Size-dependent nonlinear absorption and refraction of Ag nanoparticles excited by femtosecond lasers*

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(Received 19 August 2011; revised manuscript received 3 November 2011)

Silver (Ag) nanoparticles with different average sizes are prepared, and the nonlinear absorption and refraction of these nanoparticles are investigated with femtosecond laser pulses at 800 nm. The smallest Ag nanoparticles show insignificant nonlinear absorption, whereas the larger ones show saturable absorption. By considering the previously reported positive nonlinear absorption of 9 nm Ag nanoparticles, the nonlinear absorptions of Ag nanoparticles are found to be size-dependent. All these nonlinear absorptions can be compatibly explained from the viewpoints of electronic transitions, energy bands and electronic structures in the conduction band of Ag nanoparticles. The nonlinear refraction is attributed to the effect of hot electrons arising from the intraband transition in the s–p conduction band of Ag nanoparticles.

Keywords: nonlinear absorption, nonlinear refraction, silver nanoparticles, electronic structures

PACS: 78.67.Bf, 73.22.Dj, 42.65.Re, 42.70.Nq **DOI:** 10.1088/1674-1056/21/4/047804

1. Introduction

Noble metal (Au, Ag, and Cu) nanoparticles (NPs) possess close-lying energy bands which allow conduction electrons to move almost freely. At the excitation of light, the oscillation of the free electrons in the s–p conduction band gives rise to surface plasmon resonance (SPR).[1] The SPR of Ag NPs with wavelengths located in the range around 420 nm is determined by the size, shapes, and surrounding materials. The SPR of Ag NPs can lead to enhancement of the third-order susceptibility when they are pumped by lasers operating at the UV-visible-infrared range.[1−3] This enhancement makes Ag NPs promising for optical applications such as light-switch, optical limiting, surface-enhanced Raman scattering, etc.[4−7]

In recent years, there has been much research on the nonlinear optical properties of Ag NPs.[1−5,8−20] These studies have revealed that Ag NPs with different sizes and shapes exhibit different nonlinear properties when they are excited by lasers with different wavelengths, pulse durations, and irradiation intensities. Indeed, there are several systematic investigations concerning the nonlinear properties of Ag NPs. For example, Hamanaka and co-wokers[8] explained the nonlinear properties around the SPR of Ag NPs (with average diameters of 7 nm and 9 nm) which were excited by 150-fs laser pulses. Rativa *et al.*[20] reported the positive nonlinear absorption of 9 nm Ag NPs, which was excited by 80-fs lasers at 800 nm. References [10] and [11] reported the saturable absorption (SA) of Ag NPs, which was excited by picosecond lasers at 532 nm and attributed to intraband transition in the conduction band. This SA is intensity-dependent, which can be transformed into positive nonlinear absorption when the irradiation intensity increases. Gurudas and co-workers[11] explained this transformation.

However, in Refs. [8] and [20], the detailed electronic transitions were not explained because the corresponding models were based on classical electronics. And in Refs. [10] and [11], the SA is affected by the positive nonlinear absorption, that is, the nonlinear absorption is intensity-dependent. In fact, the nonlinear optical properties of Ag NPs can be size-dependent. However, to the best of our knowledge,

*Project supported by the Natural Science Foundation of Heilongjiang Province, China (Grant No. A200912), the Program of Excellent Team in the Harbin Institute of Technology, China, and the National Natural Science Foundation of China (Grant Nos. 60907023 and 10904027).

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for the size-dependent nonlinear absorption, a quantitative and comprehensive investigation, along with a discussion from the viewpoint of energy band and electronic structures, is still missing so far.

We prepared three batches of Ag NPs with different average sizes by employing a chemical method and a laser ablation method. The nonlinear optical properties of these NPs are investigated using the Z-scan technique with a 120-fs laser pulse at 800 nm. The nonlinear absorption of the smallest Ag NPs is insignificant, however, the two batches of larger Ag NPs are found to be pure SA even when the intensity is increased to relatively high values. By considering the nonlinear absorption of Ag NPs in our experiment, along with that of Rativa and co-workers,[20] at the excitation of femtosecond laser pulses at 800 nm, size-dependent nonlinear absorption is found. All these nonlinear absorptions can be compatibly explained from the viewpoints of electronic transitions, energy band, and electronic structures in the conduction band of Ag NPs. We have also carried out Z-scan experiments with a 30-ps laser pulse at 1064 nm, as well as light fragmentation experiments using femtosecond lasers at 800 nm to test our explanation. The nonlinear refractions of the two batches of larger Ag NPs at 800 nm are found to be self-focusing, and the nonlinear refractions are explained. The Ag NPs with the smallest size of 6 nm show insignificant nonlinear refraction.

