Nonlinear optical spectroscopy of isotropic and anisotropic metallic nanocomposites

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Abstract. In this work, we studied the nonlinear absorption and refraction of isotropic and anisotropic metallic nanocomposites, which consist of Au and Ag nanoparticles (NPs) embedded in matrices of SiO₂. We performed this study at different wavelengths using the Z-scan technique in the picosecond regime. The wavelengths were selected accordingly to the absorption spectra of the nanocomposites, choosing wavelengths into the inter- and intra-band transitions regions, including the surface plasmon (SP) resonance, as well as in the transparent region. For the anisotropic nanocomposites, the polarization and the incident angle were varied in order to evaluate the different components of the third order susceptibility tensor, \( \chi^{(3)} \). We observed dramatic changes of sign for both, nonlinear refraction and absorption, when passing from Au to Ag and/or varying the wavelength. The results accentuate the importance of the hot-electrons contribution to the nonlinear optical response at this temporal regime, when compared to inter-band and intra-band transitions contributions.

1. Introduction
Plasmonics is nowadays one of the most promising candidates to bring together photonics and nanosciences. Integrated SP nanophotonics is in continuous development mainly due to the advantages of SPs over traditional integrated photonic structures. The subwavelength confinement of light, allowing the control of light-matter interactions at the nanoscale, is one of the most powerful tools available for the development of new devices aimed to further fulfillment of the Moore’s law. On one hand, there is a growing importance in increasing the coupling efficiency at several wavelengths between an external source of light and a thin metal film [1]. On the other hand, the anisotropy of metallic NPs gives place to wavelength- and polarization-dependent optical response, as it has been predicted even for photocatalysis applications [2]. But, in our case, the anisotropy of the nonlinear optical response [3], together with a yet non-totally exploited ion implantation method of fabrication [4], may makes reality, in the short term, nonlinear optical components displaying long-range plasmonic waveguiding [5].
We have reported very recently about the possibility of fabricating integrated systems, consisting of metallic NPs embedded into a dielectric matrix, showing large and anisotropic third order nonlinear optical responses, namely nonlinear refraction and absorption [3]. But we have also discussed the relationship of this response to the electronic transitions of the NPs, namely the inter- and intra-band transitions, as well as the influence of the SP resonance on this optical response [3,6]. However, in that direction, we are still missing the dependence of this response on the wavelength, that is, how every transition shows its influence on this response when the chosen wavelength is close or far to it. In this work, we look for that dependence by performing close- and open-aperture Z-scan measurements at several wavelengths in isotropic and anisotropic metallic nanocomposites produced by ion implantation. We have observed dramatic changes of sign for both, nonlinear refraction and absorption, when passing from Au to Ag and/or varying the wavelength. The results put into evidence the hot-electrons contribution to the nonlinear optical response, when compared to inter-band and intra-band transitions contributions.

2. Experimental

2.1. Synthesis and deformation of metallic nanoparticles
As reported before [4], high-purity silica glass plates were implanted at 0° of incidence and room temperature with 2 MeV Ag$^{+}$ (or Au$^{+}$) ions at a fluence of $3.35 \times 10^{16}$ ions/cm$^2$ for Ag, and of $3.10 \times 10^{16}$ ions/cm$^2$ for Au. The depth of the Ag NPs layer was 0.94 μm with a FWHM of 0.72 μm, while for Au the depth was 0.57 μm and the FWHM was 0.36 μm. After implantation, the samples were thermally annealed for 1 hr in a reducing atmosphere 50%H$_2$+50%N$_2$ at a temperature of 600°C for Ag. In the case of Au, an oxidizing atmosphere (air) was used for 1 hr at 1100°C. The metal implanted distributions and fluences were determined by Rutherford Backscattering Spectrometry (RBS) measurements using a 3 MeV $^4$He$^+$ beam for Ag and 2 MeV $^4$He$^+$ beam for Au. Afterwards, the silica plate was cut into several pieces and each piece was irradiated at room temperature with 8 MeV Si ions at a fluence of $5.0 \times 10^{15}$ ions/cm$^2$ for Ag, and 10 MeV Si ions at a fluence of $1.2 \times 10^{16}$ ions/cm$^2$ for Au. The Si irradiation was performed under an angle off normal of θ=(0.0 or 80.0°±0.5°) for both, Ag and Au. Ion implantation, RBS analysis and Si irradiation were performed using the IFUNAM’s 3 MV Tandem accelerator NEC 9SDH-2 Pelletron facility.

2.2. Optical measurements
Optical absorption measurements were performed with an Ocean Optics Dual Channel S2000 UV-visible spectrophotometer.

