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Critical Parametric Study on Final Size of Magnetite Nanoparticles

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Abstract. The great performance of magnetite nanoparticle in varsity field are mainly depended on their size since size determine the saturation magnetisation and also the phase purity. Magnetite nanoparticles were prepared using a simple co-precipitation method in order to study the influence of synthesis condition on the final size. Variable parameters include stirring rate, reaction temperature and pH of the solution can finely tuned the size of the resulting nanoparticles. Generally, any increase in these parameters had a gently reduction on particle size. But, the size was promoted to increase back at certain point due to the specific reason. Nucleation and growth processes are involved to clarify the impact of synthesis condition on the particle sizes. The result obtained give the correct conditions for pure magnetite synthesis at nanoscale size of dimensions less than 100 nm.

1. Introduction
Magnetite nanoparticles are by and large widely looked as a potential nano candidate materials for various application notably for biomedicine. Remarkable properties of magnetite that arise at nanoscaled level provide a promising achievement in biological field. The excellent magnetism properties, good biocompatibility and the suitability to conjoint with other materials to form various nanoformulation strategies (such as liposome, micelle and dendrimer) attains a successful transportation of therapeutic agent by lessened the reticuloendothelial system (RES) clearance [1,2]. The effectiveness of nanoparticles in biomedicine field are mainly governed by their physicochemical properties. Enormous quantity of literature demonstrated that a massive portion of magnetite properties rely upon their nanoscale size. Nanoscale magnetite particles with a range of size 1-100 nm becomes the prerequisite for excellent performance in magnetofection and drug and gene delivery application [3,4,5].

Nanoparticle sizes is possible to finely control by means of both synthesis technique and varying the synthesis condition. Among the countless techniques employed for magnetite production, co-precipitation technique is the promising choice regarding of fast preparation, economical and the simplicity of the technique. However, the difficulties to tailoring the particles’ sizes is the important challenge. Thus, critical process parameter such as reaction
temperature, pH of mixture and stirring rate should be considered for the production of magnetite nanoparticles with a particular final size.

2. Experimental

2.1 Materials

Iron (III) chloride (FeCl$_3$, 98% pure, anhydrous), iron (II) chloride (FeCl$_2$.4H$_2$O, 99%), sodium hydroxide (NaOH) were obtained from Acros Organics and were used without further purification. Deionized (DI) water was used throughout the experiment.

2.2 Synthesis of magnetite nanoparticles

Generally, the chemical reaction involve for co-precipitation of magnetite from ferrous and ferric ions precursor can be represented as:

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$$  \hspace{1cm} (1)

Synthesis of magnetite were carried out using stoichiometric amount of FeCl$_3$ and FeCl$_2$.4H$_2$O at a mole ratio of 2:1. The ratio was maintain throughout the study to avoid phase transformation. Iron salts was dissolved in treated DI water for 20 minutes under continuous incoming nitrogen gas that gently bubbled at the bottom of the mixture. Influence of size under different stirring rate was studied from 300 rpm to 1100 rpm. The reaction mixture was heated up to desired temperature (30 °C, 50 °C, 70 °C and 90 °C) prior the addition of NaOH. The necessary alkaline pH of the solution was manipulated by NaOH. The mixture immediately turn into black suspension indicated that magnetite was formed. The mixture was left to react completely for 30 minutes. Final pH was recorded for each synthesis process. The precipitated magnetite was collected by centrifugation at 3000 rpm for 15 minutes and re-dispersed with DI water. The re-dispersed magnetite was again centrifuged for at least 3 times to remove unreacted ions. The as-synthesized magnetite was dried in vacuum oven for overnight at 60 °C for characterization.

2.3 Characterization

The samples crystal structure were determine by Panalytical X’pert Pro X-ray diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm) at room temperature. The samples powder were analysed over 2$\theta$ range from 20° to 80° at a scan rate of 1°/min.

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:

$$D_s = \frac{K\lambda}{\beta D\cos\theta}$$  \hspace{1cm} (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 Kα radiation), $\beta D$ is the full width at half maximum for the diffraction peak under consideration (rad) and $\theta$ is the corresponding Bragg angle ($^\circ$). For each case, the calculated crystallite sizes were tabulated in Table 1.

