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Author(s)	Ying Wang, Parvin Kaur, Augustine Tuck Lee Tan, Rajveer Singh, Lee Choon Keat Paul, Stuart Victor Springham, Raju V Ramanujan and R. S. Rawat
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Iron oxide magnetic nanoparticles synthesized by atmospheric microplasmas

Ying Wang[†], Parvin Kaur, and Augustine Tuck Lee Tan

National Institute of Education, Nanyang Technological University, 1 Nanyang Walk, Singapore 637616

[†]ying813@gmail.com

Rajveer Singh

Atmaram Sanatan Dharma College (University of Delhi) Dhaukuan New Delhi, India 110021

Lee Choon Keat, Paul and Springham, Stuart Victor

National Institute of Education, Nanyang Technological University, 1 Nanyang Walk, Singapore 637616

Raju V Ramanujan

School of Material Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

R. S. Rawat

National Institute of Education, Nanyang Technological University, 1 Nanyang Walk, Singapore 637616
rajdeep.rawat@nie.edu.sg

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This paper presents the synthesis of iron oxide nanoparticles using the atmospheric microplasma (AMP). The properties of iron oxide nanoparticles synthesized using AMP are compared with particles (i) formed in as-prepared solution and (ii) prepared using thermal decomposition method. Iron oxide nanoparticles prepared by all the 3 treatment methods exhibit quite soft ferromagnetic properties with coercivities less than 10 G. The AMP synthesis technique was found to be more efficient and better than thermal decomposition method due to ultra-shorter experiment time (around 2.5 min) as compared to 90 min required for thermal decomposition method. Moreover, AMP synthesized nanoparticles are better isolated and of smaller size than thermal decomposition ones.

The effect of plasma discharge timings on synthesized nanoparticles has also been studied in this work. Coercivity of synthesized nanoparticles decreases with the increasing plasma discharge timings from 3 to 10 min. The nanoparticles synthesized using plasma discharge timing of 10 min exhibit the smallest coercivity of around 3 G. This suggests a high possibility of achieving super-paramagnetic nanoparticles by optimizing the plasma discharge timings of AMP.

Keywords: Iron oxide nanoparticles; super-paramagnetic; nanoparticle synthesis; atmospheric micro-plasma.

1. Introduction

Super-paramagnetic iron oxide nanoparticles are regarded as a useful tool in numerous medical applications in the biomedical sector. The nature of their high magnetism is an

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asset for specifically in-vivo biomedical applications as it allows the movement through the blood to be controlled by using a magnetic field.¹ The other applications are found in the area of magnetic resonance imaging, enzyme immobilization, drug and gene targeting, cell separation, drug delivery and magnetic hyperthermia.¹ Super-paramagnetic iron oxide nanoparticles have good biocompatibility characteristics² which will be useful for the encapsulation of the particles with a suitable coating substance for controlled drug delivery.

Atmospheric micro-plasmas (AMPs) are characterized by their very high energy densities and their small discharge sizes that have unique applications for plasma processing technologies.³ AMPs produce nanostructured films which have resulted in high reproducibility where the experimental setup had shown that there were no temperature control for gas feed lines.⁴ Moreover, researches have shown that AMPs have high energy density that promotes fast reaction rates and increased throughput.⁴ The type of gas for example helium which is used in this experiment is chosen over the others because its high energy metastable state and an excellent heat conductivity.^{5,6} The AMPs are preferred to be used for iron oxide synthesis in this research due to their simple setup requirement and ease of operation. Moreover, the various techniques like hydrothermal and chemical methods, reported in other journal articles, take longer time and higher temperature for the synthesis of iron oxide nanoparticles. In addition, Liu et al.⁷ reported that specifically Fe_3O_4 particles (synthesized by thermal decomposition methods) tend to agglomerate together because of anisotropic dipolar attraction, which affects their dispersion and magnetic properties.

