Ablation and optical third-order nonlinearities in Ag nanoparticles

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Abstract: The optical damage associated with high intensity laser excitation of silver nanoparticles (NPs) was studied. In order to investigate the mechanisms of optical nonlinearity of a nanocomposite and their relation with its ablation threshold, a high-purity silica sample implanted with Ag ions was exposed to different nanosecond and picosecond laser irradiations. The magnitude and sign of picosecond refractive and absorptive nonlinearities were measured near and far from the surface plasmon resonance (SPR) of the Ag NPs with a self-diffraction technique. Saturable optical absorption and electronic polarization related to self-focusing were identified. Linear absorption is the main process involved in nanosecond laser ablation, but nonlinearities are important for ultrashort picosecond pulses when the absorptive process becomes significantly dependent on the irradiance. We estimated that near the resonance, picosecond intraband transitions allow an expanded distribution of energy among the NPs, in comparison to the energy distribution resulting in a case of far from resonance, when the most important absorption takes place in silica. We measured important differences in the ablation threshold and we estimated that high selectiveness of the SPR of Ag NPs as well as their corresponding optical nonlinearities can be strongly significant for laser-induced controlled explosions, with potential applications for biomedical photothermal processes.

Keywords: nonlinear optics, laser irradiation, metallic nanoparticles, Kerr effect, nonlinear optical absorption

Introduction

It has been noted that the physical features of formation and interaction of metallic nanoparticles (NPs) are quite specific at different wavelengths of irradiation.1 The optical response of NPs differs drastically from conventional materials2 and, particularly, they exhibit important changes strongly influenced by surface plasmon resonance (SPR) excitations.3–5 Their powerful and fast optical nonlinear response make them attractive for applications in some areas like photonics6 or plasmonics,7 but it seems that they are extraordinarily valuable for biomedical functions such as controlled drug delivery,8 genomics research,9 targeting,10 diagnosis,11 and therapeutic applications.12 Because of their distinctive optical properties and biocompatibility, Au NPs have proven to be powerful tools in various nanomedicinal and nanomedical applications.13 Nevertheless, recent advances in the use of NPs in medicine include research on Ag NPs mainly due to their interesting sensitivity given by SPR properties14,15 because excitations of the SPR could produce scattering and absorption that are easily controlled by tuning the structural orientation of the NPs.16,17 The SPR excitation of metallic NPs is an extremely useful property for in vivo imaging techniques such as photoacoustics18
and 2-photon luminescence imaging;\(^\text{19}\) besides, metallic NPs are capable of transforming the optical irradiation into heat on an ultrashort time scale, thereby inducing photothermal ablation.\(^\text{20,21}\) Nonetheless, sharp selective laser ablation for surgery and targeting has not been obtained, and therefore other alternatives which involve different media and mechanisms of optical absorption need to be developed. In this direction, several efforts have been conducted to study the energy absorption mechanisms in metallic NPs,\(^\text{22,23}\) but an in-depth description of the mechanism of nonlinear optical absorption in metallic NPs is still under investigation.\(^\text{24}\) Similarly, enhancement of the nonlinear response of an optical media with metallic NPs can be obtained by the stimulation of different mechanisms of absorptive nonlinearities.\(^\text{25,26}\) However, gigantic advances related to the enhancement of optical nonlinearities can also result from the modification of their distribution and density.\(^\text{27}\) It appears that the third-order susceptibility of metallic nanocomposites has a maximum at specific concentration of the metal, and it has been suggested that their thermal and structural properties are related to their dynamic behavior.\(^\text{28}\) More significantly, a combination of different metallic NPs, like Cu with Ag in the same media, exhibits a stronger nonlinear response in comparison to the response of only 1 kind of metallic NPs.\(^\text{29}\)

