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Synthesis of ferrofluids based on cobalt ferrite nanoparticles: Influence of reaction time on structural, morphological and magnetic properties

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ABSTRACT

In this work, for first time the ferrofluids based on the cobalt ferrite ($CoFe_2O_4$) nanoparticles were prepared by the co-precipitation method at different reaction times (0.5–6.5 h). Crystal structure, morphology and magnetic properties of the cobalt ferrite nanoparticles and the ferrofluids based on the nanoparticles were studied by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and vibrating sample magnetometer (VSM). The XRD patterns of $CoFe_2O_4$ nanoparticles synthesized at different reaction times indicated that all samples are single phase in accordance with inverse cubic spinel structure with space group Fd-3m, and no impurity phase was observed. By increasing the reaction time to 3.5 h, the lattice parameter and the average crystallites size increased and then afterwards decreased by increasing the reaction time. The microscopic studies indicated the formation of nanosized particles with nearly spherical in shape, whereas the average particle size for all samples is found to be less than 50 nm. The results of VSM also showed that the saturation magnetization and coercivity field of the cobalt ferrite nanoparticles and the ferrofluids were influenced by reaction time, whereas the ferrofluids have lower values of magnetic parameters than that of nanoparticles.

1. Introduction

Ferrofluids were firstly made by O'Connor in 1962 and they were classified by Stephen Papal in 1965 [1]. Ferrofluids are colloidal compounds in which magnetic nanoparticles such as Fe_3O_4 (magnetite), γ-Fe_2O_3 (maghemite), $NiFe_2O_4$, $CoFe_2O_4$ and etc., have consistently been scattered in an organic or aqueous fluid [2]. Due to the special magnetic properties of these materials and their fluidity, they bear wide applications in industrial and medical fields, such as solar cells, sensors, data storage, separation of materials, cooling speakers, heat transfer, magnetic drug production and hyperthermia for treatment of cancer and so on [3,4]. One of the important discussions on the applicability of ferrofluids deals with their suspension stability which is largely dependent on the size of the particles and agglomerates [5]. Since in suspensions containing nanoparticles, Brownian motions increase upon particle size reduction, they bear significant chance to get closer to each other and form agglomerated particles. Therefore for creating stability in ferrofluids and preventing particles from sticking together, surface of particles is covered with a substance called surfactant, which is made from organic materials, bearing hydrophilic and hydrophobic groups. The use of cationic and anionic surfactants makes one of the two active heads of surface attach to the colloid and the other head to the solution. Therefore, heads in the solution bear the same name and cause repulsion between colloids, thus they prevent colloids from joining and collection [6,7]. The volume fraction of magnetic nanoparticles in ferrofluids can be obtained from the following equation:

$$\phi_V = \frac{M_{fs}}{M_{ps}} \quad (1)$$

where Φ_v, M_{fs} and M_{ps} are, respectively, volume fraction of nanoparticles, saturation magnetization of ferrofluids and saturation magnetization of nanoparticles [8].

Among ferrofluids, cobalt ferrite ($CoFe_2O_4$) based ferrofluids, due to high electromagnetic performance, average saturation magnetization, high coercivity magnetocrystalline, good chemical and physical stability, became a promising candidate for many applications in commercial electronics, including video, high-density digital audio tapes, recording media, magnetic refrigerator, microwave absorbers and specially hyperthermia treatment and drug delivery [9,10]. Cobalt ferrite ($CoFe_2O_4$) bears reverse spinal structure, in which oxygen ions manufacture fcc structure and tetrahedral positions of A are occupied by half of trivalent iron ions; while, the octahedral positions of B are occupied by ions of

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cobalt and residual iron ions [11]. Recent researches showed that physical properties of nanoparticles are affected by their construction process. Since, size and distribution of particles and their spaces have the greatest impact on their magnetic properties; we should apply an appropriate production method to control such parameters [12]. In this regard, cobalt ferrite nanoparticles have been developed with various methods including sol-gel method, chemical co-precipitation, spraying co-precipitation, forced hydrolysis in a polyol system, production in micelles of oil in water, production in inverse micelle, thermal decomposition of oleate compound (Co^{2+}-Fe^{3+}), hydrothermal and thermal operation method [13–17]. However, the fundamental problem in the conventional methods deals with agglomeration of nanoparticles after production, which highly limits control of their size and shape and function. The most common way to synthesize these particles is chemical co-precipitation method using divalent cobalt salt ions and trivalent iron ions in presence of a strong base [18], which is a very simple procedure and does not need any advanced and expensive equipment's. A large number of variables are included in this process, such as reaction temperature, concentration of reactants, pH value and reaction time; in which, the effects of temperature [19], concentration [18] and pH [20] have been investigated.

