

Preparation of Fe₃O₄@SiO₂ Nanostructures via Inverse Micelle Method and Study of Their Magnetic Properties for Biological Applications

Afsaneh Sharafi^{1*}, Nazanin Farhadyar²

¹ *Ph.D., Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran*

² *Assistant Professor, Department of Chemistry, Varamin (Pishva) Branch Islamic Azad University, Varamin, Iran*

Received: 22 December 2012; Accepted: 25 February 2013

ABSTRACT

In this work, we report synthesis of superparamagnetic iron oxide nanoparticles at room temperature using microemulsion template phase consisting of cyclohexane, water, cetyltrimethylammonium bromide CTAB as cationic surfactant and butanol as a cosurfactant. Silica surface modification of the as prepared nanoparticles was performed by adding tetraethoxysilane TEOS to alkaline medium. The structure, morphology, and magnetic properties of the products were characterized by X-ray powder diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and vibrating sample magnetometer (VSM) at room temperature. The results revealed formation of iron oxide nanoparticles, with an average size of 8.8-12 nm, a superparamagnetism behavior with fast response to applied magnetic fields and Zero remanence and coercivity.

Keyword: Inverse micelle; Surface modification; Superparamagnetism; Magnetic nanoparticles; Fe₃O₄@SiO₂ Nanostructures.

1. INTRODUCTION

Magnetic drug delivery systems are a promising technology for cancer cells treatment. In such a system, some smart particles have to be associated with the magnetic core to direct magnetic nanostructures to the vicinity of the target for hyperthermia or for temperature enhanced release of the drug. The best magnetic particle size, for these kind applications has to be below a critical value, which is dependent on the material species,

but is typically around 10-20 nm [1-4]. In this condition, each nanostructure will be able to pass through the cell membrane and can acts as a single domain paramagnetic substance with a fast response to applied magnetic fields and zero remanence (residual magnetism) and coercivity (the field required to bring the magnetization to zero) [5, 6]. Multifunctional silica nanoparticles (NPs) have tremendous potential applications as magnetic

(*) Corresponding Author - e-mail: af.sharafi@yahoo.com

indicators and/or photon sources for a number of biotechnological and information technologies. Indeed, the chemistry of silica gained recently in interest in the design of new nano sized particles with functional architecture for applications in biotechnology and photonics [7, 8]. Silica NPs are actually very promising candidates in the fields of biomedical, imaging, separation, diagnosis and therapy [9-11] and band-gap photonic materials when assembled in colloidal crystals [12, 13]. These applications all require size controlled, monodispersed, bright and/or magnetic NPs that can be specifically conjugated to biological macromolecules or arranged in higher ordered structures. Also the preparation of such functional NPs involves a very good understanding of the influence of the synthesis parameters in order to control the properties of the final product such as size, morphology, effects of the shell on the core particle, etc.

In the paper, a room temperature microemulsion method has been employed to synthesize Fe_3O_4 nanoparticles, and the sol-gel processes were selected for coating magnetic nanoparticles with silica, and magnetic resonance property were investigated.

2. EXPERIMENTAL

2.1. Chemicals and reagents

Iron (III) chloride hexahydrate ($\text{Fe}_3\text{Cl}_3 \cdot 6\text{H}_2\text{O}$), Iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), aqueous ammonia (16%), cetyltrimethylammonium bromide (CTAB), n-butanol ($\text{C}_4\text{H}_9\text{OH}$), tetraethoxysilane (TEOS), in analytical grade were purchased from Merck Company (Darmstadt, Germany).

2.2. Preparation of magnetite iron oxide nanoparticles

The magnetic nanoparticles were prepared by the reverse microemulsion method. First 3 gr of cetyltrimethyl ammonium bromide (CTAB) and 10 mL n-butanol were added in 60 mL of n-hexane. The mixture was stirred at 100 rpm for 20 min and was added dropping aqueous solution of

$\text{FeCl}_2/\text{FeCl}_3$ (0.14 g /0.06 g, 2.7 mL water) under nitrogen (N_2) atmosphere and purging with N_2 for 20 min. An ammonium hydroxide solution (16% NH_4OH in water, 0.7 mL) was finally dropped in the solution under N_2 protection. By adding 1.5 mL TEOS dropwisely to the mixture and stirred for 16 h. The reaction was finally stopped by addition of ethanol and the surfactant was removed through centrifuging the solution.

