Int. J. Bio-Inorg. Hybd. Nanomat., Vol. 2, No. 3 (2013), 437-441

International Journal of Bio-Inorganic Hybrid Nanomaterials

Surface-Modified Superparamagnetic Nanoparticles Fe_3O_4@PEG for Drug Delivery

Afsaneh Sharafi[1*], Mirabdullah Seyedsadjadi[2]

[1] Ph.D., Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran 14778 92855, Iran

[2] Associate Professor, Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran 14778 92855, Iran

Received: 12 June 2013; Accepted: 19 August 2013

ABSTRACT

In this work, we report on the synthesis of superparamagnetic iron oxide nanoparticles at room temperature using microemulsion template phase consisting of cyclohexane, water, CTAB as cationic surfactant and butanol as a cosurfactant. Surface modification have been carried out by using poly(ethyleneglycol) (PEG). 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 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; Functionalize; Poly(ethyleneglycol); Nano magnetic.

1. INTRODUCTION

The relatively large surface area and highly active surface sites of nanoparticles enable them to have a wide range of potential applications magnetic iron oxide nanoparticles as a new kind of nanometer-sized material, have multiple practical applications, such as physics, medicine, and biology due to their multifunctional properties such as small size, superparamagnetism and low toxicity, etc [1-3].

In recent years, ferrofluids (FFs), colloidal suspensions of magnetic nano-ferroparticles stabilized by polymer coating,have attracted a great attention in the biomedical fields related to magnetic resonance imaging (MRI) [4-6], hyperthermia therapy of cancers [7, 8], and targeted drug delivery [9, 10]. A particular interest is placed on the superparamagnetic nano-ferroparticles (with a diameter < 10 nm) of magnetite (Fe_3O_4) because of their high magnetic saturation, negligible

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

toxicity, and easier surface modification properties. These polymers include dextran [11, 12], poly(ethylene glycol) (PEG) [13-18], and poly(vinylpyrrolidone) (PVP) [19]. In particular, PEG exhibits great predominance with improved biocompatibility, biodegradability and blood circulation times.

In this paper, we Fe_3O_4 nanoparticles coated with poly(ethylene glycol) (PEG) were synthesized. Despite the use of large quantities of poly(ethylene glycol) (PEG) is high Mghnatysty property. And also due to be dissolved in water is suitable for drug delivery.

2. EXPERIMENTAL

2.1. Preparation of magnetite iron oxide nanoparticles

The magnetic nanoparticles were prepared by the reverse microemulsion method. First 3gr of cetyltrimetyl ammonium bromid (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 $FeCl_2/FeCl_3$ (0.14 g / 0.06 g, 2.7 mL water) under nitrogen (N2) 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. The nanoparticles were isolated by centrifugating and washed with ethanol [20].

2.2. Preparation of Fe_3O_4@PEG nanoparticles

Fe_3O_4@PEG nanoparticles were prepared by the stober method. The magnetic nanoparticals Fe_3O_4 (0.01 g) was dissolved in mixed solution of water (20 mL). (0.1 g) PEG was added to the mixed solution with stirring and reactant for 15 h. The nanoparticles were isolated by centrifugating and washed with ethanol.

3. RESULTS AND DISCUSSION

3.1. X-Ray study

Figure 1 (a, b) shows the X-ray diffraction pattern of Fe_3O_4 and silica coated Fe_3O_4 nanoparticles. Figure 1(a) shows that standard Fe_3O_4 crystal with spinal structure has six diffraction peaks ((220), (311), (400), (422), (511), and (440)). The presence of diffused broad peaks of Fe_3O_4@PEG indicates lower crystalline order owing to the formation of larger fraction of PEG. The preponderance of amorphous peaks of PEG indicates that the crystalline behavior of Fe_3O_4 is suppressed due to the presence of large fraction of PEG in comparison to Fe_3O_4 nanocrystals. The average crystalline size of Fe_3O_4 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 35 nm for uncoated.

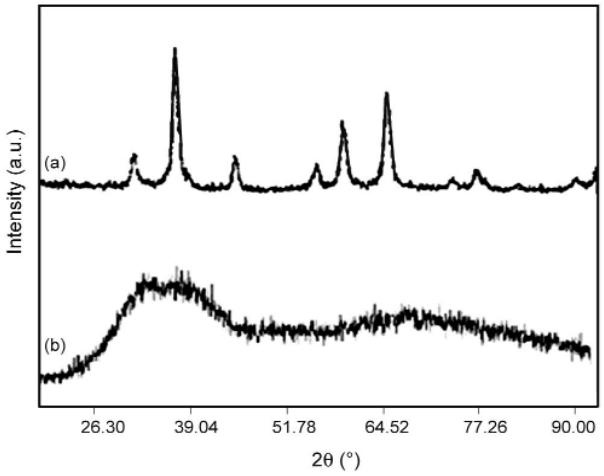


Figure 1: *X-ray powder diffraction patterns of: a) Fe_3O_4 nanoparticles and (b) Fe_3O_4@PEG composite particle.*

