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Nonlinear Refraction of Gold Nanoparticles Suspended in Water

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This paper presents the results of the experimental investigations of the surface plasmon resonances and nonlinear refraction of water suspensions of gold nanoparticles coated with a polymer shell. The linear dependence of nonlinear refraction investigated for suspensions in a wide range of beam power density has been reported.

Keywords: Nanoparticles, Nanocomposites, *Z*-scan, Nonlinear refraction.

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1. INTRODUCTION

The emergence and rapid development in recent decades of such technology as photonics, where photons play the role of signal carriers, causes permanent interest in the search of new materials with the corresponding characteristics. First of all, this refers to materials with nonlinear optical (NLO) properties, since they allow to carry out effective control of light beams and transform them. Besides traditional NLO materials, as a rule, of single-crystalline nature, composite materials have proliferated in recent years especially those containing metal nanoparticles located in a transparent matrix. Such nanocomposites are considered to be promising for the application in optical computers [1, 2], optical limiters [3, 4], optical switchers [5], modulators [6], etc.

A careful attention to metal nanoparticles (NPs) is caused, firstly, by the emergence under the action of light of collective excitations of free electrons or the so-called localized surface plasmon resonances (LSPR) as well as by the presence of an extremely fast nonlinear response. Usually, LSPR appear in the extinction spectra of metal NPs in the form of a wide band, whose position depends on the nature of the metal, sizes of NPs and dielectric properties of the medium surrounding the NPs [7]. In the spectra of NPs of noble metals (Au, Ag, Cu), LSPR band is observed in the visible region that makes them especially attractive for the use in various optical and nonlinear optical devices.

A large number of effects associated with the NLO properties of nanocomposites has been recently revealed. From the practical point of view, an important factor is the change in the refractive index of a composite under the action of powerful laser radiation. Changes in the refractive index can be associated with both the change in the absorption coefficient (through the Kramers-Kronig relation) [8] and the thermal effects (thermal lens) [9] and the Stark effect [10]. It is absolutely clear that nonlinear response depends on the concentration of NPs, state of their surface as well as on the parameters of environment. The simultaneous presence in a matrix of different-sized NPs leads to the non-uniform expansion of the LSPR band and reduces the manifestation of size effects.

The so-called *Z*-scan method, in which changes in the amplitude and phase of the focused Gaussian beam are registered when moving the sample along the optical axis, has become prevalent among many methods of study of nonlinear optical characteristics of composite materials [11]. Despite its simplicity, this method allows to determine with high precision the values of the real and imaginary parts of the third-order nonlinear dielectric susceptibility and their sign. NLO effects are significantly amplified, when frequency of incident light is close to the LSPR frequency, at that the resonance enhancement of the reduced electric field occurs in the area around NPs [12, 13]. Since in the majority of the cases LSPR band for gold NPs is found at the wavelength of 520-540 nm, then resonance interaction of light with NPs can be easily implemented using the second-harmonic radiation of YAG-Nd laser with $\lambda = 532$ nm.

2. EXPERIMENTAL

2.1 Synthesis of Au NPs

Gold NPs were synthesized by the homogeneous nucleation method by reduction of $HAuCl_4$ aqueous solution with the concentration of Au^{3+} of 1.3 g/l under the action of hydrazine hydrate N_2H_4 $0.5H_2O$ in the presence of the surface active oligoperoxide (OP). The latter was obtained by radical copolymerization of N-vinylpyrrolidone (NVP), peroxide monomer 5-tert-butylperoxy-5-methyl-1-hexen-3-yne (VEP) and glycidyl methacrylate (GMA) by the well-known technique [14]. To ensure reliable fixation of OP molecules on the surface of NPs, molecules were modified by the thiol groups ([S] = 9.6 %). Synthesis was carried out at $T = 298$ K in an alkaline medium (pH = 10.6) at the molar ratio of $[HAuCl_4] : [N_2H_4] = 1 : 20$ and mass ratio of $[Au^{3+}]$: [oligoperydoxide] = 1 : 4. The synthesis resulted in an aqueous suspension of Au NPs coated with

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a thin of about ~ 1-2 nm polymer layer, which prevents adhesion of NPs.

Size of gold NPs in the suspension was determined by the method of transmission electron microscopy using microscope TEM-100-01 at the accelerating voltage of 100 kV (resolution is 0.5 nm). In Fig. 1 we illustrate the micrographs of gold NPs, by which the size-distribution histograms of Au NPs are plotted. The distribution was defined by freely available, but quite powerful software package for image processing *ImageJ*. The histograms are shown in Fig. 1 along with related images. Suspensions are conventionally denoted as A-25 and A-27.

