

Synthesis and characteristics of a superparamagnetic multifunction core-shell, $\text{ZnMnFe}_2\text{O}_4@ \text{SiO}_2$, for use in drug delivery applications

Aqeel Al-Hamaidah

Department of Physics, Faculty of Science, University of Isfahan, Isfahan, Iran
 aqeel@sci.ui.ac.ir

Malek Bagheri Harouni*

Department of Physics, Faculty of Science, University of Isfahan, Isfahan, Iran
 bagheri.malek@gmail.com

Mahmood Rezaee Roknabadi

Department of Physics, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran
 Roknabad@um.ac.ir

Alireza Charmforoushan

Department of Physics, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran
 kourosh_charmforoushan@yahoo.com

Reza Ghanbari

Department of Physics, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran
 rezaghanbari@mail.um.ac.ir

Abstract

In this research, the core-shell of a $\text{ZnMnFe}_2\text{O}_4@ \text{SiO}_2$ nanocomposite was prepared. Due to its porous structure, and magnetic and optical properties, this nanocomposite offers unique application potential in the field of biomedicine. For this purpose, $\text{ZnMnFe}_2\text{O}_4$ nanoparticles with superparamagnetic properties have been synthesized by a hydrothermal-sonochemical method. To achieve controlling the size, shape, and distribution of nanoparticles, the choice of synthesis method becomes very important. In this research, in order to obtain nanoparticles with suitable particle distribution and magnetic properties, spinel iron oxide was doped with zinc and manganese atoms by a combination of hydrothermal and sonochemical methods. Then, core-shell nanoparticles were prepared using Stöber's method. Finally, the silica shell of the porous superparamagnetic system was characterized using an X-ray diffraction pattern, FTIR, an EDS, and VSM. The results of XRD confirmed the formation of porous silica structures. Magnetic studies of manganese ferrite nanoparticles showed superparamagnetic behavior with a magnetic saturation of 53.9 emu/g for core and core-shell saturation magnetization of 33.6 emu/g in the incidence field of approximately 10 Oe. In addition to magnetic properties, these nanoparticles have unique optical properties that can be used in bio-medical research as their porous structure with a large surface area

provides the ability to load large amounts of drugs and biological molecules, and as a result, they can be used in the field of simultaneous medical diagnosis, treatment using MRI, and targeted drug delivery.

Keywords: "core-shell" nanocomposite "superparamagnetic" targeted drug delivery "hydrothermal-sonochemical"

Introduction

Superparamagnetic materials by reducing the crystal size in ferromagnetic materials and making them single-domain, the crystal anisotropy energy is reduced until it becomes comparable to thermal energy at a certain size [1]. In such a case, the thermal energy overcomes the anisotropy energy barrier, and the magnetic moment of the entire particle can fluctuate freely, similar to the magnetic moments of a single atom in a paramagnetic material. By applying an external magnetic field, we will have an orderly arrangement of magnetic moments, which in this so-called material are superparamagnetic. Materials and multi-domains become single domains, and the superparamagnetic state is observed [2-4].

Reports say that when Zn^{2+} is added to the manganese ferrite structure, the crystallite size values drop by a lot. This is because Zn^{2+} has a smaller ionic radius (0.68) than Mn^{2+} (0.75) [5-7]. Also, it has been found that increasing the level of Zn^{2+} doping increases the surface area and porosity of $\text{Zn}_x\text{Mn}_{x-1}\text{Fe}_2\text{O}_4$ MNPs by making the crystallites smaller and the bulk density lower. Because of this, it is expected that these MNPs will be able to extract the target analyte well. To our knowledge, however, there hasn't been a report in the literature about using $\text{Zn}_x\text{Mn}_{x-1}\text{Fe}_2\text{O}_4$ MNPs in sample preparation processes.

