Nonlocality in Ag nanocubes: dependence on the concentration and incident wavelength

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Abstract

Colloidal silver nanocubes systems were analyzed by the Z-scan technique. Two systems with edge length of 99 and 215 nm were obtained by the polyol method. Concentrations 0.6, 0.4 and 0.2 mg ml\(^{-1}\) were analyzed for each particle size. Nonlinear excitation was performed with laser pulses of 26 ps, at repetition rate of 10 Hz, using wavelengths of 355, 532 and 1064 nm. The two first one wavelengths are close to surface plasmon resonance while the third one is out of resonance, for both systems. For sample featuring size of 99 nm, nonlinear absorption was observed: saturable for 355 nm and a shift from saturable to reversible for 532 nm for a specific concentration only. For 1064 nm, positive nonlinear optical refraction and saturable absorption could be observed only for sample of 215 nm. Experimental results showed that nonlinear response presents a nonlocal behavior which depends on incident wavelength. The nonlocality was affected by the concentration for 532 nm for size of 99 nm. Z-scan curves were fitted using an analytical expression for on axis far-field transmittance.

1. Introduction

Nowadays, the synthesis and study of metallic nanoparticles are state-of-the-art topics in scientific research and technology due to their potential applications in electronic industry\cite{1}, surface-enhanced Raman scattering\cite{2}, sensing\cite{3}, etc. The optical properties of this kind of systems are governed by the surface plasmon resonance (SPR). Possible applications for these materials arise from their large nonlinear susceptibilities and fast response times. The presence of SPR band enhances the third order susceptibility \(\chi(3)\) of metal nanoparticles. This kind of nonlinearity gives rise to phenomena as self-focusing, solitons generation, among others, which can be exploited for nonlinear optical signal processing, optical limiting, and optical devices\cite{4}. Silver nano-materials have potential to obtain large enhancement factors and large \(\chi(3)\) by including the size and shape of the nanoparticles insomuch as optical response of metal nanoparticles (NPs) can be tuned by controlling these characteristics and their environment. In this sense, there are several synthesis methods of NPs with which are possible to get particles with a strictly defined shape and size, by example spheres, bars, octahedrons, pyramids, cubes, etc\cite{5–8}. Among these morphologies, Ag nanocubes have attracted the attention of several research groups due to the fact that their sharp corners offer the advantage to get a better enhancement of SPR and, therefore, to do feasible their applications\cite{9,10}.

Third order nonlinear optical properties of nanocubes, with edge lengths lower and slightly higher than 100 nm, have been studied through the Z-scan technique in infrared region for femtosecond pulses\cite{11–13}. The results showed saturable (SA) and reversible absorption (RA)\cite{11}, nonlinear refraction\cite{13}, and suggest the
nanocubes as candidates for all-optical switching [12]. However, it is necessary to expand the studies about nonlinear properties for this kind of systems with the aim of finding a suitable material for power limiter or all-optical switching. In this sense, the inclusion of the nonlocal character of the nonlinear response makes more complete the characterization of nonlinear materials. The problem of the nonlocality in thin non-linear media that present nonlinear absorption and refraction had been studied in [14, 15]. In these works the authors propose a numerical model for describing the nonlocality in the nonlinear response. Based on these works, in [16] it was obtained an analytical expression for the transmittance after a thin media using the Gaussian decomposition (GD) method. This expression includes refraction and absorption nonlinear contributions.

In this work, colloidal Ag nanocubes systems with edge lengths of 99 and 215 nm synthetized by the polyl method were studied by the Z-scan technique in open (OA) and close aperture (CA) configurations. Concentrations of 0.6, 0.4, and 0.2 mg ml$^{-1}$ for each sample were studied. Nd:YAG laser of 26 ps and repetition rate of 10 Hz was used as light source; all samples were studied for several irradiances at incident wavelengths 355, 532, and 1064 nm. The samples exhibited SA, RA, and nonlinear refraction depending on their size, incident wavelength, and Ag concentration. Experimental results were fitted using the analytical expression showed in [16], which includes the nonlocality of the nonlinear response.

