Short Communication

Synthesis of Silica Coated Magnetic Nanoparticles

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Abstract
In this research controlled coating of magnetite (Fe_3O_4) nanoparticles with SiO_2 was investigated. The Fe_3O_4 nanoparticles were synthesized via chemical co-precipitation and then coated by silica according to Stober method. Effects of tetra ethyl ortho silicate (TEOS) concentration and ethanol to TEOS on the coating thickness were investigated. X-ray powder diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy and alternative gradient force magnetometry techniques were used to characterize the magnetic nanoparticles and their coating. The results showed that the Fe_3O_4 particles are in the 6-20 nm size range. Particles coating thickness increased when the TEOS concentration increased. Magnetic results revealed that the coating can prevent magnetite nanoparticles from surface oxidation and enhancement of saturation magnetization. For magnetic particles with mean diameter of 15nm coating diameter was about 7nm and the saturation magnetization of such particles was about 30emu/g.
Keywords: *Silica coating, Magnetic nanoparticles, Core-shell structure*

1. INRODUCTION

The reactivity of iron oxide particles greatly increases as their dimensions reduce. Iron oxide nanoparticles have been of great interest in a field of clinical uses [1-3]. For clinical application iron oxide nanoparticles should be discrete and super paramagnetic with sizes smaller than 20 nm and have a narrow size distribution for uniform physical and chemical properties.

However, as a result of anisotropic dipolar attraction, magnetite nanoparticles tend to aggregate into large clusters and thus lose the specific properties associated with single-domain magnetic nanostructures. Moreover, relatively small particles may undergo rapid biodegradation when they are directly exposed to biological environments [4]. In an attempt to overcome this limitation, this work explored the properties of magnetite nanoparticles embedded in a nonmagnetic matrix.

Amorphous silica (SiO_2) is probably the most interesting inorganic core, as it can be synthesized with tailored size, size distribution, and shape [5]. In addition, the chemistry of the silica surface is well established and silica-coated nanoparticles can be easily functionalized [6-8], enabling their use in a large number of applications [9]. The silica layer also provides a chemically inert surface for magnetic cores in biological systems [10].

In this article we have investigated the effect of TEOS and ethanol concentration on silica coating thickness and magnetic properties of Fe_3O_4 nanoparticles.

2. EXPERIMENTAL

2.1 Materials and method

FeCl3·6H2O and FeCl2·4H2O, tetraethyl ortho silicate (TEOS), ethanol and ammonia aqueous (25 wt.%) all were purchased from Merck company with analytical grade.

The Fe_3O_4 nanoparticles were synthesized via chemical coprecipitation[11] and dispersed in deionized water using lauric acid as surfactant. The silica coating procedure of these nanoparticles performed according to Stober Method [5]. For typical synthesis, EtOH (-mol), H_2O and $NH_3:H_2O$ were mixed in a flask. Then 2g of Fe_3O_4 particles was dispersed in it and the mixture was vigorously stirred at 40°C for 10 minutes. Then TEOS was added slowly and mixing was continued for 1 hour. The coated particles were separated by high power magnet. After several washing steps with EtOH, the coated particles were finally dried at 80°C in vacuum oven. The concentrations of reagents are summarized in table 1.

Table.1 *silica coated samples with their components.*

Sample	TEOS (g)	Ethanol(ml)	Water (ml)	Ammonia (ml)
S1	0.5	1.5	10	1.5
S2	1.5	1.5	10	1.5
S3	1	2	10	2
S4	1	3	10	2.5

2.2 Characterization

X-ray powder diffraction (XRD) measurements were carried out with Philips PW3710, using Cu-Kα radiation. Transmission electron microscopy (TEM) investigations were carried out using a Philips EM201C apparatus operating at 80 kV. Magnetization measurements were carried out with a model 155 alternative gradient force magnetometer (AGFM) at room temperature. Fourier (FTIR) was performed using a thermo Nicolet Nexus 870 FTIR spectrometer.

