

Green Synthesis of Magnetite Nanoparticles (via Thermal Decomposition Method) with Controllable Size and Shape

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Abstract

Magnetite (Fe_3O_4) nanoparticles with controllable size and shape were synthesized by the thermal decomposition method. In contrast to previously reported thermal decomposition methods, our synthesis method had utilized a much cheaper and less toxic iron precursor, iron acetylacetonate ($\text{Fe}(\text{acac})_3$), and environmentally benign and non-toxic polyethylene oxide (PEO) was being used as the solvent and surfactant simultaneously. Fe_3O_4 nanoparticles of controllable size and shape were prepared by manipulating the synthesis parameters such as precursor concentrations, reaction durations and surfactants.

Keywords: magnetic nanoparticles, magnetite, thermal decomposition, green synthesis

1. Introduction

Iron-based magnetic nanoparticles such as magnetite (Fe_3O_4) have received numerous attentions due to their unique properties and potential applications in biomedical applications[1-4]. Fe_3O_4 nanoparticles can potentially be used as magnetic targeted drug delivery carriers and magnetic resonance imaging (MRI) contrast agents due to their high saturation magnetization, low toxicity, and biocompatibility. Magnetic properties of magnetic nanoparticles can be tailored by their particle sizes and size distributions. The particle sizes and size distributions of magnetic nanoparticles are in turn, affected by the synthesis route. For these reasons, various synthesis approaches have been developed to produce Fe_3O_4 nanoparticles in order to obtain desired properties.

Synthesis methods of Fe_3O_4 nanoparticles that have been developed include co-precipitation [5-7] thermal decomposition [8,9] microemulsion route [10] hydrothermal

synthesis [11] and continuous flow technique [12]. However, success in precise particles size control of Fe_3O_4 nanoparticle has only been achieved through thermal decomposition using large quantities of toxic and expensive precursors and surfactants in organic solvent. Laborious purification steps are required before the end product can be used in biomedical applications. Thermal decomposition of iron pentacarbonyl [$\text{Fe}(\text{CO})_5$] has been used for the preparation of monodisperse $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles with average diameters from 4 to 16 nm by careful control of the molar ratio of metal precursor to surfactant, [$\text{Fe}(\text{CO})_5$] and oleic acid respectively[13]. Since $\text{Fe}(\text{CO})_5$ is very expensive and toxic, some attempts have been made to replace $\text{Fe}(\text{CO})_5$ with iron acetylacetonate [$\text{Fe}(\text{acac})_3$]. Fe_3O_4 nanoparticles of narrow size distribution have been synthesized by thermal decomposition of $\text{Fe}(\text{acac})_3$ in phenyl ether in the presence of stearyl alcohol, oleic acid and oleylamine [14].

In this study, we have attempted to synthesize Fe_3O_4 nanoparticles by the thermal decomposition method without using toxic organic

surfactants and solvents. Poly(ethylene glycol), PEO was being used as both solvent and surfactant simultaneously to synthesize Fe_3O_4 nanoparticles of controllable particle size and narrow size distribution. PEO has been widely used as a green solvent for various organic syntheses due to its low toxicity and high boiling point [15-17].

2. Experimental

2.1 Synthesis of Fe_3O_4 nanoparticles

In a typical synthesis, $\text{Fe}(\text{acac})_3$ was added to 20 mL of PEO and heated to reflux for 1 hour under a flow of nitrogen gas until a stable black suspension was obtained. The concentrations of $\text{Fe}(\text{acac})_3$ and volumes of PEO were varied in order to study their effects on the particles size of Fe_3O_4 nanoparticles formed.

2.2 Characterization of Fe_3O_4 nanoparticles

The size and morphology of the Fe_3O_4 nanoparticles were determined using a Transmission Electron Microscope (TEM) (Model JEM-1230). Size distributions were determined based on the average of particle diameters from at least 50 particle measurements per sample.

3. Results and discussion

3.1 Effect of concentration

Fig. 1 shows TEM images of Fe_3O_4 nanoparticles synthesized using various concentrations of $\text{Fe}(\text{acac})_3$ precursor. The mean size of Fe_3O_4 nanoparticles was observed to increase with increased concentrations of $\text{Fe}(\text{acac})_3$ precursor, which varied between 2 nm to 7 nm as the concentration of $\text{Fe}(\text{acac})_3$ was increased from 0.1 mmol to 8 mmol. Table 1 shows the summary of mean particles sizes synthesized at various concentrations of $\text{Fe}(\text{acac})_3$ precursor. At higher $\text{Fe}(\text{acac})_3$ precursor concentrations, Ostwald ripening of smaller particles have resulted in the formation of larger particles. Besides, the shape of the Fe_3O_4 nanoparticles was observed to be irregular and not spherical. Figure 1(f) shows the TEM micrograph of Fe_3O_4 nanoparticles prepared with fixed amount of $\text{Fe}(\text{acac})_3$ at 8 mmol and varying volumes of PEO. The mean size of Fe_3O_4 nanoparticles was observed to reduce from 9 nm to 7 nm as the volume of PEO used as solvent was increased from 10 mL to 20 mL. Increasing the volume of PEO would result in decreasing the

concentration of $\text{Fe}(\text{acac})_3$ precursor, which in turn led to the production of Fe_3O_4 nanoparticles of smaller mean sizes.

