Z-scan studies of the nonlinear optical properties of gold nanoparticles prepared by electron beam deposition

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This paper details the fabrication process for placing single-layer gold (Au) nanoparticles on a planar substrate, and investigation of the resulting optical properties that can be exploited for nonlinear optics applications. Preparation of Au nanoparticles on the substrate involved electron beam deposition and subsequent thermal dewetting. The obtained thin films of Au had a variation in thicknesses related to the controllable deposition time during the electron beam deposition process. These samples were then subjected to thermal annealing at 600 °C to produce a randomly distributed layer of Au nanoparticles. Observation of field-effect scanning electron microscope images indicated the size of Au nanoparticles ranged smallest from ∼13 to ∼48 nm. Details of the optical properties related to peak absorption of localized surface plasmon resonance (LSPR) of the nanoparticle were revealed by use of UV−vis spectroscopy. The Z-scan technique was used to measure the nonlinear effects on the fabricated Au nanoparticle layers where it strongly relates LSPR and nonlinear optical properties.

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1. INTRODUCTION

Nonlinear optics is the branch of optics that describes the behavior of light in nonlinear media, including the propagation of intense light beams in solids, liquids, and gases, and their interaction with matter. This light−matter interaction occurs when an incident laser beam has sufficiently high intensity, and can show hitherto unknown phenomena. The new phenomena possess a shared feature in that their nature bears a relation to the intensity of the incident light; a strong light field changes the optical properties of the medium, principally the refractive index n2 and the absorption coefficient O. The optics of weak light beams, where the field is insufficient to produce an appreciable change in the properties of the medium, is called linear optics. Nonlinear optics has commonalities with the nonlinear theory of oscillations, nonlinear acoustics, and other fields. Many experimental studies [1–3] have suggested that the surface of nanoparticles (NPs) plays a crucial role in determining linear and nonlinear optical properties through studies of third-order optical nonlinearities and reports in recent years have described various nonlinear properties and behavior exhibited by nanoparticles in configurations of different thicknesses, sizes, shapes, and distributions [4–7]. The nanoparticles of prominent materials such as gold nanoparticles (Au) with third-order optical nonlinearities have been investigated extensively for wide applicability. There are several methods for creating nanoparticle distributions of various types, shapes, and substrates, through e-beam lithography [8], thermal evaporation [9], laser ablation [10,11], and sputtering technique [12]. This research paper describes an investigation and demonstration regarding the modification of nonlinear optical properties due to the effects of gold nanoparticles embedded on the soda-lime glass. Based on the Z-scan technique, the nonlinearity of periodic Au nanostructure-based films [12,13] and Au colloids [14] have been studied.

In this paper, a nonlinear study of randomly distributed Au nanoparticles deposited using electron beam evaporation is reported. The Z-scan utilized in this measurement was carried out using a 800 nm femtosecond laser light source and the nonlinear optical characteristics appeared to be determined to a significant degree by the surface plasmon resonance (SPR). Effects associated with embedded nanoparticles 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 [15,16].


2. EXPERIMENTAL TECHNIQUES

A. Sample Preparation

The preparation process involves Au material being deposited onto a soda-lime glass substrate using an e-beam evaporation system (Edward 360) with pressure of 5 x 10^{-5} Torr and current 35 mV. A smooth and thin layer of gold material was first spread on a thoroughly cleaned soda-lime glass substrate via this process. The duration of deposition determined material layer thickness. An annealing process that involved exposure of the thin film of gold to a 600°C heating environment was subsequently performed, and resulted in the formation of randomly distributed nanoparticle structures. Three samples, named as S1, S2 and S3, of dissimilar layer thickness were prepared in the course of research efforts described in this paper. The peak absorption resonance of Au nanoparticles within a sample was identified by means of UV-vis spectroscopy and the size range of synthesized particles determined through field-effect scanning electron microscope (FESEM) images. The investigation of the nonlinear optical characteristics of (Au) nanoparticle suspensions was carried out using the Z-scan technique under excitation of a 800 nm femtosecond laser.

