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Application of the nonlinear optical properties of platinum nanoparticles for the mode locking of Nd:glass laser

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Abstract We analyzed the saturated absorption of a platinum nanoparticle suspension using 1064-nm, 50-ps pulses at different intensities of laser radiation. The concurrence of reverse saturated absorption and saturated absorption at high intensities allowed for defining the saturated intensity for different suspensions of Pt nanoparticles ($5 \times 10^9\ \mathrm{W\,cm^{-2}}$). This suspension was used for the mode locking of laser radiation in a Nd:glass oscillator ($\lambda = 1054$ nm). We achieved a stable generation of picosecond pulse trains with pulse duration of 5 ps using the mode locker based on the platinum nanoparticle suspension. The comparison of this nanoparticle-based mode locker with the conventional dye films showed the better stability of picosecond pulse generation and longer lifetime in the former case.

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1 Introduction

The enhanced nonlinear optical response of nanostructured materials induced by quantum confinement has attracted much interest, which induced novel applications of these structures in optoelectronics and optical switchers and limiters, as well as in optical computers, optical memories, and nonlinear spectroscopy. High values of third-order nonlinear susceptibility, especially near the surface plasmon resonances (SPRs) of nanostructured materials, are the trademark of these media, in particular metal nanoparticles.

The third-order nonlinear optical susceptibilities of different nanoparticle-containing media vary in a broad range. The nonlinearities responsible for variation of refractive and absorptive properties are of especial importance since these nonlinearities considerably change the propagation of intense light through the medium. Among them the saturated absorption attracted much interest due to the practical applications of this process. The saturated absorption in nanoparticle-containing media has previously been analyzed using various materials. In particular, the saturated absorption of Ag nanoparticles embedded in silica glass matrices has previously been observed as far as 355 nm. This process has also been reported in Ag:water suspension in the case of 397.5-nm, 1.2-ps radiation [1, 2].

In this paper, we present nonlinear optical studies of a platinum nanoparticle suspension (PNS). Our results show that this suspension could be considered as an effective mode locker for neodymium glass lasers. We present our measurements of the saturated and reverse saturated absorption of this suspension. We also demonstrate the generation of a train of picosecond pulses in a Nd:glass oscillator using this saturated absorber.

2 Experimental arrangements

A picosecond Nd:YAG laser operating at a 2-Hz pulse-repetition rate was used in most of our experiments. A single pulse ($t = 50$ ps) was amplified up to the energy of $E = 1.5$ mJ. The nonlinear optical characteristics of a nanoparticle-containing suspension were studied using the z-scan technique [3] at the wavelength of this laser ($\lambda = 1064$ nm). The experimental setup has been reported previously in [4]. The calibration of the z-scan setup was carried out using CS_2. The PNS was placed in 3-mm fused-silica

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cells to carry out the z-scan measurements. The nonlinear absorption was analyzed using the open-aperture scheme, when the sample's transmission was measured without the aperture. In this case, a detector measuring the energy of the propagated beam had a sufficiently broad aperture and was placed at such a distance from the sample that the transmitted radiation was entirely detected. The nonlinear refractive index of the suspension was measured using the closed-aperture scheme, when a small aperture was inserted in the far field after the medium. The fitting of the theoretical curves allowed for defining the nonlinear optical characteristics of this suspension.

The PNS was purchased from Wako Pure Chemical Industries, Ltd. (Japan). The initial concentration of purchased suspension was 10 mM. The molar concentration of platinum nanoparticles in the suspension in these experiments was varied between 0.05 and 1 mM. The solvents of this suspension were water and ethanol. The nanoparticles were protected against aggregation by adding polyvinylpyrrolidone (PVP). PVP has the advantage of accepting high concentrations of various guest molecules and atoms without the loss of its good optical properties (in particular a negligible scattering). PVP has been commonly used in suspensions to protect nanoparticles against aggregation. PVP also serves as a dual-functional reductant and stabilizer for the facile synthesis of noble-metal nanoparticles in liquid suspensions (see for example [5]). The analysis of nanoparticle sizes was carried out using a transmission electron microscope (JEM-2010F). The nanoparticle sizes are of crucial importance when one considers the nonlinear optical processes, since the influence of quantum confinement on the nonlinear optical properties of media strongly depends on the spatial extension of such structures. The mean size of Pt nanoparticles was defined to be 2.8 nm, close to the data presented by the manufacturer (3–5 nm), and showed a relatively narrow particle size distribution.

