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Influence of Voltage Variation on the Size of Magnetite Nanoparticles Synthesized by Electrochemical Method

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Abstract: Present research deals with the synthesis of highly pure, large scale, economical and mono-dispersed magnetite nanoparticles by using electrochemical method at a low temperature of 80 °C. We have tried to indigenously develop two-electrode electrochemical cell which was later used to synthesize Iron oxide nanoparticles with different size ranges by varying different parameters. The setup brings up the oxidation of the anode and reduction of the cathode. NaCl was used as an electrolyte. For each of the sample obtained, the structural investigation was carried out by measuring XRD (X-ray diffraction). The morphology was studied using SEM (Scanning electron microscopy) and TEM (Transmission electron microscopy). Elemental composition was verified using energy dispersive X-ray spectroscopy (SEM-EDX).

Key words: Electrochemical, magnetite, nanoparticles, Fe_3O_4, electrolyte.

1. Introduction

Magnetite nanoparticles have drawn a lot of attention due to their good biocompatibility, super-paramagnetism, and applications in hyperthermia, cancer cell therapy [1-3], and so on. Also magnetite has been already used in bulk industrial production processes as catalysts for alcohol oxidation and NH_3 production [4-6], in wastewater purification [7, 8] and as pigment and related industries [9]. In natural state, sixteen pure phases of iron oxide are known to mankind till date [10]. Due to their small size, they exhibit different electrical, chemical, magnetic and optical properties from the bulk materials [11]. Shape and size strongly affects the dispersibility in various solvents and properties exhibited by magnetite nanoparticles.

Therefore, researchers are trying to explore economical, easy and reproducible methods for synthesizing Fe_3O_4 nanomaterials. Synthesis of iron oxide nanoparticles through co-precipitation method is quite difficult due to the instantaneous nature of this reaction which makes it difficult to control the nucleation process [12]. Some of the prominent methods currently used by researchers are: hydrothermal [13, 14], wet-milling [15], sol-gel [16], pyrolysis [17], electrochemical [18, 19], etc. Among these, electrochemical method is the most promising but not exhaustively researched method for the synthesis procedure. For example, the precise influence of various parameters such as voltage, temperature, electrolyte, electrode spacing, ripples factor, stirring rate affecting the nucleation process, on the growth of Fe_3O_4 nanoparticles is not fully understood yet.

In the present study, we have synthesized magnetite nanoparticles by electrochemical process using two-electrode system. We have tried to find out the effect of voltage on the particle morphology and size of magnetite nanoparticles. A preliminary hypothesis concerning the reaction mechanism during two electrode electrochemical synthesis of Fe_3O_4 nanoparticles is also proposed. All the results and data such as crystal structure, morphology, particle size and elemental composition were investigated using, XRD

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(X-ray diffraction), SEM (Scanning electron microscopy), EDX and TEM (Transmission electron microscopy) for each prepared sample.

2. Experiment

2.1 Synthesis Procedure

Electrochemical studies were carried out in our indigenously developed classical two electrode electrochemical cell (Fig. 1). Pure iron electrodes in the form of cylindrical rods with a diameter of 10 mm and length of 70 mm were used to form anode and cathode. The experimental cell was housed in a conventional 250 ml borosil glass beaker. The electrodes were first kept in dilute nitric acid (HNO_3, Merck) for 30 min to clean and remove the oxide layer already present. Then they were polished with zero number sandpaper and further cleaned and sonicated in ethanol for 5 min before the commencement of experimental run. After drying of the electrodes, they were spaced 4 cm apart and fixed to keep the distance between electrodes constant.

Two samples were prepared under varied voltages keeping other parameters as same. The electrolyte solution was prepared by adding 2 M sodium chloride (NaCl, Merck) in double distilled de-ionized water. As such no capping agent was used. 200 ml of double distilled de-ionized water was taken as the medium for electrolyte cell to operate. Electrochemical cell was operated at a voltage of 4 V Direct Current (DC) and 2 V DC under controlled and careful stirring. The samples were named as A for 2 V DC and B for 4 V DC.

