Optical Properties of Nanostructured Sol–Gel Thin Films Doped with Fe_2O_3 and Their Ferromagnetic Characterization by Mössbauer Spectroscopy

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Sol–gel thin films containing Fe_2O_3 were deposited onto glass substrates by the dip-coating method at room temperature. Fe_2O_3 enriched with the isotope ^{57}Fe was embedded in two kinds of matrices: zinc oxide (ZnO) and silica (SiO_2). X-ray diffraction (XRD) was used for morphology and structure determination of the nanostructures and showed that the ZnO exhibit a wurtzite form when the film is annealed at 450 °C for 20 min. SiO_2 thin films at $C_{16}H_{33}PEO_{20}$:$Fe_2O_3 = 1$:2.7×10^{-1} molar concentration exhibit a hexagonal nanophase produced by the diblock copolymer Brij58 ($C_{16}H_{33}PEO_{20}$). Optical absorption and infrared spectroscopy techniques were used to evaluate the optical quality of the films. In order to determine if the Fe_2O_3 was incorporated into the matrices, room temperature Mössbauer spectra of both samples were obtained. In both cases the hematite spectrum was obtained, corroborating that the incorporation of the Fe_2O_3 to the matrices was done without chemical reaction whatsoever.

Keywords: Mössbauer Technique, Sol–Gel, ZnO, Dip-Coating.

1. INTRODUCTION

The major contaminant in coal gasification is Hydrogen Sulphide (H_2S), which is very toxic, hazardous, and extremely corrosive. Therefore cutback of hydrogen sulfide to a safe level is essential. Although the commercial desulfurization process, called liquid scrubbing, is effective for removal of H_2S, it has drawbacks such as the loss of an important amount of heat of the gas and costly wastewater treatment.[1, 2] From literature different results from Fe_2O_3 additive to alleviate the problem have been reported.[2] It was reported that SiO_2 with 45 wt% Fe_2O_3 sorbent is favourable for the removal of H_2S and regeneration.[3] Zinc ferrite ($ZnFe_2O_4$), which is composed of ZnO and Fe_2O_3 was reported to be suitable for H_2S removal.[4] Literature[2] revealed that Fe_2O_3 additive accelerated the initial rate of sulfidation, prevented a structural change such as sintering of the sorbent due to sulfidation[6] and played a significant role during oxidative regeneration.[7] Thus, the well controlled

preparation of SiO_2:Fe_2O_3 and ZnO:Fe_2O_3 materials, is important for H_2S cutback.

On the other hand, scientific and commercial interest in the manufacture of nanostructured materials has greatly increased since the discovery of their importance for numerous applications, and this aspect will be discussed in this paper. At the same time the possibility to accurately control any functional properties of nanomaterials is affected by four governing factors: the size, shape and dispersity of nanoparticles, the number of structural defects and the uniformity of chemical composition.[8]

Nanoporous silica seems to be the most challenging system for the creation of nanocomposites owing to the possibility of preparing materials with different pore sizes (2–50 nm) and structures (hexagonal, cubic or lamellar phases) using different template molecules and concentrations.[9, 10] The controllable variation of the size and shape of the pores ensures the control of the size and shape of nanoparticles formed, as well as their optical properties. Fe_2O_3-SiO_2 couples large specific surface areas and high purity with 'tunable' magnetic properties. In a flame process, nanostructured magnetic iron oxide crystals are isolated from each other within a SiO_2 matrix.

