International Journal of Nanoelectronics and Materials
In Press, Accepted Manuscript – Note to users

Preparation and Characterization of Magnetite (Fe_3O_4) nanoparticles By Sol-Gel Method

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Abstract

The magnetite (Fe_3O_4) nanoparticles were successfully synthesized and annealed under vacuum at different temperature. The Fe_3O_4 nanoparticles prepared via sol-gel assisted method and annealed at 200-400 ^{0}C were characterized by Fourier Transformation Infrared Spectroscopy (FTIR), X-ray Diffraction spectra (XRD), Field Emission Scanning Electron Microscope (FESEM) and Atomic Force Microscopy (AFM). The XRD result indicated the presence of Fe_3O_4 nanoparticles, and Scherer`s Formula calculated the mean particles size in range of 2-25 nm, the FESEM result shows the morphologies of the particles annealed at 400 ^{0}C are more spherical and partially agglomerated, the EDS result also indicates the presence of Fe_3O_4 by showing Fe-O group of elements. AFM analyzed the 3D and roughness of the sample; the Fe_3O_4 nanoparticles have a minimum diameter of 79.04 nm, which is in agreement with FESEM result. In many cases, the synthesis of Fe_3O_4 nanoparticles using $FeCl_3$ and $FeCl_2$ has not been achieved, according to some literatures, but this research was able to obtained Fe_3O_4 nanoparticles base on the characterization results

Keyword: Sol-Gel method, Magnetite nanoparticles, Particles size, Morphologies, XRD.

Introduction

Recently, the magnetite (Fe_3O_4) nanoparticles have been explored extensively due to their unlimited physical and chemical properties at the nanoscale [1]. In most of the application of magnetite nanoparticles, uniform shape and size particles are required to be well dispersed in the solvent. The major factors that influence the interest of many researchers are the particles size. However, the shape and size of the Fe_3O_4 nanoparticles usually controlled by their synthesis techniques. Therefore, this technique is the most significant method for preparation of certain materials, such as metal oxide powder and ceramic materials [2]. Magnetite nanoparticles synthesized with effective properties such as shape, size and suitable morphologies, will help to achieve a wider range of application [3]. Up to now, the focus have been made on the synthesis of iron oxide particles, because it can be crystalline in different polymorphic phases, which include hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and magnetite (Fe_3O_4) [4]. Among these inorganic nanoparticles Fe_3O_4 nanoparticles has interesting electric and magnetic properties as well as extensive potential applications in colour imaging, magnetic recording media, soft magnetic materials, ferrofluid, spintronic and biomedical applications such as drugs delivery, cell separation, imaging and therapeutic in vivo technology, among others [3, 4]. Numerous synthesis method like co-precipitation method [5], hydrothermal method [6], microwave irradiation method [7], ultrasonic method [8] and sol-gel method [9], are used to synthesized magnetite nanoparticles.

Among all synthesis method, sol-gel techniques have been chosen compare to the remaining traditional synthesis techniques due to its several advantageous properties include low cost, high purity, and suitable homogeneity [10]. However, in the quest to emerge at suitable product under sol-gel technaques many parameter need to be opimatize to keep reaction condition [11,12]. It was gathered that increasing the reactivity enhance wider surface area of the nanopaticles obtained by sol-gel technaques [13]. In recent time, the attention has been given to the preparation of magnetite nanoparticles in order to overcome certain problem, through different chemical synthesis method, although a lot of research have been published demonstrating the preparation of magnetite (Fe_3O_4) nanoparticles using several method for different applications such as drug delivery, magnetic recorder, ferro fluid and sensing application [14, 15]. Furthermore, the Fe_3O_4 nanoparticles were prepared by [16, 17] through sol-gel method using chepest materials of ferric nitrite as the precusor and the Fe_3O_4 nanoparticles was observed at 250 ^{0}C, when the temperature proroced to 350 ^{0}C the himatate (Fe_2O_3) was alos appear, this incoveniency is the major deffiency which hinder its applications [18-20]. In the research reported by [21-23], sol-gel method were used to synthesized iron oxide and its mixture using ethlylene glycol, $FeCl_3$ and $FeCl_2$, but the magnetite nanoparticles has not been observed.