2. Experimental section

2.1. Synthesis and linear properties of Ag nanocubes

The Ag nanocubes studied in this work were synthesized through the polyl method, but with a small modification reported elsewhere [8–10]. In a typical synthesis, ethylene glycol (35 ml, EG, Sigma-Aldrich 324558) was added into a 250 ml round bottom flask and heated under magnetic stirring (400 rpm), for 1 h, in an oil bath preset to 140 °C–145 °C in air. After this step, an HCl solution (411 µl, 24.35 mM, HCl, Sigma-Aldrich 320331, in EG) was added into the heated solution. 5 min later, a PVP solution was added (10 ml, 0.225 M in terms of the monomeric unit, PVP, molecular weight, 55000, 856568–100 G in EG). After another 10 min, AgNO$_3$ (15 ml, 0.1 M, Aldrich 209139 in EG) was added into the mixture. This mixture was then allowed to react for periods of 32 and 38 h in order to obtain nanocubes of different sizes. The samples were then washed, first with acetone and then with ethanol-acetone mix (1:9) and water several times to remove most of the EG and PVP by centrifugation. A set of two colloidal Ag nanocubes samples with edge sizes of 99 and 215 nm were obtained, which were labeled as S1 and S2 respectively.

The concentration of the samples was estimated through the weight by difference technique. In this case, some volume of each sample was drying at 75 °C for ∼15 h, which evaporated the solvent (water). Then, there were found the initial Ag concentrations of 0.837 and 0.552 mg ml$^{-1}$, for S1 and S2, respectively. After this process, the nanocubes were re-suspended in water preparing samples with Ag concentrations of 0.6, 0.4 and 0.2 mg ml$^{-1}$, for each particle size. Morphology of the samples was studied by means of field emission scanning electron microscope (SEM) (JEOL JSM-7200F at voltage of 10 kV. Figure 1 shows SEM images at different scales for S1, figures 1(a) and (b) show the effect of the drying and re-suspended process in S1. A similar effect was observed in sample S2, too.

The edge lengths were obtained from statistical analysis of, at least, 150 particles, obtaining approximate lengths of 99 and 215 nm for S1 and S2, respectively.

Several studies have shown that the main optical features of metallic nanostructures depend on geometry and size. For example [17] shows the optical response for spherical, cubic, and other geometrical shapes. In particular, for cubic geometry, R. Fuch found nine resonances, but only six of them had significant strength [18].

The spectra for S1 and S2 are shown in figure 2, a peak structure for both samples can be observed; the number of SPRs is related to the cubic shape and size of particle. In this sense, the vertices, playing an important role in the optical response due the sharpness of them, increase the number of resonances [19].
It is possible to see that SPRs for S1 are broader and better defined than SPRs for S2. Figure 2(a) and 2(b) show spectra corresponding to concentrations 0.6, 0.4 and 0.2 mg ml\(^{-1}\) for S1 and S2, respectively, it is possible to observe a decreasing in the extinction related to concentration.

The main characteristics of the samples are summarized in table 1. Linear optical absorption measurements were performed with a Cary 5000, using the equation, 
\[
a = \text{absorbance} L \log_{10}
\]
with L being the sample thickness, linear absorption coefficients, \(\alpha\), were calculated from the obtained experimental data.

### 2.2. Z-scan setup

The Z-scan was developed to measure the magnitude and sign of nonlinear refraction [20]. Two conventional configurations are possible for this technique; one of them measures the transmittance of a sample through a partially obscuring circular aperture (CA). The resulting beam distortion is measured and used to extract the value of nonlinear refractive index \(\gamma\). One other configuration is used to obtain the nonlinear absorption coefficient \(\beta\), in this case, care must be taken that all of the energy is collected by the detector (OA), since Z-scan measurements are very sensitive to nonlinear refractive effects that will spread the transmitted beam.

