

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Nonlinear Optical Response of Noble Metal Nanoparticles

Yachen Gao and Deigui Kong

Additional information is available at the end of the chapter

Abstract

The special nonlinear optical response of noble metal nanoparticles (MNPs) when exposed to intense laser radiation has induced novel applications in nonlinear spectroscopy, optoelectronics, and optical switchers and limiters. In this chapter, recent results on the nonlinear optical properties of MNPs (including gold, silver, palladium, and platinum) have been discussed. Some specific optical nonlinear properties, such as nonlinear refraction, saturable absorption and reverse saturable absorption, two-photon absorption, and optical limiting, for femtosecond, picosecond, and nanosecond laser pulses, have been covered.

Keywords: metal nanoparticles, nonlinear absorption, nonlinear refraction, saturable absorption, reverse saturable absorption

1. Introduction

When the light is not strong, the optical response of a material usually scales linearly with the amplitude of optical electric field. However, at high optical powers, the optical properties of material will be changed more rapidly and are no longer linearly related to the intensity of the incident light. As result, nonlinear optical effects will occur. Nonlinear optics is the study of how intense light interacts with matter. The goal of nonlinear optics is mainly the investigation of the new phenomena and effects in the interaction process of strong laser and materials, including a deep understanding of the causes and the process regularity and their possible applications in the development of disciplines. Nonlinear optics has a great value and far-reaching scientific significance. In the past two decades, people have made significant progress in nonlinear optical materials. Many optical materials with fast nonlinear response

and large nonlinear properties have been used in various photonic and optoelectronic applications such as optical communication, optical information processing, optical data storage, pulsed laser deposition, and optical limiters.

Among various nonlinear effects, nonlinear absorption and nonlinear refraction attract more attention. Ultrafast nonlinear absorption properties are of importance since the nonlinearities considerably change the propagation of intense light through the medium, which can induce novel applications in optoelectronics, optical switchers, and limiters, as well as in optical computing, optical memories, and nonlinear spectroscopy. In fact, there is also much intrinsic interest in nonlinear refractive phenomena, particularly self-focusing and self-defocusing.

The search for new materials is one of the defining characteristics of modern science and technology. Of course, in nonlinear optics field, it is the case. Seeking and investigating new nonlinear optical materials with large nonlinear optical properties and fast nonlinear response is still one of the important works concerning nonlinear optics studies. Generally, the nonlinear optical materials should exhibit high transmission at normal light, so as not to degrade normal vision while exhibiting low or high transmission at intense light to serve as optical limiting materials for protecting human eyes and sensors or as saturable absorber for mode locking. In addition, nonlinear optical materials must exhibit fast response over a broad wavelength range and a high damage threshold.

The rapid development of nanoscience and nanotechnology has provided a number of new opportunities for nonlinear optics. A growing number of nanomaterials have been shown to possess remarkable nonlinear optical properties; this promotes the design and fabrication of nanoscale optoelectronic and photonic devices. Specially, metal nanoparticles (MNPs) have attracted considerable attention as potential nonlinear optical materials. Among them, gold and silver nanoparticles (NPs) have been paid more attention because they both exhibit a broad surface plasmon resonance (SPR) absorption band in the visible region of the electromagnetic spectrum [1–10].

In the following sections, the technologies used to measure the amplitude of nonlinear absorption and nonlinear refraction of nonlinear optical materials will be introduced. And some investigations concerning nonlinear optical properties of metal nanoparticles will be discussed.

2. Z-scan technique

There are several different methods for determining the nonlinear optical response of material. The most commonly used technology is Z-scan invented by Sheik-Bahae et al. [11, 12]. Z-scan is also one of the simplest experimental methods to be employed. Because Z-scan signal can provide information not only on the magnitude of optical nonlinearity but also on its sign, the use of the Z-scan technique for nonlinear optical measurement is increasing.

The typical Z-scan setup is shown in **Figure 1**, where the lens L is used to focus the laser beam, and the smallest section of the beam crosses at the 0 point of the Z axis. O stands for the test sample placed near the 0 of the Z axis. BS is a splitter, which splits the laser into two beams.

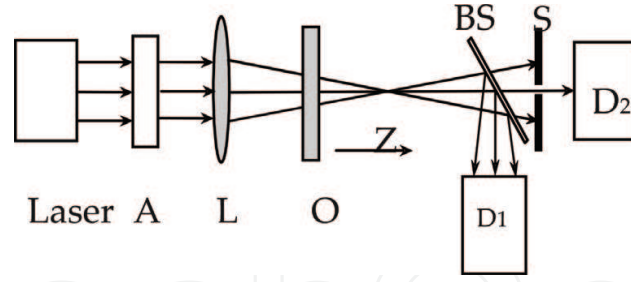


Figure 1. Setup of the Z-scan technique.

S is a small aperture used for the measurement of nonlinear refraction. D1 and D2 are photodetectors. During the test, the object to be tested moves along the Z axis, and the relationship between the light intensity and Z value is recorded.

When there is no aperture before photodetector D₁, Z-scan measurement is called open aperture Z-scan, which can provide the information about the nonlinear absorption. When there is an aperture before photodetector D₂, Z-scan measurement is called closed aperture Z-scan, which can provide the information about the nonlinear refraction of materials.

2.1. Open aperture Z-scan technique

When studying the materials' nonlinear absorption such as saturable absorption (SA) and reverse saturable absorption (RAS), we need to use open aperture Z-scan technique. Normalized open aperture Z-scan data is insensitive to beam distortion and is only a function of nonlinear absorption.

In the case of SA, the nonlinear absorption coefficient may be written as:

$$\alpha(I) = \frac{\alpha_0}{1 + (I/I_s)} \quad (1)$$

where α_0 is the linear absorption coefficient, I is the excitation intensity, and I_s is the saturation intensity. It is assumed that two-photon absorption (TPA) does not take place simultaneously with SA. The transmitted intensity is obtained from the equation:

$$\frac{dI}{dz} = -\alpha I \quad (2)$$

Here, z corresponds to the sample thickness. As shown in **Figure 2**, saturation intensity I_s can be obtained by fitting the experimental curve according to Eqs. (1) and (2). When materials show only RSA or TPA, according to open aperture Z-scan theory, the normalized transmission can be expressed as [12]:

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \approx 1 - \frac{\beta I_0 L_{eff}}{2\sqrt{2}(1 + z^2/z_0^2)} \quad (3)$$

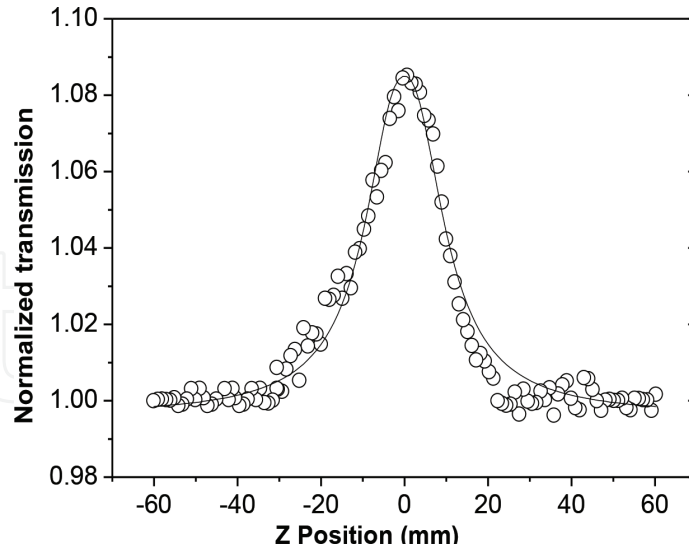


Figure 2. Theoretical and experimental result of the open aperture Z-scan for SA.

where β is the nonlinear absorption coefficient, I_0 is the on-axis peak intensity at the focus, $L_{eff} = (1 - e^{-\alpha_0 L})/\alpha_0$, L_{eff} is the effective interaction length, α_0 is the linear absorption coefficient, z is the longitudinal displacement of the sample from the focus ($z = 0$), L is the sample length, and z_0 is Rayleigh diffraction length. From Eq. (3), nonlinear absorption coefficient β can be obtained to be:

$$\beta = 2\sqrt{2}[1 - T(z = 0)]/I_0 L_{eff} \quad (4)$$

Selectively, as shown in **Figure 3**, β can also be obtained by fitting the experimental curve.