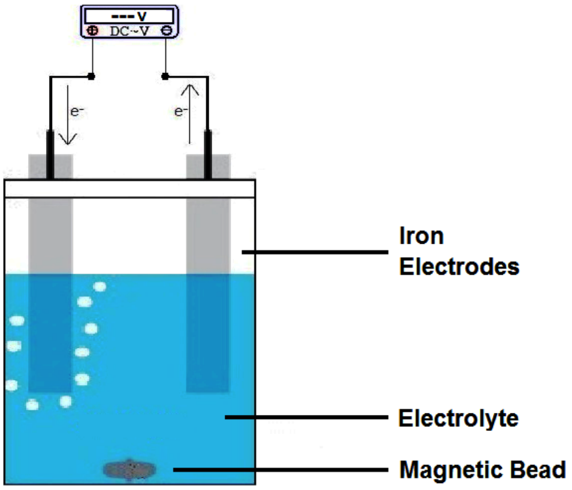

Fig. 1 Schematic diagram of our electrochemical cell.

After few minutes of operation, the electrolytic solution changed its color to yellow-brown solution before turning into black precipitate. The experimental run was carried out for 15 min and kept separately for further processing. After the experimental run, the precipitate obtained was washed and purified several times using ultracentrifugation and decantation method to achieve powder sample for further characterization.

2.2 Structural Characterization

For each of the sample obtained, crystal structure investigation was carried out by measuring X-ray diffraction using Rigaku MiniFlex™ II benchtop XRD system with a CuK_α (λ = 1.54 Å) radiation source. For XRD, powdered sample were used for both the samples. Their surface morphology and particle size was analyzed using scanning electron microscopy (Zeiss SEM for sample A and Mira 3 Tescan SEM for sample B) and transmission electron microscopy (JEM-2100F with an operating voltage of 150 kV for sample A only). Elemental composition was verified using energy dispersive X-ray spectroscopy (EDX integrated system with Zeiss EVO 40). Samples for SEM-EDX were prepared by dropping few drops of solution containing iron oxide nanoparticles upon a silicon substrate. Then the substrate was heated for 15 min to obtain a thin film. This prepared sample was further coated with a conductive thin film (< 2 nm) of gold. Samples for TEM were prepared by adding a drop of solution containing cupric oxide nanostructures to a circular carbon coated copper TEM grid. Then the as prepared grid was kept under IR lamp to dry.

3. Results

3.1 X-Ray Diffraction

X-Ray Diffractogram of sample A and B are shown in Fig. 2. Powder XRD data of the specified compositions were compared with JCPDS Card 075627. They fit well with magnetite structure with a space group Fd-3m (227). Both the powdered samples display cubic system with face-centered lattice.

3.2 Scanning Electron Microscopy

Secondary electron images of sample A (Fig. 3) and sample B (Fig. 4) revealed mono-dispersed spherical nanoparticles with an average particle size of 50 nm for low applied voltage (2 V) whereas for high applied voltage (4 V) the average particle size comes out to be 100 nm. SEM-EDX spectra of sample A and B are shown in Figs. 5a and 5b, respectively. Both of these spectra show Fe-K and O-K peaks. The Au peak at 2.2 KeV arises due to the gold coating.

3.3 Transmission Electron Microscopy

The TEM bright field images at low and higher magnification are shown in Fig. 6a and 6b respectively. They reveal nearly spherical nanoparticles with an average particle size in the range of 30 to 50 nm for low applied voltage (2 V DC) sample A in agreement with the SEM imaging. The corresponding selected area diffraction pattern (Fig. 6c) reveals 220, 311, 400 and 440 rings of magnetite structure. High resolution TEM image (Fig. 6d) of magnetite nanoparticles reveals 0.27 nm lattice spacing.

4. Discussion

Synthesis of pure and highly mono-dispersed Fe_2O_3 nanoparticles have been quite interesting task among research workers. In the present study, it has been shown that during the dissolution of iron electrode in

