Smart composites based on magnetic nanoparticles and responsive polymers

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Abstract. A comparative study of the properties of smart composites obtained by the combination of Fe$_3$O$_4$ nanoparticles with biocompatible responsive polymers is reported. Two types of magnetic composites with different morphology were obtained: (i) as core-shell nanostructures consisting of Fe$_3$O$_4$ functionalized by serine and covered with biocompatible polymer shell poly(caprolactone); (ii) as smart ferrogels, by the encapsulation of Fe$_3$O$_4$ nanoparticles into chemically cross linked polymer like poly (N-isopropylacril amide). The composites formation and their characteristics as structure, chemical composition, magnetic behaviour were investigated by XRD, FTIR, XPS and magnetic measurements. The magnetic properties of the smart composites tailor as a function of magnetite content. Both types of magnetic composites show superparamagnetic behaviour. Higher magnetization values were obtained for the composites with the functionalized magnetite core covered by poly(caprolactone) as compared with the ferrogels.

1. Introduction

Smart materials obtained by mixing the magnetic nanoparticles with an amphiphilic biocompatible polymer attracted a special interest because of the large applicability: cellular separation, the increase of the contrast in NMR imaging, hyperthermia treatment of the cancerous tumors, protein purification, targeting the drug transport, fixing the retina damages, artificial muscles, temperature and pH sensors, micro-fluidic devices [1].

In this work we present a comparative study of the properties of smart composites obtained by the combination of Fe$_3$O$_4$ nanoparticles with biocompatible responsive polymers. Magnetic composites with different morphology are investigated: (i) as core-shell nanostructures consisting of Fe$_3$O$_4$ functionalized by serine and covered with biocompatible polymer shell poly(caprolactone), PCL; (ii) as smart ferrogels, by the encapsulation of Fe$_3$O$_4$ nanoparticles into chemically cross linked polymers like poly (N-isopropylacril amide), pNIPAM.

2. Experimental

2.1. Samples preparation

The synthesis of core-shell nanostructures with magnetite core covered with polymer or copolymer shell consist first in the preparation of magnetite nanoparticles by alkaline hydrolysis of a ferrous and ferric chloride aqueous solution using a common precipitation process under inert (N$_2$) atmosphere. Magnetite particles were surface-functionalized in situ by the addition of L-serine. The magnetic
nanoparticles were mixed with freshly distilled ε-caprolactone and strongly shaken for 30 min at 1200 rotation/min. The surface initiated ring opening polymerization (ROP) of ε-caprolactone was initiated by the common catalysts, tin (II) 2-ethylhexanoate (Sn(oct)2), resulting in magnetite coated with poly(caprolactone), Fe3O4/PCL.

The smart ferrogels were prepared using ultrastable dispersions of Fe3O4 nanoparticles coated by double layer of lauric acid (LA) as ferrofluids and chemically cross linked polymer pNIPA. The monomer N-isopropylacrylamide (NIPA) and the N,N'-methylenbisacrylamide (BIS), like catalyst were dissolved in 3 ml of deionized water. After N2 gas bubbling for 10 min to deoxygenate the solution, different concentrations of ferrofluid were added and sonicated for 30 min. Ammonium peroxydisulfate (APS), 1 wt% as redox accelerator was added to the solution. The mixture was kept to react for 2 h at 60°C and after that, 24 h at room temperature. After the gelation was completed, the ferrogels was immersed in an excess amount of deionized water for 2 days to remove the residual unreacted monomers. The pNIPA ferrogels were dried for 3 days at 60°C to a constant weight.

2.2. Characterization methods
The X-ray diffraction (XRD) pattern of magnetic nanoparticles was obtained using a Diffractometer DRON 3M X-Ray, working at 35 kV and 35 mA. The Co Kα radiation, Fe filtered was collimated with Soller slits. FTIR spectra were carried out on a JASCO FTIR 610 spectrophotometer. X-ray Photoelectron spectra were recorded using a XPS spectrometer SPECS equipped with a dual-anode X-ray source Al/Mg, a PHOIBOS 150 2D CCD hemispherical energy analyzer and a multi-channeltron detector. The Mg X-ray source operated at 200 W was used for XPS investigations. The samples powder was pressed on an indium foil to allow the XPS measurements. The magnetic measurements were performed at room temperature using a Vibrating Sample Magnetometer Cryogenics.

3. Results and discussion
Figure 1 shows the XRD pattern of magnetic nanoparticles functionalized with serine. The characteristic peaks of magnetite are observed in the XRD spectrum from the figure 1. The microstructural parameters, namely effective crystallite mean size, Deff(nm) and the root mean square (rms) of the microstrains averaged along the [hkl] direction, \(\langle \varepsilon^2 \rangle_{\text{hkl}}^{1/2}\) were obtained by single X-ray profile Fourier analysis of the Fe3O4 sample [2]. The analysis of single (220) and (440) X-ray diffraction profiles gives the following values of the microstructural parameters for Fe3O4 functionalized with serine: \(D_{\text{eff}} = 9.4 \text{ nm; } \langle \varepsilon^2 \rangle_{\text{hkl}}^{1/2} = 0.546 \times 10^2\).

In the figure 2 are given the FTIR spectra of magnetite functionalized with serine (Fe3O4/serine), the composite Fe3O4/PCL and that of PCL respectively. The comparison of these spectra shows that the spectrum of the composite Fe3O4/PCL contains the characteristic absorption bands of magnetite and of PCL respectively, which evidence the composite formation.

