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Nonlinear-optical refraction of silver nanoparticle composites

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In this paper, the experimental data on nonlinear refraction of silver nanoparticle composites using a standard *Z*-scan technique are presented. It was found that the colloids of silver nanoparticles of various size possess a defocusing ability. Based on general considerations, one can conclude thermal lens nature of the nonlinear refraction of the colloids. Significantly different magnitudes of the nonlinear refractive index of silver nanoparticles suspended in water and in glycerol can be explained by differences in the specific heat capacity of mentioned fluids. The effective thickness for nonlinear-optical interaction of light with a two-dimensional silver nanoparticle array was estimated.

Keywords: silver nanoparticles, nonlinear optics, *Z*-scan.

1. Introduction

One of the most prominent features of metal nanoparticles (NPs) subjected to the electromagnetic irradiation is their ability to support specific electron excitations, termed localized surface plasmon resonances (LSPR). Noble metal nanoparticles (Au, Ag, Cu) are of prime interest since the frequency of LSPR for those metals occurs at the visible spectral range. Moreover, the resonance frequency can be tuned by varying particles' size and shape as well as the dielectric environment [1]. Unique frequency dependence of the real and imaginary parts of the dielectric function of silver makes the metal more suitable for various applications using nanoparticles, as compared to gold and copper. Indeed, the interband transition threshold for silver is about 4 eV, while the same for gold and copper occurs at 2.3 and 2.6 eV, respectively [2]. Interband transitions in latter cases substantially damp LSPR in Au and Cu nanoparticles. Resonant character of electron density oscillations in metal nanoparticles along with large curvature of the nanoparticle surface results in a giant enhancement of the local electric

field. A number of practical applications of silver NPs is based on that effect such as surface enhanced Raman scattering (SERS) [3] and IR absorption (SEIRA) [4], photovoltaics [5], biosensors [6], to name a few. Field enhancement and specific interactions of LSPR with surrounding medium give rise to the nonlinear-optical phenomena that appear at high intensities of the electromagnetic field. Therefore, studies of nanocomposite materials, *i.e.*, metal nanoparticles embedded in solids or suspended in liquids, are of great importance. In recent years such nonlinear-optical properties of silver nanoparticle colloids as high-order nonlinearities [7], two-photon absorption [8], nonlinear refraction [9], photochromic effect [10], and optical limiting [11] have been investigated. Nanocomposite films $Ag/BaTiO_3$ and Ag/SiO_2 were studied in [12, 13]. Reported studies were performed employing an experimentally simple but powerful *Z*-scan technique [14].

It should be mentioned here that the nature of the nonlinear-optical response of noble metal NPs is still disputable. Some authors interpret the results of *Z*-scan measurements by the formation of thermal lens in the medium around metal nanoparticles due to the effective heat transfer from the nanoparticles to the medium [9, 15–17] or by the difference in the refractive index of nanoparticles and the matrix [7]. BHUSHAN *et al*. suggest that the third-order nonlinearity has a thermally induced origin, while nonlinear absorption is associated with a quadrupole plasmon mode [8]. The results of nonlinear-optical measurements under resonant and non-resonant excitation are presented in [18]. In the first case, the magnitude of the third-order susceptibility exceeds that under non-resonant excitation by two orders of magnitude. This fact supports the statement that local electric field enhancement around metal nanoparticles contributes to the nonlinear optical effects rather than thermal lensing in the surroundings. Similar conclusions are also presented in [19, 20].

In our paper, we present the results of the third-order refraction *Z*-scan measurements of silver NPs suspended in water and glycerol as well as two-dimensional arrays of nanoparticles self-assembled on glass substrate.

2. Experiment

Silver nanoparticles were synthesized during the chemical reduction of silver oxide by hydrogen gas. A supersaturated aqueous solution of silver oxide was heated up to the temperature of 70°C under permanent mixing. Hydrogen gas was pressurized at ~70 kPa above atmosphere. Initially clear solution turned yellowish immediately after the reaction started, indicating the formation of silver particles 10–15 nm in diameter. Growth of the nanoparticles is accompanied by characteristic changes in color of the solution. The size of the nanoparticles was determined by the extinction UV–Vis spectra measurements and by electron microscopy as well. The particle size can be controlled simply by varying the reaction time. A detailed procedure of silver NPs synthesis can be found elsewhere [21]. The nanoparticles are mainly polyhedral in shape with no elongation along any axes; the minor fraction of the suspension includes rod-like particles (Fig. 1). Particle stability is achieved through electrostatic repulsion