3 Results and discussion

Figures 1 and 2 present the open-aperture z-scans of PNS at molar concentration 0.15 mM using different laser radiation intensities. The linear transmittance of the 3-mm-thick cell containing this suspension at the wavelength of laser radiation (1064 nm) was 40%. At low intensities (less than 2×10^{10} W cm^{-2}), the characteristic dependence of pure saturated absorption was observed (Fig. 1). With further growth of laser intensity, the normalized transmittance dependence $T(z)$ was broadened and at highest intensities the influence of an additional nonlinear optical process was observed that can be attributed to both the reverse saturated absorption and two-photon absorption (Fig. 2). The latter process could be considered insignificant since the spectral characterization of PNS did not show the absorption lines in the absorbance curve (see inset in Fig. 3). One can determine from these dependences the range of intensities at which the efficient saturated absorption can be achieved without the influence of positive nonlinear absorption (Fig. 3). The positive nonlinear absorption can be defined as the one leading to the absorption of propagated laser radiation in the medium. The negative nonlinear absorption (i.e. the saturated absorption) is the one leading to the increase of propagation of the laser radiation through the medium.

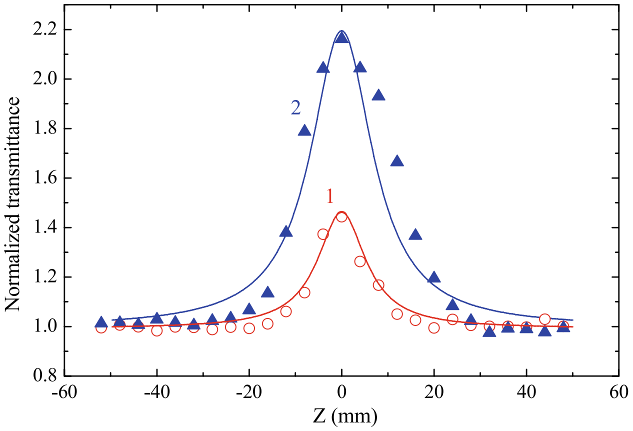

Fig. 1 The normalized open-aperture z-scan dependences measured using the (1) 0.9×10^{10} and (2) 1.73×10^{10} W cm^{-2} intensities of laser radiation. *Solid curves* are the theoretical fits

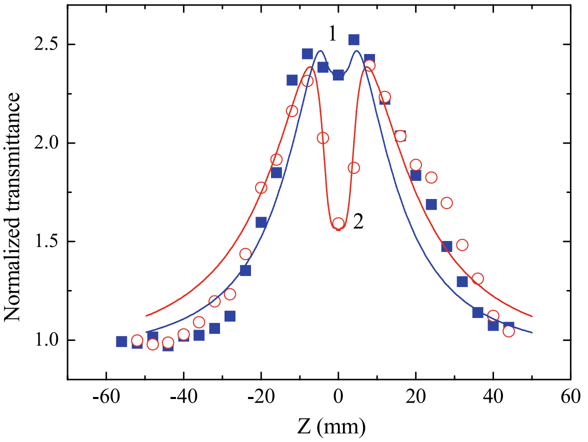

Fig. 2 The normalized open-aperture z-scan dependences measured using the (1) 3.7×10^{10} and (2) 7×10^{10} W cm^{-2} intensities of laser radiation. *Solid curves* are the theoretical fits

The Pt nanoparticle suspension showed a weak positive refractive nonlinearity, while it demonstrated a strong saturated absorption dominating over positive nonlinear refraction in the closed-aperture z-scans. The measurements of the saturated absorption were carried out using the open-aperture z-scan scheme (Fig. 1). The curves 1 and 2 presented in this figure differ from each other by the ratio of the used intensities of 0.52:1 (i.e. 0.9×10^{10} and $1.73 \times$

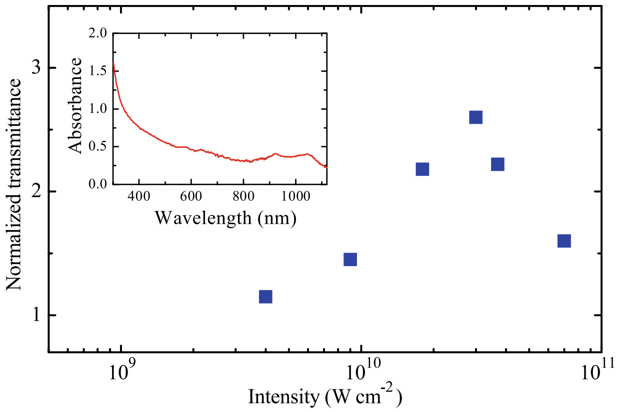

Fig. 3 Dependence of the maximum value of the normalized transmittance of 3-mm-thick PNS on the laser intensity. *Inset*: absorbance curve of the 3-mm-thick cell containing PNS

