

Preparation and stabilization of iron oxide nanoparticles using polymers

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Spherical Fe₂O₃ nanoparticles were prepared by the polyol process of organometallic precursor (Fe(acac)₃) in the presence of a reducing agent with a stabilizing agent. These were then heat-treated to make crystalline of Fe₂O₃ nanoparticles. Also, a seed-mediated growth technique was used to make them larger. TEM images of Fe₂O₃ nanoparticles made by the polyol process showed that the average particle size is 2.265 nm in diameter and the overall particle size distribution is narrow. It was confirmed that the diameter of Fe₂O₃ nanoparticles re-treated through the seed-mediated growth method had doubled by analyzing TEM images and the UV-visible spectrum. From XRD analysis, Fe₂O₃ nanoparticles transformed from amorphous to the hematite (α -Fe₂O₃) phase above 500 °C.

Key words: Fe₂O₃ nanoparticles, polyol process, reducing agent, stabilizing agent, seed-mediated growth technique.

Introduction

Nanoparticle materials have become the focus of increasing attention because the physical properties often differ significantly from those of the corresponding bulk material. Nanoparticles of metals, with a wide range of dimensions, are anticipated to yield size-dependent optical, electronic, magnetic and chemical properties suitable for applications in magnetic recording, optoelectronic devices, magnetic refrigeration, magnetic resonance imaging, as catalysts for bioprocessing [1-3]. Metal nanoparticles can be prepared in two distinct ways, that is, by division of bulk metals (a physical method) and by the growth of particles starting from metal atoms, which are obtained from molecular or ionic precursors (a chemical method). The latter method is based upon the use of soluble surfactant molecules, ligands and/or polymers, for assisting the growth of particles in the solution phase (micro emulsion technique) and it is much more suitable for tailoring small and uniform nanoparticles than the physical method.

In the synthesis of nanoparticles, important issues are particle size distribution (uniformity), size control, crystallinity/crystal structure and shape control. The particle sizes of nanoparticles can be controlled by systematically adjusting the reaction parameters, such as time, temperature, the concentration of reagents and stabilizing agents. Realizable particle sizes range in size from nanometer to a micrometer, by controlling particle size during synthesis by using competition bet-

ween nucleation and growth. Often nanocrystals are referred to as well-defined crystalline materials, whereas nanoparticles is a term used more generally for particles with diameters of 2-50 nm with variable crystallinity [4]. Transformation of the soluble precursors into the nanoparticle material has been accomplished by means such as thermal [5-7] or sonochemical [8-10] decomposition, polyol process [11, 12], electrochemical [13], chemical reduction [4, 14-15], etc. Until now noble metal colloids are prepared, and are stabilized by a particle stabilizer such as a polymer, surfactant, ligand, etc. In this way, small particle sizes and narrow size distributions of metal particles can be obtained. However, small metal particles are generally short-lived in aqueous solution as they rapidly agglomerate. Polymers or surfactants as a stabilizing agent can prevent the clustering and the destabilization of the metal colloids during storage. They use the results from the repulsive interaction between stabilizer adsorbed on the surfaces of metal particles. The stabilizer is easily dissolved in the solvent and must be thermally stable at the temperature used for the preparation and technical applications of the colloids. In particular, a polymer has been used as a stabilizing agent, and was demonstrated to have the effect of preventing aggregation and slowing down oxidation of iron nanoparticles by air. Iron particles are highly air-sensitive, both in the stable suspension and in the solid state, easily oxidizing into Fe₂O₃ [16].

In this work, in order to obtain monodispersed iron oxide nanoparticles sol, Fe(acac)₃ salts were dispersed in diethylene glycol with a reducing agent and a stabilizer under a polyol process. Also the seed-mediated growth method in which a seed nanoparticles were then grown to a larger size by the successive addition of iron oxide nanoparticles was used to grow iron oxide

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nanoparticles by adjusting the molar ratio of $\text{Fe}(\text{acac})_3$ salt to oleic acid. The molecular action of the reducing agent led to the reduction of the $\text{Fe}(\text{III})$ to the $\text{Fe}(\text{0})$ form and the stabilizing agent led to the formation of emulsion droplets possessing iron oxide nanoparticles surrounded by a stabilizing agent shell. The morphology, particle size, size distributions and structure of the nanoparticles are analyzed by transmission electron microscopy (TEM), image analysis, a UV-visible spectrometer, and X-ray diffraction (XRD).

