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Local electric field enhancements and large third-order optical nonlinearity in nanocomposite materials

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Abstract

We report local electric field calculations in nanocomposite materials. These calculations are performed by means of a recursive transfer matrix method initially developed for calculating the electromagnetic field response for three-dimensional systems of scattering spheres. Illustrative calculations are presented for various morphologies of nanocomposites composed of gold particles in a silica matrix. We particularly point out that mutual interactions between particles are responsible for large local field enhancements as compared with fields inside isolated particles. Nonlinear optical measurements, performed by using the z-scan technique, are presented afterwards. We especially study the variations of the imaginary part of the third-order nonlinear susceptibility as a function of the metal concentration and we show that these results are in agreement with the previous field calculations.

Keywords: Local electromagnetic field, nanoparticles, nonlinear optics, surface plasmon resonance, transfer matrix method

1. Introduction

Materials composed of noble-metal nanoparticles embedded in a transparent dielectric matrix have been the object of growing interest for several years because of their specific linear and nonlinear optical properties. These materials show an optical absorption band due to the surface plasmon resonance (SPR) phenomenon: collective oscillation of the conduction electrons of the metal under the influence of an applied electromagnetic (EM) wave. The enhancement of the local electric field which occurs in the particles at frequencies close to the SPR is responsible for the amplification of their nonlinear properties as compared with those of bulk metal [1, 2]. This explains the large effective third-order nonlinear susceptibility, $\chi^{(3)}$, of nanocomposite materials. Thanks to this high nonlinear response, these materials are thought to be good candidates for the realization of new photonics devices, such as all-optic switching and routing units.

The first studies devoted to the measurement of the third-order susceptibility were performed on samples with very low metal volume fraction (about 10^{-6}) in colloids [1] and in doped glasses [3]. Nowadays, several physical and chemical synthesis methods enable the elaboration of materials containing higher metal amounts [4–6]. Nevertheless, most studies still evaluate the amplification of the local fields by considering the limit case of weak metal concentrations. So far, the exact calculation of the distribution of the local field intensities has been performed only for two-dimensional semicontinuous films [7, 8].

This paper is focused on the exact calculation of local fields inside spherical metallic particles of composite materials. Calculations are based on a recursive transfer matrix method which was initially developed for calculating the electromagnetic field response for three-dimensional systems of scattering spheres [9]. In the following section, the basis of the calculation method is summarized and results

relative to gold particles embedded in a silica matrix are presented for various configurations. Experimental results of the measurement of the third-order nonlinear susceptibility of Au:SiO_2 nanocomposites by the z-scan technique are shown and connected with the previous theoretical results in section 3.

2. Local field calculations

2.1. Theoretical considerations

Let us consider an isolated metal particle embedded in a dielectric matrix, subjected to an electric field E_0. In the quasi-static limit, a simple electromagnetic calculation leads to the field, E, inside the particle:

$$E = fE_0 = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d} E_0; \qquad (1)$$

f is called the local field factor, ε_d is the dielectric function of the matrix and ε_m is that of the metal. Equation (1) can be used to calculate the field inside any metallic particle of a composite material, as long as the metal concentration remains weak. As a matter of fact, this equation does not take into account the interactions between particles. Furthermore, it cannot account for the spatial variations of the local fields.

In order to mitigate these shortcomings, we have performed calculations based on a new recursive transfer matrix approach [9]. This method was initially developed for the calculation of local fields in multiple-scattering problems: it is based on a recursive T-matrix algorithm and makes it possible to perform an exact local electromagnetic calculation of the field scattered by an assembly of interacting spheres. The theoretical considerations of this method are detailed in [10] and are only summarized here.

According to Mie theory, the incident field, E_0, impinging on a single sphere and the corresponding scattered field, E_{scat}, can be expanded in terms of spherical vector wavefunctions. The incident field expansion coefficients are converted into the expansion coefficients of the radiated scattering field by the T-matrix. In the case of an assembly of N spheres, the same T-matrix formulation leads to a system of N coupled linear equations:

$$E_{scat}^{(i)} = T_1^{(i)} \left[E_0 + \sum_{\substack{j=1 \\ j \neq i}}^{N} E_{scat}^{(j)} \right], \qquad i = 1, \ldots, N \qquad (2)$$

where $T_1^{(i)}$ is a one-body transfer matrix, the elements of which are essentially zero beyond a certain multipolarity order, n. In equation (2), the incident field is expanded in the principal co-ordinate system, whereas the scattered field from each sphere is expressed as outgoing waves centred on the corresponding scatter. The translation–addition theorem for the spherical vector wavefunctions must be invoked in order to reference all fields in the ith sphere coordinate system. This formalism usually leads to convergence problems especially associated with the dimensions of the translation matrices. It has been possible to get rid of these problems, thanks to the modification of a previous T-matrix algorithm [11], by calculating the scatter-centred transfer matrices.

