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Nonlinear optical properties of colloidal silver nanoparticles produced by laser ablation in liquids

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***Abstract*. The optical and nonlinear optical properties of colloidal solutions of silver obtained by laser ablation in water and ethanol are studied. It is shown that freshly prepared colloids experience a full or partial sedimentation by changing their nonlinear optical properties. Aqueous colloids undergo a partial sedimentation and their nonlinear optical absorption changes to nonlinear optical transmission. The obtained results are interpreted using the Drude model for metal particles taking the particle size into account and can be explained by the sedimentation of larger silver particles accompanied by the formation of a stable colloid containing silver nanoparticles with a tentatively silver oxide shell. The characteristic size of particles forming such a stable colloid is determined and its optical nonlinearity is estimated.**

Keywords: *optical nonlinearity, laser ablation in liquid, metal colloids, silver nanoparticles.*

1. Introduction

The methods for preparing metal colloids and the study of their optical parameters attract attention due to a number of their properties that are promising for the use in optics, chemistry, and biology [1]. In particular, of considerable interest are their high optical nonlinearities caused by a strong enhancement of the field near particles due to a plasmon resonance. A comprehensive description of the basic methods for preparing metal colloids is presented in paper [2]. The main disadvantage of most of these methods is a great spread in the size of prepared nanoparticles. Laser ablation is one of the perspective methods, which offers new possibilities to control the parameters of synthesised metal and semiconductor nanoparticles [3].

Studies performed to date have shown that the structural and optical parameters of colloids can be controlled by changing the regimes of their preparation. In this case, both usual colloidal systems can be prepared, which are obtained by sedimentation from solutions, and systems with variations in the shape of particles and the composition of colloids [4]. The formation of colloidal systems by laser ablation in liquid occurs under strongly non-equilibrium conditions, when a metal passes through a melt state due to ablation. This circumstance stimulates the physicochemical processes of interaction of the metal both with the liquid medium and various components added to it, which cause the formation of more complex structures instead of usual spherical particles. It is natural that such colloidal systems have optical and nonlinear optical characteristics that differ from those of colloids prepared by other methods.

This paper is devoted to the study of optical and nonlinear optical properties of colloidal silver solutions obtained by laser ablation in water and ethanol. It is shown that colloidal solutions freshly prepared by this method, as colloidal solutions obtained by other methods, have high third-order optical nonlinearities.

We studied the evolution of nonlinear optical properties of colloids during their storage, which is satisfactorily explained by the aggregation and sedimentation of colloidal particles. We found that, along with a decrease in nonlinearity (induced absorption) caused by the sedimentation of particles, the sign of nonlinearity changes (induced transmission appears) and it tends to a stationary value. It is shown that such evolution can be explained by the presence of silver particles covered by an oxide shell in the colloidal solution, which remain in a suspension after the sedimentation of larger (and/or aggregated) metal nanoparticles (without a shell).

2. Preparation of samples and experimental technique

Nanoparticles were produced by the laser ablation of a silver target in liquid. We used a copper vapour laser emitting 510.6-nm, 20-ns pulses with a pulse repetition rate of 15 kHz. The laser beam was focused through a transparent liquid on a metal target. Metal targets were 100-μm thick silver (99.99 % purity) plates. We used in experiments distilled water and ethanol. Nanoparticles were prepared at the radiation energy density of about 34 and 7.2 J cm $^{-2}$ in ethanol (samples 1 and 2, respectively) and 34 and 6.2 J cm^{-2} in water (samples 3 and 4, respectively). A silver target being ablated, the liquid changed to a yellow colour whose intensity increased with the irradiation time and laser beam energy density. The details of this method for producing metal colloids and of the preliminary study of their structural and optical properties are reported in

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Ref. [5]. The transmission spectra of colloids in the visible range were recorded with a UV-VIS Specord spectrophotometer with an error of $\sim 5\,\%$.

