Current Nanoscience, 2018, *14*, 50-53

RESEARCH ARTICLE

Photofusion and Disaggregation of Silver Nanoparticles Suspended in Ethanol by Laser Irradiation

Gabriel Ortega-Mendoza[a,*], Oscar Goiz[b], Alfonso Padilla-Vivanco[a], Carina Toxqui-Quitl[a], Plácido Zaca-Morán[c] and Fernando Chávez[c]

[a]*División de Ingenierías, Universidad Politécnica de Tulancingo, UPT, C.P. 43629, Hidalgo, México;* [b]*CIIEMAD, Instituto Politécnico Nacional, C.P. 07340, Ciudad de México, México;* [c]*Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, BUAP, C.P. 72050, Ecocampus Valsequillo, Puebla, México*

ARTICLE HISTORY

Received: June 27, 2017
Revised: August 8, 2017
Accepted: September 5, 2017

DOI:
10.2174/1573413713666171002124415

Abstract: ***Background:*** Metal nanoparticles have been widely investigated due to their unique optical, mechanical, and chemical properties compared with those of the same bulk material. These properties can be tuned by controlling their size or shape, in this sense, several nanomaterials have been obtained by means of both chemical and physical methods. For instance, silver nanoparticles have been obtained in liquid media by using laser ablation or chemical reduction techniques. Another way to obtain a colloidal silver nanoparticles is through the well-known pulsed laser irradiation method which can produce a stable colloidal solution in a few minutes of irradiation and without stabilizing molecules or ligands.

***Methods*:** Silver nanopowder suspended in ethanol was irradiated with a pulsed laser at 532 nm *via* optical fiber. Previously, the fiber was prepared by cleaving and removing its coating and then placed in the middle of a cell. The pulse width was 15 ns and the pulse repetition frequency was 10 kHz. Scanning and transmission electron microscopes were used to observe the silver nanoparticles before and after laser irradiation, respectively. The samples were analyzed by means of UV-Vis spectrophotometer to observe the absorption spectra.

***Results*:** The absorption spectra show that particle size distribution increases according to the irradiation time. The colloidal solution showed a color change (from gray to yellow) after having irradiated it for 5 minutes. From TEM images, it can be observed that silver nanopowder was transformed to semispherical particles with diameters smaller than 1μm, however, due to the wide particle size distribution the colloidal solution was centrifuged for 30 min to separate the nanoparticles.

***Conclusion*:** The pulsed laser irradiation method *via* optical fiber was successfully used to obtain a stable yellow colloidal solution. Photomelting, photofusion, and photofragmentation are the responsible phenomena for the change in morphology and size of the silver nanopowder.

Keywords: Photomelting, photofusion, photofragmentation, silver nanoparticles, optical fiber, laser irradiation, colloidal solution.

1. INTRODUCTION

Nowadays, metal nanoparticles in colloidal solutions have been widely researched due to their unique properties that are dependent on the nanoparticle features, such as composition, size, shape, among others [1]. Therefore, it is possible to change the properties of a colloidal solution by controlling the features of the metal nanoparticles [1-4].

Commonly, silver nanoparticles (AgNPs) in colloidal solutions are used in catalysis [5], chemical sensing [6, 7], nonlinear optics [8-10], surface-enhanced Raman spectroscopy [11, 12], and so forth. Nanoparticles suspended in liquids are subject to the Brownian motion. When these nanoparticles are close enough they undergo both, Van der Waals forces and Columbic forces, provoking their agglomeration and changing the properties of the colloidal solution [13, 14].

Both laser ablation and chemical reduction in the presence of stabilizing agents are two successful methods to obtain metal nanoparticles dispersed in solutions but once the metal nanoparticles are synthesized there is no way to change neither size nor morphology [15-17]. Hence, it is possible to change both size and shape of metal nanoparticles by irradiating the colloidal solution with a pulsed light laser [18-29].

It is known that metal nanoparticles interact with visible light due to its distinct surface plasmon resonance (SPR),

*Address correspondence to this author at the División de Ingenierías, Universidad Politécnica de Tulancingo, C.P. 43629, Tulancingo, Hidalgo; México, Tel.: +52-775-755-8202; Fax: +52-775-755-8321;
E-mail: jose.ortega@upt.edu.mx

1875-6786/18 $58.00+.00

therefore, the absorption of light from intense pulsed laser results in the instantaneous heating of the particle provoking melting and evaporation from the particle surface, and explosive fragmentation. These processes give rise to change in the size and morphology of the nanoparticles [18-20, 26, 29].