3.2. Edx study

The surface composition of PEG coated sample was qualitatively determined by energy dispersion spectrum (EDS) as shown in Figure 2. It shows that Fe and C and O peak are obtained and atomic (%) ratio of O/ Fe /C = 66.88/2.33/5.25. It is therefore assumed that PEG is coated onto the surface of Fe_3O_4 nanoparticles.

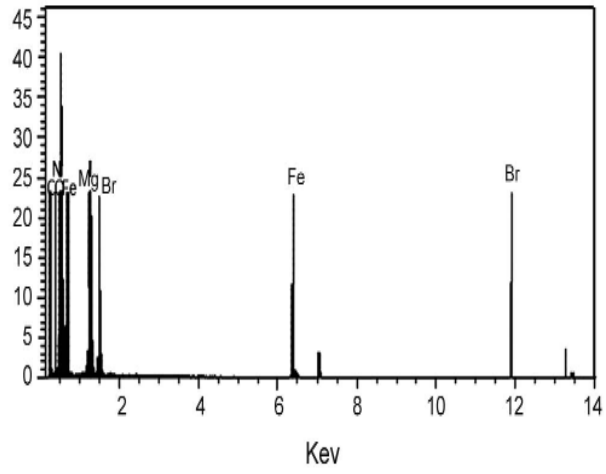


Figure 2: *Edx result of PEG coated Fe_3O_4 nanoparticles.*

Table 1: *EDAX quantification element normalized.*

Element	[Wt.%]	[At%]
O	54.07	66.88
Mg	24.27	19.76
Br	9.46	2.34
Fe	6.59	2.33
C	3.19	5.25
N	2.43	3.43

FTIR spectra of unmodified and PEG modified magnetite nanoparticles and PEG is shown in Figure 3 (a, b). The strong broad peaks at about 630 cm^{-1} and 568 cm^{-1} (in Figure a) are due to the stretching vibrations of Fe-O bonds. As shown in the (Figure b), strong peaks in the 957cm^{-1} corresponding to the stretching mode of vinyl double bonds disappeared in the spectrum of PEG-coated particles indicating that polymerization has taken place. The C-O-C ether stretch band at 1107 cm^{-1} and vibration band at 1342 cm^{-1} (antisymmetric stretch) appear in the FTIR spectrum of the nanoparticles after PEG modification. The bands around 2912 and 955 cm^{-1} correspond to CH_2 stretching vibrations and CH out- of -plane bending vibrations, respectively. The C-O-C, CH_2, and CH peaks are strong evidence that PEG-coated nanoparticles surface.

Table 2: *Assignment of FTIR spectra of Fe_3O_4 and Fe_3O_4@PEG shown in Figures 3 (a, b).*

Description	Fe_3O_4	Fe_3O_4@PEG	PEG
ν (Fe-O)	630-568	629	
ν (HO-H) stretching	3422	3415	3446
ν (HO-H) bending	1636	1632	1643
ν (C-O) symmetric stretching		1107	1110
ν (C-O) asymmetric stretching		1342	1351
ν (C-O-O)		1453	
ν (C=O) symmetric stretching			1806
ν (C=O) asymmetric stretching			1944
ν (CH vinyl)			956
ν (CH_2)			2886

3.3. Morphological study

Figure 4 (a, b) shows the SEM image of the Fe_3O_4 nanoparticles (a), the Fe_3O_4 nanoparticles Coated with PEG (b). According to the SEM image the agglomeration is very strong in the Fe_3O_4 nanoparticles. After surface modification, there is a little aggregation. This indicated that PEG molecules may help to decrease the size of adsorption of PEG chain onto the Fe_3O_4 nanoparticle surface.

3.4. Magnetic study

Figure 5 (a, b) represents magnetic-field-dependent magnetization parameters, M(H) for Fe_3O_4; and Fe_3O_4@PEG at room temperature, using vibrating sample magnetometer with a peak field of 15 kOe. The hystersis loops for Fe_3O_4 ; and Fe_3O_4@PEG with coercivity (Hc= 0.0 Oe) and remanence (Mr= 0) indicate a superparagnetism properties at 300 K with a saturation magnetization of 65 emu/g for Fe_3O_4; and 50 emu/g for Fe_3O_4@PEG.

