Journal of Nanoparticle Research (2008) 10:203–206
DOI 10.1007/s11051-007-9217-7

Brief communication

Spectroscopic and photoluminescence studies on optically transparent magnetic nanocomposites based on sol–gel glass: Fe_3O_4

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Received 27 July 2006; accepted in revised form 31 December 2006

Key words: sol–gel, nanocomposites, ferrofluids, infra red spectroscopy, photoluminescence, optical properties

Abstract

Sol–gel glasses with Fe_3O_4 nanoparticles having particle sizes laying in the range 10–20 nm were encapsulated in the porous network of silica resulting in nanocomposites having both optical and magnetic properties. Spectroscopic and photoluminescence studies indicated that Fe_3O_4 nanocrystals are embedded in the silica matrix with no strong Si–O–Fe bonding. The composites exhibited a blue luminescence. The optical absorption edge of the composites red shifted with increasing concentration of Fe_3O_4 in the silica matrix. There is no obvious shift in the position of the luminescence peak with the concentration of Fe_3O_4 except that the intensity of the peak is decreased. The unique combinations of magnetic and optical properties are appealing for magneto–optical applications.

Optically transparent magnetic materials have been the subject of many investigations during the past years because of the novel properties exhibited by them and their potential applications in areas such as optical fiber sensors, optical isolators, information storage, magneto optical switches, modulators etc (Qiu & Hirao, 1996; Guerrero et al., 1997; Beecroft & Ober, 1997). Several groups have prepared optically transparent magnets by using ion exchange resin, sol–gel synthesized aerogel, xerogel etc. (Ziolo et al., 1992; Bentivegna et al., 1999; Gich et al., 2003; Nair et al., 2005). Most of the studies were conducted on powdered specimens and therefore it is impossible to measure their optical properties. Addition of aqueous based Fe_3O_4 ferrofluid into the sol–gel silica sol and subsequent conversion into the composites results in crack free monoliths of Fe_3O_4–SiO_2 which can be used in number of technologically demanding applications (Thomas et al., 2006). The spectroscopic studies on the magnetic–silica composites have been extensively carried out inorder to study the nature of interaction of magnetic particles with silica (Bruni et al., 1999, Li et al., 2000; Moreno et al., 2002). However investigation devoted to optical studies especially photoluminescence studies are scarce or seldom reported. Magnetic luminescent materials find enormous applications in biomedical fields. In this brief communication we report on the spectroscopic and photoluminescence properties of an optically transparent magnetic nanocomposite.

Transparent magnetic nanocomposites have been prepared by sol–gel method which has been described in detail elsewhere (Thomas et al., 2006). Sol was prepared by mixing tetraethyl orthosilicate (TEOS), Ethanol and water in the molar ratio 1:2:5. HCl was added as a catalyst for promoting

hydrolysis. After complete hydrolysis Fe_3O_4 ferrofluid was added to the sol. The viscous sol obtained was then kept in a hot air oven at 45°C for aging. The monoliths obtained after 15 days were densified by the heat treatment at 70°C for 10 hours. Two sets of samples were prepared with 0.05 and 0.1 %wt Fe_3O_4 in silica. The samples are coded as SF:0.05 and SF:0.1, respectively. Pure silica samples (coded as S0) were also prepared for comparison.

The structural properties of the Fe_3O_4–SiO_2 composites were analyzed in a Joel JEM-2200 FS electron microscope operated at 200 kV. A Thermo Nicolete Avatar 370 DTGS model spectrophotometer using KBr method was employed for recording the FTIR spectra of the samples in the range 400–4000 cm^{-1}. A Jasco V 530 UV–visible spectrometer was used to determine the optical transmittance of the composites in the wavelength range 300–800 nm with 1 nm resolution. Fluorescence spectrum was recorded using a Spex-Flouromax−3 Flourimeter. All of these measurements were performed at room temperature.

Figure 1(a) shows the TEM bright field image of the composite. EDS elemental mappings in Figure 1(b, c, and d) show that Fe_3O_4 clusters of size around 50 nm is embedded in the SiO_2 matrix.

