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One step facile synthesis of ferromagnetic magnetite nanoparticles



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ABSTRACT

The ferromagnetic properties of magnetite (Fe_3O_4) were influenced by the nanoparticle size, hence importance were given to the synthesis method. This paper clearly shows that magnetite nanoparticles were successfully synthesized by employing one step controlled precipitation method using a single salt (Iron(II) sulfate) iron precursor. The acquired titration curve from this method provides vital information on the possible reaction mechanism leading to the magnetite (Fe_3O_4) nanoparticles formation. Goethite ($\alpha\text{-FeOOH}$) was obtained at pH 4, while the continuous addition of hydroxyl ions (OH^-) forms iron hydroxides ($\text{Fe}(\text{OH})_2$). This subsequently reacts with the goethite, producing magnetite (Fe_3O_4) at pH 10. Spectroscopy studies validate the magnetite phase existence while structural and morphology analysis illustrates cubic shaped magnetite with an average size of 35 nm was obtained. The synthesized magnetite might be superparamagnetic though lower saturation magnetization (67.5 emu/g) measured at room temperature as compared to bulk magnetite. However the nanoparticles surface anisotropy leads to higher remanence (12 emu/g) and coercivity (117.7 G) making the synthesized magnetite an excellent candidate to be utilized in recording devices. The understanding of the magnetite synthesis mechanism can not only be used to achieve even smaller magnetite nanoparticles but also to prepare different types of iron oxides hydroxides using different iron precursor source.

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1. Introduction

Magnetite (Fe_3O_4) phase arises from the inverse spinel structure with Fe(III) ions which is distributed randomly between octahedral and tetrahedral sites, while Fe(II) ions exists only in octahedral sites. These diverse lattices and valence states of iron (Fe(II) and Fe(III)) contributes to the magnetite magnetic properties making it very feasible for biomedical applications (drug delivery, separation, sensors), and electromagnetic materials [1–3]. The nanoparticles magnetic properties are dependent on the size, size distribution, shape and surface chemistry [4,5]. In order to control these properties, the focus has been given to synthesis parameters of iron oxide. Various methods have been reported and proven effective in synthesizing magnetite nanoparticles such as hydrothermal, solvothermal, co-precipitation, sol-gel, sonochemical and high temperature organic phase decomposition [6–10].

Magnetite nanoparticles were typically formed by complexing precipitates of goethite ($\alpha\text{-FeOOH}$) and ferrous hydroxide ($\text{Fe}(\text{OH})_2$). Existing synthesis methods involves a relatively complex synthesis route by mixing the Fe(II) and Fe(III) chloride based on the magnetite stoichiometric composition of $\text{Fe}^{(II)}/\text{Fe}^{(III)}=0.5$ [6,8–11]. Controlled precipitation is one of the simplest and highly

potential method for the synthesis of magnetite nanoparticles [12]. Parameters such as pH, salt precursor cation, concentrations, stoichiometric ratio of ferrous to ferric hydroxides and precipitating agent (base) type and concentration can be tailored and navigated to achieve different structures and phase purity (single phase) [1,13,14]. One critical parameter that plays a critical role in magnetite crystal structure formation is the iron precursor solution.

A simplified method in synthesizing magnetite nanoparticles is by using not only an organic solvent-free system but also capitalizing on the effect of one anion precursor on the $\alpha\text{-FeOOH}$ crystal growth [15]. Subsequently, by controlling the synthesis parameters, the exact ratio of $\text{Fe}(\text{OH})_2$ and $\alpha\text{-FeOOH}$ and can be achieved through in-situ hydrolysis. In this paper, single phase magnetite nanoparticles were synthesized by controlled precipitation method using sulfate (SO_4^{2-}) anion as the Fe(II) precursor. The role of sulfate (SO_4^{2-}) anion on purity, particle size and magnetic properties were investigated while the synthesis mechanism and pathway were determined from the titration curve.

2. Materials and methods

2.1. Synthesis of magnetite nanoparticles (MNPs)

All chemicals used are of analytical grade and were purchased

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from Merck. The iron oxide (magnetite) catalyst was synthesized via controlled precipitation technique. The iron oxide precursor used was 0.1 M iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) while 0.45 M sodium hydroxide (NaOH) was used as the precipitating agent. The synthesis was conducted using a water bath to regulate the temperature at 45 °C. NaOH was added to 100 mL iron solution with a fine control of rate of addition at 5 ml/min using an auto-titrator (Mettler Toledo DL50). The solution was continuously stirred and the pH changes were monitored throughout the titration process and were terminated at pH 12. The precipitated solution was then filtered under vacuum and the solid obtained were dried in an oven at 50 °C for 24 h to remove the excess water.

2.2. Characterization of magnetite nanoparticles (MNPs)

The synthesized catalyst was then subjected to structural and compound analysis using Bruker's X-Ray Diffractometer (XRD). The diffractograms were obtained using a $\theta/2\theta$ goniometer and a Scintillation counter detector. The data sets were collected in reflection geometry in the range of $2^\circ \leq 2\theta \leq 80^\circ$ with a step size of $\Delta 2\theta = 0.02^\circ$. Phase analysis was done and phase purity was determined using High Score Plus software. Fourier Transform Infrared (FTIR) employing potassium bromide (KBr) pellet technique was used to identify the functional group and Raman spectroscopy analysis was done to compliment the results from FTIR. The Raman spectra were obtained using a Renishaw inVia Raman microscope with a $50\times$ objective using 514 nm laser. The laser is set at 0.1 mW (100%) with 1800 l/mm grating. The surface morphology of the particles was observed using Scanning electron microscope (SEM) and the particles lattice plane were scrutinized using Transition electron microscope (TEM) while the particles size distribution (PSD) was calculated using Malvern Zetasizer Nano. The magnetite particle magnetism hysteresis loop measurement was conducted using Lake Shore vibrational sample magnetometer (VSM) in the solid state obtained at room temperature in a magnetic field range of -10 to $+10$ kOe.

