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Synthesis of silver nanoparticles with laser assistance

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Silver nanoparticles of different sizes and shapes have been attracting much attention due to their unusual size and shape-depending optical, electrical, and magnetic properties [1 - 4]. Up to day the majority of silver colloids are still preparing by using different chemical methods. The general idea of all these methods is chemical reduction of silver ions, Ag^+, in aqueous or non aqueous solutions by different reduction agents, like citrate [5] or borohydride [5,6]. Many promising results were obtained with this method, but like any other experimental technique, the chemical reduction has its own disadvantages and restrictions. And it was quite natural that when many researchers were working under development of chemical reduction technique, some scientists had tried to create some new, alternative methods for nanoparticle production.

One of alternative methods to chemical reduction is the method of laser ablation in liquid phase. Laser ablation in gas phase was very well known method which used successfully for many years [7 - 10]. The idea of applying this technique for liquid phase was proposed by two groups of researchers, Cotton-Chumanov group [11] and Henglein group [12] in 1993. Let's consider one of these works in more details. For their new method, authors of [11] proposed the experimental scheme which remains practically unchangeable (with small variations) up to day. This scheme is shown in Figure 1a, while in Figure 1b the other experimental scheme from the paper of Mafune et al., published in 2000 [13] is depicted for comparison. For production of silver nanoparticles in both these schemes, surface of the metal plate immobilized in water solution is irradiated by pulsed laser beam with different parameters (wavelength, pulse duration and pulse energy, pulse repetition rate). Lens is used for the beam focusing on the metal surface. Naonosecond Nd:YAG laser were used in both these experiments as well as in most of experiments accomplished up to day. Because the motivation of the work [11] was the subsequent using of nanoparticles produced in surface- enhanced Raman scattering measurements, the synthesis itself was done in pure water, without any surfactants or other stabilizers. For comparison, the same measurements were made in pure methanol and acetone. Four different metals, silver gold, platinum and cupper were studied in [11]. In case of silver plate ablated in pure water, stable colloids with average size of the particle about 20 nm (with asymmetrical distribution of sizes ranging from approximately 10 to 50 nm) were synthesized. Electron microscopy (data were not

shown in paper) indicates the presence of some amount of large particles and particle agglomerates which can be removed from colloid by centrifugation. When liquid was changed from water to methanol or acetone, the amount of large particle and agglomerates into a colloid were increased. Such colloids became unstable and precipitated completely overnight at room temperature.

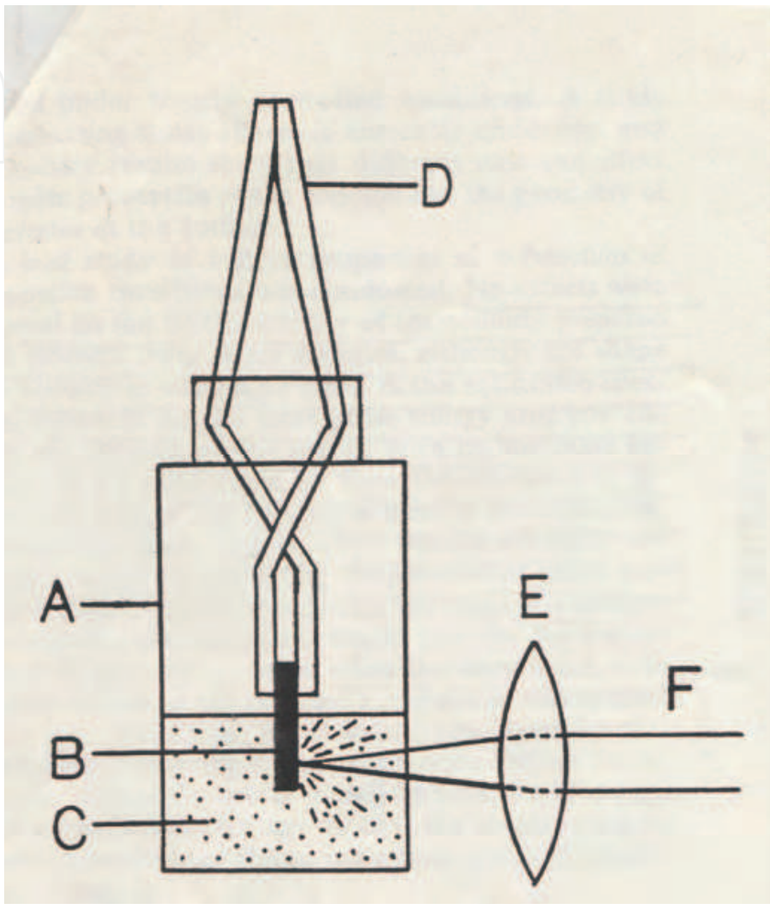


Fig. 1a. Experimental scheme proposed by Cotton-Chumanov group [11]

Further this method was developed in details by Mafune with coworkers [13 -16]. Typical experimental scheme is depicted in Figure 1b. As can be seen from Figure 1, this scheme is very similar to that one proposed by Cotton-Chumanov group [11], and is using by most of researchers in their experiments on laser ablation in liquid phase up to day. To make the process more homogeneous, some researchers rotate the metal plate or vessel or apply a stirring during an ablation [17-19].

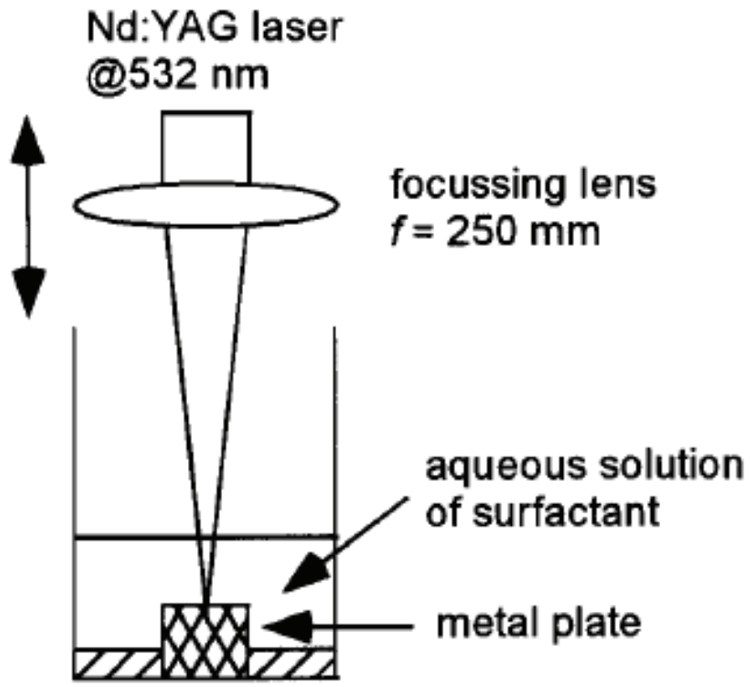


Fig. 1b. Experimental setup used in work of Mafune et al. [13]

To control the particle size, Mafune and co-authors used a surfactant. The different concentrations of surfactant, sodium dodecyl sulfate, SDS [13], or different chemical composition of surfactant [14] were used for particle size control. The following mechanism of nanoparticle's formation was proposed by Mafune et al. Absorption of laser pulse energy causes the plume formation, small cloud of hot dense plasma over metal surface contained high concentration of metal atoms and ions. Metal atoms in the plume aggregate rapidly into small embryonic particles (or nuclears) as fast as metal atoms collide mutually. After that, two concurrent processes take place: relatively slow particle growth and particle stabilization. Final average size of the particle depends on chemical composition and concentration of stabilizer. The results of experiments with different surfactant concentration are shown in Figure 2, where TEM photographs and correspondent particle size distributions are presented for three different concentrations of SDS [13].

