Spectral properties of nanocomposites based on fluorine-containing polymer and gold nanoparticles

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Abstract. The optical properties of nanocomposites of gold nanoparticles and fluorine-containing polymer have been studied. Gold nanoparticles were obtained by laser ablation of gold or terbium targets in organic solvents. The thus formed colloidal solutions were used to prepare nanocomposites of gold nanoparticles in polymer matrices of transparent and colorless fluorine-containing polymer. The polymer matrix is found to promote aggregation of nanoparticles of metal under study into elongated chains. In turn, metal nanoparticles influence on the polymer matrix. Gold nanoparticles amplify the Raman signal of the polymer matrix. In addition, the Raman spectra of nanocomposites indicate aggregation of disordered carbon around the nanoparticles obtained by laser ablation in organic solvents.

1. Introduction
Nanocomposites of metal particles in a polymer matrix have a number of unusual and unexpected properties [1–6]. As was shown previously, polymers nanocomposites containing in their composition metal nanoparticles with have a high permittivity due to the high polarizability of the metal nanoparticles [7]. This function is of interest not only for electronic and microelectronic applications, but for light-conversion technologies. The optical properties of these nanocomposites, which are of value for light-conversion technologies, have been studied less thoroughly [8]. Apparently, it can be expected that plasma oscillations of electrons in metallic nanoparticles will have an extremely short reaction to the optical excitation of nanoparticles. The typical time of this response is comparable with electron–phonon relaxation time (on the order of 1 ps). Due to such short response times, these nanocomposites can find application even as optical keys in photonic elements. If we do not consider
the main advantage of the response time, then such composites can find application in biophotonics, namely in biological and agricultural research and applications [9-10].

At present, a large number of methods are used to implant nanoparticles in solid substrates. At the heart of modern nanocomposites, as a rule, there are substances capable of forming highly ordered structures with a certain geometry (alternating flat layers, filaments, point inclusions, more complex compositions). [11]. In this study, we use technique of forming nanocomposites of gold nanoparticles in a polymer matrix, based on laser ablation of solid targets in liquids [12]. A method for obtaining metal nanoparticles and their properties before and after incorporation into a fluoroplastic polymer are described.

2. Methods
Gold nanoparticles were obtained by laser ablation in a liquid. A solid target was located at the bottom of a glass cuvette under a thin layer of working fluid (usually several millimeters) and irradiated with laser radiation (90 J/cm² at 1.06 μm, pulse width of 130 ns) [13]. The working fluids are chosen to be transparent at the laser wavelength, so the laser radiation is absorbed in the target material. In the case of volatile liquids, the cell is covered with a thin glass to slow the evaporation. This method of manufacturing nanoparticles is of a physical nature in contrast to known chemical methods. The generation rate of nanoparticles and their average size depend on a number of laser parameters. A distinctive feature of laser ablation of solids in liquids is that nanoparticles can be obtained in virtually any liquid. This feature was used in this study to form nanocomposites: metal nanoparticles embedded in polymer matrices. A distinctive feature of the laser method is the potential to generate "pure" nanoparticles that do not contain undesirable ions and surfactants [14].

![Figure 1. Experimental setup for laser ablation of solids in a liquid environment (A). An enlarged image of an experimental cell for laser ablation (B).](image)

The size of the nanoparticles was determined using an analytical centrifuge DC24000 (CPS Instruments), a fast and sensitive particle size analyzer for colloidal solutions [XXXX]. To confirm the morphology of nanoparticles, a transmission electron microscope Carl Zeiss 200FE was used. The spectrometer USB3000T (OceanOptics) was used to study the spectral characteristics of nanoparticles. The Raman spectra of the nanocomposites were recorded with a U1000 spectrometer.

3. Results
The gold nanoparticles obtained by us are characterized by size and morphology. It is shown that in our gold nanoparticle preparation there are two types of nanoparticles (Fig. 2). All our gold nanoparticles have a size of less than 50 nm. Smaller ones with a size of 6-10 nm (70%) and larger ones 15-20 nm (30%). The distribution of these groups of nanoparticles by mass is the opposite. A
group of smaller nanoparticles with a size of 6-10 nm accounts for about 30%. A group of larger nanoparticles with a size of 15-20 nm account for about 70%.

**Figure 2.** Distribution of nanoparticles by weight (A) and size (B).

The data obtained in the analytical centrifuge were confirmed by TEM microscopy. As can be seen in Figures 3 and 4, two nanoparticle fractions are observed. The average size corresponds to the particle size established by means of an analytical centrifuge.

The absorption spectra of the Au nanoparticles-fluorine-containing nanocomposite radically differ from the spectra of nanoparticles in liquids (Fig. 5). The spectrum of colloidal solution of gold nanoparticles in acetone exhibits a peak near 530 nm, which corresponds to the transverse plasmon resonance. One can also see a wide absorption wing in the red spectral region, which is indicative of the presence of some fraction of elongated Au nanoparticles in the colloid. The same nanoparticles in the nanocomposite with fluorine-containing polymer demonstrate the second plasmon resonance peak near 650 nm, which is due to elongated gold nanoparticles with an aspect ratio of about three.

The initial Raman peaks of polymer in nanocomposite have a larger amplitude. This can be explained by the enhancement of Raman scattering (the so-called surface-enhanced Raman scattering (SERS)) from composite nanoparticles. Gold nanoparticles enhancement some low-frequency vibrations in the fluorine-containing polymer.

**Figure 3.** TEM image of gold nanoparticles.
Figure 4. Size distribution averaged over 100 nanoparticles from TEM images.

Figure 5. Extinction spectra of a colloidal solution of gold nanoparticles in acetone and Au nanoparticles (Au NP)-fluorine-containing nanocomposite (A). Raman spectra of fluorine-containing polymer in the initial state and fluorine-containing nanocomposite with gold nanoparticles (B).

Figure 6. Polymer molecules align gold nanoparticles into chains in the nanocomposite. Carbon atoms are depicted in gray, fluorine atoms are green, gold nanoparticles are crimson.

Fluoroplast containing a polymer matrix apparently makes gold nanoparticles aggregated in a polymer. Nanoparticles cannot be incorporated directly into polymer chains, and the matrix flows
around them. This process is schematically shown in Fig. 6. This aggregation is accompanied by a change in the plasmon resonance spectrum of metal nanoparticles. The newly formed absorption bands overlap almost entirely the visible spectral region and partially the IR region. This circumstance makes it possible to measure the high-speed response of nanocomposites using most diverse laser sources.

4. Conclusions
Colloidal solutions of gold nanoparticles were obtained by laser ablation of gold targets in organic liquids. Nanocomposites were prepared by mixing these solutions with solutions of fluorine-containing polymer. An analysis of the extinction spectra of the nanocomposites showed that the polymer matrix changed the morphology of the nanoparticles incorporated into it in comparison with the initial morphology. The matrix aligns particles into elongated chains with a large aspect ratio. In turn, the Raman spectra of the nanocomposites show that nanoparticles also affect the polymer matrix. In the fluorine-containing matrix, gold nanoparticles increase some vibrational modes of the polymer in the low-frequency spectral region. The nanocomposites fabricated in this study have an acceptable optical quality and can be tested for ultrafast optical response.

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