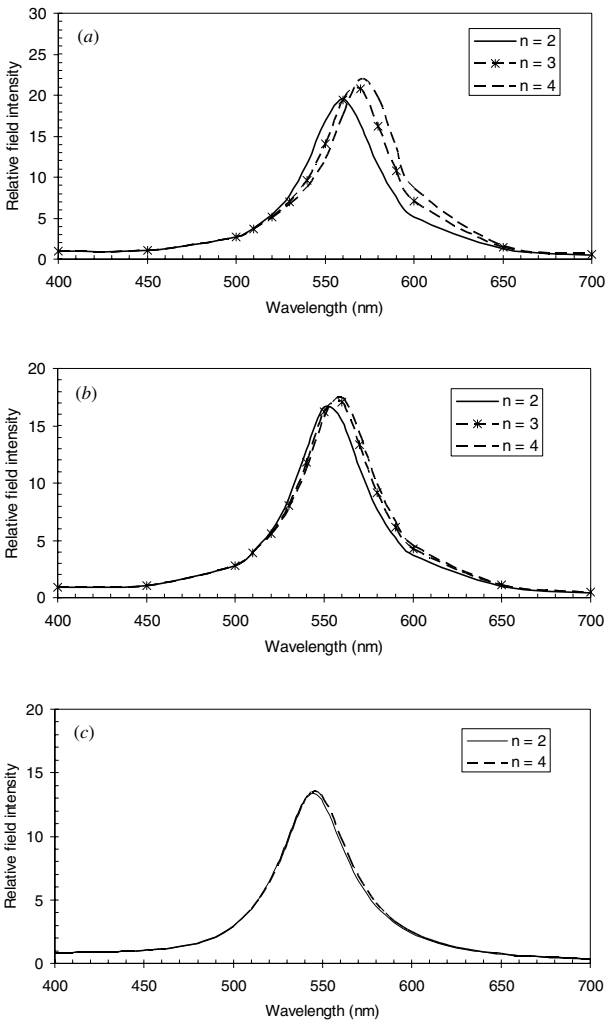

Figure 1. Relative electric field intensity inside two particles (radius $r = 2$ nm) as a function of the applied electric field wavelength for various multipolarity orders, n, and centre-to-centre distances, d: (*a*) 4.3 nm, (*b*) 4.5 nm and (*c*) 5 nm.

2.2. Results for nanocomposite materials

We have applied this method to the case of very weakly scattering spherical particles to calculate the variations of the local electric field inside metallic particles as a function of the incident wavelength. The physical system under study is composed of gold nanoparticles embedded in a silica host matrix.

First of all, we have made sure of the convergence of the results, that is their independence of the multipolarity order of the calculation beyond a certain value of n. Figure 1 shows the calculation of the relative electric field intensity, I/I_0, inside two spheres of 2 nm in radius as a function of both their centre-to-centre distance, d, and the multipolarity order. These calculations show that the convergence of the results is ensured as soon as d verifies $d \geqslant \frac{5}{2}r$, where r is the radius of the particles, and that, this condition being verified, exact calculations can be performed with $n = 3$. This will be the case for all the following calculations.

Cases of two interacting spheres with various centre-to-centre distances can be compared with the limit case of isolated

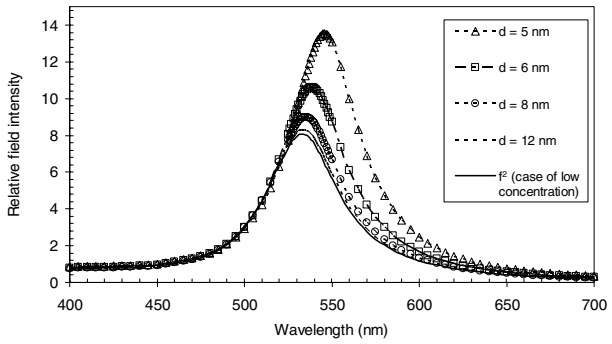

Figure 2. Relative electric field intensity inside two particles ($r = 2$ nm): comparison between isolated spheres and various cases of interacting spheres.

spheres by plotting the variations of the square of the local field factor, given by equation (1) (figure 2): between the two extreme cases, i.e. isolated spheres and interacting spheres with $d = 5$ nm, the intensity of the electric field increases almost twofold and the resonance wavelength undergoes a red-shift of about 20 nm. Besides, figure 2 shows that the field amplification decreases quickly as d increases and that it becomes negligible as soon as $d = 12$ nm.