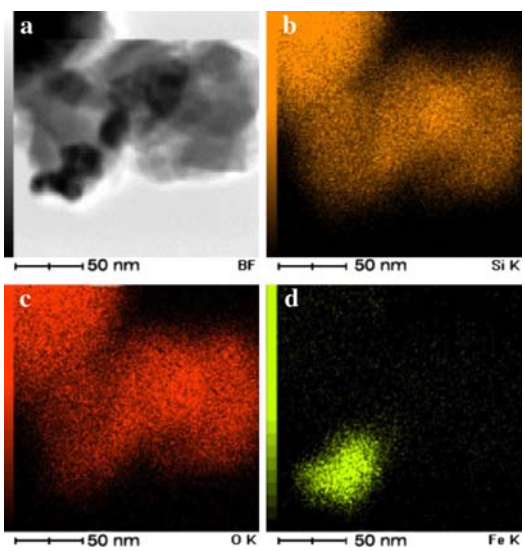

Figure 1. EDS elemental mapping of the Fe_3O_4–SiO_2 composite (a) bright field image (b) mapping of silicon (c) mapping of oxygen (d) mapping of iron.

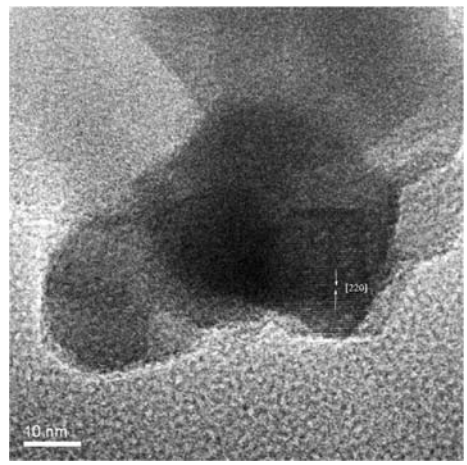

Figure 2. HRTEM image of the representative Fe_3O_4–SiO_2 composite.

HRTEM were conducted for the composites to determine the nature of the crystallite aggregates that were observed. Figure 2 shows the HRTEM image of the Fe_3O_4–SiO_2 composite. The particle diameter evaluated from the figure was found to be 20 nm. Lattice planes of the aggregates are easily recognizable and the high resolution of the image permitted assigning them to Fe_3O_4 (220) plane.

The nature of bonding present in SiO_2 and Fe_3O_4–SiO_2 can be ascertained with the help of FTIR depicted in Figure 3. The IR spectrum of the silica gel indicates the presence of three main absorption bands at 460, 800 and 1080 cm^{-1} which can be assigned to bending vibration, symmetric

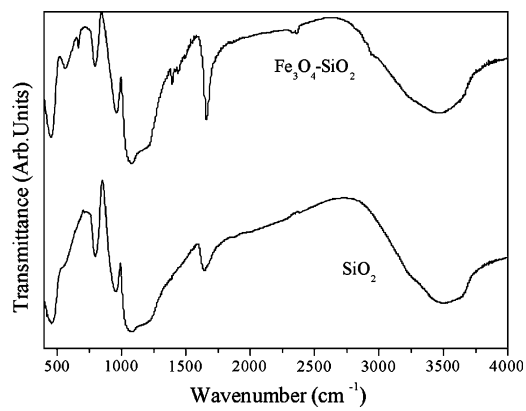

Figure 3. FTIR spectrum of a pure silica gel and a representative Fe_3O_4–SiO_2 composite.

and asymmetric stretching of SiO_2. (Bruni et al., 1999; Innocenzi, 2003). The band at 1644 cm^{-1} is due to the bending of the absorbed H_2O molecules (Bruni et al., 1999). The characteristic band for stretching (OH) groups was found at around 3500 cm^{-1} (Moreno et al., 2002; Pretsch et al., 2000). The IR spectrum of Fe_3O_4–SiO_2 has characteristic bands of Fe_3O_4 at 564 and 664 cm^{-1}. This is due to Fe–O vibrations in octahedral and tetrahedral sites of Fe_3O_4, respectively (Ardelean et al., 2004; Gillot and Bouton, 1980). It is also interesting to note the absence of a band at 857 cm^{-1} in the spectrum, which suggests that no Si–O–Fe bonds are formed (Moreno et al., 2002). From these observations it can be concluded that Fe_3O_4 is lying in the matrix without any interaction with silica. The absence of strong Si–O–Fe bonding is probably due to the low temperature used for the heat treatment (70 °C).

Room temperature hysteresis loops for the two Fe_3O_4–SiO_2 composites (not shown here) shows field dependent magnetization curves typical of an ultra fine particle magnetic composite.