The nanoparticles obtained by the laser irradiation method have a larger particle size distribution. Although is possible to carry out a certain size control varying the optical power or changing the number of laser pulses [17, 26, 27]. Furthermore, nowadays there are many methods for selecting nanoparticles with specific sizes, for instance centrifugation, size exclusion chromatography, and membrane filtration [28], among others.

In this paper, we report the well-known irradiation method to generate a stable colloidal solution [22, 23, 29] from a mix of silver nanopowder suspended in ethanol (seed solution) without the use of toxic chemical reduction agents. In this case, an optical fiber was used to irradiate the seed solution, which offers better manipulation of the laser beam since it allows to locate it in the middle of the cell. Due to a strong absorption of the laser light by the silver nanoparticles, the photomelting process arises. This procedure induces an enlargement of nanoparticles to semispherical shapes. The photomelting process starts when the laser energy is greater than 10 μJ.

2. MATERIALS AND METHODS

A scheme of the experimental setup implemented to generate a colloidal solution is shown in Fig. (**1**). A pulsed laser emitting at λ = 532 nm, with a pulse width ≈ 15 ns and oscillation frequency pulses of 10 kHz, was used. For coupling a free space laser into a multi-mode optical fiber with a core diameter of 105 μm, a fiber port collimator was used.

The optical fiber was prepared by cleaving and removing its coating before placing it into the seed solution. Previously, this solution was prepared by mixing 0.3 mg of silver nanopowder (No. 576832 from Aldrich) with 2 ml of ethanol, and later homogenized through an ultrasonic bath for 3 minutes. When the laser is turned on, and its energy is greater than 10 μJ, a colloidal solution with a characteristic color is obtained in a few minutes.

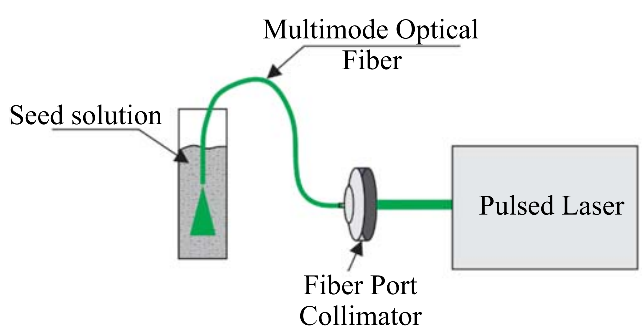

Fig. (1). Experimental setup to obtain silver colloidal solution.

Fig. (**2**) shows the morphology of the silver nanopowder used in this experiment. This image was obtained by a high

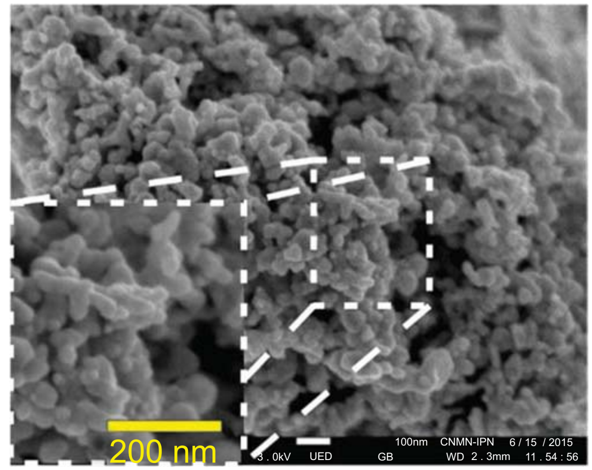

Fig. (2). SEM micrographs of silver nanopowder.

resolution scanning electron microscope JEOL model JSM 7800F. The inset shows that particle sizes are less than 100 nm and they do not determine shapes.