Due to the nanoscale size of the crystal domains, the internal thermal energy is sufficient to prevent a remnant alignment of the magnetic moment in the absence of an external magnetic field. Under a magnetic field, however, these materials can be effectively magnetized, resulting in a 'tunable' magnetism (also known as superparamagnetic behaviour).[11]

In this work, sol–gel thin films containing Fe_2O_3 were deposited onto glass substrates at room temperature by a dip-coating method. Fe_2O_3 enriched with the isotope ^{57}Fe was embedded in two kinds of matrices: zinc oxide (ZnO) and silica (SiO_2). The ZnO:Fe_2O_3 thin films were annealed at 450 °C for 20 minutes, producing the well known wurtzite crystalline phase. SiO_2 nanostructured sol–gel thin films were synthesized by using an oligo (ethylene oxide) surfactant (Brij 58) as template for silica polymerization in the synthesis of nanostructured silica material containing uniformly distributed Fe_2O_3. These magnetic particles were embedded in a long-ordered nanostructured system. The measurements of their optical and ferromagnetic properties let to us to study the effect of the nanostructure tailored into the SiO_2 matrix. Mössbauer experiments at room temperature were done to determine if the Fe_2O_3 was incorporated into the matrices.

2. EXPERIMENTAL DETAILS

Glass substrates were cleaned in boiling acidic solution of sulphuric acid-H_2O_2 (4:1) for 30 minutes. They were then placed in deionized water and boiled for 0.5 h, rinsed three times with deionized water, and stored in deionized water at room temperature. Films were dip coated to the substrates (5 cm × 3 cm) at a rate of 5 cm/min using the apparatus shown in Figure 1.

An initial solution was prepared with Fe_2O_3 dissolved in deionized water and nitric acid. A small amount of methanol, TMOS (Tetra methyl orthosilicate), and the poly (ethylene oxide) (PEO)-based non-ionic diblock copolymer Brij58 ($C_{16}H_{33}PEO_{20}$) were subsequently added. This initial solution was stirred and heated to 50–70 °C for 20 minutes to homogenize the mixture. The final molar ratio was TMOS:MeOH:Nitric acid:H_2O:$C_{16}H_{33}PEO_{20}$:Fe_2O_3 = 1:0.9:0.13:6.25:0.1:0.027 to obtain the SiO_2 thin films doped with Fe_2O_3.

ZnO thin films doped with Fe_2O_3 were prepared using zinc acetate dihydrate (Zn-(OOC-CH_3)$_2$ · $2H_2O$), ethylene glycol ($C_2H_6O_2$), *n*-propyl alcohol (CH_3CH_2-CH_2-OH), and glycerol ($C_3H_8O_3$). 2.5 ml of ethylene glycol was added to 10 g of zinc acetate dehydrate, 1 ml of *N*-(2-aminoethyl)-3-aminopropyltrimetoxysilane and 0.055 g of Fe_2O_3 in a round bottomed flask fitted with a condenser and kept at 150 °C for 15 minutes over a hot plate to obtain an uniform orange solution. During the heating, a quantity of water vapour flowed back from the mixture, equivalent to the water of hydration of zinc acetate dihydrate. On cooling to room temperature the contents of the flask solidified to an orange brittle solid which could be dissolved in 20 ml of ethanol. The solubility as well as film formation property of the sol could be enhanced by adding 0.5 ml of glycerol. The solution thus obtained was highly water sensitive and readily gels on addition of a few drops of water. Triethylamine (1 mol equivalent) was also added to the solution to assist the hydrolysis of the zinc acetate.

All films were drawn with the equipment described previously by using a hydraulic motion mechanism to produce a steady and vibration-free withdrawal of the substrate from the sol.[12] Convection-free drying was critical to obtain high optical quality films. Optical absorption spectra were recorded with a Thermo Spectronic Genesys 2 spectrophotometer with an accuracy of ±1 nm. The structure of the final films was characterized with XRD patterns recorded on a Bruker AXS D8 Advance diffractometer using Ni-filtered CuKα radiation. A step-scanning mode with a step of 0.02° in the range from 1.5 to 10° in 2θ and an integration time of 2 s was used. FTIR studies were done using a Bruker Tensor 27 FT-IR spectrometer. Room temperature transmission Mössbauer spectra of the SiO_2:Fe_2O_3 and ZnO:Fe_2O_3 samples were recorded with the aid of a constant acceleration spectrometer using a ^{57}Co source (1679 MBq). To obtain the Mössbauer spectra, thin absorbers were made with powder of the material scraped from the glass substrate, because the glass cut the signal coming from the samples.