In this work, Z-scan technique was implemented using as light source a PL2143A laser system by EKSPLA, with emission lines of 355, 532 and 1064 nm and featuring 26 ps pulses with 10 Hz repetition rate. The beam was focused by a lens with a focal length of 400 mm. The waist beam for each wavelength was determined by the knife-edge method [21]. The values obtained were \(\omega_0 \approx 25.31, 35.20\) and 60.24 \(\mu\)m for \(\lambda = 355, 532,\) and 1064 nm, respectively, and \(Z_0 = 0.550, 0.732,\) and 1.071 cm being theirs corresponding Rayleigh lengths. Since a quartz cell of 1 mm thickness was used in the experiments, the thin medium condition is fulfilled.

The transmitted beams for CA and OA for Z-scan technique were measured simultaneously according to the figure 3, with Thorlabs DET 10 A fast photodiodes, D2 and D3. An aperture of 25 mm of diameter was used for the CA measurements.

### Table 1. Nanocubes characteristic parameters.

| Sample edge length (nm) | Concentration (mg ml\(^{-1}\)) | Volume fraction \((1 \times 10^{-5})a\) | Wavelength (nm) | Linear absorption coefficient \(\alpha\) (cm\(^{-1}\)) |
|------------------------|-------------------------------|---------------------------------|----------------|---------------------------------|
| S1 (99.54 ± 25.23)     | 0.6                           | 5.7                             | 355, 532, 1064 | 5.36, 9.04, 4.19                 |
|                        | 0.4                           | 3.8                             |                | 4.09, 7.48, 3.15                 |
|                        | 0.2                           | 1.9                             |                | 1.86, 2.92, 1.88                 |
| S2 (215.60 ± 13.55)    | 0.6                           | 5.7                             |                | 2.76, 3.82, 3.82                 |
|                        | 0.4                           | 3.8                             |                | 2.55, 3.49, 3.47                 |
|                        | 0.2                           | 1.9                             |                | 1.19, 1.70, 1.71                 |

\(^a\) Density of silver 10.49 g cm\(^{-3}\).
3. Numerical methods

The characteristic CA and OA Z-scan curves are usually modeled by Sheik-Bahae et al expressions [20]; these expressions consider like-Kerr media. However, the nonlinear optical (NLO) response depends also on the material and the kind of illumination, so that this could exhibit a nonlocal character.

Several researchs about nonlocality in the nonlinear response have been performed based on numerical model. In [15], equation (1) describes the field for a Gaussian beam in the output plane of the nonlinear thin sample after the beam crosses it.

\[
E_{\text{out}} = E(r, z) e^{-\frac{r^2}{a^2}} \left[ 1 + q_m \left( -\frac{\Delta \Phi_0}{2} \right) \right]
\]

with \( q_m = \Delta \Psi_0 G_{\text{loc}}^{m/2} \) and \( G_{\text{loc}} = \frac{e^{-\gamma l_\text{eff}}}{1 + \frac{2}{\gamma l_\text{eff}}} \), where \( \Delta \Phi_0 = \frac{k I_0 L_\text{eff}}{D_0} \) is the phase shift induced by the sample, and \( \Delta \Psi_0 = \beta_0 k, L_\text{eff} = \frac{1 - e^{-\alpha l}}{\alpha} \), and \( L \) the sample thickness.