Thus, the properties of iron oxide nanoparticles synthesized by thermal decomposition and AMPs are compared in this paper. The focus of atmospheric micro-plasma treatment consists of the solution that undergoes plasma-liquid interactions⁶. This is where a direct current plasma jet formed with helium gas at the surface of the dilute aqueous solution of iron(ii) chloride and iron(iii) chloride. Moreover, the effect of plasma discharge time (3, 5 and 10 min) on the properties of synthesized iron oxide nanoparticles using AMPs is studied by using different characterization techniques.

2. Materials and Methods

2.1. Synthesis of Fe_3O_4 (iron oxide) nanoparticles:

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and ammonium hydroxide (25% NH_4OH) were purchased from Sigma-Aldrich Company, Singapore. The ammonium hydroxide (25% NH_4OH) is used to co-precipitate Fe^{2+} and Fe^{3+} ions together.⁸ 12.0g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was mixed with 4.9g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. This mixture was then dissolved in 100ml of deionized water for 30 minutes on a stirrer at a temperature of 40°C. A thermocouple was used to ensure that the temperature of the solution was at 40°C. After 30 minutes, 25ml of ammonium hydroxide (NH_4OH) was rapidly added into the solution. At that instant upon adding ammonium hydroxide, a black suspension was formed. The mixture now was stirred for 10 minutes at a temperature of 40°C. After 10

minutes, the solution was then separated and poured into 3 different beakers 20ml, 40ml and 40ml of the solution respectively. The first beaker was labelled as "as-prepared solution". The related prepared sample was mentioned as "AS" in this paper. The 40ml mixture in the second beaker was stirred at a temperature of 90°C for 90 minutes. This beaker was then labelled as "thermally decomposed solution". The related prepared sample was mentioned as "TD" in this paper. The last beaker underwent atmospheric plasma treatment with the use of direct current at 5mA and the duration of treatment was approximately 3 min. This beaker was labelled as "AMP treated solution". The related prepared sample was mentioned as "AMP1" in this paper. Two more treatments with plasma discharge timings of 5 and 10 min were performed to study the effect of plasma discharge timing on the properties of nanoparticles. The related prepared samples were mentioned as "AMP2" and "AMP3", respectively.

The setup of AMP treated method is shown in Fig. 1. The entire experiment was conducted at atmospheric conditions and room temperature. A DC discharge with constant current (5 mA) was sustained through flowing helium gas between the hollow stainless steel upper anode of Ø 300 µm bore diameter (which is essentially a commercial syringe needle) and the surface of the solution contained in a glass vessel. The tip of the upper anode was placed above the surface of the solution at a separation of 2 mm in open air. The surface of the electrolyte solution acted as the cathode. Its electrical connection is completed with a silicon substrate, which is placed half in the solution and connected to the cathode of power source (TREK 615-10, ±10kV AC/DC generator). The helium gas, at flow rate of 50 cubic centimeters per minute at STP (SCCM) with the use of a mass flow controller, was used as the discharge medium.

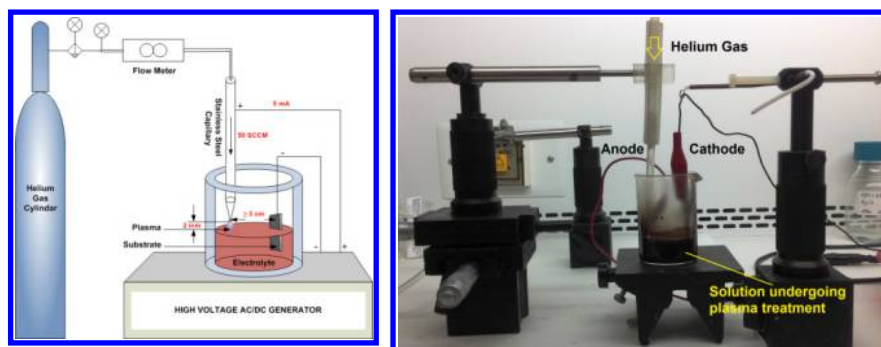


Fig. 1. Setup of AMP treated method for iron oxide nanoparticle synthesis.