3. RESULTS AND DISCUSSION

Fig. (**3a**) shows photograph of the solution (AgNPs suspended in ethanol) before and after laser light irradiation, and their corresponding absorption spectra in Fig. (**3b**). From left to right, in Fig. (**3a**), we can observe the seed solution (nonirradiated one) and colloidal solutions after irradiation of the seed solution for 30 seconds, 1, 5, 10 and 40 minutes, respectively, with a laser energy of 60 μJ. From these photographs, we can observe a change in the color of the solution mainly after 30 seconds of irradiation; this color change is due to the colloidal behavior of the solution. Furthermore, it is important to comment that nanoparticles of the seed solution precipitated after a few minutes changing the color of seed solution from gray to colorless while the yellow color of the irradiated solution did not change in months.

Fig. (**3b**) shows the absorption spectra of the samples described in Fig. (**3a**). In these spectra, an absorption peak can be seen after 5 minutes when the seed solution was irradiated, it is important to note that the peak amplitude increases according to irradiation time which means that particle size distribution (PSD) increases. Furthermore, it is important to observe that the higher the irradiation time, the higher will be the absorption peaks. This implies that the concentration of disaggregated nanoparticles is greater. The full width at half maximum (FWHM) of the absorption peak determines the AgNPs size distribution; the wider the FWHM, the broader the PSD [30]. We believe that the mechanism to produce the colloidal solution is related with a photochemical reaction where Ag-NPs can trap electrons from a molecule of the solvent [31].

Fig. (**4**) shows TEM images (obtained by a JEOL microscope, model JEM-ARM200CF) of AgNPs obtained after irradiating the seed solution for 40 minutes with a laser energy of 60 μJ. In Fig. (**4a**), we can observe that there are large particles with a smaller size than 1 μm. Metal nanoparticles absorb stronger light near the SPR. We irradiated silver

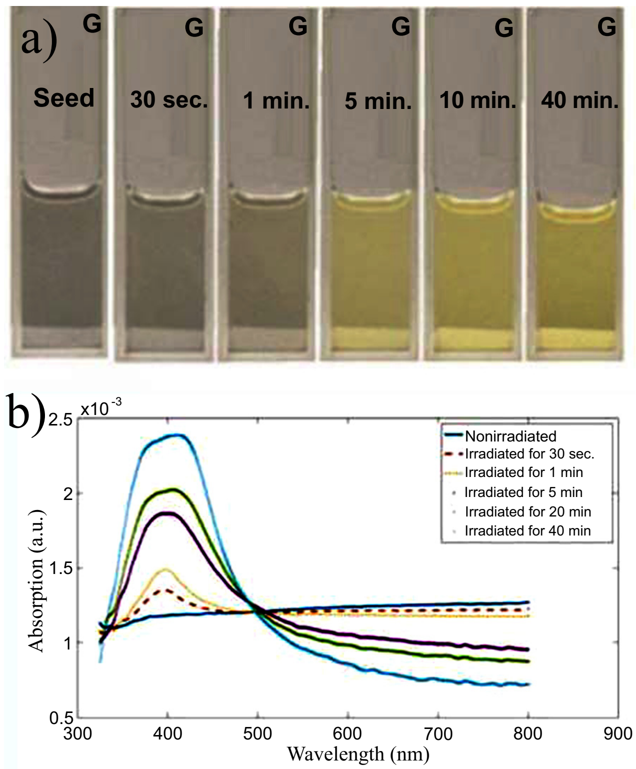

Fig. (3). **a**) Photographs of AgNPs suspended in ethanol before (seed) and after laser light irradiation with an energy of 60 µJ for 30 seconds, 1, 5, 10 and 40 minutes, respectively. **b**) Absorption spectra of the colloidal solutions.

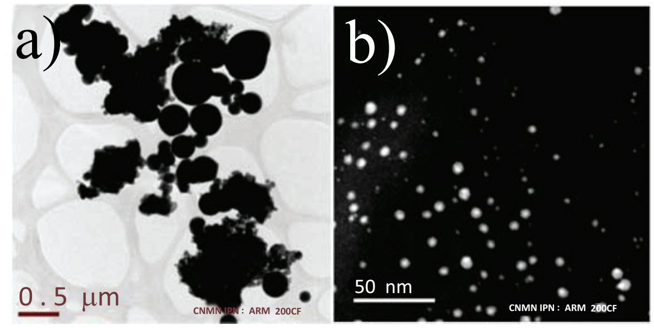

Fig. (4). TEM micrographs of AgNPs obtained by: **a**) irradiating the seed solution for 40 minutes with a laser energy of 60 µJ and **b**) centrifuging the colloidal solution for 30 minutes with a rotation speed of 300 g.

