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Third-order optical nonlinearity studies of bilayer Au/Ag metallic films

M H Mezher, W Y Chong and R Zakaria

Photonic Research Centre, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

E-mail: rozalina@um.edu.my

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Abstract

This paper presents nonlinear optical studies of bilayer metallic films of gold (Au) and silver (Ag) on glass substrate prepared using electron beam evaporation. The preparation of Au and Ag nanoparticles (NPs) on the substrate involved the use of electron beam deposition, then thermal annealing at 600 °C and 270 °C, respectively, to produce a randomly distributed layer of Au and a layer of Ag NPs. Observation of field-effect scanning electron microscope images indicated the size of the NPs. Details of the optical properties related to peak absorption of surface plasmon resonance of the nanoparticle were revealed by use of UV–Vis spectroscopy. The Z-scan technique was used to measure the nonlinear absorption and nonlinear refraction of the fabricated NP layers. The third-order nonlinear refractive index coefficients for Au and Ag are (−9.34 and −1.61) × 10⁻¹¹ cm² W⁻¹ given lower n² in comparison with bilayer (Au and Ag) NPs at −1.24 × 10⁻¹⁰ cm² W⁻¹. The results show bilayer NPs have higher refractive index coefficients thus enhance the nonlinearity effects.

Keywords: nonlinear, silver and gold, nanoparticles

(Some figures may appear in colour only in the online journal)

1. Introduction

Nonlinear optical materials have been extensively explored for many years and have been utilized in various applications. There is increased use of and interest in applying nanomaterials, based on the phenomenon related to the interaction of intense coherent light with matter in the nanoscale regime. Developments in the field of nonlinear optics hold promise for important applications in optical information processing, telecommunications and integrated optics. Nanomaterials with large nonlinear responses can be used as biosensors [1], optical limiters [2] and in photonic devices [3]. Many experimental studies [4] have suggested that the surface of nanoparticles (NPs) plays a crucial role in determining linear and nonlinear optical properties through the study of third-order optical nonlinearities, and has described various nonlinear properties and behavior exhibited by nanomaterials in configurations of different thicknesses, sizes, shapes and distributions related to the material [5]. Metal NPs possess interesting optical properties. For instance, a nanoparticle with noble materials like gold, silver and copper shows a broad absorption spectra in the visible region of the electromagnetic spectrum, where the origin of this absorption band is attributed to the electromagnetic induced collective oscillation of the free conduction electrons occupying states near the Fermi level in the conduction band (surface plasmons). Based on the Z-scan technique, the nonlinearity of periodic Au and Ag nanostructures based films [6], Au NPs colloids [7] and composite films of Au fabricated using various methods [8] have been studied. A prominent spectroscopic feature of noble metal NPs is the so-called surface plasmon resonance, which gives rise to a sharp and intense absorption band in the visible range. Surface plasmon resonance (SPR) arises in metal NPs as a collective oscillation of the surface electrons when subjected to the electric field associated with the incident light. Also, NPs should be smaller than the wavelength of the incident light in order to achieve SPR. The scattering and absorption of light depends on the polarizability of the NPs, which is a function of the size, refractive index, shape, density and surrounding medium, as demonstrated in several theoretical studies [9]. This paper describes an investigation and demonstration regarding the modification of nonlinear optical properties due to the effects of gold silver NPs embedded in materials. A Z-scan technique was utilized in the measurement of these properties and the
nonlinear optical characteristics appeared to be determined to a significant degree by the SPR. Effects associated with embedded NPs can be enhanced via an optimally chosen SPR peak, and this has significant implications for optical applications including light switch, optical limiting and surface-enhanced Raman scattering.

2. Experimental techniques

2.1. Sample preparation

The preparation process involves materials being deposited onto a glass substrate. A smooth, thin layer of Au and Ag NPs material was first spread on to thoroughly cleaned microscope glass substrate via an electron beam evaporation technique (Edward 360). An annealing process that involves exposure of the thin films of gold and silver to a 600 °C and 270 °C environment, respectively, was subsequently performed, and resulted in the formation of randomly distributed structures. Silver was then deposited on the Au layer NPs using electron beam deposition followed by thermal annealing at 270 °C to produce a randomly distributed layer of Ag on top of the Au layer. The peak absorption resonance of the NPs (Au, Ag, and Au and Ag) was identified by means of UV–Vis spectroscopy, and the size range of synthesized particles determined using field-effect scanning electron microscope (FESEM) images. The investigation of the nonlinear optical characteristics of (Au, Ag, and Au and Ag) NPs suspensions was carried out using the Z-scan technique under excitation of the 800 nm femtosecond laser.