Table 1: Summary of particle size of Fe_3O_4 nanoparticles synthesized at various concentration of $\text{Fe}(\text{acac})_3$ precursor:

Concentration of $\text{Fe}(\text{acac})_3$, mmol	Particle sizes (nm)
0.1	2
1	4
2	5
4	6
8	7

3.2 Effects of reaction duration

The reaction duration was increased from 1 hour to 2 hours to investigate the effect of reaction duration on the mean particle size. Figure 2 (a) shows well dispersed Fe_3O_4 nanoparticles of mean size of 4 nm prepared at reaction duration of 1 hour. As shown in Figure 2(b), agglomerated Fe_3O_4 nanoparticles of 6 nm in mean size were prepared at the reaction duration of 2 hours. The larger and more agglomerated nanoparticles obtained at longer reaction duration could be attributed to the Ostwald ripening of smaller particles which agglomerated and grew into larger particles.

3.3 Effects of surfactant

Although PEO had successfully served as a surfactant to prevent agglomeration of Fe_3O_4 nanoparticles through steric stabilization, the shape of Fe_3O_4 nanoparticles were observed to be less spherical. This could be due to the weak interaction of $\text{Fe}(\text{acac})_3$ with PEO polymer chains as PEO does not have any carboxylic acid (-COOH) functional group for binding to $\text{Fe}(\text{acac})_3$ precursor covalently. Thus, oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$) was added during the synthesis in order to study its effect on the size and shape of Fe_3O_4 nanoparticles. As shown in Figures 3 (a) and (b), the Fe_3O_4 nanoparticles synthesized in the presence of oleic acid were more spherical in shape. Oleic acid contains -COOH functional group which can bind covalently to iron atoms, resulting in the observed more spherical particle shape. However, the mean size of Fe_3O_4 nanoparticles synthesized with various concentrations of oleic acid remained at 6 nm, which indicated that the concentration of oleic acid had no effect on the mean size of Fe_3O_4 nanoparticles formed.