10^{10} W cm^{-2}). For the open-aperture z-scan, the normalized transmittance [3]

$$T(z) = \sum_{m=0}^{\propto} \frac{[\frac{-\beta(I) I_0 L_s^{\text{eff}}}{1+(z^2/z_0^2)}]^m}{(m+1)^{3/2}}, \tag{1}$$

together with the nonlinear absorption coefficient and absorption coefficient defined in the case of saturated absorption by the relations

$$\beta(I) = \frac{\alpha(I) - \alpha_0}{I}, \tag{2}$$

$$\alpha(I) = \alpha_0 \frac{1}{1 + (I/I_{\text{sat}})} \tag{3}$$

can be used for the fitting and definition of the negative nonlinear absorption coefficient and saturation intensity (I_{sat}) of the Pt nanoparticle suspension. Here I_0 is the laser radiation intensity at the focal plane, $L_s^{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ is the effective length of the sample, α_0 is the linear absorption coefficient, L is the length of the medium under investigation, $z_0 = k(w_0)^2/2$ is the diffraction length, $k = 2\pi/\lambda$ is the wave number, w_0 is the beam waist radius, and I is the variable laser radiation intensity along the z-axis. These curves were fitted with the experimental results. The value of the saturation absorption coefficient of PNS was found to be $\beta = -6 \times 10^{-11}$ cm W^{-1}. The relation between the nonlinear absorption coefficient and saturated intensity can be written as $\beta = -\alpha_0/I_{\text{sat}}$. The corresponding saturation intensity defined from the z-scans was 5×10^9 W cm^{-2}. The saturated absorption in Pt nanoparticle-containing media has previously been reported in [6] using nanosecond laser pulses (8 ns, 532 nm). The application of femtosecond pulses (120 fs, 800 nm) has also been demonstrated for obtaining the saturated absorption properties of these nanoparticle suspensions [7]. Our results using near-infrared picosecond laser pulses (50 ps, 1064 nm) showed stronger saturated absorption compared with the cases of shorter wavelength nanosecond and femtosecond pulses. Note that, while for nanosecond pulses the saturated absorption increased the propagation of laser radiation through the PNS only up to 1.1 times [6], this factor of propagation in the case of picosecond pulses of 1064-nm radiation was increased up to 2.6 times (Fig. 3).

In the case of PNS, the estimated volume part of metal nanoparticles was around 10^{-4}. The corresponding nonlinear absorption coefficient and nonlinear refractive index of platinum nanoparticles measured by open- and closed-aperture z-scans were estimated to be -6×10^{-7} cm W^{-1} and 4×10^{-10} cm^2 W^{-1}, respectively.

We observed the change from saturated absorption to reverse saturated absorption in PNS at the laser intensities exceeding 3.5×10^{10} W cm^{-2} (Figs. 2 and 3). The open-aperture $T(z)$ dependences at higher intensities of laser radiation can be described in terms of concurrency between the positive and negative absorption nonlinearities. The changeover from saturated absorption to reverse saturated absorption in the Pt nanoparticles protected by PVP was studied in [6] using 532-nm nanosecond radiation. Previously, it was also reported that PVP did not show the nonlinear absorption effect [6]. The total absorption coefficient, which combines the saturated absorption coefficient and reverse saturated absorption coefficient, can be presented as

$$\alpha(I) = \alpha_0 \frac{1}{1 + I/I_{\text{sat}}} + \beta_p I, \tag{4}$$

where the first and second terms describe negative and positive nonlinear absorption, respectively. β_p is the positive nonlinear absorption coefficient, which can be defined using (1). Solid curves in Fig. 2 present the theoretical fits with the experimental open-aperture z-scans using two different intensities of laser radiation. The best fit for the joint influence of the negative and positive nonlinear absorption of PNS was obtained assuming $I_{\text{sat}} = 6 \times 10^9$ W cm^{-2} and $\beta_p = 4 \times 10^{-11}$ cm W^{-1}.

