Journal of Sciences, Islamic Republic of Iran 21(3): 273-278 (2010) http://jsciences.ut.ac.ir
University of Tehran, ISSN 1016-1104

Nonlinear Responses and Optical Limiting Behavior of Ag Nanoparticle Suspension

H. Aleali and N. Mansour[*]

Department of Physics, Shahid Beheshti University, Tehran 19839, Islamic Republic of Iran

Received: 11 August 2010 / Revised: 18 August 2010 / Accepted: 30 August 2010

Abstract

In this study, the nonlinear optical properties and optical limiting performance of the silver nanoparticles (AgNPs) in distilled water are investigated. The nonlinear absorption coefficient of the colloid is measured by the Z-scan technique. The optical limiting behavior of the AgNP suspension is investigated under exposure to nanosecond laser pulses at 532 nm. The results show that nonlinear scattering can increase the performance of the optical limiting. A theoretical analysis is suggested investigating the observed nonlinear behavior of the AgNPs. It will be shown that nonlinear light scattering occurs at high beam intensity due to induced refractive mismatch between the silver nanoparticles and water. The experimental Z-scan data is fitted with the proposed theoretical model and this has allowed extracting the values of nonlinear absorption coefficient, linear and nonlinear scattering coefficients for the AgNP suspension.

Keywords: Nano-scale materials; Silver nanoparticles; Nonlinear absorption; Nonlinear scattering; Optical limiter

Introduction

Optical limiting phenomena have attracted much research effort during recent decades for promising applications in a broad range of areas such as safety protection from intense laser light [1]. An ideal optical limiting material should exhibit high transmission at normal light while exhibit low transmission at intense light to protect human eyes and sensors. The search for efficient optical limiters has lead to the study of various materials [1, 2]. Many organic materials such as phthalocyanines [3], fullerene families [4] and carbon black suspensions [5] were reported as good limiters due to their excellent nonlinear optical properties. The limiting action mechanisms can be caused by various nonlinear light-matter interactions, especially nonlinear absorption, nonlinear refraction and nonlinear scattering. Optical limiting performance is enhanced by coupling two or more of these mechanisms like self-defocusing in conjunction with the nonlinear absorption process in semiconductors [6].

Recently, various nanoscale metals and semiconductors have been extensively studied for their application as an optical limiter toward nanosecond laser pulses at 532 nm due to the enhancement in the nonlinear optical properties [7-14]. In particular, the interest in AgNPs has continuously grown due to the wide range of applications in fields of photonics [12-15], nanobiotechnology [16], electronics [17], and medicine [18]. So far, AgNPs have been successfully

---

[*] Corresponding author, Tel.: +98(21)29902774, Fax: +98(21)22431666, E-mail: n-mansour@cc.sbu.ac.ir

fabricated by a variety of methods, such as ultraviolet photochemistry, chemical reduction and laser ablation. It has been reported [19-28] that pulsed laser ablation of silver targets in liquid environment is a simple and well-suited technique to synthesize AgNPs. Laser ablation in liquids has received much attention as an effective and simple technique for producing various nanoparticles such as metals [19-30], metal oxides [31-32] and semiconductors [33-35].

In the present study, we investigate nonlinear responses and the optical limiting characteristics of the AgNPs in water. The nanoparticles were synthesized by nanosecond pulsed laser ablation of a silver plate in water. The optical limiting response of the AgNP suspension was measured under exposure to nanosecond laser pulses at 532 nm. In order to understand and to model the processes leading to optical limiting action, we have experimentally investigated linear absorption measurement using a low power CW laser (at 532 nm) and nanosecond pulsed laser measurements of the optical nonlinearities including nonlinear absorption and nonlinear scattering in the colloid. Our experimental results indicate that the nonlinear absorption and nonlinear scattering play important roles in strong optical limiting performance of the AgNPs dispersed in water. It has been reported [7, 36] that the performance of optical limiting in metal nanoparticles is enhanced by the nonlinear scattering. A theoretical analysis is suggested investigating the nanosecond pulsed laser optical limiting response of the AgNPs at 532 nm. It will be shown that our theoretical analysis based on the nonlinear absorption and nonlinear scattering is in excellent agreement with the experimental results of nanosecond Z-scan measurements of the AgNP suspension. A fit has allowed extracting the values of the linear and nonlinear scattering coefficients for the AgNPs dispersed in water.

