Nonlinear Optical Measurement of Gold Nanoparticles Using the Z-Scan Technique.

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Abstract

Metallic nanoparticles, such as Ag, Cu and Au, show characteristic optical absorption in the visible wavelength region due to the excitation of plasmons (collective oscillation of electrons). The peak position and the bandwidth of the plasmon transition depend on the size and the form of the nanoparticle. When the size decreases, the dielectric constant value is affected and it can be described by the "free path effect", which predicts a strong decreasing of the local field factor. The nonlinearity of the particle is associated with the local field factor, absorbance and the nonlinearity of the composite, using arguments of effective-medium theory. In the present work the nonlinear optical properties of colloidal gold with sub nanometer and nanometer size particles are investigated using the z-scan technique. Negative values of the nonlinear refraction and absorption coefficients are obtained. Different values of the local field factor, calculated at high intensity, originate optical bistability. Comparing our results with other in the literature for different hosts we concluded that the nonlinearity of the sub nanometer colloid is due to the particles and that quantum confinement effect plays an important role increasing the nonlinearity of the particle in two orders of magnitude compared with nanometer particles.

Introduction

Nanoparticle colloidal solution of the noble metals as Ag, Cu and Au show a very intense color, which is absent in bulk materials. The origin of this effect is the collective electron resonances induced by electromagnetic radiation denoted as plasmons.

In order to describe the nonlinear optical properties of the colloid at low concentrations it is used an extension of the Maxwell-Garnet model [1]. In this model the imaginary part of effective dielectric constant $\tilde{\varepsilon}$ of a composite medium in the limit of long-wavelength and neglecting interactions among particles can be used to express the absorption coefficient α as:

$$\alpha = \frac{18\pi p \varepsilon_h^{3/2}}{\lambda} \frac{\varepsilon_m''}{(\varepsilon_m' + 2\varepsilon_h)^2 + \varepsilon_m''^2} \tag{1}$$

where p is the volume fraction, ε_m and ε_h are the dielectric constant of the metallic particle and the host respectively, $\varepsilon_m = \varepsilon_m' + i\varepsilon_m''$ and λ is the light wavelength.

Applying a strong electric field E_0 in the composite we can obtain an expression for the electric field inside the particle, that in the electrostatic approximation is:

$$E = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} E_0 \quad . \tag{2}$$

Assuming that variations in the dielectric constant are due only to the metallic particles, we have

$$\delta\tilde{\varepsilon} = f^2 p \delta\varepsilon_m \tag{3}$$

where the local field factor is defined as

$$f = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \tag{4}$$

This variation can be associated to the nonlinearity of the composite $(\chi^{(3)})$ and the particle $(\chi_m^{(3)})$, resulting in:

$$\chi^{(3)} = p f^2 |f|^2 \chi_m^{(3)} \quad . \tag{5}$$

This nonlinearity depends strongly of the local field factor or the dielectric constant directly.

The variation of the dielectric constant of the particle at high intensity can be written as:

$$\delta\varepsilon_m = \frac{3\chi^{(3)} I}{2\varepsilon_0 c n_0 p f^2}. \tag{6}$$

Solving *f* including (6) we obtain two different solutions which correspond to an "optical bistability" [2].
When the size of the nanoparticle is decreased, the dielectric constant is affected by the collisions of the conduction electrons with the particle surfaces (the Free Path Effect - FPA). In this way, is possible to show that $\varepsilon'_m = \varepsilon_{1,bulk}$

$$\varepsilon''_m(\omega, R) = \varepsilon_{2,bulk}(\omega) + A\frac{\omega_p^2}{\omega^3}\left(\frac{\upsilon_F}{R}\right) \tag{7}$$

where ω_p is the plasma frequency , υ_F is the Fermi velocity, ω is the light frequency, R is the particle radius and A is a phenomenological factor that includes other kind of interactions such as electron-electron, electron-phonon and electron-defects.
In the gold case, ω_p = 1.37 x 10^{16} s^{-1}, υ_F = 1.4 x 10^6 $m.s^{-1}$. For colloidal gold *A* = 0.7 [3]. If the bulk values of the dielectric function are taken from [4], then from the equation (7) we obtain