From the FTIR spectrum of ferrogels, figure 3 one can observe the absorption bands characteristic of magnetite (Fe3O4) located around 580 cm\(^{-1}\) and of NIPA respectively: a carbonyl stretching vibration (amide I) at 1650 cm\(^{-1}\), N–H bending vibration (amide at 1545 cm\(^{-1}\)) and two typical peaks of C–H vibration of –CH(CH3)2 at 1372 cm\(^{-1}\) and 1385 cm\(^{-1}\), a broad peak between 3440 cm\(^{-1}\) and 3290 cm\(^{-1}\) due to N–H stretching of NIPA repeating units.
PS measurements give the surface composition of functionalized magnetite nanoparticles. The high resolution spectra of C 1s, O 1s and Fe 2p for magnetite functionalized with serine are given in the figure 4. No contribution from N1s core level was observed in the XPS spectrum of magnetite functionalized with serine, due to the deamination of serine in the presence of iron salt. The high resolution spectrum for C 1s, figure 4, can be deconvoluted into three Gaussian peaks corresponding to carbon atoms from different groups. The higher binding energy component at 288.2 eV corresponds to carbon atoms in carboxyl. The most intense component at 286.2 eV corresponds to CH/C-C, and the lower binding energy component could be ascribed to carbon atoms from CH$_2$. The oxygen spectrum in the figure 4 also exhibit three components assigned to the oxygen atoms from OH, COO$^-$ and Fe-O.

**Figure 2.** FTIR spectra of magnetite functionalized with serine (Fe$_3$O$_4$/serine), the composite Fe$_3$O$_4$/PCL and PCL.

**Figure 3.** FTIR spectra of pNIPA ferrogels prepared with different concentrations of Fe$_3$O$_4$ from ferrofluid.

XPS measurements give the surface composition of functionalized magnetite nanoparticles. The high resolution spectra of C 1s, O 1s and Fe 2p for magnetite functionalized with serine are given in the figure 4. No contribution from N1s core level was observed in the XPS spectrum of magnetite functionalized with serine, due to the deamination of serine in the presence of iron salt. The high resolution spectrum for C 1s, figure 4, can be deconvoluted into three Gaussian peaks corresponding to carbon atoms from different groups. The higher binding energy component at 288.2 eV corresponds to carbon atoms in carboxyl. The most intense component at 286.2 eV corresponds to CH/C-C, and the lower binding energy component could be ascribed to carbon atoms from CH$_2$. The oxygen spectrum in the figure 4 also exhibit three components assigned to the oxygen atoms from OH, COO$^-$ and Fe-O.

**Figure 4.** XPS spectra from C 1s, O 1s and Fe 2p of magnetite functionalized with serine.

**Figure 5.** XPS spectra from C 1s, O 1s, Fe 2p of the composite Fe$_3$O$_4$/PCL.
The Fe 2p spectrum contains the doublet Fe 2p3/2 and Fe 2p1/2 with binding energy values of 710 and 723.6 eV, typical for magnetite [3]. The peaks from Fe 2p spectrum can be deconvoluted into two components corresponding to Fe$^{3+}$ and Fe$^{2+}$ ions from magnetite. These results indicate that functionalization with serine doesn’t change the composition of the core magnetite. Figure 5 shows the high resolution spectra from C 1s, O 1s, Fe 2p of functionalized magnetite coated with poly(ε-caprolactone). The C 1s spectrum from the figure 5 contains the contribution of three components peaks located at 289.5, 286.5 and 285.7 eV, corresponding to carbon atoms from PCL [4].

The magnetic properties of the smart composites tailor as a function of magnetite content, figures 6 and 7. The value of saturation magnetization is $M_S = 69$ emu/g for Fe$_3$O$_4$/serine that contains 85 % wt. Fe$_3$O$_4$ and it decreases slightly to the value $M_S = 54.9$ emu/g for the composite Fe$_3$O$_4$/PCL containing 78 %wt Fe$_3$O$_4$. Lower values for the saturation magnetization were obtained for the pNIPA ferrogels as compared with functionalized magnetite coated with PCL due to the lower amount of magnetite that can be encapsulated into the ferrogels. The values of $M_S$ for the ferrogels are in the range 2.5-13 emu/g increasing with the increase of magnetite content. The superparamagnetic behavior of low dimensionality magnetite particles in the investigated composites is evidenced by the missing of hysteresis loop in the magnetization curves for all the investigated samples.

**Figure 6.** Magnetization vs. applied magnetic field at room temperature for magnetite nanoparticles functionalized with serine (Fe$_3$O$_4$/serine) and the composite Fe$_3$O$_4$/PCL.

**Figure 7.** Magnetization vs. applied magnetic field at room temperature for pNIPA ferrogels containing different concentrations of Fe$_3$O$_4$ nanoparticles.

4. Conclusions

Smart composites based on magnetite and biocompatible polymers like poly(caprolactone) and pNIPA were obtained. The synthesis method influences the magnetic properties of the resulting composites. Higher magnetization values are obtained for the composites with the functionalized magnetite core covered by polymer as compared with the ferrogels.

The protective coating of Fe$_3$O$_4$ nanoparticles with a shell of the biocompatible polymer poly (ε-caprolactone) represents a promising route for the development of functional hybrid particles and ferrofluids for both technical and biomedical applications.

References

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