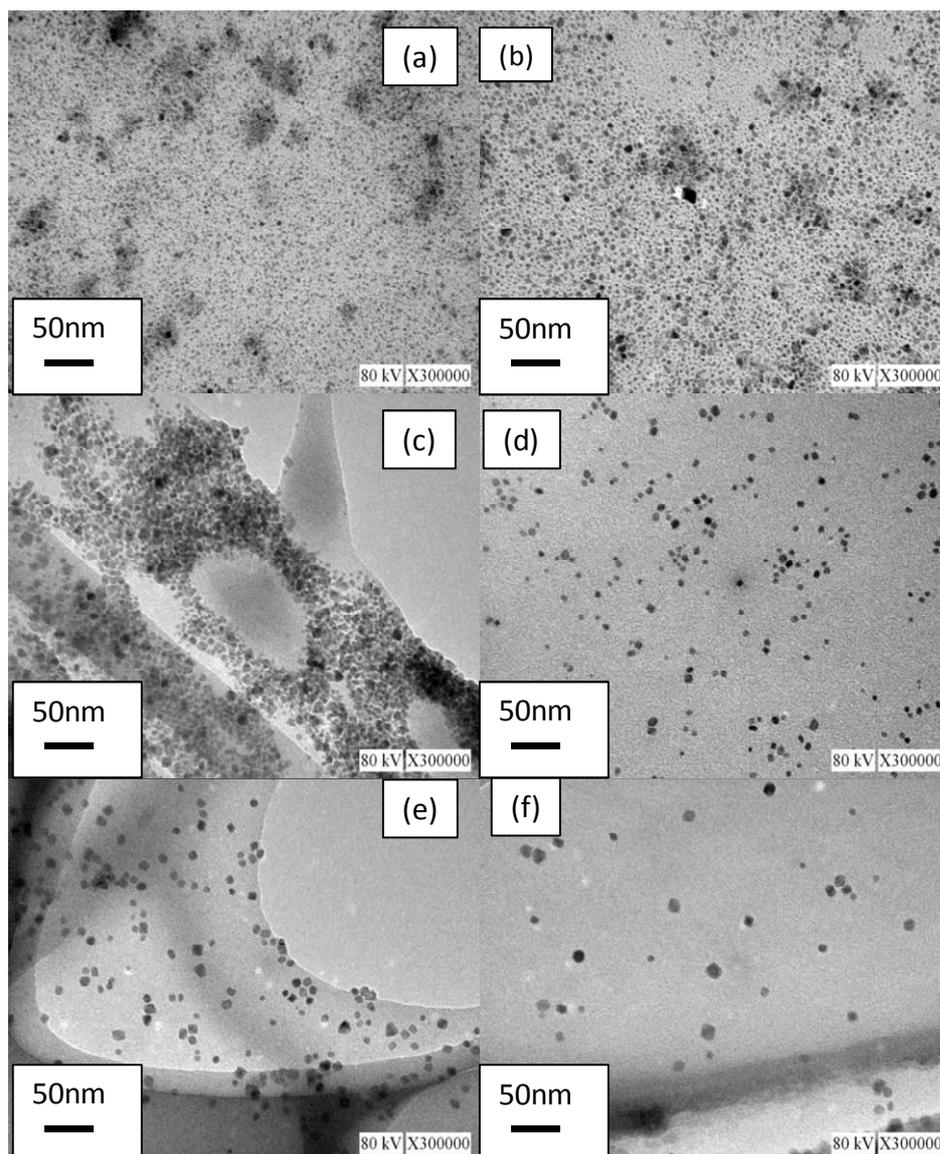


Figure 1. TEM images of Fe₃O₄ nanoparticles prepared from (a) 0.1 mmol; (b) 1 mmol; (c) 2 mmol; (d) 4 mmol; (e) 8 mmol of Fe(acac)₃ in 20 ml of PEO and (f) 8 mmol of Fe(acac)₃ in 10 ml of PEO

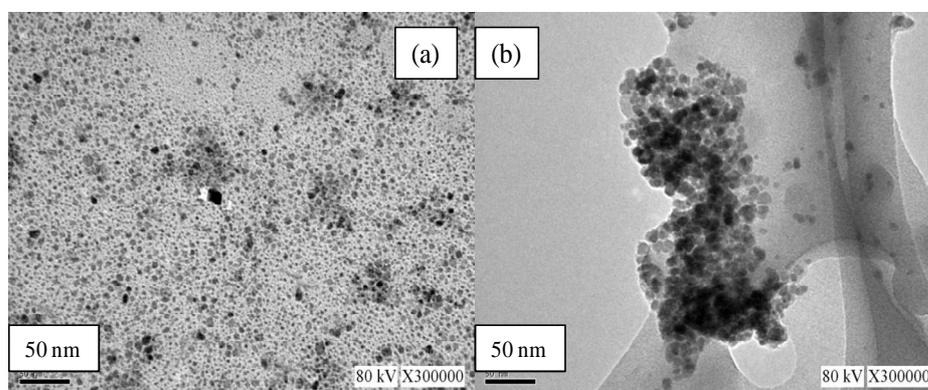


Figure 2. Fe₃O₄ nanoparticles prepared from 1 mmol of Fe(acac)₃ in 20 mL of PEO and refluxed for (a) 1 hour and (b) 2 hours.

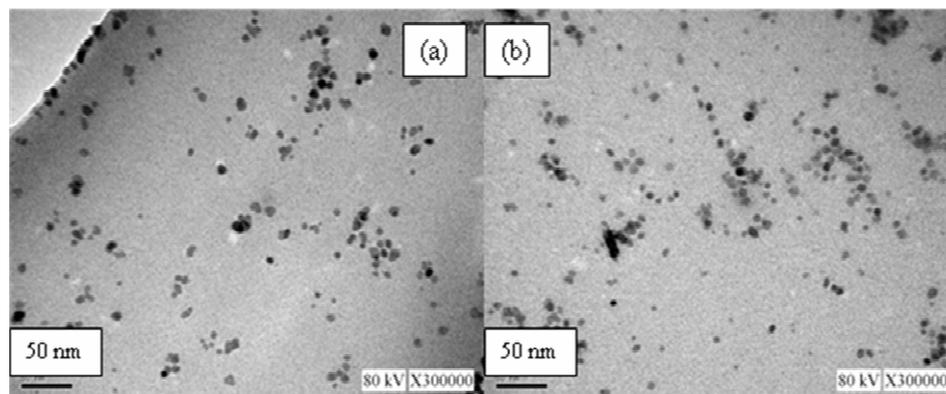


Figure 3 Fe₃O₄ nanoparticles prepared in the presence of (a) 1 mL and (b) 2 mL of oleic acid

Conclusion

In conclusion, Fe₃O₄ nanoparticles of various mean sizes were successfully synthesized by the thermal decomposition method. Our synthesis approach employed an environmental friendly solvent, PEO, as an alternative to organic solvent. PEO serves both as a solvent and a surfactant which prevents the agglomeration of Fe₃O₄ nanoparticles formed during synthesis. The size and shape of the Fe₃O₄ nanoparticles could be controlled by judicious choice of synthesis parameters such as precursor concentrations, reaction durations and surfactants.

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