Many different methods have been found to make drug delivery systems. In this field, nanomaterials have gotten a lot of attention and have been studied in depth in order to make a new generation of drug delivery systems. The first advantage of nanoparticles in medicine is their size. Their sizes range from a few nanometers to tens of nanometers, so that they are smaller than a cell (10–100 microns) or comparable to the size of a virus (45–20 nanometers), protein (50–50 nanometers), or a gene. (2 nm wide and 10–100 nm long). Core-shell nanoparticles include cores that are coated with other materials, so they are mainly designed for biomedical applications based on surface chemistry, which increases their affinity for binding with drugs and receptors and makes them ligands. This has led to the synthesis of new nanoparticles that are compatible with the biological system compared to bulk materials.

The benefit of hyperthermic treatment with superparamagnetic nanoparticles is that the changing magnetic moment inside the nanoparticles can create more heat in a specific area. Superparamagnetic

nanoparticles have a higher specific absorption rate than ferromagnetic nanoparticles, which makes them more useful. At a temperature of 42–46 °C, it gets too hot and effectively kills the solid tumor. Since superparamagnetic nanoparticles have better properties than ferromagnetic nanoparticles, they have gotten more attention [8,9].

In this report, $\text{ZnMnFe}_2\text{O}_4$ nanoparticles were well distributed and showed excellent magnetic properties. The saturation magnetization of these nanoparticles was 53.9 emu/g, and their incidence field was less than 1.9 Oe. Then we cover it with silicate oxide, and we have obtained a porous sub-magnetic core-shell for use in medical applications such as drug delivery and MRI. We have successfully obtained a superparamagnetic, porous system and "core-shell". We expect that its encapsulation in a porous system that provides sustained drug release properties will potentially reduce the frequency of drug administration, reduce side effects, and prolong its delivery and elimination time in the body. In order to use these samples for hypothermia applications, it is necessary that H_c be less than 20 Oe. It is observed that $\text{ZnMnFe}_2\text{O}_4$ and SiO_2 have a coactivity nearer 8 Oe and are very suitable for use in hypothermic applications.

Experimental methods:

1. Synthesis of nanoparticles $\text{ZnMnFe}_2\text{O}_4$:

$\text{ZnMnFe}_2\text{O}_4$ nanocomposite was synthesized using a modified version of the hydrothermal method. Iron, zinc, and manganese nitrate precursors were

irradiated with ultrasound, and deionized water was used as the solvent. The solution was stirred for half an hour under magnetic stirring at room temperature. Then ammonia was added and magnetically stirred for half an hour; then sodium hydroxide solution was added drop by drop and stirred for 10 minutes. Then the solution was exposed to ultrasonic wave radiation for 40 minutes at a temperature of 60 °C. Then the mixture was transferred to the autoclave and placed at 200°C for 5 hours. After that, the mixture was separated and washed in a centrifuge before being dried at 80°C for 12 hours.

2. Coated a non-porous silica shell on zinc-manganese ferrite core-shell nanoparticles:

In this step, the synthesized $\text{ZnMnFe}_2\text{O}_4$ was added to 60 ml of ethanol, 10 ml of water, and 2 ml of $\text{NH}_3\text{H}_2\text{O}$ and the mixture was stirred an ultrasonic device for 16 minutes. TEOS was then added dropwise to the mixture and then washed several times with ethanol and water under magnetic stirring for 14 hours before being dried in an oven at 6 °C for one hour.

Results Discussion

The diffraction pattern is based on X-ray diffraction (XRD) for the detection of crystalline materials. The XRD pattern of $\text{ZnMnFe}_2\text{O}_4$ and $\text{ZnMnFe}_2\text{O}_4@\text{SiO}_2$ nanocomposite are shown in Fig. 1.

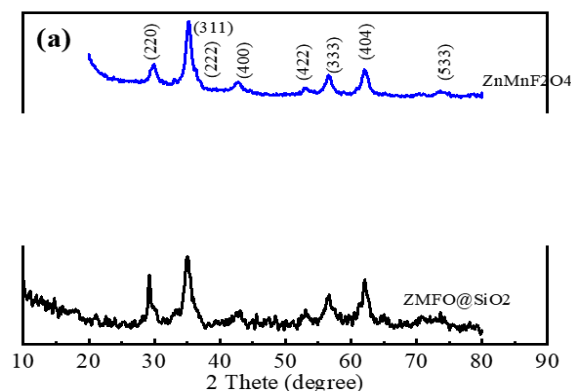


Fig. 1. The XRD pattern of $\text{ZnMnFe}_2\text{O}_4$ and $\text{ZnMnFe}_2\text{O}_4@\text{SiO}_2$ nanocomposite.

