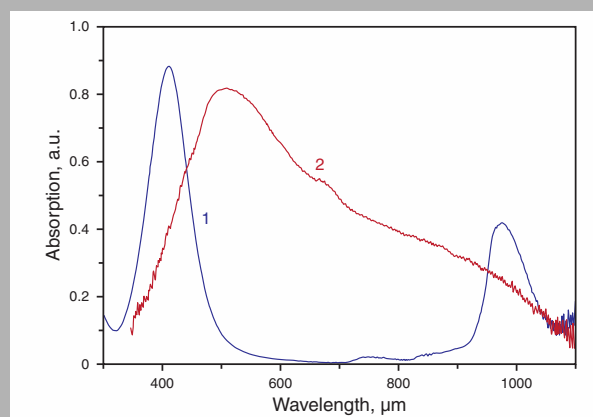


**Abstract:** Medium power (0.3–8.0 W) 970 nm in wavelength laser irradiation of water with added Ag nanoparticles (in the form of Ag-albumin complexes) through 400  $\mu\text{m}$  optical fiber stimulates self-organization of filaments of Ag nanoparticles for a few minutes. These filaments represent themselves long (up to 14 cm) liquid gradient fibers with unexpectedly thin (10–80  $\mu\text{m}$ ) core diameter. They are stable in the course of laser irradiation being destroyed after laser radiation off. Such effect of filaments of Ag nanoparticles self-organization is rationalized by the peculiarities of laser-induced hydrodynamic processes developed in water in presence of laser light and by formation of liquid fibers.



Curve 1 – absorption spectrum of initial collargol solution and curve 2 – absorption spectrum of deposit, which formed at 5 W of laser power and 10 min of irradiation

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## Laser-induced self-organization of filaments from Ag nanoparticles

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### 1. Introduction

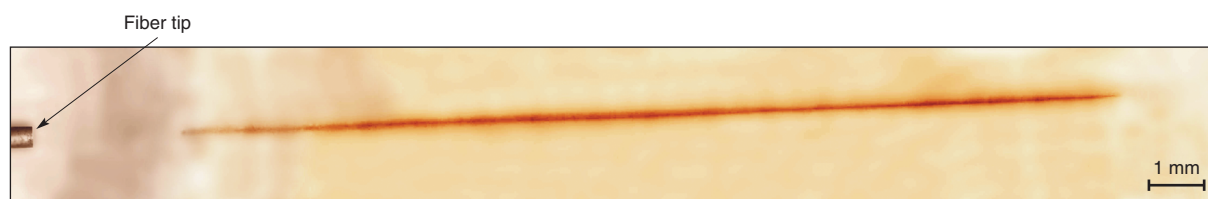
Nano-structured materials are of great interest for modern opto-electronics, sensorics, information, optofluidic, and biomedical technologies [1–6]. Different laser-based approaches have been applied to manipulation [7,8], visualization [4,9,10], structure organization [11,12], assembling, and agglomeration [13–15] of nanoparticles. Effects of nanoparticles self-organization are considered in [11,16–18].

In optical tweezers approaches [7] tightly focused laser beams have been used to control submicron particles behavior. As for metal nanoparticles, the optical tweezers

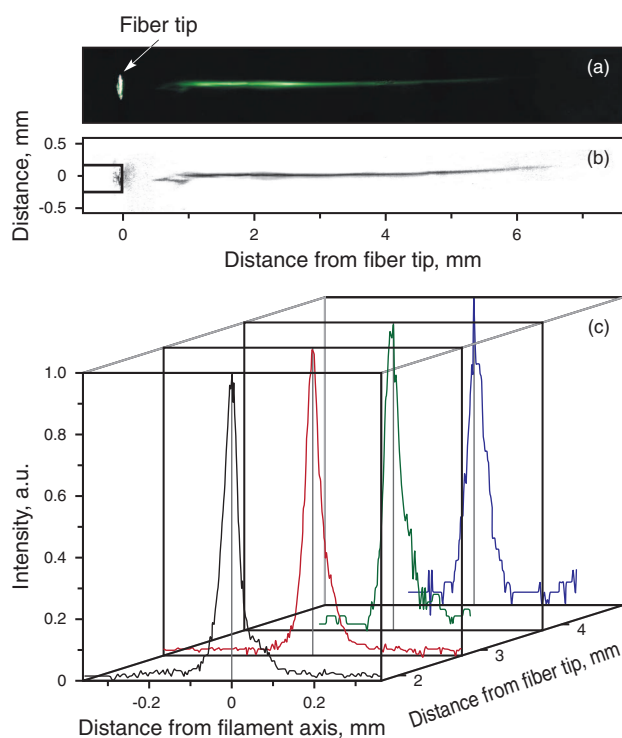
are able to trap them effectively at their sizes  $> 5$  nm [19–21]. Tightly focused laser beams are required to produce forces in piconewton range for 3-D trapping of 9.50–254 nm nanoparticles at few tens of milliwatts of laser power [22]. For example, optical tweezers with 1.05  $\mu\text{m}$  in wavelength, 0.1 W in laser power and 1.00  $\mu\text{m}$  in waist diameter allows trapping of 36 nm nanoparticle for a few seconds [19]. According to [23], 1–10  $\text{MW}/\text{cm}^2$  laser intensities are required to provide effective laser structuring of metal 30 nm nanoparticles.

