Wavelength-Dependent Nonlinear Absorption in Palladium Nanoparticles

Chunyu Chen 1,2, Jun Wang 1 and Yachen Gao 1,*

1 College of Electronic Engineering, Heilongjiang University, Harbin 150080, China; c_cy2009@163.com (C.C.); wangjun100386163.com (J.W.)
2 School of Mechatronics Engineering, Daqing Normal University, Daqing 163712, China
* Correspondence: gaoyachen@hlju.edu.cn; Tel.: +86-136-5454-0419

Abstract: This paper aims to study the nonlinear absorption characteristics of palladium nanoparticles (PdNPs) at off-resonant wavelengths. For this purpose, multi-wavelength (500–650 nm) nanosecond Z-scan technique was used. The experimental results indicate that saturated absorption (SA) and the transition from SA to reverse saturated absorption (RSA) can occur, and depends on the excitation wavelength and energy. When the excitation wavelength is constant, with the increase of excitation energy, PdNPs change from SA to RSA. When the excitation energy is constant, with the excitation wavelength approaching surface plasmon resonance (SPR), PdNPs change from SA to RSA. This phenomenon of SA and RSA under multi-wavelength excitation in the off-resonant region provides a supplement for the systematic study of the nonlinear absorption of PdNPs.

Keywords: palladium nanoparticles; nonlinear absorption; wavelength-dependent

1. Introduction

When the light is not strong, the optical response of a material usually scales linearly with the amplitude of the optical electric field. However, at high optical powers, the optical properties of material are no longer linearly related to the intensity of the incident light. As a result, nonlinear optical effects will occur. Among various nonlinear effects, nonlinear absorption is 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. Nonlinear absorption includes saturated absorption (SA) and reverse saturated absorption (RSA). The absorption with the absorption coefficient decreasing with the increase of incident light intensity is called SA. On the contrary, the absorption with the absorption coefficient increasing with the increase of incident light intensity is called RSA.

The rapid development of nanoscience and nanotechnology has provided more opportunities for nonlinear optics than ever. A number of nanomaterials possessing remarkable nonlinear optical properties have been found, which promotes the design and fabrication of nano-scale optoelectronic and photonic devices. Specially, various metal nanoparticles have been considered as potential nonlinear optical materials. Among them, gold and silver nanoparticles have received special attention because they both show a broad surface plasmon resonance (SPR) absorption band in the visible region of the electromagnetic spectrum, which can substantially enhance their nonlinear optical properties [1,2].

In the case of some transition metal nanoparticles such as platinum and palladium, although their SPR is in the ultraviolet region, they still show interesting nonlinear optical properties in the visible region. Correspondingly, many researches on the nonlinearity of platinum and palladium nanomaterials have been carried out [3–13]. In 2002, S. L. Qu et al. studied the optical properties of platinum nanoparticles (PtNPs) excited by a pulse of 8 ns and 532 nm. They found that PtNPs showed strong optical limiting properties and discussed the optical limiting mechanism in terms of the interband transition [3]. In
2005, Y. C. Gao et al. studied the PVP-Pt nanospheres using open-aperture Z-scan under 532 nm nanosecond pulsed laser with relatively weak energy. They observed the transition of optical absorption from saturated absorption (SA) to reverse saturated absorption (RSA) and theoretically analyzed the effect using a proposed formula [4]. In 2009, R. A. Ganeev et al. carried out a Z-scan measure of PtNPs using a 50 ps laser pulse with a wavelength of 1064 nm and realized mode-locking in the Nd laser using PtNPs [5]. In 2011, G. H. Fan et al. prepared palladium nanoparticles (PdNPs) with particle size 2–6 nm by a photochemical decomposition method, and studied the nonlinear optical absorption of PdNPs under the excitation of 532 nm nanosecond laser pulse. They found that PdNPs showed SA at the lower light strength of $3.28 \times 10^{11}$ W/m$^2$, and RSA at the higher light strength of $7.96 \times 10^{11}$ W/m$^2$ [6]. In 2013, K. B. Manjunatha et al. investigated the nonlinear optical properties of palladium metal-organic complex by Z-scan using a nanosecond laser with a 532 nm wavelength at different excitation energies. They found that the sample had good optical power limiting characteristics which was caused by RSA [7,8]. In 2016, Guanghua Fan et al. used 800 nm and 515 nm laser pulses to carry out Z-scan experiments. It was found that with the increase of hydrogen concentration, PdNPs changed from SA to RSA. SA was believed to be caused by single photon absorption between the d-band and conduction band of PdNPs, and RSA was caused by two-photon absorption (TPA) between the d-band and conduction band [9]. In 2019, in order to optimize the stable electrochemistry behavior of platinum and efficient plasma excitation of gold, Rheinberger et al. studied the electrochemistry and surface plasmon resonance spectroscopy of a sputtering film of Au/Pt [10]. In 2019, S. S. Cai et al. used palladium film to realize SPR excitation of fiber grating, which provides a promising technology for hydrogen detection [11].

