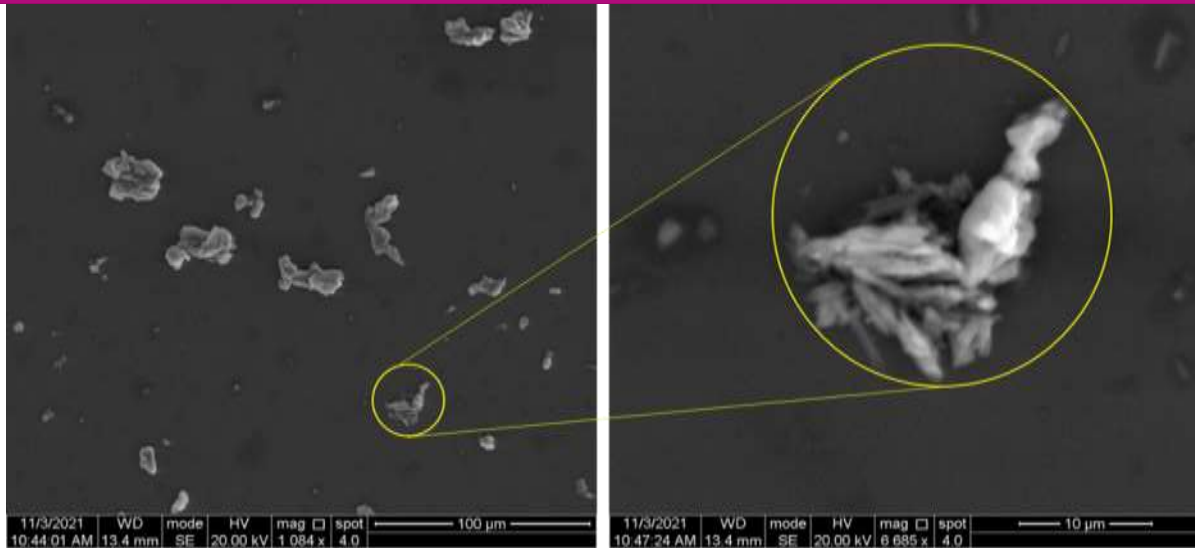
Figure 3: image of the prepared magnetite ferrofluid particles

Achieving uniformity in the size and shape of nanoparticles is crucial in obtaining the best possible ferrofluid with unique magnetic properties [23] In bulk magnetism, each nanoparticle behaves as an individual domain, resulting in a lack of uniformity and unpredictability in magnetic behavior[24]. By synthesizing nanoparticles with consistent size and shape, we can create a ferrofluid with predictable and controllable magnetic properties[25]. This is particularly important in various applications, such as targeted drug delivery and magnetic hyperthermia, where precise magnetic properties are required [26]
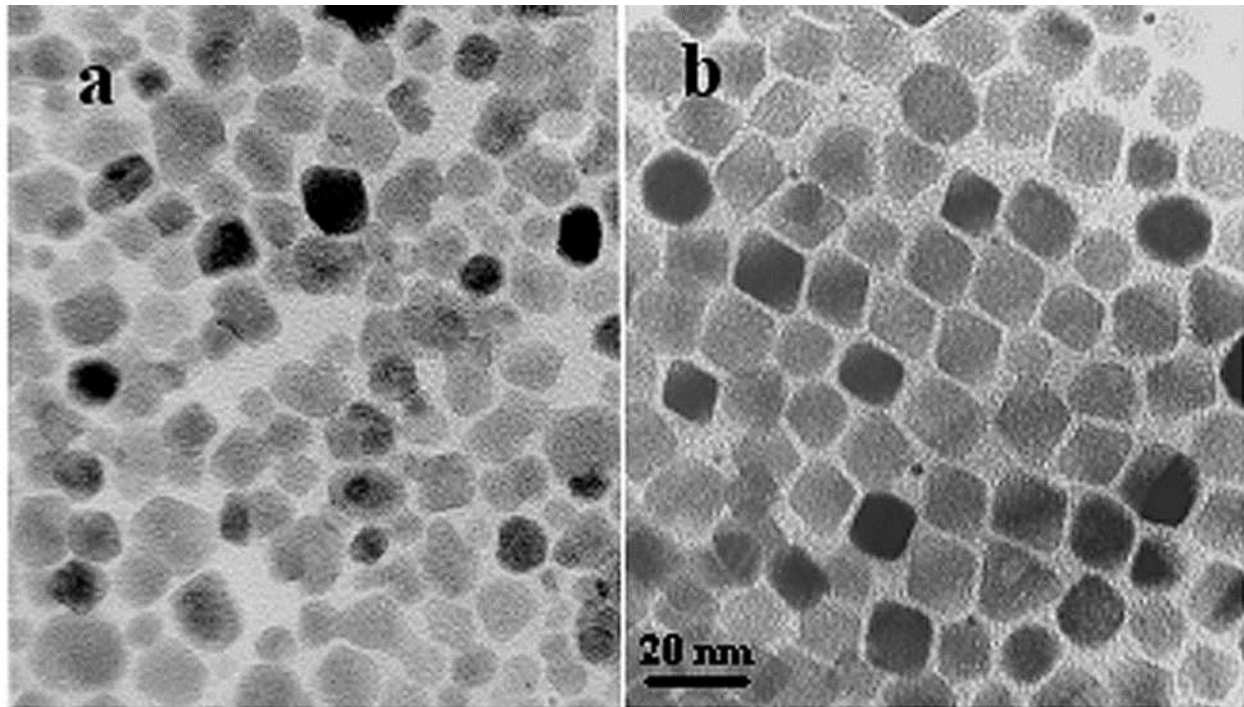

Figure 4: TEM images of magnetite nanoparticles[27]

Forming the spikes in magnetite ferrofluids in the basic test to confirm the formation of coated nanoparticles. We have performed many attempt in orders to achieve the desirable spike formation. The coated dried particles were mixed with kerosine as non-polar solvent to ensure full mixing of that the hydrophobic

particles. Then a strong magnetic were put underneath a watchglass to monitor the formation of the obvious spikes as shown in Figure 5

Figure 5: Spikes formation of the ferrofluid

Conclusion

In conclusion, we have successfully achieved our objective of synthesizing a stable form of magnetic ferrofluid under aerobic conditions using magnetite nanoparticles and a combination of bivalent and trivalent iron salts. The protective oleic acid-based coating in an alkaline environment has proven to be an effective solution to prevent undesired aggregation of the synthesized nanoparticles. By studying the optimal conditions through various tests of mixing times and Fe(III)/Fe(II) stoichiometric ratios, we have identified the 1.3:1 mixing ratio as the optimum stoichiometric ratio for synthesizing the nano-magnetite. Our results provide simple and cost-effective methods for synthesizing stable ferrofluids, which could have potential applications in various fields, such as biomedicine and environmental engineering .

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