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Synthesis of silver nanoparticles by laser ablation in pure water

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ABSTRACT We have successfully produced silver nanoparticles by irradiating an Ag target with a 532-nm laser beam in pure water. By working with high laser power and small spot sizes, we were able to synthesize very small spherical particles with a typical size of 2–5 nm. The influence of the beam spot size, the laser power, and the ablation time were studied, and the possible mechanisms of particle formation are discussed.

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1 Introduction

Sharp surface plasmon absorption of silver nanoparticles [1] makes them very attractive for bioscience and biotechnology. For such applications, the particles should be very stable and well dispersed with a very small size and a narrow size distribution. The chemical reduction method [2, 3] is most commonly used for the synthesis of such particles. Colloids produced by this method have to be purified from residual ions. Recently, a new method of nanoparticle preparation by laser ablation of a metal surface immersed in liquid has been developed [4–9]. Although residual ions are not a problem for such an approach, the size distribution of the nanoparticles tends to be broadened. To control the size of the nanoparticles, different surfactants were used [6–8]. This chemical approach for particle-size control appears very successful in synthesizing silver nanoparticles with small and narrowly distributed diameters. However, the problem of colloid purification from the surfactant arises, and was especially serious for the prospect of further biological applications. We have tried to produce silver nanoparticles in pure water without any additives. In all previous work on laser ablation in the liquid phase, the energy of a laser beam pulse was relatively low: 55 mJ/pulse in [4], 10–30 mJ/pulse in [5], and 40–90 mJ/pulse in [6–8]. In our research, we used the maximum possible energy of a laser pulse, which was about 340 mJ/pulse, and tried to understand how the laser power, as well as other parameters, affected the results of ablation.

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2 Experimental setup and procedure

The experimental setup is shown schematically in Fig. 1. The beam from a Nd : YAG laser was focused by a lens ($F = 25$ mm) on the surface of a silver target (99.99%, thickness 1.0 mm) placed inside a reactor with 170 ml of pure water. The target was slowly rotated (1/60 rpm) and its position relative to the laser beam was controlled by two X–Y sliders. The second harmonic ($\lambda = 532$ nm) was employed. The laser pulse duration was about 10 ns, the pulse-repetition rate 10 Hz, and the maximum energy of the pulse 0.34 J/pulse. The majority of experiments were accomplished at this maximum laser power. The duration of the ablation experiment was 5 min. Special experiments were conducted to understand the influence of the duration on the ablation results. In these experiments, the ablation process was terminated after each 30 or 60 s, and 5 ml of colloid were sampled. Before sampling, target rotation was continued for 1 min to make a homogeneous distribution of particles into a volume. This sampling procedure did not change the concentration of the nanoparticles in the colloid. Immediately after the ablation experiment, the UV-Vis absorption spectra of silver colloids were measured by a Shimadzu UV-1200 spectrometer. A transmission electron microscope (TEM), a Hitachi H-800, was employed to take electron microphotographs of the resultant nanoparticles.

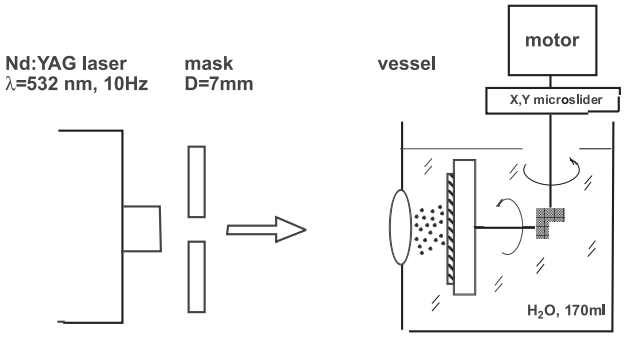

FIGURE 1 Schematic diagram of experimental setup

3 Results and discussion

First, the results of ablation strongly depended on focusing conditions, or the laser beam spot size on a metal tar-

get, D_m. Colloids synthesized for small spot sizes had a pale-yellow color and were very stable for months. On the other hand, colloids synthesized for a relatively large D_m were yellowish pink and very often precipitated after a few days or 1–2 weeks, forming a thin black layer on the bottom. UV-Vis absorption spectra were also completely different for different focusing conditions, as shown in Fig. 2. For small spot sizes, 0.6–0.7 mm, the UV-Vis absorption peaks were rather narrow (FWHM was about 50–70 nm) and rather symmetrical. When the spot size was increased, the absorption peak became wide and asymmetrical, and a red tail grew faster with D_m increase. TEM images also revealed a large difference for different focusing conditions. For small spot sizes, 0.6–0.7 mm, most of the observed particles were very small, spherical, and their sizes were rather uniform, $d_p = 2$–5 nm. A typical image is shown in Fig. 3. In some 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. 3. 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 1.5 mm, 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.