2.2. Preparation of iron oxide solution on silicon substrate:

3 ml of the 3 different solutions were taken and poured into 3 different test-tubes where it was washed with deionized water for 4 times respectively to purify synthesized nanoparticles. After each round of washing, the mixture was poured into a funnel which is covered with filter paper and surrounded with a magnet. The particles collected on the filter paper for each of 3 different solutions were then removed from the filter paper into

ethanol by ultrasounding for 20 minutes at a temperature of 40°C. The resulting solution on the petri dish was collected and 13 drops of each type of solution (20- μ l/drop) were dropped onto 3 different silicon substrates. After every drop, the solution on the substrate was placed in a spin coater (Model P6700) to ensure the uniform distribution of the solution on the substrate. After that all the samples were dried in an oven at a temperature of 50°C for 24 hours. The similar steps were performed for the plasma treated samples with varied plasma discharged timings (3, 5 and 10 min). Subsequently, 5 drops of the different plasma discharge timing solutions were placed on the silicon substrate and dried in the oven at a temperature of 50°C for 24 hours.

2.3. Characterization methods

The morphology, particle size and shape of iron oxide nanoparticles were evaluated using scanning electron microscopy (SEM; JSM6700F, JEOL 510200000437). The elemental composition of the iron oxide nanoparticles was determined using energy dispersive X-ray (EDX; JEOL510200000497). The X-ray diffraction patterns of the iron oxide nanoparticles, conducted on an X-Ray diffractometer (XRD; D5005) with Cu-K α radiation over the 2 θ range of 15-65°, aided in the estimation of the crystalline structure of the iron oxide nanoparticles. The UV-visible spectrometer was used to finalize the composition of the sample. This helps to further confirm the composition of nanoparticles formed in the solution. Magnetic properties of the iron oxide sample were measured on a vibrating sample magnetometer (VSM, Lake Shore 7400c) at room temperature.

3. Results and Discussion

3.1. Comparison of as prepared, thermally decomposed and AMP treated samples

3.1.1. Scanning electron microscope (SEM) studies

The morphologies, particle sizes and shapes of iron oxide nanoparticles obtained in 3 different treatment methods are shown in Fig. 2. Comparing the SEM images AS1, TD1 and AMP1-1 at the low magnification (~4,000), it can be seen that the particles extracted from the AMP treated solution (shown in image AMP1-1) are well separated and less agglomerated; while combined and invisible iron oxide particles are observed for as-prepared and thermally decomposed samples (shown in images AS1 and TD1, respectively). Comparison of the images for (AS2) as-prepared, (TD2) thermally decomposed and (AMP1-2) AMP treated samples at high magnification (~100,000) further proves the less agglomeration, well isolated and smaller particle size of nanoparticles synthesized using AMPs. It is also found that the shapes of prepared nanoparticles (shown in images AS2, TD2 and AMP1-2) are dominantly spherical for all the three treatment samples, while a small amount of nanotubes are observed for as-prepared and AMP treated samples. The average particle sizes for both the spherical nanoparticles and nanotubes are calculated using ImageJ (Wayne Rasband, 1.46r) software. It is noticed that the AMP treated sample shows the smaller particle size of 11.7

± 0.7 nm than the thermally decomposed one of 30.7 ± 3.0 nm. However, the as-prepared sample shows the smallest particle size of 6.4 ± 0.5 nm and the largest amount among the three samples. This might because that no further treatment was performed to the as-prepared solution resulting in less energy and mobility for the formed particles to agglomerate as compared to thermal decomposed and plasma treated samples where additional energy was available.