2.3. Preparation of $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ nanoparticles

$\text{Fe}_3\text{O}_4@/\text{SiO}_2$ nanoparticles were prepared by the stober method. The magnetic nanoparticles Fe_3O_4 (0.01 g) was dissolved in mixed solution of water (10 mL) and ethanol (50 mL). Ammonia solution (1.2 mL) and TEOS (1.8 mL) were added to the mixed solution with stirring and reactant for 1.5 h. The nanoparticles were isolated by centrifugating and washed with ethanol.

X-ray diffraction patterns (PW 1800 PHILIPS), Energy Dispersion Spectrum (Hitachi F4160, Oxford), and FT-IR spectra (A NICOLET 5700) were used to determine the crystal structure of the silica coated Fe_3O_4 nanoparticles and the chemical bonds of Fe-O-Si, respectively. The magnetic properties were analyzed with a Vibration Sample Magnetometer (VSM, Quantum Design PPMS-9).

3. RESULTS AND DISCUSSION

3.1. X-Ray study

Figure 1(a, b) represents X-ray diffraction pattern of Fe_3O_4 and silica coated Fe_3O_4 nanoparticles. All the diffraction peaks observed at (220), (311), (400), (422), (511), (440) in this Figure 1 (a, b) were consistent with those of standard XRD pattern of Fe_3O_4 crystal with spinal structure (JCPDS card No. 65-3107). Whereas, no peaks were detected for silica coated Fe_3O_4 nanoparticles which could be assigned to impurities as shown in Figure 1 (b). The average crystalline size of Fe_3O_4 and $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ nanostructures at the characteristic peak (311) were calculated by using Scherer formula:

$$D = k\lambda/\beta\cos\theta \quad (1)$$

Where, D is the mean grain size, k is a geometric factor, λ is the X-ray wavelength, β is the FWHM of diffraction peak and θ is the diffraction angle. The results of D values, using the peak (311) planes of the spinel structures was 11 nm for uncoated and 17 nm for silica coated magnetic iron oxide.

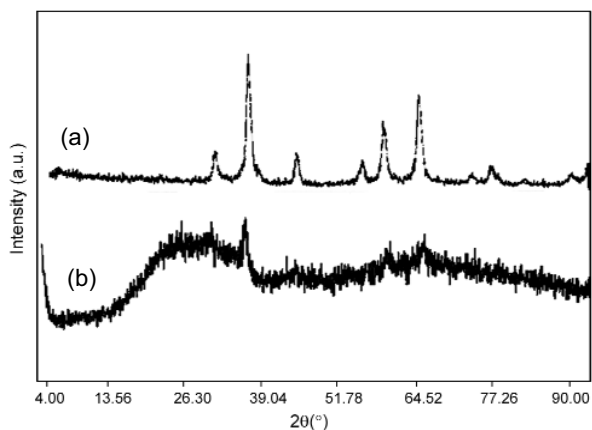


Figure 1: X-ray powder diffraction patterns of: a) Fe₃O₄ nanoparticles and (b) Fe₃O₄@SiO₂ composite particles.

3.2. Edx study

The surface composition of silica coated sample was qualitatively determined by energy dispersion

spectrum (EDS) as shown in Figure 2. It shows that Fe and Si peak are obtained and atomic (%) ratio of Fe/Si= 11.29/16.8. It is therefore assumed that silica particles are coated onto the surface of Fe₃O₄ nanoparticles.

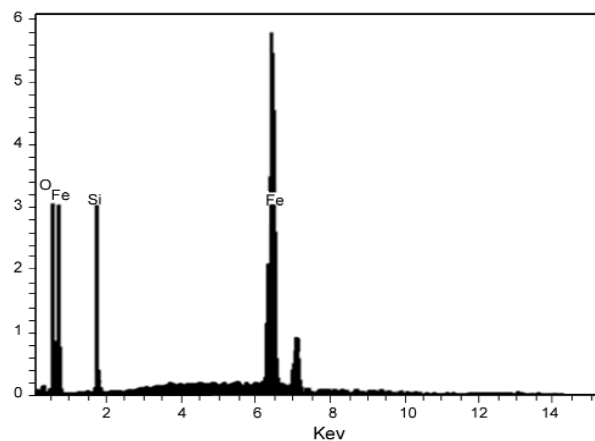


Figure 2: Energy-dispersive X-ray spectroscopy Edx result of silica coated Fe₃O₄ nanoparticles.