$$\varepsilon''_m = 2.4 + 0.7\frac{5.88}{R} \tag{8}$$

$$\varepsilon'_m = -4.7$$

with *R* in nm.
This dependence of the dielectric constant with *R* implies a dependence of the nonlinear susceptibility with the particle size. Nevertheless, measured values of the dielectric constant of the particle in different hosts [5,6] show that it is constant in the nanometric scale. On the other side, the dependence of the local field factor with *R* is strong in the subnanometric scale which and change the dielectric constant of the particle.
Thus, knowing $\chi^{(3)}$ and *α,* we can calculate *p*, *f* and $\chi_m^{(3)}$ from (3), (6) and (7).

Experimental Setup

Two different samples were used in the present study. The subnanometer colloid with gold particles in water obtained from a commercial source [7], has diameters of 0.65 nm in diameter. Each particle consists of 9 gold atoms. Colloidal gold with nanometer size was prepared using the technique introduced in [8]. Measurements of DLS (Dynamic Light Scattering) determined a diameter of 20 nm for the particles.
Determination of the nonlinear properties of the colloids was made using the z-scan technique [9]. This technique uses the self-focusing property of the material to determine the nonlinear coefficients of refraction and absorption, monitoring the transmittance with close and open aperture, respectively, as is illustrated in the figure 1. The light source used was a Q-switched, mode-locked Nd:YAG laser using a KTP crystal for measurements in 532nm with pulses of 80 ps duration. Single pulses at a repetition rate of 6 Hz were selected using a pulse-extraction system.
Optical absorption spectra was measured with a diode array spectrophotometer from 250 to 700 nm using a spectrophotometer cell of 5 mm path length.

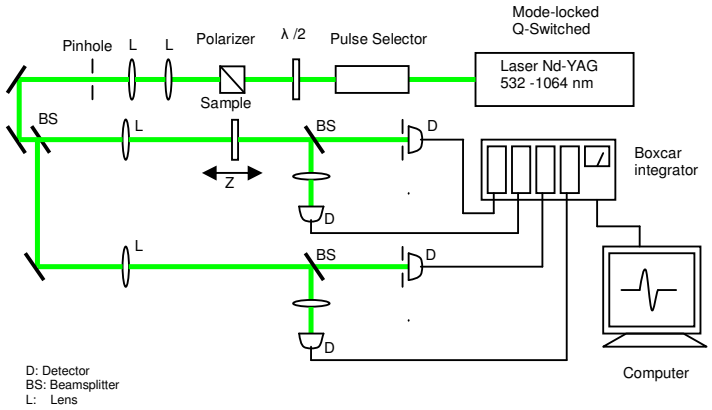

Figure 1: Experimental setup

Results and Discussions

The linear absorption spectra for nanometer and subnanometer samples are shown in figure 2. The z-scan data are shown in fig. 3. By fitting the z-scan equation for ΔT to both set of data the nonlinear refraction and nonlinear absorption coefficients are obtained. The results are given in the tables 1 and 2. A typical result of the z-scan measurement at 1.85 GW/cm^2 for the subnanometer colloid is illustrated in the figure 2. The band centered at ~516 nm is due to the surface plasmon resonance in large particles. The broad feature centered at ~350 nm is attributed to small particles [10].