The physical mechanisms of optical absorption related to NPs are dependent on the environment, wavelength, peak irradiance, and duration of the irradiation light pulse. For instance, sapphire doped by Ag NPs presents self-focusing properties,\(^\text{30}\) whereas it is interesting to observe that Ag NPs ablated in water present thermal-induced self-defocusing in the case of picosecond pulses with high pulse repetition rate, as well as in the case of nanosecond pulses. In the case of low repetition rate, self-focusing and saturable absorption of picosecond and femtosecond irradiation have been obtained.\(^\text{31}\) On the other hand, for the nanosecond regime, self-defocusing and saturable absorption have been observed when the incident light excites different SPR modes along different directions of the Ag nanorod composite.\(^\text{32}\) Reverse saturable absorption has been reported for Ag NPs precipitated in glasses, which is being related to intraband transitions.\(^\text{33}\) Nonlinear optical absorption mechanisms in silver nanosol have been associated with the excitation fluence.\(^\text{34}\) Moreover, it has been noted that metal clusters excited near the SPR can evolve from saturable absorption to induced absorption when varying the cluster size and the applied laser fluence.\(^\text{35}\) In addition, it has been reported that it is possible to change the mechanism of nonlinear optical absorption in silver nanodots with the incident irradiance.\(^\text{36}\) For example, Ag NPs show saturable absorption with moderately energetic pulses at 532 nm but exhibit strong optical limiting at higher irradiances; this latter behavior has been explained in terms of the induced optical nonlinearity and nonlinear scattering.\(^\text{37}\) In order to clarify how is the contribution of the optical nonlinearities to the ablation threshold of Ag NPs irradiated with different wavelengths and pulse durations, in this work we present results for the nonlinearities of absorption and index of refraction in a high-purity silica sample implanted with Ag ions. We used a multiwave mixing experiment with self-diffraction in the picosecond regime in order to measure the nonlinear optical response near and far from the SPR band of the Ag NPs. Additionally, we determined the ablation threshold with single pulses for different nanosecond and picosecond lasers.

Materials and methods

For the preparation of the NPs, a high-purity silica glass plate (16 × 16 × 1 mm\(^3\)) with OH content less than 1 ppm and impurity content less than 20 ppm, with no individual impurity content greater than 1 ppm, was implanted at room temperature with 2 MeV Ag\(^\text{\text{38}}\) ions, at a fluence around 2.8 × 10\(^\text{16}\) ions/cm\(^2\). After implantation, the sample was cut into identical small pieces (35 mm\(^2\)) and thermally annealed in a reducing atmosphere for 1 hour at 600°C.\(^\text{38}\) The metal distribution and fluences were determined by Rutherford backscattering spectrometry (RBS) measurements using an He\(^\text{+}\) beam in the 2–4 MeV energy range. Ion implantation and RBS analysis were performed at the 3-MV tandem accelerator NEC 9SDH-2 Pelletron at the Instituto de Física, UNAM, Mexico.

In order to identify the physical mechanism of nonlinearity of index and absorption in the sample, we measured the self-diffracted irradiances generated by a multiwave mixing experiment.\(^\text{39,40}\) Figure 1 shows the scheme of our experimental setup. We used a λ/2 phase retarder to rotate the polarization of one of the beams. Self-diffracted and transmitted optical signals were measured for 2 different wavelengths, 532 and 355 nm, which were obtained by alternating the second and third harmonic from a Nd:YAG laser with pulse duration of 26 ps. In both cases, the pulse energy was 0.1 mJ with linear polarization. The intensity rate ratio \(I_1/I_2\) was 1:1, and the radius of the beam waist at the focus in the sample was measured to be 0.15 mm.

For the experiment of optical ablation, we used an excimer laser with pulses of 40 ns at 248 nm, a Nd:YAG
laser with pulses of 13 ns at 266 nm, a Nd:YAG laser with pulses of 7 ns at 532 nm, and a Nd:YAG laser with pulses of 26 ps at 355 and 532 nm. In all cases, the pulses had linear polarization. In Figure 2, we show the scheme of our experimental setup.

**Results**

Figure 3 shows the experimental and numerical results for the self-diffraction efficiency, $\eta$, which represents the rate between the self-diffracted irradiance and the transmitted irradiance obtained for the sample; $\phi$ represents the angle...
between the planes of polarization of the incident beams. We obtained the nonlinear optical coefficients for the samples according to the equations described by Torres-Torres et al:41

\[
E_{1\pm}(z) = \left[ E_{1z0}^0 J_0 \left( \Psi_{1\pm}^0 \right) + i E_{2z0}^0 - i E_{3z0}^0 \right] J_1 \left( \Psi_{1\pm}^0 \right) - E_{4z0}^0 J_2 \left( \Psi_{1\pm}^0 \right) \exp \left( -i \Psi_{1\pm}^0 - \frac{\alpha(I) z}{2} \right),
\]

\[
E_{2\pm}(z) = \left[ E_{1z0}^0 J_0 \left( \Psi_{2\pm}^0 \right) + i E_{2z0}^0 - i E_{3z0}^0 \right] J_1 \left( \Psi_{2\pm}^0 \right) - E_{4z0}^0 J_2 \left( \Psi_{2\pm}^0 \right) \exp \left( -i \Psi_{2\pm}^0 - \frac{\alpha(I) z}{2} \right),
\]