3. Results and Discussion

3.1 Phase identification analysis

Figure 1 depicts the XRD pattern of prepared samples at different processing conditions. All the detectable diffraction peaks were compared with the standard reference data of magnetite (JCPDS card No. 89-0691). Generally, the diffraction data obtained were in good agreement with the certified standard, indexed to the inverse spinel structure with a face-centred cubic unit cells of magnetite. The formation of magnetite normally corresponded by the diffraction peaks occurring at 2$\theta = 35.4^\circ$ (311) which appeared in all samples. The narrow and sharp peaks at this
diffraction peaks suggest that the magnetite nanoparticles had a good crystallize structure. No other extraneous peaks is detected except for S4 sample which consist of (211) peak of maghemite. S4 is the smallest size found in the present study where it was noticed to easily transform into maghemite phase due to the oxidation of unstable Fe$^{2+}$ in the octahedral sublattice into Fe$^{3+}$ [6]. Maghemite and magnetite vary slightly in their structure where they share the same inverse spinel structure, but the formation of vacancies in the octahedral sites of maghemite make them different. The maghemite phase transformation experimentally reveal three low intensity additional peaks of (110), (210) and (211) [7]. In present case, partial oxidation particularly at the surface of the particles is the reason for the only (211) peaks is observed in S4 sample.

Exclude S4, the XRD patterns of the samples prepared at different stirring rate confirmed the existence of magnetite only. The observed peaks were narrower and more intense at higher agitation rate and slightly shifted to higher Bragg angle. Same issue also happened at higher temperature and molarity. The broadening of the peaks can be attributed to the ultra-small particles and imperfection in the polycrystallinity of Fe$_3$O$_4$ NPs whereas Bragg angle change was assigned to the lattice constant expansion [8].

![X-ray diffraction pattern of synthesized nanoparticles at different processing parameters.](image)

**Figure 1.** X-ray diffraction pattern of synthesized nanoparticles at different processing parameters.

3.2 Effect of stirring rate on magnetite particle size

In this study, the crystallite size decreased linearly from 13.25 nm to 9.64 nm and then increased to 11.78 nm for the stirring rate from 300 to 1100 rpm. Mostly, bigger and agglomerated particles are formed at a low stirring velocities. However, with a further increase in the stirring rate speed, significant effect on the particle size was observed. We observed that at higher mechanical stirring allowed the mixture for greater seed formation and consequently a smaller final particle size was obtained. At low stirring rate, the uniformity and regularity of the reaction solution are deteriorated. The nucleating species are not dispersed equally throughout the mixture and prone to aggregate [9]. The mobility and homogeneity are improved at elevated degree of agitation by
hastening the transport of the growth species to the nanoparticle’s surface [9]. The high energy transferred to the suspension medium caused the solution to disperse well into smaller droplets [10]. Higher shear forces resulted from the mechanical stirring greater than 900 rpm, created a lot of bubbles and splashing of the solution which cause an anomalous diffusion.

The monodispersity and growth of nanoparticles can be further explained via the growth mechanism. Essentially, size distribution of nanoparticles is controlled by their nuclei growth process where diffusion-controlled growth reaction is desired instead of adsorption-controlled growth. Therefore, increasing the stirring rates enhanced the diffusion transport of solute to the growing particle [11]. Through LaMer mechanism [12], there is a minimum degree of supersaturation ($S_c$) of the monomer species for nucleation to occur. By increasing the stirring rate will provide a rapid increase of the monomer concentration higher than $S_c$ to all location of the solution and abundance of nuclei generation are instantly formed. The blowout nucleation generation rapidly depleted the free monomers bringing the concentration back down below $S_c$. After this stage, the nucleation is almost stopped leaving the surviving particles proceed to growth. Thus, by separating the nucleation and growth stage, each nucleus is produced at just about the same time and all particles have almost indistinguishable size [13]. Consequently, monodispersed nanoparticles are yield. Generally speaking, the degree of nucleating agent mobility are enhance by raise up the stirring rate to extend their distance travel. However, further increase of stirring rate has resulted the particles which have the size below the critical nucleus to collided and suspended to make a new nuclei and increase the crystallite size [14].

| Sample | Synthesis condition | Size (nm) |
|--------|---------------------|-----------|
| S1     | 300 rpm             | 13.25     |
| S2     | 500 rpm             | 13.25     |
| S3     | 700 rpm             | 10.60     |
| S4     | 900 rpm             | 9.64      |
| S5     | 1100 rpm            | 11.78     |
| S6     | 30 °C               | 21.18     |
| S7     | 50 °C               | 11.78     |
| S8     | 70 °C               | 10.60     |
| S9     | 90 °C               | 30.26     |
| S10    | pH 11.33            | 17.66     |
| S11    | pH 11.94            | 13.15     |
3.3 Effect of solution temperature on magnetite particle size

The effect of the solution’s temperature is another parameter to take into consideration. The use of temperature from 30 to 70 °C led to a particle size decrease down from 21.28 to 10.60 nm. Low temperature strongly influence the rate of particle growth through the effect on supersaturation [15,16]. The threshold precipitation temperature for instantaneous spinel magnetite formation is at 20 °C, whereas goethite compound is the main phase found at below 20 °C instead [17]. The only magnetite phase form in this study at selected temperature range showed that the result are in agreement as previously reported [17]. We suggested that at low temperatures, insufficient energy own by the nucleating species resulted a slow diffusion rate. Thereby, allowed the nucleating species to grow larger through a mass number of aggregated ions. Gradual reduction of the size obtained when the temperature was keep increasing can be attributed to the expedited collision rate of nuclei that derived from low solution viscosity [15]. Besides that, there is more energy within the particles that can reduce the extent of aggregation.