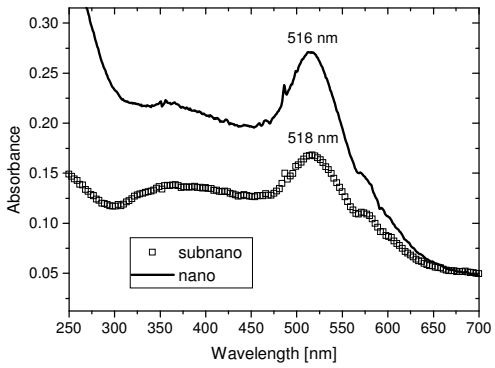

Figure 2: Linear absorption spectrum

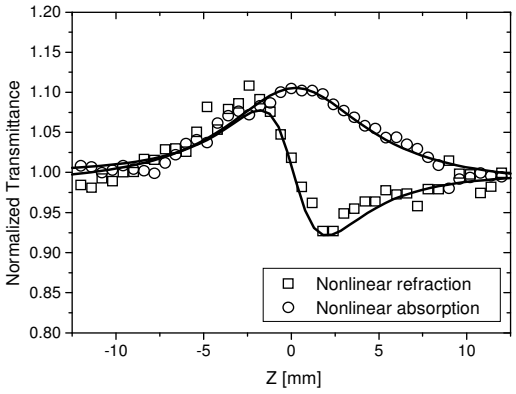

Figure 3: Results of z-scan

Intensity W/cm^2	γ cm^2 /W	β cm/W	Re[X$^{(3)}$] e.s.u.	Im[X$^{(3)}$] e.s.u.	|X$^{(3)}$| e.s.u.	Re[X$^{(3)}$] S.I.	Im[X$^{(3)}$] S.I.	|X$^{(3)}$| S.I.
1,85E+09	-4,08E-15	-3,29E-10	-1,83E-13	-6,22E-14	1,93E-13	-2,56E-21	-8,71E-22	2,70E-21
1,58E+09	-5,08E-15	-3,85E-10	-2,28E-13	-7,28E-14	2,39E-13	-3,19E-21	-1,02E-21	3,35E-21
1,48E+09	-3,60E-15	-2,74E-10	-1,61E-13	-5,19E-14	1,69E-13	-2,26E-21	-7,26E-22	2,37E-21
1,14E+09	-4,01E-15	-5,32E-10	-1,80E-13	-1,01E-13	2,06E-13	-2,51E-21	-1,41E-21	2,88E-21
8,75E+08	-4,12E-15	-6,95E-10	-1,84E-13	-1,32E-13	2,27E-13	-2,58E-21	-1,84E-21	3,17E-21
5,38E+08	-6,41E-15	-1,13E-09	-2,87E-13	-2,14E-13	3,58E-13	-4,02E-21	-3,00E-21	5,01E-21

Table 1: Nonlinear optical coefficients for subnanometer particles.

Intensity W/cm^2	γ cm^2/W	β cm/W	Re[X$^{(3)}$] e.s.u.	Im[X$^{(3)}$] e.s.u	| X$^{(3)}$| e.s.u.	Re[X$^{(3)}$] S.I.	Im[X$^{(3)}$] S.I.	| X$^{(3)}$| S.I.
1,35E+08	-1,96E-14	-3,29E-09	-8,76E-13	-6,24E-13	1,08E-12	-1,23E-20	-8,73E-21	1,51E-20
3,50E+08	-1,22E-14	-2,21E-09	-5,48E-13	-4,19E-13	6,89E-13	-7,67E-21	-5,86E-21	9,65E-21
4,08E+08	-1,28E-14	-2,83E-09	-5,72E-13	-5,37E-13	7,84E-13	-8,00E-21	-7,51E-21	1,10E-20
5,27E+08	-1,25E-14	-2,22E-09	-5,59E-13	-4,21E-13	7,00E-13	-7,82E-21	-5,89E-21	9,79E-21

Table 2: Nonlinear optical coefficients for nanometer particles.