2. Experimental details

According to the method reported by Lee and Meisl,[21] two batches of silver colloids are prepared, and the third batch of silver colloid is prepared by laser ablation on the as-produced silver colloids. Nanosecond laser pulses at 532 nm are focused by a lens with focal length of 20 cm. Part of the as-prepared silver colloid is filled in a cuvette which is placed at the focus. The focused laser pulses without any attenuation lead to the photofragmentation of silver colloids, and, accordingly, smaller Ag NPs are produced. The absorption spectra of the as-processed colloids are acquired using a spectrophotometer (Shimadzu Corporation, UV-1800). TEM observation for the size distributions of the precipitated Ag NPs are carried out with a JEM 1400 transmission electron microscope (JEOL Ltd.).

The nonlinear optical properties of silver colloids are investigated using a Z-scan technique.[22] The nonlinear absorption can be revealed by studying the transmittance of the open aperture (OA) Z-scan experiment, and the nonlinear refraction can be revealed from the transmittance of the closed aperture (CA) Z-scan experiment divided by that of the open aperture (i.e. CA/OA).[22] The open and closed aperture Z-scan can be performed simultaneously. A regenerative amplified Ti:sapphire femtosecond laser system (Coherent Inc., Legend), which produces a laser pulse at 800 nm is used to perform the Z-scan experiments. Laser pulses with repetition of 200 Hz and pulse duration of 120 fs are focused by a lens with a focal length of 20 cm.

3. Results and discussion

3.1. Characterization of the sample

For the two batches of silver colloids prepared by the method of Lee and Meisl, the absorption spectra are shown in Fig. 1, with the SPR peaks at 420 nm and 430 nm, and the colloids are labeled as S1 and S2, respectively. Part of S1 is filled in a cuvette, which is photo-fragmentated by the nanosecond laser pulse at 532 nm. The colour of the colloid turns from gray to yellow with the elapsing of continued laser irradiation. Accordingly, the absorption spectrum changes, as shown in Fig. 1, and the sharp SPR peak at 395 nm indicates that the Ag NPs are small and monodispersed. This colloid is labeled as S3. For S1 and S2, TEM photographs show that most of the Ag NPs are in the shape of hexagons, and a few of them are rod-shaped, as shown in Figs. 2(a) and 2(b). The quantitative measurements of S1 and S2 indicate that these NPs are narrowly distributed with average sizes of 33 nm and 46 nm, as shown in Figs. 2(d) and 2(e), respectively. For S3, the TEM photograph shows that the shapes of NPs are spherical with an average diameter of 6 nm, as shown in Fig. 2(c), and their size distribution is shown in Fig. 2(f).

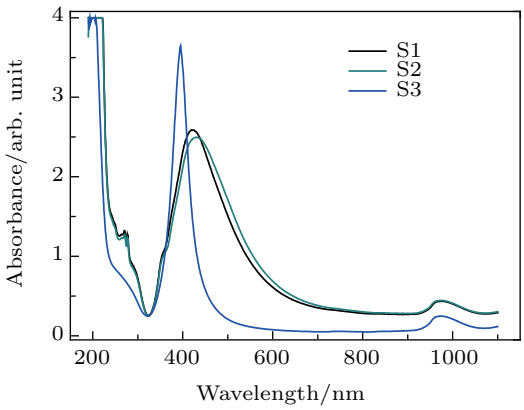


Fig. 1. (colour online) Absorption spectra of silver colloids with different nanoparticle sizes. The average particle sizes of S1, S2, and S3 are 33, 46, and 6 nm, respectively.