3. RESULTS

Figure 2(a) shows the optical absorption spectrum of the amorphous ZnO:Fe_2O_3 thin film annealed at 200 °C for 20 minutes and recorded in the range of 300–700 nm. There is a sharp decrease in intensity of the absorbed light around 360–370 nm due to band edge absorption. A typical absorption band of the ZnO matrix is observed around 349 nm. Figure 2(b) shows the optical absorption spectrum of the SiO_2:Fe_2O_3 thin film produced at room temperature which does not exhibit any absorption band.
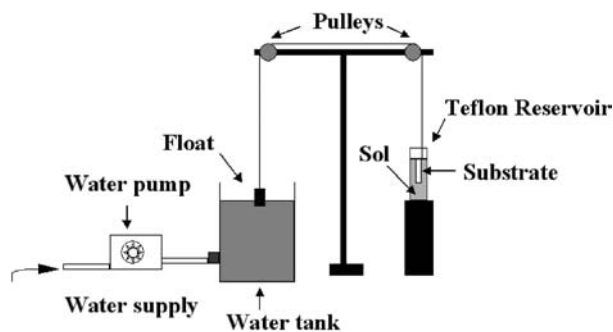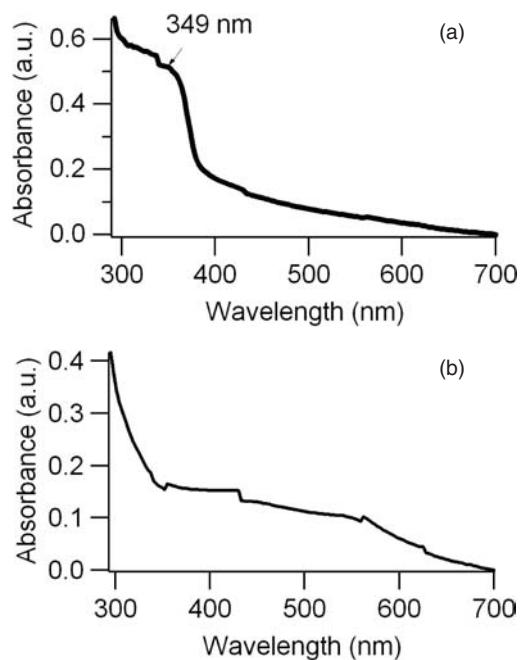

Fig. 1. Experimental apparatus setup for the preparation of the nanostructured thin films by the dip-coating method.
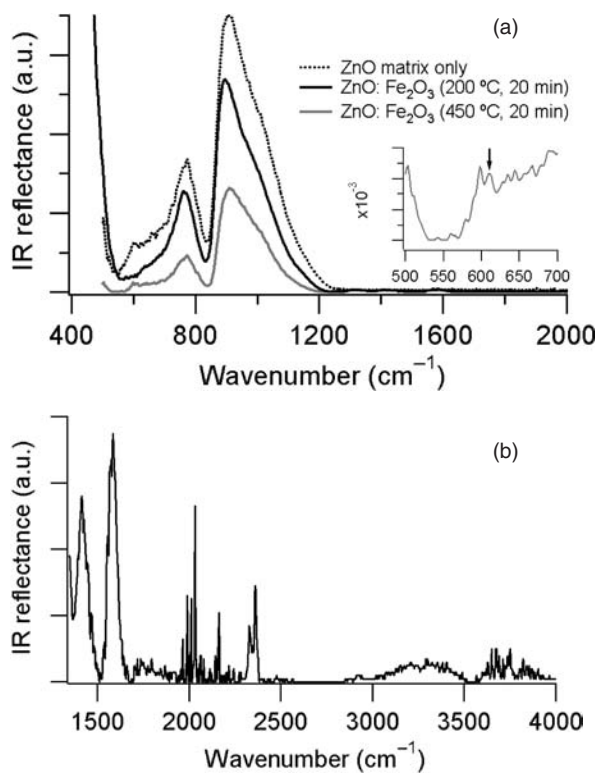
Fig. 2. Optical absorption spectra of (a) amorphous $ZnO:Fe_2O_3$ thin film deposited on glass substrate and annealed at 200 °C for 20 minutes, and (b) $SiO_2:Fe_2O_3$ thin film deposited on glass substrate at room temperature. No heat treatment.

