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Structural and magnetic characterization of electro-crystallized magnetite nanoparticles under constant current

Saba Mosivand [a,**], Iraj Kazeminezhad [b,*]

[a] Physics Department, Faculty of Science, Lorestan University, Lorestan, Iran
[b] Physics Department, Faculty of Science, Shahid Chamran University, Ahvaz, Iran

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ABSTRACT

The effect of applied current on the morphology, particle size, structure, and magnetic properties of magnetite nanoparticles prepared by electro-crystallization method was studied. The synthesis was performed in an electrochemical cell containing two iron electrodes and an aqueous solution of sodium sulfate, and either thiourea, sodium butanoate, or β-cyclodextrine as organic stabilizer. All the samples were characterized by XRD, SEM, VSM, and Mössbauer spectroscopy. X-ray diffraction patterns, clearly confirmed that all products have the cubic spinel Fe_3O_4 crystal structure. Electron microscope images of the samples showed that their mean particle size is in the range 20–80 nm, and depends critically on the applied current and type of the organic additives. Specific magnetization of the samples at room temperature ranges from 60 to 90 A m^2 kg^{-1}, depending on the growth conditions. Room temperature Mössbauer spectra are typical of nonstoichiometric $Fe_{3-\delta}O_4$, with a small excess of Fe^{3+}, $0.06 \leq \delta \leq 0.17$.

1. Introduction

It is well known that magnetic nanostructures have had a major impact on the development of modern technologies [1]. Magnetic nanoparticles because of their special properties have found many new industrial, biological and medical applications [1,2] in areas such as imaging [3], catalysis and semiconductors, pharmaceutical and cosmetic products [4,5], biosensors [6,7], cell separation and detection [8], tissue engineering, and regenerative medicine [9]. Recently, magnetic iron oxide nanoparticles have been the subject of several reviews [4,5,10–13]. Magnetite nanoparticles reported as applicable materials owning to their magnetic properties [14] and being successfully employed in magnetic resonance imaging [15,16], ferro-fluids [17], and removal of heavy metals from waste water [18,19]. Some more recent applications have been in the biomedical field [5,20,21] such as controlled drug delivery and hyperthermia-based therapy [22,23].

In the last decade, a wide range of various physical and chemical methods have been employed to synthesize iron oxide nanoparticles including ball milling [24], solvothermal synthesis [25], thermal decomposition [26], solution combustion [27], and co-precipitation [28,29]. Co-precipitation is one of the oldest and most common methods. However, it is difficult to produce particles with the same morphology and narrow size distribution and may require secondary size selection [30]. Another difficulty of this method is the tendency of generated Fe_3O_4 nanoparticles to oxidize to α-Fe_2O_3, thereby their magnetization greatly reduces. Hence, the synthesis should be performed under an inert atmosphere. Among the less conventional methods for synthesis of Fe_3O_4 nanoparticles, electro-crystallization (electro-oxidation) has begun to emerge as one of the more recent methods. With this method, it is possible to produce fine magnetite nanoparticles electrolytically using iron electrodes. A great advantage of this method is that an inert atmosphere is not required to avoid oxidation of Fe_3O_4 nanoparticles. To date, there are only a few reports on synthesis of magnetite nanoparticles using electrochemical method [31–34]. With this method, the mean particle size, particle size distribution, and their morphology can be controlled by tuning the growth conditions such as temperature and applied potential. Also, it is possible to avoid the agglomeration of particles by adding a stabilizer agent into the electrolyte solution. We have recently found that the capping agent [1], stabilizer concentration, growth temperature, and applied potential [2,31,34] influence on properties of the electro-crystallized magnetite nanoparticles.

In this study, the electro-crystallized magnetite nanoparticles were fabricated under constant current in the presence of three different stabilizer agents and their structural and magnetic properties were characterized. We are especially interested to

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* Corresponding author. Tel.: +98 61 3333 1040; fax: +98 61 3333 1040.
** Corresponding author.
E-mail address: I.Kazeminezhad@scu.ac.ir (I. Kazeminezhad).

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analyze the relationship between specific magnetization and particle size which is dependent on applying electro-oxidation current.

2. Materials and methods

2.1. Materials

Iron sheet (purity 99.5%) was purchased from Advent Research Materials Ltd., Thiourea (Tu), sodium butanoate (Bu), and β-cyclodextrine (β-CD) were purchased from Sigma–Aldrich Chemical Co., Sodium sulfate anhydrous was supplied by BDH Ltd.

