European Cells and Materials Vol. 3. Suppl. 2, 2002 (pages 19-21) ISSN 1473-2262

USE OF THE PHOTOACOUSTIC SPECTROSCOPY IN THE INVESTIGATION OF IONIC MAGNETIC FLUIDS

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INTRODUCTION: High-resolution microscopy, magnetization, and static magnetic birefringence are traditional magnetic fluid (MF) characterization techniques. Magnetic resonance and Raman spectroscopy were introduced more recently as extremely useful tools in the investigation of MF properties. However, the wide range of applications of MFs, as for instance in the biomedical field, requires more detailed investigation of their properties. In particular, the nature and interaction of the nanoparticle surface coating layer with both the surrounding medium and the nanoparticle core has attracted much attention in recent years. Photoacoustic (PA) spectroscopy is a well-established, surface-based experimental technique [1] with a wide range of application in material science. Nevertheless, only recently, has PA spectroscopy been used in the investigation of MF samples [2]. Briefly, the PA effect measures the non-radiative de-excitation processes that occur in a system after it has been optically excited by wavelength-variable modulated light. In this study, features in the PA signal obtained from thin liquid films of ionic MF samples deposited on top of inert substrates are used to draw conclusion about the suspended magnetic nanoparticles and the corresponding surface coating layer.

METHODS: Similarly to the standard procedure described in Ref. [3] three preparations containing $MnFe_2O_4$ nanoparticles, with different mean diameter values (3.8, 6.6, and 10.7 nm), were used to produce stable ionic MF samples. The $MnFe_2O_4$-based MF samples were stabilized around pH3 and labeled samples 1, 2, and 3, corresponding to mean diameter values of 3.8, 6.6, and 10.7 nm, respectively. PA spectra were taken from the three MF samples prepared as a thin liquid film on top of a polished quartz substrate. The MF samples were enclosed in a sealed, high-performance, PA cell at atmospheric pressure, coupled to a sensitive microphone. The light from a 150 watt 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. Figure 1 shows a schematic representation of the PA experimental setup. All the PAS spectra of the samples were normalized to the spectra of a highly absorbing film. For the three samples investigated, several PA features were observed in the wavelength range of 0.3 to 1 μm. In the range of 0.35 to 0.45 μm an intense band (band-C) was observed in the PA spectra. A less intense structure (band-S) was observed around 0.47 μm. Finally, in the 0.65 to 0.90 μm region a complex structure (band-L), identical in the three samples investigated, was observed in the PA spectra.

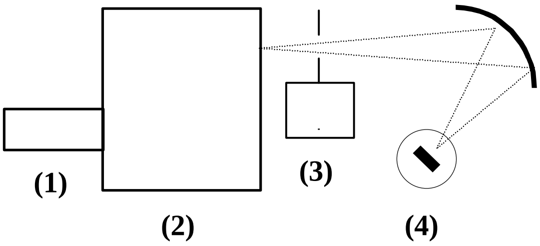

Fig. 1: Typical experimental setup of the photoacoustic experiment. (1) is the lamp, (2) is the monochromator, (3) is the chopper, and (4) is the PA cell.

RESULTS & DISCUSSION: Figure 2 shows the PA spectra of samples 1, 2, and 3 in the range of 0.3 to 1 μm. The features occurring in bands L, S, and C will be discussed as follows. Band-L shows identical features in all ferrite-based ionic MF samples we have investigated so far, including samples with divalent metal-ions as different as Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} (data not shown). It is claimed that band-L is related to the characteristics of the MF stabilizing coating layer, thus explaining the similarities observed in the PA spectra of all ionic MF samples investigated to date. The main peak (around 0.47 μm) of band-S is quite intense in manganese-ferrite-based ionic MF samples, similar to what has been observed in cobalt-ferrite-based ionic MF samples [2]. As previously stated [2], band-S is related to the metal-polyoxy-hydroxy surface layer built up at the ferrite-based nanoparticle surface, which is particularly enriched by hydroxyl groups [4]. Furthermore, the strong peak around 0.47 μm, observed in all ionic MF samples investigated, indicates the expected high surface hydroxyl grafting coefficient. Note that the PA band around 0.47 μm is typical of the crystal field band of transition-metal ions in a distorted octahedral environment [5]. Finally, the spectral features observed in band-L and band-S could be associated to higher-order Raman overtones due to molecular species in the coating layer and in the nanoparticle surface, respectively.