The appearance of saturated absorption could be caused by the bleaching of the ground state at moderate intensities, while the reverse saturated absorption can be attributed to the transient absorption caused by free carriers, which plays an important role at higher pump intensity. Currently, it is not clear what the exact phenomenon is that causes saturated absorption in platinum nanoparticles. We observed saturated absorption, which is usually linked to the SPR in nanoparticles [8]. At the same time, we note that the platinum SPR (215 nm [9]) lies far away from the excitation source (1064 nm). This process, as well as reverse saturated absorption of Pt nanoparticles, has previously been reported by different groups using various excitation conditions (8 ns, 532 nm [6, 10], 100 fs, 404 nm [11], 110 fs, 800 nm [7], and

35 ps and 28 ns, 1064 nm [12]). No exact explanations of the observed saturated processes were offered in those studies. Some speculations of the origin of the reverse saturated absorption include the consideration of the *d* band of Pt, which lies close to the $s-p$ band. This makes electron interband transitions occur easily under the excitation of the laser. The appearing free electrons strengthen the transient absorptive nonlinearity of Pt nanoparticles responsible for the reverse saturated absorption. At the same time, we note that the mechanisms leading to the saturated and reverse saturated absorption in Pt nanoparticles still remain unknown and further studies are needed for the definition of the processes leading to this phenomenon.

Our studies showed that saturated absorption and reverse saturated absorption are the main nonlinear optical processes during propagation of short laser pulses through this suspension, while the role of the optical Kerr effect was insignificant. The saturated absorption plays a crucial role in achieving the passive mode locking (PML) conditions of short-pulse generation. Previously, PML has been achieved using various techniques and materials: dyes, semiconductor saturated absorption mirrors, quantum dots, LiF F-centers, etc, while the optical Kerr effect was used for Kerr lens modulation and ultra-short-pulse generation. Variations of the nonlinear optical characteristics of some of these materials, in particular dyes, due to such factors as intense light interaction, solvents, temperature, etc, lead to the changes of parameters of the laser radiation propagating through such media. The irreversible changes in polymethine dye mode lockers lead to their nonlinear optical parameter variations (saturation intensities, nonlinear absorption coefficients, etc.), which follow by the distortion of the PML.

Below we present the application of the saturated absorption properties of PNS analyzed in this paper for achieving the PML conditions in a Nd:glass laser. To our best knowledge, it is the first time that a nanoparticle-containing medium was used for mode locking and generation of short laser pulses.

The oscillator cavity consisted of a 100% reflecting mirror-containing 2-mm-thick cell, a 6-mm aperture, a 65-mm-long Nd:glass rod, and a 70% reflecting output mirror. The cell contained two glass slides. One of these slides was the 100% reflection mirror at the wavelength of 1054 nm. The 1 mM suspension of platinum nanoparticles was pumped through the cell. Initially, we achieved the free running mode regime of generation at the conditions when pure ethanol was pumped through the cell (Fig. 4a). Once we changed the ethanol for the PNS, the PML regime was achieved and a train of picosecond pulses was generated (Fig. 4b) at 1-Hz pulse-repetition rate.

As was mentioned above, the reverse saturated absorption in a Pt nanoparticle suspension was observed at a relatively high intensity of laser radiation ($I > 3 \times 10^{10}$ W cm^{-2}). The maximum intensity of the laser field inside the oscillator cavity was considerably weaker (9×10^{9} W cm^{-2}). So, the reverse saturated absorption cannot influence the dynamics of mode locking in picosecond lasers using a Pt nanoparticle-based mode locker. The same can be said about the two-photon absorption, which could not play an important role at the intensities used in the laser cavity. In fact, Pt nanoparticles do not absorb over almost the entire UV–vis region, as their surface plasmon band exhibits a sharp feature with a maximum in the far-UV region [13–15].

