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## Preparation of surface modified magnetic Iron Oxide nanoparticles and study of their colloidal behavior

### ABSTRACT

**M. SeyedSadjadi<sup>1,\*</sup>**  
**S. E. Babaei<sup>1</sup>**  
**N. Farhadyar<sup>2</sup>**

<sup>1</sup>Department of Chemistry,  
Science and Research Branch,  
Islamic Azad University, Tehran  
14778 92855, Iran.

<sup>2</sup>Department of Chemistry,  
Varamin -Pishva Branch,  
Islamic Azad University,  
Varamin, Iran.

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In this work, we report synthesis of surface modified superparamagnetic iron oxide nanoparticles (SPION) by co-precipitation method using  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  as precursors and trisodium citrate dihydrate as surfactant. Surface modification of the as prepared samples was performed in pot by sol-gel precipitation method using tetraethoxysilane (TEOS). The structure, morphology, and magnetic properties of the products were characterized by X-ray powder diffraction (XRD), 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 parameter of 8.5 nm for naked and 37nm for silica coated particles, with a superparamagnetic behavior and fast response to applied magnetic fields with zero remanence and coercivity.

**Keywords:** *Magnetic Iron Oxid; Precipitation method; Surface modification; Trisodium citrate; Dynamic light scattering; Superparamagnetism.*

### 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 in hyperthermia or temperature enhanced release of the drug. In this purpose, various strategies have been developed for preparation of surface coated or functionalized iron oxide NPs. These kind particles should have combined properties of high magnetic saturation, stability, biocompatibility, and interactive functions on its surface. For this reason, the surface of iron oxide NPs should be modified by suitable organic or inorganic materials such as polymers, biomolecules, silica, metals, etc. [1-14].

\* Corresponding author:  
Mirabdollah SeyedSadjadi  
Department of Chemistry,  
Science and Research Branch,  
Islamic Azad University, Tehran  
14778 92855, Iran.  
Tel +98 2122285032  
Fax +98 2122285032  
Email [m.s.sadjad@gmail.com](mailto:m.s.sadjad@gmail.com)

Among the different type of functionalizing studied agents, biocompatible silica can be directly used to protect magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles from aggregation and stable  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell nanostructure has such advantages as stability at low values of pH, easy surface modification, and easy control of the shell thickness. Until now, many reports have been published on the synthesis of silica coated ultra small SPION using PVP and EDTA surfactants [15-18]. In this work we attempted to prepare high dispersive silica coated magnetic nanostructures by co-precipitation method using trisodium citrate as a surfactant.

## EXPERIMENTAL

### Materials and methods

All materials were supplied by Merck Company. X-ray diffraction patterns (PW 1800 PHILIPS), and FT-IR spectra (A NICOLET 5700) were used to determine crystal structure of SPION and its silica coated product. The morphology, particle size and particle size distribution determination were carried out using Scanning electron microscopy (Philips EM208) and Dynamic Light Scattering (Otsuka, LPA-3000, 3100, Japan). The magnetic properties were finally evaluated with a Vibration Sample Magnetometer (VSM, Quantum Design PPMS-9).

### Preparation of magnetic iron oxide nanoparticles

The  $\text{Fe}_3\text{O}_4$  nanoparticles were synthesized by co-precipitation method at 25, 50 and 90° C, by dissolving 20 g of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 4\text{H}_2\text{O}$  and 13.97 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 50mL deaerated water. The solution was then purged with nitrogen to prevent  $\text{Fe}^{2+}$  ions oxidation. After 30 min of purging, 25mL of 10M  $\text{NH}_4\text{OH}$  was added drop wise into the above cited solutions purging for an additional 10 min. Now, 35.29g of trisodium citrate dihydrate, dissolved in 200 ml of distilled water was immediately added to the prepared solution in intense stirring under nitrogen protection. During the process, the solution was gradually changed to black and the resulting black solution was maintained at different temperatures (25, 50, 90° C) for 1 h and cooled then at room temperature. The stable colloidal solution obtained was centrifuged at 9000 rpm for 10 min and the back products were

separated and washed by distilled water for several times until the pH value of the solution became neutral.