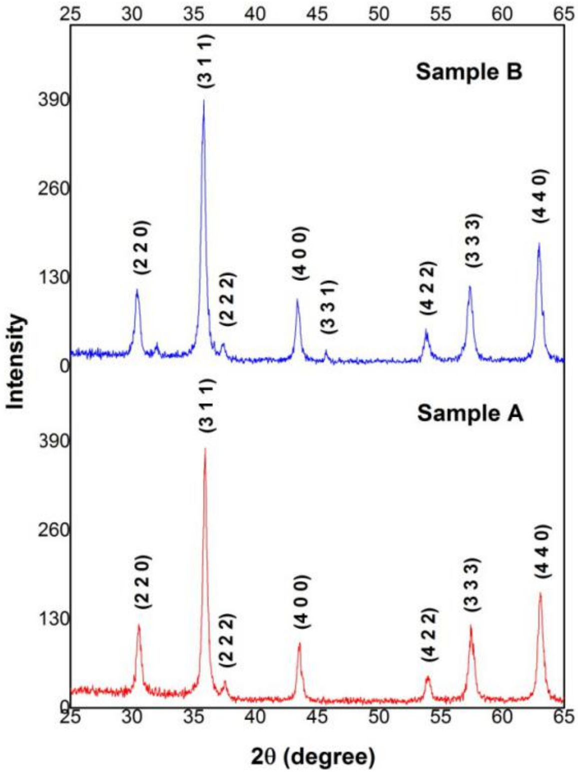

Fig. 2 X-ray diffractogram of sample A.

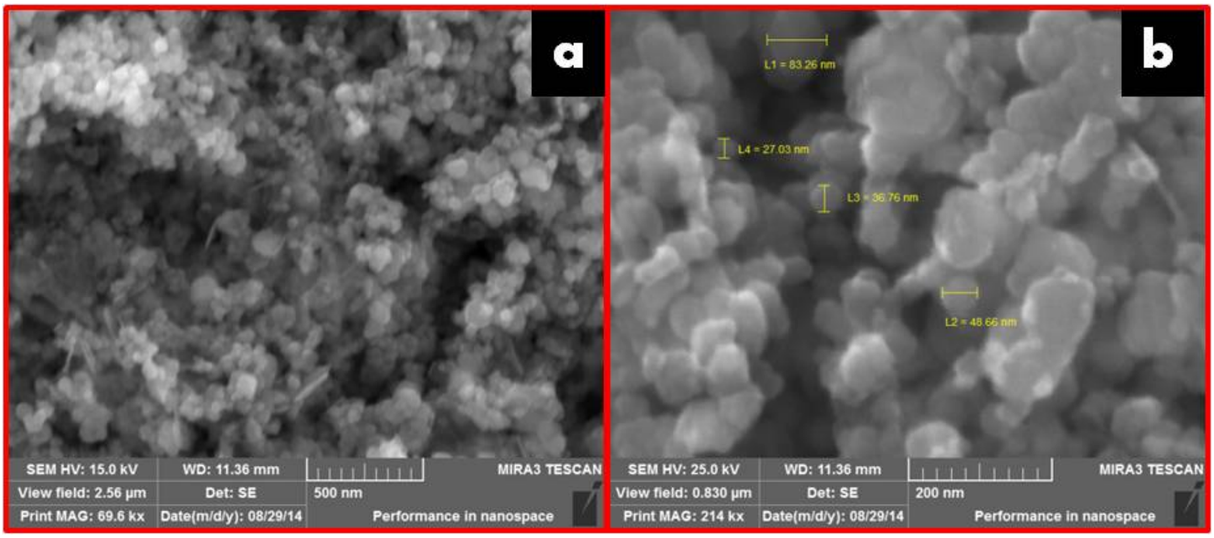

Fig. 3 SEM images of sample A: (a) at low magnification and (b) at high magnification.

