Assembly of Fe$_3$O$_4$ nanoparticles on SiO$_2$ monodisperse spheres

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Abstract. The assembly of superparamagnetic Fe$_3$O$_4$ nanoparticles on submicroscopic SiO$_2$ spheres have been prepared by an *in situ* reaction using different molar ratios of Fe^{3+}/Fe^{2+} (50–200%). It has been observed that morphology of the assembly and properties of these hybrid materials composed of SiO$_2$ as core and Fe$_3$O$_4$ nanoparticles as shell depend on the molar ratio of Fe^{3+}/Fe^{2+}.

Keywords. Fe$_3$O$_4$ nanoparticles; SiO$_2$ monodisperse spheres.

1. Introduction

Hybrid materials composed of submicrospheric cores shelled with nanoparticles are an interesting class of materials for their unique electrical, optical, magnetic, catalytic or mechanical properties (Matijević 1994; Rangel 1994; Caruso 2001; Hong *et al* 2004; Spasova *et al* 2005). There is a growing interest in the preparation of hybrid particles as the properties of these materials can be easily tailored by an appropriate choice of core and shell. The coating of nanoparticles on the suspended core submicron particles can be performed either by direct surface reactions or by controlled precipitation of the nanoparticles on the surface (Tartaj 2003; Zhu *et al* 2003). Many of the studies carried out on hybrid materials are made up of latex particles as core and iron oxide as a shell (Caruso *et al* 1999; Shiho and Kawahashi 2000; Ocana *et al* 2006). However, the use of inorganic material cores would be more advantageous from application point of view since these materials give higher thermal stability to the hybrid materials which permit to enhance their magnetic properties by a simple thermal treatment (Bizdoaca *et al* 2003). Amorphous SiO$_2$ is one of the most interesting inorganic core materials, which can be synthesized with tailored size, spherical shape, and narrow size distribution by using the Stöber procedure (Stöber *et al* 1968). The coating of uniform silica shells on iron oxide nanoparticles has been successfully carried out by different procedures (Ohmori and Matijević 1992; Philipse *et al* 1994), whereas the reverse process (iron oxide on silica) (Ramesh *et al* 2000; Tartaj 2003) is quite difficult.

We report here a process to prepare assembly of Fe$_3$O$_4$ nanoparticles on submicroscopic SiO$_2$ sphere by an *in situ* reaction using different molar ratios of Fe^{3+}/Fe^{2+} (50–200%). The structural and magnetic properties of these hybrid materials have been investigated.

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2. Experimental

The assembly of magnetic nanoparticles on silica surface was carried out in two steps. First, monodisperse spherical SiO$_2$ particles of diameter, 200 nm, were prepared by hydrolysis and condensation of tetraethoxysilane (TEOS) in water-ethanol liquor in the presence of 25% NH$_3$ solution as a catalyst, following modified Stöber process. At the beginning of the reaction, absolute ethanol, double distilled water and ammonia solution were mixed in appropriate concentration. Subsequently, TEOS was added to the above solution mixture kept under agitation by a magnetic stirrer at room temperature for 2 h. In the second step, Fe$_3$O$_4$ nanoparticles of size, 10–12 nm, were self-assembled on the surface of monodisperse silica spheres by an *in situ* reaction. The reaction solution of different molar ratios of Fe^{3+}/Fe^{2+} (50, 75, 100, 150 and 200%) in water was added to SiO$_2$ spheres well dispersed in 10% ammoniacal solution kept under continuous agitation in an ultrasonic bath. The ratio of silica to total metal ions (Fe^{3+} and Fe^{2+}) is 1 : 1 in the present work.