But when materials show transformation from SA to RSA, a nonlinear absorption coefficient including SA coefficient and TPA coefficient should be defined as [13]:

$$\alpha(I) = \frac{\alpha_0}{1 + (I/I_s)} + \beta I \quad (5)$$

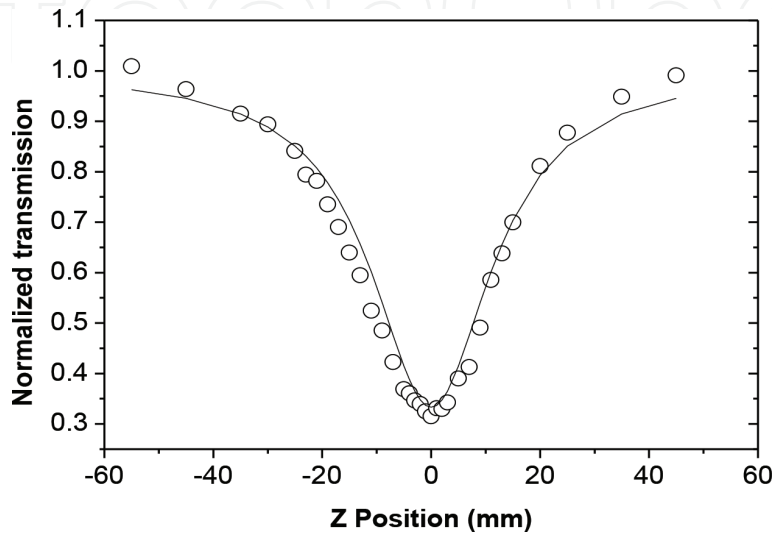


Figure 3. Theoretical and experimental result of the open aperture Z-scan for RSA.

where α_0 is the linear absorption coefficient, I is the laser intensity, I_s is the saturation intensity, and β is the nonlinear absorption coefficient. The transmission of material can be deduced to be:

$$T = 1 - \left(\frac{\alpha_0}{1 + \frac{I_0}{(1 + z^2/z_0^2)I_s}} + \frac{\beta I_0}{1 + z^2/z_0^2} \right) L \quad (6)$$

So normalized transmission can be obtained to be $T_N = T/T_0$. As shown in **Figure 4**, I_s and β can be obtained by fitting experimental data.

2.2. Closed aperture Z-scan technique

When the nonlinear refraction of materials needs to be obtained, closed aperture Z-scan experiments should be conducted. The normalized transmission of closed aperture Z-scan data can be expressed as [11]:

$$T(z) = 1 + \frac{4V\phi_0 x}{(x^2 + 1)(x^2 + 9)} \quad (7)$$

where $\Delta\phi_0 = k\Delta n_0 L_{eff}$, $k = 2\pi/\lambda$ is wave vector, $\Delta n_0 = n_2 I_0$, n_2 is nonlinear refractive index, I_0 is the on-axis peak intensity at the focus, $L_{eff} = (1 - e^{-\alpha_0 L})/\alpha_0$, L_{eff} is the effective interaction length, α_0 is the linear absorption coefficient, z is the longitudinal displacement of the sample from the focus ($z = 0$), L is the sample length, and z_0 is Rayleigh diffraction length.

The difference between normalized peak and valley in closed aperture Z-scan curve is $\Delta T_{p-v} = 0.406 (1 - S)^{0.25} |\Delta\phi_0|$, and S is aperture transmittance. The nonlinear refractive index values can be obtained to be:

$$n_2 = \frac{\alpha_0 \Delta T_{p-v}}{0.406 k I_0 (1 - S)^{0.25} (1 - e^{-\alpha_0 L})} \quad (8)$$

As shown in **Figure 5**, by fitting the experimental data using Eqs. (7) and (8), nonlinear refraction index of samples n_2 can be obtained.

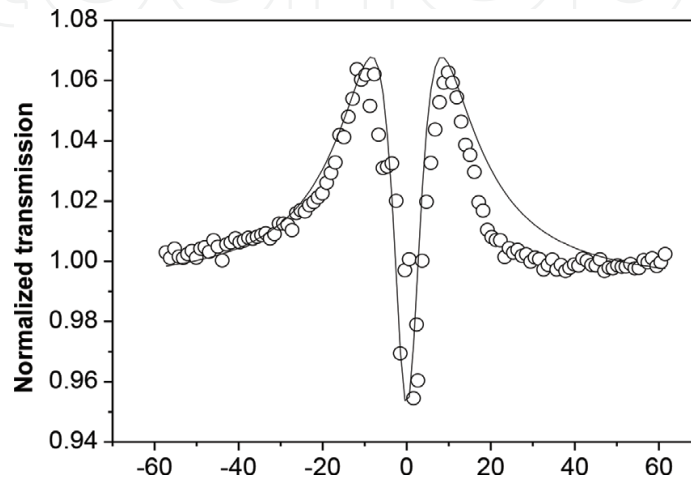


Figure 4. Normalized transmission as a function of position for open aperture Z-scan.

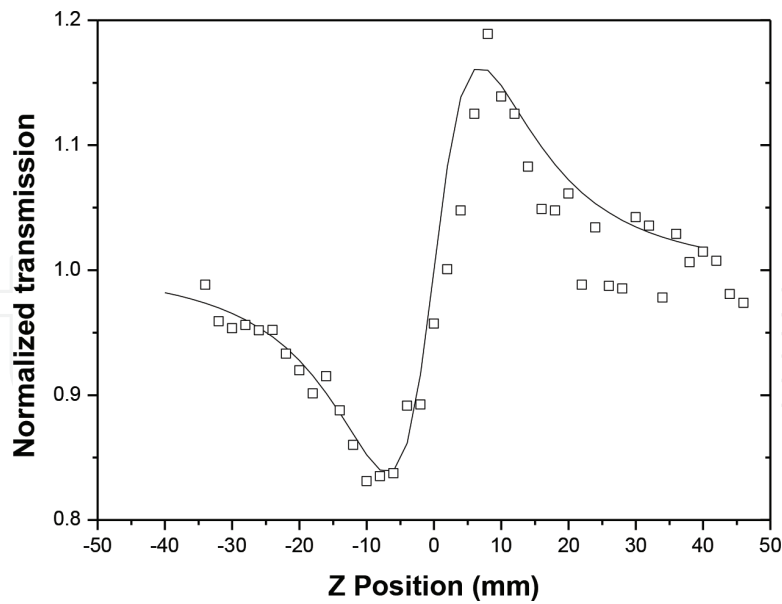


Figure 5. Normalized transmission curves of Z-scan data with an aperture divided by those without an aperture.

3. Nonlinear optical properties of metal nanoparticles

The stability combined with a large third-order susceptibility and ultrafast response means that metal nanoparticles are very promising materials for the creation of photonic devices. SPR is the main characteristics of metal nanoparticles, which strongly depend on the size, shape, and type of metal nanoparticles and the dielectric parameter of surrounding environments [14]. A huge enhancement of the nonlinear optical response in random media with metal nanoparticles is often associated with optical excitation of the SPR. Typical three metals having plasmon band in visible range are Au, Ag, and Cu. In contrast, metals such as Pt, Pd, and Cr show SPR in the wavelengths shorter than 300 nm. Therefore, large transparency and low propagation losses in the visible and infrared range are expected in Pt, Pd, and Cr nanoparticles. In many studies, composite materials with metal nanoparticles were fabricated by various methods and then generally studied using lasers operating at frequencies corresponding to the spectral range of the SPR, as listed in Ref. [15]. The review [15] has summarized the development of nonlinear optical random metal-dielectric composites based on metal nanoparticles synthesized by ion implantation.

Among the nanoparticles of noble metals, Au and Ag nanoparticles have attracted more interest and initiated more theoretical and experimental studies [1, 2, 16–31], as they both show a strong SPR band in the visible region. Moreover, their SPR absorption band can be tuned across the entire visible spectra by changing the size and shape of nanoparticles. The SPR of metal nanoparticles can lead to many interesting optical properties. For example, ultrafast nonlinear optical absorption is important since it can considerably alter the propagation of intense light in the medium, which can make metal nanoparticles be applied in optoelectronics, optical limiters and switches, as well as in optical memories, optical computing, and nonlinear spectroscopy.

