Laser forming of nanostructures in aqueous suspensions with particular optical and photoelectrical properties

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Abstract. The self-organizing forming of ordered nanostructures in the aqueous suspensions with inorganic nanoparticles of nickel, copper, silica and bio-organic particles of grinded green leaves were studied by means of the irradiation with red, green and blue lasers. Various forms of self-consistent non-homogeneous distributions of the nanocomponents and the optical flows were found. The suspensions with high density of the nickel nanoparticles demonstrated abrupt changes of their transparency and periodicity. These abrupt changes were transformed to more slow oscillations of the particles and light distributions when the nickel particles were mixed with the nanoparticles of copper. The suspensions with the nanoparticles of copper created arc-like agglomerations explained by generation of vortexes. The vortex-like distributions were found in the suspensions with silica as well. The anisotropic agglomerations were observed during the irradiations of the suspensions with the grinded green leaves. These results are promising for the developments of new kinds of optical modulators and switchers, optical memory and green solar batteries.

1. Introduction
During the last 30 years active studies of various nanostructures resulted in a wide set of applications of nanotechnologies for improved construction materials, microelectronics, nanooptics, biology and medicine [1-7]. E.g., optical computing [8] is one of the prospective directions of science and technologies where nanostructures can give essential benefits. This is due to significant decrease of energy consumption which growth is problematic for electronic computers, increased density of memory cells in comparison with magnetic systems, improves speed of the transfer and treatment of information, etc. On the other hand usual technical methods of preparation of nanostructural arrays (electron lithography, molecular beam epitaxy, etc.) are rather complicated and expensive. So fast broadening of applications of various nanostructures needs development of more economic nanotechnologies. Processes of selforganizing structuring taking place in various kinds of condensed matter subjected to mechanical, electrical, optical, thermal influences [9, 10] are capable to be a basement for simplified preparation of necessary nanostructures. Our paper is devoted to forming of ordered nanostructures in aqueous suspensions of metal, dielectric, semiconducting and biological particles by means of laser irradiation.

Various kinds of nanoparticles have been used in our experiments: diamagnetic metal copper and ferromagnetic metallic nickel, as well as dielectric silicon dioxide (silica). The mean
diameters of these nanoparticles were about 30 nm. These particles were introduced into distilled water forming colloid solutions. The volume concentrations of these solutions varied from 20% to 40%. Besides aqueous suspensions of grinded green leaves were irradiated as bioorganic material. The suspensions were deposited onto glass substrates. These substrates were placed horizontally above the exit window of semiconducting lasers. Three kinds of lasers were used: blue (450 nm wavelength), green (532 nm) and red (633 nm). The total powers of the lasers were about 0.5 w. The power density of the lasers beams at the entrance to the suspensions was about 1 w/cm². The beams of the lasers propagated through the suspensions in vertical direction. The patterns of the distributions of the laser light intensity after its propagation through the crystal were projected onto the horizontal white screen placed above the samples with the suspensions at a 3 meter distance. The variations of these patterns at the screen were registered by the video-recorder with temporal resolution 0.02 seconds and spatial resolution about 0.1 cm. The morphologies of the suspensions after the laser irradiation were studied by means of optical and scanning electron microscopes.

2. Experimental results and discussion

All the suspensions subjected to the lasers irradiation demonstrated active dynamics of registered the patterns of the laser light scattering. These dynamic variations reveal rather intensive motions of nanoparticles inside the suspensions induced by laser irradiation. On the other hand each of the samples presented several individual features. Spatial distributions of all the patterns during their fast variations demonstrate most frequently close to periodical distributions of light intensity (see for example Fig.1 with light scattering by the suspension with nanoparticles of nickel).