At present, the synthesis [12–23], characterization [12–23] and linear optical properties [13–15,17] of PdNPs have been studied a lot. And several groups have already conducted investigations on the nonlinear optical absorption of PdNPs [7–9]; these studies were performed only at the wavelengths of about 500 nm and 800 nm. In fact, nonlinear optical absorption properties are also wavelength-dependent and energy-dependent. Therefore, it is necessary to systematically study the broadband nonlinear optical absorption of PdNPs in view of its applications and theory. In this contribution, we studied the nonlinear absorption of PdNPs using a broadband wavelength laser (ranging from 500 nm to 650 nm), which allowed us to know the dependence of nonlinear absorption on wavelength. This conclusion can provide theoretical support for the application of PdNPs as a broadband saturable absorber and optical limiter.

2. Materials and Methods

PdNPs were prepared using a water bath method [24]. Firstly, 10 mL 2 mmol/L Pd(NO$_3$)$_2$·2H$_2$O solution and 10 mL 2 mmol/L H$_4$[Si(W$_3$O$_{10}$)$_4$]·xH$_2$O solution were mixed. 1 mL C$_3$H$_8$O was added. 0.2 g polyvinylpyrrolidone (PVP) was added. Aging time was 30 min, and during aging, the color of the solution did not change significantly. Secondly, the water bath was heated at 60 °C and stirred by magnetic force. The reaction lasted for about 12 min until the solution turned grey and black. Lastly, after centrifugation, the precipitates were washed with dilute NH$_3$·H$_2$O, then washed with ultrapure water and absolute ethanol several times, and then dried in a vacuum drying incubator at 60 °C for 6 h to prepare the PdNPs.

The PdNPs were observed by scanning electron microscopy (SEM). The ultraviolet-visible absorption spectrum of the PdNPs was measured by using Ocean Optical USB 4000 spectrometer. The nonlinear absorption properties of the PdNPs were studied by the typical open aperture (OA) Z-scan technique [25]. In Z-scan measurement, a nanosecond Nd:YAG laser (6 ns pulse width operating at 10 Hz) and optical parametric oscillator (OPO) were used to generate laser pulses with tunable wavelengths. The spatial distribution of the pulses was close to a Gaussian distribution. The PdNP ethanol solution was loaded into a 2 mm quartz cuvette. The linear transmission of the sample was 40% at 500 nm. The
waist radius of the laser beam was measured to be \( \omega_0 = 50 \, \mu\text{m} \) with the blade method. The sample was mounted on a mobile platform and was moved along the beam axis (Z-axis). The incident and transmitted laser pulse energies for each z position were recorded by a computer.

3. Results and Discussion

The characteristics of the PdNPs are shown in Figure 1. Figure 1a is the photo of the PdNPs, and the incident light illuminating is from the illumination of the lab. The sample is khaki-colored, which results from the selective optical absorption of the sample. Figure 1b is the SEM appearance of PdNPs, which implies the nanoparticle is sphere. The particle diameter is 16 nm \( \pm 2 \, \text{nm} \). Figure 1c shows the linear absorption spectrum of PdNPs. Obviously, there is an absorption peak at about 286 nm which is due to SPR.