Profilometer analysis of the silver targets ablated by different laser beam spot sizes showed that the depth of the hollow made by the laser beam on a target surface was independent of the focusing conditions and was always about 2–4 μm. The hollow walls were practically vertical. Therefore, it is possible to estimate its volume and, thus, the total amount of silver evaporated from the target into the water. Taking into account the total number of laser pulses during the 5-min ablation experiment, $N = 3000$, the total mass of silver transferred into a colloid during a single laser pulse was estimated. This amount ranged from 10^{-10} kg to 10^{-9} kg when

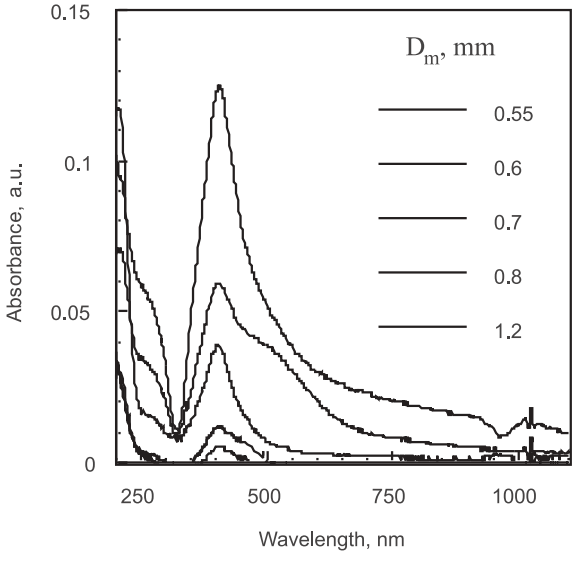

FIGURE 2 UV-Vis spectra for different beam spot sizes D_m

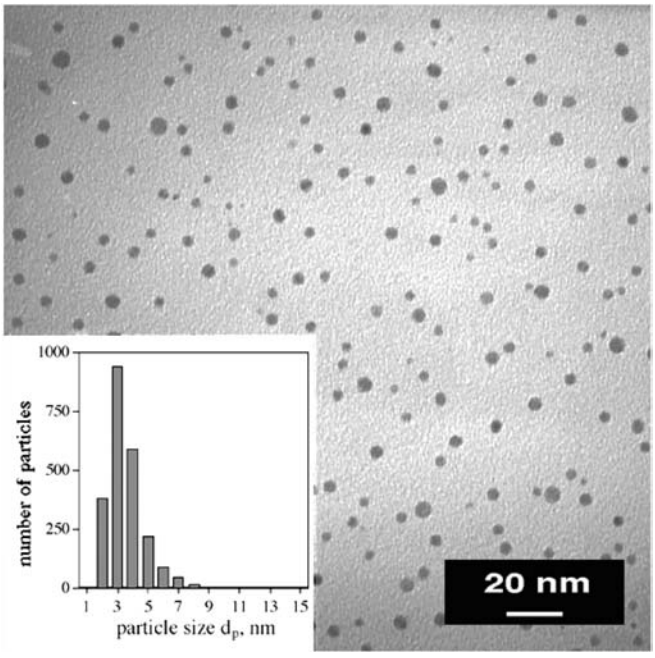

FIGURE 3 A typical TEM image of small particles synthesized for the beam spot size of 0.7 mm. *Inset* shows the particle-size distribution. The average particle diameter $d_p = 4.2$ nm

the beam spot size was varied from 0.6 to 1.7 mm, which corresponds to 10^{-9}–10^{-8} mol of Ag. This amount qualitatively agrees with the results of Mafune et al. [6], who used the first harmonic of a Nd : YAG laser, $\lambda = 1064$ nm, to demonstrate that the total amount of silver coming into the colloid ranged from 0 to 2×10^{-9} mol as the laser power was increased from 20 to 90 mJ/pulse, using a beam spot size of about 1.5–2 mm. Mafune et al. [6] did not mention that the beam spot size can affect the total amount of evaporated silver, but showed a nearly linear increase of this amount with laser power. One possible explanation of such different characteristics of laser ablation at high and low laser powers could be the following: at relatively low laser beam energies, the hollow depth could depend on the energy flow density, $J = E/S_m$, where $S_m = \pi D_m^2/4$ is the area of the spot on the target surface. When the spot size is increased, the energy flow density will decrease, causing in turn the hollow depth to decrease as well. Therefore, the volume of the hollow could remain nearly constant. When the laser power further increases, saturation could take place, and the hollow depth will be nearly constant.

