Manganese ferrite nanocubes as an MRI contrast agent

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Abstract

Facile synthesis of superparamagnetic, highly crystalline, manganese ferrite nanocubes (MnNCs) is reported. X-ray diffraction depicts single-phase face-centred cubic spinel and the electron microscopy represents the nearly monodispersed cube-like nanostructure with the size ranging from 18 to 20 nm. Vibrating sample magnetometer shows magnetization field-dependent curves at 300 K exhibiting the superparamagnetic behaviour of NCs with negligible remanence. Furthermore, the biocompatibility of NCs was proved by MTT assay. These unique characteristics make this NCs as a contrast agent ideally suited for T\textsubscript{2}-weighted MR imaging. This novel method of synthesizing NCs proves to be very attractive for various biomedical applications because of their outstanding stability and biocompatibility.

1. Introduction

Magnetic nanoferrites has become the important research area in the past two decades mainly because of their magnetic behaviour, a magneto-optical and magneto-resistive property which made its way in various fields from technology to medical applications \cite{1, 2}. Ferrites are usually metal oxides where iron is considered as the main metallic constituent. These ferrites exhibit a superparamagnetic property which makes this particle highly useable in the field of biomedical applications \cite{3}. However, most of them are susceptible to weak chemical stability, which discloses the necessity of surface modification or doping of other elements. Therefore, researchers ended up in doping elements like Co, Mg, Mn, Zn, Ni, etc, to make it chemically stable in the biological system and also for tuning the magnetic behaviour of the ferrites \cite{4}.

Among other ferrites, manganese (Mn) ferrite is a well-known soft magnetic material with high coercivity, moderate magnetization, excellent physiochemical stability and high cubic magneto-crystalline anisotropy, finding its various biological applications \cite{5}. Mn-doped ferrite is an efficient magnetic resonance imaging (MRI) contrast agent as compared to magnetite since it has same saturation magnetization as of iron oxide, but possesses a higher order of crystalline anisotropy thus causing slower magnetic moment relaxation in comparison \cite{6}. Furthermore, anisotropic nanostructures have gained much interest in recent years \cite{7}. Various synthesis techniques have been developed to produce different nanostructure shapes such as rods, prisms, octahedral and cubes etc. For example in the case of iron oxide-based nanocubes for MRI which exhibit extremely increased r\textsubscript{2} values than the other nanoshapes \cite{8}.

To the best of our knowledge, there are very few reports existing in the literature for both Mn-based ferrite structures and particularly nanocubes (MnFe NCs) by various synthesis methods and evaluated as an MRI contrast agent \cite{9–16}. Henceforth, for the first time in this work, we have investigated the possibility of using NCs as a contrast agent. In this report, MnFe NCs were synthesized by a facile thermal decomposition method employing a cationic surfactant CTAB. CTAB drastically reduces the magnetic particle aggregation by capping with their hydrophilic head and hydrophobic tail \cite{17}. The synthesized NCs are highly crystalline in nature and exhibited nearly cubic-like morphology with the size of 19.5 ± 2 nm. Besides, the synthesized MnNCs showed...
high magnetic saturation and superparamagnetic properties even at room temperature. The cytotoxic assays revealed that the synthesized NCs are biocompatible. Subsequently, these NCs were tested as an MRI contrast agent, which turned out to be an efficient T₂-weighted MR imaging.

2. Experimental details

2.1. Materials
The chemical reagents used for the synthesis are iron (III) acetylacetonate (Fe(acac)_3) ≥99.9%, manganese (II) acetylacetonate (Mn(acac)_2), hexadecyltrimethylammonium bromide (CTAB) ≥99%, benzyl ether ≥98%, isopropanol, hexane and acetone. The above-listed chemicals were purchased from Sigma, Mexico. Apart from these, the reagents used for cell culture techniques are Methylthiazolyldiphenyl-tetrazolium bromide (MTT) 98% were purchased from Sigma, Mexico and other reagents such as Dulbecco’s Modified Eagle Medium (DMEM), fetal bovine serum (FBS), and streptomycin were obtained from Gibco, Thermo Scientific, Mexico.

