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Time-modulation of surface functionalization in biocompatible magnetic fluids

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ABSTRACT

Photoacoustic spectroscopy (300–1000 nm wavelength range) was used to investigate the aging of dimercaptosuccinic acid-coated maghemite nanoparticles suspended as biocompatible magnetic fluids. The three samples investigated presented increasing surface-grafting coefficient and were water-diluted at day-0. The time evolution (from day-0 to day-40) of the areas under band-L and band-S photoacoustic features was used to draw conclusions on the changes on the relative populations of carboxyl (N_L) and hydroxyl (N_S) groups adsorbed onto the nanoparticle surface. We found the time-dependence of the relative populations of molecular species (N_L/N_S) peaking at band-L and band-S following a sigmoid-like curve with characteristic times of 2.7, 3.7 and 4.1 days for samples presenting increasing molecular surface-grafting coefficient (N).

1. Introduction

One of the key aspects related to biocompatible magnetic fluid (MF) samples, with important consequences to both fundamental and applied research, is the desorption of molecules out from the surface of the nanoparticle suspended in the carrier fluid. The surface molecular species are used not only to provide colloidal stability but specially to functionalize the colloidal magnetic particles, aiming particular biological and medical applications. However, desorption is a typical colloidal aging process which is closely related to nanoparticle clusterization, the latter tightening single nanoparticle units together in more complex agglomerates [1]. Cluster formation in MF samples, induced either by the application of an external magnetic field [2], reducing the MF sample temperature [3], increasing the MF nanoparticle concentration [4] or by changing the characteristics of the nanoparticle surface molecular layer [5–9], has been investigated to some extend though little effort has been devoted to understand the molecular surface-desorption process that may leads to nanoparticle clusterization. The influence of the surface grafting on the MF properties has been investigated using for instance static magnetic measurements [5], magnetic resonance [6], optical transmission experiments [7], static magnetic birefringence [8], and photoacoustic spectroscopy [9]. Photoacoustic spectroscopy (PAS) has been recently introduced as a promising MF characterization technique [10], for it provides important information regarding the nanoparticle core characteristics [11] as well as information related to molecular species adsorbed on the nanoparticle shell [9]. As reported in the literature [10] while the photoacoustic features related to the hydroxyl group adsorbed onto the surface of transition metal-oxide nanoparticles appears at shorter wavelengths (band-S) other adsorbed functional groups (such as carboxyl, carbonyl, and amino) reveal photoacoustic features at longer wavelengths (band-L). Therefore, as far as the time evolution of the molecular surface-grafting process is concerned PAS potentially provides a direct way to track changes on MF samples by looking at the relative intensities of band-L and band-S within the same photoacoustic spectrum. In the present study we report on the aging investigation of biocompatible magnetic fluid samples containing maghemite nanoparticle surface-coated with dimercaptosuccinic acid (DMSA) and suspended in physiological solution. Biocompatible magnetic fluid (BMF) samples with very similar maghemite core-size but presenting different DMSA grafting coefficients were used as the stock samples. Stock samples of magnetic fluids were then aqueous-diluted at day-0 while the photoacoustic spectra were recorded as a function of time in order to draw conclusions regarding changes on the molecular surface grafting.

2. Experimental

The MF stock samples were prepared and stabilized in 0.9% sodium chloride aqueous solution at pH 7, following the route already described in the literature [12]. Samples were labeled DMSA1, DMSA2 and DMSA3 with average core-diameters (size dispersion) of 7.9 nm (0.17), 7.2 nm (0.28) and 6.7 nm (0.17), respectively. The particle size (core diameter) histograms obtained from the transmission electron micrographs were curve-fitted using the log-normal distribution function [13]. Stock samples DMSA1, DMSA2 and DMSA3 were characterized in terms of the nanoparticle concentration as follow: 1.0×10^{16}, 1.7×10^{16} and 1.7×10^{16} particle/mL, respectively. Samples prepared for the PAS investigation