Figure. 4 shows the absorption spectrum of sol gel silica glass as well as of Fe_3O_4–SiO_2 composites. The composites are optically transparent in the 600–800 nm regime. An obvious red shift is noticeable when the absorption edge of SiO_2 and Fe_3O_4 loaded gels are compared. With respect to silica host, the red shift of the absorption edge for Fe_3O_4–SiO_2 composites can be mainly attributed to two factors. One of these comes from the mixing effect of the band gap of the composites (Guang-Hai et al., 2001). The other factor to be considered is the surface and interface effect between Fe_3O_4 and SiO_2 particles (Chen and Zhang, 2003; Zhou et al., 2001).

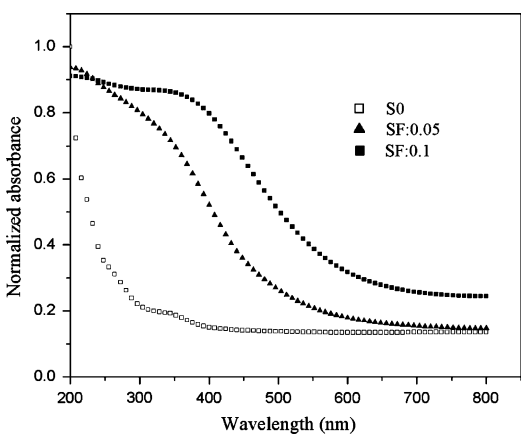

Figure 4. Absorption spectra of SiO_2 and Fe_3O_4–SiO_2 Composites.

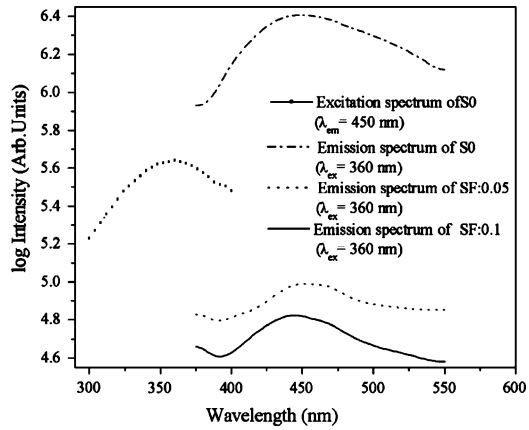

Figure 5. Excitation and emission spectra for SiO_2 and Fe_3O_4–SiO_2 composites.

Figure 5 shows the excitation and emission spectrum for silica gel as well as Fe_3O_4–SiO_2 systems. The excitation spectrum consists of a broad peak centered at around 360 nm (λ_{em} = 450 nm). The emission is centered at around 450 nm and is broad. Yang et al (Yang et al., 2001) have also found that sol–gel silica is luminescent with emission band at the same position. The blue purple emission of sol gel glass is attributed to the defect levels created in the silica glass network due to the fast and incomplete hydrolysis, condensation, polymerization process of TEOS–Ethanol–H_2O system. Si dangling bonds, nonbridging oxygen and oxygen vacancy are assumed to be the luminescent species for strong blue-purple emission of the sol gel porous silica glass.

The emission spectra of Fe_3O_4–SiO_2 composites are also broad and centered around 450 nm but the intensity is diminished. There is no obvious shift in the position but only in the intensity of the luminescence peak with the concentration of Fe_3O_4. The decrease in intensity can be attributed to the absorption of excitation (360 nm) and emission radiations (450 nm) by Fe_3O_4. The luminescence properties of silica xerogel strongly depend on the xerogel network (Han et al., 2002). As the blue emission is entirely from the silica network and the occurrence of same blue emission in the case of composites allows us to infer that the structure of the sol–gel derived silica network is

not affected by Fe_3O_4 and this has further confirmations from the FTIR studies indicating the absence of Si–O–Fe bonds.

In conclusion we have demonstrated that it is possible to obtain transparent magnetic materials exhibiting luminescence by the sol–gel method. Spectroscopic and photoluminescence studies show that Fe_3O_4 nanoparticles are in the matrix with out any interaction with silica. Optical absorption edge and luminescence intensity depend on the concentration of Fe_3O_4 in the silica matrix. Crack free monoliths of Fe_3O_4–SiO_2 can be considered as a potential candidate for magneto–optical applications. Further scope exists in modifying the preparation method to obtain Fe_3O_4 core/ silica shell particles which can act as fluorescent markers in biomedical applications.

Acknowledgements

This work was supported by Department of Science and Technology (File No. SP/S2/M-64/96 Dated 22/04/2002) and AICTE, Government of India ('Centre for ferrofluids' File No. 8023/RID/RPS-73/2004-05. Dated 29/03/2005). M R Anantharaman and Senoy Thomas acknowledge Inter University Accelerator Center, New Delhi for the financial assistance (UFUP No. 35306).

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