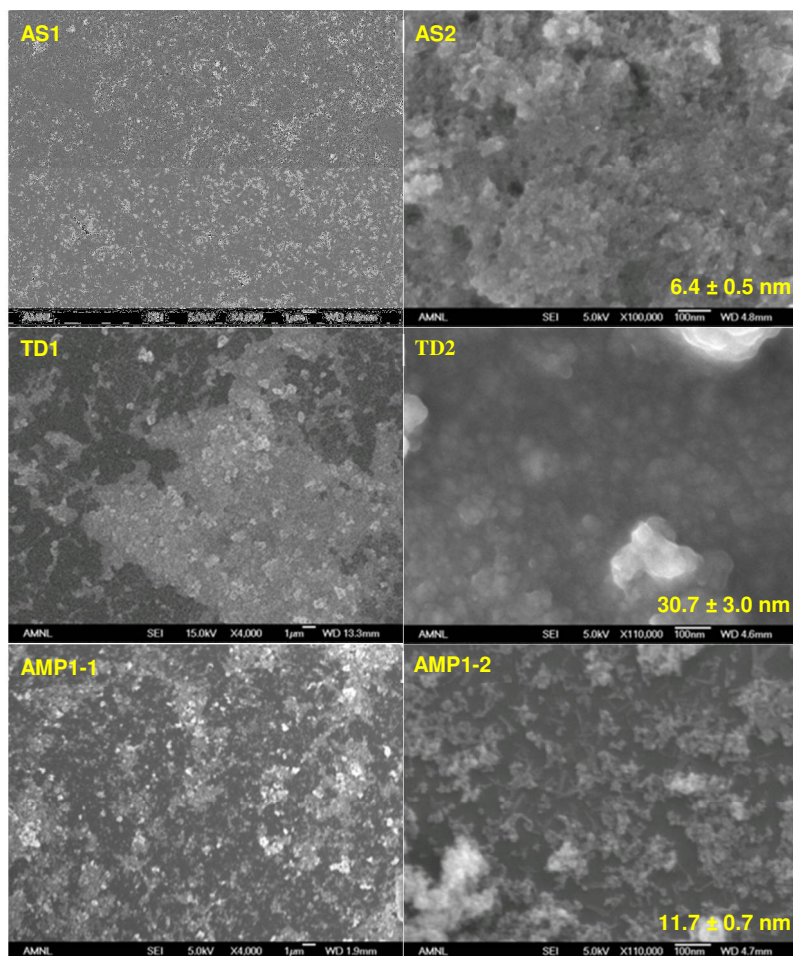


Fig. 2. SEM images of as-prepared, thermally decomposed and AMP treated samples at magnification of X4000 (AS1, TD1 & AMP1-1) and X100,000 (AS2, TD2 & AMP1-2).

3.1.2. Energy dispersive x-ray (EDX) studies

The EDX was performed to analyze the elemental composition of nanoparticle samples like iron (Fe) and oxygen (O). Elements of Fe and O are found in all 3 different treatment samples; the as-prepared, thermally decomposed and AMP treated samples as shown in

Fig. 3. This proves that pure iron oxide nanoparticles are definitely formed in all the three treatment samples. This explains the formation of black suspension, which might be iron oxide nanoparticles, observed after adding ammonium hydroxide. The values of average ratio Fe:O, Fe at.% to O at.% ratio, shown in Table 1 are the average of 12 EDX spectra collected from different part of the same sample. However, the atomic percentage of O element is higher than the standard data of 57.1–58.02 at. % for Fe_3O_4 stated by Wriedt⁹ (1991). This is normally because of the fact that the quantitative estimation for oxygen in oxides cannot be reliably arrived by direct measurement of the oxygen peak in the EDX results. From EDX results, it can be confirmed that iron oxides are formed in all the 3 different treatment samples, but the accurate type of iron oxides cannot be directly estimated.