3. RESULTS AND DISCUSSION

The X-ray diffraction pattern of synthesized nanoparticles without silica coating (S0 sample) is shown in Fig. 1.The magnetite is the unique formed phase which is correspondence with JCPC Card No.19-0629. Relatively wide peaks are related to the small particles. TEM image of these nanoparticles can be seen in Fig.2.Base on this figure, the particles are in range of 6–20 nm, with mean particle size of 11nm.
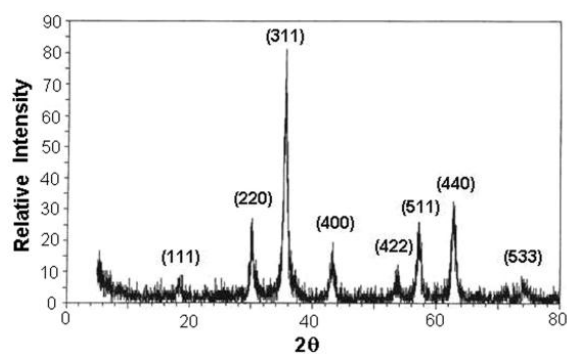

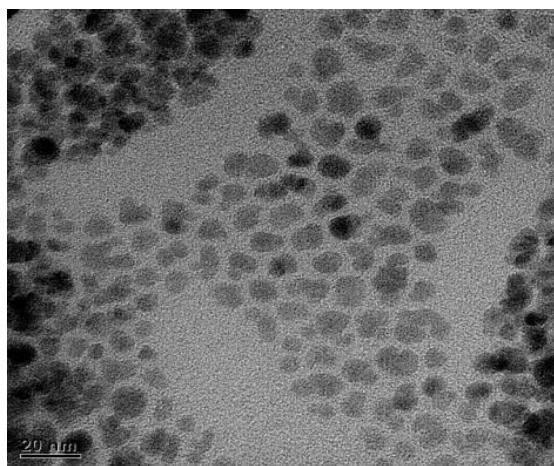**Figure 1.** *XRD pattern of synthesized iron oxide nanoparticles (S0).*

Figure 2. *TEM image of synthesized magnetite nanoparticles (S0 sample). The bar length is 20nm.*

FTIR spectroscopy was used to identify an existence of silica shell on Fe_3O_4 nanoparticles. The main absorption bands of OH ($3437cm^{-1}$), H_2O ($1632cm^{-1}$), Fe-O-Fe

($589 cm^{-1}$) groups are observed in all samples (Figure.3). Existence of OH and Fe-OH groups are so important on the core-shell structure due to their reaction with Si-OH groups in the shell.
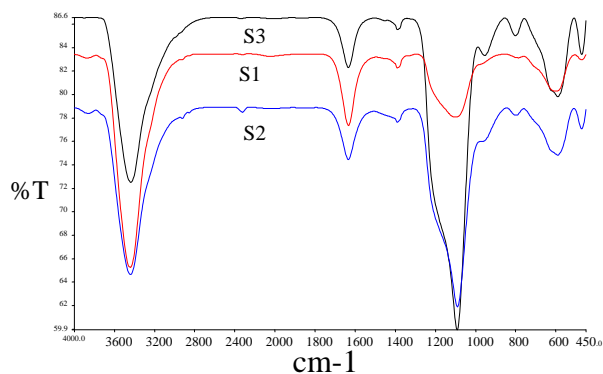

Figure 3. FTIR spectra of S1, S2 and S3 samples.

The new band was appeared in the FTIR spectra of the sample S1 at $1059 cm^{-1}$ which belongs to Si-O-Si groups. The existence of these groups in sample is a sign that shows the particles are covered. But the Si-O-Si band has a low intensity. It means that the shell thickness should be very thin. The TEM images of this sample support this idea. By increasing the TEOS (S2 and S3), the intensity of Si-O-Si band also increases and shifts to its characteristic amount ($1100 cm^{-1}$). Furthermore, the intensity of H_2O (1632 cm^{-1}) and Fe-O-Fe ($589 cm^{-1}$) bands are lower which means the silica shells are thickened on particles compared with S1.