In this work, the Fe_3O_4 nanoparticles were prepared effectivitily throgh sol-gel technaques and it was annealed under vacuum in different temperature. The major material used in the synthesis of Fe_3O_4 nanoparticles are iron(iii) chloride ($FeCl_3$), iron (ii) chloride ($FeCl_2$) and ethylene glycol (C_2H_6O). The Fe_3O_4 nanoparticles samples are prepared inform of S1, S2 and S3 with different annealed temperature 200^{0}C, 300^{0}C and 400^{0}C respectively. The morphologies of the Fe_3O_4 nanoparticles annealed at 400 ^{0}C were found to be more spherical and partially agglomerated with continues size distribution.

Experimental method

Materials

Iron (III) chloride $FeCl_3$. $6H_2O$, Iron (II) chloride $FeCl_2$ $.4H_2O$ and ethylene glycol (C_2H_6O) grade were obtained from SIGMA ALDRICH chemical cooperation. The entire reagents were used without any further purification.

Synthesis of Fe_3O_4 nanoparticles

The synthesis of magnetite nanoparticles is described as follows: 2.35g of Fe (III) and 8.35g of Fe (II) were firstly dissolved in 60 ml of ethylene glycol and vigorously stirred for a period of 3h at 45^0C to form a sol. Subsequently, the sol was heated and maintained to a temperature of 80^0 C until a dark colour gel was formed. This gel was aged for a period of 72h and later dried at $140\,°C$ for 5h. The obtained xerogel was annealed at a certain temperature ranging from 200-$400\,°C$ under vacuum condition. Finally, different size magnetite nanoparticles were successfully obtained. The synthesized Fe_3O_4 nanoparticles were washed with a certain amount of acetone and ethanol several times to enhance magnetic properties. Table 1 tabulates the effect of a change in temperature towards the mean size of magnetic nanoparticles calculated from XRD data using Scherer's formula (see Fig.4). However, from tables 1, the Fe_3O_4 nanoparticles sized increase with increase in annealing temperature

TABLE 1. Effect of change in temperature toward the mean size of magnetite nanoparticles

Sample	Annealing temperature (^OC)	Mean particles size (nm)
S1	200	2.02
S2	300	5.58
S3	400	8.35

Characterization

A sample was characterized using the Fourier Transform Infrared Spectrum (FTIR) (Perkin Elmer Spectrum 100 FTIR spectrometer). The absorption spectra of the magnetite nanoparticles were determined using Ultraviolet (Uv-Vis) spectroscopy (SHIMDZU 1800 UV-visible series). The X-ray diffraction spectroscopy (XRD) (Shimadzu XD-610) is used to determine the phase structure of the magnetite nanoparticles; the rays were radiated at a wavelength of (λ = 0.15406 nm). However, the morphological analysis of the particles were obtained by Field Emission Scanning Electron Microscope (FESEM JEOL model JDM-7600F) equipped with X-ray dispersive spectrometer (EDS). To quantitatively examine the high and three dimension (3D) profiles of the structure formed by Fe_3O_4 Atomic Force Microscopes (AFM) (Bruker 593 x 413) was used in the tapping mode to image the topography of a two-layer grid formed by Fe_3O_4. The 3D image showed the spatial profiles of the grids.