In [15], the nonlocality is included in the photoinduced phase shift profile by the parameter \( m \), which is a positive number and modify the width of the phase shift profile with respect to the width of the incident intensity profile; when the widths are equals, the NLO response is local (\( m = 2 \)); otherwise, the response will be nonlocal (\( m \neq 2 \)). In this manner, \( G_{\text{loc}} \), in equation (1) corresponds to incident intensity profile in the local case. Our group has used the model described above in previous researchs getting a good agreement with experimental results. In this sense, in reference [16] was obtained the analytical expression given by equation (2), starting from equation (1).

\[
T(z, \Delta \Phi_0) = 1 - \frac{2m \Delta \Phi_0 x + \Delta \Psi_0 (x^2 + (m + 1))}{(1 + x^2)^{m/2} (x^2 + (m + 1)^2)}
\]

The analytical expression for on axis far-field transmittance (equation (2)) was obtained using the Gaussian decomposition (GD) method, which consists in decomposing the output electric field (equation (1)), into a series of Gaussian beams with decreasing waist dimensions through a Taylor series of the photoinduced phase shift.

4. Results

4.1. Wavelengths 355 and 532 nm

From Z-scan data was possible to observe the presence of SA for S1 at \( \lambda = 355 \) nm, and SA and RA at \( \lambda = 532 \) nm. Figures 4 and 5 show experimental results for \( \lambda = 355 \) nm and \( \lambda = 532 \) nm, respectively. Sample S2 did not exhibit response for these wavelengths. Figures 4(a) and (b) show experimental results for concentrations 0.6, 0.4 and 0.2 mg ml\(^{-1}\), for incident irradiances \( I_0 = 1.5 \) and 2.8 GW cm\(^{-2}\) respectively. Values of \( m \) and \( \beta \) were obtained using equation (2). For all curves \( m = 1.9 \). In this case, the NLO is practically local. See table 2.

The presence of SA is expected in general for wavelengths close to a plasmon resonance. The pumping causes the bleach of the ground-state plasmon absorption band, which results in SA. However when intensity increases, the excited state absorption has a dominant role, so that, this intensity is enough for pumping free carriers in the conduction band to higher excited states, which drives to RSA. This can be observed in figure 5(b) for \( \lambda = 532 \) nm, where SA behavior shifted to RSA for concentration 0.4 mg ml\(^{-1}\). This shift had been reported for Ag nanoparticles [22]; it is important to mention that previous results could be observed for irradiances higher than 80 GW cm\(^{-2}\). It is remarkable that, in this work, for this wavelength, the samples were analyzed for irradiances as low as \( I_0 = 1.6, 3.2 \) and 4.7 GW cm\(^{-2}\).
Figure 5 shows experimental curves for 0.6 mg ml$^{-1}$. Opposite to the lower concentration, 0.6 mg ml$^{-1}$ exhibited a SA behavior increasing with intensity. SA is attributed to the ground state plasmon bleaching due to intraband electron excitation at moderate input intensities, while RSA at higher input intensities is attributed to various processes like, transient absorption from free carriers, two photon absorption, nonlinear scattering etc.

For $\lambda = 532$ nm, the value of $m$ was 2.6 for 0.6 mg/ml for all intensities studied, while for 0.4 mg ml$^{-1}$ the nonlocal response suffered a narrowing.

It is important to mention that since nanocubes are suspended in deionized water, NLO of deionized water was studied before performing the experiments. A negligible response was observed, in agreement with Chatzikyriakos et al [23] for deionized water, and Aloukos et al [24] for distilled water. In these works, they report nonlinear refraction at 532 nm for irradiances higher than 66 GW cm$^{-2}$, while for 1064 nm nonlinear refraction.

### Table 2. Coefficients $\beta$ for sample S1.

| $\lambda = 355$ nm | 0.6 mg ml$^{-1}$ | 0.4 mg ml$^{-1}$ |
|-------------------|------------------|------------------|
| $I_0$ GW cm$^{-2}$ | $\beta (1 \times 10^{-9})$ cm/W | $\beta (1 \times 10^{-9})$ cm/W |
| 1.58              | $-0.68$          | 1.9              |
| 2.80              | $-0.90$          | 1.9              |
| $\lambda = 532$ nm|                  |                  |
| 1.6               | $-0.05$          | 2.6              |
| 3.2               | $-0.10$          | 2.6              |
| 4.7               | $-0.33$          | 2.6              |

Figure 5(a) shows experimental curves for 0.6 mg ml$^{-1}$. Opposite to the lower concentration, 0.6 mg ml$^{-1}$ exhibited a SA behavior increasing with intensity.