Materials and Methods

AgNPs have been prepared by nanosecond pulsed laser ablation of highly pure silver target in distilled water. The laser ablation of silver was carried out using a second-harmonic radiation of Q-switched Nd:YAG laser. The laser generated 15 ns (FWHM) pulses at 532 nm with a repetition rate of 1 Hz. The laser beam was focused by a 50 cm focal length lens on the surface of a silver plate placed inside a 10 mm cell. The spatial profile of the laser pulse was Gaussian, with 300 μm (FW1/e^2M) beam waist at the target. The silver sample was irradiated with the laser fluence level of about 10 J/cm^2 for two hours. The concentration of the AgNPs is about 5.45×10^{-4} mol/L. The prepared AgNP suspension was studied using a transmission electron microscopy (TEM), and an ultraviolet-visible (UV-Vis) absorption spectrometer. A continuous wave low power (100 mW) diode-pumped Nd:YVO_4 laser operating at wavelength of 532 nm was also used to measure the linear absorption coefficient of the AgNP suspension.

The nonlinear optical properties of the prepared AgNPs were studied by transmittance and Z-scan measurements using 15 ns laser pulses at 532 nm. For nonlinear transmittance measurement, the optical geometry used in this work is shown in Figure 1. An attenuator and a beam splitter were used to control the single pulse energy of the laser beam. The beam was focused onto the sample cell by using a lens with 50 cm focal length. The spot size in the focal region was 140 μm (FW1/e^2M). Two large area energy monitors were measured the incident and transmitted energy of the laser beam. A diaphragm located before the output energy detector, was used with variable apertures to dissociate the nonlinear absorption from the nonlinear scattering effect. This experimental geometry was also used to perform Z-scan measurements. The nanoparticle-containing cell with thickness 5mm was moved using a translation system along the propagation direction (Z-axis) through the focusing area. At the focal point, the sample experiences maximum laser irradiance, which will gradually decrease in either direction from the focus.

Results and Discussion

Figure 2 shows UV-Vis absorption spectrum of the solution prepared by laser ablation of a silver plate immersed in water. One can see that the AgNPs show a surface plasmon absorption band about 400 nm in the UV-Vis region of the spectrum [12, 20].

The shape and size distribution of the AgNPs were studied by TEM and the measurements conducted just after laser ablation. The TEM image and size distribution of AgNP suspension prepared in water are presented in Figure 3. Average AgNPs radius is found to be about 9 nm, with a standard deviation of 3 nm.

Figure 4 shows linear absorption measurement of the AgNPs under exposure to low power CW laser at wavelength of 532 nm. The solid curve is plotted based on linear absorption theory and the absorption coefficient is found $\alpha = 0.11$ cm^{-1}. Typical open aperture Z-scan measurement is shown in Figure 5, with the solid curve based on Z-scan theory including the process of nonlinear absorption of Ref. [37]. The experiments were performed with nanosecond pulsed laser irradiation at wavelength of 532 nm. Moreover, the laser repetition rate was 1 Hz to prevent the influence of thermal effects. The AgNPs demonstrate high value of nonlinear responses in the nanosecond regime [38, 39]. The open aperture Z-scan measurement for the nanoparticles suspension is fitted based on the process of the nonlinear absorption using the procedure of Ref. [37] and the solid line shows the fit. The extracted values for linear and nonlinear absorption coefficients are $\alpha = 0.11$ cm^{-1} and $\beta = 5.01$ cm/GW, respectively. Note that the value of the linear absorption coefficient is the same as the value obtained us by low power laser measurements. Using the obtained values of the linear and nonlinear absorption coefficients, one can find that the contribution of the nonlinear absorption is much larger than the linear absorption.

