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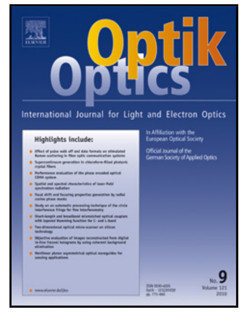

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Demonstration of variation of the nonlinear optical absorption of non-spherical silver nanoparticles

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We study the features of the nonlinear optical response of silver nanoparticles (Ag NPs) of the spherical and triangular shapes synthesized using a citrate-borohydride approach. The Z-scans were used to analyze the nonlinear optical absorption of Ag NPs of different morphology, particularly, the concurrence of saturable and reverse saturable absorption in the solution containing triangular Ag NP. We show the significant contribution to the increase in the normalized transmittance accomplished by photochemical degradation of the non-spherical Ag NPs (extinction maximum of 600 nm) and transformation into the spherical ones (extinction maximum of 400 nm). The nonlinear light scattering is analyzed as well, which showed the contribution to the variation of the sample transmission when it approaches the focal plane.

Keywords silver nanoparticles, nonlinear optical absorption, Z-scans, photochemical degradation

1. Introduction

Noble metal nanoparticles (NPs) have potential applications in the field of nanophotonics due to their strong nonlinear optical response, thus attracting a significant attention [1-5]. As a typical representative of noble metals, silver nanoparticles (Ag NPs) are particularly prominent [6-13].

Plasmon nanoparticles are an important component of such structures. The most studied regularities of these objects are mainly spectra of the extinction. In many cases, the appearance of new properties is found in the location near the plasmon nanoparticles of various objects (molecules, quantum dots, etc.) [14].

There is a variety of manifestations of the variations of the nonlinear optical response in colloidal solutions of nanoparticles, mainly silver and gold [15]. The regularities of nonlinear optical response in plasmon nanoparticles of different shapes are important for understanding the similar properties of hybrid associates. For silver and gold nanoparticles in glasses, polymers, colloidal solutions, the most frequently observed are saturable absorption (SA), reverse saturable absorption (RSA), two-photon absorption (2PA), and nonlinear refraction [16-18]. In most of these cases, studies show the change in the type of nonlinearity of spherical NPs when the intensity of the incident radiation changes.

The analysis of the nonlinear absorption coefficients and nonlinear refractive indices of spherical Ag NPs, as well as the exploration of their potential applications, were reported in a few studies [19-21]. There are experimental studies showing that particle size, morphology and surrounding medium of noble metal NPs have great influence on their nonlinear optical properties [22-25]. The change of incident intensity of probe laser pulse causes the variation of nonlinear optical properties, such as the shift from SA to RSA [26, 27]. As the incident intensity increases, the RSA leads to enhancement of nonlinear absorption in the sample.

However, the small lifetime of a localized plasmon in Ag NPs (~10^{-12} s) and the absence of metastable states in such species, which could participate in RSA, meet certain difficulties with interpretation of experimental observations of the variations of nonlinear optical response of such structures. In favor of such doubts should be added the possibility of dynamic scattering of the laser beam by the nanoparticles and their clusters, as well as the possibility of their photochemical transformation into structures of a different morphology [28].

In this paper, we report the studies of the nonlinear absorptive characteristics of silver nanoparticles of different geometry (spheres, triangular prisms and intermediate aspherical nanoparticles) in colloidal solutions using 10 ns laser pulses at the wavelength of 532 nm. Special attention is paid to the influence of additional abovementioned mechanisms capable of changing the nonlinear optical response of Ag NPs.

2. Experimental arrangements and characterization of the optical spectra of samples

The measurements of the nonlinear optical properties of our samples were carried out by applying the standard Z-scan technique [29]. The Nd:YAG laser generated single pulses (λ = 1064 nm, τ = 10 ns) at 1 Hz repetition rate. The probe second harmonic (λ = 532 nm) of this radiation generated in KDP crystal was focused by a 300-mm focal length spherical lens (Fig. 1a). The laser pulse energy was measured by a first calibrated photodiode and then registered by a digital voltmeter. The 5-mm-thick glass cells containing studied samples were moved along the z-axis through the focal plane of probe pulse using a translating stage. The open-aperture (OA) Z-scan scheme, i.e. the one without aperture in front of second photodiode allowed measuring all transmitted radiation to determine the dependence of the normalized transmittance on the position of sample on the z axis. To observe the contribution to the Z-scan from nonlinear dynamic scattering, a scheme was also used in which a second diode was installed at an angle of 4.5 with regard to the optical axis (Fig. 1b).