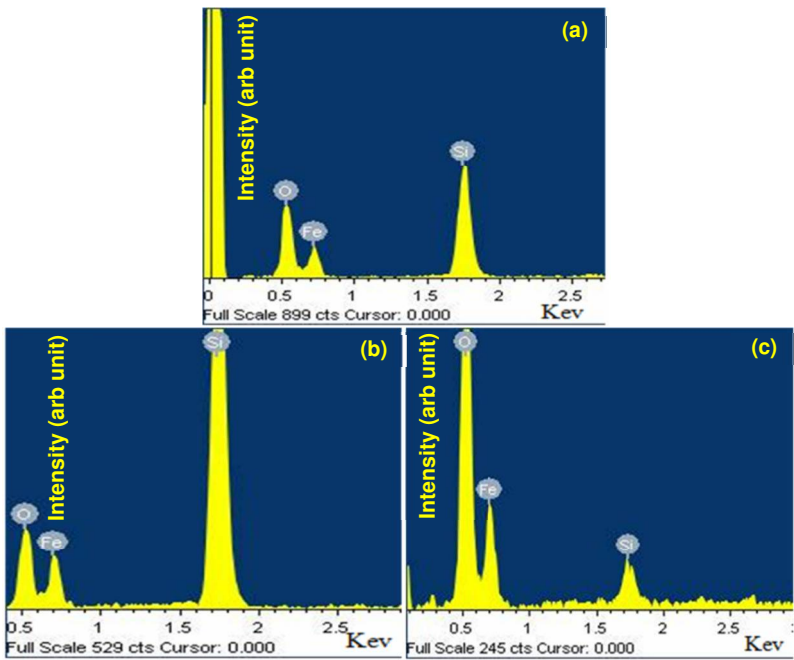


Fig. 3. EDX results of (a) as-prepared (b) thermally decomposed and (c) AMP treated samples.

Table 1. Average Values of Fe:O ratio and individual percentages from the 12 trials of the EDX samples.

	As-prepared	Thermally Decomposed	AMP Treated
Average Fe:O ratio	0.33	0.18	0.27
Fe at.%	25	16	22
O at.%	75	84	78

3.1.3. X-ray diffraction studies (XRD)

The XRD patterns of the prepared samples from 3 different treatment solutions are shown Fig. 4 at angles range of $2\theta = 15^\circ - 65^\circ$. All the diffraction peaks can be indexed to an inverse spinel structure of Fe_3O_4 nanoparticles which is in good agreement with the JCPDS Pattern No. 01-082-1533 for Fe_3O_4 . For the as-prepared diffraction peaks, 5 characteristic peaks are detected to be matched with the standard data of Fe_3O_4 , which confirms the type of formed iron oxide to be Fe_3O_4 . However, less and weaker Fe_3O_4 peaks and stronger Si peak are shown for thermally decomposed and AMP treated samples. This might be due to the exposure of surface of Si substrate resulted from the better isolated nanoparticles shown in the SEM images. Thicker thin film samples should be made by spin-coating more drops of related solutions to better characterize the crystalline structures for thermally decomposed and AMP treated samples.

3.1.4. UV-visible spectroscopic (UV-Visible) studies

UV visible spectra were recorded in aqueous solution medium on Perkin Elmer Lambda (Model EZ-221). The UV experiment was performed to further prove if nanoparticles compositions in the solution are that of iron-oxide nanoparticles. From the Fig. 5 of the AMP treated solution, it depicts an absorption band in the region 300 – 400 nm. This is due to the absorption and the scattering of UV radiation by the iron oxide nanoparticles specifically Fe_3O_4 which is in agreement with the previously reported literature review¹⁰. The broad absorption band at 326 nm indicates the formation of nanosized particles. One strange finding in Fig. 5 is that there is a sharp dip around 420 nm which is not in agreement with most literature reviews^{10, 11} for the UV-radiation graph for magnetite, Fe_3O_4 and is unable to be comment on its observation in this paper. The reason for absorbance peak at 580 nm could be due to the co-precipitation process in the initial stages of the Fe^{2+} and Fe^{3+} ions to form iron oxide nanoparticles as validated by a literature reported by Islam et al.¹².