2.2. Synthesis of manganese ferrite nanocubes (MnFe NCs)
In this work, MnFe NCs were synthesized by employing the modified protocol of thermal decomposition [18]. Initially, 2 mmol of Fe(acac)_3 and 1 mmol of Mn(acac)_2 were added into 10 ml of benzyl ether and sonicated for 15 min to achieve the homogeneous solution. Then, the CTAB concentration of 100 mM was added into the system. Finally, the reaction was carried out in a 3-neck flask at 260 °C for 1.5 h. Later, the flask was removed from the heating system and naturally cooled down to room temperature. The final black solution was precipitated and washed several times using a solvent mixture of isopropanol: hexane: acetone (2:1:2 ratio) [19] followed by a centrifugation process at 4000 rpm for 15 min and dried in an oven at 70 °C for 1 h. The black solid powder was dispersed in water by sonication and stored for further use.

2.3. Characterization techniques
The structure and crystallinity of the MnFe NCs were probed by PAN analytical, XPERT Powder x-ray diffractometer (XRD) using Cu-Kα radiation (λ = 1.54 Å) with 2θ angles ranging from 20° to 70° at a scan rate of 0.02/1 s. The morphology and size of NCs were analysed using High-Resolution Transmission Electron Microscopy (HRTEM, Jeol ARM200F). The elemental composition was measured using an energy dispersive x-ray analysis (EDAX) equipped with the HRTEM system. For TEM analysis, a drop of alcoholic NCs dispersion was placed onto the carbon-coated copper grid (Ted Pella, Inc.), and dried in a vacuum desiccator overnight. Thermogravimetric analysis was carried out using a TGA Q50 (TA Instruments) from 30 to 600 °C at a heating ramp rate of 10 °C min⁻¹ in an N₂ atm to study the % weight loss. X-ray Photoelectron Spectroscopy (XPS) analysis was employed to detect the elemental composition and their oxidation states using a K-alpha XPS System (Thermo Scientific) equipped with monochromated Al-Kα as an x-ray source and the binding energy was calibrated using C 1 s signal. The magnetization and magnetic behaviour were recorded by using Vibrating Sample Magnetometry (VSM, Quantum Design, PPMS DynaCool) with the applied field of ±50 kOe under room temperature.

2.4. MRI study parameters
The MR contrast capability of nanocubes was tested using a 1.5 T clinical MRI system by the multi-echo fast spin-echo method. Phantom agar for MRI experiments was performed with a 1.5 T clinical Signa HDxt scanner (GE Health Care). T₂-weighted images were acquired using the following parameters: 1.5 T, fast spin-echo, Repetition time TR = 2500, Echo time TE = 30–180 ms (increment of 6 ms), FOV = 16 cm², resolution = 256 × 256 points and slice thickness = 6 mm. The different concentrations of (0.01, 0.02, 0.04 and 0.08 mM) NCs were dispersed in PBS, using 1.5 ml microcentrifuge tubes and set in 2% w/v agar solution at 80 °C with agar gel as a control.

The values of various NCs T₂ relaxation time was calculated by fitting the decay curve using a nonlinear mono-exponential function, plotting the MRI signal intensities which are normalized with respect to the TE from the imaging series using the equation: M(TE) = M₀e⁻^(−TE/T₂) + C, where M(TE) is the signal intensity observed at a given TE, M₀ is the initial magnitude of MRI signal, and C is a constant.

2.5. Cytotoxicity assessment
The cytotoxic impact of NCs was performed using MTT assay by incubating various concentration of nanoparticles (50–250 µg ml⁻¹) for 24 and 48 h with L6 skeletal muscle cell line and compared with the control. The protocol for cell growth and the culturing process have been adapted from the previous studies [18]. The observations were measured in triplicates and data was obtained from their average values.
3. Results and discussion

XRD pattern (figure 1) illustrates the crystalline structure and phase of the NCs. It is clear that NCs are highly crystalline and the observed diffraction peaks correspond to (111), (220), (311), (400), (422), (511), (440) planes, of the face-centred cubic spinel manganese-ferrite phase (ICDD card no. 10-0319) [20, 21]. Besides, no impurities or secondary phases were observed which confirms the formation of pure phase MnFe NCs. The peaks broadening reveals the crystalline nature of the NCs. The average crystallite size was calculated from FWHM of the high-intensity plane (311) using Scherrer’s equation and the resulting average particle size was found to be 18 nm, which is reasonably consistent with TEM images.