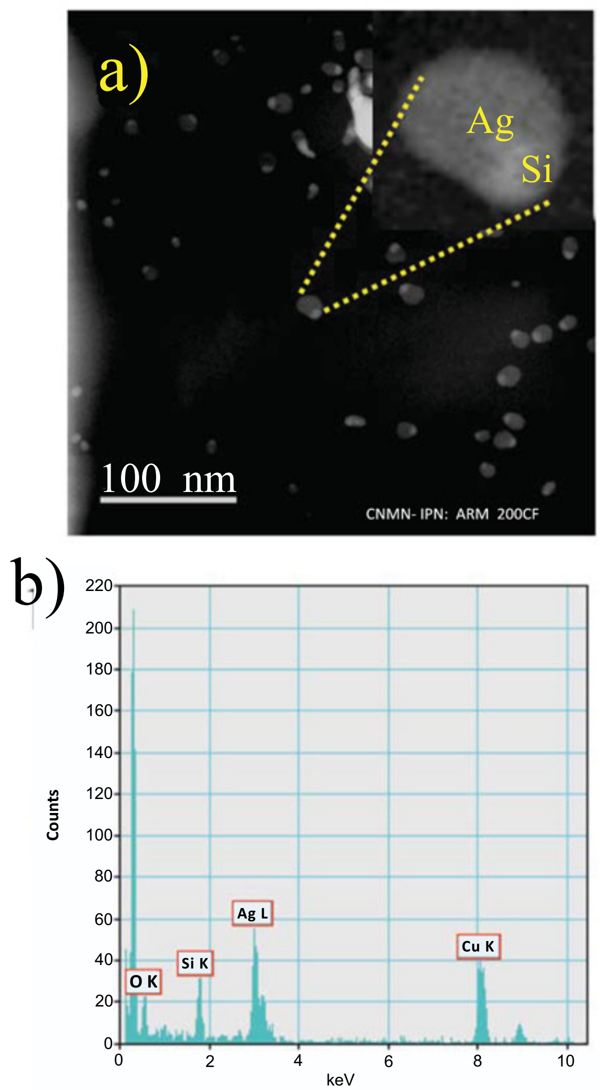

Fig. (5). **a**) AgNPs generated with a laser energy of 60 µJ for 10 minutes. **b**) EDS analysis.

nanoparticles suspended in ethanol with a pulsed laser (near to the SPR). Therefore, the AgNPs undergo super heating. This heating gives raise to coherent acoustic lattice vibrations, melting and evaporating from the particle surface, and explosive fragmentation [18-21, 26]. Both melting and fragmentation processes are responsible for the change morphology and size of particles. Furthermore, it can be observed that there is a wide PSD that is in concordance with the FWHM of the peaks in the absorption spectra. To separate nanoparticles from microparticles, the colloidal solution was placed in a centrifugal machine for 30 minutes with a rotation speed of 300 g. The separated nanoparticles are shown in Fig. (**4b**) with nanoparticles size smaller than 100 nm.

In the process to generate the colloidal solution of silver, many nanoparticles adhere onto the optical fiber end [6], provoking heating due to strong absorption of photons by silver nanoparticles, followed by explosive boiling of ethanol, and another hydrodynamic effects. Consequently, the tip of the optical fiber is degraded [32], therefore it is possible to find silicon together with the silver nanoparticles as shown in Fig. (**5a**), and it was confirmed by EDS analysis in Fig. (**5b**).

CONCLUSION

By irradiating a silver seed solution with a pulsed laser via optical fiber, a stable yellow colloidal solution was successfully obtained. Photomelting, photofusion and photofragmentation are the phenomena responsible for the change in morphology and size of the AgNPs. At the time, some selective techniques as centrifugation, size exclusion chromatography or membrane filtration can be used to separate the AgNPs with a specific size. On the other hand, with this method, it is possible to obtain a colloidal solution without stabilizing molecules or ligands, therefore it can be considered as a green method.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No Animals/Humans were used for studies that are base of this research.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

ACKNOWLEDGEMENTS

This work has been supported by CONACyT through the grant number 248214 and by PRODEP through the grant number DSA/103.5/14/10549. The authors are very grateful to the Centro de Nanociencias y Micro-Nanotecnologías of the Instituto Politécnico Nacional (CNMN-IPN) for provided TEM and SEM characterization.