Result and discussion

Fourier Transform Infrared Spectra (FTIR) analysis

The analysis of the infrared (IR) spectra confirms the monomer fixation of Fe_3O_4 nanoparticles (Fig. 1), which resulted in the formation of Fe-O bands which is proven by the appearance of the absorptions band at 476 cm^{-1}, 519cm^{-1}, 688cm^{-1}, 743$cm^{-1}$and 875cm^{-1} [7-10]. Moreover, the existence of peaks at 1069cm^{-1} to 1600cm^{-1} and 2606cm^{-1} to 2941cm^{-1} are assigned to O-H stretching, C-H stretching, C=C stretching, C=O stretching and C-O stretching bands respectively, indicating acidic medium condition of Fe_3O_4 nanoparticles preparation [19, 23]. The bonds appear at 3226cm^{-1}, 3293cm^{-1} and 3325cm^{-1} may be attributed to the H_2O molecules or O-H vibrating stretching which are probably existed due to ethylene glycol $(CH_2OH)_2$ [24].

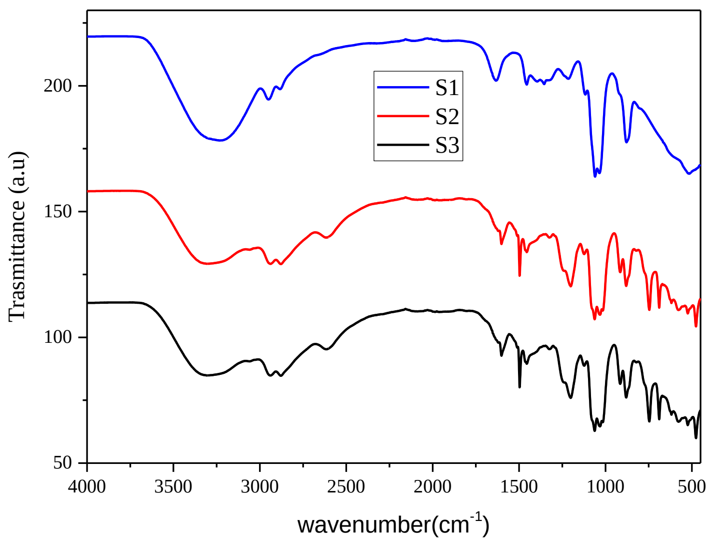

Fig. 1. FTIR spectra of the magnetite nanoparticles

UV-visible spectroscopy study

The UV-visible spectroscopy was used to characterize the structure of Fe_3O_4 nanoparticles acquired. The Fig. 2 reveals, that the absorption peaks of the prepared Fe_3O_4 nanoparticles was found within the average UV-vis absorption region [5, 17], the average lower absorption wavelength of 262.13nm and 230 nm is observed in all the samples. This can easily be assigned to the intrinsic band gap absorption of the magnetite nanoparticles.

The mobility of electrons from valence band to conduction band can be determined by the equation of the energy gap (Eg) of the Fe_3O_4 nanoparticles, was calculated using the relation

$$Eg = \frac{hc}{\lambda} \quad (1)$$

Where c is the velocity of light, h is the Planck constant, λ is the wavelength of light the estimated band gap energy result is 4.7.eV