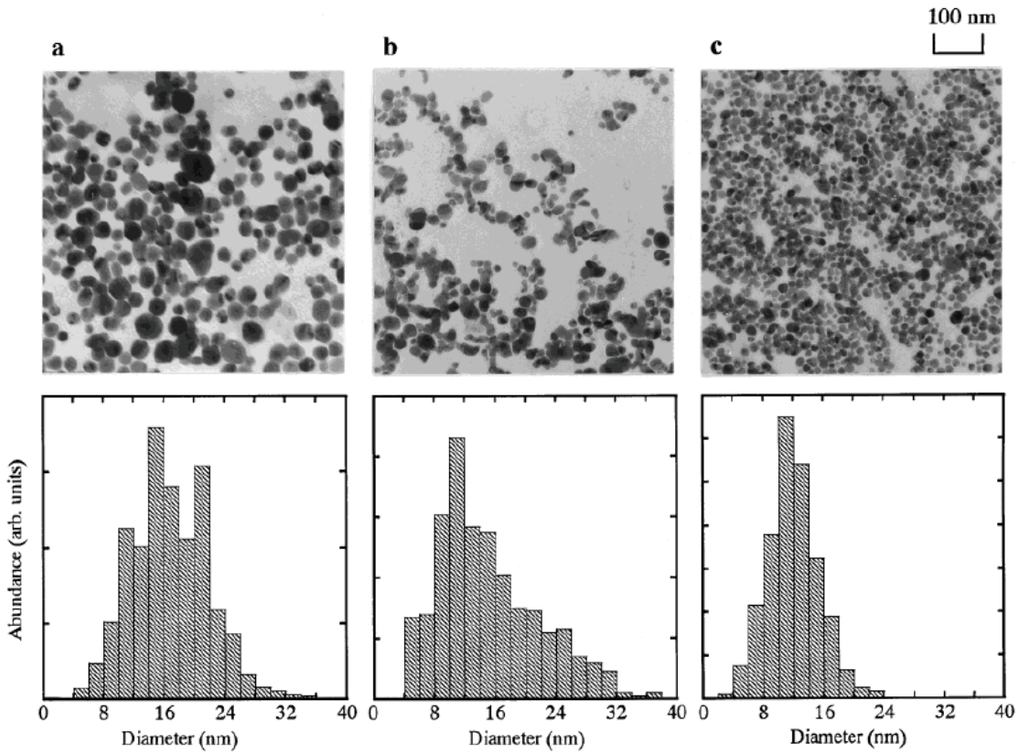


Fig. 2. Electron micrographs and size distributions of the silver nanoparticles produced by laser ablation at 90 mJ/pulse in a SDS aqueous solution at the various SDS concentrations. The concentrations of the solution in panels a-c are 0.003, 0.01, and 0.05 M, respectively. The average size decreases with an increase in the SDS concentration.From paper of Mafune [13].

Silver nanoparticles thus produced were practically spherical and had the average diameters of 16.2 ± 14.0, 14.9 ± 8.4, and 11.7 ± 5.3 nm in the 0.003, 0.01, and 0.05 M solutions, respectively. The results show that the average diameter decreases with an increase in the SDS concentration. But the relative changes in average diameter and standard deviation were very small. Moreover, further increase in SDS concentration had no effect on particle sizes [13]. Similar measurements were performed in a 0.01 M solution with changing the laser power. The results are shown in Figure 3. The average diameters of nanoparticles were found to be 7.9 ± 3.3, 10.7 ± 5.8, and 12.8 ± 4.1 nm for runs with the laser powers of 40, 55, and 70 mJ/pulse, respectively. The results show that the average diameter increases practically linearly with an increase in the laser power. Therefore, smallest and most homogeneous silver nanoparticles were produced for lowest laser pulse energy. And even at that experimental condition, the extent of particle monodispersity (42%) is not so good. Moreover, the efficiency of ablation process decreases with decrease in laser pulse energy, which puts a restriction on using of very low laser power.

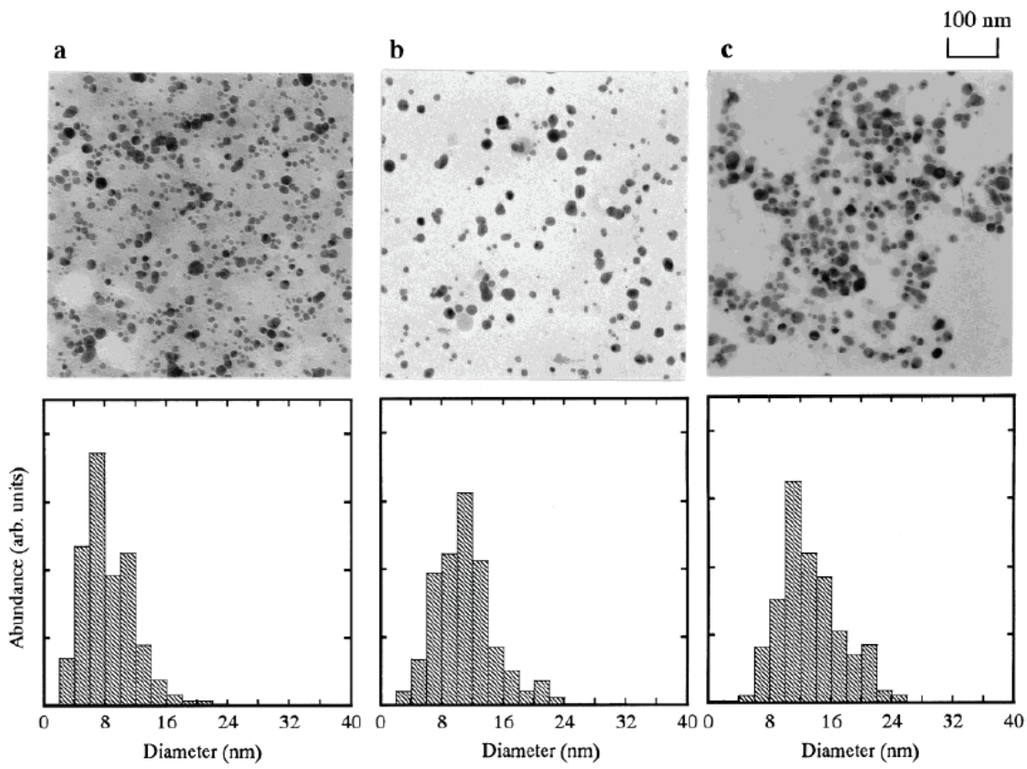


Fig. 3. Electron micrographs and size distributions of the silver nanoparticles produced by laser ablation in a 0.01 M SDS aqueous solution at the various laser powers. The laser powers in panels (a)-(c) are 40, 55, and 70 mJ/pulse, respectively. The average size increases and the distribution broadens with an increase in the laser power. From paper of Mafune [13].

Apart from the energy of laser pulse, the results of laser ablation in liquid phase depend on many other experimental parameters: laser wavelength, pulse duration, time of ablation experiment, mixing conditions and focusing conditions. Precise influence of many of these factors is not clear up to day. Let's consider the last factor, the laser focusing, in more details. Laser beam focusing was applied already in first work of Cotton – Chumanov group [11]. The authors of [11] observed that "tight focusing decreased the efficiency of ablation. It was found that the highest efficiency occurred when the laser beam with an initial diameter of 6 mm was focused into a spot about 1.5 mm." On the contrary, Prochazka et al. in their work published in 1997 [20] found that "the laser beam focusing substantially increases the efficiency of the ablation process". They found also that the colloid revealed the same optical characteristics regardless of the focusing of the beam." Let's note that the focusing conditions or the value of spot size on the metal surface did not report in [20]. Mafune et al. [13] varied the spot size of the laser beam on the surface of the metal plate in the range of 1-3 mm in diameter. Because they never mentioned how the results depend on the different focusing, it is possible to assume that in their experimental conditions the focusing does not play essential role. Pyatenko et al. in their paper published in 1994 [17] tried to vary the focusing conditions keeping the high laser beam power of 0.3 J/pulse for all experiments. In their experiments the spot size of the laser beam on the surface of a silver plate was changed

from 1.2 to 0.7 nm when the initial laser beam had the diameter of 7 mm. All the results of ablation including the ablation efficiency, colloid optical characteristics, and particle size distribution, depended strongly on focusing conditions. The efficiency increased near linearly and average particle size decreased with higher focusing. The authors reported that "for small spot sizes, 0.6–0.7mm, most of the observed particles were very small, spherical, and their sizes were rather uniform, d_p = 2–5 nm. A typical TEM image is shown in Fig. 4. In some TEM pictures mid-sized particles with d_p = 5–15 nm were observed, surrounded by smaller particles. The number of such mid-sized particles was much lower than that of the smaller ones, and had practically no influence on the particle-size distribution, which is also shown in Fig. 4.When the spot size was further increased, the number of mid-sized and large (d_p more than 20 nm) particles increased. In the case of a spot size of about 1.5mm, a typical image contains mainly large and mid-sized particles, and only a few small particles could be observed. Also, a large number of particle agglomerates was observed for such poor focusing conditions." All these results show the necessity for additional experimental study with more precise control of the focusing conditions and by varying the values of spot size of the laser beam on a metal surface in wide range.

