Volume 8, Issue 1, 2019, 541 - 544 ISSN 2284-6808

Letters in Applied NanoBioScience

www.NanoBioLetters.com

https://doi.org/10.33263/LIANBS81.541544

Original Research Article **Open Access Journal**

Received: 20.02.2019 / Revised: 22.03.2019 / Accepted: 25.03.2019 / Published on-line: 30.03.2019

Synthesis and characterization of copper ferrite nanoparticles and its application as MRI contrast agent

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ABSTRACT

Copper ferrite nanoparticles were synthesized with the use of microwave irradiation. The synthesized samples were characterized by XRD, SEM, EDS, and VSM. It was observed that at optimum condition particle size was around 30 nm and showed superparamagnetic behavior. The as synthesized samples were then applied as MRI contrast agent and it was observed that T_1 and T_2 decreased significantly.

Keywords: *nanoparticles; copper ferrite; microwave; mri; contrast agent.*

1. INTRODUCTION

Magnetic nanoparticles show different properties compared with bulk materials because of the finite number of atoms and large percentage being located at the surface [1, 2]. Giant magneto resistance, quantum tunneling of the magnetization, and superparamagnetism are some examples attributed to the small size of magnetic particles [3, 4]. Nano ferrites are considered as an important class of magnetic materials which shows good magnetic properties along with very high d.c. resistivity. Because of their optical, electronic, mechanical, thermal, magnetic and other related properties [5], spinel metal oxides (AB_2O_4) have been the subject of extensive investigation. Nano-sized spinel ferrites have received much of interests in the past few years due to their importance in understanding the fundamentals in nanomagnetism. They have also various applications in technological fields including permanent magnets, high density information storage, and magnetic drug delivery [6, 7]. One of the most important ferrites is copper ferrite ($CuFe_2O_4$) which has the prominent goodness of magnetic and semiconducting properties [8, 9]. $CuFe_2O_4$ is found in tetragonal and cubic structures. The tetragonal structure is stable at room temperature and transforms to cubic phase only at a temperature of 623 K and above due to Jahn–Teller distortion [10, 11].

The chemical and physical properties of nanoparticles (NPs) are highly depended on their size, shape, composition, crystallinity and structure. For this reason, an accurate control of these intrinsic parameters is the most important requirement for many future applications. Magnetic particle has been synthesized by different methods including chemical precipitation from aqueous or organic solutions [12]. Recently, an innovation was developed to prepare metal particles using ethylene glycol called the polyol process [13, 14]. The synthesis of such spinel phases have been developed using many approaches including sol–gel [15], combustion synthesis [16], coprecipitation [17, 18], high-energy ball milling [19], thermal plasma synthesis [20], hydrothermal method [21, 22], rapid quenching [23] and spray pyrolysis of metal nitrate solutions [24].

In current study, a synthetic route based on polyol mediated under microwave irradiation is applied to prepare $CuFe_2O_4$ nanoparticles. In recent years microwave irradiation is considered as candidate for the synthesis of nanomaterials [25–28] which provides uniform growth medium that leads to formation of products via fast and homogenous heating rate [29-31]. The dissolved reactants can be coupled with the microwave radiation which leads to higher heating rate in comparison with other conventional methods and solves temperature and concentration gradient problems [26].

2. EXPERIMENTAL SECTION

Materials and physical measurements.

All the chemical reagents used in this experiment were of analytical grade. X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered Cu Kα radiation. Fourier transform infrared (FT-IR) spectra were recorded on an EQUINOX 55 BRUKER spectrometer. Field emission scanning electron microscopy (FESEM) images were obtained on TESCAN/MIRA equipped with an energy dispersive X-ray spectroscopy. The magnetic properties of the samples were measured with a vibrating sample magnetometer (VSM).

Preparation of copper ferrite nanoparticles.

In a typical synthesis 1 mmol of $Cu(NO_3)_2.3H_2O$ was dissolved in 10 ml of PEG-200 and it was added to a 10 ml PEG-200 solution containing 2 mmol $Fe(NO_3)_3.9H_2O$. Then 0.2 g of NaOH was dissolved in 10 ml PEG-200 and finally was added to the above mentioned solution and heated at 60 °C under stirring for 15 min.

The final mixture was exposed to microwave irradiation at power of 900 W for 12 cycles consisting of 30 s on for every 60 s interval. The products were separated and washed several times with distilled water and ethanol to remove impurity and unreacted materials and finally dried in an oven for 8 h at 70 °C. To reach a crystalline product, the obtained samples were annealed at 250 °C for 5 h.

MRI measurement.

A 1.5 T MRI system (Magnetom Avanto, Siemens Medical Solutions) in Payambaran hospital was applied for imaging tests and for this purpose a knee coil was used. In vitro experiments were done with the use of four different concentration phantoms containing $CuFe_2O_4$ nanoparticles. The nanoparticles were dispersed into the wells of 4-well culture plates in which 1% agarose gel was filled and the area around was filled with distilled water. The experiments were carried out to calculate the longitudinal relaxation time (T_1) and transverse relaxation time (T_2), for all of the samples. To do T_1 mapping several T_1 weighted spin echo (SE) pulse sequences with a fixed TE=3 ms and variable TRs from 300 ms to 4000 ms, TS=5 ms, matrix size=192×256, read FOV =230 mm, phase FOV=87.5% (201.25 mm), BW=130 Hz/pixel , slice thickness=3 mm and number of average=2 were chosen. For T_2 mapping, a T_2 weighted multi spin echo (TSE) pulse sequence with fixed TR=2000 ms, 16 echoes form TE=22 ms to TE=220 ms, TS=5 ms, matrix size=192×256, read FOV=230 mm, phase FOV=87.5% (201.25 mm), BW=130 Hz/pixel, slice thickness=3 mm and number of average=1 was selected.