### Surface modifications

5 ml of ammonia 25% in 40 ml of deionized water was added to a solution of 2g SPION, obtained from previous step, in 160 ml of ethanol. The mixture obtained was homogenized by ultrasound in a bath of water for 1 hour and was added to 1ml of tetraethoxysilane (TEOS) under vigorously stirring for 12 hours. The supernatant and precipitated deposits was separated, washed with ethanol and dried in an oven for 24 hours at 60° C.

## RESULTS AND DISCUSSION

### X-Ray study

Figure 1(a, b) shows X-ray diffraction pattern of  $\text{Fe}_3\text{O}_4$  and the silica coated  $\text{Fe}_3\text{O}_4$  nanoparticles. All the diffraction peaks observed at (220), (311), (400), (422), (511), (440)) in both the case were consistent with those of standard XRD pattern of  $\text{Fe}_3\text{O}_4$  crystal with spinal structure (JCPDS card No. 65–3107). Whereas, no additional peaks were detected for silica coated  $\text{Fe}_3\text{O}_4$  nanoparticles to could be assigned to the existence of impurities as shown in Figure 1b.

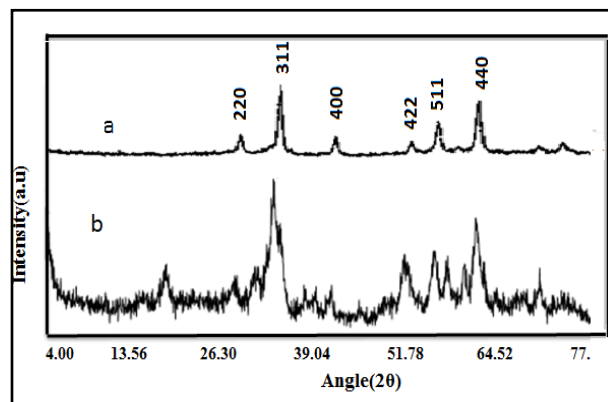


Fig. 1. X-ray powder diffraction patterns of: a)  $\text{Fe}_3\text{O}_4$  nanoparticles and (b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  composite particles

The average crystalline size of naked and silica coated  $\text{Fe}_3\text{O}_4$  nanostructures at the characteristic peak (311) were calculated by using the Scherrer formula:

$$D = k\lambda/\beta\cos\theta$$

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 8.5 nm at temperature 90 °C for uncoated and 12.99 nm for silica coated magnetic nanoparticles.

### FT-IR spectra

Figure 2, shows FT-IR spectra of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ . The strong broad peaks at about  $630\text{ cm}^{-1}$  and  $568\text{ cm}^{-1}$  (in Figure 2a) can be clearly due to the stretching vibrations of Fe(II)-O and Fe(III)-O bonds and the peaks observed at around  $3000\text{--}3500\text{ cm}^{-1}$  and  $1625\text{ cm}^{-1}$  can be assigned to the stretching and bending vibrations of the H-O-H bond respectively, showing the physical absorption of  $\text{H}_2\text{O}$  molecules on the surfaces of nanoparticles. Figure 2b shows FT-IR spectrum of silica coated iron oxide ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ) nanostructure.

This figure confirms appearance of the new ‘finger print’ bands at around  $1100\text{ cm}^{-1}$  which are characteristic of asymmetric ( $1150\text{ cm}^{-1}$ ) and symmetric ( $980\text{ cm}^{-1}$ ) stretching vibrations of framework Si-O-Si. [19] The two peaks observed at

around  $1063$  and  $786\text{ cm}^{-1}$  can be considered to be due to Fe-O-Si bond vibrations.

### Morphological study

Figures 3 and 4 show the SEM and TEM images of conjugated  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanostructures. These images clearly show spherical particle shapes and morphology with homogenous particle size and distribution.