The X-ray diffraction pattern is used to study the properties of the crystal structure of the sample, as can be seen in Fig. 1, the characteristic diffraction peaks are at 29.93, 35.40, 36.38, 42.73, 52.46, 56.59, 61.98, and 74.3, which belong to the plates (220),

(311), (222), (400), (422), (333), (404), and (533), respectively. This pattern is related to the cubic spinel structure and high crystallinity of Zn-Mn ferrite. Also, it is found that the structure of core-shell ($\text{ZnMnFe}_2\text{O}_4@\text{SiO}_2$) has not been changed.

The information obtained from this analysis can be used to determine structural parameters such as the

average size of crystal lattice. The average size of the crystals is calculated using Debye-Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where D, k, λ , β , and θ are the mean size of the ordered (crystalline) domains, dimensionless shape factor, wave number, the line broadening at half the

maximum intensity (FWHM), and peak position, respectively. The average size of crystal lattice of samples was obtained 3.62 Å.

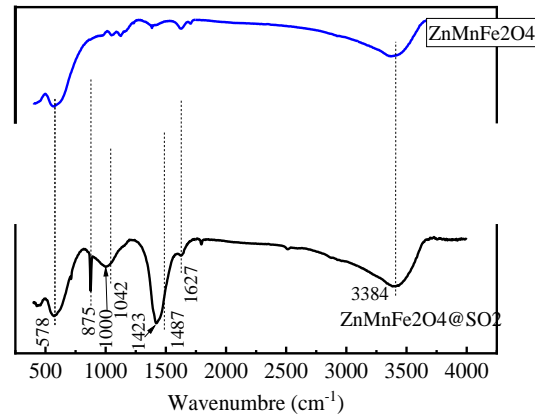


Fig. 2. FTIR spectra of $\text{ZnMnFe}_2\text{O}_4$ and $\text{ZnMnFe}_2\text{O}_4@\text{SiO}_2$ nanocomposite.

The FTIR was performed in the range of 400–4000 cm^{-1} . The IR spectrum is considered an important tool for obtaining information about the structure and status of ions in the crystal through crystal vibration modes. The formation of spinel structure in nanoparticles is shown in Fig. 2. The peaks of 551.56 cm^{-1} are related to iron-oxygen tensile vibrations (Fe-O), and the peak of the spinel nanoparticle structure of the iron and zinc oxide and zinc has a strong absorption of 400 cm^{-1} . The peak at 517 cm^{-1} is for O-F-O-Z in a four-sided location. The peak at 940 cm^{-1} is also for M-N-O vibrations [12–14]. The peak

of 1080 cm^{-1} also belongs to the O-F-O tensile mode, and the peak of 1634 cm^{-1} belongs to Zn-O at the location of octagonal bending and octagonal drilling. The results of the analysis are shown in Fig. 2, which shows the FTIR corresponding to $\text{ZnMnFe}_2\text{O}_4@\text{SiO}_2$ core-shell nanoparticles. In this spectrum, the absorption peaks at 1196 and 1000 cm^{-1} are related to Si-O-Si antisymmetric vibrations, and the peak at 955 cm^{-1} is related to Si-OH vibrations, which are caused by the bond between silica and group surface hydroxyls.