The magnetic hysteresis of silica coated samples is correlated with uncoated one in Figure. 4.

As can be seen, in all samples any appreciable hysteresis can be seen. According to the size of magnetic nanoparticles, this can be related to the super paramagnetic behavior of nanoparticles. Moreover, it is obvious that the magnetization of samples decreases as TEOS increases (samples of S1 and S2). The calculated saturation magnetization (Ms) of samples can be seen in Figure.5. The remarkable part of this figure is that the sample of S1 has higher magnetization than S0. In other word the magnetic properties of magnetite nanoparticles after being coated with silica is higher than uncoated sample. This can be related to the surface oxidation of magnetite nanoparticles and increase of the dyed layer on Fe_3O_4 nanoparticles which cause decreasing of magnetization [3].

This result illustrates that a narrow silica coating can prevent the surface of nanoparticles from oxidation or other chemical variations without decreasing of magnetization. Comparison of S2, S3 and S4 samples reveals that any major effect cannot be seen due to increasing of ethanol concentration.
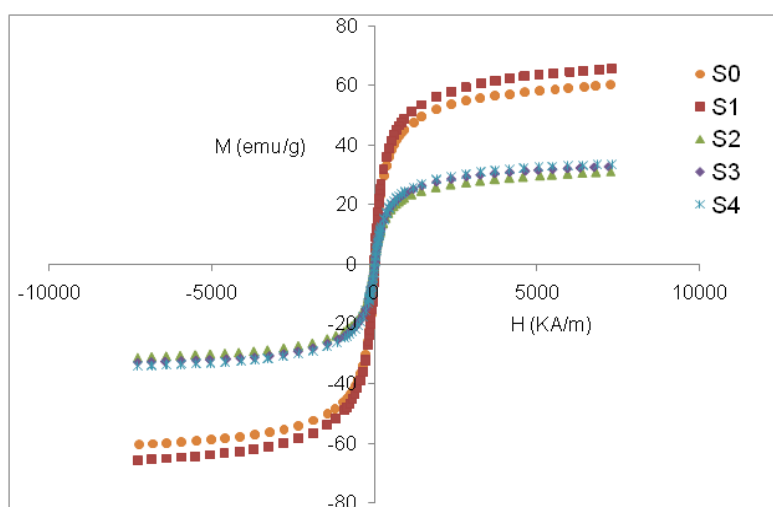

Figure 4. The magnetic hysteresis of samples. The silica coated samples are compared with uncoated sample (TAB3).

The magnetic hysteresis of silica coated samples is correlated with uncoated one in Figure. 4. It is clear that in all samples any appreciable hysteresis can be seen. According to the size of magnetic nanoparticles, this can be related to the super paramagnetic behavior of nanoparticles. Moreover, it is obvious that the magnetization of samples decreases as TEOS increases (samples of S1 and S2). The calculated saturation magnetization (Ms) of samples can be seen in Figure.5. The remarkable part of this figure is that the sample of S1 has higher magnetization than S0. In other word the magnetic properties of magnetite nanoparticles after being coated with silica is higher than uncoated sample. This can be related to the surface oxidation of magnetite nanoparticles and increase of the dyed layer on Fe_3O_4 nanoparticles which cause decreasing of magnetization [3].This result illustrates that a narrow silica coating can prevent the surface of nanoparticles from oxidation or other chemical variations without decreasing of magnetization. Comparison of S2, S3 and S4 samples reveals that any major effect cannot be seen due to increasing of ethanol concentration.