The preliminary observation of freshly prepared colloidal solutions showed that their transmission spontaneously (partially reversibly) changes during a few hours (from one to ten hours), a sediment appears, light scattering and absorption, as well as the colouring intensity decrease (in the case of colloids in ethanol, complete bleaching occurs). Because no special precautions were taken to stabilise colloids, they were kept at rest at room temperature for several days to achieve the quasi-equilibrium state (when optical absorption acquired a stationary value). Then, measurements were performed both for quasi-equilibrium colloids (the upper layer of the stored colloid was carefully removed with a pipet) and recovered colloids subjected after sedimentation to mechanical shaking up and ultrasonic processing for 10 min using a UZDN-A disperser. Such recovered colloids were again returned after a few days of storage (within the experimental error) to the quasi-equilibrium state.

We measured the nonlinear optical properties of colloids by the open-aperture z-scan technique [6, 7]. Colloidal solutions were placed into quartz cells of thickness from 1 to 5 mm. Colloids having a high extinction were studied in cells of a lower thickness. We used a nanosecond LTI-404 Nd : YAG laser with the intracavity second-harmonic generation, which emitted 25-ns pulses at 532 nm. The pulse energy incident on the measuring system was 170 μJ. When a lens with a focal distance of 20 cm was used, the radius w_0 of the laser-beam waist was 26 μm, while the power density at the lens focus was 320 MW cm^{-2}. The pulse repetition rate was 10 Hz. To reduce errors related to the scatter in the laser pulse energy, measurements were performed only for pulse energies that did not exceed 5 % of the average energy. The data obtained for each position of a cell with respect to the laser-beam waist were averaged over 20 measurements.

3. Experimental results and their processing

It is known that colloidal systems in liquids undergo to some extent the evolution during their storage (see, for example, Ref. [8], Ch. 29), which is manifested in their sedimentation, aggregation of particles to complexes, and various chemical processes proceeding on the surface of colloids. These processes can occur quite rapidly (for several hours or days) or rather slowly. In the latter case, the colloidal system can be considered quasi-stationary when small particles are uniformly distributed in the solution owing to the thermal motion, do not virtually precipitate and do not aggregate (for example, due to the presence of a charge or the corresponding shell). We studied the transmission spectra of silver colloids and measured nonlinear absorption depending on the preparation conditions of colloids. We also investigated the evolution of colloids during their storage.

Experiments were performed at two stages: the nonlinear optical characteristics of colloids were preliminary tested by the z-scan technique and then the spectral and nonlinear properties of selected colloids were measured in more detail.

The typical dependences of the relative transmission T on the coordinate z obtained by the z-scan method immediately after the ultrasonic irradiation of recovered colloids in ethanol and water and after the indicated time intervals are shown in Fig. 1. One can see that colloids first exhibit induced absorption, which is also typical for silver colloids obtained by other methods [9]. The subsequent measurements of the same samples show that induced absorption decreases with time. One can also see that the evolution of colloids in ethanol noticeably differs from that in water. While colloids in ethanol demonstrate a complete disappearance of induced absorption in the absence of induced absorption, colloids in water exhibit almost immediately after mixing a distinct combination of induced absorption and transmission. Then, induced absorption begins to dominate and acquires a stationary value.