2.2 Optical spectra of gold NPs

As known, optical spectra of spherical particles, which are smaller than the light wavelength, can be found by using the Mie theory [15]. According to the theory, cross-sections of extinction, scattering, and absorption are calculated from the expressions

$$C_{ext} = \frac{2\pi}{|k|^2}\sum_{L=1}^{\infty}(2L+1)\mathrm{Re}\{|a_L|+|b_L|\}, \quad (1)$$

$$C_{sca} = \frac{2\pi}{|k|^2}\sum_{L=1}^{\infty}(2L+1)\left(|a_L|^2+|b_L|^2\right), \quad (2)$$

$$C_{abs} = C_{ext} - C_{sca}, \quad (3)$$

in which

$$a_L = \frac{m\psi_L(mx)\psi_L'(x) - \psi_L(x)\psi_L'(mx)}{m\psi_L(mx)\zeta_L' - \zeta_L(x)\psi_L'(mx)}, \quad (4)$$

$$b_L = \frac{\psi_L(mx)\psi_L'(x) - m\psi_L(x)\psi_L'(mx)}{\psi_L(mx)\zeta_L' - m\zeta_L(x)\psi_L'(mx)}, \quad (5)$$

where $m = n / n_m$, n and n_m are the complex refractive index of the NP and the real refractive index of the medium, respectively; k is the wave vector; $x = |k|R$ is the dimensional parameter; ψ_L, ξ_L are the cylindrical Ricatti-Bessel functions, stroke denotes differentiation with respect to argument; index L specifies the order of the partial wave. If concentration N (cm^{-3}) of NPs in the suspension is known, then it is easily to find its absorption coefficient $k = C_{abs} \cdot N$ (cm^{-1}).

In Fig. 2 we show the calculated spectra of the main fractions of NPs for the sample A-27 according to the histogram. Curve 7 corresponds to the total absorption of all fractions, i.e. spectral absorption of the suspension.

The experimentally measured spectral dependence of the suspension absorption (Fig. 3) correlates well with the calculated one.

The larger width of the experimental LSPR bands compared with the calculated ones is the result of nonlinear expansion induced by the dispersion in size and deviation from the spherical shape of real NPs. A more blurred edge of the absorption spectrum of suspension A-25 is explained by the fact that particle dispersion in sizes is larger than in the sample A-27 (see Fig. 1).