REFERENCES

[1] Sau, T.K.; Rogach, A.L. Complex-shaped Metal Nanoparticles: Bottom-Up Syntheses and Applications, Wiley-VCH: Weinheim, Germany, **2012**.

[2] Gleiter, H. Nanostructured materials: Basic concepts and microstructure. *Acta Mater*., **2000**, *48*(1), 1-29.

[3] Sosa, I.O.; Noguez, C.; Barrera, R.G. Optical properties of metal nanoparticles with arbitrary shapes. *J. Phys. Chem. B*, **2003**, *107*(26), 6269-6275.

[4] Zhang, Y.; Cheng, W.; Zhang, T.; Dai, Q.; Cui, T.; Wang, Y.; Yu, W.W. Critical size of temperature-dependent band shift in colloidal PbSe quantum dots. *Curr. Nanosci*., **2012**, *8*(6), 909-913.

[5] Narayanan, R.; El-Sayed, M.A. Catalysis with transition metal nanoparticles in colloidal solution: Nanoparticle shape dependence and stability. *J. Phys. Chem. B*, **2005**, *109*(26), 12663-12676.

[6] Ortega-Mendoza, J.G.; Padilla-Vivanco, A.; Toxqui-Quitl, C.; Zaca-Morán, P.; Villegas-Hernández, D.; Chávez, F. Optical fiber sensor based on localized surface plasmon resonance using silver nanoparticles photodeposited on the optical fiber end. *Sensors*, **2014**, *14*(10), 18701-18710.

[7] Ping, H.; Zhang, M.; Li, H.; Li, S.; Chen, Q.; Sun, C.; Zhang, T. Visual detection of melamine in raw milk by label-free silver nanoparticles. *Food Control*, **2012**, *23*(1), 191-197.

[8] Karavanskii, V.A.; Simakin, A.V.; Krasovskii, V.I.; Ivanchenko, P.V. Nonlinear optical properties of colloidal silver nanoparticles produced by laser ablation in liquids. *Quant. Electron*., **2004**, *34*(7), 644-648.

[9] Deng, Y.; Sun, Y.; Wang, P.; Zhang, D.; Jiao, X.; Ming, H.; Zhang, Q; Jiao, Y.; Sun, X. Nonlinear optical properties of silver colloidal solution by *in situ* synthesis technique. *Curr. Appl. Phys*., **2008**, *8*(1), 13-17.

[10] Ganeev, R.A.; Ryasnyanski, A.I.; Kodirov, M.K.; Kamalov, S.R.; Usmanov, T. Nonlinear optical characteristics of colloidal solutions of metals. *Opt. Spectrosc*., **2001** *90*(4), 568-573.

[11] Hildebrandt, P.; Stockburger, M. Surface-enhanced resonance Raman spectroscopy of Rhodamine 6G adsorbed on colloidal silver. *J. Phys. Chem*., **1984**, *88*(24), 5935-5944.

[12] Power, A.C.; Betts, A.J.; Cassidy, J.F. Non aggregated colloidal silver nanoparticles for surface enhanced resonance Raman spectroscopy. *Analyst*, **2011**, *136*(13), 2794-2801.

[13] Jayabalan, J.; Singh, A.; Chari, R.; Srivastava, H.; Mukhopadhyay, P.K.; Srivastava, A.K.; Oak, S.M. Aggregated nanoplatelets: Optical properties and optically induced deaggregation. *J. Phys. Condens. Matter*., **2008**, *20*(44), 445222-8.

[14] Moskovits, M.; Vlckova, B. Adsorbate-induced silver nanoparticle aggregation kinetics. *J. Phys. Chem. B*, **2005**, *109*(31), 14755-14758.

[15] Huang, T.; Xu, X.-H.N. Synthesis and characterization of tunable rainbow colored colloidal silver nanoparticles using single-nanoparticle plasmonic microscopy and spectroscopy. *J. Mater. Chem*., **2010**, *20*(44), 9867-9876.

[16] Scaramuzza, S.; Zerbetto, M.; Amendola, V. Synthesis of gold nanoparticles in liquid environment by laser ablation with geometrically confined configurations: Insights to improve size control and productivity. *J. Phys. Chem. C*, **2016**, *120*(17) 9453-9463.