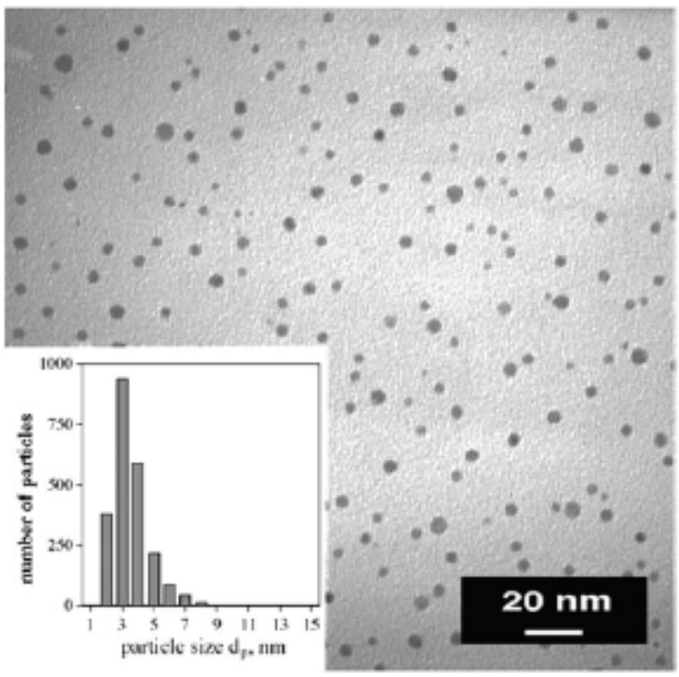


Fig. 4. A typical TEM image of small particles synthesized in [17] with strong laser focusing (spot size on the metal surface was 0.7 mm for the original beam diameter 7 mm). Insert shows the particle size distribution

As we already mentioned before, in works of Mafune et al. [13 - 16] the control under ablation process was accomplished by using the surfactant, and in particular SDS. There are two methods of particle stabilization, electrostatic (Coulombic repulsion) and steric (polymeric or other organic "overcoat") [21 - 23]. In first method, the particles prevent from

agglomeration by electrical double layer formed by negative ions absorbed on the particle surface and positive charges induced on the metal particle surface by mirror effect. In second method, the particle agglomeration prevents by absorption of polymer, surfactant or ligand molecules at the surface of the particle. Both techniques of particle stabilization are actively using in chemical reduction method. Both these techniques were employed for the ablation method in liquid phase as well. Different researchers have tried to use the different surfactants, ionic species or other molecules for stabilization of nanoparticles and more precise particle size control.

Chen and Yeh [19] compared the results of ablation made in two different surfactants, the anionic SDS and cationic CTAB. They succeeded to synthesize the colloidal silver particles with average diameter of 4.2 ± 1.9 nm and 7.8 ± 4.5 nm in SDS and CTAB solutions correspondently. Prochazka et al. [20] showed that the addition of a proper amount of $NaCl$ "increased the efficiency of the ablation process, reduces the sizes of colloidal particles, and prevents formation of large particles. However the colloids prepared in the presence of $NaCl$ were less stable than those prepared in pure water". Similar results were obtained by Bae et al. [18]. The authors [18] showed that the addition of $NaCl$ improved the results of ablation only when the concentration of $NaCl$ is below 5 mM. At higher concentrations aggregation turned out to be dominant. They also observed that silver colloids produced in pure water were much more stable than those in $NaCl$ solution. Prochazka et al. [20] have also found that some other anions such as NO_3^-, did not produce the similar effect. They attributed such differences to a substantially higher affinity of the chlorine anion to the silver surface in comparison to other ions, such as nitrates [24]. Tsuji et al. [25] performed the ablation of a silver plate in polyvinylpyrrolidone (PVP) aqueous solutions. By using the different concentration of PVP with molecular weight of 10,000, they produce the silver colloids with different average sizes of the particles. When PVP concentration was increased from 0 to 2, and then to 6 mM, the average particle size decreased from 18 ± 9 to 13 ± 10, and then to 10 ± 5 nm. Further increase in PVP concentration had no effect on average particle size (d_p was equal to 11 ± 7 and 11 ± 8 nm when the PVP concentration increased to 12 and 18 mM). Moreover, because the standard deviation in d_p was found to increase in two last experiments, it is possible to expect that the high concentration of PVP can promote particle agglomeration. This result is looked similar to result obtained by Bae et al.[18] for $NaCl$ (see above).

Analysis of all available dada shows that in spite of the different experimental conditions and different techniques for particle stabilization, the values of average particle diameter varied not so dramatically, from several nanometers in experiments of Pyatenko et al. [17], and some experiments of Mafune [13] and Chen and Yeh [19], to 10 – 15 nm in other experiments. At the same time the average value of standard deviation in average diameter was usually more than 40 %. Very often agglomeration takes place in spite of special efforts to prevent it. Also, the production of large particles additionally to the main relatively small particles was reported in most of papers. The UV-Vis absorption curves reported in almost all papers revealed the red tails, that unambiguously evident to agglomeration process and large particle formation. Therefore, it is possible to conclude that the particle size control and the particle size homogeneity are the main difficulties of laser ablation method.

If the majority of the works on laser ablation in liquid was performed in pure water (the main motivation of these works is SERS application [11, 20]) or in aqueous solutions, some researchers made their experiments in different organic solvents [26 - 33]. In such case, inside of the boundary region between plume and liquid different high temperature processes, like chemical reactions between atoms and ions of ablated material and organic molecules can take place. The molecules of organic solvent themselves can be fragmented, and the reactions between such fragments with atoms or ions of ablated material can be observed. Furthermore, some metastable phase compounds can be formed at such high temperature-high pressure conditions. Therefore, the formation of new materials such as carbides, nitrides, hydrates and others can be observed. This could be new and very interesting direction in the field of ablation in liquid phase [34, 35].

Because the colloidal particles produced in result of ablation of metal target immersed in liquid can be irradiated by subsequent laser pulses, the secondary process of particle interaction with laser beam will occur simultaneously with primary ablation process. It makes the total process more complicated. This phenomenon was recognized already in the first paper published by Cotton-Chumanov group [11]. The authors call this phenomenon "self – absorption" and tried to minimize it effect on absorption process: "In order to reduce self-absorption of the laser radiation when the pulse penetrates through the optical dense colloid, the metal was placed close to the wall". To use this phenomenon for improving the results of primary ablation was proposed by Prochazka et al. [20]. They showed that "after additional irradiation of colloid when silver foil was removed from the cell, the particle size distribution was narrowed, the average particle size was reduced, and particles larger than about 40 nm were completely absent". Further this phenomenon was studied in more details in woks of Tsuji with co workers [25, 36 -39], Smejkal et al. [40] as well as by other research groups. They showed in particular that the results of self-absorption strongly depend on the wavelength of laser irradiation. This fact can be explained by the strong dependence of particle adsorption cross section on the wavelength [41] (see bellow). The values of particle cross section for absorption of light of different wavelengths, σ_{abs}^{λ}, are completely different for fundamental wavelength, λ = 1064 nm, second, λ = 532 nm, and third, λ = 532 nm, harmonics of Nd:YAG laser, which used in these researches. Usually, the σ_{abs}^{1064} value is about two orders smaller than σ_{abs}^{532} and σ_{abs}^{355} values. This fact can be used (and have been used by some researchers, for example by Mafune [13-16] even without any explanations) to prevent secondary absorption or to divide primary and secondary processes temporary by made the primary ablation with fundamental wavelength and studying the secondary self-absorption process with second or third harmonics. More fundamental study of this phenomenon was made by Pyatenko et al. [42]. They showed that by using the process of secondary laser treatment of silver colloid at appropriate conditions, it is possible not only reduce the average size of the particle dramatically, but to made the particles near monodisperse. The authors [42] explained their results by applying the mechanism proposed by Mafune with co-workers [13] and considering the dependence of σ_{abs}^{λ} on particle size.

As it was mentioned before, the absolute majority of the experiments on laser ablation in liquid phase was accomplished with nanosecond Nd:YAG laser. Recently some researchers tried to use the femtosecond laser to study the ablation process [43-44]. According to Tsuji et

al. [43] the average size of the particles decreased from 27 nm to 41 nm when femtosecond laser was used instead of nanosecond one. At the same time, particle size distribution for colloid prepared with femtosecond laser was more narrow, and standard deviation in average particle diameter increased from 20 nm (about 70%) in case of ns to 16 nm (40%) for the case of fs laser. More detail study of this problem is needed with more detail analysis of the possible mechanisms of ablation process.