Large field enhancements can be obtained in composite materials in which each particle is subject to the influence of several others. An ideal case where mutual influences are of importance is that of spheres arranged as a linear chain. Figure 3 illustrates this case for 12 particles ($r = 2$ nm and $d = 5$ nm) aligned in the polarization direction of the incident field; the relative intensity of the electric field inside the particles is the same on both sides of the centre of the chain; it is maximum in the central spheres ($I/I_0 = 30$) at the SPR and minimum at the extremities of the chain, where its value ($I/I_0 = 11$) remains much larger than that predicted by equation (1); a shift of the spectral location of the resonance is observed for all particles and it is a maximum at the centre of the chain. It is to be noticed that the field enhancements are very large for this particular linear arrangement because the spheres are aligned along the incident polarization direction. As a matter of fact, the enhancements are lower if additional interactions between spheres arranged perpendicularly to the incident polarization direction arise. This case is illustrated by calculations performed when a second linear chain is superposed on the previous one according to the direction of the incident wavevector. In this case,

(i) for each chain, the fields are symmetric with respect to the centre of the chain,
(ii) the fields are lower in the 'second' chain than in the 'first' one,
(iii) in the 'first' chain, the fields are lower than in the case of a unique chain.

Figure 4 relates to the case of particles randomly distributed. It is the most representative case of the behaviour of ordinary composite materials. It shows results obtained for ten gold particles filling a volume fraction p of 8%. The local field value inside a sphere depends both on the distance between this sphere and the others and on the direction of the interactions between the spheres. In spite of the random distribution of the particles, the average field remains larger than that obtained in the limit case of the isolated sphere.

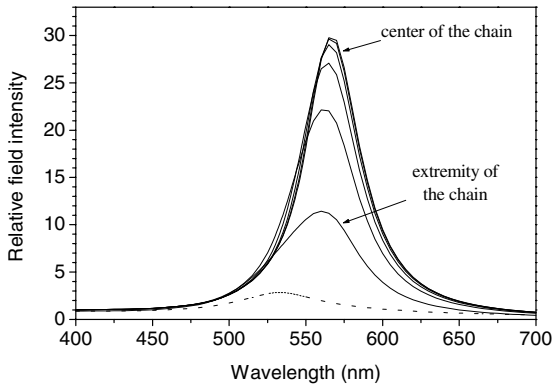

Figure 3. Theoretical variations of the relative electric field intensity as a function of the applied electric field wavelength for a linear chain of 12 particles ($r = 2$ nm). The dashed curve corresponds to the variations of the square of the local field factor in the limit case of isolated particles.

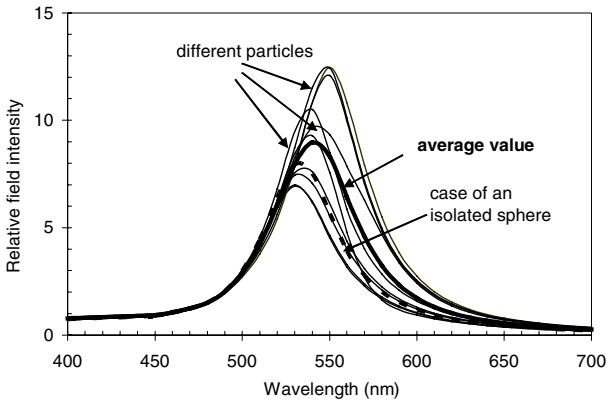

Figure 4. Theoretical variations of the relative electric field intensity as a function of the applied electric field wavelength for ten particles randomly distributed ($r = 2$ nm; metal volume fraction $p = 8\%$).

3. Nonlinear optical measurements

Besides theoretical calculations, experimental studies on the third-order nonlinear optical properties of nanocomposites have been performed in our laboratory [12]. Au:SiO_2 nanocomposites have been synthesized by radio-frequency sputtering [13], the metal concentration varying from 8 to 35%. Several characterization techniques such as TEM and grazing-incidence small-angle x-ray scattering have shown that the metal particles are spherical and randomly dispersed, the mean particle diameter varying from 2.6 to 4.8 nm as a function of the metal concentration. The third-order nonlinear properties of the films have been determined by the z-scan technique [14] according to an experimental set-up presented in a previous article [12]. This method enables us to measure both the real and the imaginary parts of $\chi^{(3)}$, proportional to the nonlinear refractive index and nonlinear absorption coefficient, respectively. Measurements have been performed at $\lambda = 532$ nm, that is close to the SPR absorption band of the materials.

