Effects of the Surface Coating and of the Size on the Nonlinear Optical Response of Magnetic Iron Oxide Nanoparticles

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ABSTRACT
In this work, new results are presented concerning the nonlinear optical properties of some recently synthesized magnetic iron oxide nanoparticles (MIONs) coated with sodium carboxy-methylcellulose (abbreviated as NaCMC) and having various sizes ranging from 7 nm to 20 nm. The present work is part of ongoing research aiming to investigate the influence of nanoparticles’ surface coating and the effect of morphological parameters such as nanoparticles’ size, geometry etc. on their nonlinear optical response. The nonlinear absorption and refraction and the third-order nonlinear susceptibility $\chi^{(3)}$ of NaCMC coated MIONs have been studied by means of the Z-scan technique employing visible (532 nm) and infrared (1064 nm), 35 ps laser pulses. The present results are compared with previously obtained results concerning similar MIONs coated with another polyelectrolyte namely poly(sodium4-styrenesulfonate) (abbreviated as NaPSS).

Keywords: nonlinear absorption, nonlinear refraction, third-order susceptibility, iron oxide nanoparticles.

1. INTRODUCTION
Recently, a considerable amount of research work is being devoted in studying the properties of magnetic iron oxide nanoparticles (MIONs) mainly because of the numerous potential applications envisaged for these systems in various scientific fields, ranging from materials science and chemistry to biochemistry, environmental remediation and medical imaging. Currently, magnetic iron oxide nanoparticles are widely used in catalysis, in pigment and ink technologies, as gas and bio-sensors, in magneto-electronics, in lithium storage, as magnetic storage media, and furthermore in magnetic targeting and separation processes in biological systems and for drug targeting. In addition, iron-based nanoparticles are very effective decontamination agents in the decontamination of water from toxic metals and organic pollutants.

Despite the various applications of iron oxide nanoparticles, their nonlinear optical (NLO) properties are relatively unexplored yet and the existing related experimental studies are limited and rather non systematic. This same situation holds also for systems based on aqueous functional colloids of MIONs. Functionalized magnetic colloids exhibiting nonlinear optical properties may have added value in biomedical applications, since NLO-responsive, biocompatible materials facilitate in vitro and in vivo imaging by e.g. NLO microscopy.

In that view, our research efforts have been initially concentrated on the characterization of the nonlinear optical response of neat and covered by poly(sodium4-styrenesulfonate) polyelectrolyte (abbreviated as NaPSS) MIONs having sizes between 7 and 20 nm using ps and ns laser excitation both in the visible and in the infrared [1,2].

In the current work, some new results are presented concerning the nonlinear optical response of some similar magnetic iron oxide nanoparticles, covered however with a relatively weaker, compared to the previously used NaPSS, bio-polyelectrolyte, namely the sodium carboxy-methylcellulose (abbreviated as NaCMC). So, both the sign and the magnitude of the nonlinear absorption, refraction and the third-order nonlinear susceptibility $\chi^{(3)}$ of NaCMC functionalized MIONs dispersed in deionised water have been determined and are compared with our previous results on NaPSS coated MIONs. The experimental technique used was the Z-scan technique, employing visible (532 nm) and infrared (1064 nm), 35 ps laser pulses.

The present experimental results reveal clearly that the MIONs’ organic coating can greatly affect their nonlinear optical response providing a very efficient way to enhance their nonlinear optical response. In addition, the present measurements indicate that MIONs’ size has also an important effect on the optical nonlinearities of these systems.

2. EXPERIMENTAL DETAILS AND DATA ANALYSIS
2.1 Materials preparation
For the synthesis of the uncoated MIONs, the following reagents (in the sequence they appear) were added in a spherical flask containing deionised H2O (40 mL): FeCl3 (0.380 g) and FeCl2 (0.140 g). The mixture was stirred at 50°C under N2 flow. An aqueous solution of NaOH (1.65 g, 10 mL) was added and after 20 min the reaction was stopped. The product was subjected to dialysis in order to remove NaCl and then subjected to
a mild centrifugation in order to separate bigger aggregates in the precipitate. The supernatant was collected with nanoparticles forming a very stable dispersion, while their hydrodynamic radii determined by Dynamic Light Scattering (DLS) measurements were found to be about 120 nm. The iron oxide inorganic cores displayed sizes of about 5.5 nm, according to TEM analysis as can be seen in Figure 1. The significant difference between the diameter from DLS and TEM is attributed to the fact that MIONs form clusters of nanoparticles in the solvent and these clusters are detected in DLS. On the contrary, in TEM the single nanoparticles (or nanocrystallites) are measured.