The AgNPs dispersed in water studied for optical limiting properties under exposure to nanosecond laser pulses at 532 nm. Figure 6 demonstrates the optical limiting experimental results of the AgNPs when different diaphragm sizes are used before the output detector. The optical limiting threshold is about 1.4 mJ. At the aperture size of 4 mm, the transmitted energy reaches a plateau as the input energy increases. At applied laser energy of the 10 mJ, the clamped energy is down to about 1.33 mJ. This implies that the transmittance decreases to about 13 percent. Namely, it gives 4 times attenuation in the applied laser energy. It is found that the AgNPs in water exhibit strong optical limiting behavior. It seems that the observed strong optical limiting action of the silver colloid can be initiated by nonlinear absorption process. Indeed, considering the applied laser beam diameter about 3 mm at the diaphragm position, it is not expected that changing the aperture size from 4 to 14 mm (open aperture) should appreciably change the transmitted energy for a nonlinear absorption process. As shown in Figure 6, it is clear here that the transmitted energy decreases with decreasing diaphragm size. This aperture dependence indicates that the nonlinear scattering may also play important role in the observed optical limiting performances of the AgNPs. At this point, one needs to consider the contribution of the nonlinear scattering which may play important role in the observed nonlinearity of the nanoparticles suspension.

During nanosecond pulse irradiation, the absorption of laser light via nonlinear process may induce a very high rise in the temperature of nanoparticles, which leads to the formation of scattering centers [7]. In the following, a theoretical analysis is suggested investigating the observed nonlinear behavior of the AgNP suspension. It has been assumed that the nonlinearity is due to the nonlinear scattering induced by nonlinear absorption process. The absorbed laser energy causes the formation of induced scattering centers due to a change in the refractive index of the AgNPs by thermal process. The equations governing the absorption losses in the forward propagating direction (the z direction) are:

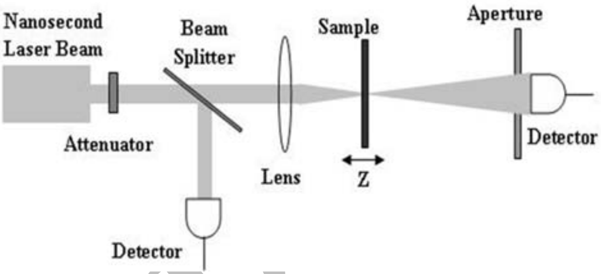

Figure 1. Optical geometry used to characterize optical limiting performance of the AgNP suspension.

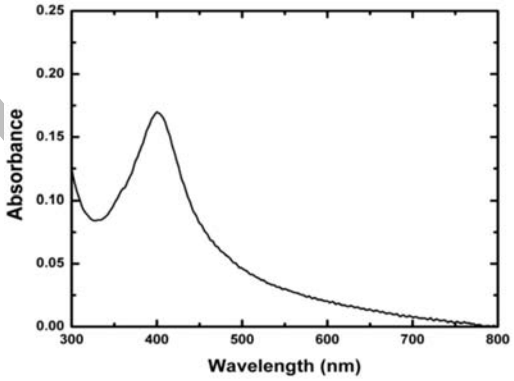

Figure 2. Absorption spectrum of the AgNP suspension obtained by laser ablation of silver plate in water.

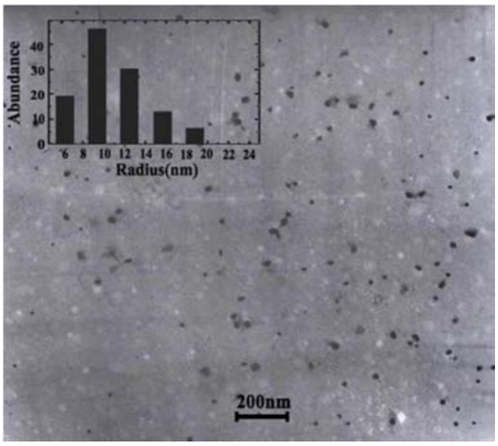

Figure 3. TEM image and size distribution of the AgNP suspension prepared by laser ablation of silver plate in water.