Experimental

$\text{Fe}(\text{acac})_3$ salt was mixed in diethylene glycol with oleic acid (1:2 molar ratios of $\text{Fe}(\text{acac})_3$ and oleic acid) and heated to reflux under nitrogen atmosphere at 200°C ; the color of the solution gradually turned from red to red-brown. After, the addition of the stabilizing agent (dissolved in diethylene glycol) it was then heated at 200°C and the solution mixture turned from red-brown to dark-brown. The resulting dark-brown solution was aged at 250°C .

The smaller Fe_2O_3 nanoparticles which were produced in the previous process were used as a seed in diethylene glycol (DEG) with $\text{Fe}(\text{acac})_3$ salt and oleic acid. At this stage, the contents of oleic acid were 1:2 molar ratios of $\text{Fe}(\text{acac})_3$ and oleic acid. This was vigorously stirred and heated to reflux under nitrogen gas at 200°C . At this stage, the color of the solution gradually changed within 20-30 minutes. After, the addition of the stabilizing agent dissolved in DEG the solution mixture was heated to turn to completely dark-brown. The resulting solution was aged at 250°C . The particle size increased by aging at the high temperature by an Ostwald ripening process, in which smaller nanoparticles dissolve and deposit on the bigger nanoparticles. The growth of Fe_2O_3 nanoparticles may be stopped by rapidly decreasing the reaction temperature. The morphology, particle size and size distribution of iron oxide nanoparticles were investigated by transmission electron microscopy (TEM, Jeol-midel JEM-2000EXII). The size distribution and mean diameter were calculated by image analysis of more than 200 particle in TEM pictures of iron oxide nanoparticles. A drop of a dispersed sample was placed on a carbon-coated TEM grid. Photomicrographs were obtained operating at 200 kV and at 200,000 times magnification.

XRD was used to examine the crystallinity/crystal structure and phase constituents of samples prepared by the two processes. The XRD measurements were performed with powders packed completely in the hole of a holder of a Rigaku D/MAX RINT 2500 X-ray diffractometer operated at 40 kV and 100 mA. The incident wavelength was $\text{Cu K } \lambda = 1.5406 \text{ \AA}$ and detector moved step by step ($\Delta 2\theta = 0.05^\circ$) between 20° and 80° . The scan speed was $4^\circ \text{ minute}^{-1}$.

To evaluate the stability of Fe_2O_3 colloids, samples were exposed to UV light (4W-254 nm tube). The UV-visible absorption spectra were recorded with a UV-visible spectroscope (Scinco CO. LTD. S-2150). The absorption spectra of the Fe_2O_3 nanoparticles were obtained by subtracting the spectrum of a blank solution of diethylene glycol plus stabilizing agent from that of the sample solution containing the Fe_2O_3 nanoparticles.

Results and Discussion

The DLVO (Derjaguin, Landau, Verwy and Overbeek) theory is well known as means of explaining the stabilization of lyophobic solids. The basic idea of the theory is that the stability of a dispersion is determined by the sum of the attractive and repulsive forces between individual particles. The mutual attraction of particles is a consequence of dispersion forces, often called London-van der Waals forces, and the mutual repulsion of particles is a consequence of the electrostatic and steric forces [17].

In the case of reduction in an aqueous solution, the prepared Fe_2O_3 nanoparticles slowly formed large agglomerates and precipitated. The Fe_2O_3 colloid have van der Waals' forces and magnetic dipole-dipole interactions generated from residual magnetic moments, which tend to agglomerate and flocculate the particles. The polymer, which was a factor that influenced the growth rate and aggregation of particles, can prevent these phenomena. In general, different polymer types have different stabilities, however polymers used in this study showed almost the same stability.

