Production of Nanoparticles with High Repetition Rate Picosecond Laser

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The fabrication of silver and gold nanoparticle colloids using the picosecond (10 ps) laser ablation in liquids was studied. The maximum productivity of 8.6 μg/s nanoparticles was achieved with the 10 ps-laser pulses at high pulse energy (110 μJ) and the repetition rate of 50 kHz. A special stirred flow chamber was constructed in order to improve reproducibility and generation speed of nanoparticles in flowing liquid during the ps-laser ablation.

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1. Introduction

Laser ablation in liquids is attracting much attention as a new technique to prepare nanoparticles. An advantage of this technique is simplicity of the procedure. In principle, nanoparticles of various species of materials can be prepared by using one procedure [1]. Nanoparticles are used in biomedical applications such as antibacterial implants or catheters, modification of textiles, and refinement of polymers. Very often the desired range of applications is restricted due to a limited availability of nanoparticle materials, their purity and their re-dispersability from agglomerates [2-6]. Over the last decade, the major effort has been directed to the production of stable solutions of small nanoparticles with narrow size distributions and controlled surface chemistry. Although 5–100 nm nanoparticles can be produced by a relatively simple chemical reduction method, the surface of these nanoparticles is likely to be contaminated with reaction by-products such as anions and reducing agents, which can interfere with subsequent stabilization and functionalization steps [7].

Compared to chemical synthesis, the advantages of the laser ablation method are the simplicity of the procedure and absence of chemical reagents in solution. Pulsed laser ablation has also appeared to be the most flexible and promising technique because of its ability to ablate almost all kinds of materials due the ultra-high energy density and control over the growth process by manipulating the process parameters such as irradiation time, duration, energy density, wavelength, etc. [8]

Furthermore, the stoichiometry (e.g. of nanoparticle alloys) is less altered during the conversion of the bulk material (alloy) into nanoparticles when ultrashort pulsed lasers are applied instead of nanosecond laser pulses [9]. It has been shown that high repetition rate picosecond (ps) lasers are advantageous compared to femtosecond (fs) lasers if the total thermal load produced by laser irradiation can be redistributed across a larger area [10]. In case of laser ablation in a liquid flow, the thermal energy is dissipated into the liquid and drained by the flow. It has been shown that laser ablation in liquid produces surface-charged nanoparticles with a shell of dipole molecules (e.g., water) formed around them, preventing agglomeration [2].

In this work, the high power and high repetition rate picosecond laser was applied for the production of silver nanoparticles in water and gold nanoparticles in n-hexane.

2. Experimental setup

A commercially available picosecond laser (Ekspla PL10100) working at 5.5 W and 1064 nm laser wavelength and the pulse repetition rate up to 100 kHz was used for the fabrication of metal colloids in liquids. A 50 mm lens focused the laser beam.

In first experiments the sample was placed on the bottom of a vessel filled with the desired liquid and mounted on a three axis positioning system. However, the production rate and size distribution of nanoparticles with this setup was badly reproducible, since laser material ablation in liquid were affected by the formation of vapor bubbles and thermal distortion of the laser beam. These disturbing effects increased with higher laser fluence and higher repetition rate.

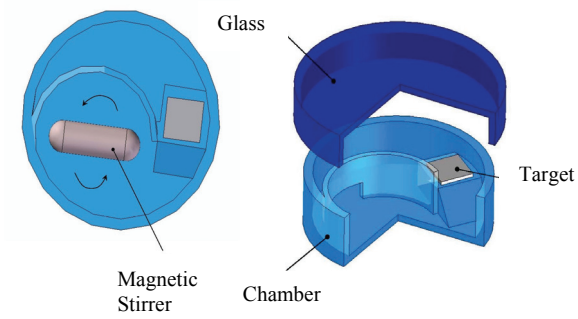

Fig.1 Design of the stirred cell for nanoparticle production.

A special cell for nanoparticle production was constructed for this experiment. Liquid in the cell (see

Fig. 1) was mixed with the magnetic stirrer. The liquid flow was accelerated in the excentered bypass by a ramp that held the target and reduced the flow cross section increasing the flow velocity, which should be as high as possible. This led to minimization of the influence of thermal-lens effects and faster bubble removal. All bubbles were caught in a special trap behind the sample and did not get into the process zone any more.

