Off-resonant third-order optical nonlinearity of Au nanoparticle array by femtosecond Z-scan measurement

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Abstract

In order to study the linear and nonlinear optical properties of metal particles, the periodic triangular-shaped Au nanoparticle array was fabricated on a quartz substrate using nanosphere lithography and pulsed laser deposition. The morphology of the polystyrene nanosphere mask (D=820 nm) and the Au nanoparticle array were investigated by scanning electron microscopy. The surface plasmon resonance absorption peak was observed at 606 nm, which is in good agreement with the calculated result using discrete dipole approximation method. By performing the Z-scan method with femtosecond laser (800 nm, 50 fs), the optical nonlinearities of Au nanoparticle array were determined. The results show that the Au particles exhibit negative nonlinear absorption and positive nonlinear refractive index with the effective third-order optical nonlinear susceptibility, \( \chi_{\text{eff}}^{(3)} \), can be up to \((8.8\pm1.0)\times10^{-10}\) esu under non-resonant femtosecond laser excitation.

Keywords: Nanosphere Lithography; Au Nanoparticles; Third-order Nonlinearity

1 Introduction

Noble metal nanoparticles such as Au, Ag and Cu have been of particular interest for a long time because of their unique optical properties called surface plasmon resonance (SPR), which is caused by the collective resonance of the conductive electrons in response to incident light and is widely used in applications such as catalysis, biological sensors and molecular rulers [1-3]. Recently, many studies have focused on the nonlinear properties of noble metal nanoparticles due to their

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large nonlinear optical effects and fast response time, which have great potential applications for such as all-optical switching and computing [4-7].

It is well known that the optical nonlinearities of noble metal nanoparticle can be greatly enhanced at the SPR position and strongly dependent on the nanoparticles' size, shape and distribution. However, among most of previous works, the metal particles are comprised of spheres of various sizes or random distributed, which leads to the broad SPR spectrum and the weak optical enhancement. The Nanosphere Lithography (NSL) has been proved to be a powerful tool developed from Natural Lithography by Van Duyne in 1995 [8,9], to fabricate periodic particle array (PPA) with tunable shape, size and height, which makes it possible to quantitatively study the optical properties of nanoparticles.

Recently, several studies on the nonlinear optical properties of metal nanoparticles array have been reported. Both theoretical [10, 11] and experimental studies [12, 13] indicate that anisotropy of the shape and geometric distribution of the metal nanoparticles could enhance greatly the optical nonlinearity, $\chi^{(3)}$. However, up to now, the measurement of the nonlinear optical properties of the Au periodic nanoparticle array excited by ultrafast laser (50fs) at a wavelength of 800nm has seldom been reported.

In this paper, we report a study of the optical nonlinearities of the Au nanoparticle array determined by femtosecond laser. The morphology of the Au nanoparticle array was observed by scanning electron microscopy (SEM). The third-order nonlinear property was measured by Z-scan method, which is a useful tool to measure the nonlinear optical properties such as the nonlinear absorption and refraction [14]. The real and imaginary parts of the third-order nonlinear susceptibility, Re$\chi^{(3)}$ and Im$\chi^{(3)}$, were determined by performing open-aperture (OA) and closed-aperture (CA) Z-Scan measurements, respectively.

## 2 Experiment

In the NSL processing step, the monodisperse polystyrene (PS) nanosphere suspensions were purchased from Duke Scientific Corp., and the diameter of the spheres used in the experiment was $820\pm5$ nm. The details of the NSL are described elsewhere [15]. For the PLD processing step, a KrF (Lambda Physik, 248 nm) laser beam was used as the laser source with the laser energy density focused on the target was about 2 J/cm2 and the laser repetition frequency was 6 Hz. The deposition time was set to be 30 min. After the deposition, the NSL mask was removed by sonicating in ethanol for 2-4 minutes to obtain the Au PPAs. The surface morphology of the NSL mask and the Au PPAs was observed by SEM (FEI QUANTA 200). The SPR spectra were measured by UV-visible absorption spectroscopy (U-3310 UV Solutions) in a wavelength range from 340 nm to 900 nm. The incident light was perpendicular to samples through a small aperture with diameter of 2 mm to measure the absorption properties of small area. In order to compare with the experimental result, the theoretical calculations based on the discrete dipole approximation (DDA) method were also performed.