The changes in temperature up to 90 °C alter the mean sizes of the magnetite from 10.60 nm to 30.26 nm. The temperature above 70 °C might be the point where the deviation from a normal growth mechanism to Ostwald ripening-type phenomenon. The size of the nanoparticles are getting bigger at temperature of 90 °C that resulted from rapid growth of nanoparticles and afterwards anomalous aggregation are formed. The mechanism of growth is caused by the increment in critical radius requirement and surface energy of particles [14]. The dissolution of unstable particles smaller than the critical radius and the redeposition of particles onto stable nuclei leads to an increased in particle size. Earlier studies also reveal that the final size was dramatically increase for the temperature of 90 °C [18] and these findings are consistent with our results. The significant size changes at elevated temperature can be hindered by introduce oleic acid as the surfactant agents during the initial crystallization phase of magnetite. Oleic acid impede the particle growth by provide the esterification process between its carboxylic acid group and the hydroxyl group on the magnetite surface [19].

3.4 Effect of pH of solution on magnetite particle size

As indicated in Table 1, the size of magnetite nanoparticles can be further tuned by varying the pH of solution. The crystallites sizes of the nanoparticles reduced from 17.66 to 10.10 nm when the pH of solution was keep increasing from 11.33 to 12.15. Darminto and his co-workers suggested that the predominant growth mechanism at low pH is the well-known Ostwald ripening process [20]. The physics driving for dissolution-crystallization process during crystal growth is the interfacial tension that results in greater final diameter [21]. On increasing the pH of the solution, excess ions are available on the growth phase which leads to lower the interfacial tension. The reaction rates are faster at this state and more initial nuclei are able to precipitate to form slightly smaller particles.

The pH of solution also controlled the protonation-deprotonation equilibria of surface introduction of hydroxyl ions [22]. Its effect was obviously seen at pH beyond 12.15 with a significant size increment. The continuous raise of pH during synthesis period promotes the diabetic barrier of electron transfer which favour the Fe$^{3+}$ ions to have higher affinity for hydroxide ions relative to Fe$^{2+}$ [23,24]. In terms of chemical reaction euphemistically the reaction followed different reaction mechanism instead of Eq. 1. Lian et al [25] proposed a new reaction pathway for magnetite production at high pH:

| S12   | pH 12.15 | 10.10  |
|-------|----------|--------|
| S13   | pH 12.25 | 17.67  |
\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \quad (3)
\]
\[
\text{Fe(OH)}_3 \rightarrow \text{FeOOH} + \text{H}_2\text{O} \quad (4)
\]
\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \quad (5)
\]
\[
2 \text{FeOOH} + \text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} \quad (6)
\]

The stabilization of Fe\(^{3+}\) ions resulted for \(\text{Fe(OH)}_3\) to first precipitated (Eq. (3)). \(\text{Fe(OH)}_3\) also can be translated into \(\text{FeOOH}\) (Eq. (4)) or well known as goethite. Then, \(\text{Fe(OH)}_2\) reach their solubility product due to the excessive hydroxyl ions in the system (Eq (5)). Lastly, \(\text{Fe(OH)}_2\) that afterwards diffuse into the surface of \(\text{FeOOH}\) nucleates to complete the reaction (Eq. (6)). Thus, the explanation for the larger particles is the proposed reaction speed up the goethite formation as compared to Eq. 1 at the same reaction time. Larger goethite nucleate was yield before introduction of \(\text{Fe(OH)}_2\). Some literature reported [24,26,27] that goethite was present at high pH which also can be explained using the same reaction pathways. Inadequate reaction time for enough \(\text{Fe(OH)}_2\) to react with \(\text{FeOOH}\) to completely form into magnetite leaves a noticeable amount of unreacted \(\text{FeOOH}\).

4. Conclusion

The experimental results suggest that the process parameters greatly control the final size of the magnetite nanoparticles ranging from 9.64 nm to 30.26 nm. Respect to this study, it can be concluded that the mean crystallite size decreases with increasing stirring rates and at some point the crystallite size was reported to raise up back. Same behaviour also observed for changes of reaction temperature and pH of solution where each findings has its particular reason. Roughly, the outcome size in the present study is suitable for biomedical application in the fact that all sizes are below 100 nm. However, phase changes can evolve such as maghemite and goethite which is due to the susceptible to oxidation for certain small size and high pH effect, respectively. In conclusion, these finding are useful for the synthesis of magnetite nanoparticles at desired size, while preserve the pure phase of magnetite for adoption of various application.

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