3. Results and discussions

In order to determine process window, straight lines were scanned on the sample at different focal heights. The line width was measured and ablation track was observed. In stationary liquid, the areas unaffected by the laser radiation appeared on the target surface (see Fig. 2), since laser radiation was shielded by hemispheric bubbles adherent to the surface and distorted by thermal effects. The incident light was also scattered by the bubbles rising upwards. They caused small ripples on the water surface, which disturbed the laser radiation. This led to unpredictable distortion of process parameters, thus leading to poor reproducibility of results.

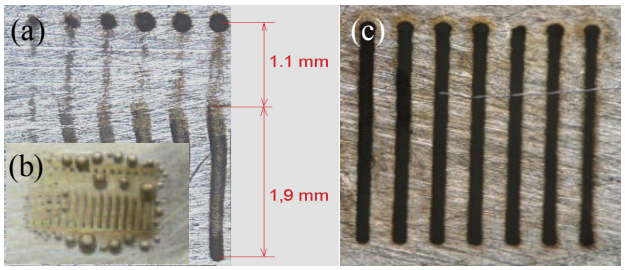

Fig.2 Ablated line geometries on the silver target produced by ps laser pulses (5.5 W, 50 kHz, 20 repetitions per line) in stationary (a,b) and flowing liquids (c). In all cases the chamber with a target was moved linearly at a constant speed of 0.5 mm/s.

To reduce thermal effects at high laser fluencies and high repetition rates, higher vessel moving speeds (0.5-2 mm/s) were required. This produced the surface water movement during experiments leading to wavy appearance of the ablated lines. The lack of repeatability was obvious in this case as could be seen in the microscope pictures shown in Fig. 2(a, b). On the contrary, using flowing liquid produced in a specially constructed stirred chamber (Fig. 1), much better ablation results and higher reproducibility can be achieved. Fig. 2c shows ablated lines generated in the stirred flow cell filled with 25 ml de-ionized water and covered with a glass window. In this case, thermal effects were minimized and generated gas bubbles were rapidly removed by the liquid flow from the processing zone.

The effective spot size (width of the ablated lines) produced in the stirred bypass flow cell is compared with the results obtained in stationary liquid in Fig. 3. In the flow cell, the ablated lines were significantly narrow due to lower scattering and distortion. The laser beam filamentation phenomenon was observed both in stationary and mixed liquid, when optical breakdown of liquid appears above the target. It caused high energy losses and narrowing of the ablated line.

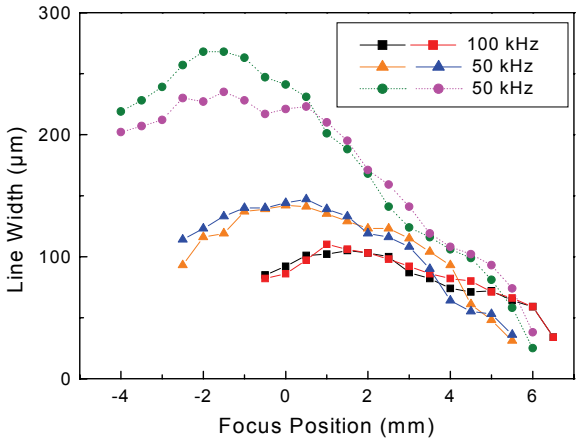

Fig.3 Width of lines produced by the 5.5 W picosecond laser ablation of a silver target in DI-water at constant pulse overlap (1 mm/s, @ 100 kHz) and (0.5 mm/s @ 50 kHz). Diamond symbols correspond to ablation in stationary liquid; squares and triangles represent results obtained in flow cell.

Another important topic is the ablation rate, which can be achieved with ultrashort laser systems. The influence of the pulse repetition rate (at 5.5 W laser power) and focus position on the mass ablation rate is shown in Fig. 4. In the flow cell, no redeposits or micron-sized fragments were observed. In this case, one can assume that the ablation rate was equal to the nanoparticle production rate.