The formation mechanism of Fe_2O_3 nanoparticles were followed. The first step for synthesis of iron oxide nanoparticles is the reduction of Fe ions to Fe atoms. Usually the synthesis of metal nanoparticles starts from reduction of metal ions to metal atoms. The reduction potential of metal ions depends on the type of metal ions and on the environment surrounding the metal ions, such as the presence ligands and solvents. In this work, we used oleic acid as a reducing agent. The molecular structure of oleic acid lead to a reduction step with the reaction $\text{Fe}(\text{acac})_3 \text{ salt} \rightarrow \text{Fe}(\text{III}) \rightarrow \text{Fe}(\text{0})$ form. The second step was, an aggregation of Fe ions to form Fe nuclei. At this stage, Fe_2O_3 nanoparticles are not produced. In the third stage, Fe nuclei grow to form Fe_2O_3 nanoparticles. The appearance of Fe_2O_3 nanoparticles could be detected by a color change. Finally, stabilization of the iron oxide nanoparticles is required. The polymer molecules played a role in preventing the Fe_2O_3 nanoparticles from aggregation.

The particle morphology, size and size distribution of the Fe_2O_3 nanoparticles were obtained by transmission electron microscopy. The TEM images and size distribution are shown in Fig. 1 and Fig. 2 for Fe_2O_3 nanoparticles in the presence of the polymer. They appear to be spherical in shape and fairly uniform in

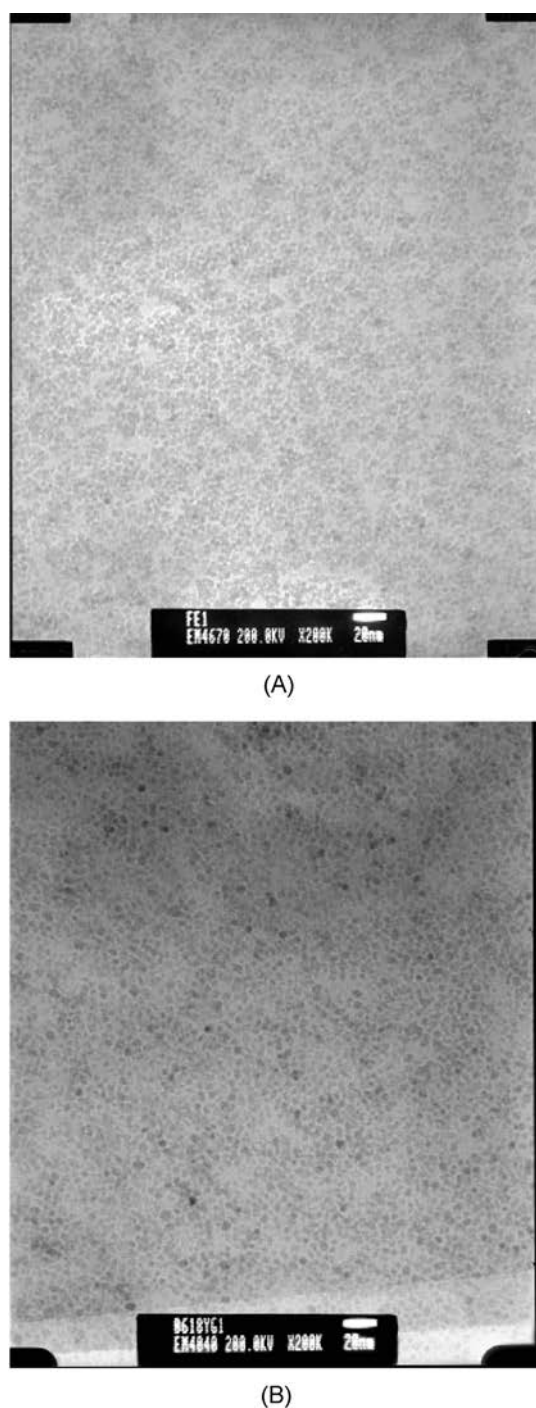


Fig. 1. TEM picture of different sized iron oxide nanoparticles. (A) Seed (B) 1st growth.