Changes in reaction time affect growth value and the final size of particles [21], therefore, it can be considered as a key factor for synthesizing of stable ferrofluids. However, to the best of our knowledge, there is no report in literature to study the reaction time effects on physical properties of nanostructured cobalt ferrite ($CoFe_2O_4$) powders and ferrofluids based on these nanoparticles. Therefore, in the present study, we try to provide valuable information about properties of ferrofluids based cobalt ferrite nanoparticles. For this purpose, the effect of reaction time on phase formation, microstructure and magnetic properties of cobalt ferrite nanocrystalline powders and their ferrofluids has been systematically studied by using the X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and vibrating sample magnetometer (VSM), respectively. According to the obtained results, the different physical properties of cobalt ferrite nanopowders and ferrofluids were changed significantly with the reaction time.

2. Experimental

2.1. Materials

The chemicals used for the synthesis of cobalt ferrite ($CoFe_2O_4$) nanoparticles are as follows: iron nitrate pentahydrate ($Fe(NO_3)_3\cdot 9H_2O$) and cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$) as inorganic reactants, sodium hydroxide (NaOH) as reducing agent and double-distilled water as dispersing solvent. Nitric acid (HNO_3) and tetramethylammonium hydroxide (TMAOH), respectively as stabilizing agent and surfactant, were also used to prepare $CoFe_2O_4$ ferrofluid. The chemicals were all of analytical grade and used without further purification.

2.2. Synthesis of $CoFe_2O_4$ nanoparticles

In this work, cobalt ferrite nanoparticles were synthesized by co-precipitation method. The schematic chemical reaction can be expressed as:

$$Co^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow CoFe_2O_4 + 4H_2O \quad (2)$$

Accordingly, the molar ratio of Co^{2+} and Fe^{3+} were controlled at 1:2. The synthesis details of nanoparticles are as follows: at first 50 ml aqueous solutions of cobalt nitrate and ferric nitrate were prepared separately to obtain precursor sols. Then both the solutions are mixed together and stirred for 1 h at room temperature in order to get a homogeneous solution. Afterwards, 100 ml of 3 M NaOH solution was added drop wise to the vigorously stirred reaction mixture at 90 °C, and at different reaction times of 0.5 (sample A), 2 (sample B), 3.5 (sample C), 5 (sample D) and 6.5 h (sample E). In the final step of the co-precipitation process, the resulting precipitates were decanted using a permanent magnet and washed with distilled water for several times.

2.3. Preparation of ferrofluids based on cobalt ferrite nanoparticles

At first, the cobalt ferrite nanoparticles obtained by the above method were stabilized with nitric acid. For this purpose, 20 ml

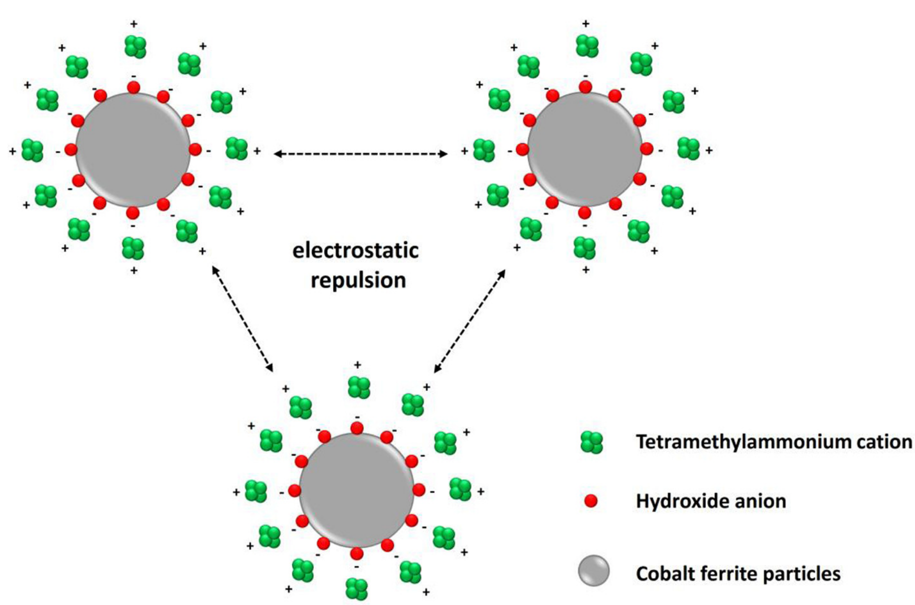

Fig. 1. The schematic model showing the repulsive forces between TMA cations.