Figure 1. The periodical pattern of light scattering corresponding to the self-consistent distributions of the nickel nanoparticles and the light photons
These periodicities correspond to internal periodical distributions of the nanoparticles in this suspensions. The rates of the changes of these structures depend of the intensity of the light and nature of the particles. The most quick re-organizations take place in the suspensions with the nanoparticles of nickel. These particles due to their magnetic moments [11] are attracted to each other forming dense agglomerations which are non-transparent for the light. So at the beginning of illumination of this suspension the laser beam can not pass through it. But after several tens of seconds the transparency appears abruptly. Our registration system with the temporal resolution of 0.02 seconds showed that this avalanche-like breakdown of the suspension proceeded faster than this interval. Then during the next 0.02 s the homogeneous spot of the light was transformed to a set of three parallel lines and at the next 0.02 to five lines (Fig. 2).

These transformations showed that the nickel nanoparticles pushed away from the laser beam at the first moment then begin returning motions arranging simultaneously linearly periodical distributions. These processes of abrupt initial pushing out of the nanoparticles followed by their partial returning can be explained by external photo-effect taking place during the illumination of the particles. At the beginning the photoelectrons removed by the light from the particles produce their positive charging. Due to the creation of positive charges the Coulomb repulsion between the nanoparticles appears in addition to the initial magnetic attraction. This repulsion is increasing in correspondence with the further photoionization of the particles. At a certain moment the Coulomb repulsion in combination with the light pressure becomes stronger than the magnetic attraction and the particles are separated and repulsed from the light beam. But after this separation the photoelectrons begin to penetrate between the particles. Hence the partial compensation of the repulsion occurs resulting in reversal approaching of the particles due to their magnetic attraction. So the particles return again into the light beam. Self-consistent interaction between the particles, the photoelectrons and the light creates their distributions close to periodical inside the suspension [12] which is transferred to the pattern of the light scattering (Fig. 2).

The suspensions with mixed nanoparticles of nickel and copper (20% of each kind) subjected to the laser irradiation demonstrated severe oscillations of their distributions, registered by the variations of the light scattering. The transverse dimensions of the light spot at the screen placed at 3 m from the suspensions oscillated between 3 cm to 30 cm with the intervals between the moments of maxima and minima from 2 to 5 seconds (Fig. 3).

It should be emphasized that in the suspensions with nickel only or with copper only (without their mixing) oscillations of this kind were not observed. We suppose that the main reason of these oscillations is connected with active repulsive interactions between ferromagnetic nickel and diamagnetic copper. The minimal light spot corresponds to the moment when the
Figure 3. The temporal oscillations of the red laser scattering by the suspension with the nanoparticles of nickel and copper. One unit at the horizontal axis corresponds to 0.5 seconds.

nanoparticles are pushed out from the laser beam and it propagates though homogeneous water without scattering. The maximal light spot corresponds to the inverse situation when the non-homogeneous mixture of the particles is returned in the beam inducing severe scattering of the light. The removal of the particles from the beam occurs due to two reasons: well known pushing out of the metal particles from the maxima of the light intensity [13] and Coulomb repulsion between them because of their electrical charging in the process of external photoeffect [14]. The mixture of nanoparticles of nickel and copper is concentrated in the vicinity of the laser beam. Here the pushing out laser forces are absent but the repulsion forces between diamagnetic and ferromagnetic particles are enhanced due to the decrease of the distances between the particles. These forces induce reversal redistribution of the particles for recovering the initial distances between them. After returning of the particle into the beam the process of their pushing out starts again, etc.

It should be noted that all other suspensions demonstrated much weaker oscillations of the light scattering in the form of slight variations redistributions of the patterns at the screen. The typical intervals between these redistributions were less than one second. For example Fig. 4 presents the light scattering patterns in the suspension with silicon dioxide nanoparticles registered with the time interval about 0.5 seconds.

Besides the periodical distributions of the light intensity (corresponding to periodical distributions of the nanoparticles in the suspensions) additional important particularities were observed. These are arcs and rings formed in the patterns of the light scattering by suspensions with copper and silicon dioxide. At Fig.4 the arcs-like rows of light spots and corresponding dark arcs between them are seen at the right and lower parts of the pattern. Fig.5 (left) presents the rings at the pattern of the light scattering in the aqueous suspension with copper nanoparticles.