2.2. Z-scan technique

The Z-scan technique is a method that takes into consideration the curve measurement of the strength of two-photon absorption (TPA) and the Kerr effect on a material, and typically it is used to measure nonlinear optics parameters for various NPs. Two phenomena that can be revealed by the Z-scan technique are nonlinear absorption (NLA) and refraction (NLR). The NLA coefficient (β) and Kerr effect induced refractive index (n2) change were both measured via the Z-scan technique in this work. TPA can occur when the level of photon energy in an insulator or semi-conductor is at least half the level of the band gap energy. NLR arises when two or more photons are absorbed simultaneously in a single absorption process, with the absorbed power being proportional to the square of the incident laser intensity, and is a NLR process observed as the change in transmittance between the peak and valley in a Z-scan [10]. As a sample moves along the z-axis, which is taken as the propagation direction of the laser beam, it experiences a phase and intensity modulation that can be observed as a transmittance measurement related to the sample position (Z). This technique depends on the occurrence of two effects, and accordingly is classified as either an open or closed aperture. If all the transmitted light is measured, only TPA will affect the Z-scan. In this case, the technique is categorized as an open-aperture Z-scan. If the transmitted light is only partially detected due to the presence of a closed aperture in front of the detector, both NLR and TPA effects can be discerned in what is termed a closed-aperture Z-scan. The TPA and NLR of this nonlinear process are only significant in situations involving high optical intensities. The Z-scan technique is performed using a femtosecond laser (Tsunami) at a wavelength of 800 nm and 82 MHz. Studies on the detection of nonlinear optics from Au and Ag have detailed an optimal laser beam profile that consists of an average power of 28.3 mW, energy of 0.15 nJ, a beam waist of 15.28 μm, with circular symmetry and low irradiance [11]. The Z-scan experimental set-up is shown schematically in figure 1 where samples were moved along the optical axis (z-direction) through the focal plane of the lens with 7.5 mm focal length. In order to measure the pure nonlinear index of refraction, the closed-aperture (S = 4.5) data was divided by the open-aperture (S = 1) parameter to obtain the Z-scan transmission [12]. These ‘divided Z-scan’ curves reveal the effect of the third-order NLR alone, which is expressed by the power series of the nonlinear phase shift at the focus ΔΦ(t) [13]. The nonlinear refractive index, n2, in the expression n(I) = n0 + n2I, was calculated as follows,
where \( n_0 \) is the linear refractive index and \( I \) is the intensity of the incident laser light. The NLA coefficient, \( \beta \), in the expression \( \alpha(I) = \alpha_0 + \beta I \), was obtained from open aperture Z-scan. Where \( \alpha_0 \) is the linear (low intensity) absorption coefficient, and \( \beta \) accounts in a phenomenological way for nonlinear processes such as induced absorption (\( \beta > 0 \)) or induced transparency (saturation of linear absorption, \( \beta < 0 \)) [14].

3. Results and discussion

(Au, Ag, and Au and Ag) NPs were characterized by their absorption in the UV–visible region due to SPR. Figure 2 shows the UV–visible spectra of (Au, Ag, and Au and Ag) NPs, where Au NPs occur at 550 nm, Ag NPs at 440 nm and the Au and Ag nanoparticle layer at 530 nm. In a metal, the conduction band is half-filled and the density of energy levels is so high that an obvious separation in energy levels within the conduction band (intraband transition) is only observed when the NPs is made up of just a few atoms [15]. Ag NPs produce a stronger plasmon resonance than Au because the SPR occurs at energies distinct from any bulk interband transitions. Also, the plasmon resonance of Ag NPs appears at a shorter wavelength than that of the Au NPs. This can provide a broader range of tunability of the plasmon resonance frequency for silver than for gold. The loss in the intensity of absorption of Au compared with Ag can be due to the large reflectivity from the metal surface. The increase in the intensity of the SPR absorption leads to an enhancement of the electric field for a bilayer of Au and Ag as \( 1.24 \times 10^{-10} \) cm² W⁻¹ (table 2) indicating that the local field is enhanced due to close interaction between Au and Ag coating. The intensity of the SPR peak depends on the number of NPs in the suspensions. If the size of NPs increases, their SPR absorption spectrum peak will be
shifted toward the larger wavelength \[16\]. Dissimilarity in absorption peaks is known to manifest as different nonlinear properties exhibited \[17\].

These different absorption peaks are related to the samples having different material. Figure 3 shows a side-by-side comparison of FESEM images for the Au, Ag, and Au and Ag layers of NPs, and figure 4 shows the size distribution of these NPs. Table 1 details the specifications of these NPs. We calculate the linear absorption \(\alpha\) by measuring the output power with a sample as a function of the power without the sample in low powers. The linear absorption in low incident powers is obtained from equation \(1\) \[18\]

\[
\alpha = -\frac{1}{L} \ln \left( \frac{P}{P_0} \right)
\]