3. Results & discussion

3.1. Mechanism of magnetite crystal growth

The route of magnetite formation was determined by scrutinizing the solution physicochemical changes through the titration curve (Fig. 1) analysis. Two inflection points were observed

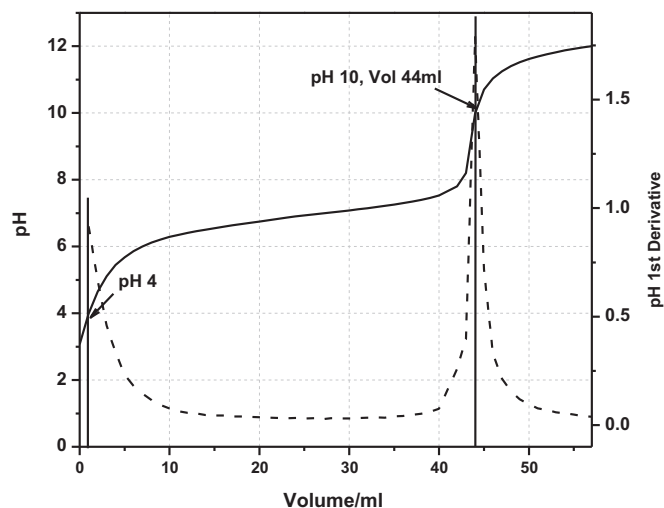
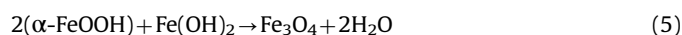
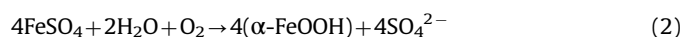


Fig. 1. Titration curve of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with a standard solution of 0.45 M NaOH.

suggesting the hydrolysis of FeSO_4 to magnetite nanoparticles occurs in kinetically control pathways. There is an immediate steep increase of pH once NaOH is added, suggesting a first change of phase equilibria. This first inflection point depicted in the titration curve is from the partial hydrolysis of FeSO_4 to goethite ($\alpha\text{-FeOOH}$) as sulfate ion promotes goethite particle growth at pH 4 as shown in Eq. (2) [16,17]. The magnetite formation mechanisms were determined as follow.



FeSO_4 continuously deprotonates, supplying Fe^{2+} and with the addition of hydroxyl ions (OH^-) from NaOH, forms iron(II) hydroxides, ($\text{Fe}(\text{OH})_2$) which is shown in Eq. (3). The goethite formed earlier serves as a crystal growth template [17]. The olation process continues with addition of hydroxide ions until the ratio of $[\text{FeSO}_4]/[\text{NaOH}]$ was 0.5 forming the magnetite nanoparticles which was concluded from the steep inflection point seen in the titration curve at pH 10 [18]. The magnetite particles continue to aggregate with excess supply of hydroxyl ions until the addition were stopped at pH 12.

3.2. Magnetite nanoparticles characterization

XRD Diffractograms (Fig. 2) shows peak characteristics indexed to Iron Oxide, Fe_3O_4 , Magnetite with cubic phase, (PDF File 089-0691). Rietveld structural analysis reveals 98% quantification. Prominent peaks that matched the magnetite phase (Table 1) were at 35.5° (311), 36.1° (220), 62.6° (440) and 57.0° (551) while the lattice constant calculated was 8.385 Å which is similar to the theoretical value of 8.396 Å [2]. There are no sulfates remaining in the sample indicating that the complexing sodium sulfate particles resulting from the hydrolysis were fully dissolved in the excess water and were able to be removed. The crystallite size was calculated based on XRD peak broadening using the Scherrer's equation. The reflection broadening at 35.5° computes the

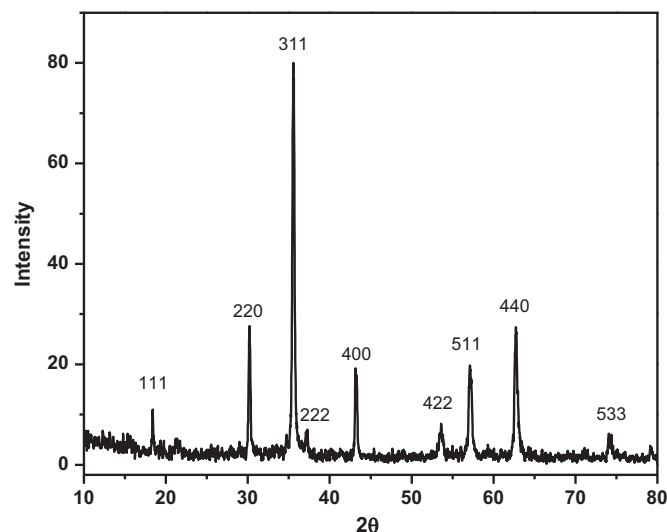


Fig. 2. X-Ray powder diffractogram of synthesized magnetite.

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