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The magnetic and oxidation behavior of bare and silica-coated iron oxide nanoparticles synthesized by reverse co-precipitation of ferrous ion (Fe^{2+}) in ambient atmosphere

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ABSTRACT

The synthesis of iron oxide nanoparticles, i.e., magnetite was attempted by using only ferrous ion (Fe^{2+}) as a magnetite precursor, under an ambient atmosphere. The room temperature reverse co-precipitation method was used, by applying two synthesis protocols. The freshly prepared iron oxide was also immediately coated with Stöber silica (SiO_2) layer, forming the coreshell structure. The phase, stoichiometry, crystallite and the particle size of the synthesized powders were determined by using X-ray diffraction (XRD) and transmission electron microscope (TEM), while the magnetic and oxidation behaviors were studied by using the vibrating sample magnetometer (VSM) and Mössbauer spectroscopy. Based on the results, the bare iron oxide nanoparticles are in the stoichiometry between the magnetite and the maghemite stoichiometry, i.e., oxidation occurs. This oxidation is depending on the synthesis protocols used. With the silica coating, the oxidation can be prevented, as suggested by the fits of Mössbauer spectra and low temperature magnetic measurement.

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1. Introduction

Nanosized iron oxide nanoparticle, especially magnetite (Fe_3O_4), is an important member of spinel type ferrite family. It has an inverse spinel structure, with $\text{Fd}3\text{m}$ space group [1] and exhibits the strongest magnetism of any transition metal oxide [2]. Thus, this particle has become an important subject in several fields of study. For example, magnetite has widespread applications in ferrofluids, targeted drug delivery, digital media recording, magnetic resonance imaging (MRI) contrast agent, magnetic hyperthermia, etc. [3–5]. It is also been used in wastewater treatment as an effective sorbent for may contaminants that can easily be separated from water by an applied magnetic field [6].

However, nanosized magnetite is highly susceptible to oxidation when exposed to air due to the large surface area [7]. This particle also easily form agglomerates due to inter-particle interaction and thus may lose/lower the properties associated with their nanostructures, such as lower magnetization values. In addition,

for certain applications, e.g., biological applications, the exposed metal ion on the surface of nanoparticles can cause metal elemental toxicities in cells (in vivo) [8]. Regarding these issues, all the protection strategies result in magnetite nanoparticles with a coreshell structure. Various coating materials have been introduced as the shell structure, including metal oxides, polymers, precious metals and silica [9]. Among those coating materials, silica has become the first option. This is due to the properties of the silica itself. It is chemically inert and has high stability against aggregation. Furthermore, surface modifications are easy due to the existence of abundant silanol groups on the silica layer that are compatible with various functional groups such as amines, thiols, carboxyl group, dyes, etc. [6,8,10–12]. Within these functional groups, molecules such as proteins, drugs, antibodies, enzymes, dyes, etc., can be covalently bonded on a functionalized silica surface and used for biomedical applications or waste-water treatments. For example, Girginova et al. [6] functionalized magnetite–silica coreshell particles with dithiocarbamate (DTC) for removal of mercury ions, Hg^{2+} , from water. Yoon et al. [8] and Lu et al. [12] used the silica coated magnetite nanoparticle for labeling of stem cells for in vivo tracking or for encapsulation of dye molecules within the silica shell, where the shell tuned the distance between nanoparticles and dyes that help to preserve the optical feature of the dye. Ashtari et al. [10] improved the method of recovery of the target single-stranded deoxyribonucleic acid

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(ssDNA) based on amino-modified silica-coated magnetic nanoparticles. The amino functional group was used in the immobilization of the DNA probe (ssDNA capture) on the coreshell particles through streptavidin conjugation using covalent bonds. During the reaction, the ssDNA target hybridized with the DNA probe to form DNA bio-conjugate and separated from the solution under a magnetic field. With a combination of these materials, an effective, selective and very fast method for the recovery of target ssDNA and other viruses was introduced. This is important for disease and mutation detection.

Many researchers have already studied the preparation of magnetite nanoparticles with different characteristics and purposes. Methods used include the thermal decomposition [13–14], hydrothermal treatment [15], co-precipitation [16–18], sol-gel [19], electro-precipitation [20], forced hydrolysis [21], solvothermal [5] and microemulsion [22] techniques. Among all these methods, chemical co-precipitation is most commonly used to produce magnetite nanoparticles due to its easiness, large volume capability and economy. The co-precipitation process involves the precipitation of iron precursors Fe^{2+} and Fe^{3+} in the ratio of 1:2 by using an alkali, usually sodium hydroxide (NaOH) or ammonium hydroxide (NH_4OH), which leads to the formation of green rust at the early stage of precipitation, followed by the black magnetite solution after precipitation process is completed. Since the pH of the alkaline solution plays an important role in controlling the growth and size of the synthesized nanoparticles [23], the reverse co-precipitation method was applied by Aono et al. [24] in synthesizing fine magnetite powder. Their work was inspired by the method reported by Teraoka et al. [25], where the reverse co-precipitation method was used in synthesizing fine powders of poly-metallic oxides. In this technique, the iron precursor solution is dropped directly into the alkaline solution, in contrast to normal co-precipitation where the alkaline solution is added into the iron precursor solution. Thus the pH of the solution can be maintained during the precipitation process.