size with a mean diameter of 2.265 nm, 5.250 nm respectively. Among these, the 2.265 nm sized particles were used as seeds to make the larger nanoparticles using the seed-mediated growth method. Figures 1-2 show the size distribution of iron oxide nanoparticles. The particle size distributions depend on the interplay between the nucleation and growth that occurs at the intermediate stage. Because the ratio of reducing agent to $\text{Fe}(\text{acac})_3$ salt and content of stabilizer influences the nucleation and growth reactions, those should be

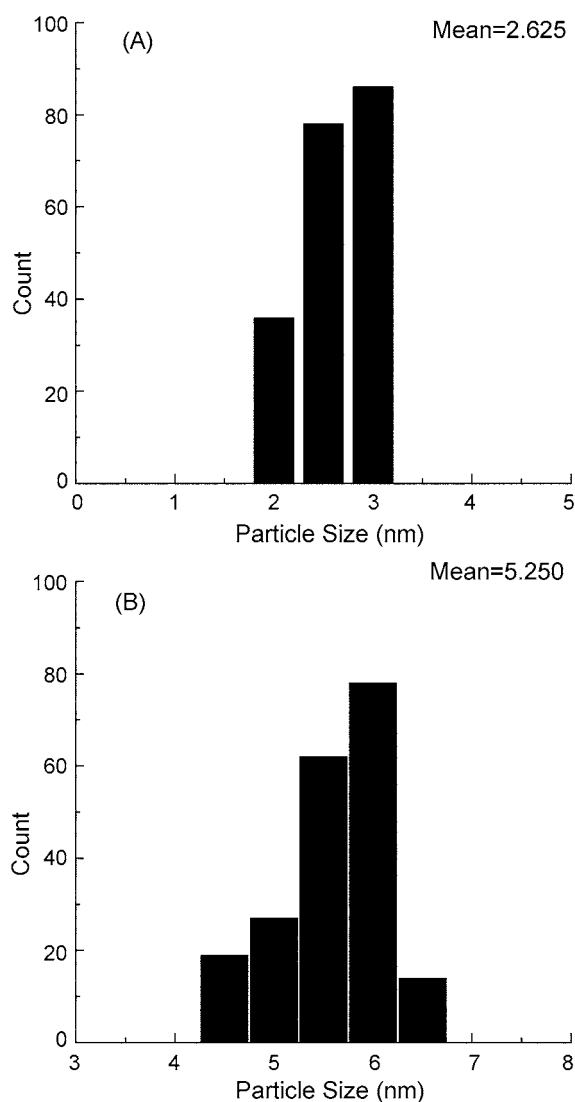


Fig. 2. Histogram of the size distributions of Fe_2O_3 nanoparticles. (A) Seed (B) 1st growth.

selected carefully. In our study, the size distribution was relatively narrow and aggregation of particles were very low due to a suitable amount of stabilizer agent and oleic acid.

Colloidal dispersions of metals exhibit absorption bands or broad regions of absorption in the ultraviolet-visible range. These bands are due to the excitation of plasma resonances or interband transitions, and they are thus a very characteristic property of the metallic nature of the particles. Figure 3 shows the UV-visible absorption spectra of Fe_2O_3 nanoparticles prepared by the reduction of oleic acid with a stabilizer in the presence of the 2.625 nm seeds. Usually, the narrow peak indicates a narrow particle size distribution and the plasmon max shifts to longer wavelength with an increase in particle size. This red shift is presumably due to the formation of larger Fe_2O_3 nanoparticles. The TEM figures showed that the nanoparticles produced through the 1st growth process had a larger diameter