The aim of this letter is to demonstrate that medium power (0.3–8.0 W) 970 nm in wavelength fiber-laser irra-

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**Figure 1** (online color at [www.lphys.org](http://www.lphys.org)) Micro-image (in transmission mode) of filament of Ag nanoparticles fabricated in water nearby optical fiber tip at 2.5 W of laser power



**Figure 2** (online color at [www.lphys.org](http://www.lphys.org)) (a) – microscopic picture of filament (in scattering mode) of Ag nanoparticles fabricated in water nearby optical fiber tip at 0.4 W of laser power, (b) – image of this filament represented in shades of gray after processing of (see text) of Fig. 2a, and (c) – normalized vertical profiles of image given at Fig. 2b

diation of water (through 400  $\mu\text{m}$  optical fiber) with added Ag nanoparticles (in the form of Ag/albumin complex – “collargol”) can stimulate the effect of self-organization filaments from Ag nanoparticles. Laser intensities at the fiber tip in this case (0.2–6.0  $\text{kW}/\text{cm}^2$ ) are much less than that in used in [23] for metal nanoparticles structuring. These filaments represent themselves long (up to 14 cm) liquid gradient fibers with unexpectedly thin (10–80  $\mu\text{m}$ ) core diameter located in water nearby laser beam axis. Possible mechanisms of such effect are discussed.

## 2. Materials and methods

Fiber laser radiation (LS-0,97 IRE-Polus, Russia) 0–10 W in output and 970 nm in wavelength was delivered into water-filled plastic cell through 400  $\mu\text{m}$  transport silica optical fiber, which was placed horizontally in the cell. Low intensity (up to 1 mW) green pilot beam from the built in diode laser was used to highlight the 970 nm laser irradiated zone in the cell. The cell was placed at the sample compartment of optical microscope (MC300, MICROS, Austria) equipped with color digital video-camera (Vision). Spectroscopic studies were performed with fiber-optic spectrum analyzer (USB4000, Ocean Optics) and UV/vis absorption spectrometer (Cary 50, Varian). To measure the refraction index of collargol we have applied the fiber-optic reflectometer FOR-11 (LaserChem, Russia), which provides  $10^{-4}$  precision of refraction index measurements at  $\lambda = 1256$  nm wavelength (see also [24]). Cleavage of transport optical fiber has been always produced just before each experiment. Ten minutes later (to provide reasonable attenuation of hydrodynamic motions in the cell) the drop (0.01–1.00 ml in volume) of brown colored collargol (complex of 25 nm in size Ag nanoparticles with albumin) has been smoothly introduced into the water cell 0.5–10.0 mm aside from the optical fiber tip.

Our in situ optical microscopic studies of laser-induced filament formation were accomplished in two different modes:

- 1) in transmission mode using illumination with white light from microscope lamp,
- 2) in scattering mode, using illumination with green light of pilot laser beam through the same transport fiber.

## 3. Results and discussions

Our experiments show that 970 nm fiber laser irradiation of water in the cell with introduced collargol drop causes in some period of time (from seconds to minutes) formation of thin and long quite homogenous filaments, growing along the axis of 970 nm laser beam in water. These filaments are brown colored (that gives the evidence of enhanced Ag nanoparticles concentration in filament) and can be seen even with unaided eye.

Fig. 1 demonstrates the microscope image (in transmission mode) of one of such filaments. This filament is located along the axis of output laser beam and is about 17 mm in length. The measured profile of optical density of this filament is triangular in its shape with about the same widths along filament (determined at half-maximum) of  $\sim 200 \mu\text{m}$ .