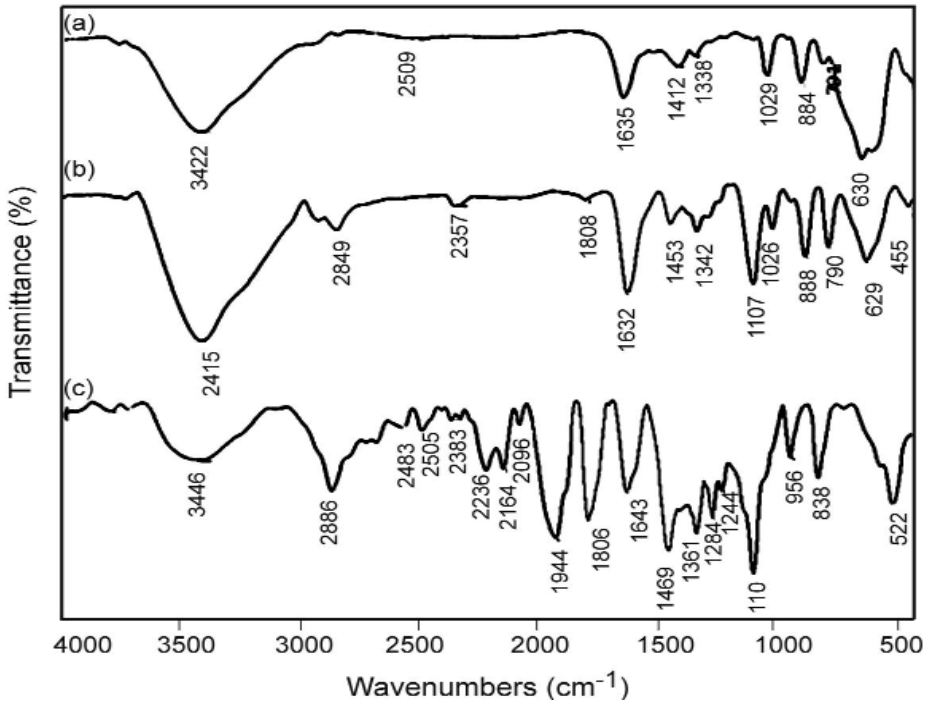
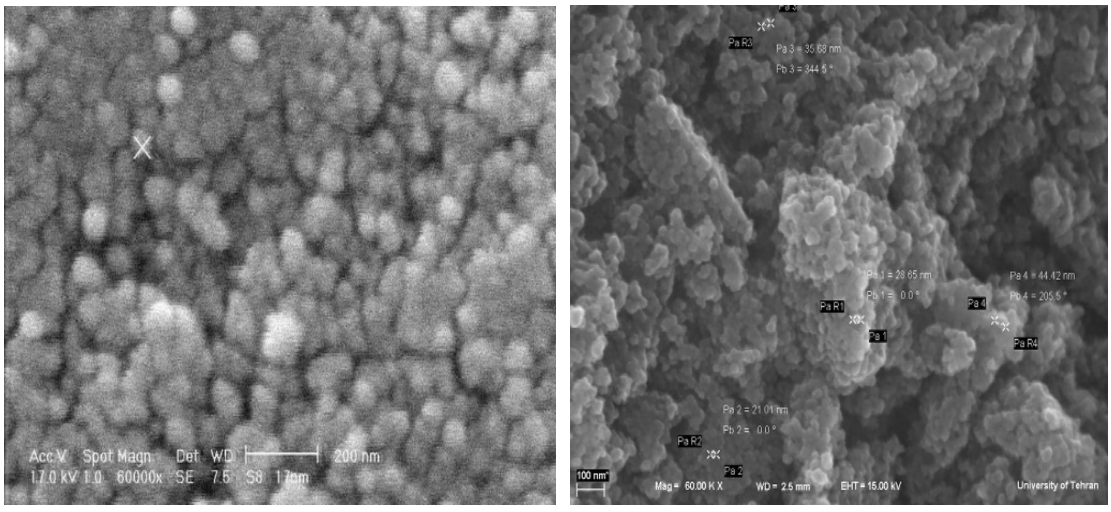


Figure 3 (a, b): *FT.IR Spectra a) Fe_3O_4 b) Fe_3O_4@PEG c) PEG.*



(a) (b)

Figure 4 (a, b): *a) SEM image of Fe_3O_4 ; b) SEM image of Fe_3O_4@PEG Core-Shell nano-structures.*

