

## **Preparation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Nanostructures via Inverse Micelle Method and Study of Their Magnetic Properties for Biological Applications**

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### **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; Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Nanostructures.

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### **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

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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<sub>3</sub>O<sub>4</sub> 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 (Fe<sub>3</sub>Cl<sub>3</sub>.6H<sub>2</sub>O), Iron (II) chloride tetrahydrate (FeCl<sub>2</sub>.4H<sub>2</sub>O), aqueous ammonia (16%), cetyltrimethylammonium bromide (CTAB), n-butanol (C<sub>4</sub>H<sub>9</sub>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

FeCl<sub>2</sub>/FeCl<sub>3</sub> (0.14 g /0.06 g, 2.7 mL water) under nitrogen (N<sub>2</sub>) atmosphere and purging with N<sub>2</sub> for 20 min. An ammonium hydroxide solution (16% NH<sub>4</sub>OH in water, 0.7 mL) was finally dropped in the solution under N<sub>2</sub> 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 Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles were prepared by the stober method. The magnetic nanoparticles Fe<sub>3</sub>O<sub>4</sub> (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<sub>3</sub>O<sub>4</sub> 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).

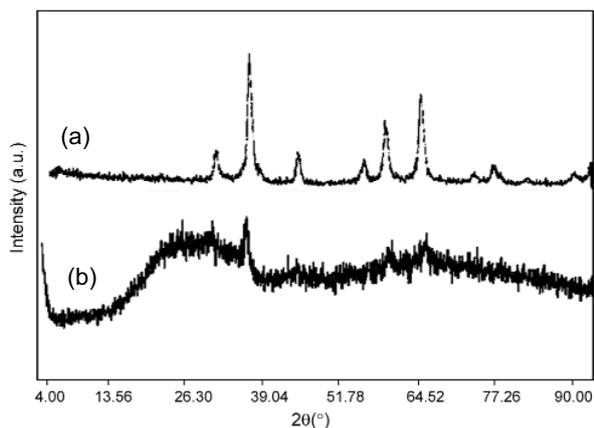
## 3. RESULTS AND DISCUSSION

### 3.1. X-Ray study

Figure 1(a, b) represents X-ray diffraction pattern of Fe<sub>3</sub>O<sub>4</sub> and silica coated Fe<sub>3</sub>O<sub>4</sub> 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<sub>3</sub>O<sub>4</sub> crystal with spinal structure (JCPDS card No. 65-3107). Whereas, no peaks were detected for silica coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles which could be assigned to impurities as shown in Figure 1 (b). The average crystalline size of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> 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,  $\lambda$  is the X-ray wavelength,  $\beta$  is the FWHM of diffraction peak and  $\theta$  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.

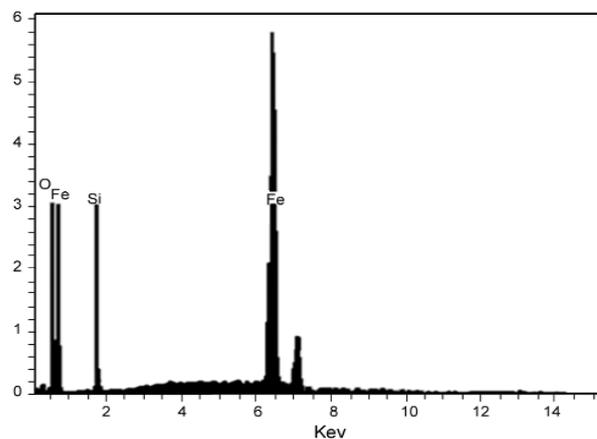


**Figure 1:** X-ray powder diffraction patterns of: a) Fe<sub>3</sub>O<sub>4</sub> nanoparticles and (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> composite particles.

### 3.2. Edx study

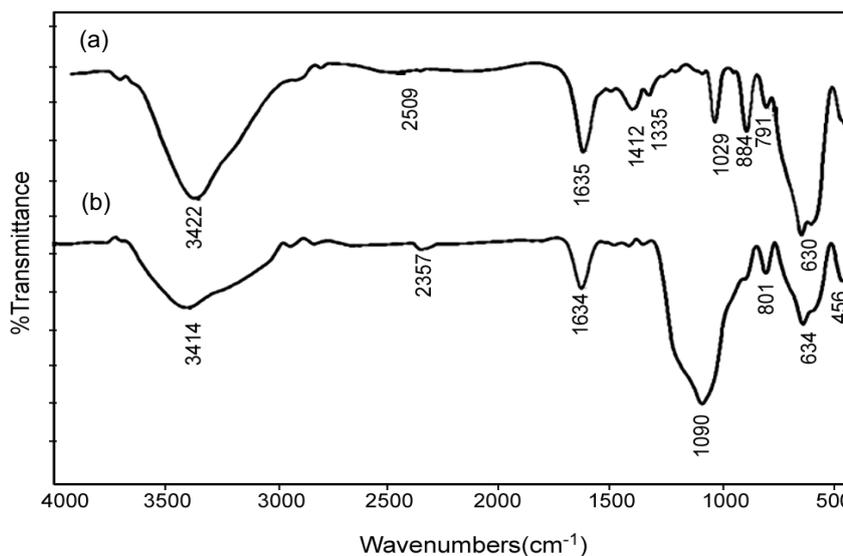
The surface composition of silica coated sample was qualitatively determined by energy dispersion

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 Fe<sub>3</sub>O<sub>4</sub> nanoparticles.



