Synthesis of poly (ethylene glycol) (PEG)-capped Fe$_3$O$_4$ nanoclusters by hydrothermal method.

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Abstract. In the present work, we report the synthesis of poly (ethylene glycol)-capped iron oxide nanoclusters of spherical morphology by hydrothermal method. The synthesized particles were characterized by X-ray powder diffraction (XRD), Dynamic Light Scattering (DLS), Field Emission Scanning Electron Microscope (FESEM)/Energy dispersive spectroscopy (EDS) and Fourier Transform Infrared Spectroscopy (FT-IR). The effects of reaction parameters such as reaction temperature, time and hydrolysis ratio on the properties of PEG capped Fe$_3$O$_4$ have been studied. XRD confirms the presence of cubic spinel structure of Fe$_3$O$_4$ phase. FESEM images show spherical morphology of particles and particle sizes are ~ 100 to 200 nm. DLS analysis shows the hydrodynamic size to be ~ 151 to 512 nm for PEG capped Fe$_3$O$_4$ nanoclusters dispersed in water. FT-IR confirms coating of PEG on Fe$_3$O$_4$ surface.

1. Introduction

Magnetic nanoparticles (MNPs) have widespread applications like magnetic recording, defect sensors[1], ion sensors[2], optical devices[3], contrast agent for magnetic resonance imaging (MRI)[4], biomedical applications such as therapeutic agents for hyperthermia[5], targeted drug delivery[6], etc. At a particular size they show superparamagnetic behaviour where the particle will react only when the field is applied and do not exhibit any coercivity, this behaviour is highly preferred for magnetic hyperthermia and magnetic drug targeting. The two highly preferred phases of iron oxide nanoparticles are magnetite (Fe$_3$O$_4$) and maghemite ($\gamma$-Fe$_2$O$_3$) because of their excellent superparamagnetic behaviour and biocompatibility. Bare magnetic nanoparticles have a tendency to aggregate due to strong magnetic dipole-dipole and van der Waals interactions between particles. Therefore it is necessary to coat it with surfactants to prevent aggregation. One of the common approaches undergone for coating nanoparticles is by core-shell method. The outer shell coating can be organic (e.g., polymers) or inorganic (e.g., carbon, silica) materials [7].

Many synthesis techniques have been developed for the preparation of capped iron oxide nanoparticles. These techniques include hydrothermal[7], co-precipitation followed by reduction[8], microemulsion, thermal decomposition and sol-gel[3]. By hydrothermal method nanocrystals of a broad range can be easily synthesized through liquid-solid-solution reaction [9]. The method works on the basis of phase separation (crystallization) at the interfaces of three phases above. The advantage of
hydrothermal method over other techniques is that it can give very narrow size distribution and very good shape control. These advantages along with a good coating can employ these particles for applications where stability is a concern. In this work, we synthesized poly (ethylene glycol) (PEG)-capped magnetite nanoparticles of spherical morphology using hydrothermal method. The properties of the obtained particles where studied using X-ray powder diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM), Fourier Transform Infrared spectroscopy (FT-IR), and Dynamic Light Scattering (DLS).

2. Experimental Details
2.1 Materials
For synthesis, FeCl₃·6H₂O, Ethylene Glycol, Sodium Acetate and poly (ethylene glycol) (MW: 600) has been procured from E-Merk and used without further purification. Milli-Q water with a resistivity of 18MΩcm was used in all experiments.

2.2 Preparation procedure
Magnetite nanoclusters are synthesized by hydrothermal method[10]. The precursors were prepared with 0.003mol FeCl₃·6H₂O, 0.80mol ethylene glycol, 0.018mol of Sodium acetate, 0.0003mol of PEG and different amounts of water was added for different samples to vary hydrolysis ratio water. The mixture of precursors is mixed homogeneously at a constant stirring speed of 600 rpm and temperature of 45°C. Once the mixture forms a clear homogeneous solution it is transferred in to a teflon lined autoclave and was made to undergo reaction at different temperatures (160°C, 180°C, 200°C) at different times (8h, 16h, 24h) for different samples. Once the reaction is completed it is allowed to cool down to room temperature. Further the sample was washed with ethanol and distilled water 3 times to remove impurities. The PEG coated samples were dried in vacuum oven at 50°C for 45min.