B. 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 Au nanoparticles. 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 research work. TPA can occur when the level of photon energy in an insulator or semiconductor is at least half the level of the bandgap 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 a nonlinear refraction process observed as the change in transmittance between the peak and valley in a Z-scan [17,18]. As a sample moves along the Z-axis, it 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 classed 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 transmitted light is 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 (Spectra-Physics Tsunami) at a wavelength of 800 nm, duration 100 fs, and 80 MHz repetition rate. Studies on the detection of nonlinear optics from Au and Ag have 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, circular symmetry, and low irradiance. The Z-scan experimental setup is shown schematically in Fig. 1 with the samples moved along the optical axis (Z-direction) through the focal plane of the lens with 7.5 mm focal length and polarizer. In order to measure the pure nonlinear index of refraction, an aperture is used to get a closed signal [19]. Behind the aperture, a Thorlabs S154 is placed to measure transmitted power to calculate the closed signal. The closed-aperture (S = 0.245) data was divided by the open-aperture (S = 1) parameter to obtain the Z-scan transmission. These “divided Z-scan” curves reveal the effect of the third-order nonlinear refraction alone, which is expressed by the power series of the nonlinear phase shift at the focus ∆Φ0(τ) [20]. The sample will change position with respect to the focal plane of a field lens, which is set at position Z = 0. The measurement starts far away from the focus (negative Z), where the transmittance is relatively constant. Then the sample is moved toward the focus and then to the positive Z. The nonlinear refractive index, n2 in the expression n(1) = n0 + n2I, was calculated as follows: where n0 is the linear refractive index and I is the intensity of the incident laser light. The nonlinear absorption coefficient, β in the expression α(I) = α0 + βI, was obtained from the open-aperture Z-scan. Where α0 is the linear (low-intensity) absorption coefficient, and β accounts for a phenomenological way for nonlinear processes, such as induced absorption (β > 0) or induced transparency (saturation of linear absorption, β < 0) [20,21].

3. RESULTS AND DISCUSSION

Nonlinear optics characteristics of Au nanoparticles are dominated by the localized surface plasmon resonance (LSPR) effect. The UV-vis absorption spectra (recorded using Perkin Elmer) of Au nanoparticles films are shown in Fig. 2. The localized

Fig. 1. Schematic diagram of the Z-scan experimental technique.

Fig. 2. Spectrum of SPR for layers of Au nanoparticles with different time of exposure.
plasmon resonance for a single Au NP is 510 nm [12]. Since the Au nanoparticles were isotropic in shape, the associated LSPR peaks could be suitably determined from the obtained absorption data. As the spacing of two particles in closed-packed sample S1 with time exposure of 6 s, this narrow gap between NPs concentrates the electromagnetic field and shifts plasmon resonance to 540 nm. The absorption peaks of the Au NPs further redshift to 550 nm for S2 (8 s) and 590 nm for S3 (10 s). Peak absorption of the Au nanoparticles layer was dissimilar among the samples, attributed to absorption of the different particles size diameter and spacing. It is well known that the plasmon band of metal nanoparticles arises from the oscillations of free electrons in the conduction band which occupy energy states near the Fermi level. Mie theory [22] has considered the effects of particle size on the plasmon band. As the theory predicted, here, for sample S3, it has experimentally confirmed that the peak position shifts to the red and the band broadens indicating that the size of the particles increases [23]. Dissimilarity in peak absorption is known to manifest as different nonlinear properties exhibited.

These different peak absorptions, related to the samples having nonidentical averaged sizes of nanoparticles and layer thicknesses, are a result of the dissimilar period of depositions during the sample preparation process. Figure 3 shows a side-by-side comparison of FESEM images for the S1, S2, and S3 layers of Au nanoparticles. Figure 4 depicts size distribution of Au nanoparticles on each sample. Table 1 details the specifications of these nanoparticles.

The nonlinear refractive index $n_2$ can be measured by a Z-scan technique, which can simultaneously measure nonlinear absorption and nonlinear refraction in various media, such as in solids, liquids, and liquid solutions. It is a single-beam technique that furnishes sign and magnitude of refractive index for nonlinearities.

In a typical open aperture of Z-scan, the open-aperture transmission normalized to the linear transmission of the sample is plotted against the sample position measured relative to the beam focus. Nonlinear absorption will be indicated by a smooth valley-shape curve, symmetric about the focal ($Z = 0$) position [23].