Most of experimental results obtained up to day in study of the process of laser ablation in liquid can be explained by using the mechanism proposed by Mafune et al. [13]. With this mechanism it is possible also to understand the difficulties with particle size control that arise in laser ablation method (see above). In dead, if embryonic particles were born and subsequently grown in a plume, hot and dense region just above the ablated surface, where the strong non homogeneity existed, the conditions for particle formation and growth are very non homogeneous. And because the process of particle formation and growth strongly depends on the temperature, pressure and concentrations, it is quite natural to expect that the particle sizes will vary in wide range even though the macroscopic parameters will control very precisely. However, nucleation and growth do not represent the only mechanism of nanoparticle formation. Some experimental data show that another formation process, consisting in the ejection of metal drops or solid fragments from the target, so called "explosive boiling", are also take place at particular experimental conditions [45-48]. This second mechanism can be responsible for the formation of large (with sizes larger than about 100 nm) particles, that in turn, leads to the bimodal particle size distribution. Let's emphasize again, that the particle size control, decreasing the width in particle size distribution, and the preventing of the particle agglomeration are still the main challenges in laser ablation method.

In our previous papers [41, 42, 49], we proposed a new approach to the synthesis of noble metal spherical particles. In our new method we did not ablate a metal plate immersed into a liquid, but undergo by laser treatment a colloid consisted from metal particles, synthesized by chemical reduction method. By chousing appropriate parameters of laser irradiation, we can transform the initial colloid, prepared by standard citric reduction method, to the colloid contained only small monodisperse spherical particles. We used these particles further as seeds for their subsequent growth by adding to the colloid appropriate amount of silver nitrate (as a metal precursor) and citrate (as a reduction agent). For final precise control of the particle size and sphericity, the secondary laser treatment of colloid with appropriate parameters was applied. Let's consider this new method in details now.

At the beginning the initial silver colloid was synthesized with standard citric reduction method [5, 6]. For this purpose 450 ml of pure water was mixed with 50 ml of 0.01M $AgNO_3$. The mixture was heated up to boiling with intensive stirring. After boiling started, 10 ml of trisodium citrate water solution (1g of trisodium citrate dissolved in 100 ml of pure water) was added to boiling solution. The boiling with stirring then continued for one hour. To prevent large evaporation of solution, a glass was closed with alumina foil during this 1 hour boiling process. After about 3 min of boiling, the solution turned yellow, and after about 5 min it turned gray-yellow and became opaque. The extinction spectrum of this initial colloid diluted 10 times with water is shown in Figure 5. The peak shape and position clearly shows that the colloid was composed of large, nonspherical particles. The results of TEM observation, shown in Figure 2, proved that the main component of the colloid was

large spheroid particles with typical size of about 120 nm and an aspect ratio of about 1.5. Apart from these particles, a relatively large amount of nanorods with different lengths and thicknesses were observed.
Seed particles were prepared then by "hard" laser treatment of initial colloid.
Here we have to stop talking about experimental procedure and explain about "hard" and "soft" laser irradiation regimes, which we used in our method for primary and secondary laser treatment of colloids synthesized in different stages.

Both these regimes were calculated in frame of particle heating-melting-evaporation model, proposed by Takami et al. [50] and further developed in our works [41, 42, 49] for interaction of nanosecond laser pulse with colloidal particles. As it was shown in [41] , when the laser intensity is smaller than the critical value of 10^{12} W/cm^2 (this condition is valid practically every time when we use a nanosecond Nd:YAG laser), namely this model adequately describes the process of colloidal nanoparticle interaction with laser beam. Thus, if we work with laser intensity lower than the limit value, we can use thermodynamics to calculate the parameters of laser beam for which the particle evaporation process will start and completed. The conditions corresponded to evaporation threshold or evaporation start we call "soft", when the conditions corresponded to evaporation completed or full evaporation call "hard". As it was shown in [41], the laser fluence (not laser power) is the value responsible for these processes, therefore, both "soft" and "hard" processes can be accomplished with different laser beam diameter and different laser power. Laser fluences for "soft" and hard regimes can be calculated by equations (1a) and (1b):

$$J^{soft} \cdot \sigma_{abs}^{\lambda} = \rho \cdot \frac{\pi d_p^3}{6} \cdot \left\{ c_p^s (T_m - T_0) + c_p^l (T_b - T_m) + \Delta H_m \right\} \tag{1a}$$

$$J^{hard} \cdot \sigma_{abs}^{\lambda} = \rho \cdot \frac{\pi d_p^3}{6} \cdot \left\{ c_p^s (T_m - T_0) + c_p^l (T_b - T_m) + \Delta H_m + \Delta H_{ev} \right\} \tag{1b}$$

All physical and thermodynamic constants used in equation (1), i.e., silver density, ρ, heat capacities, c_p^s for solid, and c_p^l for liquid silver, heat of melting, ΔH_m, and heat of evaporation of silver, ΔH_{ev} can be found in reference books. The values of particle cross section for absorption of light of different wavelengths, σ_{abs}^{λ}, can be calculated for spherical silver particles by classic Mie theory [1, 51, 52]. The results of such calculations are shown in Figure 7 for fundamental wavelength, λ = 1064 nm, second, λ = 532 nm, and third, λ = 355 nm, harmonics of Nd:YAG laser. It can be seen from this Figure that the absorption cross sections are strongly depends on particle size, and their size dependences are completely different for different wavelengths. When particle cross sections for light absorption are known, the "soft" and "hard" laser fluences can be calculated for particles of different sizes for different laser wavelengths. The results of these calculations are shown in Figure 8 for three main wavelengths of Nd:YAG laser. Let's note that the strong dependences of

J^{soft} and J^{hard} on particle size and laser wavelength are the direct consequence of these dependences for the absorption cross section, σ_{abs}^{λ}.

Now we can return to the experimental procedure of nanoparticle synthesis. As we already said, seed particles were prepared from initial colloid irradiating it with "hard" conditions. Because the initial colloid was very non homogeneous in particle sizes and shapes, the maximum "hard" laser fluence of 0.8 J/pulse·cm^2 for second harmonic of Nd:YAG laser (λ = 532 nm), was used. According to Figure 4, at such conditions all spherical particles will be evaporated completely independently on their sizes. As concern to non spherical particles, we assumed that at first these particles will be melted becoming spherical, and after that will be evaporated completely as other spherical particles. After 30 min of such "hard" treatment of initial colloid we produce the colloid contained only very small spherical nanoparticles. The average size of these particles was about 10 nm with average standard deviation ± 2 nm. Typical TEM photograph for this colloid is shown in Figure 13, and typical UV-vis absorption spectrum is shown in Figure 10. Because the measurement of particle size distribution for such small particles needs a time (sometimes totally more than 2 weeks), preliminary check has to be done by measuring the UV-Vis absorption spectra. Absorption peak for seed particle colloid has to be very narrow (FWHM is about 35-37 nm) without any shoulder and tail. Peak maximum is about 387-390 nm. All other results will show that some other particles existed into a colloid or agglomeration of seed particles takes place.

