Dependence of lattice strain of magnetite nanoparticles on precipitation temperature and pH of solution

A H M Yusoff\textsuperscript{1,2}, M N Salimi\textsuperscript{1} and M F Jamlos\textsuperscript{2}

\textsuperscript{1}School of Bioprocess Engineering, Universiti Malaysia Perlis, 02600 Arau, Malaysia.
\textsuperscript{2}School of Computer and Communication Engineering, Universiti Malaysia Perlis, 02600 Arau, Perlis.

Abstract. Magnetite nanoparticles were prepared by co-precipitation method at different precipitation temperature and pH of solution. The produced inverse spinel cubic structure can be denoted to magnetite structure as deduced from X-ray diffraction (XRD) result. X-ray peak broadening analysis was utilized to determine the crystallite sizes and lattice strain present by the Williamson-Hall method. The results showed that the average crystallite size and tensile strain of the nanoparticles was first decrease before rising again at a certain temperature. The same phenomenon of size was experienced on the pH variation of the solution with compressive and tensile strain was displayed. It was observed that the almost perfect structure (very low strain) and relatively small nanoparticles was synthesized at temperature of 70 °C and pH of 11.94 with 8.89 nm in size.

1. Introduction
Among the various magnetic nanoparticles, magnetite is being widely studied due to its ability to magnetically guidance their movement into the targeted site. This attractive property has made magnetite a potential material to use in bioseparations\textsuperscript{[1]}, magnetic resonance imaging \textsuperscript{[2]}, hyperthermia \textsuperscript{[3]}, drug delivery agent \textsuperscript{[4]} and magnetofection\textsuperscript{[5]}. Thus, understanding to control nanoparticles motion is a beneficial knowledge to cure various disease at maximum performance. Magnetism property of magnetite exhibit size-dependent properties. Research to have magnetism property appropriate to the ideal size that suited for biomedical application has been greatly discussed. Besides size, magnetism also strongly influenced on their crystal imperfection \textsuperscript{[6]}. Lattice distortion, grain boundary, dislocations and faulting are some example that lead to distribution of imperfect crystallinity of nanoparticles \textsuperscript{[7]}.

Having a perfect structure (unstrained particle) and additionally small size of particle are two remarkable parameter to yield well magnetism properties. It is noticed that the defects in structural properties can cause peak broadening and shift the Bragg peak angle of the X-ray diffraction (XRD) data. Thus, the crystallinity defect and the strain distribution in the sample can be resolved by analysing the peak width. Williamson-Hall (WH) method is one of the existing way to extract the size and strain from the diffraction peak. Hence, in the present study, the well-known Scherrer method and WH analysis was employed for estimating crystallite size and lattice strain.

This paper accounts for the synthesis of magnetite nanoparticles using a simple co-precipitation route. The role of precipitation temperature and pH condition was studied by evaluating the strain and stress distribution as less work is done in respect of this.
2. Methodology

2.1. Magnetite nanoparticles preparation

Iron (III) chloride (FeCl$_3$, 98% pure, anhydrous), iron (II) chloride (FeCl$_2.4$H$_2$O, 99%), sodium hydroxide (NaOH) were obtained from Acros Organics. All chemical reagents applied in this work were of analytical grade and the chemicals used without further purification.

The magnetite nanoparticles were prepared through co-precipitation method from FeCl$_3$ and FeCl$_2.4$H$_2$O. Both iron precursors were dissolved in treated deionized water (DI) at a mole ratio of 2:1. The resulting yellowish solution was refluxed at different temperature (30 °C, 50 °C, 70 °C and 90 °C) for 20 minutes prior NaOH was added. The stirring rate was maintained at 700 rpm throughout of the experiment. pH of the mixture was manipulated by addition of pH (pH = 11.33, 11.94, 12.15 and 12.25). Synthesis processed are performed under oxygen free condition to prevent the formation of maghemite. The black suspension formed were collected by centrifuge at 3000 rpm for 15 minutes and washed several times with DI water. Lastly, the precipitated was redispersed and dried in a vacuum oven for overnight at 60 °C for further characterization.