Determination of phase purity and their identification was done by X-ray diffraction (XRD) studies using Philips powder diffractometer, PW3040/60 with CuK$_\alpha$ radiation. The crystallite size was determined from the X-ray line broadening using Scherrer formula given below

$$D = 0{\cdot}9\lambda/\beta \cos\theta\,,$$

where D is the average crystalline size, λ the X-ray wavelength used, β the angular line width at half maximum intensity and θ the Bragg's angle. The infrared spectra of the synthesized materials were obtained using a Nicolet spectrometer (Magna IR, 550). The micrographs were taken using transmission electron microscope (CM 200, Philips). The room temperature magnetization was measured by vibrating sample magnetometer (VSM, Lake Shore, Model-7410). The magnetization vs temperature was measured in an applied magnetic field of 500 Oe.

3. Results and discussion

The XRD patterns of the samples (figure 1) show single phase Fe_3O_4 spinel structure along with amorphous nature of SiO_2 particles. However, since the XRD patterns of Fe_3O_4 and γ-Fe_2O_3 are very similar, it is difficult to distinguish the two phases simply from XRD patterns. Even so, by comparison with the *d* values of the experiment and those of standard magnetite (JCPDS card no. 19–629) and maghemite (JCPDS card no. 39–1346) data, it can be found that the results of the experiment are much closer to those of magnetite. Variation in intensity of diffraction peaks is clearly observed from XRD patterns, which may be due to different ratios of Fe^{3+}/Fe^{2+} used during the synthesis process. The Fe^{3+}/Fe^{2+} ratio strongly affects the formation of Fe_3O_4 spinel structure. The crystallite size of Fe_3O_4 particles estimated from X-ray line broadening was in the range of 10–12 nm.

The typical room temperature magnetization loops of assembled Fe_3O_4 particles on silica surface are depicted in figure 2. The inset shows a typical magnetization vs temperature plot of assembled Fe_3O_4 particles on silica surface prepared with Fe^{3+}/Fe^{2+} = 75% and measured in an applied field of 500 Oe. The results show zero coercivity, zero remanence and also non saturation up to 20 kOe, indicating superparamagnetic nature of ferrite particles. The specific magnetization value of samples prepared with different Fe^{3+}/Fe^{2+} ion ratios is given in table 1. It is observed that the specific magnetization depends on the ratio of Fe^{3+}/Fe^{2+} ions used during synthesis process. The low value of magnetization is due to the presence of nonmagnetic SiO_2 core. The magnetization vs temperature measurements show that the Curie temperature (T_C) is

about 580°C, which is in agreement with that reported for Fe_3O_4 (Liu *et al* 2003), whereas the T_C of γ-Fe_2O_3 is around 645°C (Ebisu and Watanabe 1987; Özdemir 1990). These results suggest that the phase formed is of Fe_3O_4 rather than γ-Fe_2O_3. The slight hump observed in the *M/T* curve at around 400°C may be assigned to the atomic rearrangement inside the sample because of the removal of organic moiety like ethoxy (–OC_2H_5) and hydroxyl group (–OH)

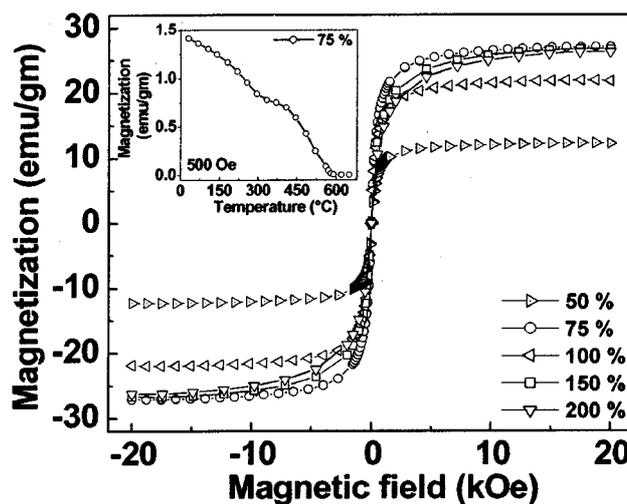**Figure 2.** Room temperature magnetization loops of samples prepared with different ratios of Fe^{3+}/Fe^{2+} ions. Inset shows the magnetization vs temperature plot of sample prepared with Fe^{3+}/Fe^{2+} = 75% measured in an applied field of 500 Oe.