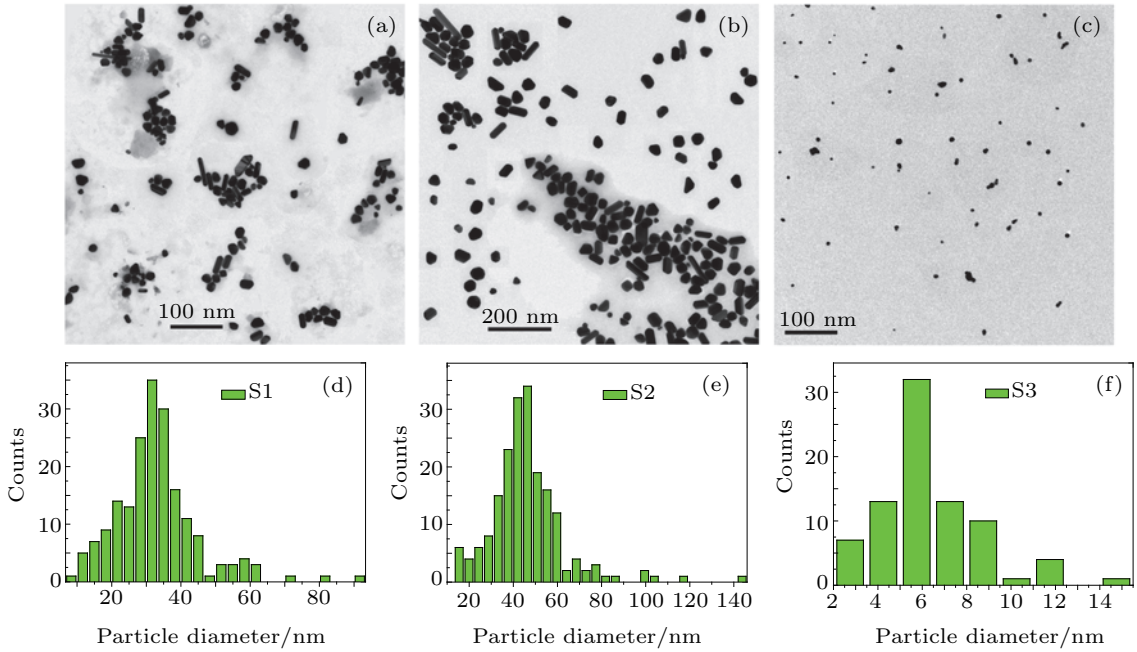


Fig. 2. (colour online) TEM pictures of Ag nanoparticles and their corresponding size distributions. (a), (b), and (c) are the TEM pictures of S1, S2, and S3, respectively; and (d), (e), and (f) are the size distributions of S1, S2, and S3, respectively.

When the large Ag NP is irradiated by the high-intensity and long-duration laser pulses, electrons in the NP can be highly excited. The energy absorbed from the laser pulse leads to an increase in the temperature of NP, and the NP melts at great heat. Part of the electrons can be sufficiently excited, and some of the electrons can even be photoejected out of the NP and rest on the interface of NP and the solvent. The accumulated electrons on the surface of the molten NP lead to an explosion, so the molten fragments are sputtered into the solvent and cooled down, and the surface tension will result in the formation of smaller spherical NPs. At a given value of the irradiation intensity, this process can be repeated until the majority of Ag NPs become too small to absorb the energy sufficient for their melting from the laser beam.[23] Ultimately, small spherical Ag NPs with narrow size distribution are produced.

3.2. Nonlinear optical properties of Ag NP solution

The as-prepared silver colloids are filled in a glass cell with an inner optical path of 1 mm; and the values of linear transmittance for S1 and S2 at 800 nm are 83% and 80%, respectively. Herein we present the results of the Z-scan experiments in Figs. 3 and 4. Figure 3(a) shows the OA Z-scan results of S1 obtained at intensities of 8.32×10^{14}, 1.66×10^{15}, and 2.5×10^{15} W/m^2, which are the peak radiation intensities at the focus. The symmetrical peaks in the curves indicate that SA dominates the nonlinear

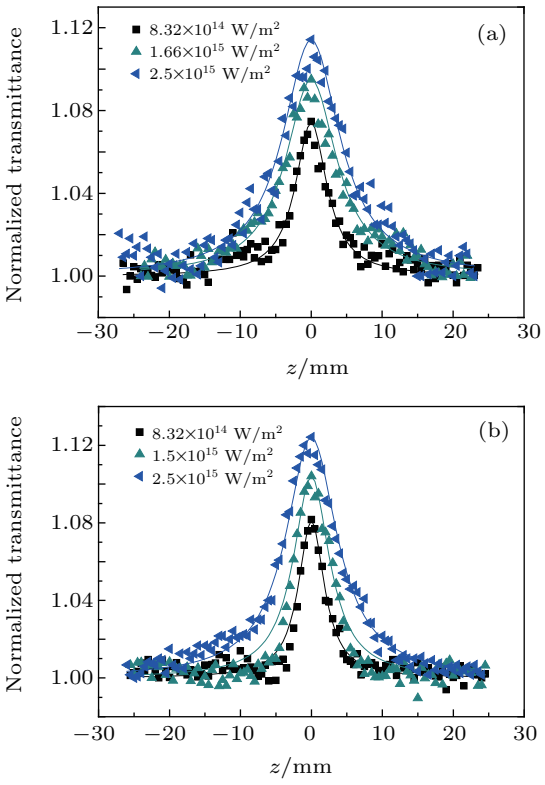


Fig. 3. (colour online) The OA Z-scan experimental results (triangles and squares) and theoretical fits (solid lines) of different Ag nanoparticles at different irradiation intensities: (a) experimental results and theoretical fits of S1 at 8.32×10^{14}, 1.66×10^{15}, and 2.5×10^{15} W/m^2; (b) experimental results and theoretical fits of S2 at 8.32×10^{14}, 1.5×10^{15}, and 2.5×10^{15} W/m^2, respectively.