Alibeigi et al. [26] reported on reverse co-precipitation of ferrous/ferric ($\text{Fe}^{2+}/\text{Fe}^{3+}$) mixed salt in sodium hydroxide solution in an oxidizing environment, which resulted in the formation of maghemite, $\gamma\text{-Fe}_2\text{O}_3$, instead of magnetite particles due to the oxidation of Fe^{2+} to Fe^{3+} . They also found that reverse co-precipitation from a solution of only ferrous ions (Fe^{2+}) in air can be used to produce Fe_3O_4 phase nanoparticles. Their claim is in agreement with Mizukoshi et al. [27], who reported on an ultrasonic-assisted reverse co-precipitation of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in a NaOH solution in various types of atmospheres, including air, with the addition of surfactant, which also results in formation of Fe_3O_4 structures. The precipitation of magnetite from only Fe^{2+} salts has also previously been reported by Sugimoto et al. [28] but with different method. In their work, they used amorphous ferrous hydroxide gel in producing the crystallize magnetite nanopowders. The amorphous ferrous hydroxide is first precipitated and the aqueous gel is aged at 90 °C for various periods of time in presence of nitrate ions in both inert and ambient atmosphere.

Our previous study [29] focused on synthesis of magnetite nanoparticles in air by using a reverse co-precipitation method. Ferrous ion (Fe^{2+}) of various concentrations was used as a magnetite precursor while ammonium hydroxide (NH_4OH , 25%) was used as a precipitating agent. Results indicated that the synthesized magnetite nanoparticles were in a non-stoichiometric state, $\text{Fe}_{3-\delta}\text{O}_4$, with the stoichiometries varying between the magnetite and maghemite ($\gamma\text{-Fe}_2\text{O}_3$ @ $\text{Fe}_{2.67}\text{O}_4$) structure; $\text{Fe}_3\text{O}_4 < \text{Fe}_{3-\delta}\text{O}_4 < \text{Fe}_{2.67}\text{O}_4$. In this study, the most oxidized magnetite that was synthesized in Ref. [29] is further characterized by using a low temperature magnetic measurement and Mössbauer spectroscopy. The oxidized magnetite then was re-synthesized, and immediately coated with an amorphous silica layer in the form of coreshell structure. The oxidation behavior and the magnetic properties at room and lower temperature of the bare and silica-coated iron oxide nanoparticles were studied and compared.

2. Experimental

2.1. Synthesis of iron oxide nanoparticles

Reverse co-precipitation method was used in synthesis of magnetite nanoparticles [30]. An amount of 50 ml deionized water was put in a beaker followed by the addition of 50 ml of ammonium hydroxide. The pH of the solution was approximately 13. The ferrous ion (Fe^{2+}) precursor of 0.05 M concentration was prepared separately. In a 50 ml beaker, about 0.7 g of ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was mixed with the deionized water, magnetically dispersed for 15 min, followed by 10 min of ultrasonic agitation to ensure that all the ferrous salt was dissolved. Two synthesis protocols were applied in the precipitating process [29]. In Synthesis Protocol 1 (SP1), each of 10 ml of Fe^{2+} solution was added drop-wise in every 10 min to the magnetically stirred base solution. After the last addition, the mixed solution was allowed to react under constant stirring for 1 h, and was aged overnight. Then, the black solution were washed few times with deionized water to remove the excess ammonia by decantation, dried at 323 K and ground. While in Synthesis Protocol 2 (SP2), the Fe^{2+} precursor was added at once into the base solution, and mixed for 1 h. Then, the black solutions were washed few times with deionized water to remove the excess ammonia by decantation and re-dispersed to its original volume.

2.2. Synthesis of iron oxide-silica coreshell structures

The synthesis technique was based on a modified Stöber method [30]. 100 ml of ethanol (98%) was mixed with 1 ml of tetraethylorthosilicate (TEOS) under mechanical mixing for 5 min followed by the addition of 7 ml of NH_4OH . The stirring process was continued for 15 min followed by the addition of 20 ml of the as-prepared iron oxide solutions from SP2. In order to complete the hydrolysis and condensation of TEOS, the solution was mixed for 12 h. The obtained product was washed with ethanol and dried in oven at 323 K and ground. The remaining iron oxide was also dried at 323 K and ground prior to the characterizations.

2.3. Characterizations

The phase of the obtained products were determined by using powder XRD Philips (PW1710) over a 2θ range from 10° to 90°, using $\text{Cu}_{K\alpha}$ ($\lambda=1.5046 \text{ \AA}$). Refinement of the iron oxide powder patterns were made by using PowderCell 2.4 software. The crystallite sizes were determined by using the Scherrer equation. Mössbauer spectroscopy in the transmission mode was used to determine the magnetic phase in the sample. The Mössbauer spectra measurement was carried out in the transmission mode with ^{57}Co diffused into a Rh matrix as a source moving with constant acceleration at room and helium temperatures. The spectrometer (Wissel) was calibrated by means of a standard $\alpha\text{-Fe}$ foil, and the isomer shift was expressed with respect to this standard at 293 K. The fitting of the spectra was performed with the help of the CONFIT program [31]. CONFIT program utilizes a convolution algorithm in the fitting of overlapped Mössbauer spectra at different temperatures and using by also external magnetic fields. It is also significant that the program integrates the fitting of crystalline and amorphous (distribution) models in a single fit menu system. At the moment the program is able to accept 1024 experimental points per spectrum; the number of fitted parameters must not exceed 105 and the number of spectrum components must be less than or equal to 99. The room and low temperature magnetic measurements were done by using a vibrating sample magnetometer (PPMS Quantum Design and Cryogenic). Average particle size and morphologies of the nanoparticles were evaluated by using transmission electron microscopy (TEM Tecnai F20) operated at 200 kV.

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