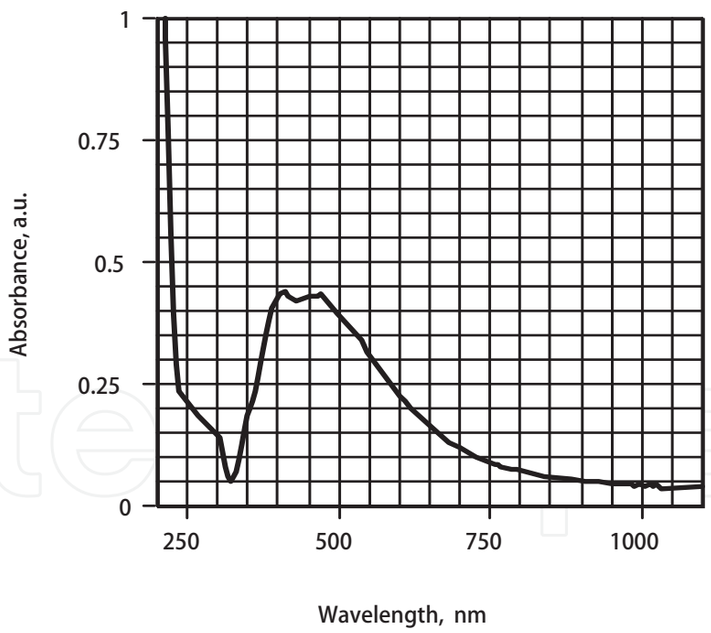


Fig. 5. UV-Vis absorption spectrum of initial colloid

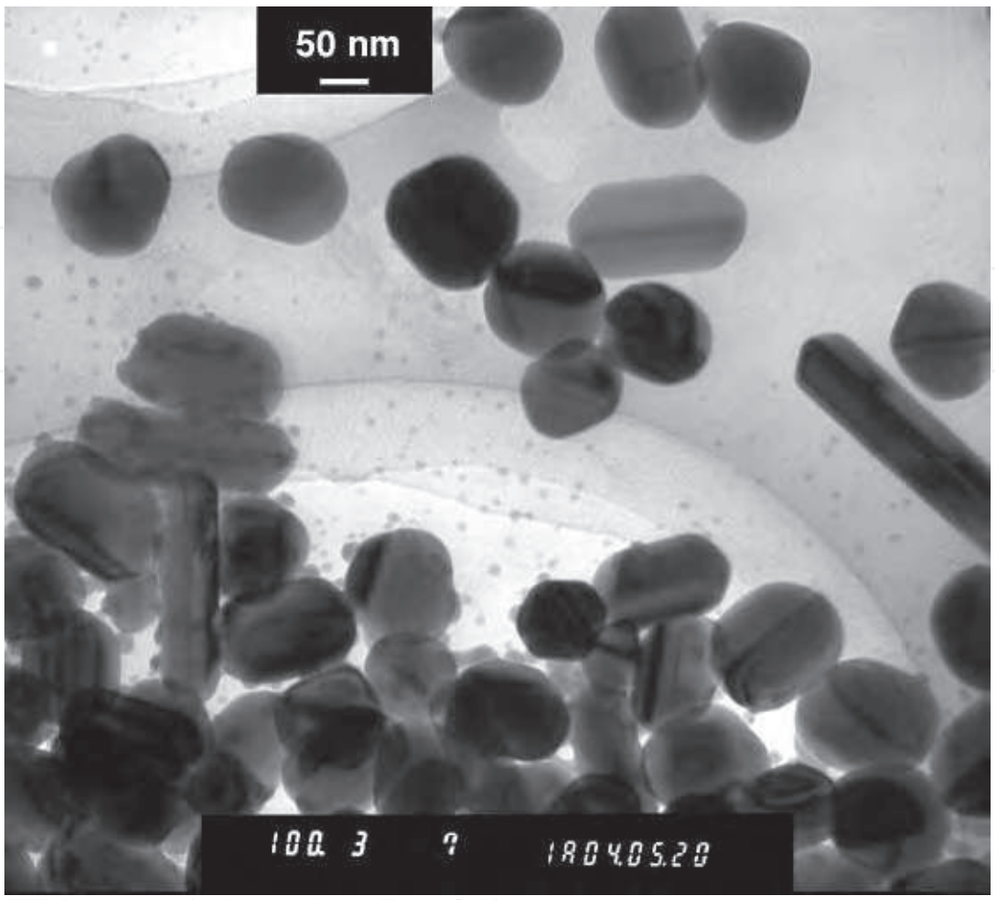


Fig. 6. TEM picture of initial colloid (From [42])

Further growth of seed particles was accomplished by applying seed method. Seed method has a long history [5, 53-55, 22]. Recently it was further developed by the groups of Marphy [56-58] and El-Sayed [59-60] mainly for the synthesis of noble method nanorods. The base of this method can easily be explained for a colloid consisted of monodisperse spherical metal particles (with initial diameter d_0). For subsequent growth of these particles, the appropriate amount of metal precursor (in our case it will be silver nitrate, $AgNO_3$) and reduction agent (in our case - citrate) are added to the colloid. The experimental conditions must be appropriate for reduction process (in our case – colloid boiling). Assuming there is no bulk nucleation and the reduction of silver ions occurs only on the surface of seed particles, that is total number of silver particles in colloid remains the same and only the homogeneous growth of seed particles takes place, we can write:

$$\frac{\Delta N_{Ag}}{N_{Ag}^0} = \frac{\Delta m_{Ag}}{m_{Ag}^0} = \frac{\Delta V}{V_0} = \frac{V - V_0}{V_0} = \frac{d^3 - d_0^3}{d_0^3} = \left(\frac{d}{d_0}\right)^3 - 1 \qquad (2)$$

where d_0 and V_0 are the diameter and volume of the seed particle; d and V the diameter and volume of the particle after growth; N_{Ag}^0 and m_{Ag}^0 are total amount of

silver atoms in seed colloid and their total mass; ΔN_{Ag} and Δm_{Ag} are the total amount of silver atoms in precursor (silver nitrate) added to seed colloid and the total mass of these silver atoms. Therefore, the value of relative particle growth, $\left(\frac{d}{d_0}\right)$, can easily be calculated by knowing the mass of seed particles and the total mass of silver in silver nitrate added to seed colloid:

$$\left(\frac{d}{d_0}\right) = \left(1 + \frac{\Delta m_{Ag}}{m^0_{Ag}}\right)^{1/3} \quad (2a)$$

Writing the equation (2) we assume also that the particle density, ρ, does not depend on the particle size. This assumption is quite natural for large particles, but could be not so obvious when the size order became less or about few nanometers.

Thus, we tried to increase the size of seed particles by using such seed technique. The experimental procedure was similar to that one used or preparation of initial colloid: some amount of silver nitrate water solution was heated up to boiling with intensive stirring. After that some amount of seed colloid and appropriate amount of citrate solution were added to boiled nitrate. The boiling with stirring then continued for one hour. The appropriate amount of seed colloid was calculated by using equation (2a), relative amount of citrate added was the same as for classic citric reduction method [5,6] (1 ml of citrate solution for 5 ml of 0.01M silver nitrate solution).

Several syntheses were achieved by changing the $\frac{\Delta m_{Ag}}{m^0_{Ag}}$ ratio in equation (2a). The results of TEM observation for four different syntheses are presented in Fig. 11. For small $\Delta m_{Ag} / m^0_{Ag}$ ratios, most of the particles were spherical, and the average size of a spherical particle increased with the $\frac{\Delta m_{Ag}}{m^0_{Ag}}$ ratio. When this ratio exceeded 20, however, the synthesis of spherical particles was accompanied by the synthesis of nanorods. The relative concentration and aspect ratio of these nanorods increased with the $\frac{\Delta m_{Ag}}{m^0_{Ag}}$ ratio.

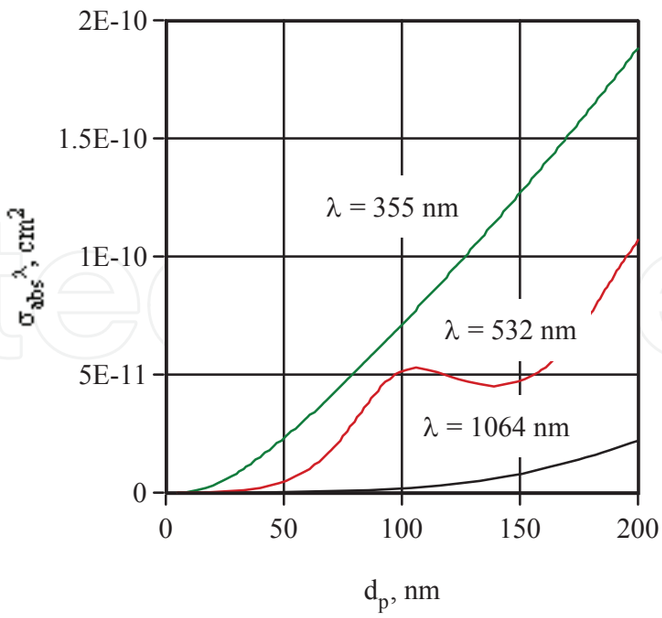


Fig. 7. Absorption cross sections, σ_{abs}^{λ}, for spherical silver nanoparticles calculated as a function of particle diameter, d_p, with Mie theory [51,52] for three characteristic wavelengths of Nd:YAG laser

Table 1 compares the average sizes of spherical particles measured from TEM photographs with the sizes calculated by equation (2a). The good coincidence between experimental and calculated values of d_p proves that the main process was the reduction of silver ions on the surface of seed particles and that the main products were the spherical particles, at least while the $\frac{\Delta m_{Ag}}{m_{Ag}^0}$ ratio did not exceed 100. Very small particles with sizes of few nanometers can be seen in Fig. 11d. These particles can be identified as the result of bulk nucleation, which can already start at $\frac{\Delta m_{Ag}}{m_{Ag}^0}$ ratio about 50. However, the total amount of these very small particles is still rather small, and those particle were not observed in most of other TEM photographs made for $\frac{\Delta m_{Ag}}{m_{Ag}^0}$ = 45.