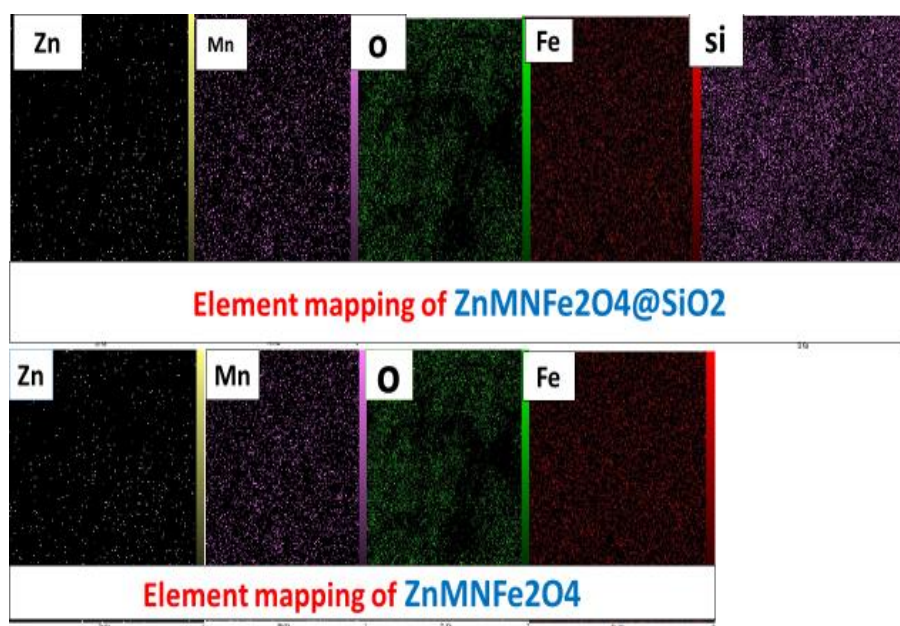


Fig. 3. The elemental mapping of $\text{ZnMnFe}_2\text{O}_4$ and $\text{ZnMnFe}_2\text{O}_4@\text{SiO}_2$ nanocomposite.

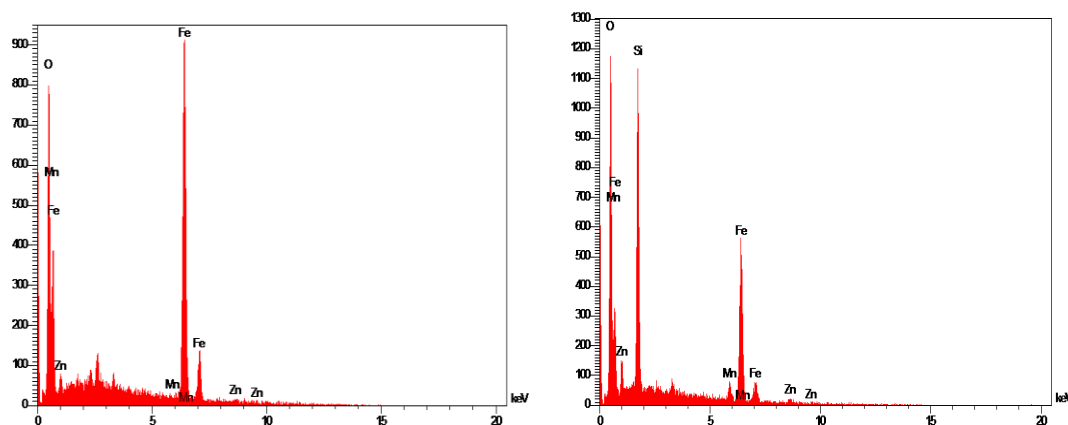


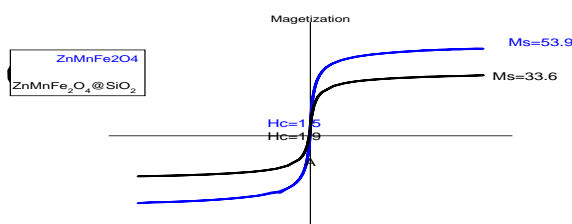
Fig. 4. The EDS spectra of $\text{ZnMnFe}_2\text{O}_4$ and $\text{ZnMnFe}_2\text{O}_4@\text{SiO}_2$ nanocomposite.

The elemental mapping of samples are shown in Fig. 3. This analysis shows that the sample elements have uniform distribution. Also, in order to know more nanoparticles and to prove the presence of silicate in the sample, EDS elemental composition analysis

about the chemical composition of $\text{ZnMnFe}_2\text{O}_4@\text{SiO}_2$ core-shell

should be used. The presence of Mn, Fe, Zn, O, and Si elements show in the EDS spectra in Fig. 4.

