INVESTIGATION ON PREPARATION OF 2D SHAPED MAGNETITE NANOPARTICLES BY PRECIPITATION OF MOHR'S SALT

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Abstract

The investigation on the formation and morphology changes of magnetite nanoparticles is done in this work in order to estimate the origin of earlier observed phenomena resulting in the formation of 2D shaped nanoparticles of magnetite at certain conditions during one-step precipitation of magnetite nanoparticles from Mohr's salt solution with strong base (NaOH). The impact of temperature, mixing and amount of base added during the precipitation reaction is evaluated in this study. Moreover, the intermediate phases formed during the precipitation reaction are studied. For characterization of the prepared particles, SEM-EDS, XRD and PCCS analysis are performed on prepared particles.

Keywords: Magnetite, structure tailoring, nano-sized flakes, mohric salt

1. INTRODUCTION

Thanks to the multiply use in various applications such as sensors development, memory devices, catalysis and electronics nano-sized iron oxide particles preparation is extensively studied. Among them, nanoparticles of Fe_3O_4 and γ-Fe_2O_3 has drawn a lot of attention due to their mesoscopic effect, small object effect, quantumsize effect and high surface, remarkable magnetic properties, low toxicity, and biocompatibility [1, 2].

Various methods for preparation of these particles have been developed, including coprecipitation, microemulsion, laser pyrolysis and hydrothermal synthesis [3, 4]. The most common technique is coprecipitation where ferrous and ferric salts in water solutions have been reported to produce quite uniformed particles with ranging size between 10nm to 150 -200 nm [5, 6]. The coprecipitation is kinetically driven process, influenced by chemical reaction rate, therefore to monitor chemical reaction and control of produced iron oxides and size distribution together with their magnetic properties is of great interest. Easy one step processes for the preparation of these nanoparticles by precipitation of ferrous salts has been also developed [7, 8].

In order to estimate the impact on the formation of 2-D shaped magnetite nanoparticles, the method of stirring either by mechanical stirrer or ultrasonification is studied as well as the amount of base added and pH of reaction mixture during precipitation together with temperature impact during the precipitation.

2. SYNTHESIS PROCEDURE

For synthesis of magnetic particles following chemicals were used in this study. Purchased from Sigma Aldrich: $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ pure, NaOH p.a. Precipitation of nanoparticles was done according to method, developed in earlier work of Author of thesis. [9] Stock solution of Mohric salt was prepared with concentration of 0.030 mol·dm^{-3}. The yellow to orange colored solution was stabilized adding droplets of sulfuric acid to reach pH ≤ 3 resulting in transparent colorless solution. Stock solutions of bases were prepared with concentration of 0.1 mol·dm^{-3}.

Furthermore the apparatus consisting of water bath, three necked flask with thermometer, heater and bubble cooler has been used for measurements of pH upon increasing amount of base added and the temperature impact on the rate of precipitation and appearance of magnetic particles was evaluated while varying the temperature of precipitation reaction.

2.1. Impact of temperature and stirring conditions

In each synthesis, stock solution of Mohric salt and NaOH were tempered at different temperatures (50°C, 60°C, 70°C), after 20 minutes of tempering were added together into the apparatus and immediately vigorously stirred (800 rpm) for 30 seconds. After this procedure, resulting green solutions were either placed into the beaker and put into the temperated ultrasonification bath, or left vigorously stirred in the apparatus or left in the apparatus without any stirring for further 60 minutes. During this time, the change of colour indicated precipitation of nanoparticles of magnetite by turning colour from dark green to black. After that, the nanoparticles were separated by magnetic force and washed several times with deionized water and dry - heated at 50°C on heated plate for 120 minutes. XRD and SEM analysis was performed on the prepared samples.

2.2. Impact of amount of base added

Using the data earlier published in [7], the different amount of base was added to observe the change of the particles formed during the different pH during precipitation. The selected pH of precipitating solutions are presented in **Table 1** and showed in **Figure 1** adapted from [7].