$\frac{\Delta m_{Ag}}{m^0_{Ag}}$	d_p, nm		
	measured		calculated by equation (2a)*
	before soft laser treatment	after soft laser treatment	
3.6	14.2	14.0	13.3
18.9	20.2	19.8	21.7
32.4	27.1	28.7	25.8
45	29.6	28.8	28.7
90	34.0	33.5	36.0

Table 1. Average size of the spherical particles synthesized in one-step experiments

UV-Vis extinction spectra of different colloids are presented in Fig. 8a. The positions of all plasmon peaks correspond well to Mie's theory for spherical particles [1]: the maximums were close to 400 nm and shifted to red as the particles became larger. However, a red tail appeared when the $\frac{\Delta m_{Ag}}{m^0_{Ag}}$ ratio exceeded 20. Small peaks can be distinguished in the tail region for curves 2 to 5 in the insert of Fig. 8a. The maximums of these peaks shifted from 600 to 700nm as the n^+/n_s ratio became larger. These peaks can be identified as the longitudinal peaks of the plasmon absorption of nanorods [61]. The low intensity of these peaks also proves the small relative amount of nanorods.

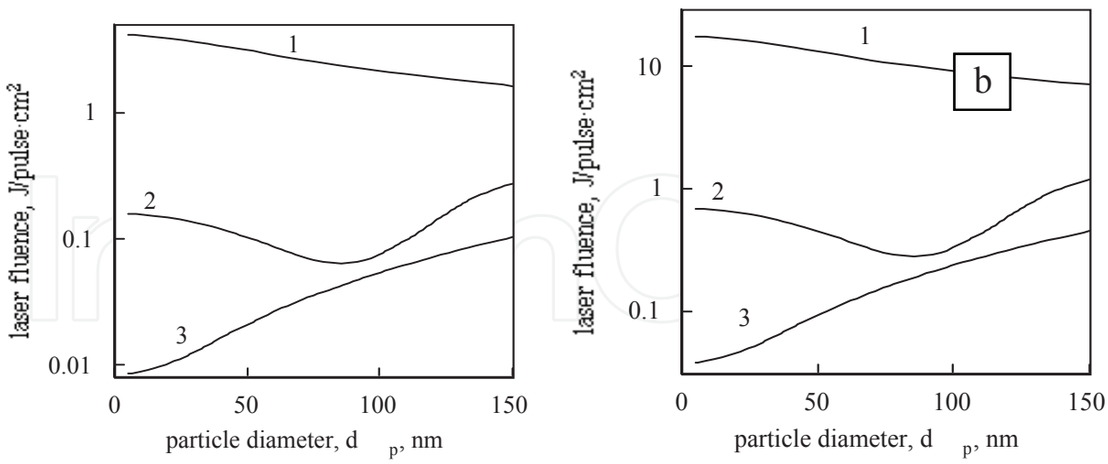


Fig. 8. "Soft" (a) and "hard" (b) laser fluences calculated as the functions of particle diameter for 3 characteristic wavelengths of Nd:YAG laser. (1) λ = 1064 nm, (2) λ = 532 nm, and (3) λ = 355 nm.

To eliminate these nanorods from colloid, we need to irradiate a colloid with "soft" laser irradiation. Second harmonic of Nd:YAG laser (λ = 532 nm) is used again for this irradiation, but the value of laser fluence will depend on the particle size as shown in Figure 8b. For particle size of 20, 30 and 40 nm this "soft" laser fluence will be equal to 0.14, 0.13 and 0.12 $J/puls \cdot cm^2$ correspondently. Normal duration time for such "soft" irradiation is 40 min.
During this irradiation all nanorods were melted and became spherical, thus only spherical particles with the same (or practically the same) particle size distribution will remain into the colloid after such "soft" laser treatment. It can be checked by UV-Vis absorption spectra (see Figure 12b). All the red tails, as well as the small red peaks, have disappeared. At the same time, small red shifts of the primary peaks and their widening corresponding to increase in particle size can still be observed. Direct TEM observations shown in Figures 9 for synthesizes 4 from Table 1, also demonstrate that only spherical particles with practically the same particle size distribution remain into a colloid after "soft" irradiation.
Thus, by applying one-step synthesis and subsequent treatment of the synthesized colloid with soft laser irradiation, we obtained stable colloids containing only spherical and almost mono-disperse particles. The average particle size can be well controlled by varying the $\frac{\Delta m_{Ag}}{m^0_{Ag}}$ ratio and can easily be changed from 8 to 40nm. These results are summarized in Table 1.

A further increase in the $\frac{\Delta m_{Ag}}{m^0_{Ag}}$ ratio leads to a further increase in nanorod concentration, diameter and aspect ratio. The treatment of such colloids with soft laser irradiation cannot melt those nanorods completely. Increase in laser power starts the spherical particle evaporation and produces many very small particles. The following multi-step procedure was designed to produce larger particles.
In first step seed particles prepared as described before were used. For each further step, the particles synthesized in previous step used as the seed particles for the next step. Excluding first 3 steps, where relatively small particles were synthesized, all next synthesis includes two procedures: chemical synthesis and laser treatment of colloid synthesized. "Soft" conditions for laser treatment of different colloids were estimated by using the particle sizes calculated from equation (2b) and using the dependence of "soft" laser fluence on particle size depicted in Figure 8a.

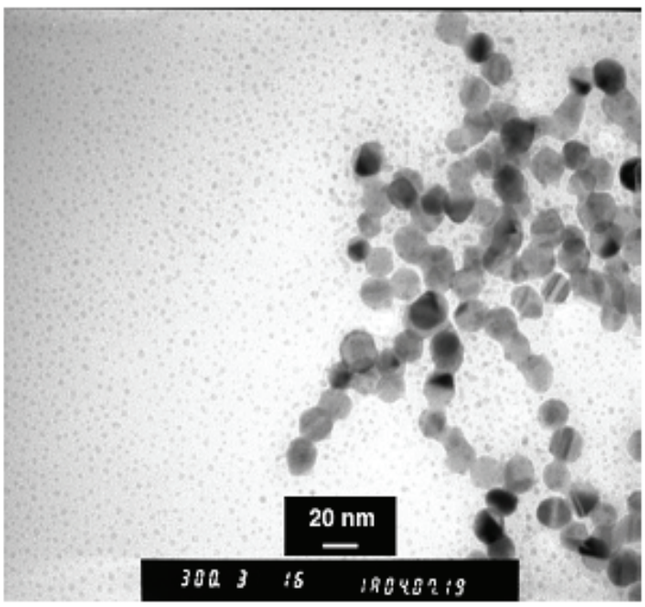


Fig. 9. TEM image of seed colloid (initial colloid treated by "hard" irradiation at λ =532 nm for 30 min).(From [42])

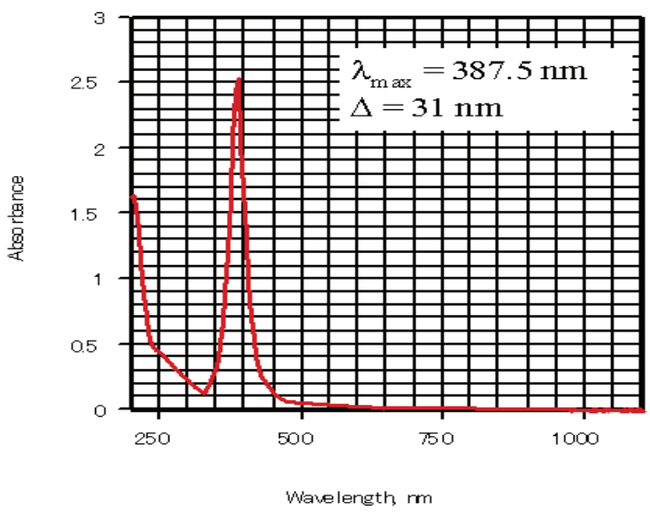


Fig. 10. Typical UV-Viis absorption spectrum of seed colloid (initial colloid treated by "hard" irradiation at λ =532 nm for 30 min).