Figure 3 represents FT-IR spectra for Fe₃O₄ and Fe₃O₄@SiO₂, The strong broad peaks at about 630 cm⁻¹ and 568 cm⁻¹ (in Figure 3a) are due to the stretching vibrations of Fe-O and Fe-O bonds and

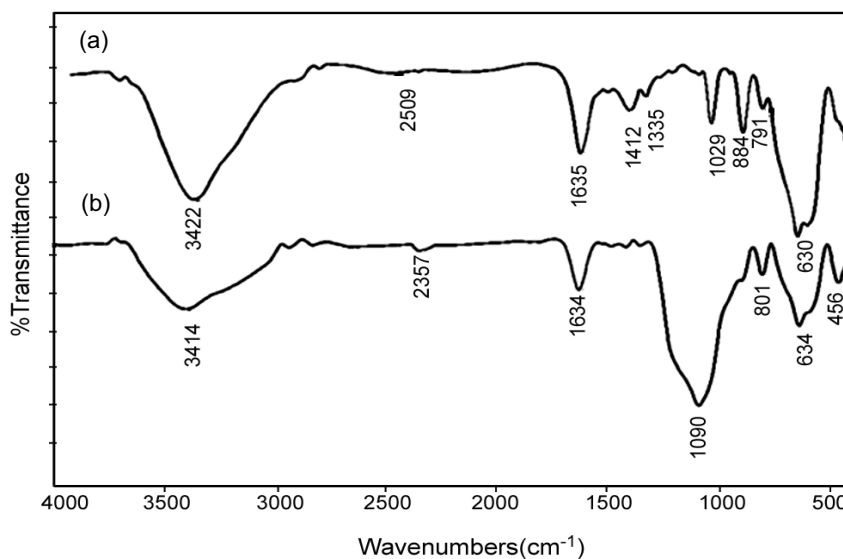


Figure 3: Fourier transforms infrared (FT-IR) spectra of: a) Fe₃O₄; b) Fe₃O₄@SiO₂.

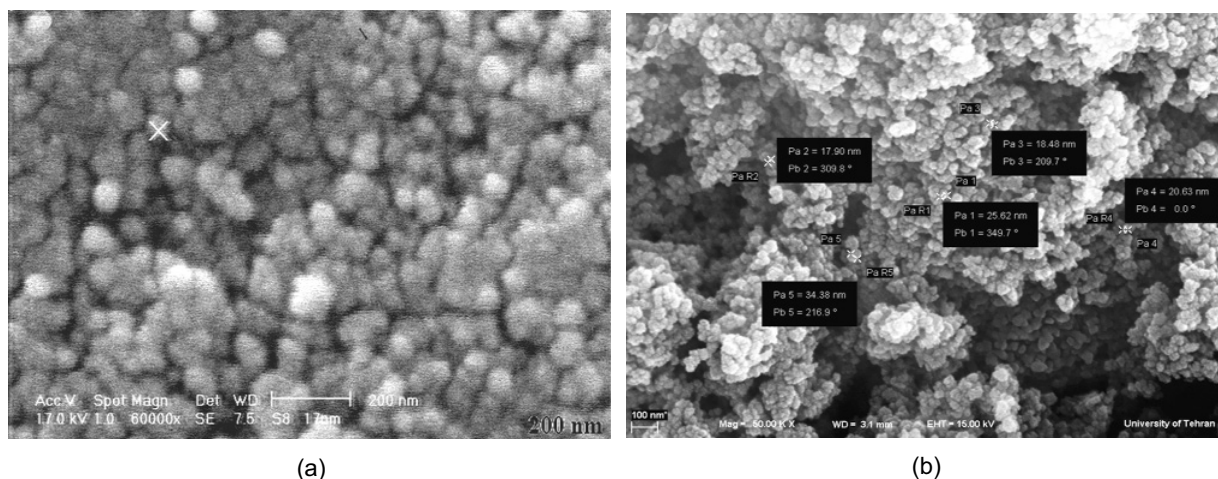


Figure 4 (a, b): a) SEM image of Fe₃O₄; b) SEM image of Fe₃O₄@SiO₂ Core-Shell nanostructures.

the peaks around 3000-3500 cm⁻¹ and 1625 cm⁻¹ have been assigned to the stretching and bending vibrations of the H-O-H bond, respectively, showing the physical absorption of H₂O molecules on the surfaces. In Figure 3b shows IR spectrum of silica coated Fe₃O₄@SiO₂ nanoparticles confirms the presence of the finger print bands at around 1090 cm⁻¹ which are characteristic of stretching vibrations of framework Si-O-Si. Peak 634 cm⁻¹ (in Figure 3b) not absorbed indicates the formation of Si-O-Fe, Si-O-Si bond was assumed that absorption bands in (1090 cm⁻¹), (989 cm⁻¹), (801 cm⁻¹), respectively, assigned to stretching vibration of Si-O-Si bond, Si-OH bond, Si-O-Fe bond.