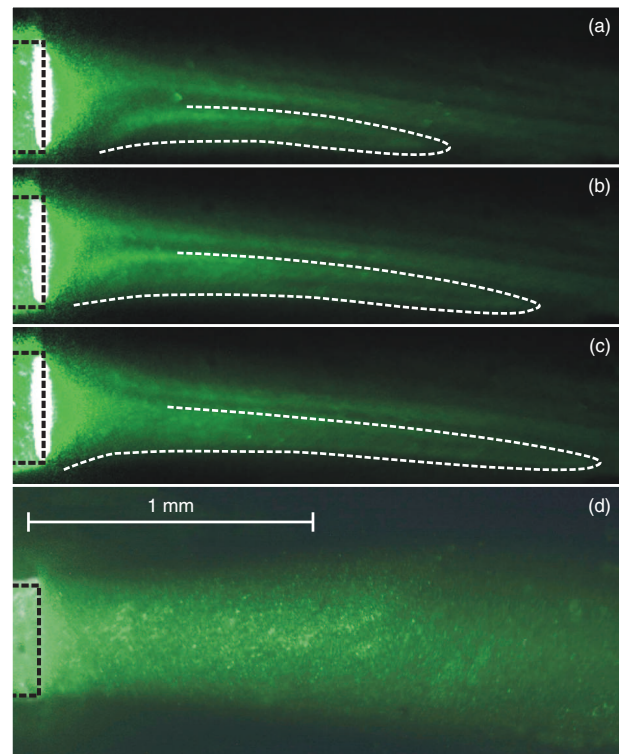
Fig. 2a demonstrates the micro-image of another laser fabricated filament in scattering mode. Intensity of light scattered from this filament decreases gradually with the distance from fiber tip. Attenuation of green light in this case is caused by absorption and scattering of green light in the course of its propagation through the filament. To reveal the peculiarities of filament (given in Fig. 2a) we have performed the following processing of its microscope image: all vertical profiles of image were normalized to local maximum (Fig. 2c); the microscope image was represented in shades of gray (Fig. 2b). As it follows from Fig. 2b and Fig. 2c the length of given filament is about 6 mm, its average width is about  $40 \mu\text{m}$ , and scattering intensity decreases rapidly with the distance from filament axis. Notice that vertical profiles of all fabricated filaments (in both transmission and scattering modes) are almost triangular with a sharp top. It was also established that the end of filament has always a needle-like shape and, the width of filament obtained in transmission mode measurements exceeds 3–5 times that obtained in scattering mode.

It is of importance that filaments of Ag nanoparticles have been formed in our experiments only in the case of existence of initial collargol concentration gradient in laser irradiated water (when collargol drop was introduced initially into water aside from fiber tip). When collargol drop was premixed in water cell before laser irradiation, formation of filaments has never been observed (at any collargol concentrations in the cell and at any laser powers and doses).

The initial stage of filament self-organization process can be clearly seen in scattering mode (Fig. 3). Intense hydrodynamic flows take place nearby the fiber tip when laser power is on. Such flows result in intrusion of collargol from neighboring area into the area in front of the fiber tip. The slanting filament structure is clearly seen in Fig. 3. One can also see here the initial process of new intrusion formation (outlined with dashed line). The rate of rise-up front of a given intrusion (which is about  $150 \mu\text{m}$  in average thickness) is found to be described by exponential law  $V = 0.6\exp(-1.5r)$ , where  $r$  is the distance from fiber tip: at 1 mm from fiber tip  $V = 1.5 \times 10^{-2} \text{ cm/s}$ , while at 2 mm from fiber tip  $V$  falls down to  $3 \times 10^{-3} \text{ cm/s}$ .

It was revealed that filaments of Ag nanoparticles self-organized in the course of 970 nm laser irradiation can exist in the cell (in the presence of laser beam and with no external mechanical distortions of liquid in the cell) for quite a long period of time. We have supported such filaments for tens of minutes. Notice that both rectilinear and curved filaments were self-organized in our experiments.

After 970 nm laser radiation being off, the filaments of Ag nanoparticles have been completely destroyed for



**Figure 3** (online color at [www.lphys.org](http://www.lphys.org)) Microscope pictures (in scattering mode) of intrusions of Ag nanoparticles in water (outlined with dashed line) stimulated by laser induced hydrodynamics nearby optical fiber tip at 1.0 W of 970 nm laser power in 6 s (a), 12 s (b), and 18 s (c) of laser irradiation. (d) – scattering of green light beam in diluted collargol with no 970 nm laser irradiation. Fiber tip is shown by dashed line