The third order nonlinear optical spectroscopy was performed by the Z-scan method at 355, 500, 532, 600 and 750 nm [7]. A picosecond pulsed laser system (PL2143A) and an optical parametric generator (PG 401/SH), both from EKSPLA, were used in the Nonlinear Optics Laboratory at IFUNAM as light sources. These sources were focused with a focal length of 500 mm, where in each case the beam waist was estimated by using the Knife’s edge method. The Rayleigh length was calculated to be around 1 cm for all the wavelengths considered, much larger than the thickness of the nanocomposite. It was verified that the nonlinear optical response from only the SiO$_2$ matrix was negligible when compared to that from the nanocomposite (matrix+NPs layer). The reference and transmitted beams (open- and close-aperture) were measured with Thorlabs DET210 fast photodiodes.

3. Results and discussion
In figures 1-3, we show the linear optical absorption spectra of our nanocomposites. Figure 1 displays the optical absorption from isotropic Au and Ag nanocomposites, while figures 2 and 3 show the optical absorption from anisotropic Au and Ag nanocomposites, where the NPs were deformed at 0° and 80°, respectively. In these figures, it is also shown the wavelength position of the laser beam used for performing the Z-scan measurements in each case.
Before reporting the nonlinear optical responses, it is necessary to put in clear that our materials consistently presented positive and negative nonlinear absorption at the same time. The importance of this is that, when fitting and estimating the nonlinear optical coefficients, if the presence of both types of absorption simultaneously is not considered, the fitting is rather poor. This is illustrated in figures 4 and 5 for the case of Au isotropic nanocomposites, when increasing the incident irradiance. It can be seen how one passes from positive to negative nonlinear absorption when increasing the irradiance, but if one fits considering only one type of absorption, this is bad for both, the nonlinear refraction and absorption, figure 4. Otherwise, if one considers both types of nonlinear absorption, the fitting improves radically in both cases and, for the nonlinear absorption, it shows clearly the presence of the two types for both irradiances; figure 5. Therefore, we considered that fact when calculating the nonlinear absorption and refraction from the experimental data throughout the measurements.
In the first case, the fitting was made accordingly to the normal procedure [7], where nonlinear coefficients are directly related to the distance between peak and valley, once the nonlinear absorption has taken into account by dividing the curves obtained for closed- and open-aperture configurations. While in the second case, the fitting was made following [8], where the superposition of third-order nonlinear absorption types is given by the following relationship

\[
\frac{dI}{dz} = -\left[ \frac{\alpha_0}{1 + I/I_s} + \beta I \right] I_m,
\]

where \( \alpha_0 \) is the linear absorption coefficient at the proper wavelength, \( \beta = \beta_0 \sqrt{1 + (I/I_s)^2} \) is the two-photon absorption coefficient, \( \beta_0 \) is the two-photon absorption coefficient at low intensity and \( I_s \) and \( I_m \) are the saturation intensity for the saturation absorption and two-photon absorption processes, respectively.

\[\text{Figure 4. a) Closed- and b) open-aperture Z-scan transmittance measurements for isotropic Au nanocomposite, for 1.0 (black) and 6.7 (green) } \times 10^{15} \text{ W/m}^2, \text{ considering only one type of nonlinear absorption when fitting.}\]

\[\text{Figure 5. a) Closed- and b) open-aperture Z-scan transmittance measurements for isotropic Au nanocomposite, for 1.0 (black) and 6.7 (green) } \times 10^{15} \text{ W/m}^2, \text{ considering both types of nonlinear absorption when fitting.}\]

In figure 6, it is shown the nonlinear refraction and absorption, respectively, for the isotropic Au nanocomposites. There is a clear evidence of the presence of both types of nonlinear absorption into the open-aperture measurements for all the wavelengths studied. For the case of 532 nm, it is worth mentioning that for a higher irradiance, it was observed saturable absorption (negative nonlinear absorption), as it can be seen in figure 5. Therefore, we can say that the only case presenting a dominating positive nonlinear absorption was for 750 nm, that is, far from resonance. For the nonlinear refraction, a negative value was observed only for 355 nm, while for the rest of the wavelengths it was positive.
For the isotropic Ag nanocomposites, the situation is different. Concerning the nonlinear refraction, at 500 nm, and also at 532 nm but at small irradiance, this is negative, becoming positive at 532 nm for higher irradiances, as seen in figure 7, being also positive for the other wavelengths. For the nonlinear absorption, it is positive for 355 and 532 nm, while it is negative for 500 and 600 nm; in the case of 750 nm, it is clearly visible the superposition of both types, although it looks like that the positive value dominates over the negative.