Figure 3(a) shows the XRD of a $ZnO:Fe_2O_3$ thin film annealed for 20 minutes at 450 °C. The spectrum shows well defined diffraction peaks showing crystallinity. The crystallites are randomly oriented and the *d*-values
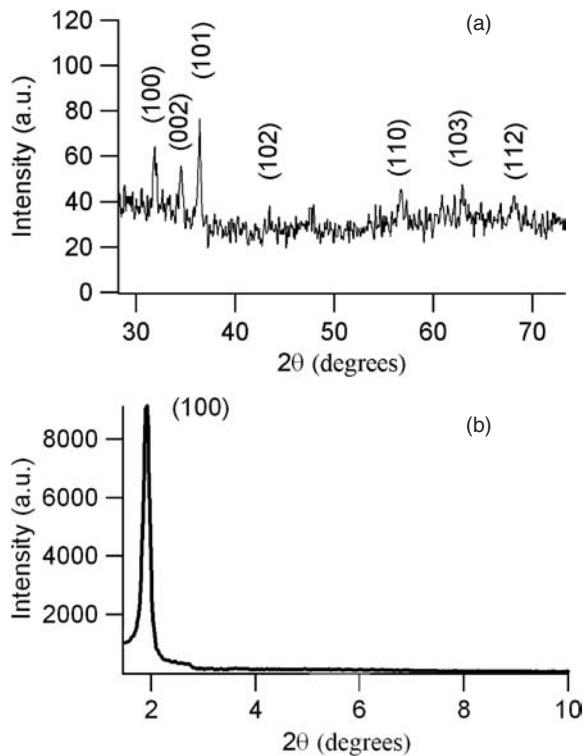
Fig. 3. XRD spectra of (a) $ZnO:Fe_2O_3$ thin film annealed at 450 °C for 20 min. (b) $SiO_2:Fe_2O_3$ thin film produced at room temperature.

Fig. 4. (a) FTIR spectra of ZnO pure thin film (dotted line), amorphous $ZnO:Fe_2O_3$ thin film annealed at 200 °C for 20 minutes (black solid line) and $ZnO:Fe_2O_3$ thin film annealed at 450 °C for 20 minutes deposited on glass substrate (gray solid line). In the inset the region from 500 to 700 cm^{-1} was magnified, it contains the band at 611 cm^{-1}. (b) From $ZnO:Fe_2O_3$ thin film annealed at 450 °C, an in the region from 1300 to 4000 cm^{-1} is shown.

calculated for the diffraction peaks are in good agreement with those given in ASTM data card (#5.0664) for ZnO. This means that ZnO has been crystallized in a hexagonal wurtzite form. But, the slightly orange color of the thin film indicated that the initial Fe_2O_3 quantity decreased during the annealing treatment. For this reason, these samples were not studied by Mössbauer spectroscopy until enough amount of Fe_2O_3 can be obtained.

On the other hand, $ZnO:Fe_2O_3$ thin films were annealed at 200 °C for 20 minutes contained enough Fe_2O_3 into the ZnO matrix, but their crystallinity was very poor. The wurtzite phase was not obtained in these samples.

Table I. IR frequencies [in cm^{-1}], of the ZnO thin film, and the amorphous $ZnO:Fe_2O_3$ thin film.