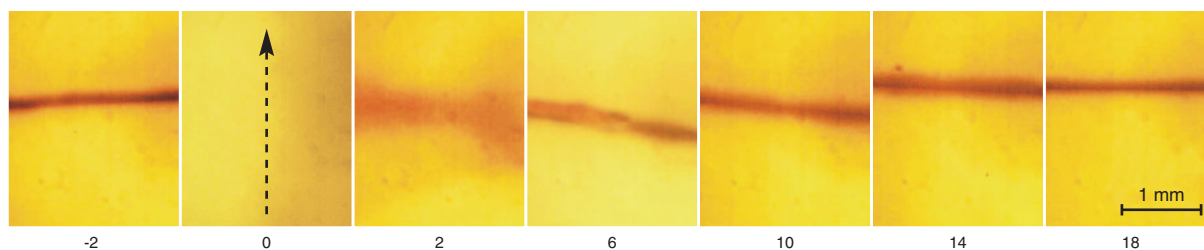
10–30 s period of time. Notice that time  $\Delta t$  of diffusion blooming of filament by  $\bar{x}$  value, estimated by the formula

$$\bar{x}^2 = D\Delta t = \frac{kT}{3\pi\mu d}\Delta t,$$

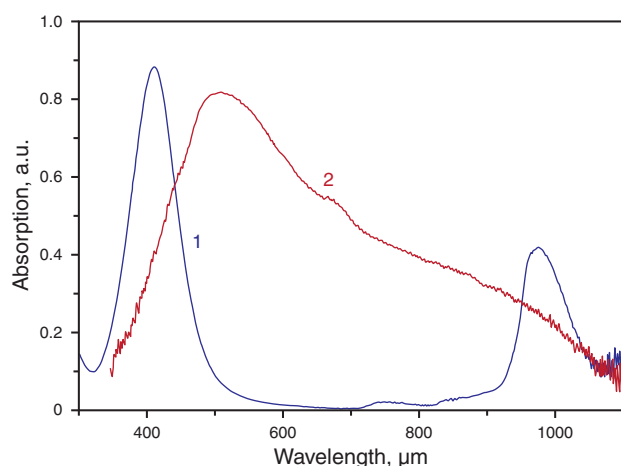
where  $D$  is diffusion coefficient of nanoparticle,  $k = 1.38 \times 10^{-23} \text{ J/K}$  – Boltzmann constant,  $T(K)$  – absolute temperature,  $\mu = 1.002 \times 10^{-3} \text{ (N s/m}^2\text{)}$  – dynamic viscosity of water, and  $d = 25 \text{ nm}$  Ag nanoparticle diameter. This formula gives  $\Delta t = 25 \text{ s}$  for  $\bar{x} = 100 \mu\text{m}$ .

External mechanical distortions of filament of Ag nanoparticles results in its destruction. However, after mechanical distortion being off, the filament can be renewed completely in presence of 970 nm laser radiation. Fig. 4 shows the dynamic of such filament renovation after distortion of self-organized filament (produced by its rapid crossing with thin a metal needle). As one can see from Fig. 4, complete renewal took place for quite a short period of time (about 20 s).

Our experiments have shown that there is some range of 970 nm laser powers, for which the effect of laser-induced filament self-organization takes place and is, also,



**Figure 4** (online color at [www.lphys.org](http://www.lphys.org)) Renewal of destroyed filament of Ag nanoparticles in water nearby the tip of optical fiber

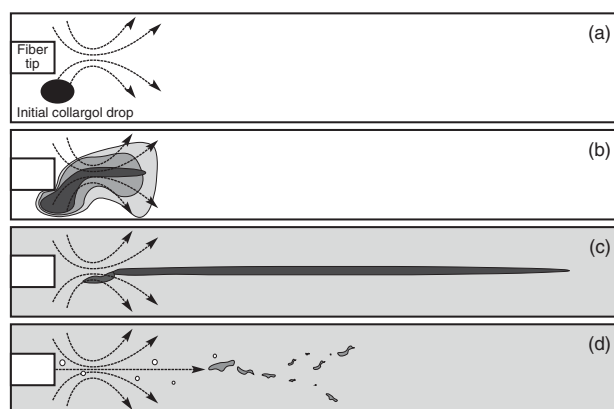


**Figure 5** (online color at [www.lphys.org](http://www.lphys.org)) Curve 1 – absorption spectrum of initial collargol solution and curve 2 – absorption spectrum of deposit, which formed at 5 W of laser power and 10 min of irradiation

stable and reproducible. At laser power higher than 8 W we have never observed filament formation. At 0.2–0.5 W laser power filaments have been formed but have been unstable. The most stable and long-living filaments were observed in 0.5–3.0 W laser power range. At laser power less than 0.2 W we have never observed such filament formation.