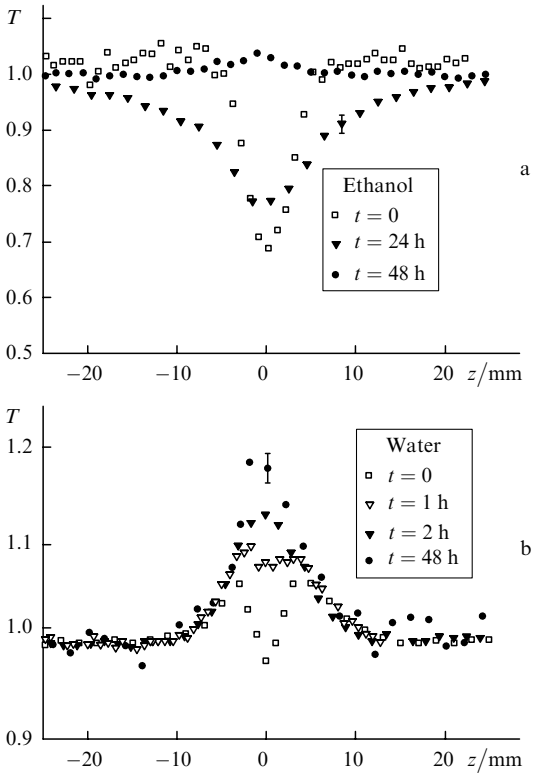

Figure 1. Typical dependences of the relative transmission on the coordinate z obtained by the z-scan method for recovered silver colloids in ethanol immediately after processing and 24 and 48 h later (a), as well as in water immediately after processing and 1, 2, and 48 h later (b).

While induced absorption and transmission in metal colloids were earlier observed by other researchers [10], the appearance of induced transmission instead of induced absorption during the storage of colloids was observed here for the first time to our knowledge. The study of the properties of such colloids is the aim our paper. Note that a detailed information on the state of colloids during experiments (time after their preparation, mixing conditions, presence of light scattering, precipitation, etc.) is often absent in the literature available. One can assume that during ablation, along with large silver particles (which are readily subjected to sedimentation and aggregation and can be easily detected in experiments), silver particles are produced which are virtually always in a suspended state.

Therefore, we found that aqueous solutions of silver colloids form after sedimentation a phase that is more stable in time and has a noticeable nonlinear transmission. We separated this phase from the sediment and measured its optical and nonlinear characteristics.

The typical absorptions spectra of colloidal solutions of the phase obtained after sedimentation and separation from the sediment are shown in Fig. 2 (samples 3 and 4). One can see that these spectra are typical for metal colloids and represent almost symmetric bands described by plasmon absorption in metal particles. We interpreted the absorption spectra using a classical model for metal spheres considered, for example, in Ref. [11]. This model describes the spectrum of the colloid permittivity in terms of the spectra of the permittivity of a bulk metal and the environment, while the influence of the particle size is taken into account as the increase in the frequency of electron collisions in the metal. Finally, the plasma frequency of the metal and the refractive index of the environment specify the position of the absorption maximum of the colloidal solution. The intensity of the absorption band is determined by the volume fraction of the metal, while its width is determined by the frequency of electron collisions taking into account the contribution related to the nanoparticles size. The absorption spectrum of the colloidal solution in this approximation has the form [11]

$$\alpha(\omega) = 9\frac{f\omega n^{3/2}}{c}\frac{\varepsilon_2(\omega)}{[2n+\varepsilon_1(\omega)]^2+\varepsilon_2^2}, \qquad (1)$$

where

$$\varepsilon_1(\omega) = \varepsilon_1^{\mathrm{L}}(\omega) + 1 - \frac{\omega_\mathrm{p}^2}{\omega^2+\omega_\mathrm{c}^2};$$

$$\varepsilon_2(\omega) = \varepsilon_2^{\mathrm{L}}(\omega) + 1 - \frac{\omega_\mathrm{p}^2\omega_\mathrm{c}}{\omega(\omega^2+\omega_\mathrm{c}^2)};\ \omega_\mathrm{c} = \frac{v_\mathrm{F}}{l_\mathrm{e}} + \frac{2v_\mathrm{F}}{D};\ \omega = 2\pi\frac{c}{\lambda};$$

f is the volume fraction of the metal in the colloidal solution; $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the metal permittivity, taking into account the contribution of electrons with the surface of metal colloidal particles; $\varepsilon_1^{\mathrm{L}}(\omega)$ and $\varepsilon_2^{\mathrm{L}}(\omega)$ are the real and imaginary parts of the metal permittivity caused by the contributions from the lattice and bound electrons; n is the refractive index of the liquid environment; ω_p is the plasma frequency, which is equal to 1.39×10^{16} s^{-1} for silver; ω_c is the frequency of electron collisions; v_F is the Fermi velocity, which is equal to 1.38×10^{6} m s^{-1} for silver; l_e is the mean free path for electrons, which is equal to 57 nm for bulk silver; D is the silver particle diameter; λ is the radiation wavelength (in nm); and c is the speed of light in vacuum.