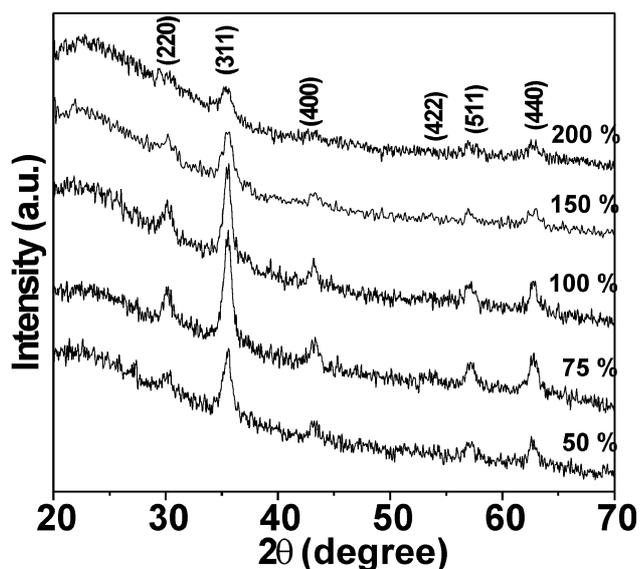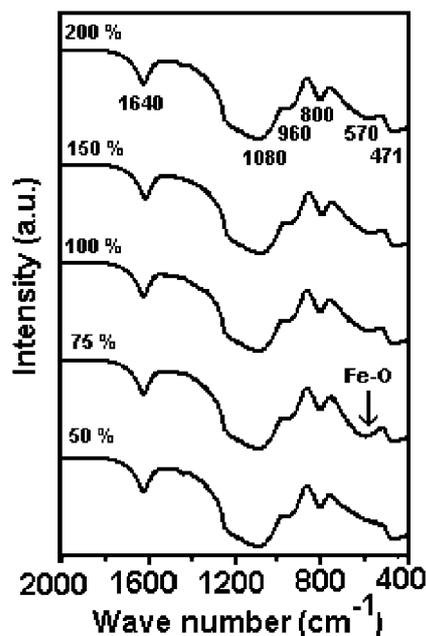**Figure 1.** XRD patterns of the samples prepared with different ratios of Fe^{3+}/Fe^{2+} ions.

Figure 3. FTIR transmission spectra of assembled samples prepared with different ratios of Fe^{3+}/Fe^{2+} ions.

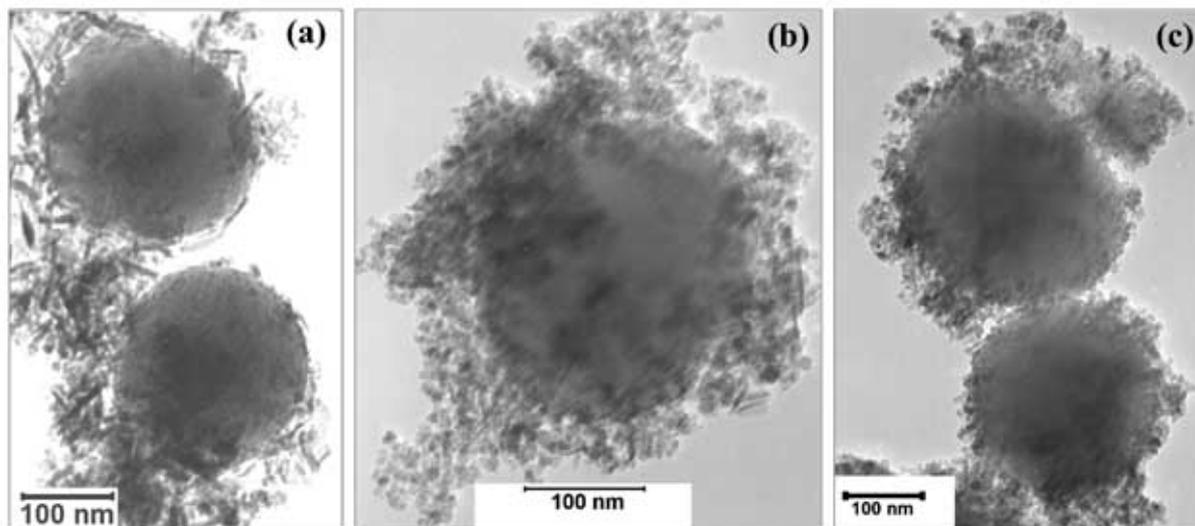**Figure 4.** TEM micrographs of samples prepared with Fe^{3+}/Fe^{2+} ratios: (**a**) 50, (**b**) 75 and (**c**) 100%.