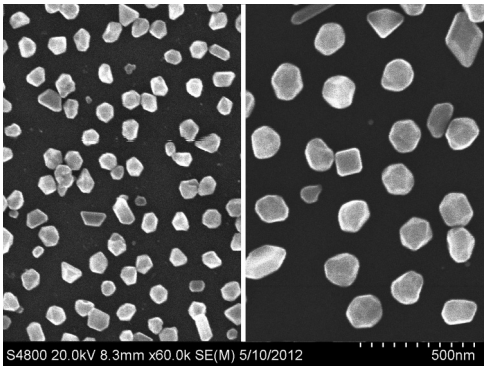

Fig. 1. SEM image of silver nanoparticles synthesized by chemical reduction. Left panel corresponds to the sample Ag-1; right panel – sample Ag-3 (for sample assignment see Table 1).

between the thick electrical double layers that result from the limited dissociation of silver oxide [21]. Since hydrogen, water and silver oxide are the only components used in the reaction, no other chemicals (*e.g.*, surfactants) that may strongly affect the optical response of the NPs are present in the final colloidal suspension. Mass fraction of silver metal in the suspension was determined by thermogravimetric analysis. Sample characterization is presented in Table 1.

T a b l e 1. Characterization of the samples.

	Sample			
	Ag-1	Ag-2	Ag-3	Ag-4
Average NP diameter [nm]	80	100	144	215
NP concentration [cm^{-3}]	2.3×10^{10}	1.1×10^{10}	1.7×10^{10}	4.7×10^{10}
Average interparticle distance in colloid [nm]	3500	4540	3900	2800
Surface concentration of NPs in 2D array [cm^{-2}]	4.9×10^{9}	3.9×10^{9}	1.4×10^{9}	7.0×10^{9}
Average interparticle distance in 2D array [nm]	143	160	270	380
Nonlinear refraction n_2 suspension of NPs [cm^2/W]	-1.64×10^{-8}	-1.498×10^{-8}	-1.297×10^{-8}	-0.65×10^{-8}

Two-dimensional arrays of Ag NPs were prepared by self-assembling of the nanoparticles onto glass substrate. Prior to the self-assembling, the surface of the glass slides was modified with poly(vinyl pyridine) (PVP), which is capable of simultaneous interaction with various substrates via hydrogen bonding and with metal particles through donor–acceptor interactions of the nitrogen atom on the pyridyl group [22]. Self-assembly of the nanoparticles on PVP modified surfaces results in the formation of a single layer of randomly distributed nanoparticles with an average interparticle distance comparable to their diameter [23].

Extinction spectra of the samples were measured using MDR-23 monochromator (LOMO, Saint Petersburg, Russia) equipped with a halogen lamp as a source and a photomultiplier tube as a photon counting mode detector. The signal linearity was observed in the range of 10^2–10^6 photons·s^{-1}. Integrating sphere was mounted between the monochromator and the detector to measure the absorption spectra. Quartz cuvette with an optical path of 1 mm was used for the experiments.

Nonlinear refraction was measured employing a standard single beam *Z*-scan technique [14]. It relies on the measurement of the intensity of the focused laser beam passed through the sample when the latter moves along the beam. Nearby the focal point, where the power density of the laser beam reaches its maximal value, the transmittance of the sample increases or decreases relatively to that in the linear regime depending on the sign of nonlinearity.

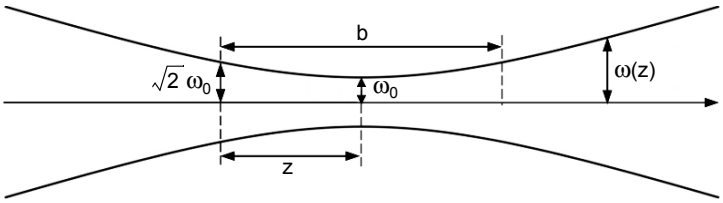

Fig. 2. Parameters of the focused laser beam used in *Z*-scan experiments.

Z-scan measurements were carried out at room temperature using second harmonic 532 nm radiation of CW neodymium laser with diode pumping. The output power of laser radiation was 45 mW. The beam was focused by lens with a focal length of 75 mm. Parameters of the focused laser beam used in the experiments are presented in Fig. 2. Here ω_0 is the radius of Gaussian beam at the focal point, $2\omega_0 = 22.3$ μm, β is the Rayleigh length. It is essential that the thickness of the sample is less than the Rayleigh length ($1 < b = 1.197$ mm). Power density of the laser beam at the focal point is about $I_0 = 1.04\times10^4$ W/cm^2.