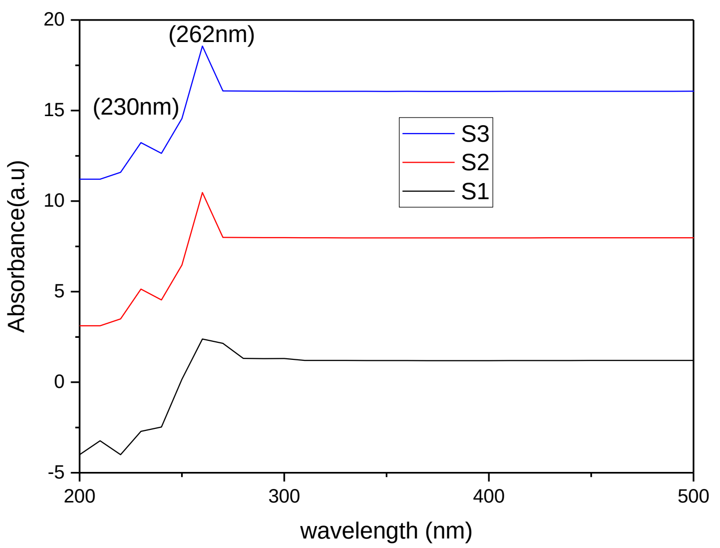

Fig. 2. UV-visible spectra of the magnetite nanoparticles

The analysis pattern of XRD in magnetite (Fe_3O_4) nanoparticles

The X-ray diffraction (XRD) pattern of the Fe_3O_4 nanoparticles was obtained at different annealing temperatures as shown at diffraction peak of 2θ = 26.75^0, 32.67^0, 35.44^0, 55.88^0, and 62.55^0. This can be assigned to (310), (110), (311), (440), and (330) crystal planes of pure Fe_3O_4 nanoparticles with spinal structure of (JCPDS98-3969) [7, 21], respectively in $200\,°C$ and $300°C$. At $400°C$ some peaks are also observed at 46.54^{0}and 55.98^0 which can be easily be assigned to (331), and (240). This indicates that these peaks are related to γ–Fe_2O_3 of (JCPDS98-0625) and α-Fe_2O_3 of (JCPDS98-2012) [22, 23] respectively, these data are in agreement with what was reported by [16, 18]. This reveals that the resultants nanoparticles in the first sample (S1) is purely Fe_3O_4 nanoparticles [25], while the remaining second (S2) and third (S3) samples are probably γ-Fe_2O_3 and α-Fe_2O_3 nanoparticles, respectively [26]. The peak of the sample S1 in Fig.3 marched very well with Fe_3O_4 of (JCPDS98-3969) nanoparticles, same peaks are shifted slightly to the higher angle in the S2 , which is possibly due to oxidation of Fe_3O_4 in air at $300°C$ resulted to γ-Fe_2O_3 same result of this transformation of Fe_3O_4 to γ-Fe_2O_3 have been reported in the literature by [13, 25] . The XRD pattern of the S3 indicates the oxidation of Fe_3O_4 at $400°C$ in air. The diffraction peaks marched well with α-Fe_2O_3 (JCPDS98-2012), showing the transformation of Fe_3O_4 to α-Fe_2O_3 at $400°C$ in air [8, 11].

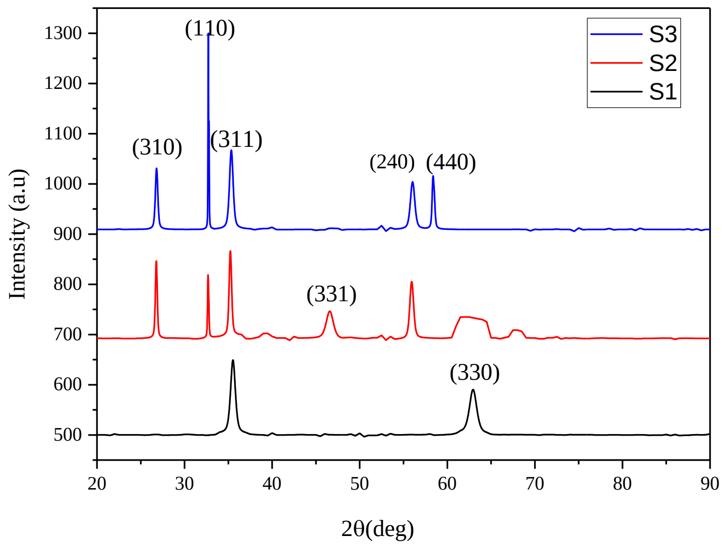

Fig. 3. XRD analysis of Fe_3O_4 nanoparticles obtained at different temperature

Scherer's formula calculated the crystalline particles size

$$D = \frac{K \cdot \lambda}{\beta \cdot Cos\theta} \qquad (2)$$

Where K (0.94) is a dimensionless quantity, λ is the X-ray wavelength, β is the line broadening at half-maximum intensity (FWHM) and θ is the Bragg angle. Therefore, the obtained particles size result is plotted as the function of temperature in (Fig 5). As been observed in the plot, the magnetite nanoparticles size is increase of temperature from 200 $°C$ to $400°C$. Therefore, the average particles size as calculated by Scherer`s formula is 2.02nm, 5.58nm and 8.35nm for S1, S2, and S3 respectively. This shows that with rising annealing temperatures, the size of the Fe_3O_4 nanoparticles is gradually increasing as shown.