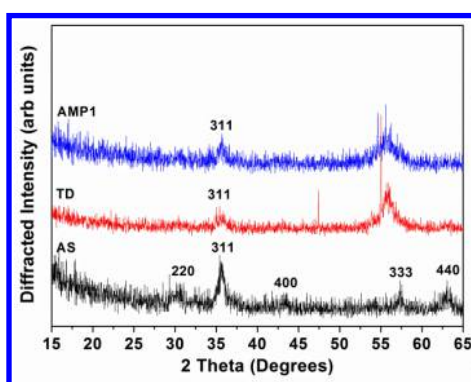


Fig. 4. XRD patterns for as-prepared, thermally decomposed and AMP treated solutions.

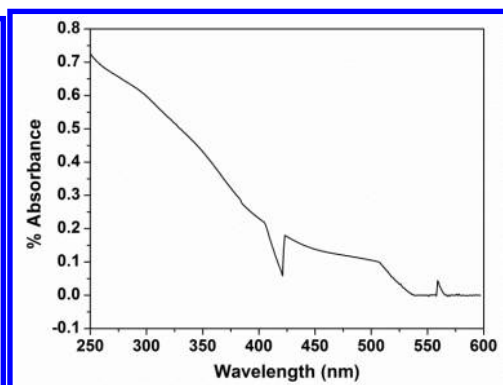


Fig. 5. UV-Visible spectrum of plasma-treated solution.

3.1.5. Vibrating sample magnetometer (VSM) studies

The magnetic properties of the 3 different treatment samples were characterized by vibrating sample magnetometer (VSM, Lakeshore's 7400c) at room temperature. Fig. 6 shows the graph of the combinations of the magnetic properties of the samples using the plots of magnetic moment 'M' versus the applied magnetic field 'H' (between -12 000 and 12000 G). The VSM shows the formation of a hysteresis loop for the samples of Fe_3O_4 nanoparticles with coercivities less than 10 G, exhibiting a quite soft magnetic behavior. When the applied field (H) is increased from 0 to 2500 G, the magnetization (M) increases sharply and nearly becomes saturated at approximately 2500 G. It can be seen that all the 3 samples have strong magnetic responses to a varying magnetic field. The hysteresis curves for the thermally decomposed and AMP treated samples show smooth changes in magnetization (M) with the applied field (H). The similar magnetic behavior of thermally decomposed and AMP treated samples suggests the potential big interest of AMP technique in the synthesis of iron oxide nanoparticles because of the ultra-shorter synthesis time (~ 3 min) used. However, the as-prepared nanoparticles show the smallest coercivity of about 3 G among the three samples, the reasons of which should be further studied.

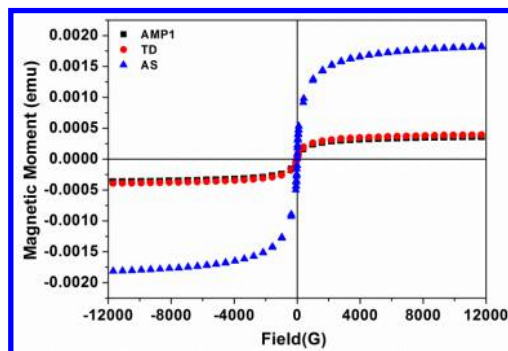


Fig. 6. Vibrating sample magnetometer curve of Fe_3O_4 nanoparticles from 3 different treatment solutions at room temperature.