According to [6], the absorbance at a wavelength of 250 nm, I_{250}, could be used as a measure of the total amount of silver coming to the colloid (in the form of nanoparticles of different sizes as well as free silver atoms). When the I_{250} values, measured from Fig. 2, are plotted against the area of individual spots on the silver target, S_m, as shown in Fig. 4, a linear dependence can be assumed. This means that in our experiments the depth of the individual spot produced by a single laser pulse does not depend on the spot size.

The influence of the laser power on the ablation results was checked in another experiment. Because a simple decrease of laser power made the particle concentration in the colloid undetectably small, the duration of ablation, t, was increased simultaneously with a decrease of the laser power

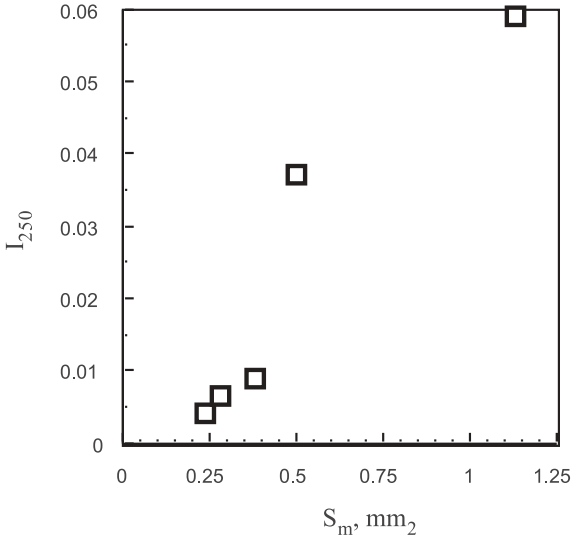

FIGURE 4 I_{250} values vs. beam spot area S_m

to keep the total energy irradiating the target nearly constant. The I_{250}/t value was used as a measure of the total amount of silver evaporated into the colloid after a single laser pulse. The results of the experiment conducted with a beam spot size of about 0.7 mm are shown in Fig. 5. Because the peaks obtained for different laser powers had rather similar characteristics (FWHM, λ_{max}), the maximum absorbance, I_{max}, could represent the total amount of nanoparticles in the colloid. As can be seen from Fig. 5, both values, I_{250}/t and I_{max}/t, increase linearly with laser pulse energy up to 0.2 J/pulse, in good agreement with results of [6], and above that the growth is more rapid. Therefore, by working with high laser power, we have two possibilities to change the total amount of silver evaporated in a water colloid during a single laser pulse: to change the laser power or to change the focusing conditions and, therefore, the beam spot size. In the first case, we change the depth of the spot, and in the second case the depth of the spot remains constant.

Another important factor, which can strongly affect the results of ablation experiments, is the duration of ablation. Our measurements showed that the results strongly depended on sampling time. For a sampling time of 30 s, the λ_{max} values remained practically constant (the average being equal to 402.5 nm), independent of the spot size during the first 7 min. The peak width slowly increased in time, with the growth rate related to the spot size. Thus, for $D_m = 0.6$ mm, the FWHM increased from 60 to 70 nm in the first 5 min and, for $D_m = 1.2$ mm, from 80 to 120 nm. I_{max} values increased practically linearly with time during the first few minutes, as shown in Fig. 6. Their growth rate was proportional to the beam spot area, S_m, in good agreement with previous results. When the sampling time was increased from 30 to 60 s, the results were changed dramatically: I_{max} values revealed a saturation, λ_{max} values began to increase rapidly (to 415 nm for $D_m = 1$ mm and to 437 nm for $D_m = 0.7$ mm), and the peak width also showed a rapid increase.

All these results could be explained in terms of the dynamic formation mechanism of particle growth [6–8]. According to this mechanism, immediately after the ablation, a dense cloud of silver atoms (plume) accumulated over the ablation spot. Silver atoms in the plume aggregate rapidly into small embryonic nanoparticles as fast as silver atoms collide mutually. After the rapid growth ceases, the embryonic particles grow slowly while collecting free silver atoms, which diffuse to them through water. In our case, when D_m was small, the particle concentration was low, and we dealt with the process of slow growth of small embryonic nanoparticles toward secondary mid-size ones. But when D_m was increased, the particle concentration became large, and another possibility for particle growth arose. Free silver atoms could precipitate not only onto the embryonic particles but onto the secondary, mid-sized nanoparticles already existing in the colloid as well, forming large tertiary nanoparticles. These two processes, formation of secondary and tertiary nanoparticles, could be responsible for the change in UV-Vis absorption spectra observed for large spot sizes when the