![Figure 1. Characteristics of PdNPs. (a) Photo of the sample. (b) SEM image. (c) Linear absorption spectrum.](image)

The nonlinear absorption characteristics of PdNPs were studied in the wavelength range of 500 nm to 650 nm by using OA Z-scan. Representative experimental results at wavelengths of 500 nm, 550 nm, 600 nm and 650 nm were shown in Figure 2a–d where the normalized transmission changing with the Z position was given under different excitation energies of 630 \( \mu\text{J} \), 730 \( \mu\text{J} \) and 752 \( \mu\text{J} \), respectively. The normalized transmission is the measured transmission divided by the linear transmission of 40%.

As shown in Figure 2a, when the wavelength of the laser used in the experiment is 500 nm, under three excitation energies (630 \( \mu\text{J} \), 730 \( \mu\text{J} \), 752 \( \mu\text{J} \)), the Z-scan traces recorded show an increasing transmission around the focal point (sample position, \( z = 0 \)), but a dip appears at the focal point. The shape of the Z-scan curve suggests that the sample exhibits the transformation from SA to RSA. With the increase of excitation energy, the peak value of both wings decreases and the bandwidth increases, while the valley becomes deeper and deeper, which indicates that the sample shows stronger RSA at higher laser energy. Figure 2b shows the experimental results obtained at 550 nm laser wavelength, whose curves are basically similar to those in Figure 2a. But the amplitude of peaks and valleys in Figure 2b are smaller than those in Figure 2a. Figure 2c shows that when the wavelength is 600 nm and the excitation energy is weaker (630 \( \mu\text{J} \), 730 \( \mu\text{J} \)), the sample displays SA. But when the excitation energy increases to 752 \( \mu\text{J} \), the transmission of the sample increases firstly and then decreases, which means the transformation from SA to RSA. Figure 2d is the experimental result obtained at wavelength of 650 nm. Similarly, when laser energy is weaker (630 \( \mu\text{J} \), 730 \( \mu\text{J} \)), the sample exhibits SA, but transforms from SA to RSA at higher energy (752 \( \mu\text{J} \)). Relatively, the amplitude of peaks and valleys in Figure 2d are smaller than those in Figure 2c.

In order to better understand the results above, the relationship between the normalized transmission of PdNPs and the incident laser pulse energy density was shown in Figure 3a–d.
Figure 2. Normalized transmission of PdNPs for open aperture Z-scan measurement under different wavelengths of (a) 500 nm, (b) 550 nm, (c) 600 nm and (d) 650 nm. The dotted lines are experimental data while the solid lines are theoretical fits.

Figure 3. The relationship curve between the normalized transmission of PdNPs and the incident laser pulse energy density under different wavelengths of (a) 500 nm, (b) 550 nm, (c) 600 nm and (d) 650 nm. The dotted lines are experimental data.

From Figure 3a,b, we can found that the transmission of the sample first increases with laser influence, then decreases, which means the transformation from SA to RSA. In
Figure 3c,d, when laser energies are 630 μJ, 730 μJ, the normalized transmission increases with laser influence, which means only SA. At 752 μJ, the transmission increases first and then decreases, which implies transformation from SA to RSA.

The results of the Z-scan experiment above can be analyzed via a hypothetical energy level diagram shown in Figure 4. Under the excitation of the laser pulse, the external field causes the collective oscillation of electrons in the conduction band. As the sample approaches the focal point, the light strength increases, which leads to nonlinear absorption. Most of the outermost electrons in the d-band and the quasi-electrons in the sp conduction band near the Fermi-level transitions from the ground state to the excited state, resulting in the reduction of free electrons in the ground state and the plasma bleaching of the ground state. The light intensity is so high that all the electrons available for absorption of photons have been excited. Hence, there are no other electrons to absorb photons. The transmission is the largest at the focal point and SA is formed. With the increase of excitation energy, the electrons in the d-band absorb two photons simultaneously and transition to sp-band, or transition to the excited state. In these processes, there are also two-photon absorption [6,9]. In the two-photon absorption process, the free carriers in the excited state continue to absorb photons, and the electrons transition from the excited state to the higher second excited state. The transmission increases to a certain extent (this part is SA) before the focal point, and then begins to decline until it reaches the focal point with the maximum light strength and the lowest transmission, forming RSA. The excitation wavelength is from 500 nm to 650 nm, while the SPR wavelength of PdNPs is 286 nm, which makes the nonlinear absorption of PdNPs happen easier at 500 nm and 550 nm, which are closer to SPR under the same excitation energy. At the same excitation wavelength, the excitation energy is larger, and the electrons get the interband transition energy more quickly, which makes it easier to realize the nonlinear absorption of PdNPs. Since 600 nm and 650 nm are far from SPR wavelengths of PdNPs, nonlinear absorption incurs difficulty and results in a small Z-scan signal, as shown in Figure 2c,d.