Table 1: EDAX quantification element normalized.

Elements	Wt.%	At.%
Fe	95.39	11.29
O	4.08	68.15
Si	0.53	16.8

3.3. Morphological study

Figure 4 (a, b) represents SEM images of Fe₃O₄ and Fe₃O₄@SiO₂ nanoparticles. These images clearly show spheric particle shapes and morphology with

a homogenous particle size and distribution. This result has been confirmed by Dynamic Light Scattering analysis data.

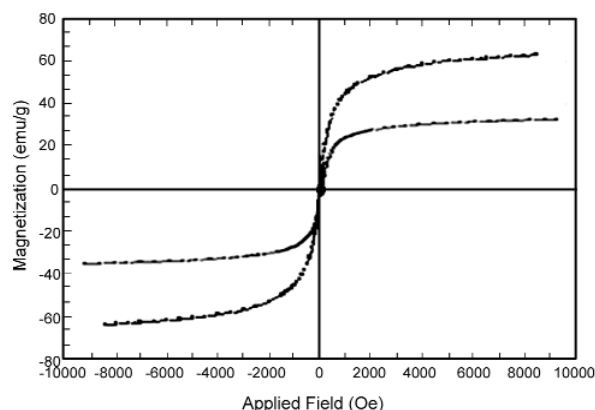


Figure 5: Magnetization vs. applied magnetic field for a) Fe₃O₄; b) Fe₃O₄@SiO₂ at room temperature.

3.4. Magnetic study

Figure 5 (a, b) represents magnetic-field-dependent magnetization parameters, M(H) for Fe₃O₄; and Fe₃O₄/SiO₂ in the size of 13.26, 21.06 and 34 nm at room temperature, using vibrating sample magnetometer with a peak field of 15 kOe. The hysteresis loops for Fe₃O₄; and Fe₃O₄@SiO₂ in the size of 11 nm, with coercivity (H_c= 0.0 Oe) and remanence (M_r= 0) indicate a superparamagnetism

properties at 300 K with a saturation magnetization of 65 emu/g for Fe₃O₄ and 34 emu/g for Fe₃O₄@SiO₂.

4. CONCLUSIONS

Fe₃O₄ nanoparticles were prepared by the microemulsion technique using Fe³⁺ and Fe²⁺ and silica coated uniformly by hydrolysis and condensation of TEOS in a sol-gel process. Using this method nanosized Fe₃O₄ in 11 nm size and 17 nm size silica coated Fe₃O₄ were prepared successfully. FT-IR spectra showed formation chemical bonds of Fe-O-Si on to the surface of Fe₃O₄ nanoparticles and FT-IR spectra, edx analysis data showed the presence of silica in our prepared sample. Microemulsion (inverse micelle) is a suitable way for obtaining the uniform and size controllable nanoparticles.

REFERENCES

1. Yamguchi K., Matsumoto K., Fiji T., *J. Appl. Phys.*, **67**(1990), 4493.
2. Odenbach S., *Adv. Colloid Interface Sci.*, **46**(1993), 263.
3. Atarshi T., Imai T., *J. Magn Magn Mater.*, **85**(1990), 3.
4. Caceres P.G., Behbehani M.H., *Appl. Catal A*, **109**(1994), 211.
5. Chikov V., Kuznetsow A., *J. Magn Magn Mater.*, **122**(1993), 367.
6. Fan R., Chen X.H., Gui Z., *Mater Res Bull.*, **36**(2001), 497.
7. Burns A., Hooisweng O., Weisner U., *Chem. Soc. Rev.*, **35**(2006), 1028.
8. Wang L., Zhao W., Tan W., *Nano Res.*, **1**(2) (2008), 99.
9. Yan J., Estevez M.C., Smith J.E., Wang K., He X., Wang L., Tan W., *Nano Today*, **2**(3) (2007), 44.
10. Trewyn B.G., Slowing I.I., Giri S., Chen H.T., Lin V.S.Y., *Acc. Chem. Res.*, **40**(2007) 846.
11. Slowing I.I., Trewyn B.G., Lin V.S.L., *J. Am. Chem. Soc.*, **129**(2007), 8845.
12. Masse P., Pouclet G., Ravaine S., *Adv. Mater.*, **20**(2008), 584.
13. Ge J., Yin J., *Adv. Mater.*, **20**(18) (2008), 3485.