The results shown in table 1 and table 2 refer to high intensity measurements and are not valid to compare with most literature results obtained at smaller intensities. In order to obtain $\chi^{(3)}$ at low intensity, a saturation model was used to fit our results. The model used was

$$\chi^{(3)} = \frac{\chi_0^{(3)}}{1+\frac{I}{I_{s,o}}} \tag{9}$$

where $\chi_0^{(3)}$ is the nonlinear susceptibility at low intensity and $I_{s,o}$ is the saturation intensity. The Intensity inside a particle is $I_s=|f|^2 I_{s,o}$. The best fit for the subnanometer particles gives $I_{s,o}$= 8.2 x 10^8 W/cm^2, Re[$\chi_0^{(3)}$]=-4.7±0.4 x 10^{-13} e.s.u. and Im[$\chi_0^{(3)}$]= -2.5±0.3 x 10^{-13} e.s.u. The best fit for the nanometer particles gives $I_{s,o}$= 7 x 10^8 W/cm^2, Re[$\chi_0^{(3)}$]=-9.5±0.5 x 10^{-13} e.s.u. and Im[$\chi_0^{(3)}$]= -7.4±0.4 x 10^{-13} e.s.u .

For silver particles with diameter less than 2nm it was shown that the position as well as the width of the surface plasmon absorption band becomes independent of the cluster size [11]. However, for gold particles smaller than 2nm it is expected very large change in the electronic structure [12]. Then we can expect that the dielectric constant doesn't vary below of this size or that the interactions electron-electron, electron-phonon and electron-defects affect the phenomenological factor *A*. As the two situations mentioned are not completely understood, we performed calculus of $\left|\chi_m^{(3)}\right|$ for subnanometer particles using the free path model using equation (8) and equations (1), (4) and (5). The results obtained were $\left|\chi_m^{(3)}\right|$ = 8.4 x 10^{-6} e.s.u and $\left|\chi_m^{(3)}\right|$ = 7.0 x 10^{-7} e.s.u. for *R*=0.325 and *R*=1 nm, respectively. In both cases the nonlinearity of the particle increased in comparison with the results for the nanometer colloid.

For nanometer particles the obtained value was $\left|\chi_m^{(3)}\right|$ = 8.6 x 10^{-8} e.s.u. In order to compare with literature results the figure of merit (FOM) $|\chi^{(3)}_m|/\alpha$ is considered. The present results are plotted in Fig. 4 with results reported by other authors.

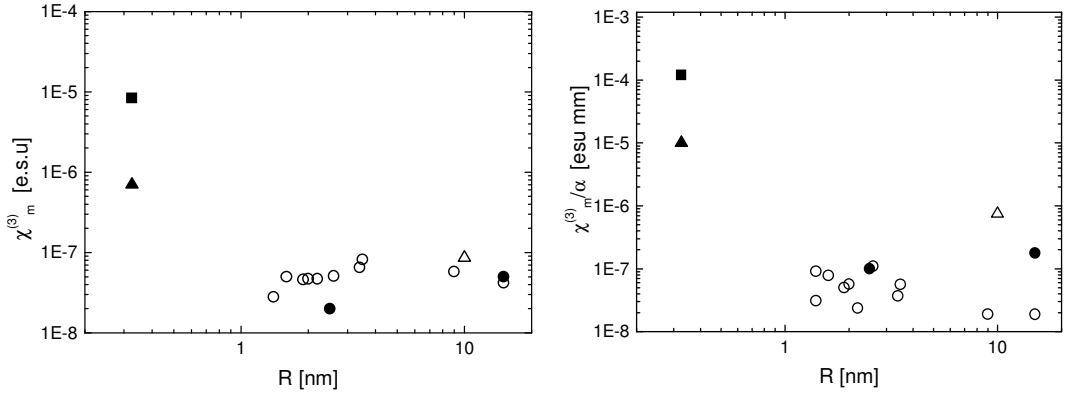

Figure 4: Nonlinearities of the particle in different hosts. Solid circle is the result for particles in water [6]. Open circles for particles in glass [5]. Solids square and triangle are the present work for subnanometer particles using R=0.325nm and R=1nm respectively. Open Triangle is the present work for nanometer particle with R=10nm.

According with our results the FOM of the particle in the subnanometer regime is enhanced by two orders of magnitude due to local field effects.

Acknowledgements

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