These kinds of the light scattering distributions correspond usually to ring or spiral distributions of the phases and amplitudes of light in the scattering medium [15]. These distributions of the light parameters are connected with corresponding particularities of
Figure 4. The two patterns of the light scattering by the silica nanosuspension with the time interval of 0.5 seconds

Figure 5. The laser light scattering (left) and the electron microscopy (right) of the distribution of the nanoparticles of copper

distributions of the nanoparticles themselves. For example, Fig. 5 (right) presents electron microscopy of the copper nanoparticles left after evaporation of water from the suspension. It is seen clearly that the most part of the nanoparticles arrange arcs and rings of nanoscopic dimensions. Forming of these arc-like or ring-like agglomerations can be explained by generation of turbulence vortices due to local heating of the particles with the absorbed light, resulting in convection flows of the suspension as well as due to local maxima of the light pressure created by self-consistent redistributions of the nanoparticles and the light flow. These semi-ring and arc agglomerations of copper nanoparticles which possess high electric conductivity due to their nanoscopic dimensions are capable to create meta-materials with the negative refractive index in the visible range [16]. The metamaterials of this kind are promising for developments of optical microscopy with nano-resolution, new kinds of optical memory and information treatment, etc. [17]. The local increase of the light intensity is described in several publications as soliton-like excitations combining nanoparticles and light redistributions [18-21]. The silica nanoparticles are
transparent for the laser light, so the participation of the local heating induced by the laser light is excluded. But on the other hand nanoparticles of quartz are capable to arrange comparatively long chains [22]. Single crystals of quartz are characterized by screw symmetry [23]. So it is possible to imagine that the nanoparticles of quartz subjected to irradiation by the laser light with relatively high electrical field are capable to reproduce screw-like internal structure. The electrical polarization of this structure can induce attraction between the particles with creation of the screw-like chains. These chains will modify in their turn the light flow inside the suspension arranging spiral distributions of the amplitude and phase [24]. Generally speaking the possibility of generation of self-consistent states of spiral distribution of nanoparticles, turbulent vortexes inside the suspensions and corresponding optical vortexes can not be excluded [25].

Aqueous suspensions with bioorganic components of green tissues of plants are of especial interest for laser irradiation because their illumination induces high electrical activity in the process of photosynthesis [26] (separation and migration of electrical charges followed by creation of large dipole moments). During irradiation of the suspensions from water and grinded green leaves with blue and red lasers we found that at the beginning of the process the components of the green tissue decreased their dimensions resulting in broadening of the light scattering spot. If the suspension is irradiated with circularly polarized laser light total circular motion of the pattern of the light scattering is observed in addition to described above periodicity. This phenomenon can be attributed to the inducing of high dipole moments inside the green nanocomponents by electrical field of the light with subsequent rotation of these components due to their involvement by the rotating electrical field. These involvement is possible because the density of the green nanocomponents is close to the density of water. So due to compensation of the gravitation and low mass the involvement of these particles to rotation is much more probable in comparison with metal nanoparticles. After several minutes of irradiation optical microscopy with polarized light of the suspension revealed the creation of anisotropic microparticles (Fig.6).

Figure 6. The optical polarization microscopy of the microparticles created during irradiation of the suspension of the grinded green leaves by the blue laser. The dimensions of the microphoto are 100x100 micrometers
These particles are oriented easily with relatively weak external electrical field. Earlier we found that illumination of green leaves of plants induce internal electrical potentials. Forming of anisotropic microparticles can be explained by two processes. The thylakoids containing molecules of chlorophyll after their absorption of photons transfer photoexcited electrons to the outer surface. So positive charges are left inside the thylakoids. When the amount of these charges exceeds a certain threshold its membrane due to Coulomb repulsion is destroyed and forms a sort of a plate with one side charged positively and the opposite side charged negatively. Then these plate-like membranes are assembled to oriented arrays due to Coulomb attraction between positive and negative sides. These arrays are capable to produce macroscopic electrical polarization being illuminated due to oriented separated of the charges by the membranes. This scheme describes the possibility of preparation of solar batteries using cheap raw materials and relatively simple equipment.

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4. References
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