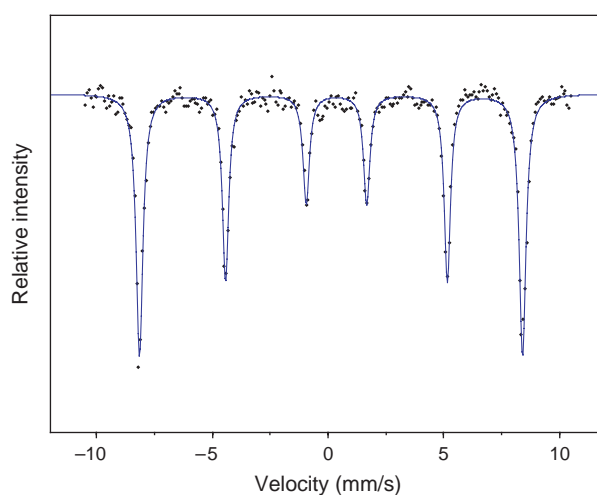| ZnO	$ZnO:Fe_2O_3$	Assignment
773	762	—
908	895	—
—	1315	—
—	1414	C-O stretching
—	1582	Asymmetric Stretching of C=O bond
2341	2326	—
2361	2359	—
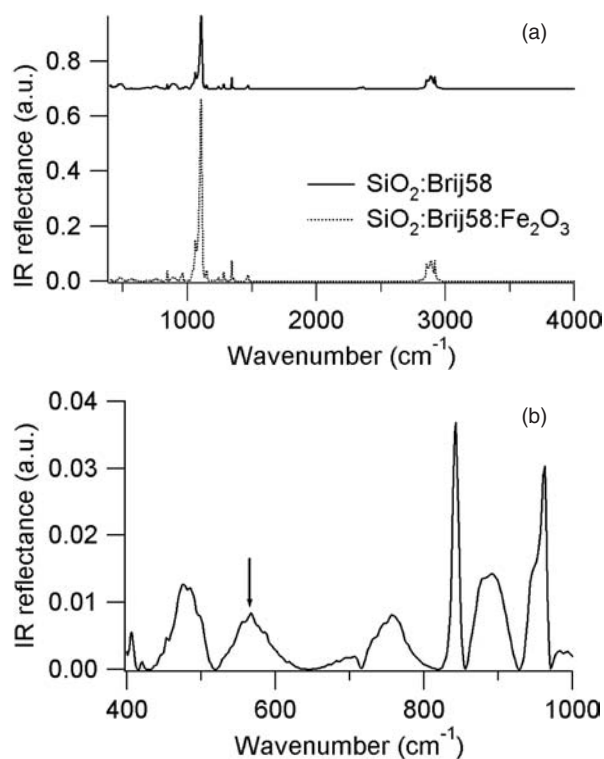
Fig. 5. FTIR spectra of (a) SiO$_2$:Brij58:Fe$_2$O$_3$ thin film (dotted line) and SiO$_2$:Brij58 thin film (solid line) at room temperature in the range of from 400 to 4000 cm^{-1}. (b) An enlargement of the FTIR spectrum showed in 5(a) from SiO$_2$:Brij58:Fe$_2$O$_3$ thin film in the range of 400–1000 cm^{-1}. The band located at 567 cm^{-1} is indicated with a black arrow.

Figure 3(b) shows the XRD patterns of the SiO$_2$:Fe$_2$O$_3$ thin film templated with Brij 58 at room temperature. The peak at $2\theta = 1.92°$, with a d-spacing of 46.0 Å, corresponds to the (100) peak of the $2d$-hexagonal-phase structure.

Figure 4(a) shows FTIR spectra of ZnO pure thin film, and ZnO:Fe$_2$O$_3$ thin films annealed at different temperatures. IR bands of the ZnO pure thin film (without heat treatment) exhibit two bands located at 773 and 908 cm^{-1}. From amorphous ZnO:Fe$_2$O$_3$ thin film annealed at 200 °C

Table II. IR frequencies [in cm^{-1}], of the Brij 58 powder and the SiO$_2$:Fe$_2$O$_3$ thin film.

