Study of the interactions between the surface chemisorbed layer and the surrounding media in magnetite-coated nanoparticles using Raman spectroscopy

S.W. da Silva[a],*, M.A.G. Soler[a], C. Gansau[b], N. Buske[b], P.C. Morais[a]

[a]Universidade de Brasília, Instituto de Física, Fisica Aplicada, CEP 70919-970 Brasília-DF, Brazil
[b]Mediport Kardiotechnik GmbH, Wiesenweg 10, D-12247 Berlin, Germany

Abstract

Raman spectroscopy is used to investigate surface-coated magnetite nanoparticles (9 nm diameter) dispersed in aqueous medium. In a first sample, the magnetite nanoparticle is coated with dextran. In a second sample the magnetite nanoparticle is double-coated with a dodecanoic layer following an ethoxylated polyalcohol layer. The Raman measurements were focused on the typical intra-molecular OH-stretching mode chemiosorbed at the nanoparticle surface. The data are discussed in terms of the suppression of the symmetric and asymmetric hydrogen bonded mode in both samples. © 2001 Elsevier Science B.V. All rights reserved.

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In recent years, the interest in magnetic fluids (MFs) for biomedical applications has grown enormously [1,2]. However, the development of specific biocompatible magnetic fluids (BMFs) has to go over the challenge of surface-coating the nanomagnetic particles with bioactive molecules. In addition, the physico-chemical nature and properties of the molecular layer chemisorbed at the nanoparticle surface play a central role on the chemical activity and physical stability of MFs [3]. In particular, the first molecular layer around the magnetic nanoparticle need to be engineered in order to bind effectively to specific biomolecules in the synthesis of BMFs. Therefore, the nature and the properties of the first molecular coating represent one of the main issues in the MF research, as far as the biomedical applications are concerned. The biological specificity and the grafting coefficient of a particular bioactive molecule depend upon the efficiency of the link between the nanoparticle surface and the biomolecule. Furthermore, before the nanoparticle can be coated with a particular biomolecule, at a specific grafting coefficient, its surface has to be molecular designed using pre-coating species. However, little effort has been done to investigate theoretically [4,5] and experimentally [6,7] the structure and the interaction of the chemisorbed layer with the nanoparticle surface from one side and with the surrounding medium from the other side. In Ref. [7] we started this study using pre-coated magnetite-based MF samples with dodecanoic acid (single coated) in hydrocarbon and dodecanoic acid plus ethoxylated polyalcohol (double coated) in aqueous medium. In this study, however, we investigated magnetite-based nanoparticles pre-coated with dextran, which allows the dispersion in aqueous medium. The effective hydroxyl grafting coefficient and the hydrogen bonding strength of both the double-coated and the dextran-coated MF samples are discussed here. The Raman spectra of aqueous-based system are dominated by hydrogen bonding as well as by non-hydrogen bonding. Gaussian analysis has indicated that liquid water presents five intra-molecular OH-stretching modes [8]. The two OH-stretching Raman components at the higher end frequency of the spectra (v^s and v^a) describe non-hydrogen bonded modes. In contrast, the three Raman components

*Corresponding author. Tel.: + 55-613072363; fax: + 55-3072900.

E-mail address: sebas@fis.unb.br (S.W. da Silva).

(v_d^s, v_d^a and v_b) at lower frequencies describe hydrogen bonded modes [8]. Therefore, the Raman measurements were focused on the typical intra-molecular OH-stretching mode associated to the hydroxyl group chemiosorbed at the nanoparticle surface. The data are discussed in terms of the suppression of the symmetric and asymmetric hydrogen bonded mode in both samples.

The samples used here were obtained by chemical co-precipitation of Fe(II) and Fe(III) ions in alkaline medium, following coating with dextran (dextran-MF) or with a double layer of dodecanoic acid an ethoxylated polyalcohol (d-MF). After coating, both sample were diluted in water in a concentration of about 2.5×10^{16} particle/cm^3. The interest in these two samples is mainly due to the biological effects they presented when in vivo tests are performed. The dextran-coated magnetite-based MF sample presented a reduced toxicity when compared to the double-coated magnetite-based MF sample [9]. Besides the toxicity, the double-coated magnetite strongly interacts with tissues, thus resulting in severe organ adherence, when administrated in the peritoneal cavity of female Swiss mice [9].