Regarding the nonlinear spectroscopy of the anisotropic nanocomposites, the measurements were performed only at 355 and 532 nm. Let us first examine the case of deformation at 0° for both, Au and Ag. Figures 8 and 9 show the nonlinear optical measurements for these cases. The first thing to remark for both cases is the independence of the measurements on the incident polarization, confirming the isotropy of the deformed NP into its transversal section. In the case of Au, for the nonlinear refraction, there is a clear change of sign when passing from 355 to 532 nm. The first wavelength is located into the inter-band transition region, while the second is clearly located into the plasmon resonance. For the nonlinear absorption, at 355 nm the negative value dominates over the positive; however, at 532 nm, their values are very close, almost neutralizing each other.

In the case of Ag, the nonlinear refraction is positive at both wavelengths, however, the nonlinearity is larger at 355 nm. On the other hand, for the nonlinear absorption, the positive value dominates at 355 nm, opposite to what happens for Au; while, at 532 nm, again, there is a counterbalancing response, as for Au.
Figure 8. a) Closed- and b) open-aperture Z-scan transmittance measurements for anisotropic Au nanocomposite, deformation at 0°.

Figure 9. a) Closed- and b) open-aperture Z-scan transmittance measurements for anisotropic Ag nanocomposite, deformation at 0°.

For the deformation at 80°, figures 10 and 11 show the nonlinear optical measurements for the Au and Ag anisotropic nanocomposites, respectively. For the irradiances used, there is not a clear change when exploring the different components of the third-order nonlinear tensor as in [3]. In the case of Au, there is not a change of sign for the nonlinear absorption at 532 nm when passing from the NP major axis tensor component (polarization at 0°) to the minor axis tensor component (polarization at 90°), although the response is slightly larger for the major axis tensor component. Also, at this wavelength, the response is clearly negative, while for 355 nm, although the negative sign still dominates, there is a clear contribution from the positive one. Looking at the nonlinear refraction, at both wavelengths, the response is positive but it is larger for 532 nm. Now, there is not a change of sign as it happened for the deformation at 0°.

In the case of Ag, for the nonlinear refraction, it can be observed the same behaviour as for deformation at 0°: it is still positive, but is larger at 355 nm than at 532 nm; however, this is an opposite performance when compared to Au deformed at 80°. For the nonlinear absorption, the response is different with respect to deformation at 0°, now, at 355 nm, the response is positive, but smaller than the one obtained in the previous case: deformation at 0°, and there is a clear positive response superposed to the negative one, although this last dominates the combined response. The negative response also dominates, but now clearly, at 532 nm, in opposition to what happened for deformation at 0°, when both responses counterbalanced to each other. As in Au, in Ag the response associated with the major axis of the deformed NPs is larger than the one associated with the minor axis.

Concerning a quantitative analysis of these results, the order of magnitude of $\chi^{(3)}$ is quite independent of the wavelength used for the measurements, for both Au and Ag nanocomposites. However, in the case of Au, this order of magnitude is around $10^{-10}$ esu, while for Ag it is around $10^{-11}$ esu. It is worth remarking that the real part of $\chi^{(3)}$ contributes the most, with an order of magnitude of around $10^{-10}$-$10^{-9}$ esu for Au, and of around $10^{-11}$-$10^{-10}$ esu for Ag. Regarding the imaginary part, for
Au, the order of magnitude is around $10^{-12}$-10$^{-11}$ esu, while for Ag it is around $10^{-13}$-10$^{-12}$ esu. Nevertheless, it is necessary to remember that the real and imaginary parts change of sign as it has been showed all along this work.

![Figure 10](image.png)

**Figure 10.** a) Closed- and b) open-aperture Z-scan transmittance measurements for anisotropic Au nanocomposite, deformation at 80°.

![Figure 11](image.png)

**Figure 11.** a) Closed- and b) open-aperture Z-scan transmittance measurements for anisotropic Ag nanocomposite, deformation at 80°.

All these results need a deeper analysis considering the different electronic transitions, inter- and intra-band ones, but also the influence of the hot-electrons contribution, which may have a different sign [6]. However, in this work we are only presenting the experimental results, leaving for a larger manuscript such a complete analysis.

4. Conclusions

We have studied the nonlinear absorption and refraction of isotropic and anisotropic, Au and Ag, nanocomposites at 355, 500, 532, 600 and 750 nm by using the Z-scan method in the picosecond regime. These wavelengths explored the inter- and intra-band transitions regions, including the SP resonance, as well as the transparent region. We have presented results showing changes of sign when passing from Au to Ag, and also when varying the wavelength. These results shall be more deeply analyzed taking into the account the contribution from each type of transition, but also the contribution, maybe different in sign, from the hot-electrons.

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