3.1. Nonlinear optical studies of Au nanoparticles

The first experimental results on the nonlinear optical effects of Au nanoparticle were obtained by Ricard et al. in 1985 [32]. They prepared the Au nanoparticle with an average diameter of 10 nm and measured the third-order nonlinear susceptibility using phase conjugation to be 1.5×10^{-9} esu at 530 nm. They traced the enhancement to the nonlinearities of the electrons in Au particles.

Among all composite materials, those made out of gold NPs embedded in a dielectric matrix are more important, because of their strong SPR absorption band in the visible region [33]. The coexistence of unique linear and nonlinear (especially third-order) optical properties makes the material be well suited for the potential applications ranging from optical limiter [20, 34], quantum information processing [35, 36], cancer treatment [37–39], on to all-optical switching [33, 40, 41]. In this direction, Au NPs embedded in dielectric media have been widely put more attention for their SPR, which depends strongly on the NPs environment and geometry [42].

Many investigations were performed in Au nanoparticles to study the nonlinear refractive index and nonlinear absorption [2, 16–22]. Moreover, the optical limiting of Au nanoparticles has also been studied widely for protection of human eyes and optical devices from laser damage. The contents studied mainly include the effects of sizes, matrices, and shapes on the nonlinear optical properties in Au nanoparticles [43].

Sánchezdena O et al. studied the size dependence of nonlinear optical response in Au metallic nanoparticles with diameters of 5.1, 13.4, and 14.2 nm synthesized and embedded in sapphire by using ion implantation [43]. Under 532-nm, 26-ps pulses, they found that the Au NPs exhibited a negative nonlinear absorption, which increases with size and size-independent positive nonlinear refraction.

For larger Au nanoparticles than those above, a systematic study of the size-related nonlinear optical properties of triangular Au particles was performed by S.H. Yoon et al. who fabricated the triangular Au nanoparticle arrays with four larger sizes of 37, 70, 140, and 190 nm on SiO₂ substrates using nanosphere lithography [44]. **Figure 6** shows the absorption spectra of the Au nanoparticles of different sizes. It can be seen that the SPR absorption peaks lie at 552, 566, 580, and 606 nm for the 37, 70, 140, and 190 nm Au nanoparticles, respectively. With the increasing particle size, the absorption peak shifts to longer wavelength.

Figure 7 shows the typical OA Z-scan experiment results of the four samples. The curve of the 37-nm sample showed a TPA with an additional SA component. For the samples with size of 70 and 140 nm, TPA component turned weaker and SA became dominant. The curve of the 190-nm sample showed only the SA component. These differences occur because the absorption in the excitation region is much weaker than that at 400 nm for the Au nanoparticles sized 37 nm, and herein, the interband transition to the TPA process plays a key role. However, the absorption at 800 nm is larger than that at 400 nm for the 190-nm Au nanoparticles; this is because the SA process becomes dominant. The curves of the samples of 70 and 140 nm showed a transition in this variation of the two nonlinear mechanism contributions.

Figure 8 shows the CA Z-scan data for four Au nanoparticles of 37, 70, 140, and 190 nm. For the 37 and 70 nm Au nanoparticles, a self-defocusing occurs, and the nonlinear refraction index

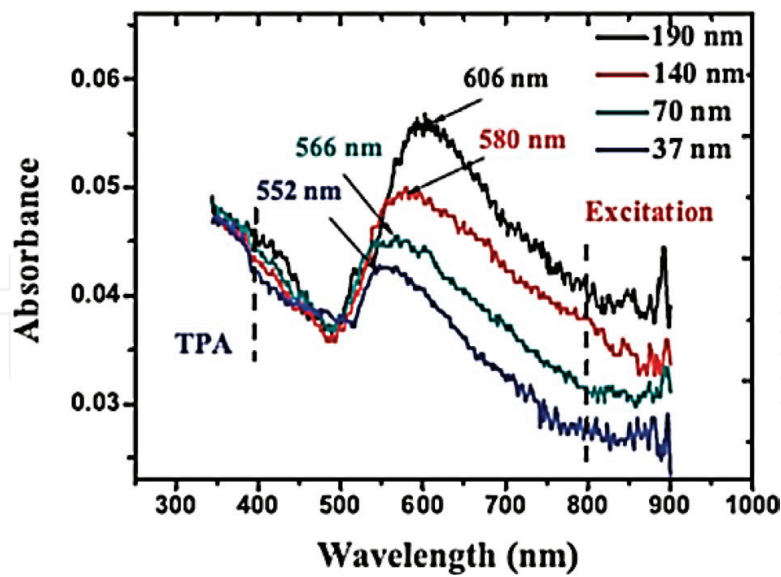


Figure 6. Absorption spectra of Au periodic particle arrays with sizes of 37, 70, 140, and 190 nm.

decreases due to the dominant interband transition caused by the TPA process. However, for the 140 and 190 nm Au nanoparticles, self-defocusing occurs. With the increase of particle size, the SA becomes dominant. The increase of refractive index is due to the excited electrons, resulting in the self-focusing.

It is obvious that the size of Au nanoparticles influences the nonlinear optical properties of Au nanoparticles. Hence, the optical limiting of Au nanoparticles should be size-dependent. Mostafavi et al. prepared gold nanoparticles with 2.5, 9, and 15 nm radii and studied the nonlinear optical response of resulting nanoparticles [8]. They found that the optical limiting threshold and the amplitude depend strongly on size. The 2.5-nm clusters do not limit light even at very high fluence, while the larger clusters do at 530 nm.

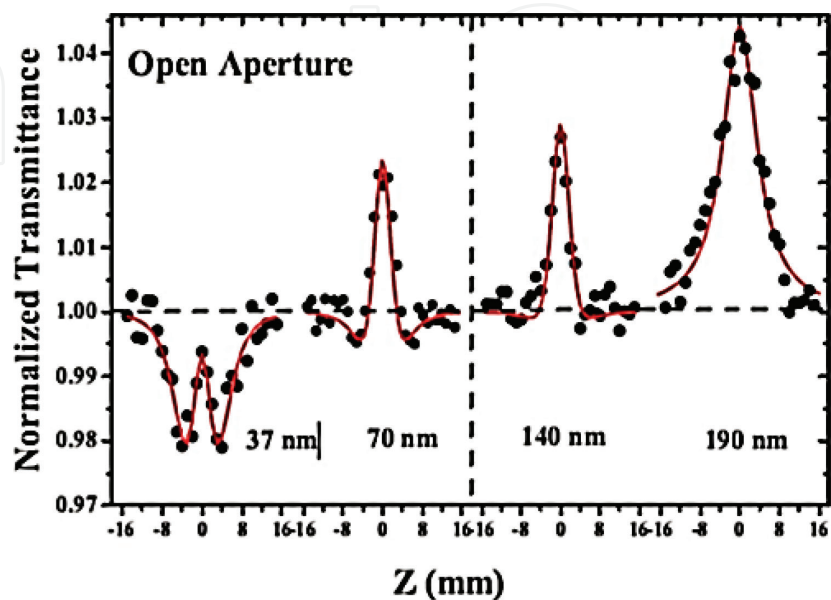


Figure 7. The OA Z-scan results of four samples with sizes of 37, 70, 140, and 190 nm.

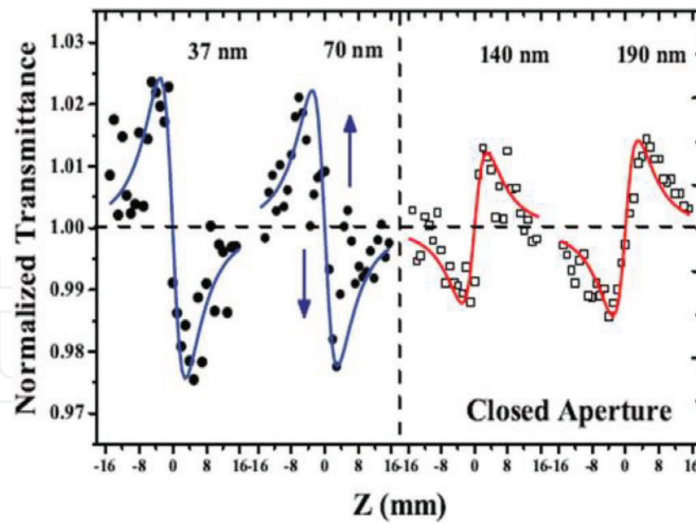


Figure 8. The CA Z-scan results of the four samples at exciting intensity $I_0 = 55 \text{ GW/cm}^2$.