2.2. Characterization

The sample crystal structure were determine by PanalyticalX’pert Pro X-ray diffractometer using Cu Kα radiation (λ = 0.15406 nm) at room temperature. The prepared Fe$_3$O$_4$ powders were pressing over the sample holder and the analysis was recorded over $2\theta$ range of 20° to 80° at a scan rate of 1°/min.

3. Results and Discussion

All the X-ray diffraction (XRD) pattern under study were compared with the standard reference data of magnetite (JCPDS Card No. 89-0691). The significant diffraction peaks were appeared at Bragg angles that corresponding to Miller indices of (220), (311), (400), (511) and (440) which consistent with the standard pattern. Thus, all the samples possessed the spinel structure of Fd3m group. No additional peaks were observed indicated that no impurities phases such as maghemite or goethite except the only magnetite phase was found in the final product. During the nanoparticles preparation, growing crystallites of magnetite may take a specific crystallographic direction that normally noticeable through the highest intensity of the diffraction data. The preferred direction of crystallite growth was influence by the ions compositi ons and the synthesis condition. Earlier studies [8] show that the growth orientation is found to be preferentially in the direction of (110) prior change to (104) crystallographic direction. Thermal treatment during nanoparticle preparation were observed to have that serious change of growth orientation where hematite phase was evolved after calcination at 650 °C and above. Another study reveal that the calcination time [9] and high pH of solution [10, 11] also change the final phase into maghemite or goethite, respectively. Besides that, Wang et al. [12] suggest that the change of growth orientation may relate to the strain developed in nanoparticle grains. Nonetheless, in present case, the preferred growth orientation shows along the (311) crystallographic direction which verified the only magnetite phase was formed.

The average crystallite size and lattice strain distribution in the material can be find out through the peak broadening. But, the breadth of the Bragg peak must be refined due to the convolution of the profiles with instrumental error and sample dependent effects. Thus, line broadening of standard material such as silicon was employed to correct and eliminate both contributions in $\beta_D$ calculation through the following equation:

$$\beta_D = \sqrt{\frac{\beta^2_{measured} - \beta^2_{instrumental}}{K \cos \theta}} \quad (1)$$

 Mostly, the trend of change of crystallite size is determined by a well-known Scherrer formula. Values of full width at half maximum (FWHM) of diffraction peaks at $2\theta = 35.4^\circ$ was chosen for calculation of the crystallite size using Scherrer’s formula:

$$D_S = \frac{K \lambda}{\beta_D \cos \theta} \quad (2)$$
where $D_s$ is the crystallite size (nm), $K$ is the shape parameter which is 0.94 for spherical shape, $\lambda$ is X-ray wavelength ($\lambda = 0.15406$ nm for Cu $K\alpha$ radiation), $\beta_D$ is the full width at half maximum for the diffraction peak under consideration (rad) and $\theta$ is the corresponding Bragg angle (°). The average crystallite size ($D_s$) from the Scherrer method is tabulated in Table 1.

In addition, Williamson-Hall (WH) plot was also employed to determine the crystallite size and effect of strain in the as-synthesized magnetite nanoparticles. Each XRD result were fitted with Lorentzian curve shape and the total broadening ($\beta_{hkl}$) is obtained as the following equations:

$$\beta_{hkl} = \beta_s + \beta_D$$

(3)

where $\beta_s$ is crystallite size broadening and $\beta_D$ is lattice strain broadening. A Williamson-Hall’s mathematical relation is employed that relate between strain-induced broadening in the sample and average crystallite size as follows:

$$\beta_{hkl} = \frac{K\lambda}{D\cos\theta} + 4\varepsilon \tan\theta$$

(4)

By rearranging the Equation(4):

$$\beta_{hkl}\cos\theta = \frac{K\lambda}{D_{WH}} + 4\varepsilon \sin\theta$$

(5)

where $\varepsilon$ is lattice strain and $D_{WH}$ is crystallite size computed from WH relation. This strain was assumed to have a uniform strain in all crystallographic directions. A plot of $4\sin\theta$ versus $\beta_{hkl}\cos\theta$ were plotted in figure 1 and figure 2 for different reaction temperature and different pH of solution, respectively. The slope from the straight line represent the value of strain in the sample while y-intercept was utilised for $D_{WH}$ measurement corresponding to zero strain. The $D_{WH}$ and lattice strain computed through the WH method were shown in table 1. The small difference of crystallite size between $D_s$ and $D_{WH}$ is owing to the crystal strain involvement[7]. Scherrer method ignores the microstrain in the lattice that originating from the imperfection of structure whereas Williamson-Hall method isolates the instrumental and sample broadening effects in calculation.