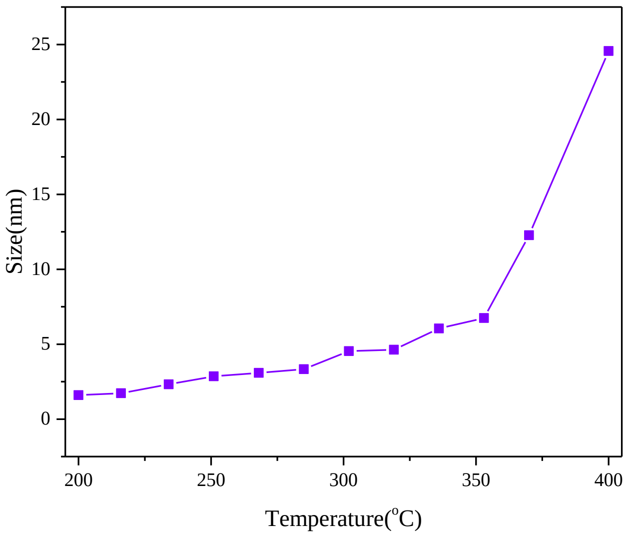

Fig. 4. Size of Fe_3O_4 nanoparticles calculated using Scherer's formula as a function of annealing temperature.

Field Emission Scanning Electron Microscope (FESEM) and Energy dispersive spectrometer (EDS) image of magnetite (Fe_3O_4) nanoparticles

FESEM observed the morphologies of the (Fe_3O_4) nanoparticles; the obtained image is shown in (Fig. 5).The Fe_3O_4 nanoparticles sample (S3) annealed at 400 ^{0}C were appeared to be in a spherical structure and nearly agglomerated. However, the spherical nanoparticles exhibit magnificent internationalisation rate and highest cellular take up instead of another shape such as nanorods, nanocubes or nanodisk [25]. Moreover, due to strong inter-particles

Van der Waals force and magnetic attraction among the Fe_3O_4 nanoparticles, some agglomeration is detected in the samples (S3). The irregular shapes are observed at elevated changes in temperature (see S1 and S2) due to agglomeration process [22, 23]. The image obtained through EDS analysis shown in (Fig. 5) confirmed the appearance of Fe_3O_4 nanoparticles by indicating Fe-O group of the element.