But we believe that the increasing trend of optical limiting capability with size will terminate somewhere, and there should be an optimal size for optical limiting. To testify the hypothesis, we synthesized the gold nanoparticles with even larger radii of 15, 25, 50, and 70 nm and studied the optical limiting performance of the nanoparticles with different size at 532 nm for 8-ns laser pulses [45].

As shown in **Figures 9** and **10**, the optical limiting effect is found to be size-dependent. Compared with what Francois et al. have found [8], however, the results in our experiments are more complicated. When the size of gold nanoparticles increases from 15 to 25 nm, optical limiting capability increases. But when particle size increases further, optical limiting capability decreases instead. Visual description for the comparison of optical limiting ability is shown in **Figure 10**.

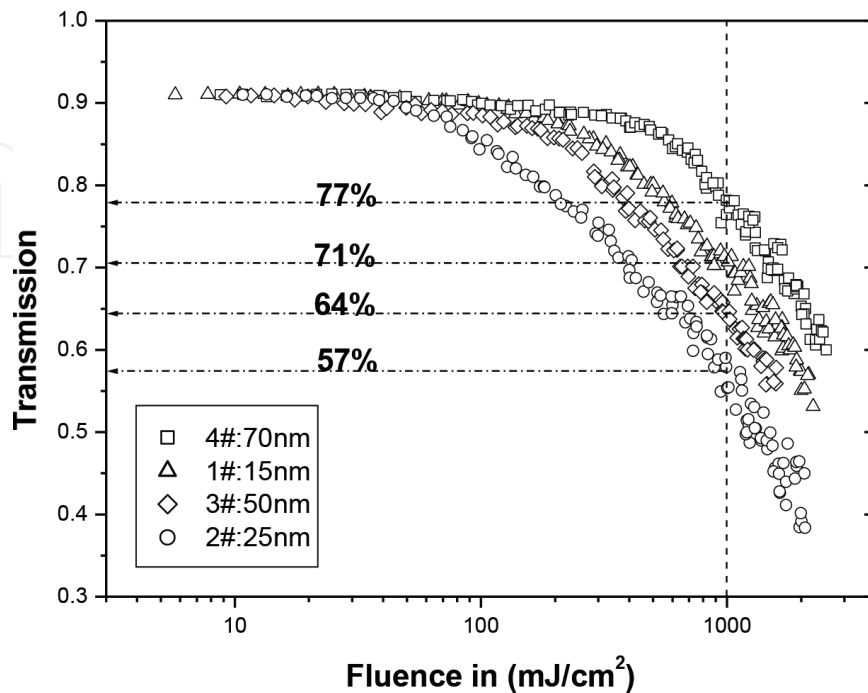


Figure 9. Optical limiting curves of gold nanoparticles with the radii of 15, 25, 50, and 70 nm.

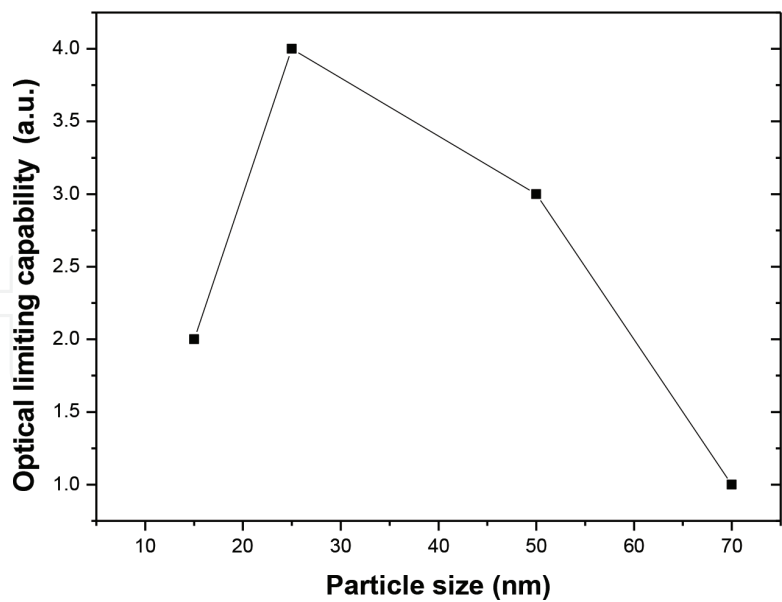


Figure 10. Optical limiting capability changing with particle size.

We analyzed the results in terms of the surface layer of nanoparticles. We assume that only surface layer of the particle can respond to outside light. We think of the thickness of the surface layer to be d_s . The absorption region of gold nanoparticles with different sizes is shown in Figure 11. When gold nanoparticle has the radius less than d_s , light energy can be absorbed by whole particle. Then, the absorbed energy transfers to surrounding solvent and leads to solvent bubbles. Moreover, the larger the size is, the stronger the nonlinear scattering is, and gold nanoparticles exhibit size-enhanced optical limiting. This is in consistent with the results in 15- and 25-nm gold nanoparticles. But when the radius of gold nanoparticle increases to be larger than d_s , only outer layer d_s can absorb light energy. The energy will first transfer to the core (black part in Figure 11) of gold nanoparticles. The transferring energy from gold nanoparticle to solvent decreases, which will obstruct the surrounding solvent to form bubbles. The obstruction makes the optical limiting weaker in larger particle.

Based on the analysis above, we found that, when the radius of nanoparticle is equal to the surface layer d_s , the absorption-induced scattering is the strongest, correspondingly the optical limiting is most effective. That means, the optical limiting optimal size of metal nanoparticles equals to surface layer thickness d_s . For gold nanoparticles, it is 25 nm. The investigation may be helpful for the synthesis of metal nanoparticles for optical limiting. Undoubtedly, more studies are required to find out the exact reasons for this behavior.

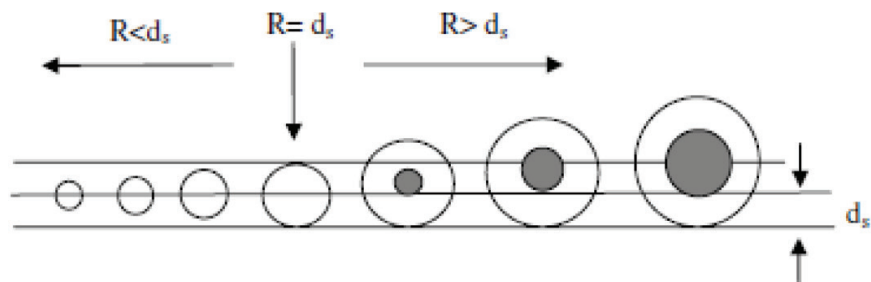


Figure 11. Absorption regions in gold nanoparticles with different sizes.

3.2. Nonlinear optical studies of Ag nanoparticles

For Au nanoparticles, there is significant overlap between the interband absorption and the plasmon resonance absorption, which decreases substantially the efficiency of plasmon excitation. In the case of Ag, however, the interband transition absorption at about 320 nm is far from its SPR wavelength of about 400 nm. This makes the plasmon excitation in Ag nanoparticles more efficient than that in Au nanoparticles. Moreover, the separation of two kinds of absorption facilitates the separate investigation of the nonlinear optical effects arising from interband transitions and those due to SPR. Hence, many groups conducted research on the nonlinear absorption and optical limiting in silver nanoparticles [1, 22–31].