TEM analysis was carried out to study the morphology of as-synthesized nanostructures. Figure 2(a) represents the nearly cubic-shape of the particles, that could be due to the cubic crystal structure of MnFe observed from XRD [22] with negligible aggregation. The aggregation of NCs are due to the strong magnetic dipole-dipole interactions or maybe weak van der Waals forces by the function of surfactant [23]. The inset shows the single nanocube. The histogram (figure 2(b)) depicts the average diameter of 19.5 ± 2 nm and narrow size distribution. As can be seen in figure 2(c), the selected area electron diffraction (SAED) pattern revealed the spinel planes of the ferrite crystal phase (Fd-3m), demonstrating a highly crystalline structure supported by well-pronounced diffraction rings [24]. The inset shows d-spacing of 0.49 nm, consistent with the (111) plane of the Mn crystal structure. EDAX analysis from HRTEM represents the presence of Mn, Fe and O elements in figure 2(d) and the compositional analysis (table 1) represents the weight and atomic % of element distribution in the system [25, 26]. From which, it is found that the Fe to Mn ratio was 2.16:1 that is close to the stoichiometry of theoretical ratio.

Considering the synthesis route, the formation mechanism of NCs is favoured by the preferential growth of surfactant molecules adsorption. Here CTA⁺ ions help in directional growth of NCs. In detail, the growth is always favoured by adsorption of different amount of surfactant during the synthesis [27]. The formation of NCs occurs as follows: At the initial stage of the reaction, nanoparticles grow equally in all the facets, but after the adsorption of CTA⁺ ions on specific crystal facets (100) transforms the spherical nanoparticles to nanocubes by controlling the growth rates along different crystal axes and allowing growth only in the easy axes direction of [111] which dominates the growth at this facet and diminishes the growth in other facets. This process is continued until surface energies were completely elapsed [22, 28–30].

The oxidation state and elemental composition of MnNCs were identified using XPS analysis. Figure 3(a) represents the complete survey of NCs with the presence of elements such as Fe, Mn and O. The in-depth analysis of each element is represented in figures 3(b)–(d). In case of Fe 2p scan, the two high intense peaks (711 eV and 724.7 eV) of Fe 2p3/2 and Fe 2p1/2 and one satellite/shake-up peaks (718 eV) were observed. These peaks prove that the pure form of magnetite with a low detection limit of Fe²⁺. From Mn 2p spectra, the two core level peaks (641.3 and 653.3 eV) of Mn 2p3/2 and Mn 2p1/2 were obtained which proves the doping of
Mn ions in the NCs. Finally, in case of O 1 s peaks, we observed unusual bond splitting into two peaks (529.8 and 532.8 eV) which denotes that the formation of ionic bonds between metals (Mn/Fe) with oxygen and hydroxyl group respectively. These results suggested that the Mn and Fe are in the oxidation state of +2 and +3 ions respectively [8, 24, 31, 32].

The as-synthesised NCs were evaluated using TGA thermal analysis. As can be seen in figure 4, 21% of initial weight loss was observed which may be due to the release of physisorbed water and other organic components of benzyl ether. Later, the weight loss of 8% was seen from 200 °C–350 °C which is a pure decomposition of CTAB molecules in the reaction solution. As usual, the NCs were highly stable at higher temperatures [17, 33].