In order to obtain useful data using the Z-scan technique, the sample was moved forward or backward along the direction of the femtosecond laser beam and through its focal point. Nonlinear optical effects occurred in the region around the focal point where the laser intensity was very high. Both open- and closed-aperture Z-scans were conducted in order to distinguish the NLA and NLR effects for each nanoparticle layer. In the closed-aperture Z-scan measurement, a peak followed by a valley was observed in the normalized transmittance results, and this trend indicated a negative nonlinear refractive index (also known as self-defocusing). The aperture linear transmission in this case was 0.45.
Table 1. Specifications of Au Nanoparticles within S1, S2, and S3 Samples with Different Layers of Thickness

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au Deposition Duration (Seconds)</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>S1</td>
<td>6</td>
<td>24.39</td>
<td>14.19</td>
<td>7.7</td>
<td>540</td>
</tr>
<tr>
<td>S2</td>
<td>8</td>
<td>33.23</td>
<td>15.14</td>
<td>9.7</td>
<td>550</td>
</tr>
<tr>
<td>S3</td>
<td>10</td>
<td>47.82</td>
<td>27.40</td>
<td>13.4</td>
<td>590</td>
</tr>
</tbody>
</table>

To determine the nonlinear coefficients, we carried out the open- and closed-aperture Z-scan measurement of Au NP films having thickness of 7.7, 9.7, and 13.4 nm (Table 1). An open-aperture transmission of the Au NP films was measured in the far field to obtain their respective nonlinear absorption coefficients. Figure 5 shows decreases of transmittance around the focal point of the scanned samples at different thickness, which indicates the nonlinear absorption in Au NP films [1]. S1 and S2 shows a trend of increment, which differed from S3. S3 shows a shift on peak and distinct absorption, which denotes the presence of reverse saturable absorption character in all the films [24]. The entire open-aperture graphs represented peak and valley, which are asymmetric in trend.

To evaluate the refractive nonlinearity, we focus our scope on the magnitude of the nonlinear refractive index \( n_2 \) of Au NP films. For this purpose, closed-aperture measurements were performed and normalized transmittance is shown in Fig. 6. Au NP films exhibit post focal peak and valley, which is a direct indication of positive \( n_2 \) (positive lens).

The Z-scan measurement using both CW and pulse laser has also been performed at the same average power, which yield almost trivial and flat Z-scan curves for the CW laser. Therefore, the measured transmittance signal in this work stems from a nonlinear effect rather than a thermal effect [12].

Consideration of the gold nanoparticle linear absorption involved a comparison of the linear absorption for samples containing such particles and the substrate without nanoparticles.

For a percentage of power transmitted through the sample containing particles, \( p \), and percentage of power transmitted through the substrate material, \( p^0 \), the equation for linear absorption, \( \alpha \), is calculated as shown in Eq. (1):

\[
\alpha = \frac{-1}{L} \ln \left( \frac{p}{p^0} \right).
\]

Nonlinear refractive index \( n_2 \) can be calculated from the difference between the normalized peak transmittance and valley transmittance, peak to valley \( \Delta T_{(p-v)} \). The empirical relationship between the induced phase distortion, \( \Delta \Phi^0 \), and \( \Delta T_{(p-v)} \) for a third-order nonlinear refractive process in the absence of NLA is also can be determined from the following equation [2],

\[
T_{(p-v)} = 0.0406(1 - j)^{0.25}(\Delta \Phi^0),
\]

in which \( j \) is the transmittance of the aperture in the absence of a sample \( \Delta \Phi^0 \) while \( I_o \) is on the axis of the nonlinear phase shift and irradiance with the sample at focus \( Z = 0 \), respectively. The sign of \( \Delta \Phi^0 \) is determined from the position of the peak and valley relative to the Z-direction.

Where \( \Delta T_{(p-v)} \) can be defined as the difference between the normalized peak and valley transmittances \( (T_p - T_v) \), \( \Delta \Phi^0 \) is the on-axis phase shift at the focus.

The linear transmittance of the aperture is given by

\[
S = 1 - \exp \left( -\frac{2r_a^2}{w_a^2} \delta \right),
\]

where \( r_a \) is the radius of the aperture and \( w_a \) is the beam radius at the aperture.