Table 1. The specific magnetization value of samples prepared with different ratio of Fe^{3+}/Fe^{2+} ion.

Ratio of Fe^{3+}/Fe^{2+} (%)	Specific magnetization at 20 kOe (emu/g)
50	12·2
75	26·8
100	21·8
150	26·5
200	26·2

from the surface of silica coated Fe_3O_4 particles at this temperature.

The FTIR transmission spectra of assembled Fe_3O_4 particles on silica surface are shown in figure 3. The transmission spectra show bands at 1080 cm⁻¹, 800 cm⁻¹ and 471 cm⁻¹, which are presumably due to asymmetric stretching (v_{as}), symmetric stretching (v_s) and bending modes of Si–O–Si, respectively (Barick *et al* 2005). The broad band at 1640 cm⁻¹ is due to the bending modes of H_2O adsorbed at the silica surface. The weak band at 960 cm⁻¹ is due to non-bridging oxygen (Si–O) stretching vibration of silanol. The band at 570 cm⁻¹ is associated with the stretching vibration of Fe–O (Lopez *et al* 1992). The intensity of Fe–O band is higher in case of sample prepared with Fe^{3+}/Fe^{2+} = 75% which implies that Fe_3O_4 phase is well developed in this case. This result strongly supports the observed XRD patterns.

Figure 4 shows the TEM micrographs of Fe_3O_4 nanoparticles assembled on the silica surface prepared with Fe^{3+}/Fe^{2+} ratio of (a) 50, (b) 75 and (c) 100%. The Fe_3O_4 nanoparticles prepared with Fe^{3+}/Fe^{2+} = 75% assembled throughout the surface of ~ 200 nm silica sphere

whereas in other ratios, Fe_3O_4 nanoparticles did not assemble throughout the surface of silica sphere. This shows that Fe^{3+}/Fe^{2+} ratio as well as total iron ion to silica ratio plays an important role on the assembling structures. The assembled morphology of Fe_3O_4 nanoparticles on silica surface is disordered and non-uniform. We are currently looking into different aspects to achieve perfect uniformity and ordering of Fe_3O_4 particles on silica surface. It is observed that 50% ratio of Fe^{3+}/Fe^{2+} mainly gives needle shaped Fe_3O_4 whereas other ratios give almost spherical Fe_3O_4 particles of size, 10–12 nm.

4. Conclusions

Monodisperse spherical silica particles of size, 200 nm, were prepared by modified Stöber process. The Fe_3O_4 nanoparticles were assembled on the surface of silica spheres by an *in situ* reaction using different molar ratios of Fe^{3+}/Fe^{2+}. The XRD analysis confirmed the formation of single phase Fe_3O_4 nanoparticles along with the amorphous nature of silica. Both XRD and FTIR analysis suggest that Fe_3O_4 phase is well developed in case of sample prepared with Fe^{3+}/Fe^{2+} = 75%. The assembled morphology of Fe_3O_4 nanoparticles on silica surface is non-uniform and disordered. The assembled morphology and magnetization strongly depends on molar ratio of Fe^{3+}/Fe^{2+} used during synthesis process.

Acknowledgements

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