absorption, which keeps saturable even when the intensity is as high as 4.2×10^{15} W/m^2. These results are distinctly different from those in previously reported works.[11,13,14,20] The OA Z-scan results of S2 are presented in Fig. 3 (b), where the nonlinear absorption evolution with the increase in intensity is similar to that of S1. The CA/OA Z-scan results of S1 and S2 are presented in Figs. 4 (a) and 4 (b), respectively. Their nonlinear refractions are self-focusing, and they remain unchanged as the intensity increases. The Z-scan experiment is also performed with S3. However, there is no nonlinear absorption and refraction can be observed even when the radiation intensity reaches 4.2×10^{15} W/m^2. And the supernatant layer without Ag NPs also shows insignificant nonlinear absorption and refraction, indicating that the nonlinear optical properties of S1 and S2 arise mainly from Ag NPs.

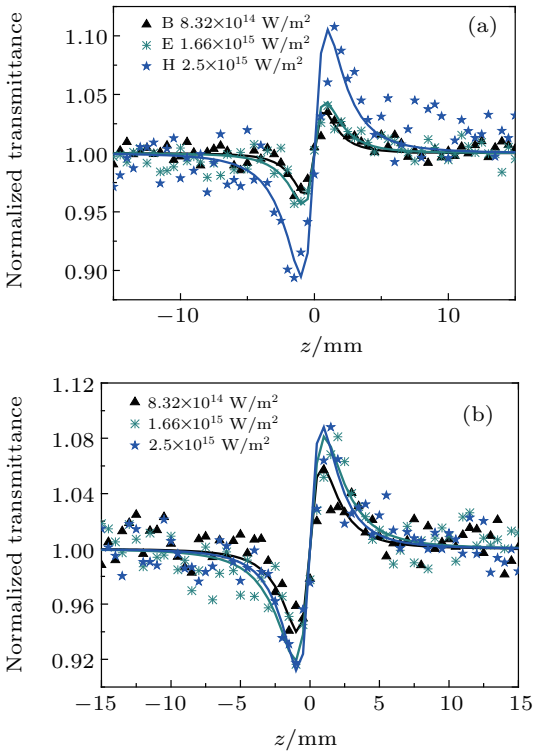


Fig. 4. (colour online) The CA/OA Z-scan experimental results (triangles, crosses, and stars) and theoretical fits (solid lines) of different Ag nanoparticles at 8.32×10^{14}, 1.66×10^{15}, and 2.5×10^{15} W/m^2; (a) experimental results and theoretical fits of S1, (b) experimental results and theoretical fits of S2.

Because the SA dominates the nonlinear absorption in a wide range of intensities, we can adopt a commonly accepted method to describe the OA Z-scan results with the total absorption coefficient expressed as

$$\alpha(I) = \alpha_0 + \beta I. \tag{1}$$

Typically, this expression is used to describe the TPA, with β being the TPA coefficient and α_0 being the linear absorption coefficient.[22] However, this expression can also be used to describe SA, in which β is negative and viewed as an effective nonlinear absorption coefficient.[10,11,15,18,24,25] According to formula (1), the normalized transmittance in the OA Z-scan experiment can be expressed as[22]

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}}, \tag{2}$$

where $q_0(z,0) = \beta I_0 L_{\rm eff}/(1+z^2/z_0^2)$, I_0 is the peak irradiance at the focus of the Z-scan experiment, $L_{\rm eff} = (1-{\rm e}^{-\alpha L})/\alpha_0$, with L being the sample length; z is the position of the sample and z_0 is the diffraction length of the beam. The results of OA Z-scan experiments can be well fitted by formula (2), as shown by the solid lines in Fig. 3, which indicates that β is proper for describing the SA. The extracted β's for S1 and S2 are found to be unchanged with increasing excitation energy of laser pulse, as depicted in Fig. 5. The average value of β is -1.94×10^{-13} m/W for S1 and -2.11×10^{-13} m/W for S2.