$$\frac{dI}{dz} = -(\alpha + \alpha_s(I))I - \beta I^2 \tag{1}$$

$$\frac{dT}{dt} = \frac{\beta I^2}{\rho C_p} \tag{2}$$

where I is the input laser irradiance, β is the nonlinear absorption coefficient, $\alpha_s(I)$ assumed to be the effective scattering coefficient, T is the temperature, ρ is the density and C_p is the specific heat of the AgNPs. The effective scattering coefficient is given by Rayleigh-Gans relations and is proportional [8, 40, 41] to the square of the effective refractive index, Δn_{eff}, given by:

$$\alpha_s(I) = g_s(\Delta n_{eff})^2 = g_s[\Delta n_L + \Delta n_{NL}]^2 \tag{3}$$

where the g_s parameter is independent of intensities but depends on the size, shape, and concentration of particles and wavelength of the laser light. Δn_L, Δn_{NL} are the difference in linear refractive indices and nonlinear refractive indices of the nanoparticles and the surrounding medium, respectively. In the following, we present a calculation for the nonlinear part of the effective refractive index, Δn_{NL}.

Under assumption that the ΔT can remain constant during the laser pulse, Eq. (2) is approximately:

$$\Delta T \approx \frac{\beta I^2 \tau}{\rho C_p} \tag{4}$$

where τ is the laser pulse width. The nonlinear change of the refractive index, Δn_{NL} as a function of temperature is given by [42]:

$$\Delta n_{NL} = (\frac{dn}{dT})\Delta T \tag{5}$$

where $\frac{dn}{dT}$ is the thermo-optic coefficient. Substituting Eq. (4) into Eq. (5) we have:

$$\Delta n_{NL} = (\frac{dn}{dT})\frac{\beta I^2 \tau}{\rho C_p} \tag{6}$$

Using Eq. (3) and Eq. (6), the resulting differential equation for absorption of laser beam in the nanoparticles suspension would be:

$$\frac{dI}{dz} = -\alpha_{eff} I - \beta I^2 - \gamma_s I^3 \tag{7}$$

where $\alpha_{eff} = \alpha + \alpha_s$, $\alpha_s = g_s(\Delta n_L)^2$ and $\gamma_s = 2g_s \Delta n_L (\frac{dn}{dT})\frac{\beta\tau}{\rho C_p}$. Finally, Eq. (7) is solved numerically for an initial Gaussian pulse.

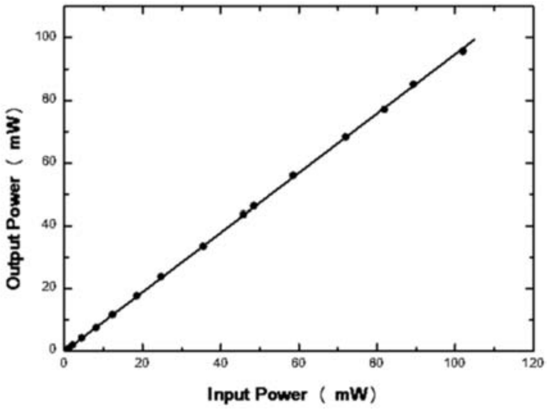

Figure 4. Linear transmittance measurement of the AgNP suspension using a low power CW laser at 532 nm.

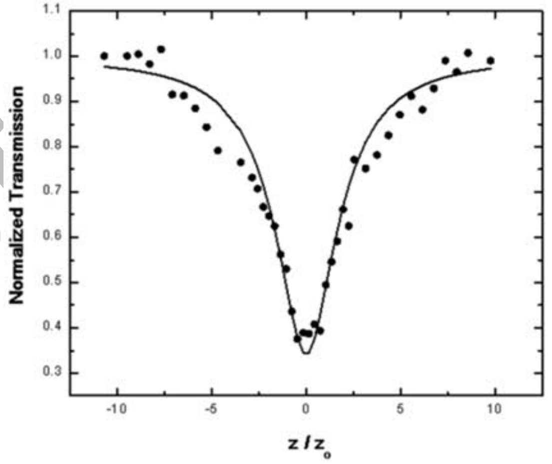

Figure 5. Shows open aperture Z-scan measurement of the silver nanoparticles dispersed in water. The solid curve is the theoretical fit for the nonlinear absorption process.