For example, Gurudas et al. studied the picoseconds optical nonlinearity in silver nanodots prepared by pulsed laser deposition at 532 nm [22]. The nonlinear refraction and nonlinear absorption of these nanoparticle films were measured by using the Z-scan technique. The broad SPR absorption indicates that there are different-sized and different-shaped nanoparticles in the samples. At 532 nm, the SA and RSA are found to be dependent on sample properties. So by designing properly nanoparticles with different sizes and shapes, it may be possible to use these materials for various applications such as mode locking and optical limiter to protect sensors or eyes from the damage of high-power laser. Zheng et al. have investigated the shape-dependent NLO behaviors of nanostructured Ag nanoplates, nanowires, and nanoparticles suspensions (as shown in **Figure 12**) and their silica gel glass composites at both 532 and 1064 nm [23, 24] by using Z-scan.

NLO abilities of the nanostructured suspensions are found to be shape-dependent at 532 and 1064 nm. **Figure 13** shows the OA Z-scan experiment results of the nanostructured Ag in aqueous suspensions. All the samples exhibit typical RSA, but the deepness of the valleys differs from one to another, indicating different RSA abilities. As shown in **Figure 14**, they also investigated the NLO properties of the Ag/silica gel glass nanocomposites. In contrast to corresponding suspensions, the composites show more complicated OA Z-scan curves and the curves are insensitive to the nanostructured shapes. To a different extent, all the traces show

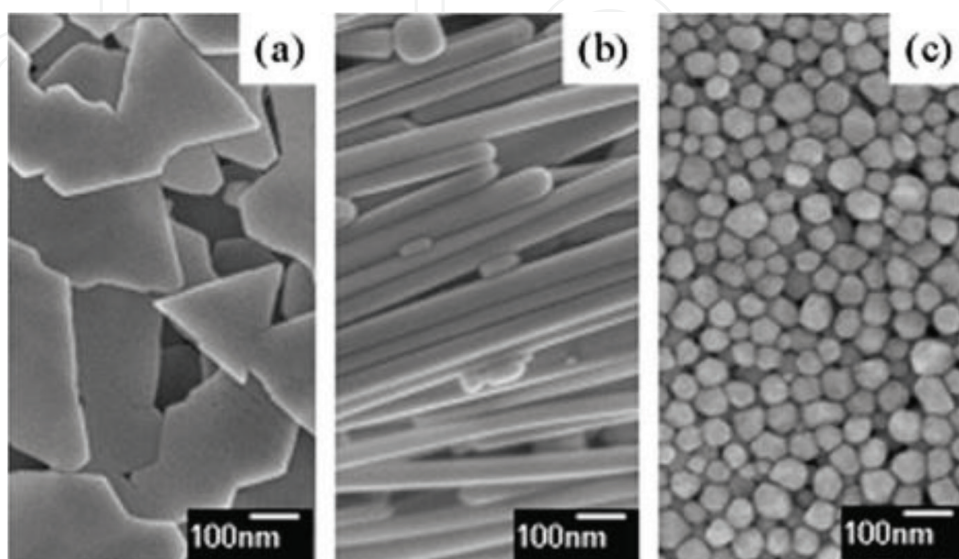


Figure 12. SEM images of the investigated Ag (a) nanoplates, (b) nanowires, and (c) nanoparticles.

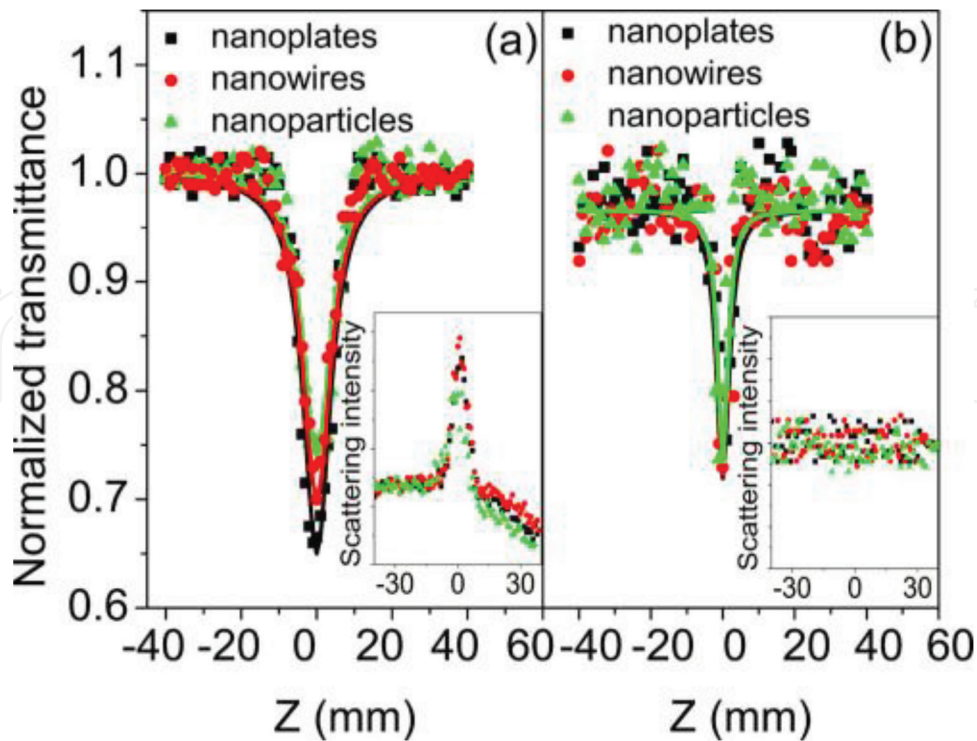


Figure 13. OA Z-scan curves of the investigated nanostructured Ag suspensions at 532 (a) and 1064 nm (b).

two symmetrical humps flanking the valley near the focus, where hump indicates SA and valley RSA. When the input energy increases gradually from 0.6 to 1.5 mJ, the NLA signals switch from SA to RSA. Besides, they have studied the NLO properties of Ag nanowire/silica

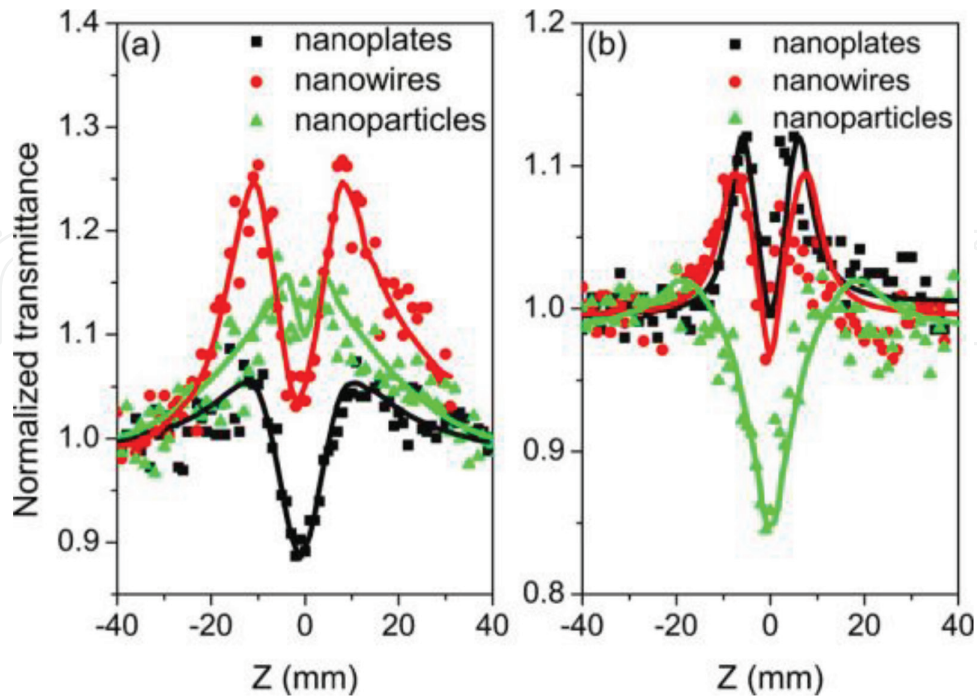


Figure 14. OA Z-scan curves of the investigated Ag/silica gel glass nanocomposites at 532 (a) and 1064 nm (b).

gel glass composite and Ag nanowires (NWs) suspension at both 532 and 1064 nm in Ref. [24]. In the Ag NWs suspension, only RSA is found, while in the Ag NWs/silica gel glass composite, a switch from SA to RSA is observed. The origin of this phenomenon was discussed from the viewpoint of electronic dynamics of Ag NWs in liquid and solid-state matrices. The solid-state environment of the gel glass composite greatly enhances the fluorescence of Ag NWs, retards the electronic relaxation process, and results in surface plasmon bleaching, which causes SA.