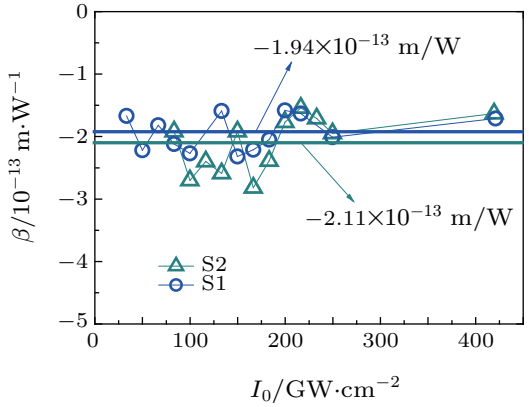


Fig. 5. (colour online) The effective nonlinear absorption coefficient (β) as a function of the peak irradiance at focus (I_0). The circles represent the data of S1 and the triangles the data of S2.

In distinct contrast with the results we obtain in this work phenomenologically, Rativa *et al.* reported the positive nonlinear absorption of Ag NPs with an average diameter of 9 nm, which was excited by the 80-fs laser at 800 nm.[20] They did not explain the origin of the nonlinear absorption in view of the electronic transition, but only mentioned that it was mainly due to the creation of hot electrons; they said their results were in good agreement with those of Hamanaka *et al.* Hamanaka and co-wokers proposed a model based on classical electronics to explain the nonlinear optical properties around the SPR of Ag NPs (with diameters of 7 nm and 9 nm) excited by a laser pulse of 150 fs. They attributed the nonlinear properties to the creation of hot electrons; however, the detailed electron transitions were also not interpreted.[8]

From our experiments and the work of Rativa *et al.*, as well as that of Hamanaka *et al.*, it can be clearly seen that at excitation of the femtosecond laser under almost the same condition, the Ag NPs with sizes smaller than 6 nm exhibit insignificant nonlinear absorption, and the 9 nm NPs exhibit positive nonlinear absorption; whereas the NPs larger than 30 nm exhibit SA. As shown experimentally, it is evident that the nonlinear absorption of Ag NPs are related closely to their sizes, but the size effects still remain to be further explored. Nevertheless, all the above-mentioned size-related nonlinear absorptions, despite the fact that they are phenomenologically different, can be compatibly explained from the viewpoint of electronic transition mechanisms as proposed in the following. However, before we start the discussion, we should first introduce the energy band and electronic structures, as well as the electronic relaxation of Ag NPs.

The optical properties of Ag NPs are determined by the localized outmost electrons in the d bands and quasi-free-electrons in the s–p conduction bands. The d bands are fairly flat in the k space and lie about 4 eV below the Fermi level, and the d electrons have relatively large effective masses which can only influence the transition probabilities when the excitation is intense enough. Whereas the s–p bands are extremely uneven, which intersects the Fermi level in some region of the k space,[26,27] the s–p electrons possess effective masses which are very close to those of the free electrons, therefore the s–p electrons can be easily influenced by the incident radiation.[1,27]

The occupied density of states (DOS) near the Fermi level can be revealed by X-ray photoemission spectroscopy (XPS),[28–31] and the unoccupied DOS near the Fermi level can be revealed by bremsstrahlung isochromatic spectroscopy (BIS).[29,30] The isolated Ag atom with d bands filled and the 5s level partly filled, possesses the outermost electronic configuration of $4d^{10}5s^1$, which changes into energy band structures when many atoms assemble together to form Ag NP and bulk Ag. The bulk Ag has spatially compact 4d bands and more extended 5s bands,[28] therefore the 4d states are nearly filled and the states near the Fermi level are primarily due to the 5s state.[29] The evolution of electronic structures with the increase in size of NP can be well characterized by XPS and BIS. The XPS of Ag NP is similar to that of bulk Ag, and it changes little with the increase in NP size,[28] which indicates that the occupied DOS of the 4d band of the Ag NP is nearly filled. And the XPS shows the occupied DOS of the 4d band with a peak at about 4 eV below the Fermi level.[28] However, the BIS changes dramatically with the increase in Ag NP size,[29] indicating that the unoccupied DOS of 5s states are closely related to NP size. For Ag NPs smaller than 10 nm and larger than 20 nm, the unoccupied DOS of 5s states is schematically shown by the orange and blue curves in Figs. 6(a) and 6(b), respectively.[29–31]