[17] Mafuné, F.; Jun-ya, K.; Takeda, Y.; Kondow, T. Formation and size control of silver nanoparticles by laser ablation in aqueous solution. *J. Phys. Chem. B*, **2000**, *104*(39), 9111-9117.

[18] Link, S.; Burda, C.; Mohamed, M.B.; Nikoobakht, B.; El-Sayed, M.A. Laser photothermal melting and fragmentation of gold nanorods: Energy and laser pulse-width dependence. *J. Phys. Chem. A*, **1999**, *103*(9), 1165-1170.

[19] Kamat, P.V. Photophysical, photochemical and photocatalytic aspects of metal nanoparticles. *J. Phys. Chem. B*, **2002**, *106*(32), 7729-7744.

[20] Hashimoto, S.; Werner, D.; Uwada, T. Studies on the interaction of pulsed lasers with plasmonic gold nanoparticles toward light manipulation, heat management, and nanofabrication. *J. Photoch. Photobio. C*, **2012**, *13*(1), 28-54.

[21] Takimi, A.; Yamada, H.; Nakano, K.; Koda, S. Size reduction of silver particles in aqueous solution by laser irradiation. *Jpn. J. Appl. Phys*., **1996**, *36*, L781-L783.

[22] Pyatenko, A.; Wang, H.; Koshizaki, N.; Tsuji, T. Mechanism of pulse laser interaction with colloidal nanoparticles. *Laser Photon. Rev*., **2013**, *7*(4), 596-604.

[23] Pyatenko, A.; Wang, H.; Koshizaki, N. Growth mechanism of monodisperse spherical particles under nanosecond pulsed laser irradiation. *J. Phys. Chem. C*, **2014**, *118*(8), 4495-4500.

[24] Swiatkowska-Warkocka, Z.; Pyatenko, A.; Koga, K.; Kawaguchi, K.; Wang, H.; Koshizaki, N. Various morphologies/phases of Au-Based nanocomposite particles produced by pulsed laser irradiation in liquid media- insight in physical processed involved in particles formation. *J. Phys. Chem. C*, **2017**, *121*(14), 8177-8187.

[25] Zhang, D.; Lau, M.; Lu, S.; Barcikowski, S.; Gökce, B. Germanium sub-microspheres synthesized by picosecond pulsed laser melting in liquids: Educt size. *Sci. Rep*., **2017**, *7*, 40355.

[26] Ortega-Mendoza, J.G.; Hernández-Álvarez, C.; Padilla-Vivanco, A.; Toxqui-Quitl, C.; Zaca-Moran, P.; Chávez, F.; Goiz, O. In: Photomelting and photofragmentation of silver nanoparticles suspended in ethanol. *In: Proceedings SPIE 9545 of the Nanophotonic Materials XII SPIE*, San Diego California, United States, **2015**.

[27] Tsujia, T.; Iryob, K.; Watanabeb, N.; Tsuji, M. Preparation of silver nanoparticles by laser ablation in solution: Influence of laser wavelength on particle size. *Appl. Surf. Sci*., **2002**, *202*, 80-85.

[28] Amendola, V.; Meneghetti, M. Controlled size manipulation of free gold nanoparticles by laser irradiation and their facile bioconjugation. *J. Mater. Chem*., **2007**, *17*(44), 4705-4710.

[29] Ishikawa, Y.; Koshizaki, N.; Pyatenko, A. Submicrometer-sized spherical iron oxide particles fabricated by pulsed laser melting in liquid. *Electron. Comm. Jpn*., **2016**, *99*(11), 37-42.

[30] Agnihotri, S.; Mukherji, S.; Mukherji, S. Size-controlled silver nanoparticles synthesized over the range 5-100 nm using the same protocol and their antibacterial efficacy. *RSC Adv*., **2014**, *4*, 3974-3983.

[31] Takeuchi, Y.; Ida, T.; Kimura, K. Colloidal stability of gold nanoparticles in 2-propanol under laser irradiation. *J. Phys. Chem. B*, **1997**, *101*(8), 1322-1327.

[32] Yusupov, V.I.; Chudnovskii, V.M.; Bagratashvili, V.N. Laser-induced hydrodynamics in water-saturated biotissues: 2. Effect on delivery fiber. *Laser Phys*., **2011**, *21*(7), 1230-1234.