Table 1 Selected nanoparticles of magnetite with different pH

Sample	1	2	3
pH	8.9	10.1	12.0

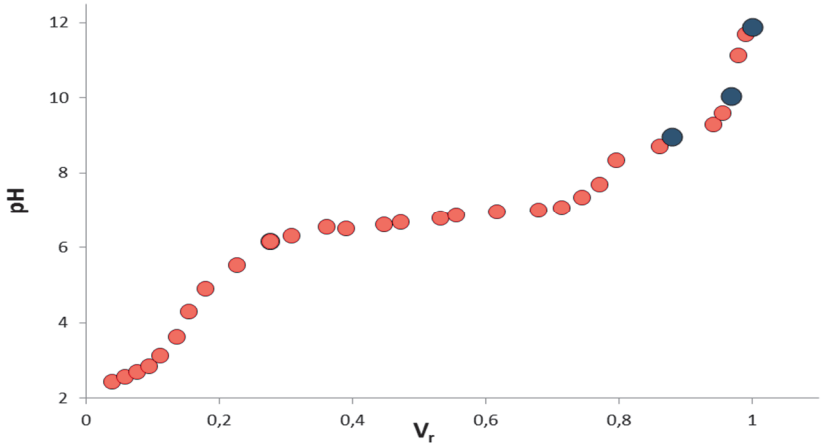

Figure 1 Measurement of pH during precipitation synthesis, emphesized are samples 1, 2 and 3 [7]

Relative volume of hydroxide added V_r is used in the **Figure 1** for constructing the titration curve. Three points are marked according to the samples 1, 2 and 3, where the magnetic particles were collected for the XRD analysis. Equation below depicts the relative volume evaluation. V_a stands for volume of hydroxide added, V_t stands for total volume of added hydroxide in measurement.

$$V_r = \frac{V_a}{V_t} \quad (1)$$

3. RESULTS

3.1. Impact of temperature

In **Figure 2**, the particles morphology is shown by SEM analysis considering the different temperatures, A - 50°C, B - 60°C and C - 70°C. Moderate stirring (250 rpm) was applied to the prepared samples and the pH of reaction was set to be 10.1 by addition of base.

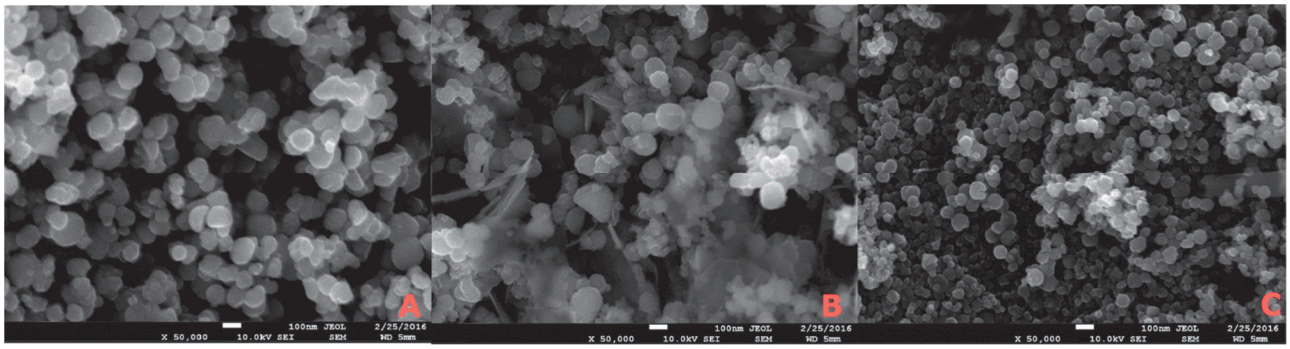

Figure 2 Moderately stirred nanoparticles with different temperature of precipitation (A - 50°C, B - 60°C, C - 70°C)

Mixture of 2D shaped particles of magnetite appeared at temperature 60°C, while with other temperatures, there was not reported any significant presence of 2D shaped particles.In order to estimate any difference in XRD diffraction pattern, the XRD was performed. In **Figure 3**, the results of XRD analysis over samples A, B and C is showed.