Unnikrishnan et al. studied nonlinear optical absorption in Ag nanosol at selected wavelengths of 456 nm (inside the SPR band), 477 nm (on the edge of SPR), and 532 nm (outside the SPR) using open aperture Z-scan technique [25]. They all found a flip over from SA to RSA behavior at higher input excitation. Similar switching behaviors have also been previously observed for Ag nanoparticles in ZrO_2 by Anija [26] and for Ag nanoparticles in PMMA by Deng [27] under nanosecond laser pulse at 532 nm.

All the above studies were conducted at 532 nm far from the SPR wavelength of 400 nm. While at resonant wavelength, Ganeev and Rysanyansky have investigated the nonlinear optical absorption of Ag nanoparticles [28]. They found that Ag nanoparticles exhibit either SA for 1.2-ps pulsed laser or RSA for 8-ns pulsed laser. In fact, the nonlinear optical properties of materials depend strongly on wavelength and pulse width.

In 2012, we studied the nonlinear absorption of Ag nanoparticles using open-aperture Z-scan method with femtosecond laser pulses at 400 nm [29]. As shown in **Figures 15 and 16**, when laser intensities are relatively weaker, Ag nanoparticles show SA, but when laser intensities are strong, a switch from SA to RSA occurs. Moreover, when the repetition rate of pulse laser is high, open-aperture Z-scan curves become asymmetric. The switch and asymmetry were interpreted in terms of plasmon bleaching, free carrier absorption, and migration of Ag nanoparticles. The peak of the SPR of the Ag nanoparticles is at about 400 nm near the laser excitation. So the observed SA is due to the ground-state plasmon bleaching. It is the effect that causes an increase in transmission. When the laser intensity increases further,

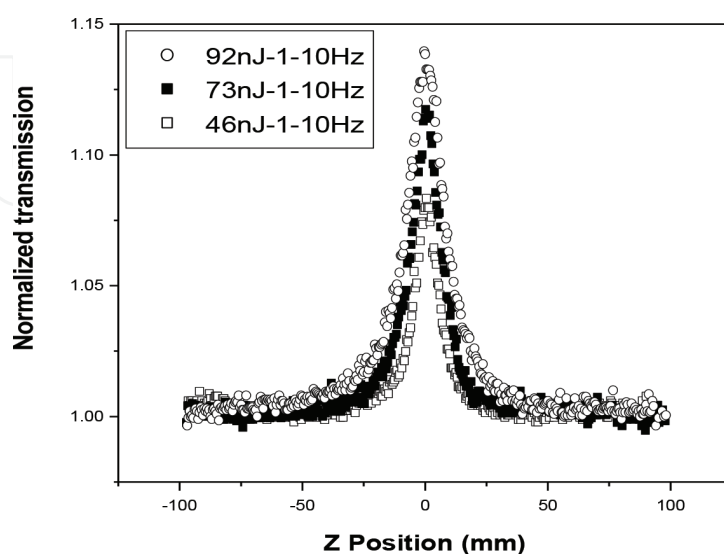


Figure 15. Open-aperture Z-scan curves at relatively low energies (46, 73, 92 nJ) using 1- and 10-Hz pulsed laser.

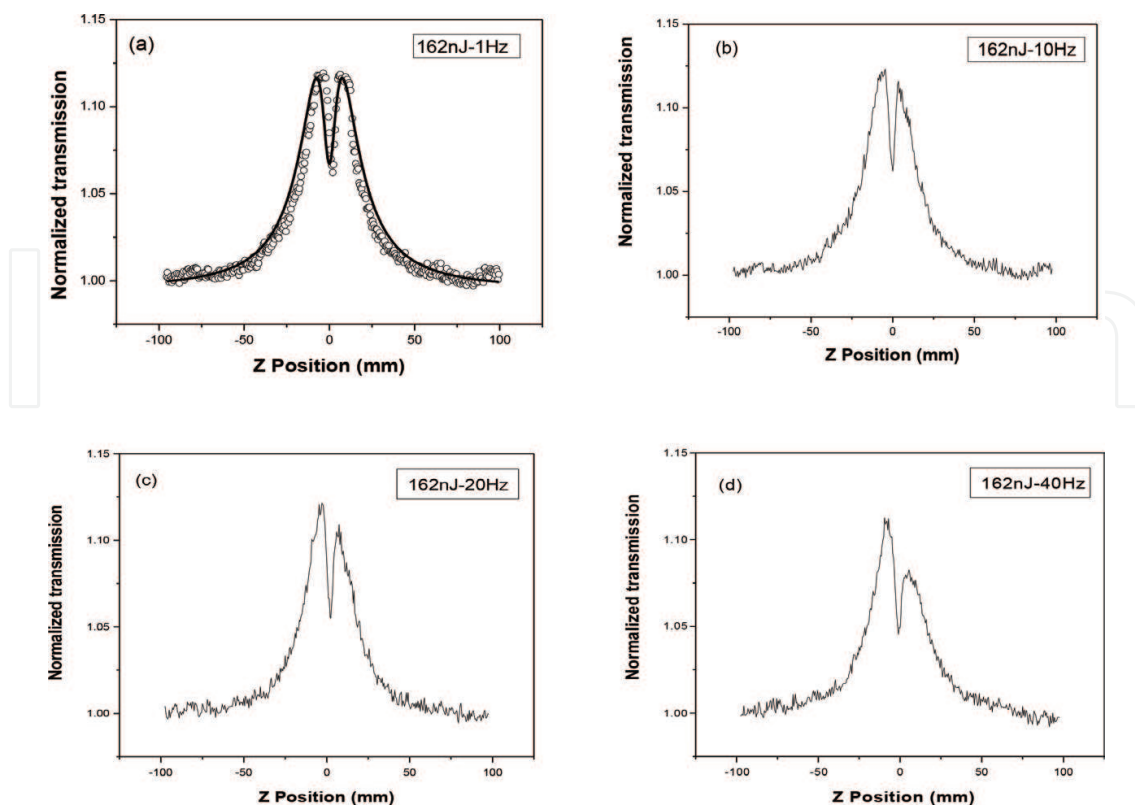


Figure 16. Open-aperture Z-scan curves obtained at energy of 162 nJ using (a) 1-, (b) 10-, (c) 20-, and (d) 40-Hz pulsed laser.

RSA begins to happen because the excitation can easily cause free carrier responsible for the RSA. This is a typical optical limiting effect, which can be applied to protect eyes and sensors from the damage of intense laser. Besides, asymmetrical open-aperture Z-scan curves were observed by using laser with higher repetition rate, which was thought to be due to the migration of nanoparticle following the impulsive optical excitation. More work is needed to study how laser causes the migration of nanoparticle and make a theoretical fit of the asymmetrical curves.

3.3. Nonlinear optical studies of Pd and Pt

It is well known, because both Au and Ag nanoparticles show a strong surface plasmon resonance (SPR) absorption band in the visible region, they have attracted more interest and initiated more theoretical and experimental studies concerning nonlinear optical properties. Though the SPR of transition metal nanoparticles is located in the ultraviolet range, the NLO response cannot be resonantly enhanced, but instead, it can be influenced by other nonlinear processes. Pd and Pt nanoparticles have also been found to exhibit interesting nonlinear optical properties such as two-photon or multiphoton processes [46–49], RSA [50] and SA [13, 51–53]. Correspondingly, Pt nanoparticles can be used in optical limiting [50, 53, 54] and mode locking [52, 53].

Even though platinum's SPR at 215 nm [55] lies away from excitation wavelength of 532 nm, as shown in **Figure 17**, we still observed SA at lower fluences, which is usually linked to SPR in gold nanoparticles [13]. Furthermore, as shown in **Figure 18**, we found the changeover from SA to RSA at higher input pump intensities.