3. Results and discussion

Figure 3 depicts the extinction, scattering, and absorption spectra of the suspension (sample Ag-1). Absorption band centered at $\lambda = 410$ nm is associated with the dipole mode of the LSPR in Ag NPs. Linear absorption spectrum provides a basis for calculating the nonlinear-optical parameters.

Two types of *Z*-scan arrangement were employed to determine nonlinear refraction (NLR), namely closed aperture and eclipsing Z-scan. In latter case the aperture is replaced with an opaque disc blocking the central part of the beam [24–26].

Concentration dependence of NLR of the Ag NP suspensions was studied. The concentration was varied simply by diluting the initial colloid with distilled water or glycerol. Assuming a spherical shape of the NPs, one can easily calculate the absolute

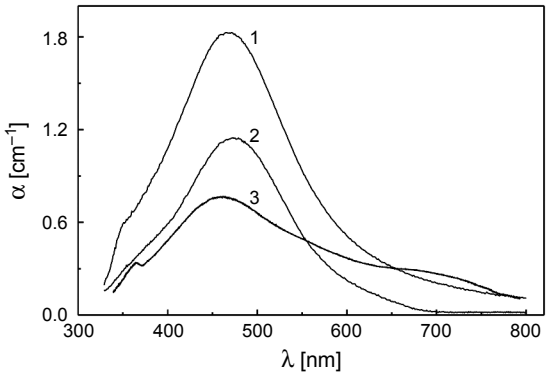

Fig. 3. Extinction (curve 1), scattering (curve 2), and absorption (curve 3) spectra of silver NPs aqueous suspension (sample Ag-1).

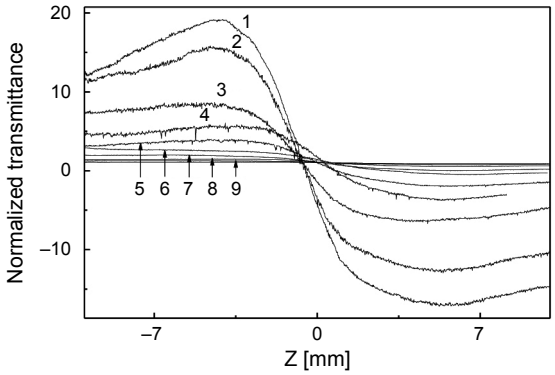

Fig. 4. *Z*-scan transmittance of the Ag-4 suspension in water:glycerol solution (curve 1 – 35:65, curve 2 – 38:62, curve 3 – 44:56, curve 4 – 47:53, curve 5 – 54:46, curve 6 – 62:38, curve 7 – 70:30, curve 8 – 79:21, curve 9 – 89:11). All curves are normalized by the same concentration of the nanoparticles.

Ag NPs concentration in the suspension using experimentally determined mass fraction and an average size of the nanoparticles. Corresponding results are presented in Table 1. Refractive index of the water-glycerol solution was measured using Abbe refractometer. As shown in Fig. 4, the amplitude of *Z*-scan transmittance increases with increasing the glycerol fraction in the solution. In other words, the nonlinear-optical response of Ag NP suspension becomes stronger with the increase in the refractive index of the medium. Z-scan plots presented in Fig. 4 are typical of the NLR of a negative sign, *i.e.*, the colloid possesses defocusing properties [14].

According to SHEIK-BAHAE *et al.*, the nonlinear refractive index of the third order n_2 can be extracted from normalized *Z*-scan dependences and is given as [14]

$$n_2 = \frac{\Delta \Phi_0}{k L_{\text{eff}} I_0} \tag{1}$$

where $\Delta\Phi_0$ is the nonlinear phase distortion, $k = 2\pi/\lambda$ is the wave vector, I_0 is the peak intensity of the laser beam at the focal point, L_{eff} is the effective length of the sample

$$L_{\text{eff}} = \frac{1 - \exp(-\alpha L)}{\alpha} \tag{2}$$

where α is the linear absorption coefficient, L is the sample thickness.