Because of direct measurements of PSD rather time-spending process, the results of synthesizes can be checked preliminary by measuring the UV-Vis absorption spectra. The results of these measurements are shown in Figure 14a. It can be seen that for each next step excluding first two ones, the absorption peak became more and more wide and shifted to red compare with the previous one. The peaks for synthesis 1 and 2 are very similar to each other and very similar to the peak obtained for seed particles (not shown here). It shows that only spherical relatively small particles were synthesized in first two steps. It can be seen also that peak for synthesis 4 has small red shoulder indicating that some small amount of

nanorods with small aspect ratio were formed along with spherical particles. Figure 14b demonstrates how the absorption peaks changed after the "soft" laser treatment of colloids. These results indicate that all nanorods were removed from a colloid as well as all other non spherical particles. Very small shifts of peak maximum show also that the average sizes of the particles remain unchanged after such "soft" treatment. Direct TEM observation also proves that only spherical particles with nearly the same sizes remain into a colloid after "soft" irradiation. The fact that average size of the particle remains unchanged after "soft" treatment can be seen in Table 2 where the results of such multi- step procedure are summarized. Finally the TEM pictures of colloids obtained in Synthesis 4,5,6, and 7 are shown in Figure 15.

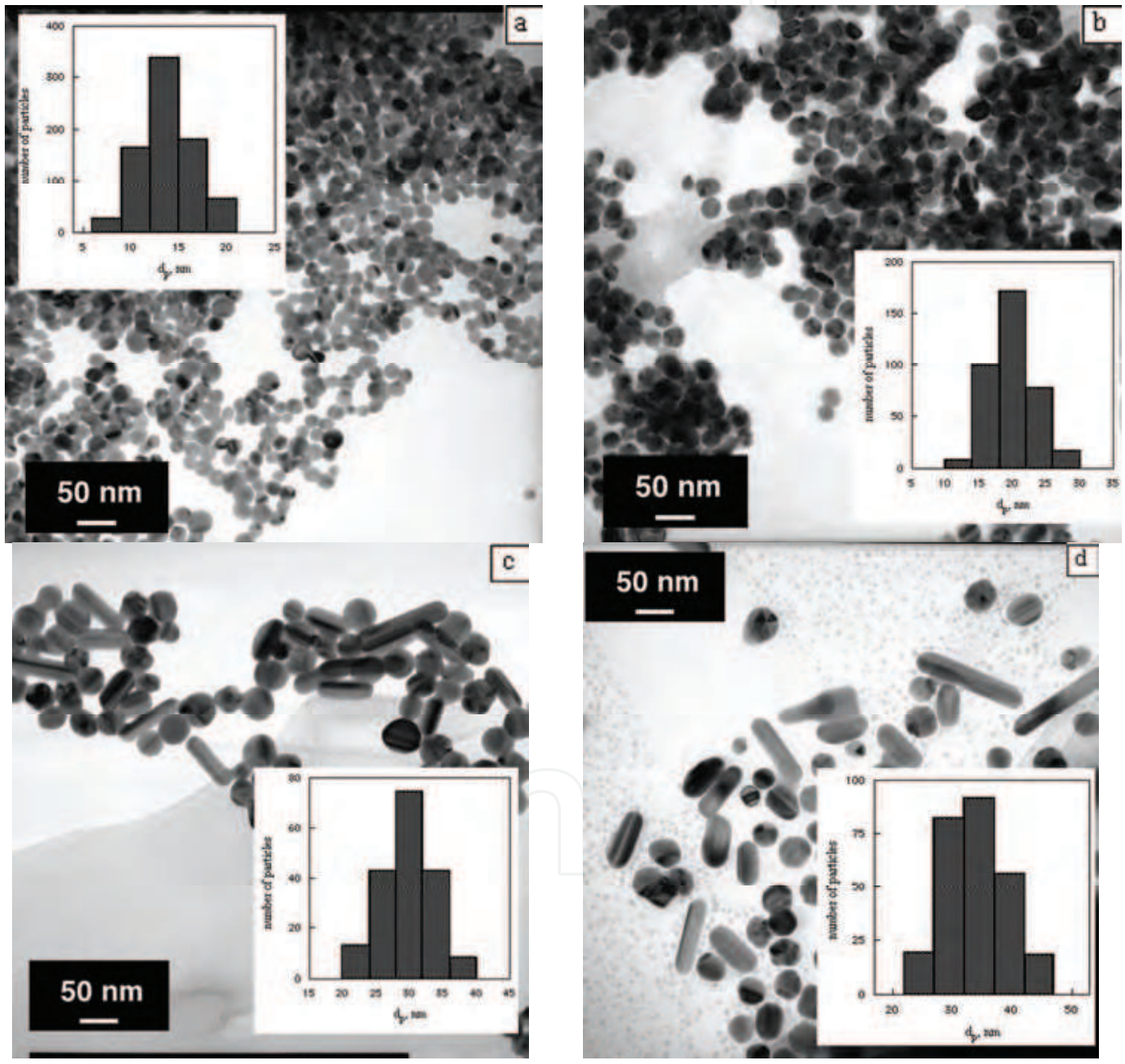


Fig. 11. TEM photographs for four colloids prepared in one-step syntheses with different $\Delta m_{Ag} / m^{0}_{Ag}$ ratios: a) 3.6; b) 18.9; c) 32.4; d) 45. All photos have the same magnification. The inserts are the histograms for particle size distribution.(From [49])

Step number	d_p, nm		
	measured		calculated by equation (2a)*
	before soft laser treatment	after soft laser treatment	
Syn1	23.3 +/- 3.0	-	21.5
Syn2	27.1 +/- 3.8	-	27.1
Syn3	35.9 +/- 4.3	-	34.1
Syn4	40.3 +/- 4.0	39.5 +/-3.5	43.0
Syn5	58.5 +/-5.4	53.6 +/- 5.0	54.2
Syn6	73.1 +/- 6.5	74.5 +/- 7.0	68.3
Syn7	84.1 +/-6.9	-	86.1

* d_{p0} = 10.0nm

Table 2. Average size of the spherical particles synthesized in multi-step experiments

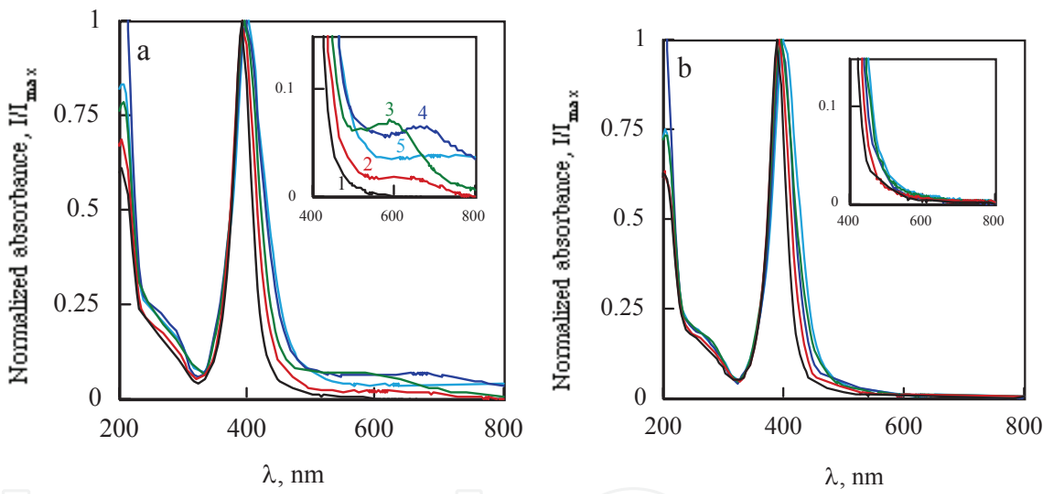


Fig. 12. UV-Vis absorption spectra of colloids synthesized in one-step synthesis, (a) before, and (b) after soft laser treatment. The inserts display details in the 400 to 800nm region. Curves 1 to 5 correspond to Synthesizes 1-5 in Table 1. (From [49])

Thus, we can conclude that our new developed procedure permits to synthesize spherical silver nanoparticles with different desirable size from 10 to 100 nm. All particles are monodisperse, with standard deviation in particle size of about 10%. For synthesis of relatively small particles with size from 10 to 40 nm one-step synthesis with "soft" laser treatment of final colloid can be used, while for synthesis of larger particles with sizes more than 40 nm, multi-step procedure with "soft" laser treatment of intermediate products has to be applied. The new method that we described here is more complicated and more time-spending compare with laser ablation technique, but it has one great advantage compare with laser ablation - the possibility of particle size control, and production of colloids with different desirable size of monodisperse nanoparticles.