2.3 Characterization
The XRD measurements were carried out using Rigaku Ultima IV instrument. A scan rate 20°/min with a step size of 0.005° was maintained for the 2θ values in the range 20° to 75° using Cu Kα (λ = 1.54 Å) radiation in the Bragg- Brentano geometry. FESEM images were obtained from Zeiss Field Emission Scanning Electron Microscope, with field emission gun operating at 10 kV. Energy Dispersive spectroscopy for elemental analysis was done using Bruker attachment on SEM machine, EHT was set at 20 kV. FT-IR studies to evaluate the surfactant species were done using Thermo Scientific iS10 FT-IR spectrometer from the spectral range 4000 cm⁻¹ to 500 cm⁻¹. Pellets made with KBr powder and magnetite nanoparticles were used for IR absorption studies. The hydrodynamic size distribution of the nanoparticles was measured using Malvern Zeta Sizer which uses backscattering technology.

3. Results and discussions
Hydrothermal method is one of the most versatile and convenient method to synthesis iron oxide nanoparticles. Polyol-mediated hydrothermal synthesis has been followed in this work[11]. Precursors were dissolved in ethylene glycol to form a homogeneous solution. The solution was then transferred to an autoclave and was heated for temperatures above 160°C and for times from 8 to 24h. As the solution is heated, the precipitation of particle proceeds by two steps: 1) Nucleation and 2) Particle growth. The relative rates of nucleation and particle growth decides size, shape and degree of aggregation. When the concentration of the reduced species in the solution reaches supersaturation, nucleation occurs spontaneously and is followed by particle growth. Particle growth mainly depends up on the time of the process. In the present study, hydrolysis ratio (ratio of water involved to the amount of metal precursor) was varied there by changing the supersaturation level thus controlling nucleation and particle growth. Also, syntheses were carried out at two different process times, 8h and 24h, to examine the change in particle sizes. Temperature was also been varied to probe the effect of
reaction rate on the size and morphology of the particles. Table 1 lists the different experimental conditions and the corresponding sample labels.

**Table 1.** Experimental conditions for hydrothermal synthesis of iron oxide nanoclusters

| Sample | Hydrolysis ratio (h) | Time (hr) | Temperature (°C) |
|--------|----------------------|-----------|------------------|
| S1     | 12                   | 8         | 200              |
| S2     | 12                   | 8         | 160              |
| S3     | 6                    | 24        | 180              |
| S4     | 6                    | 8         | 180              |
| S5     | 18                   | 8         | 180              |
| S6     | 6                    | 8         | 180              |

3.1 *X-ray Powder Diffraction (XRD) Analysis*

Figures 1(a-c) show the XRD patterns of the PEG-capped Fe₃O₄ nanocluster samples S1 to S6. The diffraction peaks at 2θ value of 29.83°, 35.19°, 42.95°, 56.84° and 62.44° correspond to (200), (311), (400), (511) and (440) planes of cubic spinel structure of Fe₃O₄ (JCPDS: 79-0419).

![Figure 1](image-url)