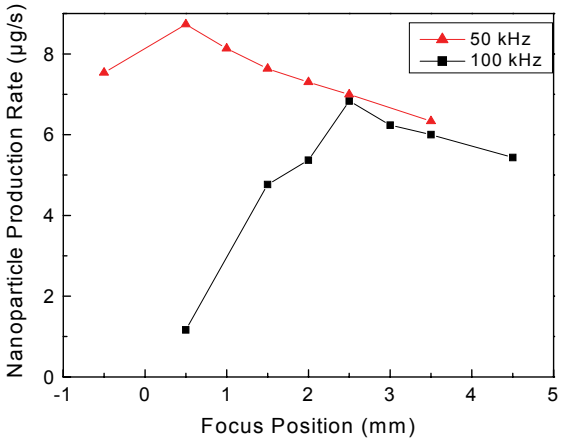

Fig. 4 Silver nanoparticle production rate as function of focus position determined in air.

The ablation rate strongly depends on the pulse overlap [11], therefore the ablation trajectory was designed in such a way, that all the time the tangential scanning speed was kept constant and the system was moving without stops during the experiments. Other parameters, such as liquid flow, energy density and liquid temperature were kept as constant as possible, in order to avoid their influence on the ablation rate and nanoparticle size distribution.

The maximum nanoparticle productivity obtained for 10 ps laser pulses was 8.6 μg/s at the 50 kHz repetition rate (110 μJ) and 6.8 μg/s at the 100 kHz repetition rate (60 μJ). The difference appeared due to higher ablation efficiency at the higher laser pulse energy. A shift

of the productivity maximum (see Fig. 4) closer to the sample surface at higher pulse energies was observed. This can be attributed to the nonlinear effects, such as filamentation and thermal lens formation.

The produced nanoparticles were analyzed with the scanning electron microscope (SEM). A drop of nanoparticle colloid solution was placed on a glass substrate and dried out. The shape of observed nanoparticles was close to spherical (Fig. 5). The spatial resolution of SEM was about 20 nm, therefore there is no information about smaller nanoparticles.

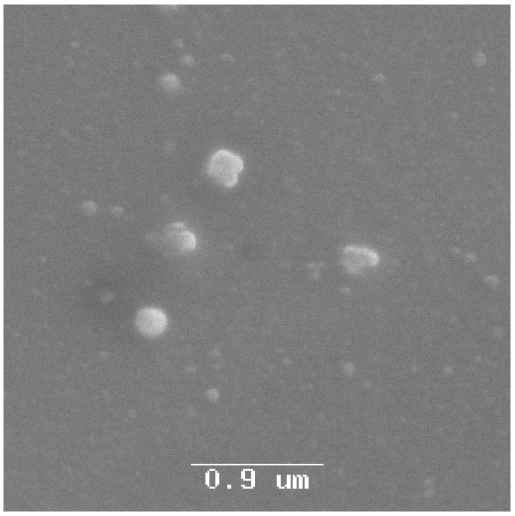

Fig. 5 SEM picture of silver nanoparticles made at 100 kHz, 5.5W and focal position of 0.5 mm above the sample.

Size distribution of silver nanoparticles was obtained from SEM pictures and is given in Fig. 6. The most probable diameter was 50 nm and the size of nanoparticles varied from 30 to 80 nm.

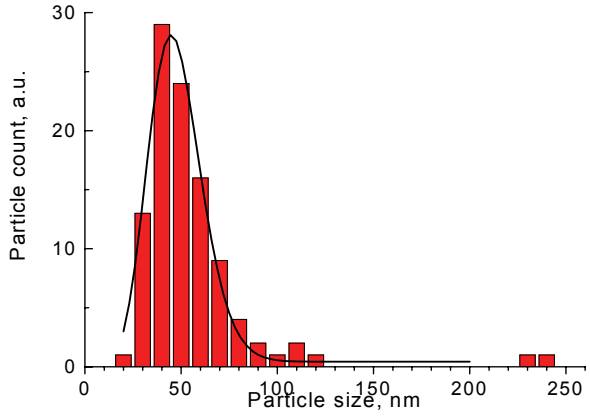

Fig. 6 Size distribution of silver nanoparticle produced by the picosecond laser ablation in water, at 100 kHz, 5.5W and focal position of 0.5 mm above the sample.