2.2. Experimental method

Magnetite nanoparticles were synthesized by electro-crystallization of iron from an aqueous medium using a chronopotentiometric technique. Two purified 1 cm^2 and 4 cm^2 iron plates were used as sacrificial anode and cathode, respectively. The electrodes were first polished mechanically with fine-grain emery paper and then cleaned with ethanol in an ultrasonic bath. The cleaned electrodes were placed in an electrochemical cell containing a solution of 0.25 M Na_2SO_4 salt as the electrolyte and 0.04 M of one of the three organic stabilizer agents listed above and then the reaction was conducted galvanostatically. In order to study the effect of current on the structure and magnetization of particles three different series of samples were synthesized in the presence of either Tu, Bu, or β-CD under five different current of 0.4 A, 0.8 A, 1.2 A, 1.6 A, and 2 A, using a Solartron Instruments SI 1280B electrochemical measurement unit. The reaction time was chosen 30 min. At the beginning of the experiment the solution was colorless. As the reaction takes place, water is reduced to hydrogen and hydroxyl anions at the cathode, while iron metal is oxidized to Fe^{2+} and Fe^{3+} at the anode. In the solution, Fe^{2+}, Fe^{3+}, and OH^- react to form an orange-brown iron hydroxide precipitate which then dehydrates to produce a black magnetite (Fe_3O_4). The black precipitate was separated from the electrolyte solution using a Nd–Fe–B permanent magnet and washed for several times with a copious amount of deionized (DI) water and left to dry.

2.3. Characterization methods

The crystal structure of the samples was determined by a Philips X-ray diffractometer, using CuKα radiation ($\lambda = 1.5405$ Å)

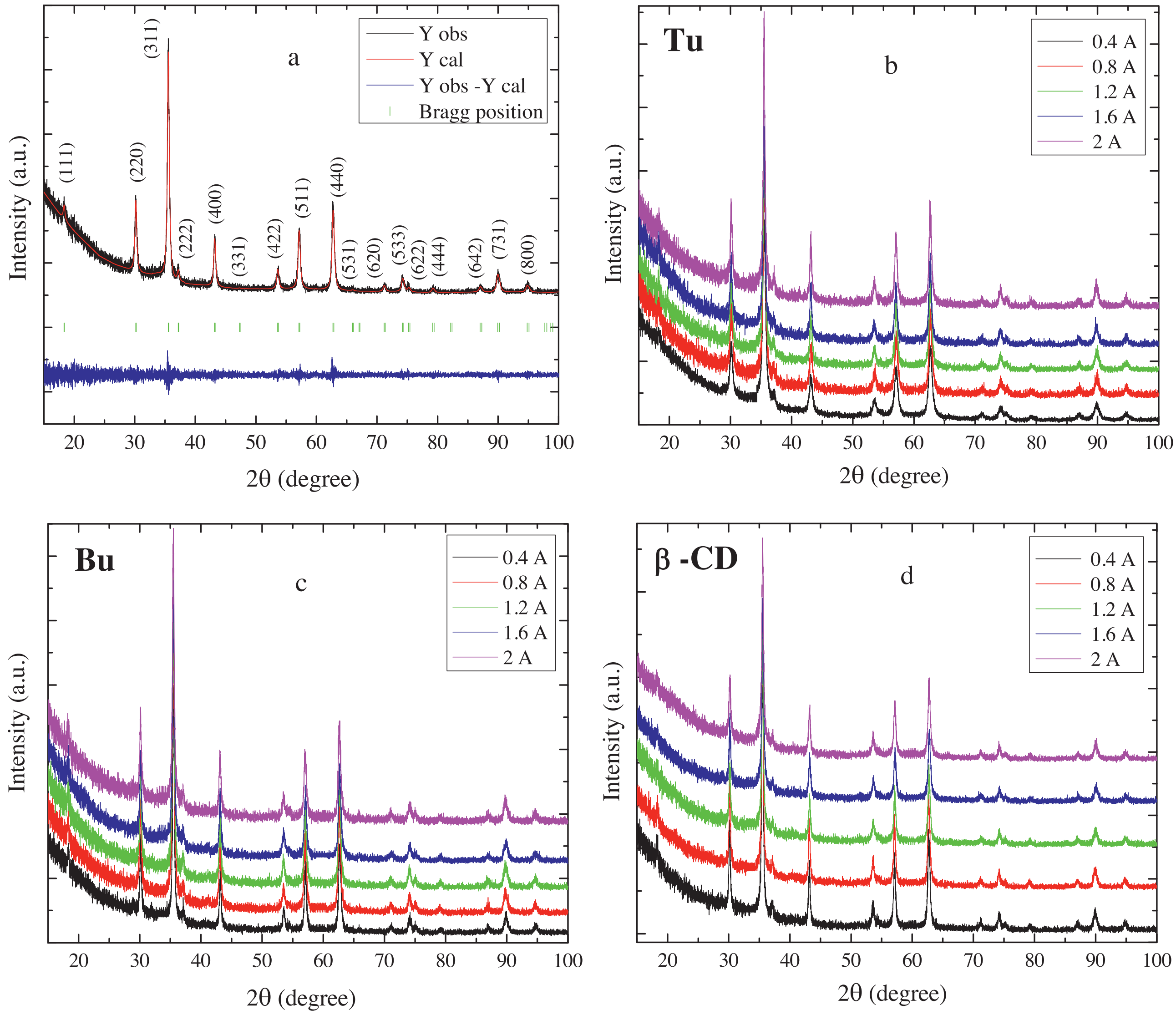

Fig. 1. XRD pattern and the Rietveld profile refinement, using the Fullprof program for magnetite nanoparticles prepared at 0.8 A with Bu and XRD patterns of the samples prepared under different currents in the presence of Tu, Bu, and β-CD.