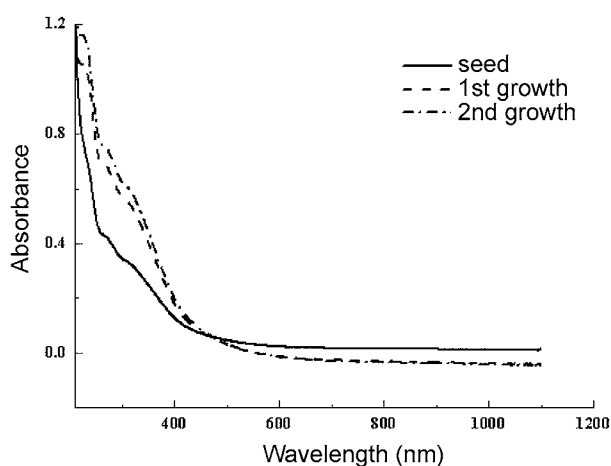


Fig. 3. UV-visible spectra of Fe_2O_3 nanoparticles of various sizes.

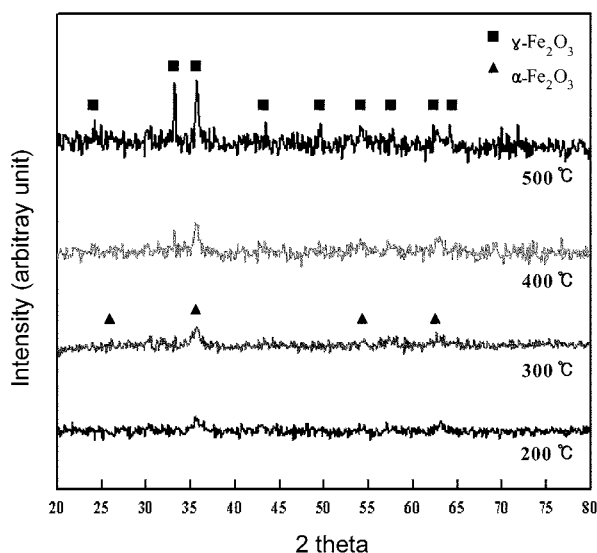


Fig. 4. X-ray diffraction pattern of Fe_2O_3 nanocrystallites.

than the seed particles. Continuously growing the nanoparticles by using a 2nd growth process, the particle size became increasingly larger which was verified through the UV-visible spectroscopy study.

Figure 4 shows the XRD patterns of calcined iron oxide particles heated at a rate of 4 K minute^{-1} under a nitrogen atmosphere, which was then quenched to room temperature. Samples were annealed at 200, 300, 400, and 500°C for 4 hours. Before the calcination, iron oxide powders are amorphous, exhibiting extremely broad diffraction maxima. However, it is clear that calcination of the iron oxide powder show diffraction peaks corresponding to an extended crystalline structure. Although our iron oxide powders do not show sharp peaks, still diffraction peaks can be resolved. In the X-ray diffraction analysis reflections of iron oxide were noted, corresponding to $\gamma\text{-Fe}_2\text{O}_3$ and transformed Fe_2O_3 through oxidation at temperatures around 300°C. Then phase transformation from maghemite ($\gamma\text{-Fe}_2\text{O}_3$) to hematite ($\alpha\text{-Fe}_2\text{O}_3$) occurred at 500°C. A further increase

in temperature, above 500°C, gave only $\alpha\text{-Fe}_2\text{O}_3$.

Conclusions

Spherical iron oxide nanoparticles with a narrow size distribution were prepared by a polyol process of $\text{Fe}(\text{acac})_3$ salt in the presence of a polymer and oleic acid. To make larger Fe_2O_3 nanoparticles, a two-step seed-mediated growth method was used. Polymers were used as a stabilizing agent, and demonstrated to have the effect of preventing aggregation. The results demonstrated that a seed-mediated growth process can generate size-controlled nanoparticles. Moreover, in the case of crystal structures, magnetite was formed at 200°C and transformed to $\gamma\text{-Fe}_2\text{O}_3$ through oxidation at 300°C. Later the Fe_2O_3 structure changed from maghemite to hematite (γ to α -phase) when the annealing temperature was 500°C. The seed-mediated growth technique or its modified version may be useful for other systems of nanoparticles for producing particles of desired sizes.

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