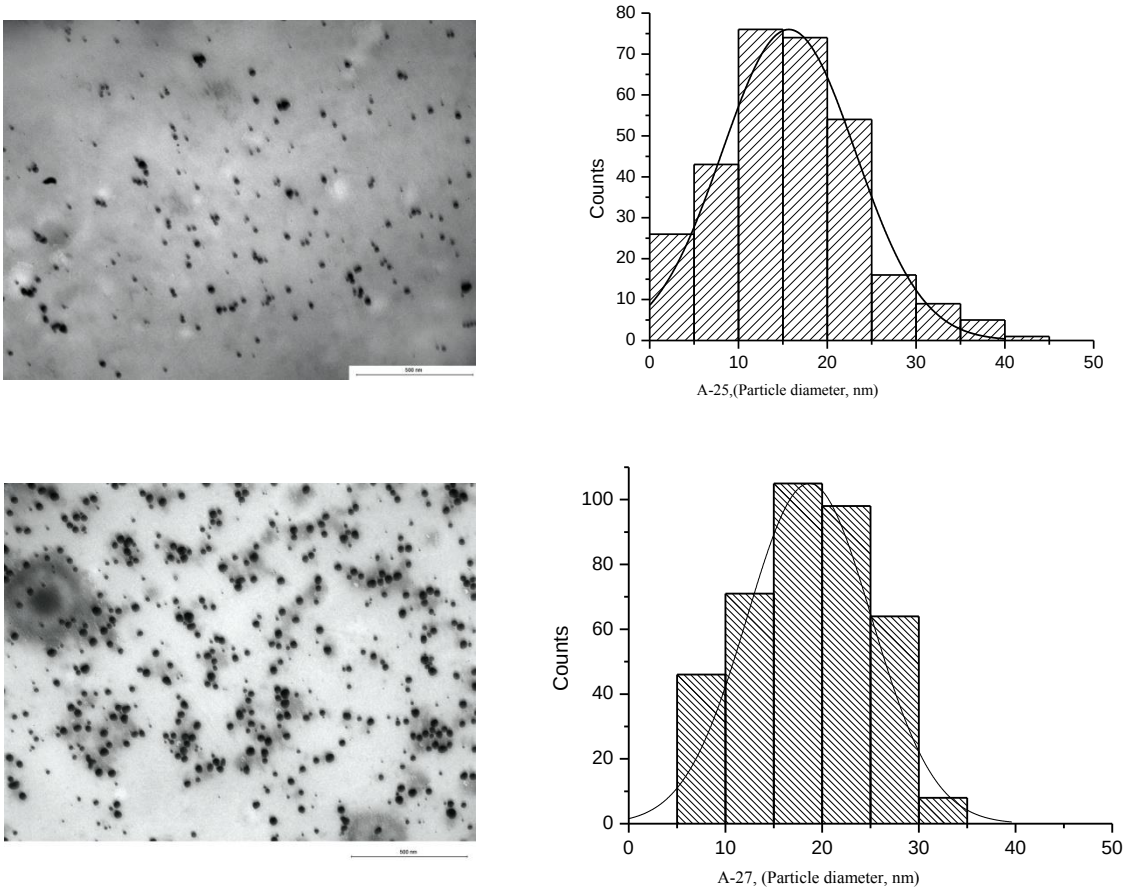

Fig. 1 – Micrographs and size distribution of gold NPs in the suspension: samples A-25 (above) and A-27 (below)

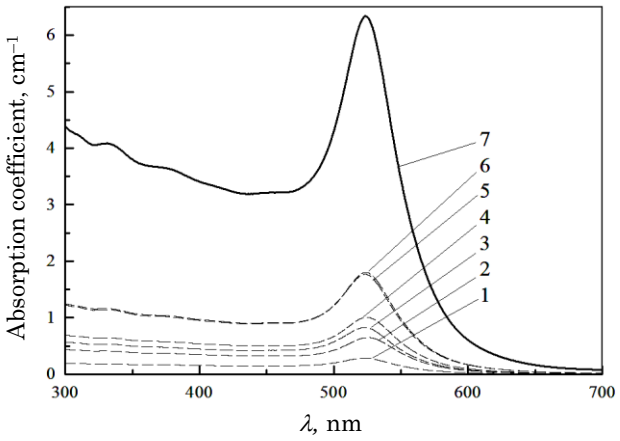

Fig. 2 – Absorption spectra for the suspension of gold NPs A-27 calculated according to the Mie theory (1 – d = 5 nm; 2 – d = = 7.5 nm; 3 – d = 10 nm; 4 – d = 12.5 nm; 5 – d = 15 nm; 6 – d = 17.5 nm; 7 – total absorption)

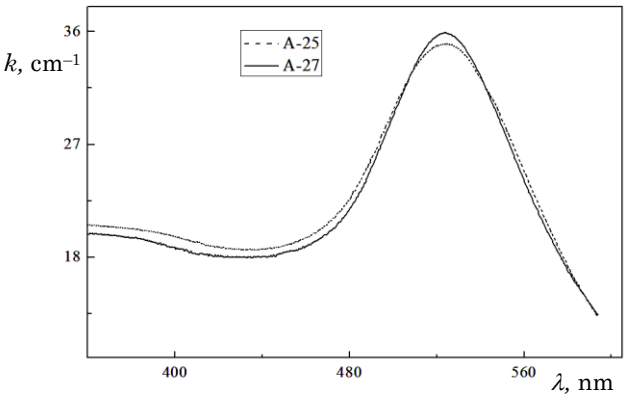

Fig 3 – Experimental absorption spectra of the suspension of gold NPs

Absorption spectra were measured by monochromator MDR-23; quartz cell with the suspension was placed into the integrating sphere photometer. Stabilized halogen lamp served as the light source, signal was registered by photomultiplier in the photon-counting mode.

2.3 Measurements of the nonlinear refraction

The standard Z-scan technique with a closed aperture was used to measure the nonlinear refraction (NLR) [11]. Scheme of the Z-scan experiment is shown in Fig. 4.