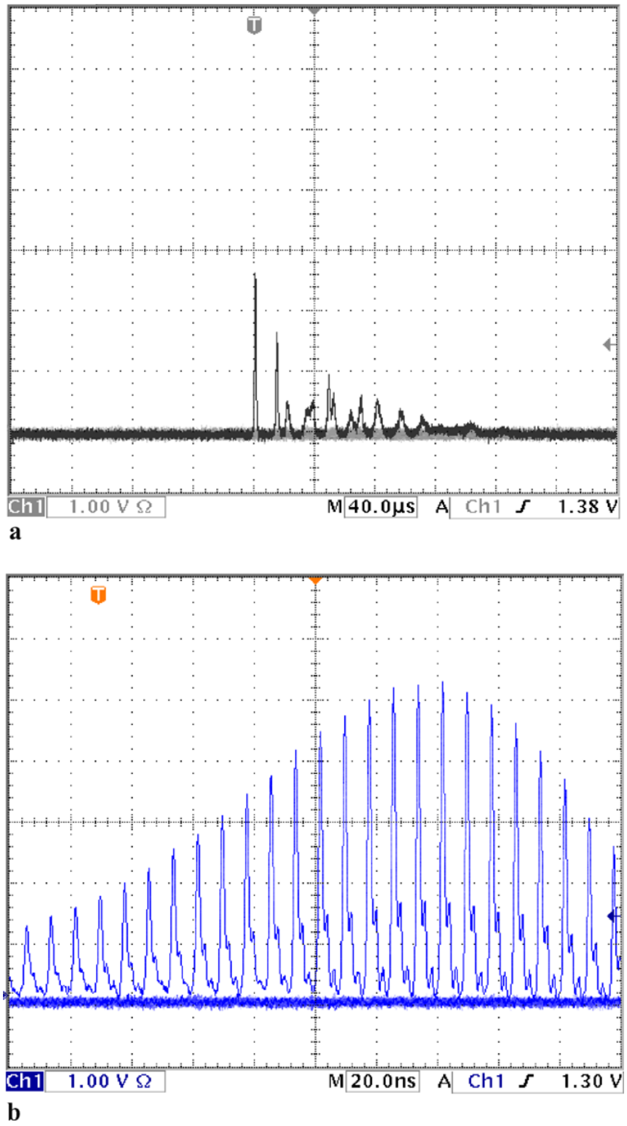

Fig. 4 Oscilloscope traces of the **a** free-running mode and **b** mode locking of the Nd:glass laser

We did not observe considerable variations of picosecond pulse generation at different pumps of the laser cavity. The mode locking was achieved at different concentrations of the platinum nanoparticle suspension. Note that we analyzed other nanoparticle suspensions purchased from the same manufacturer (i.e. Au, Ag, and Pd nanoparticle suspensions) and did not observe the mode locking in the neodymium glass laser.

The stability of picosecond pulse generation was analyzed for a period of one month. No visible degradation or change of the dynamics of picosecond pulse train generation was observed during this period. We also used this suspension without the pumping through the cell, but just using the filled cell inside the cavity. In the second scheme, we filled the cell containing two transparent glass substrates (without the mirror) with the platinum nanoparticle suspension and inserted it inside the cavity of the laser oscillator containing a Nd:glass rod and 100% and 70% reflecting mirrors (without any electro-optic or mode-locking elements). The cell was placed close to the 100% reflecting mirror. The generation conditions remained the same; however, the pulse-repetition rate was decreased to 0.2 Hz to achieve the stable regime of lasing of the picosecond pulse train. Single-shot autocorrelation measurements of pulse duration showed that the pulse duration was 5 ps. The comparison of this nanoparticle-based mode locker with the conventional dye films demonstrated the better stability of picosecond pulse generation and longer lifetime in the former case.

The application of PNS in a Nd:YAG laser was less favorable and did not allow us to achieve the same results as in the case of the neodymium glass laser. This was probably due to the higher amplification cross section in the Nd:YAG laser, which did not allow the achievement of the optimal relations between the induced losses and renewable enhancement of radiation intensity inside the cavity.

4 Conclusions

In conclusion, we presented studies of the nonlinear optical properties of a commercially available platinum nanoparticle suspension using 1064-nm picosecond laser radiation. The basic mechanisms involved in the nonlinear optical response of nanoparticle-containing materials are quite different. However, among the mechanisms involved, the excited-state saturation and reverse saturated absorption play a crucial role in the variation of the absorption of the platinum nanoparticle suspension. The simultaneous appearance of the saturated and reverse saturated absorption of PNS was observed in the case of high laser intensity. We defined the saturated absorption and reverse saturated absorption coefficients and saturated intensity of PNS.

We applied this suspension as a saturated absorber for achieving mode locking in a Nd:glass laser ($\lambda = 1054$ nm). Among the most important properties of saturated absorbers are the modulation depth, unsaturable losses, recovery time, saturation fluence and intensity, as well as damage threshold. The new saturated absorber studied in the present paper showed stable characteristics of saturation intensity and unsaturated losses, high modulation depth, long lifetime, and high damage threshold. Further optimization of the application of such a saturated absorber can pave the way for the application of platinum nanoparticles as solid-state structures, for example after drying the suspension.

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