In the photographs presented in Figure 2 the colour of various concentrations’ dispersions of uncoated MIONs in deionised water are shown. The formation of fine colloidal dispersions is also evident by the optical transparency if the samples.

For the synthesis of the coated MIONs, FeSO₄·7H₂O (0.72 g) and sodium carboxymethyl cellulose (NaCMC, 0.5 g) were dissolved in H₂O (40 mL) at 30 °C under magnetic stirring. In this mixture, NH₄OH 30 % was added. The temperature was raised to 50 °C. After 1h the reaction stopped. The fine NaCMC-coated MIONs were separated from the byproducts and higher order aggregates with centrifugation. By varying the amount of NH₄OH added, NaCMC coated MIONs with different mean nanocrystallite sizes were obtained (~7 to ~13 nm), while their hydrodynamic diameter (measured by DLS) was slightly smaller compared to that of the uncoated MIONs, that is ~100 nm. Figure 3 presents some representative TEM images and the corresponding size distribution diagrams of the prepared coated MION colloids. Following an identical procedure, replacing NaCMC with sodium poly(styrene sulfonate) (NaPSS), coated MIONs with a nanocrystallite size of ~18 nm and Dₜ=115 were also obtained[1,2]. In this case of polymer coated MIONs the polymer chains attached on their surface contribute significantly in the hydrodynamic size.

Figure 1. TEM image of the uncoated magnetic colloid, the size distribution diagram obtained thereof and the lognormal fit.

Figure 2. Photographs of uncoated MIONs at various concentrations.

Figure 3. TEM images and size distribution diagrams from the ~7 nm (left) and ~13 nm MagCMC colloid.
2.2 Z-scan technique

For the determination of the nonlinear optical properties of the MIONs, several water deionised dispersions with various concentrations of MIONs have been prepared and measured using Z-scan technique employing 35 ps laser pulses, at 532 and 1064 nm, from a mode-locked Nd:YAG laser operating at a repetition rate of 10 Hz[4,5]. For each prepared sample, several Z-scan measurements were performed at different incident laser energies. The Z-scan technique and the details of the experimental setup and the procedure for the analysis of the Z-scan data have been described in details elsewhere [5] and will not be presented here. The samples were placed into 1 mm thick quartz cells and the laser beam was focused into the sample by means of a 20 cm focal length quartz lens. The stability of the prepared dispersions was checked periodically by measuring their UV-Vis-NIR optical absorption spectra.

3. RESULTS AND DISCUSSION

The nonlinear absorption parameter \( \beta \) of the samples was determined from the ‘open-aperture’ Z-scan measurements while from the corresponding “divided” Z-scans the nonlinear refraction parameter \( \gamma' \) was deduced, the nonlinear absorption parameter \( \beta \) being determined previously, according to the procedures described in detail in ref. [5]. In addition, from the shapes of the ‘open-aperture’ and “divided” Z-scans, the signs of the absorptive and refractive parts of the optical nonlinearity were also determined.

As an example, in Figure 4, two representative “divided” Z-scan recordings are presented corresponding to a 0.052 % wt/v MION dispersion in deionized water, measured under 532 and 1064 nm laser excitation respectively. In this case the inorganic core of the MIONs had a diameter of about 7 nm. As can be seen from the curve of Fig. 4(a), the “divided” Z-scan recording obtained under 532 nm laser excitation was found to exhibit a transmission peak followed by a post-focal valley, indicative of defocusing behaviour corresponding to negative nonlinear refractive index (i.e. \( \text{Re}\chi^{(3)}<0 \)), while the “divided” Z-scan recording obtained under 1064 nm laser excitation, shown in Fig. 4(b), was found to exhibit a pre-focal transmission valley followed by a post-focal transmission peak revealing self-focusing behaviour corresponding to positive nonlinear refractive index (i.e. \( \text{Re}\chi^{(3)}>0 \)). In other words, the nonlinear optical response of MIONs dispersions was found to switch from defocusing to self-focusing depending upon the laser excitation wavelength, e.g. defocusing under visible excitation and self-focusing under infrared excitation.