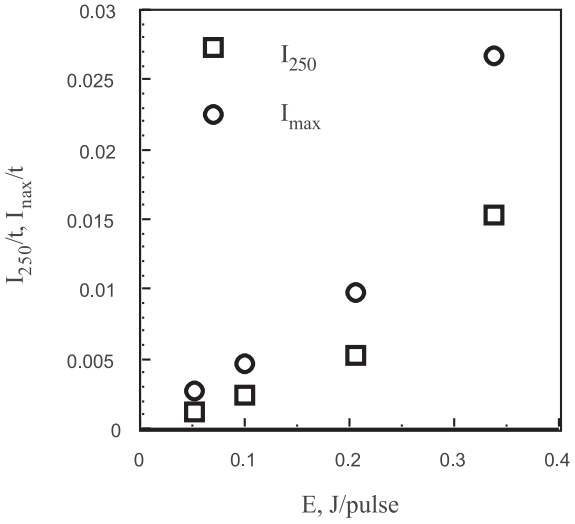

FIGURE 5 I_{250}/t and I_{max}/t values vs. laser pulse energy. Beam spot size, D_m, is 0.7 mm

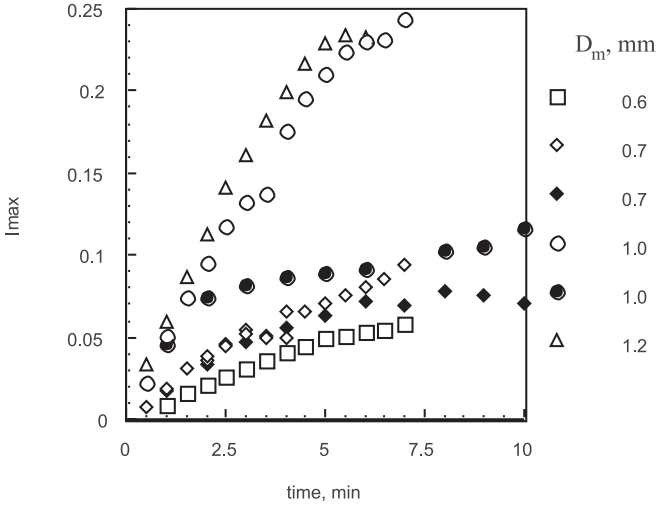

FIGURE 6 Time dependence of I_{max} for different beam spot sizes. *Open symbols* correspond to a sampling time of 30 s, *closed* to 60 s

sampling time was equal to 30 s. Another process that can strongly affect the ablation results is particle agglomeration. Our results revealed the existence of a gradient of the nanoparticle concentration in the vicinity of the plume. Because of the nonideal mixing conditions, the particles formed in previous plumes did not have enough time to move far from the place where nanoparticles and free atoms from the new plume were injected into the colloid. In such conditions, the particles accumulated in the vicinity of the plume and their local concentration could be much higher than their average concentration in a colloid. When the local concentration became high enough, the particle-agglomeration process began. During the 30 s of ablation, the number of these agglomerates was not high compared to the total number of particles. But the rate of agglomerate formation and growth can be nonlinear. When the sampling time was increased to 60 s, the agglomeration became essential, especially for large beam spot sizes (large particle concentration). Therefore, it is possible to conclude that the most important factor affecting the size of the nanoparticles is the particle concentration. By working with a low concentration of nanoparticles and by improving the mixing conditions (preventing high local particle concentration), it will be possible to produce mainly primary, embryonic nanoparticles.

The most essential difference between our results, obtained for high laser power, and all previous results [4–9], obtained for lower laser power, is the average size of the primary embryonic nanoparticles. Mafune et al. [6] reported that the average diameter of the embryonic particles was 11 nm and that, in experiments conducted with pure water, all these primary particles further grow up to 20 nm. As a result, strong agglomeration occurred, and silver colloids produced using pure water were unstable. In our experiments, the average size of the embryonic particles was 3.5 nm, some growing up to 10 nm (average size of secondary particles). As a result, the silver colloids contained mainly primary particles (synthesized using small beam spot sizes) and were very stable for months. The only possible explanation of such a difference could be the difference in experimental conditions. Working with a much higher laser power, we produced a hotter and denser plume, which could, in turn, change dramatically the size and concentration of the embryonic particles.

4 Conclusion

By working with high laser power and small laser beam spot sizes, we succeeded in producing small silver nanoparticles with a narrow size distribution in pure water without any chemical additives. After surface modification these particles can be used in many applications in bioscience and biotechnology.

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