SiO$_2$:Brij58	SiO$_2$:Brij58:Fe$_2$O$_3$	Assignment
467	476	δ(O-Si-O)
567	567	—
762	756	ν_s(Si-O-Si)
842	843	—
893	891	—
962	962	ν(Si-O-Si)
1061	1061	ν_{as}(Si-O-Si)
1105	1105	—
1148	1146	—
1281	1291	—
1342	1344	—
1468	1468	—

Fig. 6. Room temperature Mössbauer spectrum of Fe$_2$O$_3$ incorporated into the amorphous ZnO matrix annealed at 200 °C for 20 minutes.

for 20 minutes, the bands are slightly shifted towards lower frequencies located at 762 and 895 cm^{-1} in comparison to those from the ZnO pure sample. The shifts are 11 and 13 cm^{-1} respectively. When the ZnO:Fe$_2$O$_3$ thin film was annealed at 450 °C for 20 minutes, the bands come back to the initial position of 773 and 908 cm^{-1}, and a new band was located at 611 cm^{-1}. The appearance of this band implies the rearrangement of the matrix. This band is attributed to the spinel Fe-O stretching, and is associated to the presence of hematite.[13] The band seen at 1582 cm^{-1} is due to a C=O bond, due to the bridging type metal-acetate bonding (M-OCOOM). The band at 1414 cm^{-1} is the C-O stretching frequencies and that at 1315 cm^{-1} is due to weakly bond acetic acid molecule (HOOC-R). Table I contains the characteristics bands of the ZnO pure thin film and the ZnO:Fe$_2$O$_3$ thin films.
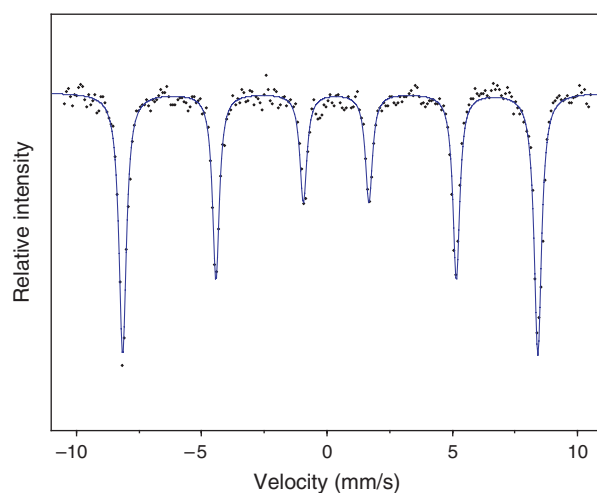
Fig. 7. Room temperature Mössbauer spectrum of Fe$_2$O$_3$ incorporated into the nanostructured SiO$_2$ matrix.

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Table III. Mössbauer parameters of Fe_2O_3 incorporated into the amorphous ZnO matrix, annealed at 200 °C for 20 minutes. The isomer shift is with respect to α-Fe.

Isomer shift δ (mm/s)	0.3668 ± 0.0053
Quadrupole splitting ΔQ (mm/s)	0.1173 ± 0.0053
Hyperfine field H (kOe)	513.43 ± 0.39
Half width $\Gamma/2$ (mm/s)	0.167 ± 0.024

Figure 5(a) shows the FTIR spectrum of SiO_2 pure film (solid line) and $SiO_2{:}Fe_2O_3$ film (dotted line) templated with Brij 58 deposited on glass substrates measured in the range of 400 to 4000 cm^{-1}. The most intense band is located at ~1105 cm^{-1} due to asymmetric stretching of the Si-O-Si chain; its intensity increases by the presence of transition metal ions.[13]