![Figure 4](image-url) Energy diagram for optical transition in Pd NPs. Under the excitation of light pulse, the external field causes the collective oscillation of electrons in the conduction band. Most of the outermost electrons in the d-band and the quasi-electrons in the sp-band near the Fermi-level transition from the ground state to the excited state resulting in the reduction of free electrons in the ground state and the plasma bleaching of the ground state. SA is formed. With the increase of excitation energy, the electrons in the d-band absorb two photons simultaneously and transition to sp-band, or transition to the excited state. These processes are two-photon absorption processes.

In addition to the qualitative discussion of nonlinearity, it is necessary to analyze quantitatively the nonlinear absorption characteristics of PdNPs. Herein, the total absorption coefficient α(I) can be expressed using Equation (1) [3].

\[
α(I) = \frac{α_0}{1 + I/I_s} + βI
\]  

(1)
where $\alpha_0$ is the linear absorption coefficient, $I_s$ is the saturation strength, $\beta$ is the nonlinear absorption coefficient, $I$ is the laser intensity. The first term on the right side of Equation (1) is SA, and the second term is RSA.

The intensity of the Gaussian beam used in the experiment is expressed using Equation (2) [26].

$$I(z) = \frac{I_0}{1 + \frac{z^2}{z_0^2}}$$

where $z$ is the displacement of the sample relative to $z = 0$; $z_0$ is the Rayleigh diffraction length. By combining Equation (1) with Equation (2), the nonlinear absorption coefficient can be expressed using Equation (3).

$$\alpha(I) = \alpha_0 \left(1 + \frac{I_0}{1 + \frac{z^2}{z_0^2}}\right) + \frac{\beta I_0}{1 + \frac{z^2}{z_0^2}}$$

The relationship between absorption and transmission [25] is expressed using Equation (4).

$$T(z) = 1 - \alpha(I) L_{eff}$$

where $L_{eff}$ is the effective length of the sample. By combining Equation (3) and Equation (4), the normalized transmission can be expressed using Equation (5).

$$T(z) = 1 - \frac{\alpha_0 L_{eff}}{1 + \frac{I_0}{(1+\frac{z^2}{z_0^2})I_0}} - \frac{\beta I_0 L_{eff}}{1 + \frac{z^2}{z_0^2}}$$

Equation (5) is used to fit the experimental data, where $\alpha_0 = 0.0458 \text{ m}^{-1}$, $L_{eff} = 0.0013 \text{ m}$, $z_0 = 15.7 \text{ mm}$ and the theoretical fitting results are shown in Figure 2 with solid lines. It can be found that the theoretical fitting curve is in good agreement with the experimental data. Correspondingly, the saturation strength $I_s$ and the nonlinear absorption coefficient $\beta$ are obtained and shown in Table 1.