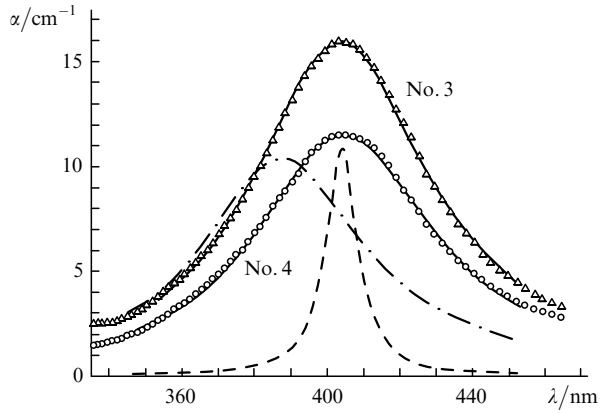

Figure 2. Absorption spectra of colloidal silver solutions in water (samples No. 3 and 4). Circles and triangles are the experiment; solid curves are the best fits; the dashed curve is calculated for large particles of diameter 200 nm (with a shell, $n = 1.45$); the dot-and-dash curve is calculated for particles of diameter $\sim$30 nm, but in the aqueous environment (without a shell, $n = 1.33$).

The absorption spectra were simulated using the known empirical data for the real and imaginary parts of the refractive index of bulk silver. By comparing the empirical spectra of the permittivity with the simulated spectra, we determined the values of $\varepsilon_1^{\mathrm{L}}(\omega)$ and $\varepsilon_2^{\mathrm{L}}(\omega)$. Expression (1) was used to simulate the absorption spectra of colloids by fitting then the calculated and experimental spectra by the method of least squares (the fitting parameters were D, f, and n).

The calculated absorption spectra of colloidal Ag particles are also presented in Fig. 2 (solid curves). The parameters D, f, and n at which the minimum root-mean-square deviation was achieved, were equal to 15.5 nm, 4.6×10^{-6}, and 1.45 for sample No. 3 and 15.2 nm, 3.3×10^{-7}, and 1.46, respectively, for sample No. 4 (with an error of ±2 in the second decimal place). A comparison of the calculated and experimental absorption spectra shows that the approximation used describes satisfactorily the plasmon absorption peak of colloids under study. One can see that the parameters of particles remaining in the solution after sedimentation are virtually the same for both colloids, only their volume fraction being different, which are rather small ($\sim10^{-6}$). A the same time, the simulation gives the value of the refractive index of the environment of metal particles equal to $n \sim 1.45-1.46$, which is substantially higher than the refractive index of water ($n \sim 1.33$).

We can assume that upon ablation not only particles of different sizes are formed in solution but also particles with a thin shell of oxidised silver. This shell can appear, in particular, due to oxidation of the surface of melted small silver particles (directly during ablation or even during the subsequent action of laser radiation on colloidal particles). It seems that a greater part of particles are subjected to sedimentation and aggregation, while particles with the shell remain in a suspension. Such a colloidal solution can be stable due to the presence of the shell and the charge states of particles on their boundary caused by the shell, which prevent their aggregation. As follows from calculations [12], a thin shell strongly affects the position of the plasmon peak (for silver particles in the air, a 1-nm thick shell with the refractive index $n = 1.496$ causes the long-wavelength shift of the peak by $\sim$10 nm). For the shell thickness of no less than 15 nm, the shift becomes maximal, and the environment parameters no longer affect the plasmon peak. One should bear in mind that the model that we use here does not take the shell into account directly but gives the effective values of n for the shell and water. Therefore, either the shell should be sufficiently thick or the shell material should have even greater refractive index. This well agree with the data reported in paper [13], where it was pointed out that the refractive index of silver oxide depends on the stoichiometry and can achieve 2.8 at high contents of oxygen. To obtain more accurate data, further studies are required. Figure 3 shows the experimental dependences of the relative transmission on the coordinate z obtained by the z-scan method for silver colloids in water (samples No. 3 and 4).