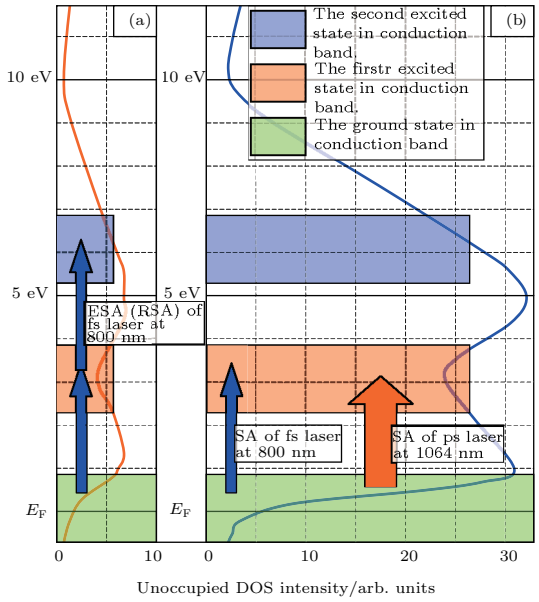


Fig. 6. (colour online) The s–p conduction band electronic structures and intraband transitions of Ag nanoparticles with different sizes: (a) nanoparticles smaller than 10 nm, and (b) nanoparticles larger than 20 nm. The orange and blue lines are the unoccupied DOS intensities of small and large Ag nanoparticles, respectively. The green, orange, and blue boxes denote the ground state, the first and second excited states in the conduction band in Ag nanoparticles, respectively. The two blue arrows in panel (a) are the ESA of the femtosecond laser at 800 nm, which leads to RSA. The blue and orange arrows in panel (b) are the SA of the femtosecond laser at 800 nm and the SA of the picosecond laser at 1064 nm, respectively.

When the electrons in the ground state of the conduction band are excited, they transit instantly to excited states. During the early stage of these excited states, the electronic gas is in non-equilibrium and not in Fermi–Dirac distribution. The excited electrons exchange energy through electron–electron collisions to form an internally thermalized electronic gas; this is shown to take place with a characteristic time constant of 350 fs.[32,33] After the thermalization and partly during this process, the electronic gas transfers the energy absorbed from the laser further to the lattice through electron–phonon coupling, which cools

the electronic gas, and the electron–phonon coupling time constant is 2 ps. The subsequent cooling of the excited phonons is through phonon–solvent interaction, which is completed with a decay time constant of 40 ps.[34]

Now, we come to explain the nonlinear absorption of Ag NPs in our work and that of Rativa *et al.*, along with that of Hamanaka *et al.* The interband and intraband transitions can only take place distinctly when the occupied DOS in the ground state and unoccupied DOS in the excited state are sufficient.[35] So in all cases we can safely exclude the presence of intraband absorption in the 4d band because the 4d states are nearly filled. In addition, according to the energy band and electronic structures mentioned above, the possible interband transition of electrons between the d bands and s–p conduction band has to overcome the band gap of Ag NP, which is 4 eV, and does not change with the size of the NP. The interband three-photon transition at 800 nm (1.55 eV) may surely cause a valley in the curve of the OA Z-scan.[36,37] For the positive nonlinear absorption reported by Rativa *et al.*, a representative peak radiation intensity at the focus is 1.8×10^{15} W/m^2; whereas in our experiments, the SA dominates the nonlinear absorption of S1 and S2, even if the intensity increases to 4.2×10^{15} W/m^2. This indicates the absence of interband three-photon transition. So the positive nonlinear absorption of Ag NPs with an average diameter of 9 nm, and the SA of NPs with diameters larger than 30 nm, may both originate from the intraband absorption in the s–p conduction band.

For the small Ag NPs with a diameter of 9 nm, the conduction electrons will be excited to higher excited states because there are not sufficient unoccupied DOS in the first-excited state to accommodate these excited electrons, as shown by the orange box in Fig. 6(a). This excitation is the excited state absorption (ESA),[38] as shown by two blue arrows in Fig. 6(a), which can be referred to as reverse saturable absorption (RSA) when the ESA decreases the transmittance of the sample and induces an overall effect opposite to that of SA. So the valley in the OA Z-scan experiments of Rativa *et al.*,[20] and the positive Im $\chi^{(3)}$ predicted by Hamanaka *et al.*,[8] both originate from the RSA in the conduction band. In our experiments, the duration of laser pulse is 120 fs, shorter than the time constant of the electron–electron collisions in Ag NP, and the single pulse vanishes before the thermalization of the excited electronic gas. When electrons in the ground state in the conduction band are excited to the first-excited state in the conduction band, all the excited electrons can be accommodated in this excited state because the excitation of the femtosecond laser is insufficient and the unoccupied DOS in the first-excited state is enough, as shown by the orange box in Fig. 6(b), which leads to the SA of intraband transition, as shown by a blue arrow in Fig. 6(b). This SA remains unchanged even when the irradiation intensities are high, which leads to a total absorption coefficient proportional to the irradiation intensity, and β is independent of intensity. For S3, the occupied and unoccupied DOS in the conduction band is insufficient, so the nonlinear absorption is insignificant. Accordingly, we believe that when the wavelength of the excitation laser is much larger than that of the SPR of Ag NPs, the nonlinear absorption of Ag NPs may receive little contribution from the interband transition between the d bands and the s–p conduction band, regardless of the difference in pulse duration of the excitation laser and the size of the NPs. This conclusion is helpful to clarify the argument about the contribution of TPA and RSA to the positive nonlinear absorption of Ag NPs.[11]