Figure. 6 shows the TEM images of coated nanoparticles for two samples of S1 and S2. It is clear that for S1 sample the coating is not obvious which can be related to small thickness of coating. According to the FTIR and magnetic properties (Figure.3 and 4), the presence of coating is imperative. For sample S2 a uniform coating on the magnetic cores is clear. The thickness of coating is about 7nm. This reveals that the shell thickness has been increased with TEOS from sample S1 to S2 which confirms the FTIR results. The lower magnetization of S2 relative to S1 can be related to the thickness of silica shell.

4. CONCLUSION

Silica coated magnetite nanoparticles were prepared via a simple method. The microstructure studies show that the uniform coating can be obtained via control of TEOS concentration. However, the ammonia concentration is not so effective for thickness of coating.
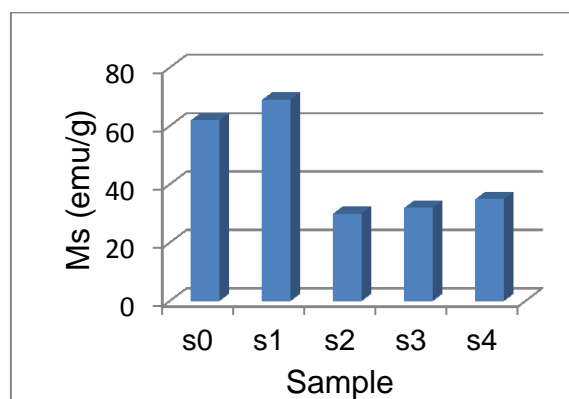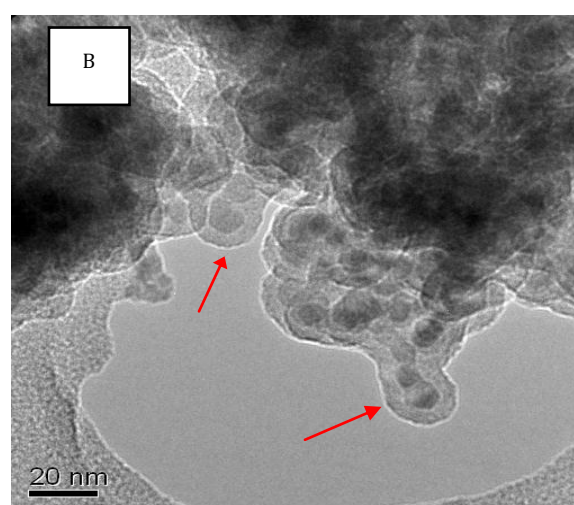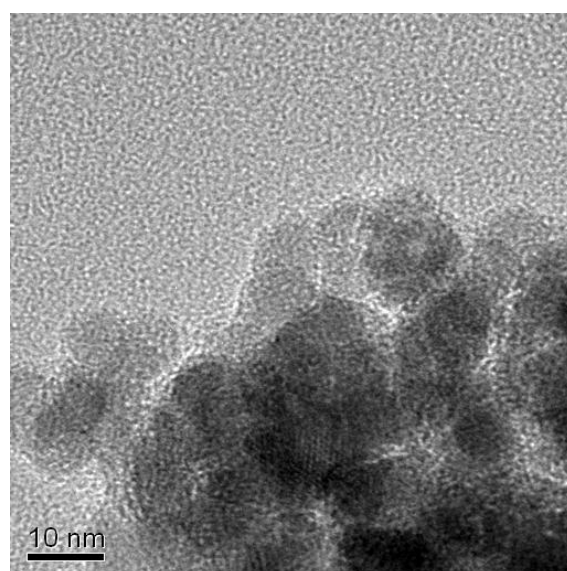
Figure 5. *Ms Variation for samples*.

Figure 6 *TEM images of (A) S1 and (B) S2 Samples*.

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The magnetic properties reveal that the coating prevents the oxidation of magnetite nanoparticles however the Ms of coated nanoparticles decreases when the silica thickness increases.

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