Fig. 5. VSM analysis of $\text{ZnMnFe}_2\text{O}_4$ and $\text{ZnMnFe}_2\text{O}_4@\text{SiO}_2$ nanocomposite.



VSM analysis was used to find out about the magnetic properties of core-shell nanoparticles and the magnetic receptivity needed in these nanoparticles because of their magnetic ability in biomedical applications. So, even though this material has been covered with porous silica, it is still superparamagnetic. It is, but because silica is not magnetic, its saturation magnetization has gone down. The saturation magnetization for the core is equal to 9.53 emu/gr, and the repulsion field is 1.5 Oe, but the saturation magnetization and repulsion field for the core are 33.6 emu/gr and 1.9 Oe, respectively. The figure shows that the above samples are superparamagnetic. The saturation magnetization in these nanoparticles combined with their magnetic property makes them have many applications, especially in therapeutic fields.

Conclusions

The goal of this research project was to find out if it was possible to make core-shell nanoparticles so that a nanocomposite with magnetic, optical, and porous properties could be made. For this purpose, first, manganese ferrite superparamagnetic nanoparticles were made using the hydrothermal-sonochemical method for the sample with the best magnetic properties, and a superparamagnetic sample of HC about 1 with good particle distribution was used as a magnetic core. Then, making solid silica coating conditions and then putting porous silica on the surface of core-shell nanoparticles made it possible, and it was made successfully. In this step, first a thin layer of silica was placed on the surface of the nanoparticles using Stöber's method, and then a porous layer of silica was coated on the surface of these nanoparticles with manganese ferrite.

Structural, magnetic, and optical properties. The characterization of these nanoparticles (VSM, FTIR, EDS, and XRD) was performed, and the results of the characterization are summarized in an example of a porous superparamagnetic core-shell and atomic distribution. The saturation magnetization in these nanoparticles combined with their magnetic property makes them have many applications, especially in therapeutic fields.

References

- [1] H. Yan, J. Zhang, Ch. You, Zh. Song, et al. "Influences of different synthesis conditions on properties of Fe₃O₄", Materials Chemistry and Physics 113, (2009), 46-52.
- [2] H. Mei Xiao, X. Ming Liu, S. Yun Fu. "Synthesis, magnetic and microwave absorbing properties of core-shell structured MnFe₂O₄/TiO₂ nanocomposites", Composites Science and Technology 66 (2006) 2003–2008.
- [3] ST. Senz, W. Blum, D. Hesse. "The effect of stress on cubic-to tetragonal phase transitions in Mg₂TiO₄ and Mg₂GeO₄ spinel films", Philosophical Magazine A, (2001), VOL. 81, NO. 1, 109-124.
- [4] S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser. "Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocrystal Superlattices", Science 287, (1989).
- [5] M. Sugimoto, J. Am. Ceram. Soc. 82 (1999) 269.
- [6] W.B. Cross, L. Affleck, M.V. Kuznetsov, I.P. Parkin, Q.A. Pankurst, J. Mater. Chem. 9 (1999) 2524.
- [7] O.A. Shlyakhtin, I.N. Vjunitsky, Y.J. Oh, Y.D. Tretyakov, J. Mater. Chem. 9 (1999) 1223.
- [8] G.F. Goya, H.R. Rechenberg, J. Magn. Magn. Mater. 203(1999) 141.
- [9] D.J. Fatemi, V.G. Harris, V.M. Browning, J.P. Kirkland, J. Appl. Phys. 83 (1998) 6867.
- [10] Li, X., Xie, C., Xia, H. & Wang, Z. (2018a). pH and ultrasound dual-responsive polydopamine-coated mesoporous silica nanoparticles for controlled drug delivery. *Langmuir* 34, 9974-9981
- [11] Sukumaran, S., Neelakandan, M., Shaji, N., Prasad, P. & Yadunath, V. (2018). Magnetic nanoparticles: Synthesis and potential biological applications. *JSM Nanotechnology & Nanomedicine* 6, 1068.