In the approximations determining the applicability of the z-scan method (Gaussian beam, sample thickness is

smaller than the waist length in the focus, second-order nonlinearity, nonlinear changes in the amplitude and phase in a sample are much smaller than unity and π, respectively), the change in the transmission in a sample for an open aperture is described by the expression [6]

$$\Delta T(x) = -\frac{2(x^2+3)}{(x^2+9)(x^2+1)}\Delta\Psi_0, \qquad (2)$$

where $\Delta\Psi_0 = \beta I_0 L_{\text{eff}}/2$; $x = z/z_0$ is the coordinate of a sample with respect to the focus normalised to the focus waist length $z_0 = (2\pi/\lambda)w^2/2$; w is the waist radius of the Gaussian beam; β is the nonlinear absorption (transmission) coefficient; $L_{\text{eff}} = (1 - e^{-\alpha l})/\alpha$; α is the linear absorption coefficient at the wavelength of measurements; l is the cell thickness; and I_0 is the radiation intensity in the lens focus. Away from the focus (where the contribution of nonlinearity can be neglected), the transmission T tends to unity and ΔT tends to zero.

By approximating the experimental curves by the method of least squares, we can determine from (2) the parameter $\Delta\Psi_0$ of the curve, and, knowing the parameters of the laser beam and optical system, find also the coefficient β. The solid curves in Fig. 3 demonstrate the numerical fitting of experimental data by expression (2). The values of β obtained for colloids No. 3 and 4 were -10.4 and -3.7 cm GW^{-1}, respectively (with the error of ± 1 in the first decimal place).

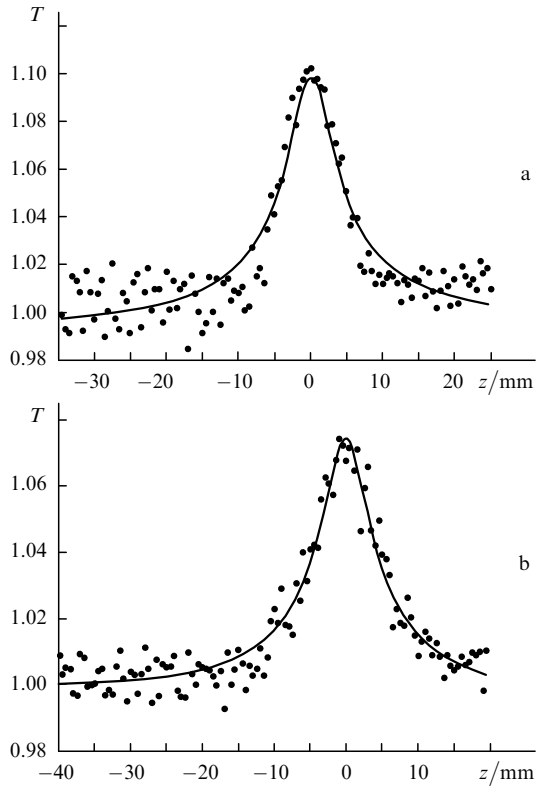

Figure 3. Dependences of the relative transmission T on the coordinate z obtained by the z-scan method for samples No. 3 (a) and 4 (b). Dots are the experiment; the solid curve is the best fit by expression (2).

4. Discussion of results

Based on the method for preparing colloids and their optical spectra considered above, we can conclude that upon laser ablation of silver in water, a component is formed in colloids, which is not subjected to noticeable aggregation and sedimentation. This component consists of particles having a shell, which is formed probably by silver oxide and has the refractive index that is substantially higher than that of water. The numerical simulation showed that the plasma absorption peak of this colloid is well described by the spectrum of an ensemble of silver spheres of the same size in water. This can be explained by assuming that small particles are not formed during ablation (or they are completely oxidised), whereas large particles without a shell are subjected to sedimentation and aggregation. The question about the conditions and reasons resulting in such quasi-stability of precipitated colloids requires a more detailed study. We can only assert that under conditions described above, a spontaneous selection of particles occurs in the colloid. In this case, the parameters of particles (obtained from optical spectra) only weakly depend on the ablation power density. The study of nonlinear properties of silver colloids showed that, unlike colloids recovered by mechanical shaking and ultrasonic irradiation, silver colloids exhibit induced bleaching.