3. RESULTS SECTION

XRD analysis was applied to study the crystallinity and phase structure of the as-synthesized samples. All of the diffraction peaks in Fig.1 can be indexed to the tetragonal structure of $CuFe_2O_4$ (space group $I4_1/amd$) which is very close to the values in the literature (JCPDS No. 34-0425 with lattice parameters a = b = 5.844 Å and c = 8.302 Å). Acceptable matches are observed for compound indicating the presence of only one crystalline phase in the samples. As can be seen there is broaden and sharp peaks indicating the small size and high crystallinity of the as synthesized products. The average crystallite diameter of the obtained product was estimated from Debeys-Scherrer equation: $D_c=k\lambda/\beta\cos\Theta$; Where β is the breadth of the observed diffraction line at its half-intensity maximum, K is the so-called shape factor, and λ is the wavelength of X-ray source used in XRD. The average crystallite diameter of the obtained products was about 38 nm.

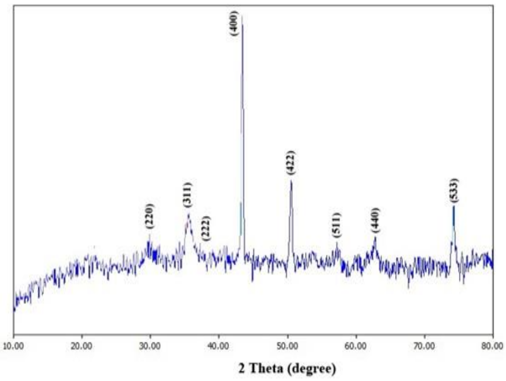

Figure 1. XRD pattern of the as synthesized $CuFe_2O_4$ nanoparticles.

SEM images of the products synthesized before and annealing process are presented in Figure. 2. It can be seen in the case of the samples obtained before annealing, nanoparticles are agglomerated and size distribution is not uniform (Figure. 2a, b). After annealing process particle size distribution was improved and agglomeration was decreased significantly (Figure. 2c, d).

EDS spectrum of the nanoparticles is presented in Figure. 3. The presence of the Cu, Fe, and O can be seen in this figure. The presence of Au is originated from coating of the particles with Au for SEM analysis.

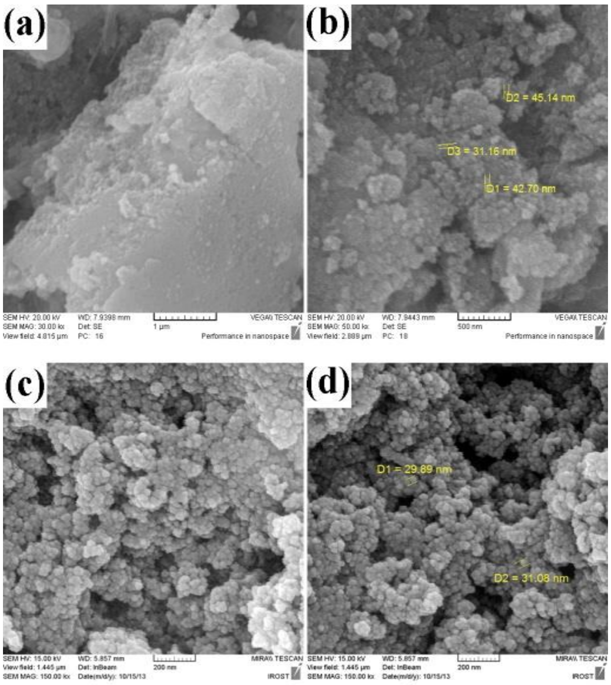

Figure 2. SEM images of the samples (a, b) before annealing process, and (c, d) after annealing at 250 °C.

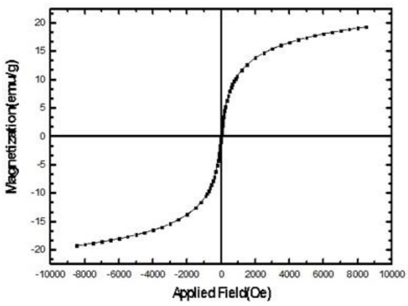

Figure 4. Magnetization curve of the annealed nanoparticles.

Magnetic property of the nanoparticles was analyzed by VSM (Figure. 4). The hysteresis loops measured at room temperature confirms a superparamagnetic behavior of product. The saturation magnetization (Ms) is about 19.3 emu/g which is smaller than bulk material. The small saturation magnetization can be attributed to the much smaller size of $CuFe_2O_4$ nanoparticles [18]. MR images of the synthesized samples which were fixed in phantoms are shown in Figure 5. In comparison with pure water, the synthesized nanoparticles decreased T_1 and T_2 which were calculated 1716 and 831 ms, respectively. As can be seen nanoparticles performance in decreasing of T_2 is much better than T_1. This means that the samples can lead to more signal enhancement for T_2 weighted images than T_1 weighted images.

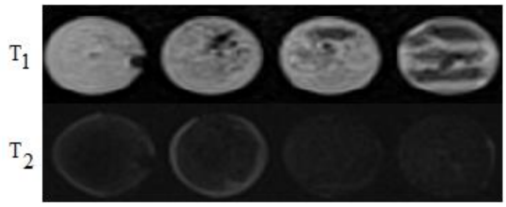

Figure 5. MRI images of the synthesized nanoparticles fixed in phantoms.

4. CONCLUSIONS

Nanoparticles of $CuFe_2O_4$ were synthesized via polyol mediated medium in the presence of microwave irradiation. The crystal size was calculated from XRD pattern which was about 38 nm and confirmed by SEM images. The synthesized were then applied as MRI contrast agent and T_1 and T_2 decreased significantly.

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