In the Z-scan experiment, the sample was moved forward or backward along the direction of the laser beam around the focus \((z = 0)\). By properly monitoring the transmittance change through a small aperture placed at the near and far field position (open and closed aperture) as shown in figures 5 and 6, one is able to determine the amplitude of the phase shift. Experimental results of Z-scan data with an aperture is divided by those without an aperture to obtain pure NLR. The peak followed by a valley-normalized transmittance obtained from the closed aperture curves indicates that the sign of nonlinear refractive indices is negative, i.e. self-defocusing. The value of aperture linear transmission, \(S\), is 4.5 and the nonlinear refractive index \(n_2\) \(\text{cm}^2\text{W}^{-1}\) can be obtained from equations \(2\) and \(3\):

\[
\Delta T_{p-v} = f \Delta \phi^o \quad \text{for} \quad \Delta \phi^o < \pi \quad \text{(2)}
\]

where \(\Delta T_{p-v}\) is the difference between the normalized peak transmittance and valley transmittance, \(f = 0.406(1 - S)^{0.25}\) is an experimental constant and \(\Delta \phi^0\) is the plane distortion. \(\Delta \phi^0\) relates to \(n_2\) through the following expression:

\[
\Delta \phi^o = \frac{2\pi L_{\text{eff}} n_2 I^5}{\lambda} \quad \text{(3)}
\]

where the effective thickness \(L_{\text{eff}}\) of the sample is defined as \[19\]

\[
L_{\text{eff}} = \frac{1 - e^{-\alpha L}}{\alpha} \quad \text{(4)}
\]

Table 1. Specifications of Au, Ag, and Au and Ag NP samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Au deposition duration (s)</th>
<th>Average size of particles (nm)</th>
<th>Standard deviation</th>
<th>Sample thickness (nm)</th>
<th>SPR (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>2.3</td>
<td>24.39</td>
<td>9.3</td>
<td>14.8</td>
<td>540</td>
</tr>
<tr>
<td>Ag</td>
<td>6</td>
<td>33.23</td>
<td>15.95</td>
<td>21.6</td>
<td>420</td>
</tr>
<tr>
<td>Au and Ag</td>
<td>2.5 and 2</td>
<td>47.82</td>
<td>27.40</td>
<td>22.4</td>
<td>530</td>
</tr>
</tbody>
</table>

Table 2. Nonlinear refractive index and NLA coefficient and nonlinear for Au, Ag, and Au and Ag samples subjected to incident laser beam.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(P_1) (mW)</th>
<th>(\lambda) (nm)</th>
<th>(w^0) ((\mu)m)</th>
<th>(I_0) (MW cm(^{-2}))</th>
<th>(\alpha) (cm(^{-1}))</th>
<th>(\Delta \phi^0)</th>
<th>(n_2) (\text{cm}^2\text{W}^{-1})</th>
<th>(\beta) (cm W(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>33</td>
<td>800</td>
<td>15.28</td>
<td>444.628</td>
<td>10.1 (\times) 10(^4)</td>
<td>0.44</td>
<td>(-9.34 \times 10^{-11})</td>
<td>0.000231</td>
</tr>
<tr>
<td>Ag</td>
<td>33</td>
<td>800</td>
<td>15.28</td>
<td>444.628</td>
<td>9.8 (\times) 10(^4)</td>
<td>0.19</td>
<td>(-1.61 \times 10^{-11})</td>
<td>0.000329</td>
</tr>
<tr>
<td>Au and Ag</td>
<td>33</td>
<td>800</td>
<td>15.28</td>
<td>444.628</td>
<td>9.5 (\times) 10(^4)</td>
<td>0.64</td>
<td>(-1.24 \times 10^{-10})</td>
<td>0.000597</td>
</tr>
</tbody>
</table>

Figure 5. Open aperture Z-scan curve for samples Au, Ag, and Au and Ag.

Figure 6. Close aperture Z-scan curve for samples Au, Ag, and Au and Ag.
was determined by performing the open aperture Z-scan from the open aperture Z-scan data, the NLA coefficient is estimated as

$$\beta = \frac{2\sqrt{2}}{I_0 L_{eff}} \Delta T$$

where $\Delta T$ represents the peak value at the open aperture Z-scan curve. The intensity dependent absorption is measurable as a change of transmittance through the sample for a closed aperture Z-scan, although it can be determined more accurately via an open aperture Z-scan. The values of $\beta$ and $n_2$ depend on the light–matter interaction that occurs when a laser of sufficiently high intensity is incident on a sample, and thus the interaction can change the optical properties of the medium. This study provides evidence for the $\beta$ and $n_2$ values of (Au, Ag, and Au and Ag) NPs; which Au NPs had lower $\beta$ and $n_2$ than in the Ag NPs and Au and Ag. Table 2 tabulates the measurement conditions and associated results regarding values of NLA, for which $P_1$ is the input power and the laser intensity at the focus has been calculated.

4. Conclusion

This paper describes an easy way to shift the peak absorption (right and left) of Au and Ag, and how adding very thin layers of Ag on top of Au also shows enhancement effects of the nonlinear optics for this sample. The samples had different peak absorptions, which were related to different materials resonance. The single layer of nanoparticle shows low nonlinear optics rather than the two layers showing high NLA and NLR. As such, the magnitudes of nonlinear optics effects were considered to relate to the interaction between the materials to obtained data where it shows the SPR for Au is 520 nm, Ag 436 nm and tuned to red-shift of 526 nm for the bilayer of Au and Ag. This work has detailed a simple and fast method to determine the nonlinearity of NPs, and the authors anticipate it will act as a reference for further investigations in similar future research.

Acknowledgments

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References