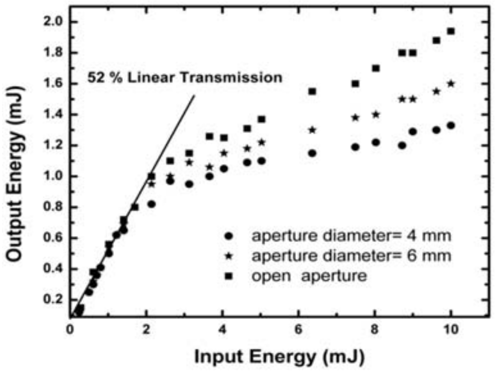

Figure 6. Optical limiting performance for the same AgNP suspensions illustrating the aperture dependence and the presence of nonlinear scattering.

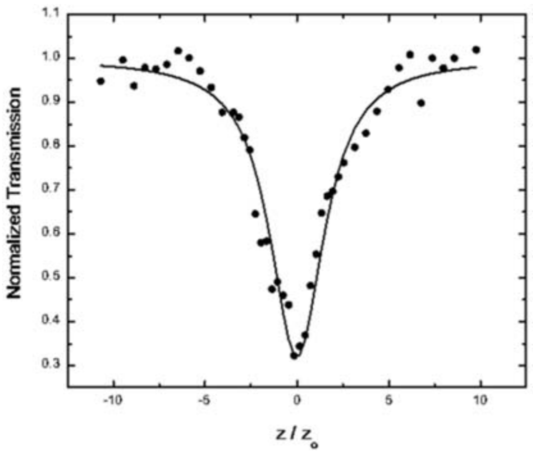

Figure 7. Shows Z-scan measurement at aperture size of 4 mm of the silver nanoparticles dispersed in water. The solid curve is fitted to the presented model.

Figure 7 shows the Z-scan measurement of AgNPs when the aperture size is 4mm. The theoretical nonlinear transmission and the experimental data for the observed nonlinear transmission of the AgNPs are compared. The solid curve illustrates the theoretical fit to the experimental Z-scan data for the AgNPs. The extracted fit parameters, nonlinear absorption coefficient, linear and nonlinear scattering coefficients are β = 5.01 cm/GW, α_s = 1.01 cm^{-1} and $\gamma_s = 7.5\times10^{-18}$ cm^3/W^2, respectively. As clearly shown in this figure, the experimental results for transmission measurement are in excellent agreement with the prediction of the proposed theoretical analysis. It seems that the observed strong optical limiting in the AgNPs under nanosecond laser irradiation is mainly nonlinear scattering which induced by nonlinear absorption process.

In summary, AgNPs were fabricated by laser ablation of a silver plate in distilled water. Image obtained by TEM shows narrow size distribution of the nanoparticles with radius centered at about 9 nm with a standard deviation of 3 nm. The nanoparticle solution has strong optical limiting behavior towards nanosecond pulsed laser irradiation at 532 nm. Our results show that the performance of optical limiting is enhanced by nonlinear scattering. We have developed a theoretical model based on nonlinear scattering induced by nonlinear absorption process. It is found that our theoretical analysis is in excellent agreement with the experimental results. A fit has allowed extracting the values of nonlinear absorption coefficient, linear and nonlinear scattering coefficients for the AgNP suspension.