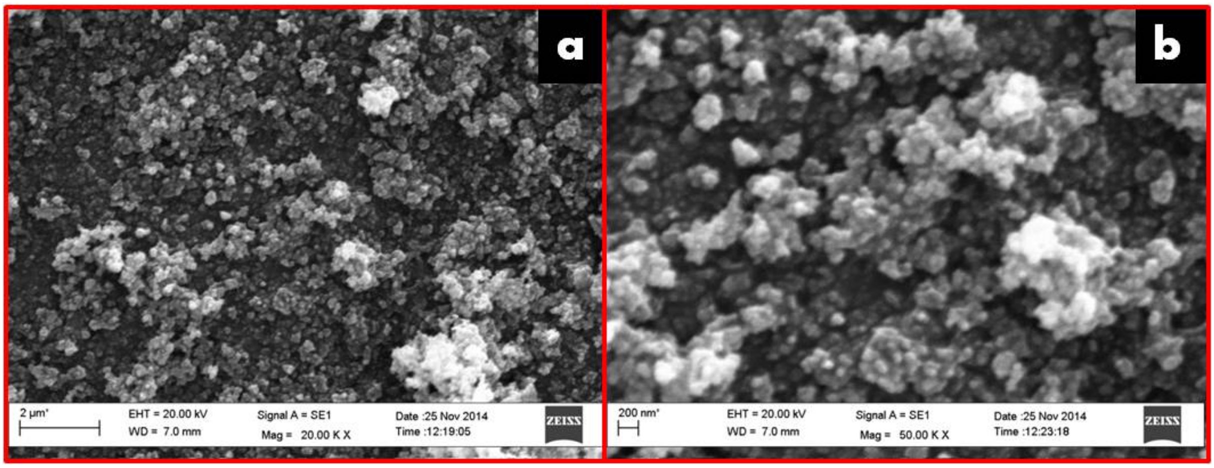

Fig. 4 SEM images of sample B: (a) at low magnification and (b) at high magnification.

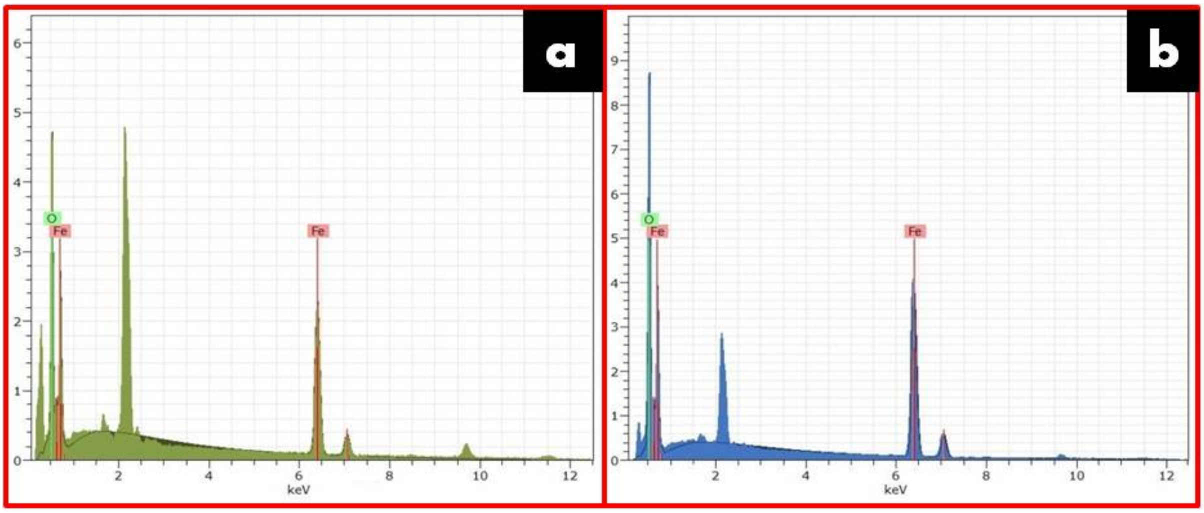

Fig. 5 SEM-EDX spectra of (a) sample A and (b) sample B.

distill water; Fe_3O_4 may be formed by an alkalization reaction of ferrous ions under a condition of excess of OH^- ions [20]. Hence, the concentration of OH^- ion forms one of the most important factor in synthesis procedure. It means that if we increase the concentration of OH^- ions by adding NaOH or KOH, it leads to better synthesis of magnetite nanoparticles.

Another approach for increasing OH^- ions is by decreasing the distance between two electrodes so that OH^- ions produced by the reduction of H_2O at the cathode can react with Fe^{2+} ions to form $Fe(OH)_2$. We adapt the later approach by keeping the distance of 3 to 4 cm approximately for different set of reactions.

There is chain of reactions which take place in the formation of magnetite nanoparticles. At each and every step, the change in color of the solution was noted.

At the beginning of the experiment, when the potential difference is zero, the solution is transparent. As the reaction started, the iron anode was oxidized:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

And the reduction of water occurs at the cathode according to the following reaction:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

Then, solution color changes to yellow-brown and marks the formation of $Fe(OH)_2$, due to the arrival of OH^- ions produced at the cathode to the anode by diffusion, creating the basic medium necessary for the reaction.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (3)$$