\[
E_{3\pm}(z) = \left[ E_{3z0}^0 J_0 \left( \Psi_{3\pm}^0 \right) + i E_{4z0}^0 - i E_{2z0}^0 \right] J_1 \left( \Psi_{3\pm}^0 \right) - i E_{4z0}^0 J_2 \left( \Psi_{3\pm}^0 \right) \exp \left( -i \Psi_{3\pm}^0 - \frac{\alpha(I) z}{2} \right),
\]

\[
E_{4\pm}(z) = \left[ E_{4z0}^0 J_0 \left( \Psi_{4\pm}^0 \right) - i E_{2z0}^0 - i E_{1z0}^0 \right] J_1 \left( \Psi_{4\pm}^0 \right) + i E_{4z0}^0 J_2 \left( \Psi_{4\pm}^0 \right) \exp \left( -i \Psi_{4\pm}^0 - \frac{\alpha(I) z}{2} \right),
\]

where \( E_{1\pm}(z) \) and \( E_{3\pm}(z) \) are the complex amplitudes of the circular components of the transmitted waves beams; \( E_{4\pm}(z) \) and \( E_{4\pm}(z) \) are the amplitudes of the self-diffracted waves; \( E_{1z0}^0 \), \( E_{2z0}^0 \), \( E_{3z0}^0 \), and \( E_{4z0}^0 \) are the amplitudes of the incident and self-diffracted waves at the surface of the sample; \( \alpha(I) \) is the irradiance-dependent absorption coefficient, where \( \alpha_0 \) and \( \beta \) are the linear and nonlinear absorption coefficients, respectively; \( I \) is the total irradiance of the incident beams; \( J_m(\Psi_{1\pm}^0) \) stands for the Bessel function of order \( m \); \( z \) is the thickness of the nonlinear media; and the following equations (5) and (6) are the phase increments.

\[
\Psi_{1\pm}^{(0)} = \frac{4 \pi^2 z}{n_0 \lambda} \left[ A + \frac{n_0 \beta}{2 \pi} \sum_{j=1}^{4} |E_{j\pm}|^2 \right]
\]

\[
\frac{4 \pi^2 z}{n_0 \lambda} \left[ A + \frac{n_0 \beta}{2 \pi} \sum_{j=1}^{4} |E_{j\pm}|^2 \right] + \left[ A + B + \frac{n_0 \beta}{2 \pi} \sum_{j=1}^{4} |E_{j\pm}|^2 \right],
\]

\[
\Psi_{1\pm}^{(1)} = \frac{4 \pi^2 z}{n_0 \lambda} \left[ A + \frac{n_0 \beta}{2 \pi} \sum_{j=1}^{4} |E_{j\pm}|^2 \right] + \left[ A + B + \frac{n_0 \beta}{2 \pi} \sum_{j=1}^{4} |E_{j\pm}|^2 \right],
\]

Figure 3 Self-diffraction efficiency at 355 nm and at 532 nm.
Here, $A = 6\chi^{(3)}_{1122} = 3\chi^{(3)}_{1122} + 3\chi^{(3)}_{1212}$, and $B = 6\chi^{(3)}_{1122}$, which are the independent components of the third-order susceptibility tensor $\chi^{(3)}$ for an isotropic material. The optical wavelength is represented by $\lambda$ and the refractive index is $n$. 

Table 1 shows the nonlinear optical coefficients obtained for the sample according to the equations (1–6). The best fit for the sign and magnitude of the nonlinear parameters in our numerical simulations indicates that a saturable absorption and a self-focusing effect were exhibited by the sample for both wavelengths 355 and 532 nm. The nonzero self-diffraction signal for orthogonal polarizations of the incident beams allows us to identify an electronic polarization responsible for the nonlinear refraction; besides, the maximum value obtained for parallel polarizations of the incident beams at 355 nm allows us to observe that an additional contribution, such as a thermal process or an excited-state population, could also be added to the nonlinearity of index. The resulting parameters have an error bar of approximately ±10%.

Concerning the ablation measurements, Figure 4 shows the experimental results for the linear absorption spectra associated with the sample after it had been exposed to the different irradiation studies. One can clearly observe the changes in the SPR band related to the Ag NPs in the silica sample.

Table 2 shows the ablation threshold obtained for the sample, and it is related to the spectra shown in Figure 4. These magnitudes have an error bar of approximately ±20%.