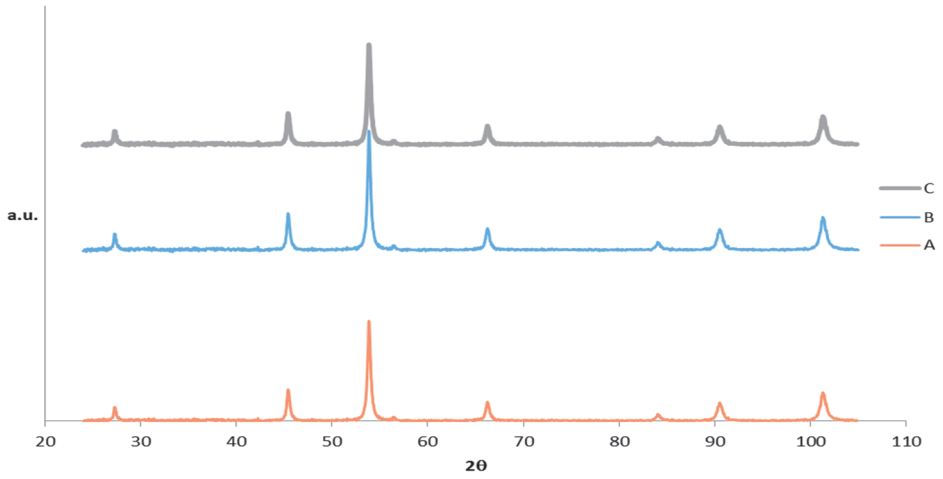

Figure 3 XRD analysis of samples A, B, C

Considering the results of XRD analysis, there was no reported difference between the particles quality. The only one phase (magnetite) was presented in samples.

3.2. Impact of stirring

To evaluate stiring conditions, the sample B was prepared at 60°C with different stirring conditions. Ultrasonification (US), vigorous stirring (VS) and non-stirred (NS) samples were prepared and analysed by SEM as shown in **Figure 4**.

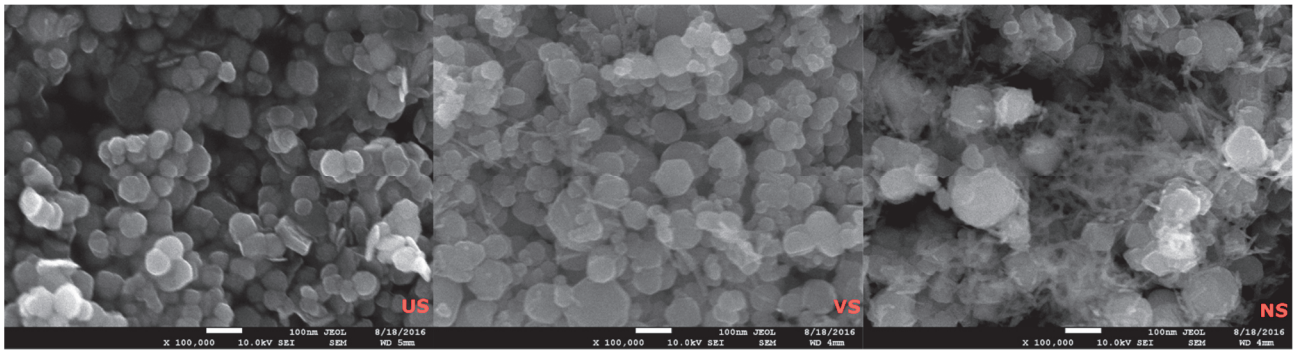

Figure 4 Different stirring conditions applied during precipitation at 60°C
(US - ultrasonified, VS - vigorous stirring, NS - non-stirred)

During ultrasonification of the particles there are barrely any 2D shaped particles observed. Increasing number of these structures can be observed with vigorous stirring conditions and highest observed amount is presented in non-stirred sample of magnetite. For further analysis, the non-stirred samples with different pH were selected.

3.3. Impact of amount of base added

Figure 5 represents the analysis of samples from the **Table 1** vigorously stirred and non-stirred.