The Raman setup consists of a double 0.85 m 1401 Spex monochromator equipped with the usual photo-counting system. The samples were optically excited with the 514 nm line from an Argon ion laser, at an optical power on the order of 150 mW, outside the sample holder. Fig. 1 shows that only two Raman modes, at the higher energy side of the Raman spectra (v_b and v^a), were observed in the two samples. The presence of these two modes, in comparison to five Raman modes observed in liquid water, is partly explained considering the replacement of a hydrogen atom from the water molecule by the nanoparticle surface, as discussed elsewhere [6]. Suppression of the two symmetrical Raman modes (v_d^s and v^s) from coated MFs is expected, for the surface site is no longer symmetrical. Suppression of the v_d^a Raman mode from coated MFs is straightforward, once the coating layer prevents water molecules from the medium to bound to the OH-group at the nanoparticle surface. Therefore, the two Raman modes left behind in coated MFs are the anti-symmetric non-hydrogen bonded (v^a) plus the anti-symmetric hydrogen bonded (v_b) ones.

From the fitting procedure it was found that the spectra of the two samples are very much similar, except for the relative intensities. From both samples, the OH-stretching Raman mode at the higher end frequency (v^a) have about the same frequency (around 3685 cm^{-1}), thus showing that different coatings do not affect this vibration mode. However, the Raman mode v_b associated to the dextran-MF sample (3650 cm^{-1}) presents a wave number upshift of about 30 cm^{-1} when compared with the d-MF sample (3620 cm^{-1}). In qualitative grounds, the wave number upshift reflects a weaker interaction between the OH-group at the nanoparticle surface and the coating layer. In reasonable agreement with the up-
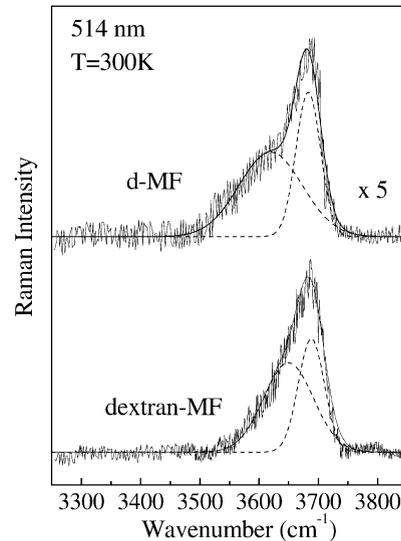

Fig. 1. Raman spectra in the OH-stretching region of MF coating with dextran (dextran-MF) or with a double layer of dodecanoic acid an ethoxylated polyalcohol (d-MF).

shift result, the estimated hydrogen bonding strength is larger for the dextran-MF sample (2.48 kcal/mol) in comparison with the d-MF sample (2.38 kcal/mol). Details of the calculation of the enthalpy change can be found elsewhere [6].

On the other hand, it was found that the intensity of the Raman lines in the dextran-MF sample is about five times the intensity of the Raman lines in the d-MF sample. This is a strong indication that the hydroxyl-grafting coefficient was reduced in the d-MF sample when compared to the dextran-MF sample. To link to the nanoparticle the dextran molecule has to replace hydroxyl groups previously bounded at the nanoparticle surface. Once dextran is a huge molecule compared to the typical surface hydroxyl–hydroxyl distance it is conceivable that the dextran links to the nanoparticle surface by removing just a small fraction of hydroxyl groups, i.e., a high hydroxyl-grafting coefficient is left behind even after the dextran coating process. On the other hand, the surface nanoparticle coating with dodecanoic acid plus ethoxylated polyalcohol has a quite different approach, making possible the removal of a higher fraction of hydroxyl groups. That explains the reduced hydroxyl grafting coefficient observed in the d-MF sample compared to the dextran-MF sample.

In conclusion, it was found that the effective hydroxyl grafting coefficient in the dextran-MF is about five times higher than the effective grafting coefficient in the d-MF sample. The wave number upshift observed for the v_b modes in the dextran-MF sample goes parallel with the increase on the enthalpy change associated to the hydrogen bonding involving the OH-group.

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