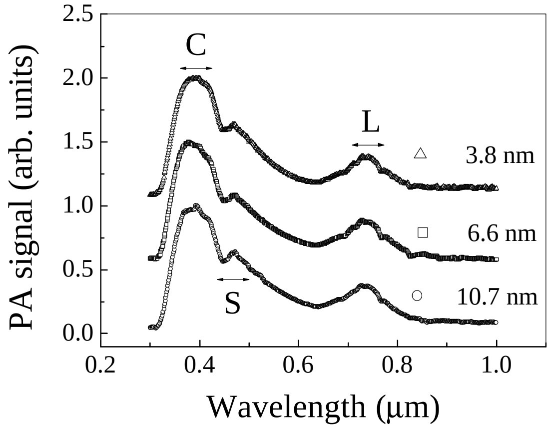

Fig. 2: PA spectra of ionic magnetic fluid samples based on $MnFe_2O_4$ nanoparticles with different average sizes.

Whereas band-L and band-S have been respectively ascribed to the stabilizing coating layer and the nanoparticle surface layer, band-C has been related to the absorption of the incident light by the core nanoparticle [2]. At this point we should 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. Further, the optical absorption edge of most bulk ferrite-based crystals falls in the range of 0.3 to 0.4 μm. It is important to mention that a semiconductor quantum dot model has been successfully used to explain the charge-discharge mechanism as well as the stability of aqueous colloids based on ferrite nanoparticles. Moreover, the PA signal represented by band-C has been previously attributed to a charge-transfer band [5]. Therefore, the main features of band-C in the PA spectra shown in Figure 2, namely, the presence of structures and the rapid rise of the PA signal at decreasing wavelength, are the signatures of optical processes near the semiconductor absorption edge. One aspect that deserves attention with regard to band-C (see Figure 2) is the presence of structures. A more detailed analysis of the features appearing in Figure 2 can be performed after imaging the PA signal in the the wavelength window of 0.41 to 0.46 μm. Figure 3 shows the first derivative of the PA signal in the 0.41-0.46 μm range. The first derivative of the PA signal, probably gaussian in shape, does improve the band deconvolution procedure into several components. The right-hand side arrows in each PA spectrum (see Figure 3) are claimed to be signal fundamental optical transitions in the band-C region, quoted at 0.432, 0.436, and 0.439 μm for samples 1, 2, and 3, respectively. This is exactly the wavelength order one should expect for the size-dependence of the fundamental optical transition in quantum-confined semiconductor systems. In Figure 3 extra arrows are pointing to features occurring at higher energies. These features are claimed to be due to optical transitions between excited energy states. In support to the view described above, the PA features in sample 1 (3.8 nm particle size) appear much more widely spaced in energy, compared to those for samples 2 and 3. This is due to the quantum confinement effect, which is expected to be stronger in sample 1 in comparison to samples 2 and 3.

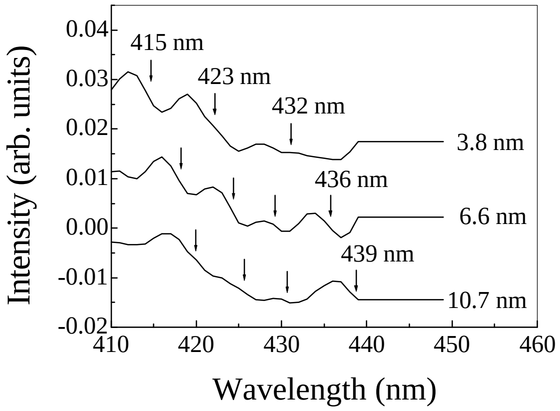

Fig. 3: First derivative of the PA spectra, in the range of 0.41 to 0.46 μm.

At this point it is important to stress that a more detailed analysis (a quantitative analysis) of the PA features revealed in Figure 3 requires knowledge of several parameters, not only for the nanoparticle core but also for the nanoparticle surface layer. Among the parameters are the electron and hole effective masses, conduction and valance band offsets, dielectric constants, and fundamental band-gaps. In addition to these parameters the pH of the magnetic fluid sample is extremely important in order to include the surface charge density and thus the effects due to band-bending and band-gap renormalization. Not only is such analysis far beyond the scope of the present study, but to date the required parameters are not available.

CONCLUSIONS: In summary, this study shows that PA spectroscopy emerges as a powerful technique to investigate magnetic fluid samples. Three main bands (L, S, and C) were identified in the 0.3 to 1 μm spectral range. Bands L, S, and C were ascribed to the coating layer, to the metal-polyoxy-hydroxy thin layer at the nanoparticle surface, and to the nanoparticle core, respectively. Features in band-C were associated with the fundamental and excited optical transitions in the quantum-confined semiconductor system (quantum dot). Indeed, PA spectroscopy requires relatively low-cost instrumentation and most of the systems in operation are home made.

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ACKNOWLEDGEMENTS: This work was supported by the Brazilian agencies FAP-DF, CNPq, and FINATEC.