### Dynamic Light Scattering

Figure 5 represents Dynamic Light Scattering (DLS) peak corresponding to a hydrodynamic diameter of the nanoparticles for the as prepared silica coated magnetic iron oxide sample in an initial small size of nanoparticles resulted from TEM image. The result obtained showed that the small size of nanoparticles originated from TEM image disappeared and larger particles were formed. This agglomeration seems to be reversible, and the original nanoparticles may be formed by addition of appropriate reagents [20]. Attempt to perform more experiment in this subject will be necessary since, preparation non-agglomerated homogenous dispersion is very important for the biological application, for example, in DDS application.

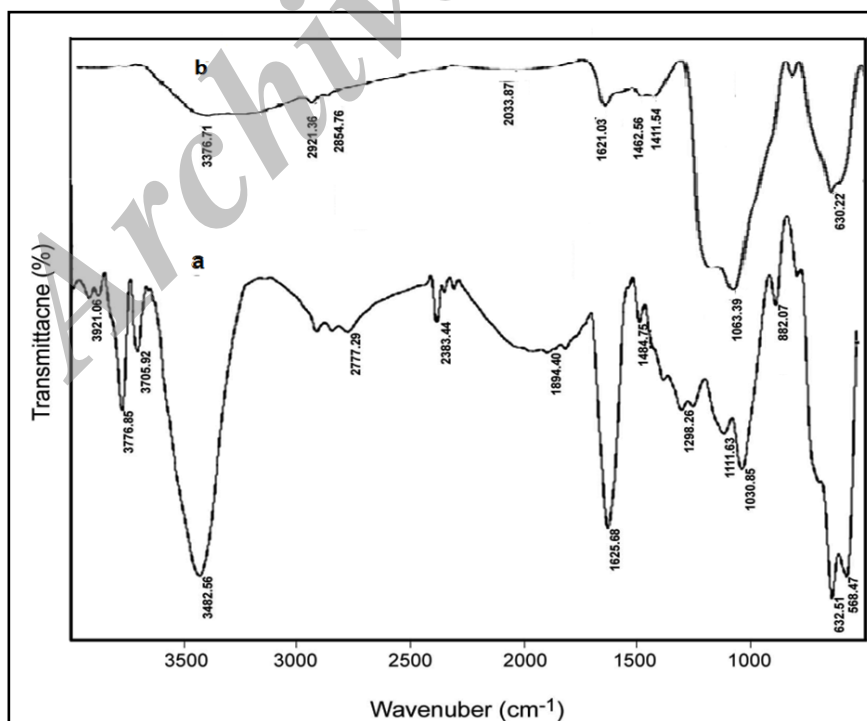


Fig. 2. FT-IR spectra of: a)  $\text{Fe}_3\text{O}_4$ ; b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanoconjugate

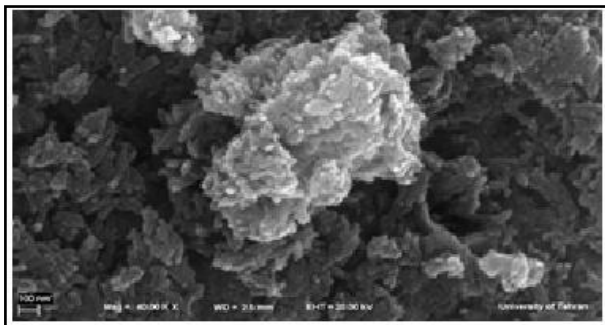


Fig. 3. SEM image of core-shell  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  aggregate

