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# Saturable absorption and reverse saturable absorption in platinum nanoparticles

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#### Abstract

The optical nonlinear absorption of the aqueous solution of platinum nanospheres protected by poly (*N*-vinyl-2-pyrrolidone) was investigated using open aperture *Z*-scan method with nanosecond pulse laser at the wavelength of 532 nm. A shift from saturable absorption to reverse saturable absorption was observed at higher input pump intensities. The transition process was analyzed using a phenomenological model based on nonlinear absorption coefficient and saturation intensity.

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#### 1. Introduction

Nanostructured materials have unique physical and chemical properties as a result of their small size. These properties differ largely from those of the corresponding single molecules and bulk materials [1]. In recent years, nanomaterials have attracted substantial attention, due to their possible applications in optoelectronics and anticipated versatility in providing a deeper understanding of size-sealed structure–function relationships [2]. For example, intensive studies are currently being pursued in the nonlinear optical properties of noble metal nanoparticles

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[2–13], owing to their potential use in optical and nonlinear optical devices [3].

In this context, gold and silver nanoparticles have received special attention [2–12] because they both show a broad absorption band in the visible region of the electromagnetic spectrum. This is substantially different from the flat absorption spectra of the corresponding bulk metals in the same region. The broad absorption band is due to the electromagnetic field-induced collective oscillation of the free conduction electrons occupying states near the Fermi level in the conduction band, which is referred to as surface plasmon resonance (SPR) absorption [4]. Ya-Ping Sun et al. [5] investigated silver-containing metal-halide clusters and nanosols. The optical limiting in the material for nanosecond laser pulses was found to be even stronger than that in the benchmark materials fullerenes and metallophthalocyanine. It has also been demonstrated by Ispasoiu et al. [2] and Zhang et al. [6], respectively, that silver-dendrimer nanocomposite and nanosized polyicosahedral gold-silver cluster could exhibit large optical limiting. On the other hand, we have recently studied the optical nonlinearities and optical limiting behavior in gold and silver nanoparticles based on C<sub>60</sub> [7–10], and found stronger optical limiting in them than that in C<sub>60</sub>. Philip et al. [4] studied the picosecond optical nonlinearity in monolayer-protected gold, silver and gold-silver alloy nanoclusters at 532 nm. They observed the changing from saturable absorption to reverse saturable absorption in gold nanoparticles using Z-scan technique. Because the wavelength of SPR in the gold nanoparticles is 520 nm, and very near the excitation wavelength of 532 nm used in their experiments, they interpreted the flip of saturable absorption to reverse saturable absorption in terms of SPR. Specifically, they attributed the origin of the saturable absorption to the bleach of the ground-state plasmon band occurring at moderate intensities, while attributed reverse saturable absorption to the transient absorption (caused by free carriers) which is significant at higher pump intensity. To our knowledge, however, the research concerning optical nonlinearity in platinum nanoparticles is still rarely reported [11,13]. Moreover, only reverse saturable absorption was observed in [11,13]. In general compounds [14–17], the simultaneous appearance of both saturable absorption and reverse saturable absorption was found and discussed. But the novel phenomenon in platinum nanoparticles has not been reported anywhere.

In this paper, we conduct the investigation on platinum nanoparticles in aqueous solution using 532 nm nanosecond laser pulses. Even though platinum's SPR at 215 nm [18] lies away from excitation wavelength of 532 nm, we still observed saturable absorption at lower fluences which is usually linked to SPR in gold nanoparticles [4]. Furthermore, we found the changeover from saturable absorption to reverse saturable absorption at higher input bump intensities.

#### 2. Samples and experiments

The sample used in our experiment is platinum nanoparticles stabilized by poly (N-vinyl-2-pyrrolidone), denoted as Pt-PVP, which is synthesized by microwave irradiation. Details of sample synthesis and characterization have been discussed in [19]. The average size of Pt-PVP was estimated by transmission electron microscopy (TEM) to be of the order of 2 nm. PVP is a macromolecular polymer with an average molecular weight of 40,000, with which Pt nanoparticles in small size and with narrow size distribution can be obtained. In Pt-PVP, the ratio of PVP to Pt is 5:1 in mole numbers. Pt-PVP was dissolved in water, and the concentration of Pt-PVP aqueous solution is  $2.5 \times 10^{-5}$  M. The sample was contained in a quartz cuvette with a 2 mm thickness, and the linear transmittance of the sample is 70%. The linear absorption spectrum of Pt-PVP aqueous solution is shown in Fig. 1.

The laser used is a frequency-doubled and Q-switched Continuum ns Nd:YAG laser, operating at the repetition rate of 1 Hz and producing 8 ns laser pulses at 532 nm wavelength. The laser pulses are spatially and temporally Gaussian. The open aperture Z-scan experiments were conducted using a typical setup [20]. A lens with a focal length of 308 mm was used to focus laser beam to 110  $\mu$ m in diameter as determined by CCD. The sample cuvette was fixed on a

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