![Figure 1. The WH analysis of magnetite nanoparticles prepared at 30 °C (S1), 50 °C (S2), 70 °C (S3) and 90 °C (S4).](image-url)
Figure 2. The WH analysis of magnetite nanoparticles prepared at pH = 11.33 (S5), pH = 11.94 (S6), pH = 12.15 (S7) and pH = 12.25 (S8).

The strain observed in all samples were relatively small as compared to another literature. Synthesis technique is one of the factor that contribute to the microstrain broadening of diffraction peak. Vives et al. [13] studied the line profile of iron ball milled powders and obtained high internal microstrain in their sample. It is obvious that the samples were allowed to receive high rotation speed (150, 250 and 350 rpm) that can induce high residual stress in the compacted part. Contrary to the chemical synthesis technique that not required heavy mechanical process and thermal stress such as quenching during the sample preparation. Our result were consistent with Jafari et al. [8] and Khorsand et al. [14] which both prepare the nanoparticles using co-precipitation method and sol-gel method, respectively.

Table 1. A slightly more complex table with a narrow caption.

| Sample code | Processing condition | D_S (nm) | D_WH (nm) | Strain ($\times 10^{-4}$) |
|-------------|----------------------|----------|-----------|--------------------------|
| S1          | 30 °C                | 21.18    | 28.30     | 82                       |
| S2          | 50 °C                | 11.78    | 25.21     | 38                       |
| S3          | 70 °C                | 10.60    | 8.89      | 1                        |
| S4          | 90 °C                | 30.26    | 18.24     | 18                       |
| S5          | pH 11.33             | 17.66    | 18.74     | 17                       |
| S6          | pH 11.94             | 13.15    | 8.89      | 1                        |
| S7          | pH 12.15             | 10.10    | 8.45      | –9                       |
| S8          | pH 12.25             | 17.67    | 10.83     | –22                      |

It is noted that inhomogeneous strain either compressive or tensile strain give rise to peak widths broadening and shift the 2θ peak position. As can be observed in Figure 1 and Figure 2, the lattice strain has a positive slope when the crystal lattice experience tensile forces whereas lattice shrinkage due to the compressive strain was indicated by the negative slope. Samples at different precipitation temperature showed a continuous lattice expansion where the strain decreases when temperature was keep increasing. The increase in temperature is likely to drive proper modification of atom arrangement in the lattice since the atoms receive more energy at high temperature. However, tensile stress was increases again that arising from the Ostwald ripening-type phenomenon. The phenomenon
is the predominant growth mechanism at higher precipitation temperature that results in greater final diameter of particles. Increase in strain may be associated with the change in lattice strain number where the number was increasing during the growth phase correspondingly to their size.

On the other hand, samples at variation of pH showed the contribution of both type of strain. pH at 11.33 and 11.94 showed a reduction of tensile strain whereas sample at pH 12.15 and 12.25 showed an increment in compressive strain. Lian et al. [15] reported that goethite was formed first before magnetite formation at very high pH. It is noted that goethite has an orthorhombic crystal structure and this is expected to induce intense atomic competition during magnetite formation. Structural clashes generate lattice shrinkage in the structure and keep increasing at higher pH.

4. Conclusion
Simple way to obtain magnetite nanoparticles by co-precipitation method which enhance their structural properties at small particle size was presented. The result demonstrate that the parameter under study have significant influence on crystallite size and strain distribution of synthesized nanoparticles. For particles with less strain distribution resulted in less surface imperfection. Generally, surface defects have decreased to a certain temperature because of energy gain in the system. While, same pattern was observed at change of pH but the compressive strain evolved can be explained by the overlap structure formed at high pH. Therefore, respect to this study, it could be concluded that such well structure of magnetite can be obtained at 70 °C and pH = 11.94 with 8.89 nm in size.

5. References
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