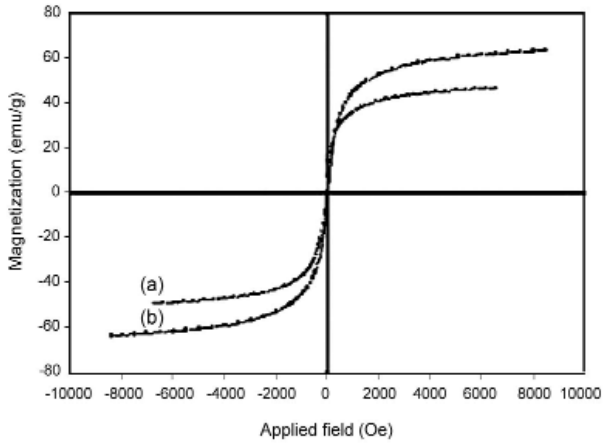


Figure 5: *Magnetization vs. applied magnetic field for a) Fe_3O_4; b) Fe_3O_4@PEG, at room temperature.*

4. CONCLUSIONS

✓ Fe_3O_4 nanoparticles were prepared by the microemulsion technique using Fe^{3+} and Fe^{2+} and surface modification have been carried out by using poly(ethyleneglycol) (PEG).
✓ X-ray diffraction pattern showed formation of spinal structure for prepared Fe_3O_4.
✓ FTIR spectra showed formation PEG on to the surface of Fe_3O_4 nanoparticles.
✓ Edx analysis data showed the presence of PEG in our prepared sample.
✓ Microemulsion (inverse micelle) is a suitable way for obtaining the uniform and size controllable nanoparticles.
✓ Preparation of homogeneous particle size and particle distribution has been possible using microemulsion method.

REFERENCES

1. Chomchoey N., Bhongsuwan D., Bhongsuwan1 T., *Kasetsart J.*, *Nat. Sci.*, **44** (2010), 963.
2. Hoa L.T.M., Dung T.T., Danh T.M., Duc N.H., Chien D.M., *J, Phys.*, **187** (2009), 012048.
3. Acar H.Y.C., Garaas R.S., Syud F., Bonitatebus P., Kulkarni A.M., *J. Magn. Magn. Mater*, **293** (2005), 1.
4. Herve K., Douziech-Eyrolles L., Munnier E., Cohen-Jonathan S., Souce M., Marchais H., Limelette P., Warmont F., Saboungi M.L. ,Dubois P., and Chourpa I., *Nanotechnology*, **19** (2008), 465608.
5. Feng B., Hong R.Y., Wang L.S., Guo L., Li H.Z., Ding J., Zheng Y., Wei D.G., *Colloids Surf., A*, **328** (2008), 52.
6. Chertok B., Moffat B.A., David A.E., Yu F.Q., Bergemann C., Ross B.D., Yang V.C., *Biomaterials*, **29** (2008), 487.
7. Zhang L.Y., Gu H.C., Wang X.M., *J, Magn Magn Mater*, **311** (2007), 228.
8. Hergt R., Dutz S., *J, Magn Magn Mater*, **311** (2007), 187.
9. Alexiou C., Arnold W., Klein R.J., Parak F.G., Hulin P., Bergemann C., Erhardt W., Wagenpfeil S., Lubbe A.S., *Cancer Res.*, **60** (2000), 6641.
10. Son S.J., Reichel J., He B., Schuchman M., Lee S.B., *J, Am Chem Soc.*, **127** (2005), 7316.
11. Kaufman C.L., Williams M., Ryle L.M., Smith T.L., Tanner M., Ho C., *Transplantation*, **76** (2003), 1043.
12. Berry C.C., Wells S., Charles S., Aitchison G., Curtis A.S., *Biomaterials*, **25** (2004), 5405.
13. Zhang Y, Kohler N, Zhang M, *Biomaterials*, **23** (2002), 1553.
14. Butterworth MD, Illum L, Davis SS, *Colloids Surf A*, **179** (2001), 93.
15. Xie J, Xu C, Kohler N, Hou Y, Sun S, *Adv Mater*, **19** (2007), 3163.
16. Mondini S, Cenedese S, Marinoni G, Molteni G, Santo N,Bianchi CL, Ponti A, *J, Colloid Interface Sci*, **322** (2008), 173.
17. Zhang Y., Kohler N., Zhang MQ, *Biomaterials*, **23** (2002), 1553.
18. Peng J., Zou F., Liu L., Tang L., Yu L., Chen W., Liu H., Tang J.B., Wu L.X., *Trans Nonferrous Met Soc China*, **18** (2008), 393.
19. D'Souza A.J., Schowen R.L., Topp E.M., *J, Controlled Release*, **94** (2004), 91.
20. Sajadi M.S., Sharafi A., Farhadyar N., *J, Nano Research*, **21** (2013), 37.