Figure 5(b) is an enlargement of FTIR spectrum shown in Figure 5(a) from $SiO_2{:}Brij58{:}Fe_2O_3$ thin film in the range of 400–1000 cm^{-1}. The spectrum exhibits peaks around 476, 756 and 843 cm^{-1} that are characteristic of the silica network. Symmetric stretch and bending vibration of the Si-O-Si chain are observed at 476 and 756 cm^{-1}, respectively. The shoulder at 962 cm^{-1} is composed of the contributions from Si-O-H stretching vibrations and from Si-O-Fe vibrations. The Fe-O-Si bonds are also apparent from the presence of a weak band at 567 cm^{-1} associated with the Fe-O stretching in Fe-O-Si bonds. This band is associated to the presence of hematite.[14] Table II contains the bands of $SiO_2{:}Brij\ 58$ which were identified on the nanostructured $SiO_2{:}Fe_2O_3$ thin film.

The Mössbauer spectra for amorphous $ZnO{:}Fe_2O_3$ and nanostructured $SiO_2{:}Fe_2O_3$ samples are shown in Figures 6 and 7, respectively. The obtained spectra were almost identical. Both samples have the same ferromagnetic phase (sextet). The continuous line is the result of the fitting process done with the Recoil program.[15] As can be seen in Tables III and IV, the Mössbauer parameters correspond to hematite,[16] so then, taking into account the FTIR bands for hematite observed in the $ZnO{:}Fe_2O_3$ and $SiO_2{:}Fe_2O_3$ thin films (Figs. 4 and 5, respectively), we can assure that the Fe_2O_3 was incorporated into the matrices without any chemical reaction with the other compounds present during the process.

The diblock copolymer allowed the generation of magnetic particles distributed uniformly in the SiO_2 matrix. This result suggests an important influence of the nanophase on the magnetic particles obtained in nanostructured silica films. In general, the nanostructured sol–gel thin films, prepared with a diblock copolymer, contain three

Table IV. Mössbauer parameters of Fe_2O_3 incorporated into the nanostructured SiO_2 matrix. The isomer shift is with respect to α-Fe.

Isomer shift δ (mm/s)	0.3725 ± 0.0072
Quadrupole splitting ΔQ (mm/s)	0.0947 ± 0.0072
Hyperfine field H (kOe)	514.73 ± 0.55
Half width $\Gamma/2$ (mm/s)	0.167 ± 0.029
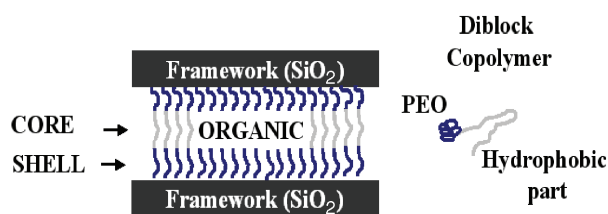
Fig. 8. Schematic representation of the three regions of nanostructured sol–gel thin films prepared with diblock copolymers (PEO = poly (ethylene oxide)).

distinct regions (Fig. 8): the framework that consists of silica or modified silica, the shell that is formed by the hydrophilic part of the surfactant (EO blocks which are water soluble) with the residual solvent, and the core that is formed by the hydrophobic part of the surfactant.

4. CONCLUSIONS

In conclusion, it can be stated that dense, transparent and crack free zinc oxide thin films can be synthesized by the sol–gel process with excellent optical and ferromagnetic properties. An annealing temperature of 450 °C was necessary to remove organics as well as to crystallize the films to obtain the wurtzite form. Mössbauer parameters were calculated and they correspond to hematite (α-Fe_2O_3). This is reinforced by FTIR results. Mössbauer studies reveal that the Fe_2O_3 was incorporated into the oxide matrices without any chemical reaction with the other compounds present during the sol–gel process. The ferromagnetic phase was found in both kinds of samples. The response measured in both kinds of films is similar to that detected in powdered samples.[17, 18]

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