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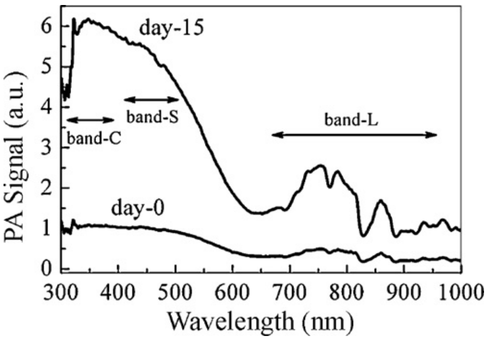

Fig. 1. Typical photoacoustic (PA) spectra of sample DMSA1 at day-0 and day-15.

were obtained by diluting the stock BMF samples using pure water as solvent. The dilution procedure was accomplished by adding three volumes of pure water in one volume of the stock sample. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy was used to quantify the relative DMSA surface grafting in both BMF stock samples, as described in the literature [12]. From the ATR-FTIR data we found sample DMSA1 presenting the lowest surface-grafting coefficient whereas sample DMSA3 presented the highest surface-grafting coefficient. Among all three BMF samples investigated sample DMSA2 presented intermediate surface-grafting coefficient. After dilution the three BMF samples were used for recording the PAS data at day-0, day-2, day-5, day-8, day-15, day-20, day-30, and day-40. The photoacoustic (PA) spectra were recorded for all three aqueous-diluted BMF samples prepared as a thin film on top of a polished quartz substrate. The samples were enclosed in a sealed, high-performance, PA cell at atmospheric pressure, coupled to a sensitive microphone. The light from a 150 W Xe lamp was dispersed by a 0.22 m double monochromator (Spex model 1680) and used as the variable wavelength light source. The light was chopped at a frequency of a few hertz to improve the signal-to-noise ratio. All the PA spectra were normalized to the spectra of a highly absorbing (black) film.

3. Results and discussion

Fig. 1 shows typical PA spectra of sample DMSA1 recorded at day-0 and day-15. The usual region of band-C, -S and -L are also indicated in Fig. 1. Band-C has been related to the absorption of the incident light by the core nanoparticle [11]. We emphasize that the PA signal scales with the optical absorption coefficient and, under low optical excitation intensities, the PA signal scales linearly with the optical absorption coefficient. The optical absorption edge of most bulk ferrite-based crystals falls within the range of 300–400 nm. Band-S is related to the metal-polyoxy-hydroxy surface layer built up at the co-precipitated ferrite-based nanoparticle surface, which is particularly enriched by hydroxyl groups [10]. The strong peak around 470 nm, observed in all ionic magnetic fluid samples investigated to date, indicates the expected high surface hydroxyl grafting coefficient. Note that the PA band around 470 nm is typical of the crystal field band of transition metal ions in a distorted octahedral environment [9]. Finally it is claimed that band-L is related to the characteristics of the nanoparticle stabilizing molecular coating layer, thus allowing characterization of a particular BMF sample.