From the discussion mentioned above, we can see that the proposed transition mechanism can be extended to compatibly interpret the nonlinear absorption of Ag NPs in our experiments and that of Refs. [8] and [20], even though the particle sizes and phenomena of nonlinear absorption are quite different. For our experiments, we can conclude that the combination of sufficient occupied DOS in the ground state and unoccupied DOS in the first-excited state, along with the insufficient excitation of electrons in the conduction band of Ag NPs, is the reason the nonlinear absorption remains saturable. In the following, we will conduct two experiments to test our explanations mentioned above.

The first experiment is an OA Z-scan experiment, which is performed under almost the same conditions as before, but replacing the femtosecond laser with a picosecond laser. The picosecond Nd:YAG laser (Continuum Inc., Surelite) can produce a 30-ps laser pulse at 1064 nm at a repetition rate of 10 Hz. In this experiment, the peak irradiation intensity at focus will take 1.46×10^{13}, 2.08×10^{13}, and 3.54×10^{13} W/m^2, respectively. For S1 and S2, in all cases, the nonlinear absorptions are dominated by SA because a peak emerges in each transmittance curve, as can be seen in Fig. 7, at an intensity of 3.54×10^{13} W/m^2. For S3,

no nonlinear absorption can be observed.

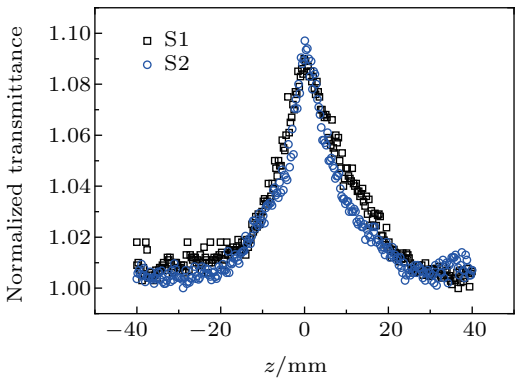


Fig. 7. (colour online) The OA Z-scan experimental results of different Ag nanoparticles due to the excitation of a picosecond laser at 1064 nm. The irradiation intensity is 3.54×10^{13} W/m^2, and the squares and circles are the experimental data for S1 and S2, respectively.

The photon energy at 1064 nm is 1.165 eV, so the possible interband absorption between the d bands and the s–p conduction band is four-photon absorption, which can only happen when the irradiation intensity is very high. And the intraband transition in the d bands is negligible because the d bands are almost filled. So at relatively low intensity, the nonlinear absorption is dominated by intraband absorption in the conduction band. Because the pulse duration of 30 ps is longer than the electron–phonon coupling time constant of Ag NPs, and much longer than the pulse duration of the femtosecond laser used in the previous Z-scan experiments, the excitation of electrons in the conduction band is more sufficient than that of the femtosecond laser. Consequently, the SA of S1 and S2, as shown by an orange arrow in Fig. 6(b), can definitely lead to the conclusion that the occupied DOS in the ground state and the unoccupied DOS in the first-excited state in the conduction band are sufficient, as shown by the green and orange boxes in Fig. 6(b), respectively. Whereas the insignificant nonlinear absorption of S3 confirms that the occupied and unoccupied DOS in the conduction band of small Ag NPs is insufficient.

According to the work of Kamat *et al.*,[39] laser pulses can smash Ag NPs when the irradiation intensity is high. They attribute the fragmentation to the photoejection of electrons, which is physically due to insufficient DOS in the excited states. We have performed an experiment to investigate the possible fragmentation of Ag NPs using a 120-fs laser at 800 nm and a repetition rate of 1000 Hz. In this experiment, 0.1 ml of sample is filled in a glass cell which is placed at the focus of a lens. The peak irradiance at focus is 4.2×10^{15} W/m^2, which is equal to the maximum intensity in our Z-scan experiments. S1, S2, and S3 are irradiated by the laser for 3 hours, and then examined with a transmission electron microscope. However, we cannot find any evidence of the possible fragmentation from the TEM micrograph. These results indicate again that, for S1 and S2, at an irradiation intensity smaller than 4.2×10^{15} W/m^2, the unoccupied DOS in the excited state is sufficient to support the SA of a 120-fs laser at 800 nm; however for S3, the occupied DOS in the ground state is insufficient.