The sample itself acts as a thin lens with varying focal lengths as it moves through the focal plane [25]. By moving the sample through the focus and by placing an aperture before the detector (a closed-aperture configuration) the value of \( n_2 \) was calculated based on consideration of three elements. The first element was \( I_o \), which depends on the beam waist \( w_a \) [5] of
11.9 μm in this case. The second element was ΔΦ, which can be calculated from the normalized peak and valley transmittances, as detailed in Eq. (1). The third element was I_{eff}, the effective thickness, which can be calculated via the linear absorption in low incident power, as obtained from Eqs. (1)–(3):

\[ I_{eff} = \frac{1 - e^{-\alpha t}}{\alpha}. \]  

(4)

The resulting Eq. (4) is shown as

\[ n_2 = \frac{\Delta \Phi \lambda}{2 \pi I_{eff} I_0}, \]  

(5)

where \( \lambda \) is the incident beam wavelength and \( I_0 \) is the incident beam on the axis of the nonlinear phase shift and irradiance with the sample at focus \( Z = 0 \). The open-aperture transmittance is symmetric in relation to the focal point, \( Z = 0 \), where minimum transmittance occurs.

The coefficient of nonlinear absorption is calculated by Eq. (5),

\[ \beta = \frac{2 \sqrt{2}}{I_{0eff}} \Delta T(Z), \]  

(6)

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 the \( \beta \) and \( n_2 \) values of samples altered in relation to the size and thickness of depositedAu nanoparticles; relatively larger Au nanoparticles in S2 had lower \( \beta \) and \( n_2 \) than in the S1 nanoparticles.

Table 2 tabulates the measurement conditions and associated numbers regarding values of nonlinear absorption, where \( n_2 \) increases with the thickness of the samples from \( n_2 = 1.77 \times 10^{-8} \text{ cm}^2 \text{ W}^{-1} \) to \( n_2 = 2.16 \times 10^{-8} \text{ cm}^2 \text{ W}^{-1} \) for which pl is the input power and the laser intensity at the focus has been calculated.

Comparing the measured nonlinear absorption of the Au NP thin films with reported nonlinear absorption of the Au NPs using the thermally managed Eclipse Z-Scan (TM-EZ scan) [7] (\( n_2 = -5.5 \times 10^{-11} \text{ cm}^2 \text{ W}^{-1} \)), we can see our value is significantly enhanced.

### Table 2. Nonlinear Refractive Index and Nonlinear Absorption Coefficient and Nonlinear for S1, S2, and S3 Samples Subjected to Incident Laser Beam of (\( \lambda = 800 \text{ nm}, \text{ PI} = 12.7 \text{ mW}, \text{ no} = 11.9 \mu m, \) and \( I_0 = 329.35 \text{ MW cm}^{-2} \))

<table>
<thead>
<tr>
<th>Samples</th>
<th>( \alpha ) (cm(^{-1} ))</th>
<th>( \Delta \Phi^* )</th>
<th>( n_2 ) (cm(^2) W(^{-1}))</th>
<th>( \beta ) (cm(^2) W(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2:1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T2:2</td>
<td>1.63 \times 10^5</td>
<td>0.33</td>
<td>1.77 \times 10^{-8}</td>
<td>2.26 \times 10^{-4}</td>
</tr>
<tr>
<td>T2:3</td>
<td>1.57 \times 10^5</td>
<td>0.42</td>
<td>1.82 \times 10^{-8}</td>
<td>2.58 \times 10^{-4}</td>
</tr>
<tr>
<td>T2:4</td>
<td>1.93 \times 10^5</td>
<td>0.66</td>
<td>2.16 \times 10^{-8}</td>
<td>2.62 \times 10^{-4}</td>
</tr>
</tbody>
</table>

### 4. CONCLUSION
In conclusion, various thickness of Au NPs deposited using an e-beam evaporation system is reported and its nonlinear optical property is measured by the Z-scan method with a femtosecond laser. The Au films are composed of randomly distributed Au NPs which induce wide absorption and predominantly contribute to large nonlinear absorption. The samples had different peak absorptions, with redshift for larger size samples showing effect on surface plasmon resonance of Au. Nanoparticle size appeared to affect nonlinear optics properties as well, which indicates that samples with the smallest gold nanoparticles showed lower nonlinear response in comparison to the sample with the largest size nanoparticles. As such, the magnitudes of nonlinear optics effects were considered to relate to sample nanoparticle sizes and layer thicknesses based on the obtained data. This research work has detailed a simple and fast method to determine the nonlinearity of nanoparticles, and the results shows Au NP films could be a promising candidate as a nonlinear optical material.

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### REFERENCES


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