SA is attributed to the ground state plasmon bleaching due to intraband electron excitation at moderate input intensities, while RSA at higher input intensities is attributed to various processes like, transient absorption from free carriers, two photon absorption, nonlinear scattering etc.

For $\lambda = 532$ nm, the value of $m$ was 2.6 for 0.6 mg/ml for all intensities studied, while for 0.4 mg ml$^{-1}$ the nonlocal response suffered a narrowing.

Figure 4. Z-scan curves at $\lambda = 355$ nm for three concentrations, (a) $I_0 = 1.5$ GW cm$^{-2}$, (b) $I_0 = 2.8$ GW cm$^{-2}$.

Figure 5. Z-scan curves at $\lambda = 532$ nm for several irradiances (a) 0.6 mg ml$^{-1}$, (b) 0.4 mg ml$^{-1}$.
refraction and negligible absorption were reported above 80 GW cm$^{-2}$. These results correspond to pulses in the ps regime and a repetition rate between 1–10 Hz.

4.2. Wavelength 1064 nm

For this wavelength, only S2 exhibited a response for concentration 0.6 mg ml$^{-1}$. Positive nonlinear refraction and SA were observed. Since the equation (2) contains the refractive and absorptive contributions, it should reproduce curves containing said contributions simultaneously. For this reason, equation (2) was used to reproduce experimental results for OA and CA, but this last one with the absorptive component. Figure 5 shows results for the irradiances $I_0 = 8.64$ and 11.59 GW cm$^{-2}$. Figures 6(a) and (b) correspond to irradiance $I_0 = 8.64$ GW cm$^{-2}$, while figures 6(c) and (d) correspond to $I_0 = 11.59$ GW cm$^{-2}$.

In this case, the value obtained for $m$ was 4.5. The increase in the intensity stimulated the SA.

From the values for $\Delta \Psi_0$ and $\Delta \Phi_0$ obtained from fitting, it is possible to observe the decrease in the nonlinear refraction, figures 6(b) and (d), with the irradiance.

The experimental results showed for this wavelength are very interesting: we can observe that the mechanism which gives origin to the nonlinearity is not thermal. This is because thermal processes are commonly associated with strong nonlocalities ($m < 2$), and in this case the sample exhibit a weak nonlocality ($m > 2$). On the other hand, nonlinearity cannot be associated with plasmonic effects, as can be seen from the spectrum, figure 2(b). The presence of SA is contrary to results shown previously for Ag nanomaterials for wavelengths off-resonant region [25, 26]. One possible reason is related to the two-photon process, which was used to interpret the positive optical nonlinear refractive index in [27]. This shall be investigated as a continuation of this work.

5. Conclusions

We have used an analytical expression to reproduce experimental results obtained by Z-scan technique. This expression reproduces in a good approximation the results obtained. The nonlinear optical response depends on the incident wavelength, irradiance and concentration of nanoparticles. In other hand, nonlocality was effected by the concentration for sample of 99 nm with $\lambda = 532$ nm; this sample showed a local behavior for $\lambda = 355$ nm and nonlocal for $\lambda = 532$ nm, at this wavelength a shift from SA to RSA was observed for 0.4 mg ml$^{-1}$, this concentration could be considered as a possible candidate for optical limiting applications.

SA and RSA were observed in the sample of smallest size. While for the largest size sample, SA and positive nonlinear refraction for wavelength off resonance could be observed.

Sample of 215 nm showed a weak nonlocality for $\lambda = 1064$ nm, which is a behavior not yet reported. It is worth mentioning that the results obtained in this work were obtained for irradiances lower than those previously reported.
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