The question about the mechanisms of nonlinearity of colloidal silver solutions is still open. Different researches have reported both the observation of induced absorption (in most cases, the second harmonic of a neodymium laser was used in experiments) and induced bleaching (especially, near the plasmon resonance frequency) in liquids or the formation of silver colloids in a spherical solid matrix. According to the modern model concepts, the nonlinearity of metal colloids can be caused both by the metal itself and a matrix, whose bulk nonlinearities increase by several orders of magnitude due to the field enhancement upon the plasmon resonance. As for metal particles themselves, in the short pulse approximation, three processes determine a change in absorption: the dimensional restriction of conduction electrons, interband transitions, and a change in the imaginary part of the permittivity due to the energy redistribution of electrons [14].

The first two processes lead to bleaching, being substantial only in the resonance case (for plasmons and interband transitions), while the third process causes induced absorption over the entire wavelength range and its contribution exceeds that of the first two processes away from the resonance. The situation becomes more complicated if the environment also has nonlinear properties or the charge properties of the surface depend on the incident field intensity. In the case of nanosecond pulses, it is assumed that nonlinearity caused by a cumulative heat release (strong heating and even the local boiling of liquid near nanoparticles) is high. A change in the sign of phase nonlinearity observed in silver colloids is explained by the contribution of heating, while the heating of a metal itself enhances induced absorption.

Finally, it is necessary to consider the integrated extinction because local boiling enhances scattering as well. For settled colloids, bleaching was observed, although measurements were performed in the region outside the resonance. Therefore, the induced absorption in colloids

under study is not related directly to the silver nonlinearity and requires a more detailed study, including analysis of the structural properties of colloids and the charge state of their surface. We can, however, assume that the oxide shell plays a key role in this case. One of the explanations is that the local heating of the shell resulting in a change in the refractive index causes the blue shift of the plasmon peak, thereby reducing absorption at the measurement wavelength. In addition, an increase in the local field in the shell also leads to this effect. Both these effects can combine. These assumptions can be verified in experiments using short, for example, picosecond laser pulses at different wavelengths to observe the dynamics of induced absorption with a high time resolution.

5. Conclusions

Our study of the optical and nonlinear optical properties of colloidal silver solutions prepared by laser ablation in water and ethanol has shown that:

(i) freshly prepared (or recovered by mixing and ultrasonic irradiation) silver particle colloids have the third-order nonlinearity (induced absorption);

(ii) the optical characteristics of freshly prepared (or recovered) colloids relax in time; the intrinsic and induced absorption for colloids in ethanol disappears almost completely after a few days (and the sediment appears simultaneously), which can be explained by the aggregation and sedimentation of colloid particles;

(iii) the time dependence of nonlinearity for colloidal solutions in water has special features compared to that in a solid matrix: the nonlinearity changes the sign and acquires a stationary value, which can be explained by the presence of an ensemble of particles in the colloid, which remain in the suspended (quasi-stationary) state for a long time;

(iv) the transmission spectra of quasi-stationary silver colloids in water are well described by the classical model of silver spheres, in which the refractive index of the environment corresponds not to water but most likely to silver oxide (which probably forms shells around silver particles). The presence of such a shell (and possibly the charge states on the particle surface caused by the shell) can prevent the aggregation of particles, thereby providing a greater stability of colloids;

(v) quasi-stationary silver colloids in water have nonlinearity of the opposite sign (induced bleaching instead of induced absorption) with respect to freshly prepared (recovered) colloids; we assume that the oxide hell plays a key role in the change of the nonlinearity sign.

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