**Discussion**

From our results shown in Table 1, we can say that saturable absorption was the dominant nonlinear optical effect exhibited by the sample at these wavelengths in the picosecond regime. Near to resonance, a stronger nonlinear response was found, and even when a significant nonlinear refraction was present, the largest magnitude for $n_2$ was exhibited far from resonance. Since $n_2$ is stronger for 532 nm, higher self-diffraction efficiency is found in this case in comparison with the 355 nm experiment. Although in the latter case, the total nonlinearity is stronger, the nonlinear refraction produced by the interaction of the incident waves in the sample is mainly responsible for the modulation of the grating of index from which the self-diffraction effect is generated. Classically, in a nonlinear media, a decrement in its linear absorption leads to a decrement in the nonlinearity of absorption, but an increment in the nonlinear refractive index. Meanwhile, the nonlinear optical response and their mechanisms exhibited for a specific wavelength can also be modified by changing the size and distribution of NPs.

Previous analytical and experimental results on nanosecond laser ablation suggest that the linear absorption in metallic nanostructures is the main process involved. It has been shown that the ablation threshold is closely related to the temperature and the thermal stress reached within the sample. The maximum temperature depends on the energy absorption of the NPs, the fluence, and pulse duration. In consequence, for nanosecond pulses, the ablation threshold decreases with the linear absorption and with the pulse duration. The behavior of the ablation threshold shown in Table 2 is consistent with this scenario, at least qualitatively, for the nanosecond pulses and even for the picosecond pulses at 532 nm. On the other hand, the high ablation threshold measured with 26 ps pulses at 355 nm cannot be understood unless one takes into account the fact that this wavelength is in the region of the SPR, and therefore an induced transparency could be partially associated with a strong saturable absorption. Our calculations (with $\beta = -9.5 \times 10^{-10} \text{m/W}$ and ablation threshold of $3.96 \text{J/cm}^2$ at 26 ps in propagation through the $5 \times 10^{-7} \text{m}$ thickness of the nanocomposite) indicate that reduction in the absorption coefficient should be considered negligible. Nevertheless, a significant additional energy transfer mechanism by intraband transitions associated with the optical nonlinearities could also be present during picosecond irradiation. The results in this work show that when the incident irradiance is high on the samples, strong values of the optical nonlinearities of the NPs are important in the modification of the ablation threshold. This is exactly the case in our experiments when the 355 nm wavelength excites the SPR of the NPs with approximately 100 GW/cm² in the picosecond regime, and in consequence, the ablation threshold becomes astonishingly elevated. Predictable consequences in nanomedicine can take advantage from high intensity excitations of the SPR in order to reach an ultrafast control of optical signals. Collateral damages in the neighborhood of laser irradiation zones can be reduced by using laser systems with ultrashort temporal response. Enhancement of the optical effects in biological media can be obtained by the stimulation of different mechanisms of

| Table 1 Optical nonlinearities exhibited by the sample |
|---------------------------------|
| **Experiment** | $\alpha$ (m⁻¹) | $\beta$ (m/W) | $n_2$ (m²/W) | $|\chi^{(3)}|$ (m²/W) |
|-----------------|----------------|---------------|---------------|-------------------|
| 355 nm, near the resonance | $1.5 \times 10^{-2}$ | $-9.5 \times 10^{-10}$ | $1.6 \times 10^{-17}$ | $4.64 \times 10^{-17}$ |
| 532 nm, far from the resonance | 20 | $-1 \times 10^{-10}$ | $2 \times 10^{-17}$ | $2.97 \times 10^{-17}$ |
absorptive nonlinearities. Nowadays, these physical phenomena are still under investigation.

**Conclusion**

A fascinating modification in energy transfer and high sensitivity measurements can be obtained with the use of the nonlinear optical SPR properties of metallic NPs. We measured the nonlinear absorptive and refractive responses near and far from the SPR for a high-purity silica sample containing Ag NPs. The main mechanisms of nonlinear absorption in the sample are dependent not only on the properties of metallic NPs but also on the influence of the surrounding media, which should be considered in the mechanism of nonlinearity exhibited by the system. Saturable optical absorption and self-focusing were present in the nanocomposite in both cases, near and far from the resonance. Besides, electronic polarization was identified as mainly responsible for the nonlinear refraction. We estimated that in the nanosecond regime, the optical linear absorption plays the main role in the ablation of the sample, but with high intensity ultrashort pulses (picosecond and femtosecond), the nonlinear absorption and refraction can have important and even dominant contributions in the change of the mechanism of ablation and in the ablation threshold for nanostructured media. Given the high sensitivity of the SPR properties of Ag NPs, and their corresponding strong consequences in the ablation threshold, we consider that they can be useful for laser-induced controlled explosions with potential applications for biomedical photothermal processes. An attempt to stress the importance of the optical nonlinearities of metallic NPs in ablation applications is made in this article.

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**Disclosure**

The authors report no conflicts of interest in this work.

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