**Figure 1.** (a), (b) and (c) shows XRD comparison for S1 and S2, S3 and S4, S5 and S6.

For S1 and S2 hydrolysis ratio and reaction time was kept constant at 12 and 8h while temperature was varied. The crystallite size for the most dominant peak as calculated from Scherer equation are 38.1 nm
and 20 nm, respectively. This shows that increasing reaction temperature will permit a higher nucleation rate allowing more particles of smaller size to form and grow rapidly. For sample S3 and S4 hydrolysis ratio and temperature were fixed at 6 and 180°C and time was varied, here the crystallite sizes are 21 nm and 16 nm, respectively, which shows that increasing reaction time increases crystallite size owing to better diffusion of particle atoms which helps to grow the precipitated particles. For S3 some amount of γ-Fe$_2$O$_3$ phase has been formed this may be due to the oxidation of Fe$_3$O$_4$ at longer times. For S5 and S6 the time and temperature are kept constant at 8 h and 180°C and hydrolysis ratio was varied. Increasing the hydrolysis ratio has seen to increase the crystallite size, for S5 crystallite size is 25.1 nm and for S6 it is 16.0 nm. Increasing the water content could delay the supersaturation of the reaction mixture facilitating nucleation to continue even after the concentration drops below supersaturation. This would allow more particles to diffuse into already formed ones. Table 2 shows a detailed comparison of sizes obtained from XRD, FESEM and DLS for samples S1 to S6.

3.2 Field Emission Scanning electron microscope studies

Figure 2 (a), (b), and (c) corresponds to FESEM images of S1, S3 and S5 respectively. The images show that particles are not perfectly spherical in shape and are highly polydisperse. This can be due to poor stabilization owing to the lower molecular weight of PEG (600) used for steric stabilization. Cluster formation is clearly visible from the images; this can be attributed to the strong dipole-dipole interactions between each particle. For all the cases cluster size is ~100 to 200 nm (Table 2). Figure 3 shows a typical EDS analysis for PEG capped Fe$_3$O$_4$ (sample S1) giving 63% of Fe and 37% of O.
Figure 3. EDS analysis for PEG capped Fe$_3$O$_4$ nanocluster (S1)

Table 2. Comparison of crystallite size, particle size and hydrodynamic diameters of samples S1 to S6

| Sample | Crystallite size (nm) | Particle size (nm) | Hydrodynamic diameter (nm) |
|--------|----------------------|--------------------|---------------------------|
| S1     | 38.1                 | ~150               | 392.2                     |
| S2     | 20                   | ~100               | 240.8                     |
| S3     | 21                   | ~98                | 413.1                     |
| S4     | 16                   | ~88                | 151.3                     |
| S5     | 25.1                 | ~200               | 512.2                     |
| S6     | 16                   | ~170               | 468.7                     |

3.3 Dynamic Light Scattering Studies

Figure 4 shows hydrodynamic diameters of PEG capped Fe$_3$O$_4$ (sample S1). Table 2 shows detailed comparison of hydrodynamic sizes for sample S1 to S6. In all the cases the hydrodynamic sizes are higher as compared to particle size obtained from FE-SEM. The higher diameter value obtained in DLS measurement may due to aggregation and the contributions from solvent molecules being adsorbed on particle surface, canted surface or may be due to surfactant layer. There is a significant distribution at higher sizes which can be attributed to aggregation and polydispersity.

3.4 FT-IR Studies

Figure 5 shows the FT-IR spectra of PEG-capped Fe$_3$O$_4$ nanocluster (S1). Peaks at 3424.55cm$^{-1}$, 1631.58cm$^{-1}$, 1399.87cm$^{-1}$, 1086.3cm$^{-1}$ and 564.95cm$^{-1}$ confirms that poly(ethylene glycol) is successfully coated over Fe$_3$O$_4$. The characteristic peak at 564.95cm$^{-1}$ and 1399.87cm$^{-1}$ is due to Fe-O bending and Fe-O stretching. The peak at 3424.55cm$^{-1}$ can be attributed to the presence of -OH group on the surface of Fe$_3$O$_4$ nanoparticles. The peaks at 1631cm$^{-1}$ and 1086.3cm$^{-1}$ represents -COO-stretching and -C-O-C-stretching respectively.
4. Conclusion
PEG-capped Fe$_3$O$_4$ nanoclusters have been successfully synthesized using hydrothermal method. The effect of reaction parameters like hydrolysis ratio, time and temperature were studied. The size, morphology, organic contents and hydrodynamic size were studied using XRD, FESEM, FT-IR, and DLS, respectively. The experiments revealed that higher temperature, hydrolysis ratio and longer time will increase the particle size due to enhanced reaction kinetics, continued nucleation below supersaturation, and more diffusion, respectively.

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