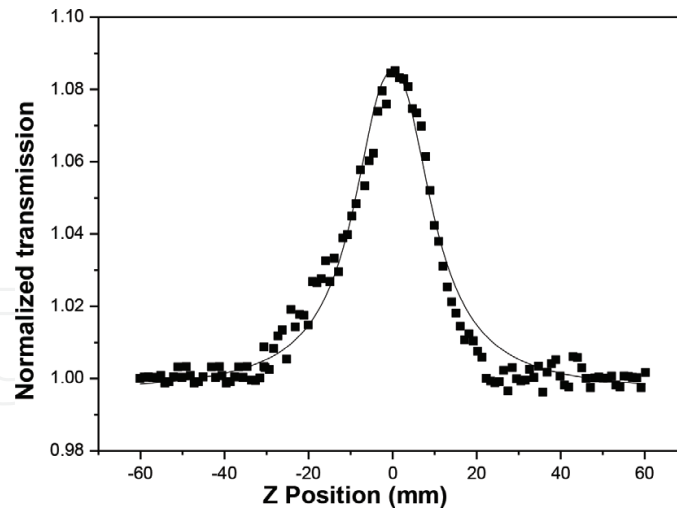


Figure 17. The normalized open-aperture Z-scan curve at lower fluences.

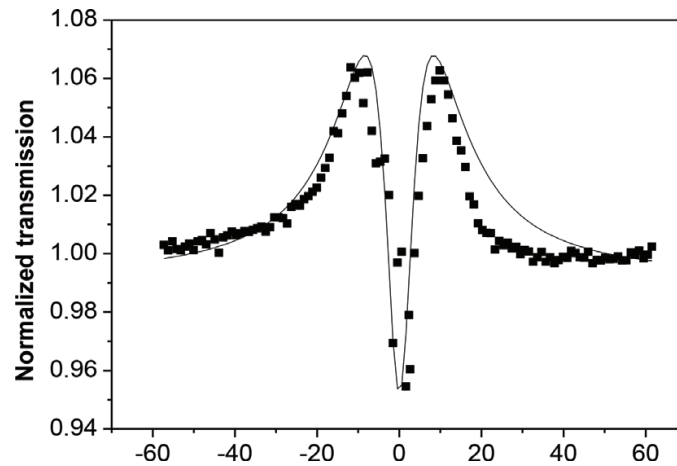


Figure 18. The normalized open-aperture Z-scan curve at higher fluences.

To interpret the flip of SA around the beam waist, we phenomenologically combine a saturable absorption coefficient and the two-photon absorption (TPA) coefficient, yielding the total absorption coefficient as shown by Eq. (5). Solid lines in **Figures 17** and **18** are the theoretical fitting. It can be found that the theoretical fit is in good agreement with the experimental results, indicating the model used is reasonable. For Pt nanoparticles, the SPR wavelength is at about 215 nm far from 532 nm, which implies that the ground plasma bleaching cannot occur in Pt nanoparticles. So we think that the SA in Pt nanoparticles has different origins from that in gold and silver nanoparticles and cannot be interpreted in terms of SPR. Although we have no ideal about the special phenomena, we think that Pt nanoparticles may be employed in not only optical limiting but also mode locking. In fact, the proposal has been proved by Qu and Ganeev et al.

4. Conclusions

In this chapter, nonlinear optical properties of metal nanoparticles were reviewed. Most of these studies were conducted in liquid matrices. However, from the viewpoint of practical

applications, it is important and indispensable to homogeneously disperse the nanostructured metals in solid-state matrices to avoid their easy agglomeration and instability in suspensions. In this case, investigation on NLO behaviors of metal nanoparticles in solid matrices becomes the most significant step toward the development of practical optoelectronic components and devices.

Conflict of interest

The author declares no competing financial interest.

Author details

Yachen Gao* and Deigui Kong

*Address all correspondence to: gaoyachen@hlju.edu.cn

College of Electronic Engineering, Heilongjiang University, Harbin, PR China

References

- [1] Sun Y, Riggs JE, Rollins HW, Guduru R. Strong optical limiting of silver-containing nanocrystalline particles in stable suspensions. *The Journal of Physical Chemistry. B.* 1999; **103**(1):77-82
- [2] Philip R, Kumar GR, Sandhyarani N, Pradeep T. Picosecond optical nonlinearity in monolayer-protected gold, silver, and gold-silver alloy nanoclusters. *Physical Review B.* 2000; **62**(19):13160-13166
- [3] Anija M, Thomas J, Singh N, Sreekumaran Nair A, Tom RT, Pradeep T, et al. Nonlinear light transmission through oxide-protected Au and Ag nanoparticles: An investigation an nanosecond domain. *Chemical Physics Letters.* 2003; **380**:223-229
- [4] Zhang H, David EZ, Deng LG, Liu HK, Teo BK. Optical limiting behavior of nanosized polyicosahedral gold-silver clusters based on third-order nonlinear optical effects. *Journal of the American Chemical Society.* 2001; **123**:11300-11301
- [5] Ispasoiu RG, Balogh L, Varnavski OP, Tomalia DA, Goodson T. Large optical limiting from novel metal-dendrimer nanocomposite materials. *Journal of the American Chemical Society.* 2000; **122**:11005-11006
- [6] Shiliang Q, Chimin D, Song Y, Wang Y, Gao Y, Liu S, et al. Optical nonlinearities in gold nanoparticles protected by ligands. *Chemical Physics Letters.* 2002; **356**:403-408
- [7] Gao Y, Wang Y, Song Y, Li Y, Qu S, Liu H. Strong optical limiting property of a novel silver nanoparticle containing C60 derivative. *Optics Communications.* 2003; **223**:103-108

- [8] Francois L, Mostafavi M, Belloni J, Delouis J-F, Delaire J, Feneyrou P. Optical limitation induced by gold clusters. 1. Size effect. *The Journal of Physical Chemistry. B.* 2000;**104**: 6133-6137
- [9] Francois L, Mostafavi M, Belloni J, Delaire JA. Optical limitation induced by gold clusters. 2. Mechanism and efficiency. *Physical Chemistry Chemical Physics.* 2001;**3**:4965-4971
- [10] Gao Y, Song Y, Li Y, Wang Y, Liu H, Zhu D. Large optical limiting of the [60]fullerene-substituted tripyridine palladium nanoparticles. *Applied Physics B.* 2003;**76**:761-763
- [11] Sheik-Bahae M, Said AA, Van Stryland EW. High-sensitivity, single-beam n² measurements. *Optics Letters.* 1989;**14**(17):955-957
- [12] Sheik-Bahae M, Said AA, Wei TH, Hagan DJ, Van Stryland EW. Sensitive measurement of optical nonlinearities using a single beam. *IEEE Journal of Quantum Electronics.* 1990; **26**(4):760-769
- [13] Gao Y, Zhang X, Li Y, Liu H, Wang Y, Chang Q, et al. Saturable absorption and reverse saturable absorption in platinum nanoparticles. *Optics Communications.* 2005;**251**(4-6): 429-433
- [14] Hodak JH, Henglein A, Hartland GV. Tuning the spectral and temporal response in PtAu core-shell nanoparticles. *Journal of Chemical Physics.* 2001;**114**(6):2760-2765
- [15] Zhang Y-x, Wang Y-h. Nonlinear optical properties of metal nanoparticles: A review. *RSC Advances.* 2017;**7**:45129-45144
- [16] Elim HI, Yang J, Lee JY, Mi J, Ji W. Observation of saturable and reverse-saturable absorption at longitudinal surface plasmon resonance in gold nanorods. *Applied Physics Letters.* 2006;**88**(8):083107-083110
- [17] Karthikeyan B, Anija M, Philip R. In situ synthesis and nonlinear optical properties of Au: Ag nanocomposite polymer films. *Applied Physics Letters.* 2006;**88**(5):053104-053107
- [18] Wu DJ, Liu XJ, Liu LL, Qian WP. Third-order nonlinear optical properties of gold nano shells in aqueous solution. *Applied Physics A: Materials Science & Processing.* 2008;**92**(2): 279-282
- [19] Polavarapu L, Xu QH. A single-step synthesis of gold nanochains using an amino acid as a capping agent and characterization of their optical properties. *Nanotechnology.* 2008; **19**(7):075601-075607
- [20] Seo JT, Yang QG, Kim WJ, Heo J, Ma SM, Austin J, et al. Optical nonlinearities of Au nanoparticles and Au/Ag coresells. *Optics Letters.* 2009;**34**(3):307-309
- [21] Lee YH, Yan YL, Polavarapu L, Xu QH. Nonlinear optical switching behavior of Au nanocubes and nano-octahedra investigated by femtosecond Z-scan measurements. *Applied Physics Letters.* 2009;**95**(2):023105-023105
- [22] Gurudas U, Brooks E, Bubb DM, Heiroth S, Lippert T, Wokaun A. Saturable and reverse saturable absorption in silver nanodots at 532 nm using picosecond laser pulses. *Journal of Applied Physics.* 2008;**104**(7):073107-073125