3.2. Effect of different discharge timings (3, 5 & 10 min) for AMP treatment

3.2.1. Scanning electron microscope (SEM) and (EDX) studies

The morphologies, particle sizes and shapes of iron oxide nanoparticles from the plasma treatment of different discharge timings (3, 5 and 10 min) are shown respectively in Fig. 7 using SEM. Comparing the SEM images (AMP1-1), (AMP2-1) and (AMP3-1) at low magnification, it can be seen that as the plasma discharge timing increases, the amount of particles increase and the particles start to agglomerate as clearly show in (AMP3-1) where the particles are mostly formed in small blocks as compared to more scattered distribution in (AMP1-1). Comparison of the images for (AMP1-2), (AMP2-2) and (AMP3-2) further shows the high agglomeration of particles at longer plasma discharge timing (AMP3-2) as compared to (AMP1-2). Also, from this magnification, it is also observed that the particles in (AMP1-2) are made of different shapes like spherical and

nanotubes whereas for (AMP2-2) and (AMP3-2), the particles are mostly of the same spherical shape and more evenly distributed as compared to (AMP1-2). In (AMP3-2), although nanoparticles agglomerate more the particle size still is district. The calculated average particle size for the three samples with plasma discharge timings of 3, 5 and 10 min are 11.7 ± 0.7 , 5.2 ± 0.2 and 6.3 ± 0.3 nm respectively. The smallest particle size is shown for the sample with plasma discharge timings of 5 min.

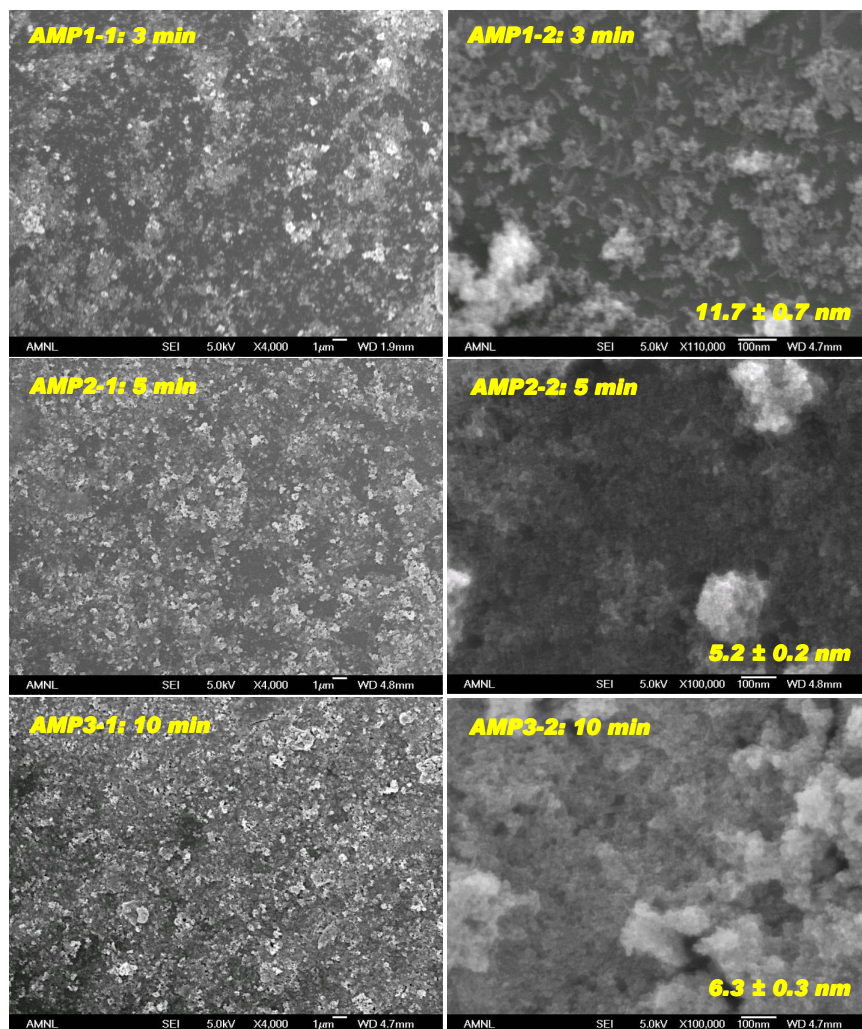


Fig. 7. SEM images of AMP treated samples for different plasma discharge timings at magnification of X4000 (AMP1-1, AMP2-1 & AMP3-1) and X100,000 (AMP1-2, AMP2-2 & AMP3-2).