The third-order nonlinear optical properties of the sample were determined by the Z-scan method. In our experiments, a femtosecond laser system, which consisted of a mode-locked Ti: Sapphie oscillator and a regenerative amplifier (Spitfire, Spectra-Physics, 800 nm, 50 fs, 1 kHz) were used as the light source. The sample was scanned along the optical axis (z-direction) and focused by a
lens with a focal length of 200 mm. When there is no aperture in front of the detector, OA Z-scan curves are obtained and the nonlinear absorption coefficient $\beta$ can be determined, while the nonlinear refractive index, $\gamma$, is determined by CA Z-scan curves using a small aperture. The radius of the beam waist ($\omega_0$) was 33 $\mu$m, which is calculated from the equation, $\omega(z)^2 = \omega_0^2 (1 + z^2/z_0^2)$, where $z_0 = \pi \omega_0^2/\lambda$ is the Rayleigh length. The value of $z_0$ was calculated to be 4.2 mm, much larger than the thickness of either the 0.2 mm-thickness substrate or the sample. The transmitted beam energy through OA or CA is received by silicon diodes (PC20-6, Silicon Sensor GmbH) and double-phase lock-in amplifier (SR830, Stanford Research System).

3 Results and discussion

Figure 1 shows a SEM image (20×15 $\mu$m$^2$) of the polystyrene nanosphere mask. It can be seen that most of the area is occupied by well-packed nanospheres. The inset in Fig. 1 shows details of the mask that the triangular-shaped gaps between nanospheres can only allow the deposited source to go through. Figure 2 shows the SEM image of the Au nanoparticles at a large scale of 25×20 $\mu$m$^2$ and the Au PPAs can be observed clearly. The area of these PPAs can be as large as several hundred square micrometers. The inset in Fig. 2 shows clearly the shape and the size of the Au triangular prism. The size of the nanoparticle can be defined with two parameters: the in-plane perpendicular bisector ‘a’ and the out-of-plane particle height ‘b’. By a simple geometrical calculation, $D = 0.233a$, the value of ‘a’ is calculated to be 190 nm, which is in good agreement with the experimental results showed in the inset in Fig. 2.

FIG. 1. SEM image of large area (20×15 $\mu$m$^2$) of well-packed nanosphere mask with diameter D=820 nm. The inset shows SEM image of the details of the nanosphere mask.

FIG. 2. SEM image of large area (25×20 $\mu$m$^2$) of Au nanoparticle array. The inset shows the cell of triangular Au nanoparticle array.
The linear absorption of the Au PPAs was measured in the wavelength range from 340 nm to 900 nm and the black line shows the absorption spectrum in Fig. 3. It can be seen that the absorption peak due to SPR of Au particle is found to be located at 606 nm. With the Mie theory, when $\epsilon_r(\lambda)+2\epsilon_d=0$ and $\epsilon_i(\lambda)$ is small, the SPR condition occurs. $\epsilon_d$ is the dielectric constant of the medium surrounding the metal nanoparticle, $\epsilon_r(\lambda)$ and $\epsilon_i(\lambda)$ is the real and the imaginary parts of dielectric function of the metal particles. The optical enhancement under laser excitation near the SPR position is much stronger than that in the off-resonant position such as $\lambda=800$ nm. In comparison, the optical properties of Au particles with the same cross section and particle height of 14 nm, 16 nm and 18 nm were calculated using the DDA method [16, 17]. The red line shows absorption spectrum for a single 16nm-height particle. It can be seen that the position of SPR peak is located at 606 nm, which is the same with the experimental results. The green line shows the average DDA results of three Au particles with different height: 14 nm, 16 nm and 18 nm. The deviation of the Au particles shape and height from perfect one leads to the SPR peaks shifting and a broader SPR spectrum. So it is reasonable that the particle height is estimated to be 16±2 nm.