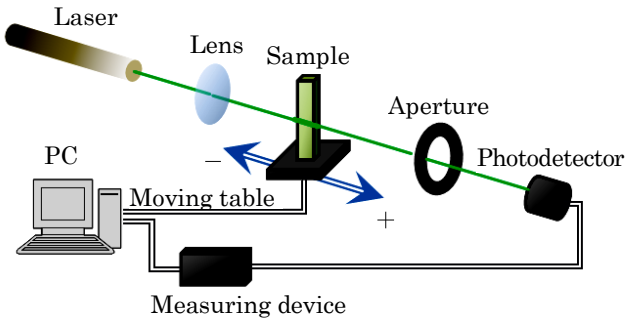

Fig. 4 – Measurement scheme by the Z-scan technique

The expression proposed by Sheik-Bahae, et al. [11] was used in order to calculate the nonlinear third-order refractive index n_2 by the normalized Z-scan curves

$$n^2 = \frac{\Delta\Phi_0}{kL_{eff}I_0}, \qquad (6)$$

where $\Delta\Phi_0$ is the nonlinear phase distortion; $k = 2\pi/\lambda$ is the wavenumber; I_0 is the maximum of the laser radiation intensity in focus; L_{eff} is the effective sample thickness,

$$L_{eff} = \frac{1-e^{-\alpha L}}{\alpha}, \qquad (7)$$

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

Nonlinear phase distortion $\Delta\Phi_0$ is empirically associated with the change in the normalized transmission $\Delta T_{pv} = T_p - T_v$ obtained from the experimental Z-scan curve

$$\left|\Delta\Phi_0\right| \cong \frac{\Delta T_{pv}}{0.406\left(1-S\right)^{0.27}}, \qquad (8)$$

where S is the aperture transmission in the absence of the sample. In our experiment with a closed aperture, the transmission was equal to 0.07 of the light intensity incident on the aperture. The measurement results are represented in Table 1.

3. RESULTS AND DISCUSSION

In Fig. 5a we show the normalized absorption curve, in Fig. 5b – the normalized curve of nonlinear refraction for the suspension A-27 of gold NPs. For the sample A-25, the corresponding spectra have the same form, but with another amplitude.

An interesting feature is manifested during Z-scan measurements of suspensions of gold NPs. In the plane of the detector aperture one can observe several interference rings that is especially noticeable under illumination of the cell with suspension by convergent beam. The number of observed rings in the sample plane is determined by the power density of a laser beam and concentration of NPs (Fig. 6). The appearance of interference rings can be understood from the following considerations. It is seen by the shape of the Z-scan curve of nonlinear refraction that aqueous suspension of gold NPs possesses the defocusing (dissipates light) properties. As a result of the interference of coherently scattered light and main beam, there appear the interference rings.

Dependence of the change in the phase of the scattered light on the power density was measured by the attenuation of laser radiation by neutral light filters. The obtained results are illustrated in Fig. 7.

A similar interference was observed in passing of the powerful laser beam through the film of rare crystals [16, 17], where large changes in the phase are conditioned by a spatial self-modulation of the laser beam, but for rare crystals dependence of the phase change on the intensity undergoes a jump due to the Frederikc phase transition. In our case, change in the phase on the beam intensity is linear (see Fig. 7) in a wide range of intensities. This allows to suggest a large nonlinear susceptibility of the nanocomposite.

Table 1 – The values of the nonlinear refraction for the studied suspensions

Sample	ΔT	α, cm^{-1}	L_{eff}, cm	$\Delta\Phi_0$	n_2, cm^2/W
A-25	1.79	34.3	$2.82\cdot10^{-2}$	4.499	$1.30\cdot10^{-7}$
A-27	2.58	34.8	$2.78\cdot10^{-2}$	6.484	$1.90\cdot10^{-7}$