From the EDX results in Fig. 8, it clearly portrays that there is formation of iron oxide nanoparticles in plasma discharge timing of 10 min. The atomic percentages of Fe and O are listed in Table 2. As compared to the EDX results in Table 1 for specifically the AMP treated sample for discharge timing of 3 min, it can be seen that the values are approximately the same. Thus, with different plasma discharge timings, the percentage of the Fe:O ratio remains the same.

3.2.2. Vibrating sample magnetometer (VSM) studies

Fig. 9 shows the graph of the hysteresis loops of 3 different discharge timings of the plasma treated solutions. The VSM shows coercivities of 10, 6 and 3 G for the plasmas discharge timings of 3, 5 and 10 min, respectively. This exhibits a decreasing trend with the increasing plasma discharge timings. This indicates that superparamagnetic properties might be totally achieved if the plasma discharge timing is increased a bit more. It can be seen that the magnetic moment are increased with the increasing plasma discharge timings from 3 to 10 min. This might be due to increased amount of nanoparticles with the increasing plasma discharge time, as shown in SEM results.

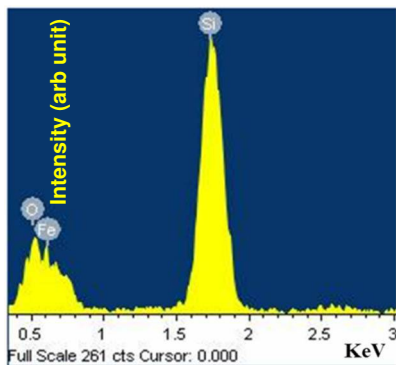


Fig. 8. EDX results of the plasma treated samples at 10 min.

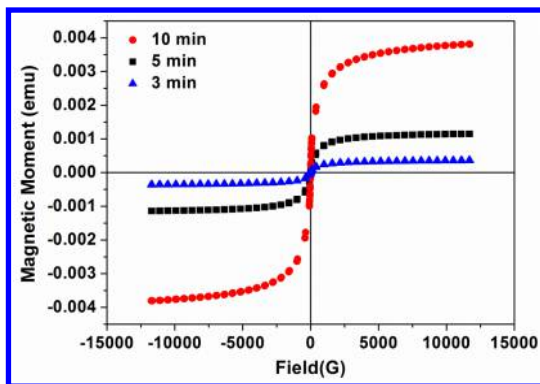


Fig. 9. VSM curve of Fe_3O_4 nanoparticles for the 3 different discharge timings of plasma treated samples.

Table 2. Average Values of Fe:O ratio and individual percentages from the 4 trials of the 10 min plasma-treated EDX samples.

Plasma treated samples	
Average Fe:O ratio	0.25
Fe at. %	20
O at. %	80

4. Conclusion

In summary this research has proved the significance of using AMPs treatment compared to thermally decomposed method. The Fe_3O_4 (magnetite) nanoparticles are formed and display quite soft magnetic properties (< 10 G) for both AMP treated and thermally

decomposed samples. But since, (i) the nanoparticles synthesized by AMPs treatment show smaller size (~ 6 nm) and smaller coercivity (~ 3 G) than that of thermally decomposed sample (~ 31 nm and ~ 10 G); and (ii) AMPs treatment takes a shorter time (~ 10 min) than that of thermally decomposed method (~ 90 min); thus in future, scientists could adopt AMPs technique for the formation of iron oxide nanoparticles efficiently. Moreover, based on the study that the plasma discharge time effect on the particle size, distribution and magnetic properties of the samples, it is found that with the increasing plasma discharge timing a trend of transition from soft ferromagnetic to superparamagnetic properties is exhibited. This further suggests the worth able study of AMPs treatment using for the synthesis of iron oxide nanoparticles.

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