FIG. 3. Absorption spectrum of Au nanoparticle array with SPR peak at 606nm. the red line shows the DDA calculation result of absorption properties for a single Au particle with the same cross section, and a particle height of 16 nm. The green line shows the average DDA results of three Au particles with the same cross section and different height: 14 nm, 16 nm and 18 nm.

Figure 4 shows typical OA and CA Z-scan results for the Au PPAs. The black dots indicate the experimental data and the solid curve represents the theoretical fit. The laser pulse energy at the focal spot, $E_0$, was 100 nJ and the laser intensity at the focal point, $I_0=\frac{E_0}{\pi\omega^2\tau}$, was calculated to be 59.5 GW/cm². Under the repetition rate of 1 kHz, the accumulative thermal effects can be neglected. The transmitted energy at each position was measured 16 times to obtain a reliable average value.

![Absorption Spectrum](image1)

![OA and CA Z-scan Results](image2)
FIG. 4. Z-Scan measurements at $I_0=59.5$ GW/cm$^2$. (a) Open-aperture Z-Scan results of Au nanoparticle array, the solid line indicates the theoretical fit. (b) Closed-aperture Z-Scan result of Au nanoparticle array, the solid line indicates the theoretical fit.

One can see that the curve in Fig. 4 (a) comprises a normalized peak, indicating the presence of saturation of absorption (SA) in the Au PPAs. Under these conditions, as the shape of the Z-scan results for the substrate is flat, the substrates have a very small nonlinear optical effect that can be neglected and the large nonlinear absorption observed here results from the Au PPAs.

Figure 4(b) shows the CA Z-scan data for Au PPAs. In order to obtain nonlinear refraction information, an approximate method was used where the closed-aperture transmittance was divided by the corresponding open-aperture data. It can be seen that the shape of the curve exhibits a positive value for the nonlinear refractive index. From Fig. 4(b), one can find that the distance between the peak and the valley ($\Delta Z_{p,v}$) is about 7.6 mm as compared to $1.71z_0$, which indicates that the observed nonlinear effect is the third-order response. The difference between normalized transmittances at peak and valley $\Delta T_{p,v}$ is 0.04, and $S=0.18$ is the transmittance of the small aperture.

The nonlinear absorption coefficient $\beta$ (m/W) and the nonlinear optical refractive index (m$^2$/W) can be calculated using the method described in details elsewhere$^{14}$. The value of $\beta$ and $\gamma$ of Au PPAs were calculated to be $(-1.3\pm0.1)\times10^{-8}$ m/W and $(1.3\pm0.2)\times10^{-15}$ m$^2$/W, respectively. The real and imaginary parts of the $\chi^{(3)}$ of the Au PPAs can be obtained by the following equations $\text{Re}\chi^{(3)}$ (esu)=$cn_0^2\gamma/120\pi^2$ and $\text{Im}\chi^{(3)}$ (esu)=$cn_0^2\beta/240\pi^2k$, where $k=2\pi/\lambda$ is the wave vector. The values of $\text{Re}\chi(3)$ and $\text{Im}\chi(3)$ were calculated to be $(7.4\pm1.0)\times10^{-10}$ esu and $(-4.7\pm0.4)\times10^{-10}$ esu, respectively. The absolute value of $\chi^{(3)}$ was obtained to be about $(8.8\pm1.0)\times10^{-10}$ esu, indicating the large third-order nonlinear optical properties in Au PPAs using the femtosecond laser excitation.

FIG. 5. (a) Open-aperture Z-Scan results of Au nanoparticle array in different exciting energy. (b) Intensity dependence of the nonlinear absorption coefficient $\beta$ (m/W).