For the nonlinear refraction in our experiments, the index of refraction n is expressed as[22]

$$n = n_0 + \gamma I, \tag{3}$$

where γ is the nonlinear refractive index, and n_0 is the linear refractive index. The normalized transmittance of the CA/OA Z-scan scheme can be written as[22]

$$T(z, \Delta\Phi_0) = 1 - \frac{4\Delta\Phi_0 x}{(x^2+9)(x^2+1)}, \tag{4}$$

where $\Delta\Phi_0 = k\gamma I_0 L_{\text{eff}}$, k is the wave number, and I_0 and L_{eff} have been defined in formula (2); $x = z/z_0$, z and z_0 have also been defined in formula (2). To Eq. (4), the experimental results of S1 and S2 can be well fitted, as shown by the solid lines in Fig. 4; and the calculated values of γ at different intensities are listed in Table 1. We can see that the values of γ are positive and small, which accords with the results of Rativa *et al.*[20]

Table 1. Nonlinear refractive indexes of S1 and S2 at different irradiation intensities.

$I_0/10^{14}$ W·m^{-2}	8.32	16.6	25
γ of S1/10^{-20} m^2·W^{-1}	2.31	2.29	4
γ of S2/10^{-20} m^2·W^{-1}	3.18	4.78	3.13

Generally, the nonlinear refraction arises from the thermal effect and/or electronic mechanisms.[22] The commonly mentioned thermal effect in solution is a slow accumulative process which is associated with the non-radiative relaxation of the energy absorbed via linear and/or nonlinear absorption by the metal NPs. According to the work we have reported previously,[35] for the aqueous solution in our experiments, the buildup time of the thermal effect is about 30 ns, which is much longer than the duration of the laser pulse at 120 fs. In addition, the repetition rate of 200 Hz in our Z-scan experiments is low enough to

reduce the accumulation of the thermal effect. Therefore, the thermal effect can be neglected.

The nonlinear refractions of Ag NPs have been reported by many researchers,[3,8−13,16,17,19,20] and most of the nonlinear refractions can be attributed to the electronic mechanisms. The previously mentioned model proposed by Hamanaka and co-workers provided various cases in the nonlinear refraction around the SPR of Ag NPs.[8] According to their model, the nonlinear refraction arises from the creation of hot electrons. When the excitation wavelength is far from the SPR peak of Ag NPs, the nonlinear refractive index is small, and the nonlinear refraction can be self-focusing. The self-focusing in our experiments is well consistent with their theory.

As discussed in the nonlinear absorption, the creation, transition, and relaxing of the hot electrons have been discussed in detail. The intraband transition in our experiments is a pure third-order nonlinear optical process which can also lead to the nonlinear refractive index independence of irradiation intensity.[40] The nonlinear refractive indexes of S1 and S2 listed in Table 1 confirm this independence, although these indexes are not constant. The variation of these indexes is induced by other experimental conditions than irradiation intensity. For example, for some reasons the spatial distribution is not so strictly Gaussian. This distortion of the laser beam affects the results of CA Z-scan experiments more remarkably than those of the OA Z-scan. As for S3, the insignificant nonlinear absorption leads to the insignificant nonlinear refraction. In a word, the self-focusing of Ag NPs originates from the creation of hot electrons in the conduction band, and this is a pure third-order nonlinear optical process with the nonlinear refraction index independent of the irradiation intensity.

4. Conclusion

In this paper, the nonlinear optical properties of Ag NPs with different sizes have been investigated. By considering the insignificant nonlinear absorption of the smallest Ag NPs, and the pure SA of the two larger sizes of Ag NPs, along with the previously reported positive nonlinear absorption of 9 nm Ag NPs, the size-dependent nonlinear absorptions are found. These nonlinear absorptions can be compatibly explained from the viewpoint of the electronic transition mechanisms we proposed. These mechanisms can bring new and deep insight into realizing and predicting the nonlinear absorption of Ag and other noble metal NPs. The nonlinear refractions of the larger Ag NPs are self-focusing, which can be attributed to the creation of hot electrons in the s–p conduction band.

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