The instability of filaments and even their absence at high laser powers is caused by intense laser-induced hydrodynamic processes nearby the fiber tip. Curve 1 in Fig. 5 shows collargol absorption spectrum (400 nm band is attributed to Ag nanoparticle plasmon resonance and 980 nm absorption band – to absorption by water), while curve 2 shows absorption spectrum of deposit, which was formed at 5 W of laser power and 10 min of irradiation.

The wide absorption band of deposit observed at fiber tip can be caused by island film of Ag nanoparticles, and, possibly, by elementary carbon absorption (deposited at fiber tip due to albumin thermo-decomposition). As a result of such deposits, the fiber tip becomes an intense heat source. That causes explosive water boiling, intense for-



**Figure 6** (online color at [www.lphys.org](http://www.lphys.org)) To the explanation of the effect of laser-induced formation of filaments of Ag nanoparticles (a)–(c). (a) – formation of water flow nearby the fiber tip, (b) – formation of Ag nanoparticles intrusions, (c) – fabrication of filaments from Ag nanoparticles, and (d) – intense formation of micro-bubbles hampering filament formation and destructing fabricated filaments at high laser power

mation of micro-bubbles [25], moving rapidly away from fiber tip to liquid and destroying filament.

We rationalize the observed effect of laser-induced self-organization of filaments from Ag nanoparticles by the following mechanisms. Initially (Fig. 6a), laser light absorption by water (the absorption coefficient in water at 970 nm is about  $0.5 \text{ cm}^{-1}$ ) causes its heating with the  $2 - 10^\circ\text{C/s}$  rate. Besides, the intense transfer of impulse from laser light to water molecules takes place in this case. As a result, the closed axis-symmetric liquid flows are developed being directed from fiber tip. These flows promote Ag nanoparticles intrusion into the laser beam nearby the fiber tip (Fig. 6b). Such intrusions are clearly seen in scattered green laser light (Fig. 3).

Another factor dominates at the second stage of filament self-organization. The refractive index for collargol  $n_c$  is higher than that for clean water  $n_w$ . The value of  $n_c - n_w = 0.0044$  at  $\lambda = 1256 \text{ nm}$  was directly measured in our experiments using fiber-optic densitometer. Due to the effect of total internal reflection, laser light is concentrated

inside intrusion, which is, in fact, a liquid optical fiber. Channeling of laser light inside intrusion with Ag nanoparticles results in deeper propagation of laser light into water. Light pressure promotes faster movement of intrusion front giving rise to filament (Fig. 6c). As it was shown in [26,27], for example, laser light pressure is also able to force through the boundary between two unmixed liquids, and to form thin channel of one liquid inside another one, thus forming liquid optical fiber with gradient core. The image of filament in transmission mode shows thus optical density of filament from Ag nanoparticles. At the same time the image of filament in scattering mode clearly demonstrate channeling effect in fabricated filament which is in fact a liquid gradient fiber. Such liquid gradient fiber provides also effective channeling of 970 nm laser beam, thus promoting filament elongation and spatial stability.

Laser induced formation of micro-bubble streams 10–50  $\mu\text{m}$  in thickness and up to a few millimeters in length [25] can also promote the filaments fabrication observed in our experiments. It is clear, however, that too intense chaotic formation of micro-bubble streams observed at high laser intensities [25] can hamper filament fabrication (Fig. 6d).

We believe that such filaments of nanoparticles can be developed not only in water media but, also, in other fluids, with other laser wavelength and particles types. The indispensable conditions in this case are the availability of sufficient level of laser light absorption in irradiated medium nearby fiber tip and possibility of liquid fiber formation.

#### 4. Conclusion

We found that medium power (0.3–8.0 W) 970 nm in wavelength laser irradiation of water with added Ag nanoparticles (in the form of Ag-albumin complexes) through 400  $\mu\text{m}$  optical fiber stimulates self-organization of the unexpectedly thin (10–80  $\mu\text{m}$ ) and lengthy (up to 14 cm) filaments of Ag nanoparticles in the form of liquid gradient fibers. These filaments in water are stable in the course of laser irradiation being destroyed after laser radiation off. Such effect of filaments from Ag nanoparticles self-organization is rationalized by the peculiarities of laser-induced hydrodynamic processes developed in water in presence of laser light.

The effect of laser-induced self-organization of filaments of Ag nanoparticles revealed in this letter can be expanded on filaments of other particles types and, also, at even more complicated filament structures, for example, photon crystal structures. Implementation of laser-induced filament self-organization in photo-polymerized monomers can give an opportunity to provide solidification of liquid filaments.

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