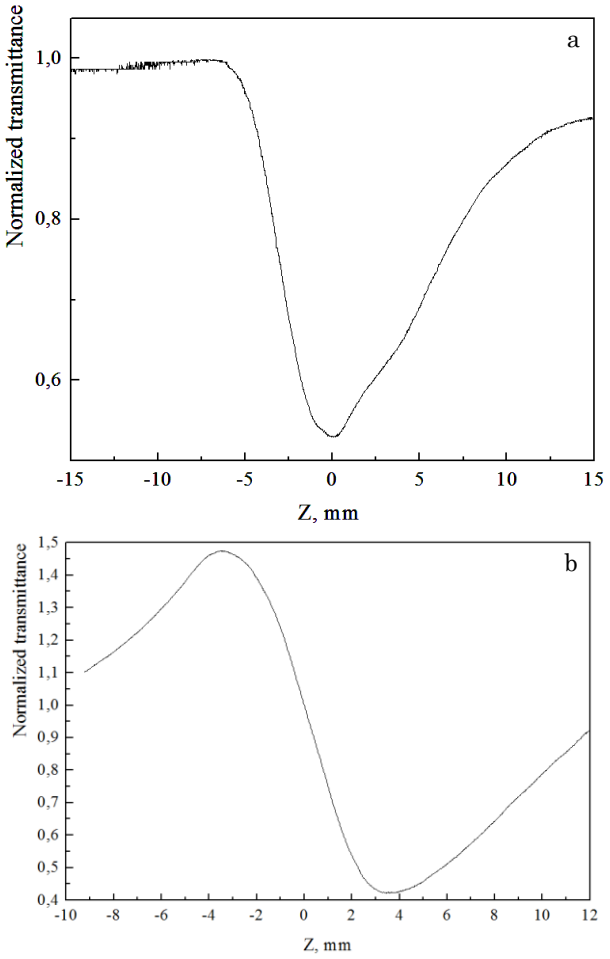

Fig. 5 – Normalized Z-scan dependences of the nonlinear absorption (a) and nonlinear refraction (b) for the sample A-27

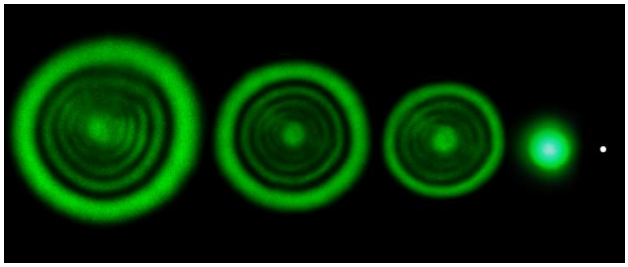

Fig. 6 – The interference pattern in the plane of the aperture. From left to right images are obtained for the power densities of 79.0 W/cm², 67.0 W/cm², 61.8 W/cm², 53.0 W/cm², respectively; the right light circle is the aperture size in the measurement of the refraction

The presence of interference rings in the plane of observation creates certain peculiarities in the measurement of the nonlinear refraction and nonlinear absorption. In both cases, intensity pulsations of smaller amplitude will overlap Z-scan dependences of a traditional form. Such pulsations are not observed for small intensities of the probing beam or for low concentrations of NPs in the suspension. We should note that the value of the nonlinear refraction depends linearly on the concentration of NPs in the suspension (Fig. 8).

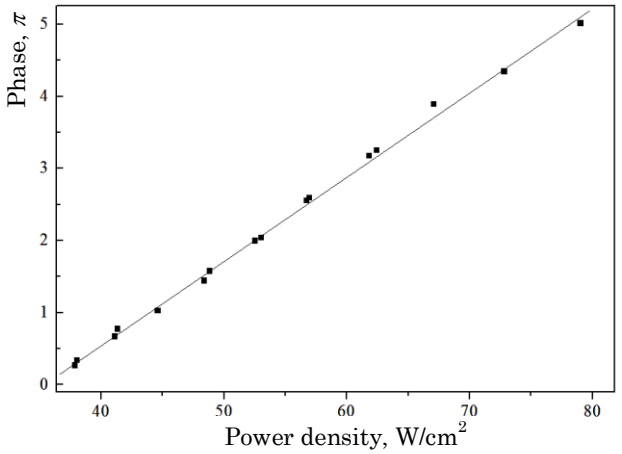

Fig. 7 – Change in the phase of the scattered light depending on the power density of laser radiation for the suspension A-27

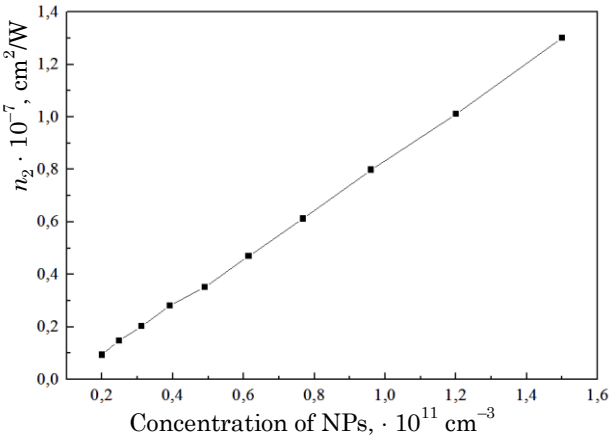

Fig. 8 – Concentration dependence of the nonlinear refraction of the suspension A-25

4. CONCLUSIONS

The nonlinear refraction of aqueous suspensions of Au NPs during excitation in the surface plasmon resonance region has been studied by the Z-scan method. The obtained value of the nonlinear refraction indicates a great nonlinearity of the studied systems. The linear (in a wide range) dependence of the nonlinear refraction on the concentration of NPs in the suspension and power of the exciting beam has been established.

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