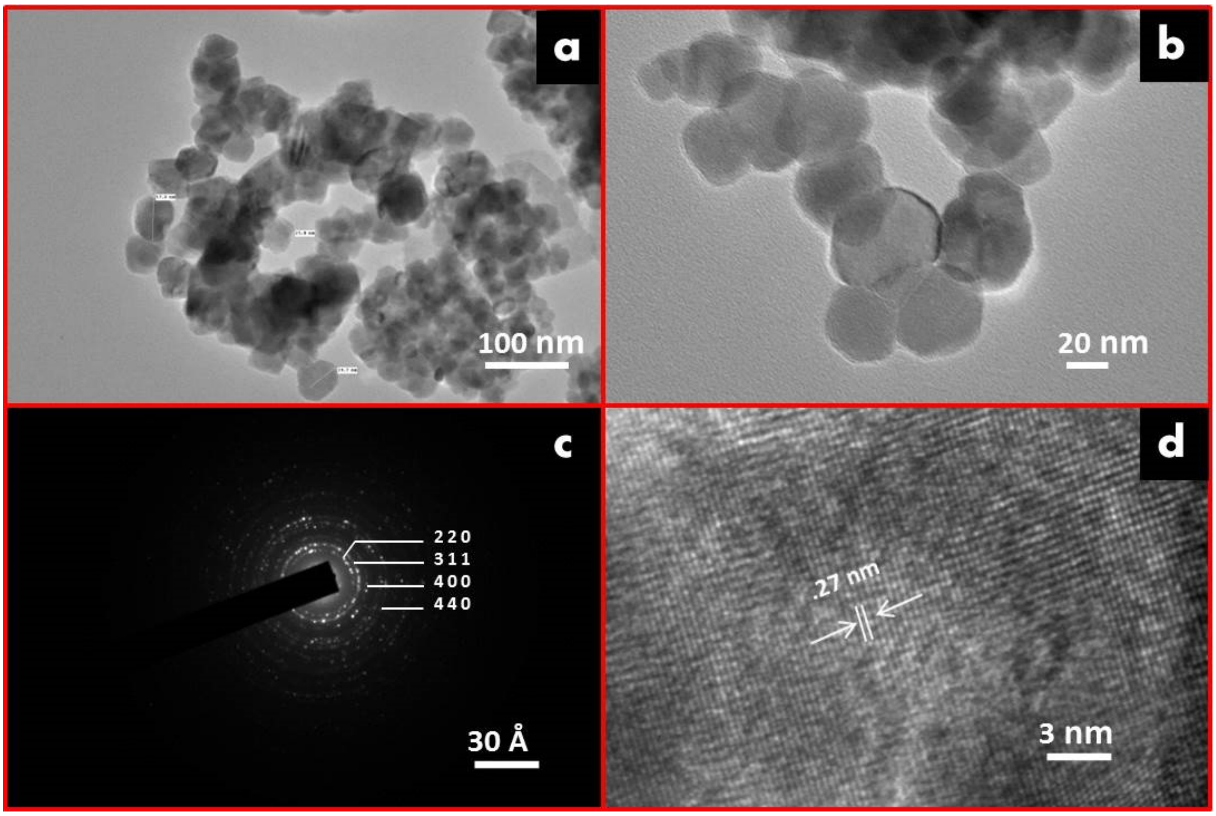

Fig.6 TEM bright field images of sample A: (a) at low magnification, (b) at high magnification, (c) corresponding selected area diffraction pattern and (d) High resolution TEM image.

After the formation of ferrous hydroxide, the color changes to reddish-brown, this slightly marks the presence of FeOOH which comes from:

$$3Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe(OH)_2 + 2FeOOH + H_2O \tag{4}$$

And finally, the precipitate becomes black indicating the formation of magnetite nanoparticles by the reaction between ferrous hydroxide and FeOOH:

$$Fe(OH)_2 + FeOOH \rightarrow Fe_3O_4 + 2H_2O \tag{5}$$

For better yield of Fe_3O_4, current density and supporting electrolyte plays an important role. It was observed that at higher current density, the Fe_3O_4 nanoparticles formation rate comes out to be faster. In our studies, we had also taken into account the role of supporting electrolyte and used sodium chloride (NaCl) for that purpose. At higher concentrations of sodium chloride (NaCl), the synthesis rate was faster and vice versa.

5. Conclusions

Magnetite nanoparticles with average particle size of 50 nm at operating voltage of 2 V DC and 100 nm at operating voltage of 4 V DC have been successfully synthesized. The achieved nanoparticles are mono-dispersed and crystalline in nature with face-centered cubic structure. With increase in operating voltages, the particle size increases and vice versa.

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