Colloidal solution of silver nanoparticles made using the laser ablation in water showed excellent stability against agglomeration. It remained stable even after two months from their manufacturing. In our opinion, the mechanism of stabilization is very simple. They get electrical charge during ablation process and form a shell from dipole water molecules. The presence of electrical charge was proved by applying the electrical field to the colloidal nanoparticle solution. When the electrical field was applied to the solution in the nanoparticle tracking analysis system LM10 (Nanosight), they started to move immediately towards the negative pole.

The same laser equipment was used to produce gold nanoparticles in n-hexane. A stabilizing agent was used to prevent agglomeration because the hexan molecules have no dipole moment. Concentration of the stabilizing agent dodekantiol was changed in order to check stabilization properties. It was varied from 8 to 2 mmol/l. The processing time was 240 s and mass removal varied at about 0.9 mg (ablation rate 3.75 μg/s) at the 5.5 W output power and the 50 kHz pulse repetition rate. Colloid samples were analyzed with a visible spectrum spectrometer and the resonant wavelength of nanoparticle surface plasmons was measured. All samples showed resonant wavelength at 520 nm and a broad absorption peak which shows broad nanoparticle size distribution. Nanoparticles were found to be stable for a long time at all stabilizing agent concentrations.

4. Conclusions

The high repetition rate picosecond laser showed very high productivity of nanoparticles, up to 8.6 μg/sec of silver nanoparticles at the 5.5W output power and the 50 kHz pulse repetition rate. High energy density led to bubble formation and caused thermal effects, and the laser beam was strongly distorted. When the target material was immersed in stationary liquid, non-reproducible ablation spot was obtained. A high flow chamber was designed to mix the liquid. Bubbles were removed from the workfield and the thermal and bubble related problems were successfully solved.

Silver particles made by this method were of round shape and their sizes varied from 30 to 80 nm. The most probable diameter of nanoparticles was 50 nm. They were electrically charged during the ablation process and surrounded by dipole water molecules immediately. The charging led to stabilization against agglomeration. Colloidal solution of silver nanoparticles in water showed excellent stability over a long period.

Colloid solutions of gold nanoparticles in n-Hexan with stabilizing agent dodekantiol were made. The ablation rate of gold nanoparticles was lower than that of silver and was about 3.75 μg/sec at the 5.5 W output power and the 50 kHz pulse repetition rate.

Acknowledgements

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References

[1] T. Tsuji, T. Hamagami, T. Kawamura, J. Yamaki and M. Tsuji: Appl. Surf. Sci. 243, 214-219 (2005).
[2] F. Mafunè, J. Kohno, Y. Takeda, and T. Kondow: J. Phys. Chem. B 104, 9111 (2000).
[3] A.V. Simakin, V.V. Voronov, G.A. Shafeev, R. Brayner, and F. Bozon-Verduraz: Chem. Phys. Lett. 348 (2001).

[4] A.V. Kabashin, and M. Meunier: J. Appl. Phys. 94, 7941 (2003)
[5] B. Liu, Z. Hu, Y. Che, Y. Cheng, and X. Pan: Appl. Phys. Lett. 90, 44103 (2007).
[6] S. Barcikowski, A. Hahn, A.V. Kabashin, and B.N. Chichkov: Appl. Phys. A 87, 47 (2007)
[7] J.-P. Sylvestre, A.V. Kabashin, E. Sacher and M. Munier: Appl. Phys. A 80, 753-758 (2005).
[8] J. Lin, S. F. Lim, S. Mahmood, T. L. Tan, S. V. Springham, P. Lee and R. S. Rawat: 33rd EPS Conference on Plasma Phys. Rome, 19 - 23 June 2006 ECA Vol.30I, P-2.087 (2006).
[9] J. Koch, A. Bohlen, R. Hergenröder, K. Niemax: J. Anal. At. Spectrom., 19, 267–272 (2004).
[10] A. Ostendorf; G. Kamlage; U. Klug, F. Korte, B.N. Chichkov: Proceeding of SPIE 5713, 1-8 (2005).
[11] G.Račiukaitis, M.Brikas: Proc. SPIE, 5662, 717-721 (2004).

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