| $\lambda$ (nm) | $E$ (µJ) | $I_0$ (W/m²) | $I_s$ (W/m²) | $\beta$ (m/W) |
|---------------|-----------|--------------|-------------|----------------|
| 500           | 630       | $2.51 \times 10^{13}$ | $1.32 \times 10^{12}$ | $1.46 \times 10^{-11}$ |
|               | 730       | $2.91 \times 10^{13}$ | $4.16 \times 10^{11}$ | $1.1 \times 10^{-11}$ |
|               | 752       | $2.99 \times 10^{13}$ | $1.36 \times 10^{12}$ | $2.53 \times 10^{-11}$ |
| 550           | 630       | $2.51 \times 10^{13}$ | $3.59 \times 10^{11}$ | $5.14 \times 10^{-12}$ |
|               | 730       | $2.91 \times 10^{13}$ | $2.43 \times 10^{11}$ | $9.59 \times 10^{-12}$ |
|               | 752       | $2.99 \times 10^{13}$ | $1.2 \times 10^{12}$ | $2.8 \times 10^{-11}$ |
| 600           | 630       | $2.51 \times 10^{13}$ | $1.05 \times 10^{12}$ | $0$ |
|               | 730       | $2.91 \times 10^{13}$ | $8.32 \times 10^{11}$ | $0$ |
|               | 752       | $2.99 \times 10^{13}$ | $4.47 \times 10^{11}$ | $4.92 \times 10^{-12}$ |
| 650           | 630       | $2.51 \times 10^{13}$ | $1.26 \times 10^{12}$ | $0$ |
|               | 730       | $2.91 \times 10^{13}$ | $8.32 \times 10^{11}$ | $0$ |
|               | 752       | $2.99 \times 10^{13}$ | $5.99 \times 10^{11}$ | $1.8 \times 10^{-12}$ |

In Figure 5a, the linear absorption spectrum of PdNPs and the saturation strength $I_s$ at excitation energies of 630 µJ, 730 µJ and 752 µJ are plotted as double Y-axis characteristic curves, and the colored dotted lines represent the saturation strength curve varying with the wavelength. The black line is the linear absorption spectrum. In Figure 5b, the characteristic curves of the linear absorption spectrum and the nonlinear absorption coefficient $\beta$ at the excitation energies of the PdNPs at 630 µJ, 730 µJ and 752 µJ are plotted as a double Y-axis characteristic curve, and the colored dotted lines represent the nonlinear
absorption coefficient curve varying with the wavelength. The black line is the linear absorption spectrum.

![Figure 5](image.png)

Figure 5. The characteristic curve of wavelength-dependent nonlinear absorption. Double Y-axis characteristic curves are shown in (a), where colored dotted lines represent the saturation strength $I_s$, and for comparison, the black line represents linear absorption spectrum. Double Y-axis characteristic curves are shown in (b), where colored dotted lines represent the nonlinear absorption coefficient $\beta$, and for comparison, the black line represents linear absorption spectrum.

Figure 5a shows that at different energies, with the increase of the wavelength away from SPR, the saturated absorption coefficient first decreases and then increases. From Figure 5b, we can see that when the excitation wavelength is near the SPR peak value, the nonlinear absorption coefficient is larger. At a fixed excitation wavelength, when energy is greater, the nonlinear absorption coefficient is larger. The increase of saturation strength near the SPR wavelength is due to the nonlinear resonant enhancement. When the excitation energy is moderate, the bleaching of the ground state plasmon will lead to SA. However, when the excitation wavelength is different, the number of electrons in the conduction band is different. The wavelength is near SPR; it is easier to realize the ground state plasma bleaching. The greater the excitation energy is, the more electrons will be transferred to the conduction band to realize the ground state plasma bleaching. In the process of plasma ground state bleaching, the absorptivity decreases and the saturation strength increases. At the wavelength far away from SPR, the decrease of the nonlinear absorption coefficient is due to the enhancement of free carrier absorption.

4. Conclusions

The nonlinear absorption of PdNPs was studied by the OA Z-scan method using 500 nm, 550 nm, 600 nm and 650 nm nanosecond pulsed lasers. The results show that, although the SPR wavelength of PdNPs is far away from the excitation wavelength, the SA and the transition from SA to RSA can still occur. Moreover, the nonlinear absorption is wavelength- and energy-dependent. This research implies that PdNPs can be used to develop broadband saturable absorbers and optical limiters.

Author Contributions: Methodology and writing—original draft preparation, C.C.; investigation, Y.G.; data curation, J.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Provincial Natural Science Foundation: F2018027.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The experimental data were measured in the Femtosecond Laser Laboratory of Heilongjiang University.

Conflicts of Interest: The authors declare no conflict of interest.