In order to analyze the time evolution of the relative population of carboxyl-to-hydroxyl groups, both directly adsorbed onto the nanoparticle surface, the areas under band-L (*AuL*) and -S (*AuS*) were investigated as a function of time. Fig. 2 shows the time-dependence of the *AuL*/*AuS* ratio. The area under the corresponding spectrum band scales with the surface-grafting coefficient (N) of the adsorbed groups, namely carboxyl (N_L) and hydroxyl (N_S) groups while $AuL/AuS = N_L/N_S$. All data in Fig. 2 were normalized to 0.5 for day-0 in order to provide better comparison among different samples. Note in all three cases (see Fig. 2) the general tendency for saturation at longer times, though sample DMSA1 follows a quite different profile in comparison to samples DMSA2 and DMSA3, whose behavior is very much close together. In addition, note that all the data shown in Fig. 2 follow a sigmoid-like function, characterized by different parameters. One can easily derive a sigmoid-like function describing the aging process shown in Fig. 2 using a very simple model, as follows. Firstly, as already described in the literature, the surface of co-precipitated (alkaline medium) nanoparticles is fully coated with hydroxyl groups. Secondly, the surface-coating of the maghemite nanoparticle with DMSA is accomplished because, under favorable chemical conditions, the carboxyl group shifts the surface-adsorbed hydroxyl group to some extend. Therefore, the BMF samples under investigation in this study contain maghemite nanoparticle surface-coated with hydroxyl and carboxyl groups, the steady-state relative population of them established by the conditions under which the coating process took place. Third, as far as the steady-state relative population of the surface molecular species is concerned water-dilution of the as-produced BMF samples take the sample out from the equilibrium. The driving force restoring the system to another equilibrium position is the gradient of the osmotic pressure between the bulk solution (π_B) and the nanoparticle surface at the two distinct linking sites (π_L, π_S). Here we have two different molecular species (hydroxyl and carboxyl) in two different compartments (nanoparticle surface plus bulk solution). Note that the DMSA molecule normally has the first carboxyl group adsorbed onto the nanoparticle surface while the second one is facing the bulk solution.

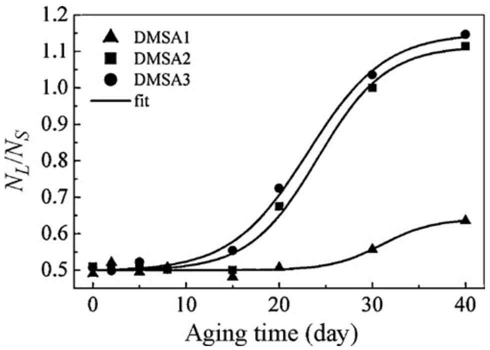

Fig. 2. N_L/N_S versus aging time. Symbols are the experimental values whereas solid lines are the best curve-fitting using Eq. (2).

The model picture assumes the rate (dN_S/dt) scaling with $\{(\pi_L - \pi_B) - (\pi_S - \pi_B)\}$. In other words, the differential equation describing the rate for reaching the steady-state condition is:

$$\frac{dN_S}{dt} = -\frac{N_S - N_L}{\tau}, \tag{1}$$

where τ is the characteristic time for approaching the steady-state condition. Solution of Eq. (1) gives:

$$\frac{N_L}{N_S} = B + (T - B)\left\{1 + \exp\left[\frac{t_0 - t}{\tau}\right]\right\}^{-1}, \tag{2}$$

where B (bottom) and T (top) describe the range of the N_L/N_S data and t_0 is the time at which the ratio N_L/N_S is halfway between bottom and top. The solid lines in Fig. 2 represent the best curve-fitting of the data ($AuL/AuS = N_L/N_S$) using Eq. (2), thus providing the characteristic time of $\tau = 2.7$, 3.7 and 4.1 days for samples DMSA1, DMSA2 and DMSA3, respectively. This finding indicates that (for all samples investigated here) the relative number of carboxyl groups (N_L/N_S) tight to the nanoparticle's core increases after the dilution procedure. Further, the higher the initial surface-grafting coefficient the higher the typical time (τ) for approaching the steady-state condition.

4. Conclusion

In summary, photoacoustic spectroscopy was used in this study to follow and evaluate the aging of dimercaptosuccinic acid-coated maghemite nanoparticle suspended as biocompatible magnetic fluid samples. Photoacoustic spectra of water-diluted samples were recorded as a function of time, thus providing information for the time evolution of the relative population of molecular species (carboxyl versus hydroxyl) adsorbed onto the nanoparticle surface. We found the area under the photoacoustic band-L (band-S), which scales with the number of adsorbed carboxyl (hydroxyl) species, the appropriated variable to investigate the samples aging. A simple model picture, based on the gradient of osmotic pressure, is proposed in the present study to fit the experimental data in order to provide the characteristic time constant for the aging process.

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