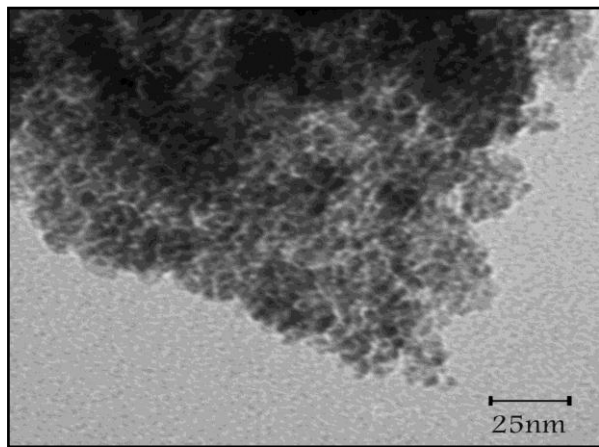


Fig. 4. TEM image of core-shell  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  aggregate

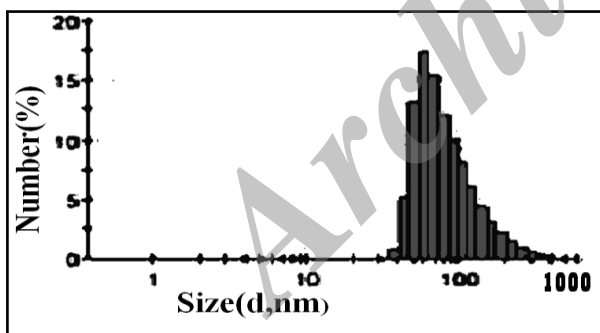


Fig. 5. particle size and distribution for silica coated  $\text{Fe}_3\text{O}_4$  nanoaggregate

### Magnetic study

Figure 6 (a, b) shows magnetic-field-dependent magnetization parameters,  $M(H)$  for  $\text{Fe}_3\text{O}_4$ ; and  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  using a vibrating sample magnetometer with a peak field of 15 kOe. The hysteresis loops for  $\text{Fe}_3\text{O}_4$ ; and  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , with coercivity ( $H_c=0.0$  Oe) and remanence ( $M_r=0$ )

indicate superparamagnetism properties at 300 K with a saturation magnetization of 65 emu/g for  $\text{Fe}_3\text{O}_4$ ; and 50.6 emu/g for  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ .

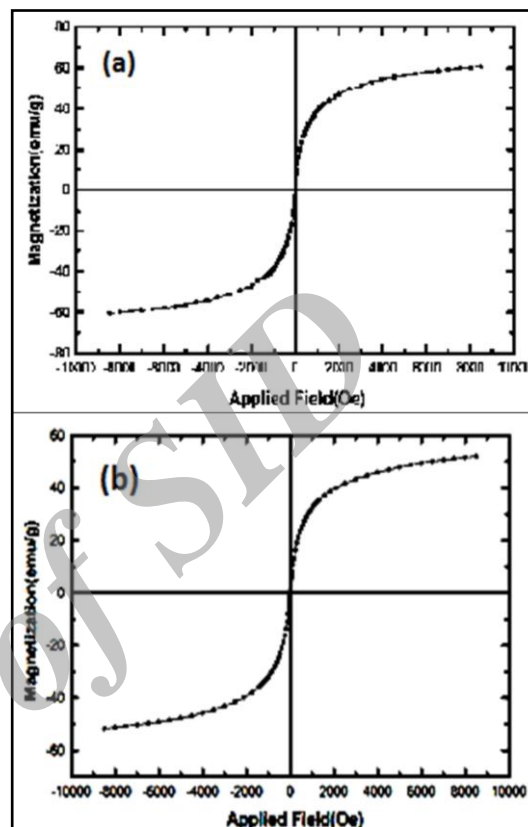


Fig. 6. Magnetization vs. applied magnetic field for a)  $\text{Fe}_3\text{O}_4$ ; b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , at room temperature

### CONCLUSIONS

This study revealed increase of the small-size of silica modified superparamagnetic iron oxide in its colloidal form due to the agglomeration process and stabilization of the prepared nanoparticles depends on their molecular structure. The ligands used in this work, citric acids through its carboxylic or alcohol-type OH-groups was suitable to bind each other and agglomerate to form larger particles. Acquiring more information in this subject is necessary since preparation of the no - agglomerated homogenous dispersions is very important for biological application, for example, in DDS application.

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