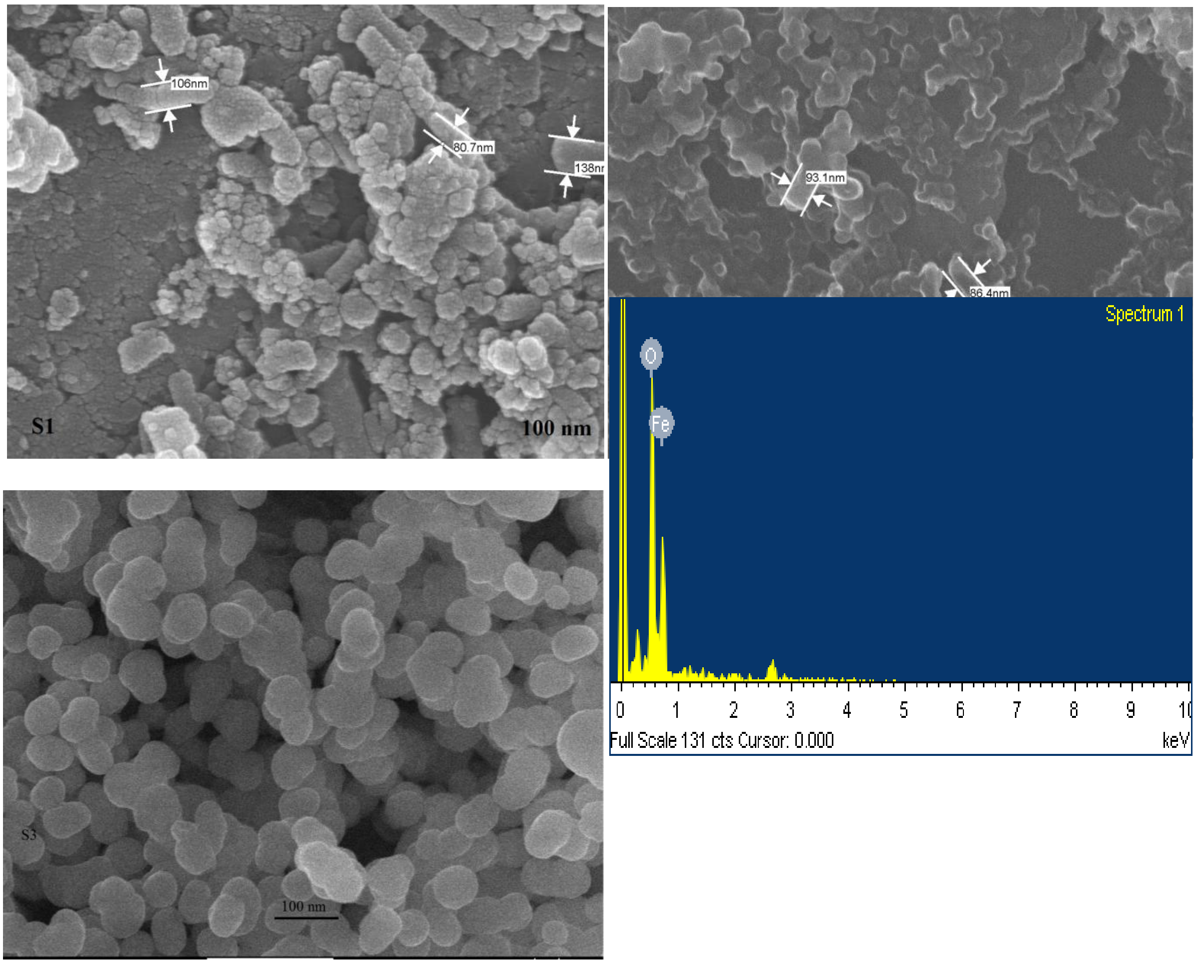

Fig.5. FESEM image of magnetite nanoparticles annealed under vacuum at 200 for S1, 300 for S2 and 400 ^{0}C for S3 and the EDS image of magnetite (Fe_3O_4) nanoparticles

Atomic Force Microscope (AFM) characterization

The magnetite nanoparticles were deposited and dried on the glass for AFM characterization. The results were obtained to determine the three dimensions (3D) and roughness of the samples. Fig. 5 shows the resulting 3D images of the sample, the maximum high of the particles is about 10.4 nm and the diameter of 79.09 nm for the scanned area of $1 \mu m \times 1 \mu m$

according to histogram in Fig.6. This results is in line with particles size obtained by FESEM, the knobs spots (yellow spots) indicate the present of small agglomeration of Fe_3O_4 nanoparticles, which also seen as a yellow area at phase contrast of the 3D image as reported by [23]. The light yellow area is obtained due to the high moisture content in the ethylene glycol; the sample was melted down because of heat absorption from the laser light [26].