References

1. Tutt L. W., Boggess T. F. A review of optical limiting mechanisms and devices using organics, fullerenes, semiconductors and other materials. *Prog. Quantum. Electron.*, **17**: 299-338 (1993).
2. Perry J. W. *Nonlinear optics of organic molecules and polymers*, CRC Press, NewYork, pp. 813-841 (1997).
3. Perry J. W., Mansour K., Lee I. Y. S., Wu X. L., Bedworth P. V., Chen C. T., Marder D. Ng. S. R., Miles P., Wada T., Tian M., and Sasabe H. Organic optical limiter with a strong nonlinear absorptive response. *Science*, **273**: 1533-1536 (1996).
4. Tutt L. W., and Kost A. Optical limiting performance of C_{60} and C_{70} solutions. *Nature*, **356**: 225-226 (1992).
5. Mansour K., Soileau M. J., and Van Stryland E. W. Nonlinear optical properties of carbon-black suspensions (ink). *J. Opt. Soc. Am. B.*, **9:** 1100-1109 (1992).
6. Van Stryland E. W., Vanherzeele H., Woodall M. A, Soileau M. J., Smirl A. L., Guha S., and Boggess T. F. Two-photon absorption, nonlinear refraction, and optical limiting in semiconductors. *Opt. Eng.* **24**: 613-623 (1985).
7. Francois L., Mostafavi M., Belloni J., Delouis J. F., Delaire J., and Feneyrou P. Optical limitation induced by gold clusters. Size effect., *J. Phys. Chem. B.*, **104**: 6133-6137 (2000).
8. Joudrier V., Bourdon P., Hache F., and Flytzanis C. Nonlinear light scattering in a two-component medium: optical limiting application., *Appl. Phys. B.*, **67**: 627-632 (1998).
9. Jia W., Douglas E. P., Guo F., and Sun W. Optical limiting of semiconductor nanoparticles for nanosecond laser pulses. *Appl. Phys. Lett.*, **85**: 6326-6328 (2004).
10. Qu S., Du C., Song Y., Wang Y., Gao Y., Liu S., Li Y., and Zhu D. Optical nonlinearities and optical limiting properties in gold nanoparticles protected by ligands. *Chem. Phys. Lett.*, **356**: 403-408 (2002).
11. Venkatram N., Rao D. N., and Akundi M. A. Nonlinear absorption, scattering and optical limiting studies of CdS nanoparticles. *Optics. Express.*, **13**: 867-872 (2005).
12. Sun Y. P., Riggs J. E., Rollins H. W., and Guduru R. Strong optical limiting of silver-containing nanocrystalline particles in stable suspensions. *J. Phys.Chem. B.*, **103**: 77-82 (1999).
13. Gao Y., Wang Y., Song Y., Li Y., Qu S., Liu H., Dong B., and Zu J. Strong optical limiting property of a novel silver nanoparticle containing C_{60} derivative. *Opt. Commun.*, **223**: 103-108 (2003).
14. Martin R. B., Meziani M. J., Pathak P., Riggs J. E., Cook D. E., Perera S., and Sun Y. P. Optical limiting of silver-containing nanoparticles. *Opt. Mater.*, **29**: 788-793 (2007).
15. Wang J., and Blau W. J. Inorganic and hybrid nanostructures for optical limiting. *J. Opt. A: Pure Appl. Opt,*. **11**: 024001 (2009).
16. Tom R. T., Samal A. K., Sreeprasad T. S., and Pradeep T. Hemoprotein bioconjugates of gold and silver nanoparticles and gold nanorods: structure-function correlations. *Langmuir*, **23:** 1320-1325 (2007).
17. Li Y., Wu Y., and Ong B. S. Facile synthesis of silver nanoparticles useful for fabrication of high-conductivity elements for printed electronics. *J. Am. Chem. Soc.* **127:**