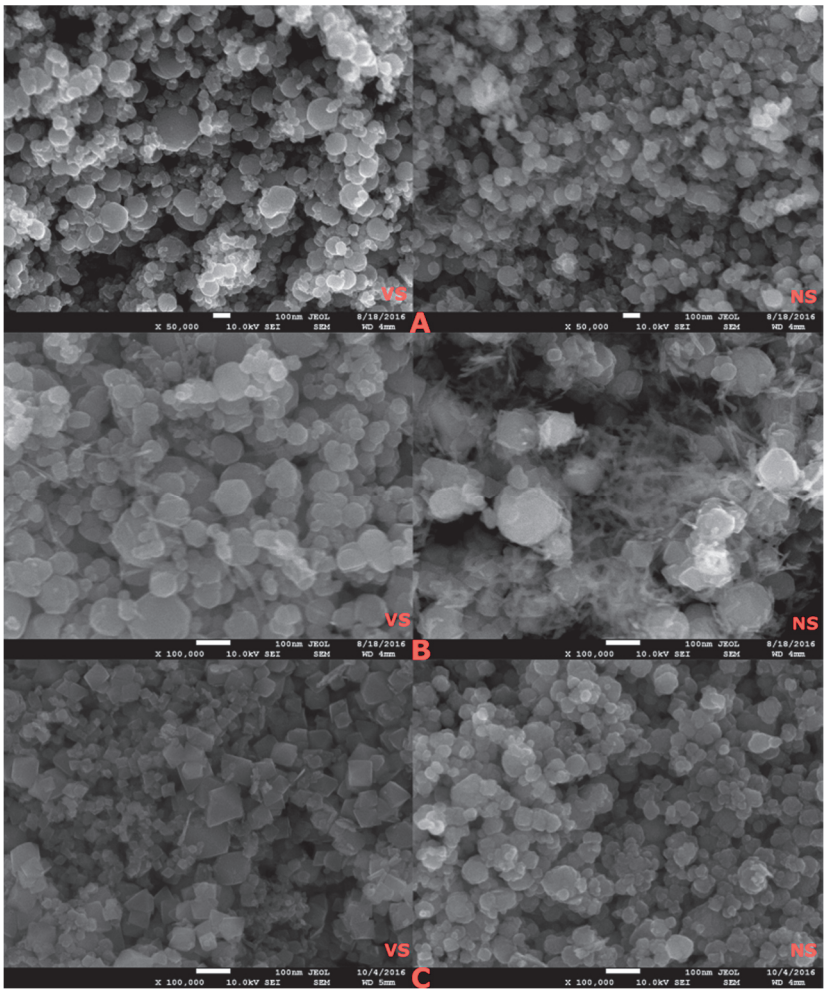

Figure 5 Analysis of vigorously stirred and non-stirred samples with various pH during precipitation

It can be observed,that during vigorous stirring the incidence of the 2D shaped structures is lower and at high pH values octahedral particles were formed, which is consistent with the work done by Lai, Z.,T. et all. [10]. Highest amount of 2D particles was observed for the pH 10.1, hence some particles were round shaped. Prepared non-stirred particles size was measured by photon cross correlation spectroscopy (PCCS) and were dispersed by the ultrasonification in the deionized water for 10 minutes prior to the measurement. Results are mentioned in the **Table 2** and are expressed in x_{50} quantile.

Table 2 Size of particles with increasing pH

Sample	1	2	3
x_{50} (nm)	695	981	351

Comparing the results from the SEM and PCCS analysis, the aglomeration of particles probably happened in case of PCCS measurement, hence the results are consistent with SEM study.

4. DISCUSSION

The formation of magnetite nanoparticles is well explained in previous works [7,8,10] by previous formation of goethite $Fe(OH)_2$, and reaction of hydroxylic groups from base with pre-hydroxylated goethite resulting in formation of magnetite Fe_3O_4. Adding the base in one step, with different temperatures and amount, different particles shape can be obtained. When reaching high pH around 12, pure magnetite in form o octahedral shaped crystals appears, whereas at lower pH (10.1) the 2D shaped particles of magnetite can be observed with increasing amount acording to the method of stiring of reacting solution.

When ultrasonification field is applied to the precipitating solution, the prepared particles are quite uniformed round shaped and there is no incidence of the 2D shaped structures considering the conditions of highest incidence of 2D shaped structures. When precipitated solution is stirred vigorously, there is less amount of 2D shaped particles than in case, that moderate stirring or no stiring is applied to the precipitated solution. PCCS study of size is non-appropriate for the estimation of the single particle diameter, as probably agglomeration of particles happens. XRD analysis showed no difference in XRD pattern of prepared particles, showing the one-phase systems composed of magnetite Fe_3O_4. With higher temperature of the precipitated solution, the particle size is reduced as can be observed in **Figure 2**. Also, the size of particles is reduced with increasing pH of reaction expect the 2D structures appearance.

5. CONCLUSION

2D structured magnetite nanoparticles can be successfully prepared by the precipitation from the Mohr´s salt solution with NaOH solution. The incidence of these interesting particles is at given concentration dependent on the temperature of reaction, methods of stirring of these solutions and amount of added base. At high basic conditions with vigorous stirring the octahedral particles are observed while at lower pH = 10.1 the particles are forming 2D shaped structures similar to the shape of Goethite particles reported elsewhere. It can be assumed, that probably the 2D shaped structurs of magnetite can be attributed to the reaction of formation of magnetite by the hydroxylic groups reaction with the prehydroxylated goethite structures in shape of rods. It is well observed, that this growth happens in majority only at several fullfilled conditions, such as moderate pH for reaction (pH = 10.1), method of stirring (no stirring after intensive mixing of solutions) and temperature of reacting solution (60°C). It is well observed, that tunning of particles shape can be accomplished by variation of forementioned conditions in studied system.

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