Magnetic properties of MnNCs were evaluated using VSM by the magnetic hysteresis curve. Magnetization field-dependent curve obtained at room temperature (300 K). Figure 5 displays the characteristics attributable to a soft ferromagnet, showing superparamagnetic behaviour with a magnetic saturation, $M_s = 59 \text{ emu g}^{-1}$ with

![Figure 2.](image-url)  
Figure 2. (a) Low magnification TEM image of cube-like MnFe NCs (inset represents the single nanocube scale bar of 20 nm), (b) Histogram of average particle size calculated using Image J software of 336 particles, (c) SAED pattern of MnFe NCs (inset: d-spacing of MnNCs), (d) EDAX spectrum of the elements.

Table 1. Elemental composition of MnFe NCs from HRTEM.

| Element | Weight% | Atomic% |
|---------|---------|---------|
| O K     | 38.38   | 65.29   |
| Mn K    | 18.08   | 11      |
| Fe K    | 43.54   | 23.71   |
| Total   | 100     | 100     |

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negligible coercivity and remanence (Mr = 14 emu g⁻¹, figure 5, inset) [10, 34] with the absence of hysteresis loop. And the obtained Ms is very much acceptable for various biological applications like drug delivery, hyperthermia, and MRI etc.
Nanocubes showed darkening as T2-weighted MR images in a concentration-dependent manner (figure 6(a)). On evaluating the T2-weighted images in the phantom gels, a noticeable darkening and thereby negative contrast was observed with increasing Mn\(^{2+}\)Fe concentrations. However, the T2 signal intensity was relatively strong because of Fe concentration doped with Mn ions, thus proving to be an efficient MRI contrast agent. Figure 6(b) represents the normalised MRI signal (experimental data) versus echo time (s) for the various NCs concentrations, along with the nonlinear exponential fitting decay curves. The r\(_2\) relaxivity values shown in figure 6(c) calculated from obtained 1/T\(_2\) values which were perfectly linear with the increasing concentration of NCs and the slope was made using the linear regression line. The calculated r\(_2\) value was found to be 296.11 mM\(^{-1}\)s\(^{-1}\). The obtained r\(_2\) value at 1.5 T is lower when compared to some of the published work 347.5 mM\(^{-1}\)s\(^{-1}\), 301 mM\(^{-1}\)s\(^{-1}\) [10, 12] which can be attributed to shape of the nanoparticle, as because of the cube-shaped structure has a relatively smaller surface to volume ratio which in turn lead to lower contact of hydrogen nuclei in the water proximity [28]. However, the obtained r\(_2\) value was much larger than other Mn doping with iron oxide [13] which is due to high Ms value of NCs and also the thickness of surfactant organic layer around the NCs [15].

Practically, the manganese doped nanoferrite represented as a T\(_1\) contrast agent. Some of the reports clearly state that the size is the deciding factor. For example, when the particle size is greater than 9 nm and larger Ms represents higher r\(_2\) value due to the aggregation in the suspension [35]. Li et al and Zhang et al reported the synthesis of ultra-small size Mn-doped iron oxide showed enhanced T\(_1\) contrast property [36, 37].

The biocompatibility of these nanocubes was demonstrated by analysing the rate of cell viability (MTT assay) using L6 cells. These cells were exposed to NCs at different concentrations ranging from 50–250 \(\mu\)g ml\(^{-1}\) for 24 h and 48 h time period. Figure 7 demonstrates more than 80% of the cell viability even at highest concentrations of 250 \(\mu\)g ml\(^{-1}\). It is seen that the nanoferrite does induce cytotoxicity, the concentration-dependent negligible toxicity may be by means of Mn ions in the NCs solution [38].
4. Conclusion

In summary, manganese ferrite nanocubes were synthesized by a facile thermal decomposition method. The smooth nucleation, regulated growth and adsorption of CTA$^+$ ion on a particular plane at high temperature, thermodynamically favour the formation of cubic nanostructures. The magnetic characteristics depict superparamagnetic features at room temperature. MR imaging showed an enhanced contrast property. Therefore, the results suggested that the MnFe NCs can be efficiently used in biomedical applications. Further investigations are underway by tuning the CTAB concentration and its impact of nanostructure formation. We also intend to change the Mn doping concentration and the size, to enhance the nanocube either as a strong positive or dual contrast agent.

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Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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