Nonlinear phase distortion can be empirically determined from normalized transmittance Z-scan curves as

$$|\Delta\Phi_0| \cong \frac{\Delta T_{pv}}{0.406(1-S)^{0.27}} \tag{3}$$

where S is the aperture transmittance in the linear regime. In our experiments with closed aperture, the transmittance amounts to 0.07 of the incident beam. In the case of eclipsing Z-scan, the nonlinear phase distortion is given as

$$|\Delta\Phi_0| \cong \frac{\Delta T_{pv}}{0.68(1-S)^{-0.44}} \tag{4}$$

where S is the fraction blocked by the disk.

Figure 5 depicts the concentration dependence of the NLR of the nanoparticles Ag-3 suspended in water-glycerol solution (curve 1) and in water (curve 2). One can see a drastic difference between mentioned dependences. Despite the fact that the concentration of the nanoparticles decreases with diluting of the solutions, the NLR of Ag/water-glycerol suspension rapidly increases. This somewhat unexpected behavior can be explained by more favorable thermal lensing conditions in glycerol environment rather than that in water. Indeed, glycerol possesses substantially lower specific heat capacity ($c_p = 2.43$ Jg^{-1}K^{-1}) than water ($c_p = 4.18$ Jg^{-1}K^{-1}), which provides fast and effective heat transfer from Ag nanoparticles to glycerol environment. On the other

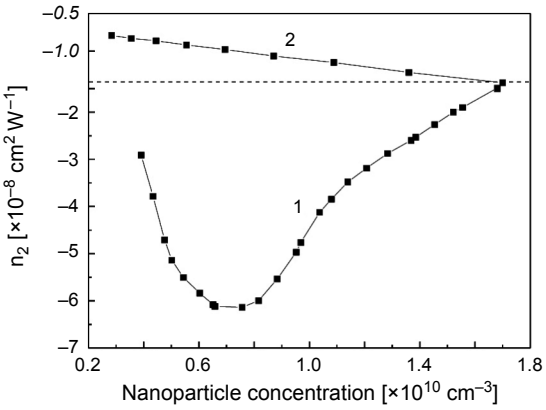

Fig. 5. Nonlinear refraction of Ag-3 NPs suspended in water-glycerol solution (1) and in water (2) for various nanoparticle concentrations. Different scale for the curves along y axis is used for clarity.

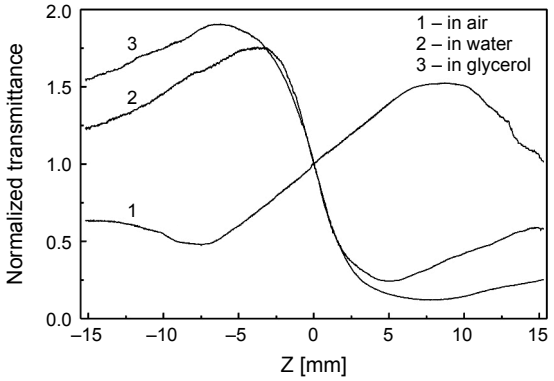

Fig. 6. *Z*-scan transmittance of silver NPs array (sample Ag-3) self-assembled on a glass substrate in air (n = 1), in water (n = 1.33), and in glycerol (n = 1.47).

hand, the refractive index of glycerol (n = 1.47) is higher than that of water (n = 1.33), which also contributes to the increase in the nonlinear refraction. Note also highly nonlinear concentration dependence of n_2 for Ag NPs suspended in water-glycerol mixture (curve 1 in Fig. 5). U-like shape of the curve 1 can be explained by the contribution of two competitive processes, namely the increase in the glycerol abundance in the mixture and the decreasing in nanoparticles concentration.

Analogous measurements were carried out for two-dimensional arrays of Ag nanoparticles self-assembled on glass substrates (samples Ag-1–Ag-3). The sample was placed into an empty quartz cuvette. First, *Z*-scan measurements were done in air environment (n = 1). Later the cuvette was gently poured with water (n = 1.33) using a syringe. After the measurements the cuvette was evacuated and poured with glycerol (n = 1.47), so the sample did not change its position relatively to the beam. Therefore, all measurements were done at the same spot of the sample. Normalized transmittance of a two-dimensional array of silver NPs in different environments is shown in Fig. 6. It is worth noting that 2D array placed in liquid (water, glycerol) and in air has an opposite sign of the nonlinear refraction. Indeed, water and glycerol as well as their mixture possess a negative thermo-optic coefficient [27], while air environment possesses a positive one [28].