- [23] Zheng C, Du YH, Feng M, Zhan HB. Shape dependence of nonlinear optical behavior of nanostructured silver and their silica gel glass composites. *Applied Physics Letters*. 2008; **93**(14):143108-143111
- [24] Zheng C, Ye XY, Cai SG, Wang MJ, Xiao XQ. Observation of nonlinear saturable and reverse-saturable absorption in silver nanowires and their silica gel glass composite. *Applied Physics B: Lasers and Optics*. 2010; **101**(4):835-840
- [25] Unnikrishnan KP, Nampoory VPN, Ramakrishnan V, Umadevi M, Vallabhan CPG. Non linear optical absorption in silver nanosol. *Journal of Physics D: Applied Physics*. 2003; **6**(11):1242-1245
- [26] Anija M, Thomas J, Singh N, Sreekumaran Nair A, Tom RT, Pradeep T, et al. Nonlinear light transmission through oxide-protected Au and Ag nanoparticles: An investigation in the nanosecond domain. *Chemical Physics Letters*. 2003; **380**(1-2):223-229
- [27] Deng Y, Sun YY, Wang P, Zhang DG, Jiao XJ, Ming H, et al. Nonlinear optical properties of silver colloidal solution by in situ synthesis technique. *Current Applied Physics*. 2008; **8**(1):13-17
- [28] Ganeev RA, Rysanyansky AI. Nonlinear optical characteristics of nanoparticles in suspensions and solid matrices. *Applied Physics B: Lasers and Optics*. 2006; **84**(1-2):295-302
- [29] Gao Y, Wu W, Kong D, Ran L, Chang Q, Ye H. Femtosecond nonlinear absorption of Ag nanoparticles at surface plasmon resonance. *Physica E: Low-dimensional Systems and Nanostructures*. 2012; **45**:162-165
- [30] Polavarapu L, Xu Q-H, Dhoni MS, Ji W. Optical limiting properties of silver nanoprisms. *Applied Physics Letters*. 2008; **92**(26):263110-263113
- [31] Porel S, Venkatram N, Narayana Rao D, Radhakrishnan TP. Optical power limiting in the femtosecond regime by silver nanoparticle-embedded polymer film. *Journal of Applied Physics*. 2007; **102**(3):033107-033113
- [32] Ricard D, Roussignol P, Flytzanis C. Surface-mediated enhancement of optical phase conjugation in metal colloids. *Optics Letters*. 1985; **10**(10):511-513
- [33] Wang K, Long H, Fu M, Yang G, Lu PX. Intensity-dependent reversal of nonlinearity sign in a gold nanoparticle array. *Optics Letters*. 2010; **35**(10):1560-1562
- [34] Philip R, Kumar GR, Sandhyarani N, Pradeep T. Picosecond optical limiting in monolayer protected cluster gold, silver and gold-silver alloy nanoclusters. *Physical Review B*. 2000; **62**:13160-13166
- [35] Gisin N, Thew R. Quantum communication. *Nature Photonics*. 2007; **1**(3):165-171
- [36] Li Y, Zhang S, Liu J, Zhang K. Quantum correlation between fundamental and second-harmonic field via second-harmonic generation. *Journal of the Optical Society of America B: Optical Physics*. 2007; **24**(3):660-663
- [37] Hirsch LR, Stafford RJ, Bankson JA, Sershen SR, Rivera B, Price RE, et al. Nanoshell-mediated near-infrared thermal therapy of tumors under magnetic resonance guidance.

Proceedings of the National Academy of Sciences of the United States of America. 2003;**100**(23):13549-13554

- [38] Lal S, Clare SE, Halas NJ. Nanoshell-enabled photothermal cancer therapy: Impending clinical impact. *Accounts of Chemical Research*. 2008;**41**(12):1842-1851
- [39] Huang X, Neretina S, El-Sayed MA. Gold nanorods: From synthesis and properties to biological and biomedical applications. *Advanced Materials*. 2009;**21**(48):4880-4910
- [40] Gibbs HM. *Optical Bistability: Controlling Light with Light*. London: Academic Press; 1985
- [41] Midwinter JE. *Photonics in Switching*. London: Academic Press; 1993
- [42] Noguez C. Surface plasmons on metal nanoparticles: The influence of shape and physical environment. *Journal of Physical Chemistry C*. 2007;**111**(10):3806-3819
- [43] Sánchezdena O, Motasantiago P, Tamayorivera L, et al. Size-and shape-dependent nonlinear optical response of Au nanoparticles embedded in sapphire. *Optical Materials Express*. 2013;**4**(1):92-97
- [44] Jun HS, Lee KS, Yoon SH, et al. 3rd order nonlinear optical properties of Au:SiO₂ nanocomposite films with varying Au particle size. *Physica Status Solidi A: Applications and Materials Science*. 2010;**203**(6):1211-1216
- [45] Gao Y, Chang Q, Ye H, et al. Size effect of optical limiting in gold nanoparticles. *Chemical Physics*. 2007;**336**(2):99-102
- [46] Papagiannouli I, Potamianos D, Krasia-Christoforou T, Couris S. Third-order optical nonlinearities of PVP/Pd nanohybrids. *Optical Materials*. 2017;**72**:226-232
- [47] Iliopoulos K, Chatzikyriakos G, Demetriou M, Krasia-Christoforou T, Couris S. Preparation and nonlinear optical response of novel palladium-containing micellar nanohybrids. *Optical Materials*. 2011;**33**:1342-1349
- [48] Papagiannouli I, Demetriou M, Krasia-Christoforou T, Couris S. Palladium-based micellar nanohybrids: Preparation and nonlinear optical response. *RSC Advances*. 2014;**4**: 8779-8788
- [49] Papagiannouli I, Chatzikyriakos G, Iliopoulos K, Demetriou M, Krasia-Christoforou T, Couris S. Palladium micellar nanohybrids with tunable nonlinear optical response. *Optical Materials*. 2014;**36**:123-129
- [50] Qu S, Song Y, Liu H, Wang Y, Gao Y, Liu S, et al. A theoretical and experimental study on optical limiting in platinum nanoparticles. *Optics Communication*. 2002;**203**:283-288
- [51] Ganeev RA, Suzuki M, Baba M, Ichihara M, Kuroda H. Low- and high-order nonlinear optical properties of Au, Pt, Pd, and Ru nanoparticles. *Journal of Applied Physics*. 2008; **103**(6):063102
- [52] Ganeev RA, Tugushev RI, Usmanov T. Application of the nonlinear optical properties of platinum nanoparticles for the mode locking of Nd:glass laser. *Applied Physics B: Lasers and Optics*. 2009;**94**(4):647-651

- [53] Chehrghani A, Torkamany MJ. Nonlinear optical properties of laser synthesized Pt nanoparticles: Saturable and reverse saturable absorption. *Laser Physics*. 2014;**24**(1): 015901-015909
- [54] Ganeev RA, Ryasnyansky AI, Kamalov SR, Kodirov MK, Usmanov T. Nonlinear susceptibilities, coefficients and refractive colloidal metals. *Journal of Physics D: Applied Physics*. 2001;**34**(11):1602-1611
- [55] Henglein A, Ershov BG, Malow M. Absorption spectrum and some chemical reactions of colloidal platinum in aqueous solution. *The Journal of Physical Chemistry*. 1995;**99**: 14129-14136