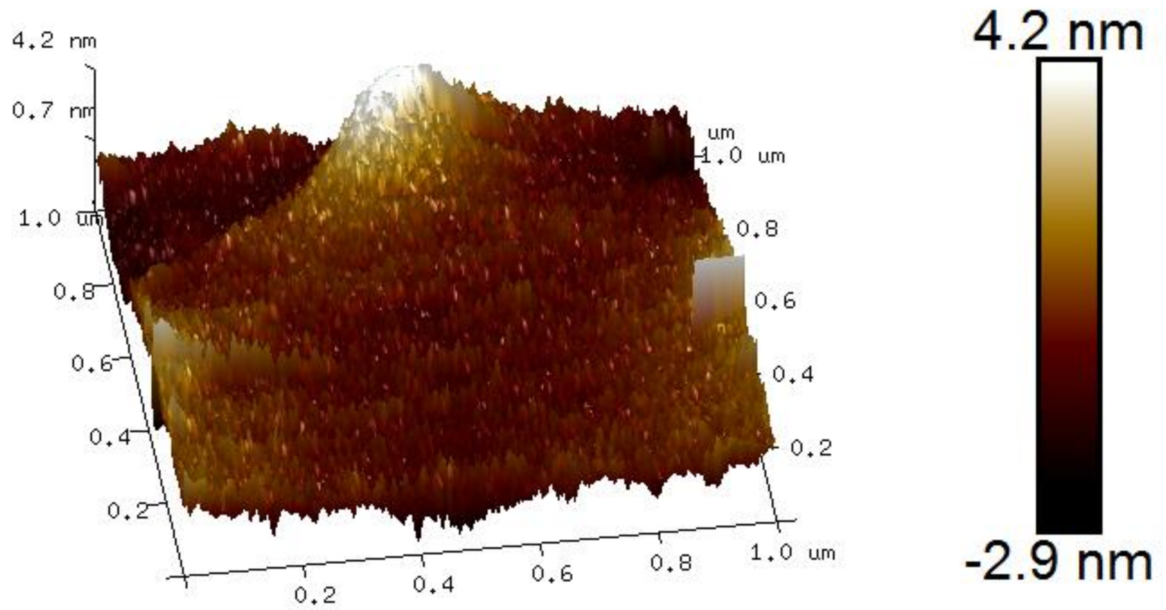

Fig 5. AFM 3D image of the magnetite nanoparticles annealed at 400 ^{0}C

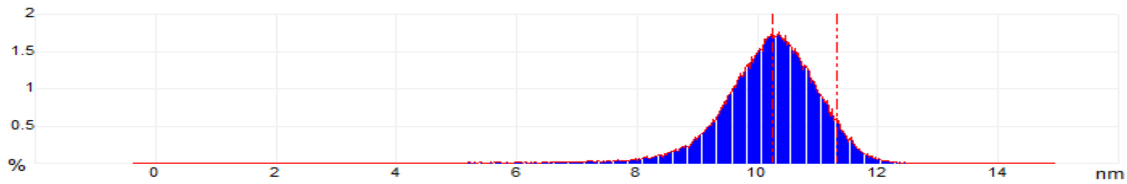

Fig. 6 Histogram obtained from AFM Analysis

Acknowledgement

This research was supported by the Centre for Graduate Studies (CGS) Universiti Tun Hussein Onn Malaysia (UTHM).

Conclusion

This research has demonstrated the preparation of Fe_3O_4 nanoparticles by sol-gel assisted method and annealed under vacuum at different temperature 200-400^0 C. The Phase and molecular structure, functional group, morphologies and roughness analysis of the Fe_3O_4 nanoparticles were successfully characterized; the results indicated that the different sized Fe_3O_4 nanoparticles were obtained, simply by varying annealing temperature. The morphologies observed by FESEM shows that the sample S3 annealed at 400 ^{0}C is more spherical and different size Fe_3O_4 nanoparticles were observed in S1, and S2 annealed at 200 and 300 ^{0}C respectively. This method offers several significant properties for the preparation of Fe_3O_4 nanoparticles. Firstly, the synthetic method is economically important and environmentally friendly, because it includes cheaper and toxic free iron salts; secondly, the size of the obtained Fe_3O_4 nanoparticles can easily be controlled by varying the annealing temperature.

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