Figure 5 shows the variations of the imaginary part of $\chi^{(3)}$ as a function of the metal concentration p. Results reveal a very large enhancement of $\mathrm{Im}\,\chi^{(3)}$ with increasing p: a hundredfold increase in $\mathrm{Im}\,\chi^{(3)}$ as p rises from 8 to 35%. It is to be noticed that, with increasing metal concentration,

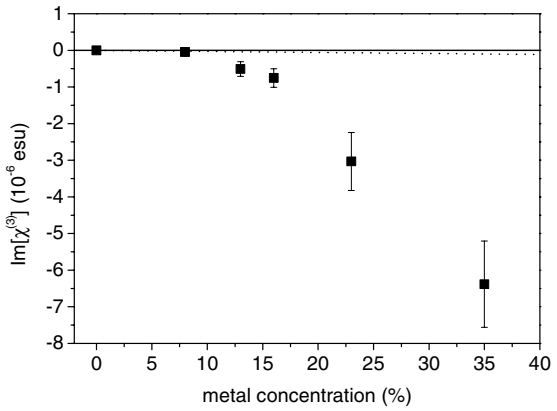

Figure 5. Variations of Im $\chi^{(3)}$ as a function of metal concentration. The dashed line corresponds to the dilute media theory (equations (1) and (3)).

results diverge from the theoretical prediction [3] (dashed line on figure 5) suited for weakly concentrated materials. The corresponding theoretical expression, determined in the quasi-static approximation through a mean-field approach, and usually considered to explain the nonlinearities of composites, is given by

$$\chi^{(3)} = p|f|^2 f^2 \chi_m^{(3)}, \tag{3}$$

where $\chi_m^{(3)}$ is the intrinsic third-order nonlinear susceptibility of gold particles. Its value, measured on a bulk gold film [15], was taken to be equal to $\chi_m^{(3)} = (-1 + 5\mathrm{i}) \times 10^{-8}$ esu. Equation (3) predicts a linear variation of $\chi^{(3)}$ with the metal concentration. Our measurements reveal that Im $\chi^{(3)}$ no longer varies linearly with p as soon as p reaches 5–10%. The discrepancy between the theoretical prediction and the experimental results has to be attributed to the large enhancement of the local electric field. As a matter of fact, we have previously shown that from $p = 8\%$ (figure 4) this enhancement is no longer evaluated by the local field factor defined by equation (1), because this equation, and therefore equation (3), does not take into account the mutual influence between particles. The link between field calculations and experimental results remains qualitative at this date. As a matter of fact, simulations with a large number of particles (at least 50) are necessary to be able to predict values of $\chi^{(3)}$ from field calculations. This work requires much computing time and is in progress.

4. Conclusion

We have applied a recursive transfer matrix method initially developed for calculating the electromagnetic field response for three-dimensional systems of scattering spheres to the study of nanocomposite materials. We have thus studied the variations of the local electric field inside gold particles embedded in a silica matrix as a function of the frequency of the applied EM field for various configurations. These calculations show that mutual interactions between particles are responsible for large local field enhancements as compared with fields inside isolated particles. In the case of particles 2 nm in radius, we have determined that mutual interactions have to be considered as soon as particles are closer than $d = 12$ nm.

For the ideal case of materials composed of linearly arranged particles, we have shown that very large enhancements can be obtained provided that the particles are aligned in the polarization direction of the incident field. In this case, very high intensities are induced inside the particles at the centre of the linear chain and the local field amplification is accompanied by a shift of the spectral location of the resonance.

For the case of randomly distributed particles, we have pointed out that the average field remained larger than that obtained for the limit case of isolated particles, even for a low metal concentration such as $p = 8\%$.

Finally, we have presented experimental results relating to the measurement of the third-order nonlinear susceptibility of Au:SiO_2 nanocomposites by the z-scan technique. These results show that Im $\chi^{(3)}$ values diverge from the theoretical predictions and do not vary linearly with p. This discrepancy, attributed to the large enhancement of the local electric field, proves the qualitative agreement between the local field calculations and the experimental nonlinear measurements.

Work is in progress in order to establish a quantitative relationship between the theoretical calculations and the experimentally determined values of the third-order nonlinear susceptibility.

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