In order to study the influence of the size of the iron oxide nanocrystallites on the third-order nonlinear optical response of the NaCMC coated MIONs different samples have been prepared having nanocrystallite inorganic cores with mean sizes of about 7, 10 and 13 nm. In all cases, the resulted final products had hydrodynamic diameters in the range of about 100 nm. They were all found to exhibit a third-order nonlinear susceptibility \( \chi^{(3)} \) of the order of \( 10^{-12} \) esu, clearly decreasing with increasing the size of the nanocrystallite. Moreover, their nonlinear optical response at 532 nm was found to be about five times stronger compared with that measured under 1064 nm excitation. In addition, all samples studied were found to exhibit only nonlinear refraction, their nonlinear absorption being negligible within the range of incident laser energies used. It is important to notice at this point that similar sizes MIONs covered with NaPSS did not show any nonlinear optical response under ps laser excitation conditions [2], clearly suggesting that the nature of the coating is greatly affecting the nonlinear optical response of the MIONs, most probably due to changes occurring at the density of surface states created at the surface of the nanoclusters forming the final product. It is also very important to note that NaPSS coated
MIONs displayed nanocrystallite size of 18 nm, further supporting our results that by increasing the size, the nonlinear response drops.

For comparison purposes, further measurements have been performed under identical conditions on deionised water dispersions of some commercially available uncoated magnetite (Fe₃O₄) nanoparticles (Ferrotec’s EMG 605 Ferrofluid) having nominal size of about 10 nm, as reported by the manufacturer. From these measurements a third-order nonlinear susceptibility of about 10⁻¹³ esu has been determined under 532 nm laser excitation a value almost an order of magnitude smaller than that of NaCMC coated MIONs. DLS measurements of the commercial uncoated magnetite nanoparticles have revealed the formation of clusters having hydrodynamic diameter of about 64 nm. It should be noted here that MIONs coated with NaCMC are most probably less aggregated than uncoated ones, since the polymer absorbs on their surface preventing interparticle interactions. This culminates into smaller free surface area of uncoated MIONs, and in turn into reduced percentage of surface states, to which the nonlinear optical properties are most probably ascribed. Based on this rational, (free surface area per unit mass of MIONs) the increase in nonlinear optical properties as particle size decreases, discussed in the previous paragraph, is also explained.

Comparing the uncoated MIONs, the commercial ones (Dₚ = 64 nm) and those prepared in the lab according to the previously described route (Dₚ = 120 nm), the latter displayed much lower response despite the fact that their inorganic core size was smaller (5.5 nm over 10 nm). Nevertheless, attention should be paid in this case to the significantly lower Dₚ of the commercial sample, which interprets into lower aggregation and thus higher free surface area. Undoubtedly, further investigations should and are being carried out in order to study possible effects of Fe²⁺/Fe³⁺ ratios in MIONs, as well as to experimentally investigate by TEM the commercial sample, in order to strengthen our conclusions.

4. CONCLUSIONS

In conclusion, in this work the nonlinear optical response of some recently synthesised magnetic iron oxide nanoparticles coated with a relatively weak polyelectrolyte c.a. the NaCMC is investigated. The prepared MIONs had iron oxide cores with diameter ranging between 5 and 13 nm. Their nonlinear absorption and refraction have been determined both at 532 and 1064 nm using 35 ps laser excitation. They have been found to exhibit only refractive nonlinearity of the order of 10⁻¹² esu greatly enhanced compared with similar nanoparticles coated with NaPSS polyelectrolyte, probably due the smaller nanocrystallites size in the case of NaCMC coated MIONs, which determines the free surface area of the material and thus the population of surface states.

REFERENCES