**Figure 2:** Energy-dispersive X-ray spectroscopy Edx result of silica coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

Figure 3 represents FT-IR spectra for Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, The strong broad peaks at about 630 cm<sup>-1</sup> and 568 cm<sup>-1</sup> (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) Fe<sub>3</sub>O<sub>4</sub>; b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>.

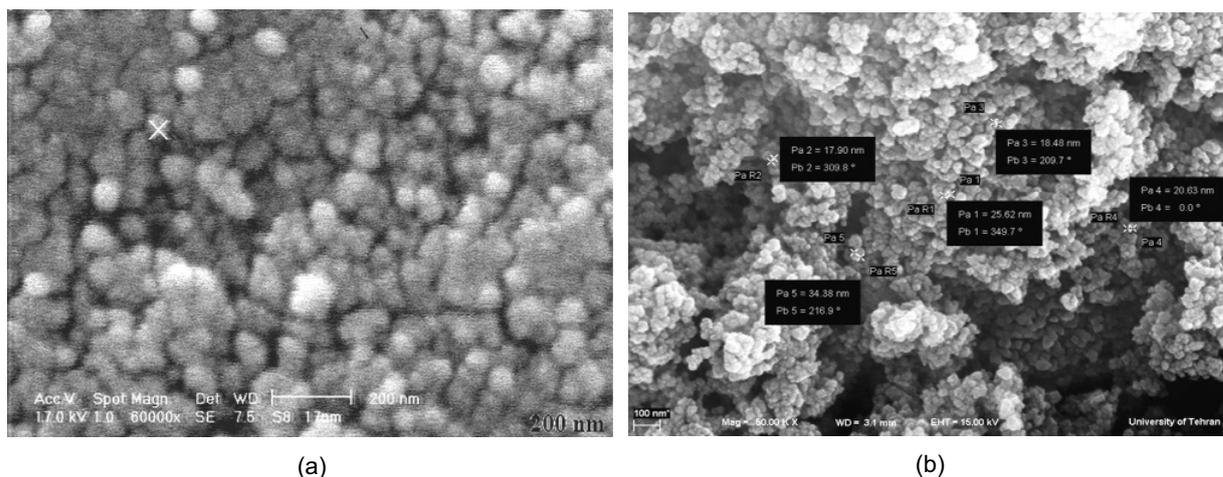


Figure 4 (a, b): a) SEM image of Fe<sub>3</sub>O<sub>4</sub>; b) SEM image of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> Core-Shell nanostructures.

the peaks around 3000-3500 cm<sup>-1</sup> and 1625 cm<sup>-1</sup> have been assigned to the stretching and bending vibrations of the H-O-H bond, respectively, showing the physical absorption of H<sub>2</sub>O molecules on the surfaces. In Figure 3b shows IR spectrum of silica coated Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles confirms the presence of the finger print bands at around 1090 cm<sup>-1</sup> which are characteristic of stretching vibrations of framework Si-O-Si. Peak 634 cm<sup>-1</sup> (in Figure 3b) not absorbed indicates the formation of Si-O-Fe, Si-O-Si bond was assumed that absorption bands in (1090 cm<sup>-1</sup>), (989 cm<sup>-1</sup>), (801 cm<sup>-1</sup>), 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 Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> 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.

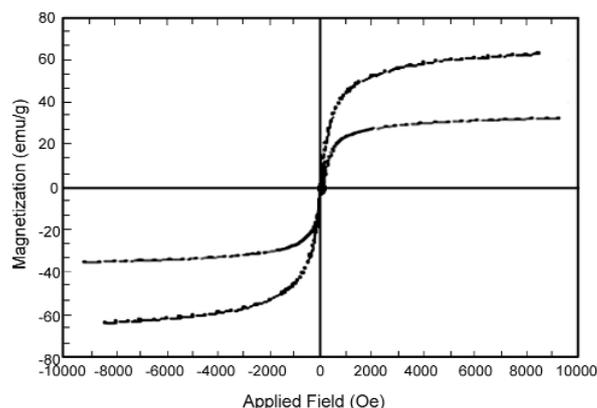


Figure 5: Magnetization vs. applied magnetic field for a) Fe<sub>3</sub>O<sub>4</sub>; b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> at room temperature.

### 3.4. Magnetic study

Figure 5 (a, b) represents magnetic-field-dependent magnetization parameters, M(H) for Fe<sub>3</sub>O<sub>4</sub>; and Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> 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 Fe<sub>3</sub>O<sub>4</sub>; and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> in the size of 11 nm, with coercivity (H<sub>c</sub>= 0.0 Oe) and remanence (M<sub>r</sub>= 0) indicate a superparamagnetism

properties at 300 K with a saturation magnetization of 65 emu/g for Fe<sub>3</sub>O<sub>4</sub> and 34 emu/g for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>.

#### 4. CONCLUSIONS

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by the microemulsion technique using Fe<sup>3+</sup> and Fe<sup>2+</sup> and silica coated uniformly by hydrolysis and condensation of TEOS in a sol-gel process. Using this method nanosized Fe<sub>3</sub>O<sub>4</sub> in 11 nm size and 17 nm size silica coated Fe<sub>3</sub>O<sub>4</sub> were prepared successfully. FT-IR spectra showed formation chemical bonds of Fe-O-Si on to the surface of Fe<sub>3</sub>O<sub>4</sub> 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.

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