3266-3267 (2005).
18. Choi W. S., Koo H. Y., Park J. H., and Kim D. Y. Synthesis of two types of nanoparticles in Polyelectrolyte capsule nanoreactors and their dual functionality. *J. Am. Chem. Soc*. **127**: 16136-16142 (2005).
19. Mafunê F., Kohno J. Y., Takeda Y., Kondow T., and Sawabe H. Formation and size control of silver nanoparticles by laser ablation in aqueous solution. *J. Phys. Chem. B.*, **104**: 9111-9117 (2000).
20. Mafunê F., Kohno J. Y., Takeda Y., Kondow T., and Sawabe H. Structure and stability of silver nanoparticles in aqueous solution produced by laser ablation. *J. Phys. Chem. B.*, **104**: 8333-8337 (2000).
21. Simakin A. V., Voronov V. V., Shafeev G. A., Brayner R., and Bozon-Verduraz F. Nanodisks of Au and Ag produced by laser ablation in liquid environment. *Chem. Phys. Lett.*, **348**: 182-186 (2001).
22. Tsuji T., Iryo K., Nishimura Y., and Tsuji M. Preparation of metal colloids by a laser ablation technique in solution: influence of laser wavelength on the ablation efficiency (II). *J. Photochem. Photobiol. A: Chem.*, **145:** 201-207 (2001).
23. Tsuji T., Iryo k., Watanabe N., and Tsuji M. Preparation of silver nanoparticles by laser ablation in solution: influence of laser wavelength on particle size. *Appl. Surf. Sci.* **202:** 80-86 (2002).
24. Tsuji T., Tsuboi Y., Kitamura N., and Tsuji M. Microsecond-resolved imaging of laser ablation at solid–liquid interface: investigation of formation process of nano-size metal colloids. *Appl. Surf. Sci*., **229**: 365-371 (2004).
25. Kazakevich P. V., Simakin A. V., Voronov V. V., and Shafeev G. A. Laser induced synthesis of nanoparticles in liquids. *Appl. Surf. Sci*., **252:** 4373-4380 (2006).
26. Bae C. H., Nam S. H., and Park S. M. Formation of silver nanoparticles by laser ablation of silver target in NaCl solution. Appl. Surf. Sci., **197-198:** 628-634 (2002).
27. Chen Y. H., and Yeh C. S. Laser ablation method: use of surfactants to form the dispersed Ag nanoparticles. *Colloids Surf. A: Physicochem. Eng. Asp*., **197**: 133-139 (2002).
28. Pyatenko A., Shimokawa K., Yamaguchi M., Nishimura O., and Suzuki M. Synthesis of silver nanoparticles by laser ablation in pure water. *Appl. Phys. A.*, **79:** 803-806 (2004).
29. Kabashin A. V., Meunier M., Kingston C., and Luong J. H. T. Fabrication and characterization of gold nanoparticles by femtosecond laser ablation in an aqueous solution of Cyclodextrins. *J. Phys.Chem. B.*, **107:** 4527-4531 (2003).
30. Nichols W. T., Sasaki T., and Koshizaki N. Laser ablation of a platinum target in water. I. Ablation mechanisms. *J. Appl. Phys.*, **100**: 114911-1-6 (2006).
31. Tsuji T., Hamagami T., Kawamura T., Yamaki J., and Tsuji M. Laser ablation of cobalt and cobalt oxides in liquids: influence of solvent on composition of prepared nanoparticles. *Appl. Surf. Sci.*, **243:** 214-219 (2005).
32. Sasaki T., Shimizu Y., and Koshizaki N. Preparation of metal oxide-based nanomaterials using nanosecond pulsed laser ablation in liquids, *J. Photochem. Photobiol. A: Chem*., **182**: 335-341 (2006).
33. Ganeev R. A., Ryasnyanskiy A. I., and Usmanov T. Optical and nonlinear optical characteristics of the Ge and GaAs nanoparticle suspensions prepared by laser ablation. *Opt. Commun.*, **272:** 242-246 (2007).
34. Anikin K. V., Melnik N. N., Simakin A. V., Shafeev G. A., Voronov V. V., and Vitukhnovsky A. G. Formation of ZnSe and CdS quantum dots via laser ablation in liquids. *Chem. Phys. Lett.*, **366:** 357-360 (2002).
35. Ruth A. A., and Young J. A. Generation of CdSe and CdTe nanoparticles by laser ablation in liquids. *Colloids. Surf. A: Physicochem. Eng. Asp.*, **279:** 121-127 (2006).
36. Pan H., Chen W., Feng Y. P., Ji W., and Lin J. Optical limiting properties of metal nanowires. *Appl. Phys. Lett.*, **88:** 223106 (2006).
37. Sheik-Bahae M., Said A. A., Wei T. H., Hagan D. J., and Van stryland E. W. Sensitive measurement of optical nonlinearities using a single beam. *IEEE J. Quantum Electron.*, **26:** 760-769 (1990).
38. Scalisi A. A., Compagnini G., D'Urso L. and Puglisi O., Nonlinear optical activity in Ag–SiO_2 nanocomposite thin films with different silver concentration. *Appl. Surf. Sci.*, **226**: 237-241(2004).
39. Qu S., Zhang Y., Li H., Qiu J., and Zhu C. Nanosecond nonlinear absorption in Au and Ag nanoparticles precipitated glasses induced by a femtosecond laser., *Opt. Mater*., **28**: 259-265 (2006).
40. Ishimaru A. *Wave Propagation and scattering in Random Media.* Vol 1, Academic Press, New York, 22 p. (1978).
41. Bohrn G.F., and Huffman D.R. *Absorption and Scattering of Light by Small Particles*, Wiley, New York, 159 p. (1983).
42. Boyd R.W. *Nonlinear Optics*, 3nd Ed., Academic Press, New York, 220 p. (2003).