Figure 5 (a) shows the OA Z-scan results for Au PPAs at different excitation energies. With the increasing of the laser intensity at the focal point $I_0=29.5$ GW/cm$^2$, 46.4 GW/cm$^2$, 59.5 GW/cm$^2$, 89.3 GW/cm$^2$ and 178 GW/cm$^2$, the normalized transmittance peak becomes progressively larger and exhibits SA process. The excited intensity induces ground-state plasmon to be bleached that leads to the OA transmittance increasing with the increasing excited intensity. Figure 5(b) shows the laser intensity dependence of the values of $\beta$ that are independent of the laser intensity when the
intensity is relatively low (<60 GW/cm²) and start to decrease when the laser energy is higher. The high (>60 GW/cm²) intensity results in the free carrier absorption dominating the region and the transmittance decreases with the increasing intensity and the reverse saturation of absorption (RSA) process becomes considerable.

In the ultrashort pulse temporal regime (smaller than a few picoseconds), the contribution of the hot electron phenomenon to χ² is expected to be significant [15]. χ² and the corresponding susceptibility response to the local field Eloc, χeff², are related through [18]:

\[ \chi_{eff}^{(2)} = pf^2 |F|^2 \chi_m^{(2)} \]  

where p is the metal volume fraction and f the ratio between the local field Eloc and the applied field E₀.

\[ E_{loc} = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d} E_0 \]  

But, in the case of triangular-shaped nanoparticle arrays, the local-field factor f cannot be calculated using equation (3). However, using the following equation, the value of local-field factor can be estimated:

\[ \alpha = p\frac{\omega}{n_0 c} |F|^2 \varepsilon_m^{-1} \]  

where α₀=8.5×10³ cm⁻¹ is the linear absorption coefficient at the wavelength of 800 nm, ω is the angular frequency of the incident light, c is the velocity of light. For the nanoparticle array in this experiment, p=0.08, which is a very low value of volume fraction of metal nanoparticles. The value of local-field factor |f| is estimated to be 1.6, which is about 11 times larger than that for the spherical particles. So the enhancement observed in Au PPA is probably due to the stronger local field in the triangular-shaped nanoparticles.

For comparison, the nonlinear coefficients of several thin films in the near infrared region under the excitation of femtosecond laser pulses are listed in table 1. It suggests that the Au nanoparticle array exhibits large optical nonlinear coefficients and have great potential applications in nonlinear photonics devices.

<table>
<thead>
<tr>
<th>Films/Particles</th>
<th>λ(nm)</th>
<th>Pulse width</th>
<th>β (m/W)</th>
<th>γ(m²/W)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Au PPA</td>
<td>800</td>
<td>50 fs</td>
<td>-1.3×10⁻⁸</td>
<td>1.3×10⁻¹⁵</td>
<td>This work</td>
</tr>
<tr>
<td>DWNT*</td>
<td>800</td>
<td>50 fs</td>
<td>1.4×10⁻¹⁰</td>
<td>&lt;2.6×10⁻¹⁵</td>
<td>21</td>
</tr>
<tr>
<td>BiFeO3</td>
<td>780</td>
<td>350 fs</td>
<td>1.6×10⁻¹⁰</td>
<td>1.5×10⁻¹⁷</td>
<td>22</td>
</tr>
<tr>
<td>LGF*</td>
<td>800</td>
<td>150 fs</td>
<td>3×10⁻⁸</td>
<td>2×10⁻¹⁷</td>
<td>23</td>
</tr>
<tr>
<td>VO2</td>
<td>800</td>
<td>120 fs</td>
<td>2.7×10⁻⁹</td>
<td>-7.1×10⁻¹⁶</td>
<td>24</td>
</tr>
</tbody>
</table>

TABLE 1. Femtosecond optical nonlinearities of several films/particles in the near infrared
4 Conclusion

In summary, triangular-shaped Au nanoparticle array was fabricated by NSL and the PLD technique. The nonlinear optical properties of the sample were investigated by the Z-scan method at a wavelength of 800 nm with pulse duration of 50 fs. The third-order nonlinear optical susceptibility was determined to be \((8.8 \pm 1.0) \times 10^{-10}\) esu. The large third-order nonlinearity shows that Au nanoparticles array has great potential applications in ultrafast nonlinear photonics devices such as all-optical switching and computing.

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References