It was experimentally found that illuminating conditions play a key role in the nonlinear-optical response of 2D Ag NPs array, when the latter is placed in air environment. Figure 7 depicts normalized *Z*-scan transmittance curves for Ag-3 sample under front (the NPs are exposed directly to the laser beam) and back (laser beam passes glass substrate first) illumination. In the former case, the array exhibits lower nonlinear refraction ($\Delta T_{1pv} < \Delta T_{2pv}$ in Eqs. (3) and (4)) in comparison with back illumination condition. This phenomenon can be explained by a stronger thermal lensing effect in air rather than that in glass.

Note that the nonlinear refraction n_2 is determined, among other parameters, by the effective thickness L_{eff} of a sample, which in turn is connected with its geometrical thickness (see Equations (1) and (2)). It is not clear however, what geometrical thick-

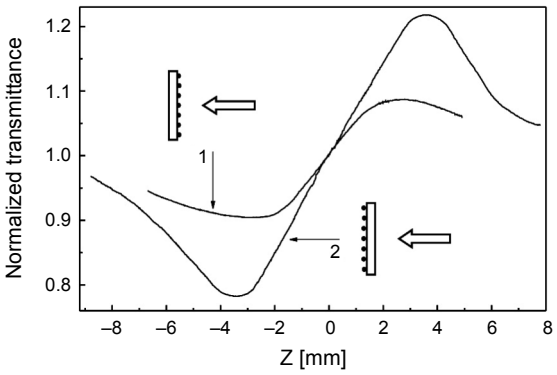

Fig. 7. Normalized *Z*-scan transmittance of silver NPs array (sample Ag-3) in air environment at different illuminating conditions: 1 – front illumination, 2 – back illumination.

ness should be taken into account for the calculations of L_{eff} in the case of a single 2D layer of nanoparticles. Assuming the thickness to be equal to nanoparticle's diameter ($d \approx 144$ nm for Ag-3 sample), the L_{eff} value is unreasonably small. This immediately leads to the overestimated value of the nonlinear refraction coefficient n_2. For instance, the calculations yield $n_2 = -1.297\times10^{-8}$ cm^2/W for Ag-3 colloid and $n_2 = -1.47\times10^{-4}$ cm^2/W for 2D array. Apparently, the interaction between the intense laser beam and the composite medium (suspension of metal nanoparticles in a liquid) takes place within a finite volume. That means that the nanoparticles surrounding is also involved in the nonlinear response of such a medium thus increasing the effective thickness. Let us estimate L_{eff} from following considerations. One can expect an equal nonlinear optical response for the same number of nanoparticles probed by the beam either suspended in water or self-assembled on the surface in water surrounding. According to SEM image analysis, the surface concentration of the nanoparticles for Ag-3 array amounts to 1.4×10^9 cm^{-2} (see Table 1). Nonlinear refraction for Ag-3 NPs aqueous suspension with the volume concentration of 1.4×10^9 cm^{-3} determined from *Z*-scan experiments is $n_2 = -0.73\times10^{-8}$ cm^2/W (curve 2 in Fig. 5). Substituting the determined n_2 value into Eq. (1), one can find the effective thickness to be $L_{\text{eff}} \approx 340$ nm, which overlaps nanoparticle's near-field zone of ~$2d$ [29]. On the other hand, the near-field interaction between the adjacent nanoparticles in a 2D nanoparticle array gives rise to the cooperative surface plasmon mode that manifests itself as an intense narrow absorption spectral band [23]. Therefore, near-field interactions cannot be neglected when considering nonlinear-optical properties of 2D self-assembled arrays of silver nanoparticles.

4. Conclusions

Nonlinear refraction of different composites containing silver nanoparticles was studied employing a *Z*-scan technique. Suspensions of Ag NPs in water and water-glycerol solution as well as two-dimensional arrays of the NPs self-assembled on glass substrates

were investigated. It was found that Ag NP suspensions exhibit negative nonlinear refraction, *i.e.*, possess defocusing properties. Concentration of the nanoparticles in the suspensions was varied by diluting the initial colloids with water or glycerol. The experiments reveal a substantial difference in NLR magnitude for the NPs suspended in water and in glycerol, which is due to more favorable thermal lensing conditions in the latter case. The estimated effective thickness of a two-dimensional array of self-assembled Ag nanoparticles is twice the nanoparticle's diameter. Near-field interparticle interactions should be taken into account when considering NLR of two-dimensional arrays of Ag NPs.

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