Fig. 13. TEM photographs of colloid obtained in one-step Synthesis 4 (Table 1), before and after "soft" laser treatment.

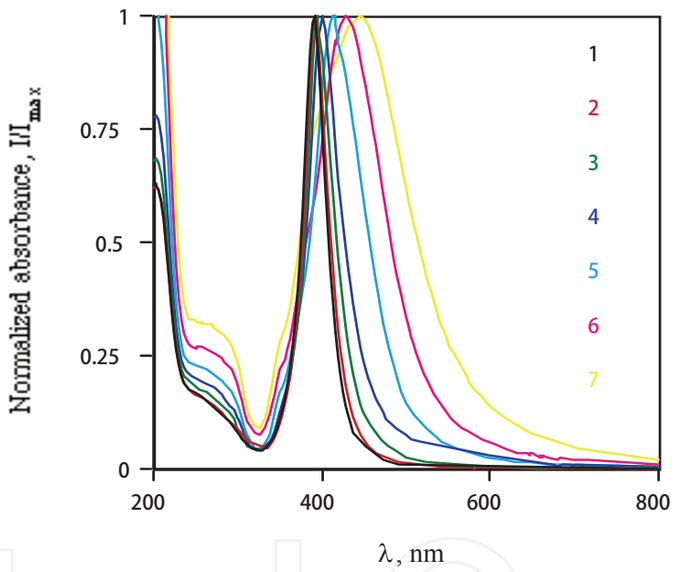


Fig. 14a. UV-Vis absorption spectra of colloids synthesized in multi-step synthesis, Curves 1 to 7 correspond to Synthesizes 1-7 in Table 2.

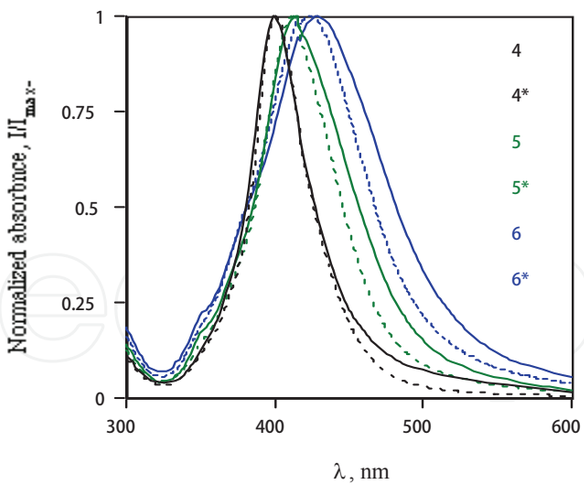
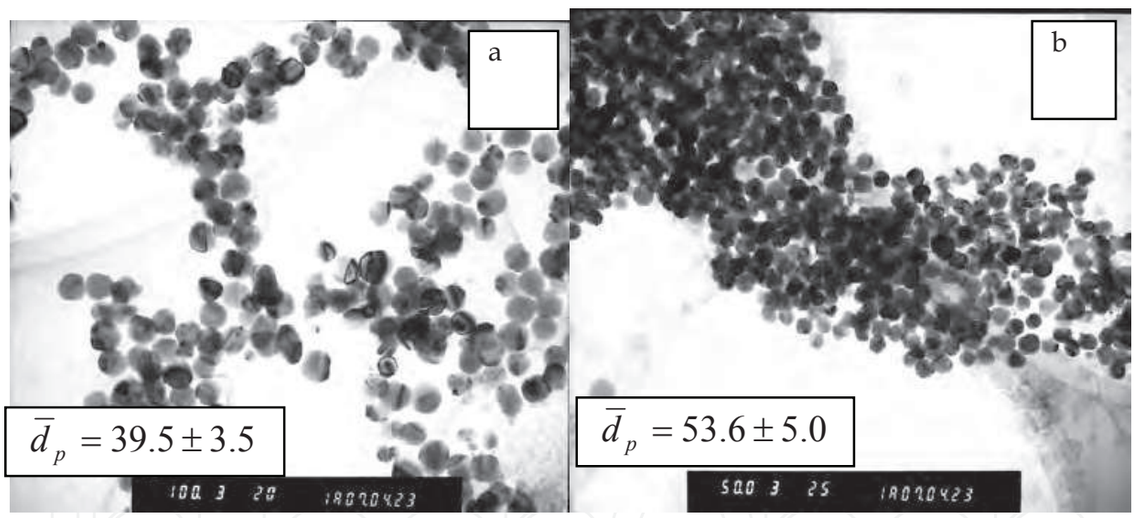


Fig. 14b. UV-Vis absorption spectra of colloids synthesized in multi-step synthesis before (4,5,6) and after (4*,5*,6*) "soft" laser treatment. Curves 4,5,6 correspond to Synthesizes 4,5,6 in Table 2.



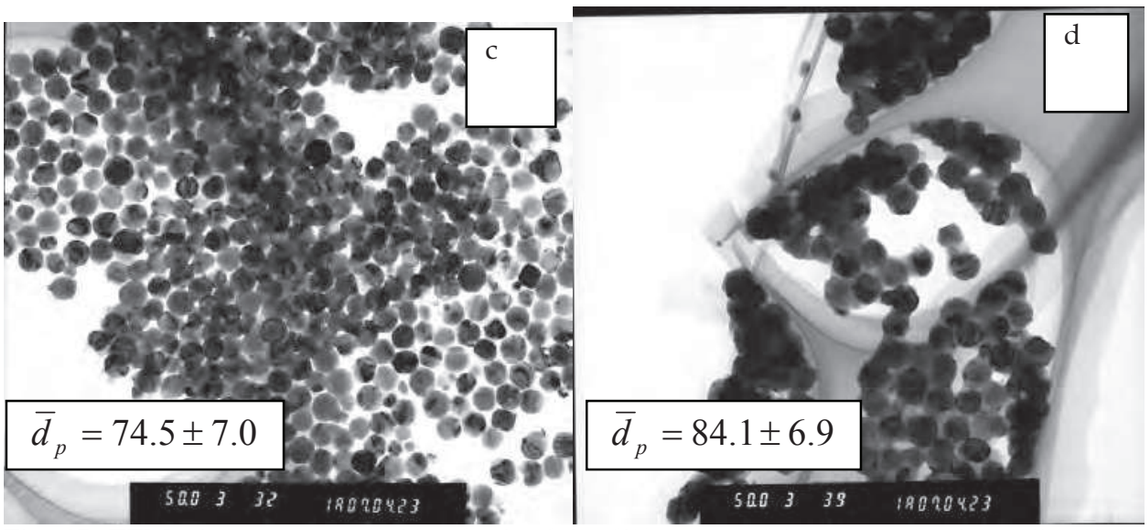


Fig. 15. TEM pictures for colloids obtained in different multi-step synthesis: a) Syn4*; b) Syn5*, c) Syn6* and d) Syn7. Magnification in picture a) is $100x10^3$, in other pictures $50x10^3$.

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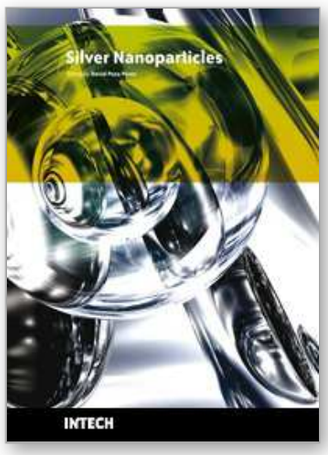

Silver Nanoparticles

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Nanotechnology will be soon required in most engineering and science curricula. It cannot be questioned that cutting-edge applications based on nanoscience are having a considerable impact in nearly all fields of research, from basic to more problem-solving scientific enterprises. In this sense, books like “Silver Nanoparticles” aim at filling the gaps for comprehensive information to help both newcomers and experts, in a particular fast-growing area of research. Besides, one of the key features of this book is that it could serve both academia and industry. “Silver nanoparticles” is a collection of eighteen chapters written by experts in their respective fields. These reviews are representative of the current research areas within silver nanoparticle nanoscience and nanotechnology.

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