Femtosecond laser ablation in aqueous solutions: a novel method to synthesize non-toxic metal colloids with controllable size

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Abstract:
We review results of the femtosecond laser ablation of noble metals in pure water to synthesize colloidal nanoparticles. We show that such ablation leads to the formation of two different populations of nanoparticles (low and highly size-dispersed ones), while their mean size and relative contribution are strongly affected by the intensity of pumping radiation. Analyses of ablation craters on the target surface enables to relate the appearance of these populations to photon- and plasma-induced ablation mechanisms, respectively. The nanoparticles produced are of importance for biological sensing and imaging applications.

1. Introduction
Laser ablation has shown itself as one of the most efficient physical methods for nanofabrication. The method consists in the ablation of a target (mostly solid) by an intense laser radiation, yielding to an ejection of its constituents, and to the formation of nanoclusters and nanostructures (for review, see e.g., [1]). In the case of liquid ambience, this process leads to the release of nanoclusters to the environment and the formation of colloidal nanoparticle solution [2-17]. In contrast to conventional chemical reduction methods, this method enables us to avoid the use of toxic chemical reduction agents to control the growth of the colloidal nanoparticles. In particular, the laser ablation-based synthesis can be implemented in pure deionized water [7-14] or even in biologically-compatible aqueous solutions [15-17]. The independence of laser-based synthesis of dirty colloidal chemistry makes it unique for the fabrication of markers of bioanalytes for sensing and in vivo imaging applications.

In pure water, however, or any other aqueous solution exempted of additional chemically active components, the size of nanoparticles produced tends to be relatively large, since a natural coalescence of hot ablated nanoclusters can not be easily overcome. In particular, nanosecond laser-based ablation used in most works, generally gives relatively large (10-300 nm) and strongly dispersed (50-300 nm) particles [6-14]. Although certain size control can be achieved by decreasing the wavelength of pumping radiation [9,12] or varying the laser fluence [2,7,8], the range of size variations stays rather moderate in the nanosecond radiation case.

We recently applied a femtosecond laser technique to synthesize gold nanoparticles in aqueous solutions [14-18]. Our studies demonstrate much better flexibility in controlling the size and size dispersion of nanoparticles produced [14,18]. In this paper, we summarize data on properties of metal
nanoparticles prepared by the femtosecond laser ablation in pure water. In addition to gold, we give some new data on the laser ablation of silver in order to generalize the analysis of the phenomenon.

2. Experimental setup
The experiments were carried out with a Ti/Sapphire laser (Hurricane, Spectra Physics Lasers), which provided 110 fs full width at half maximum (FWHM) pulses (wavelength 800 nm, maximum energy 1 mJ/pulse, repetition rate of 1 kHz). The radiation was focused by an objective with the focal distance of 7.5 cm on the top of a rod of Ag or Au (purity 99.99%) with the height of 1.5 mm and the diameter of 6 mm, which was placed on the bottom of a 2-mL glass cuvette filled with pure 18 MΩm deionized water. In most experiments, the target was placed slightly ahead of the focus to decrease the radiation intensity on the surface. The thickness of the water layer above the rod was 10 mm. The vessel with the rod was placed on a horizontal platform, which executed repetitive circular motions at a constant speed of 0.5 mm/s to form a circle-like region of the ablated material on the target surface.

A Transmission Electron Microscope (TEM) with 0.23 nm point-point resolution (model Philips CM30) was used to take electron images of the nanoparticles in the solution. A drop of a sample solution was placed on a carbon-coated copper grid and then dried at room temperature. Normally, the diameters of 1000 particles were measured and the distribution of particle size (diameter) distribution was obtained. Target surface was examined by scanning electron microscopy (SEM, model Phillips XL20). In addition, we recorded absorption spectra in 250-1000 nm range using Lambda 19 Spectrometer (Perkin Elmer).

3. Experimental results
The laser ablation of metals in water was accompanied by the presence of a plasma plume on the target surface, easily visible by a naked eye. Nevertheless, we did not observe any additional plume along the optical path related to the laser-induced breakdown of water or air on the water surface. The color of aqueous solutions changed within a few seconds of the experiment and the solution became green and red in the case of Ag and Au targets, respectively. The increase of the laser fluence could also lead to the appearance of metallic tints in the solution under high radiation fluences. Absorption spectra from the solutions are characterized by the presence of sharp peaks at 400 and 520 nm for Ag and Au, respectively. The appearance of these peaks is generally attributed to the generation of localized plasmon resonances in metal nanoparticles [19, 20]. Note that the plasmon-related absorption peaks slightly broadened and red-shifted under the increase of the laser fluence, suggesting the increase of the mean size and size dispersion of nanoparticles produced.

More detailed information on size properties of nanoparticles produced was obtained from Transmission Electron Microscopy data. We found, the main feature of the femtosecond ablation-based synthesis consisted in the presence of two different populations of nanoparticles [14]. An example of such populations for the ablation of Ag in deionized water is shown in Fig. 1. The first “low-dispersed” population is characterized by small mean size and narrow size dispersion; whereas the second, highly dispersed one, has much larger mean size and broader dispersion. Fig. 2 shows the dependence of the mean size of silver (a) and gold (b) nanoparticles, corresponding to two different populations, as a function of the radiation fluence. Here, the increase of the mean size under an increase of the fluence is clearly visible. However, the increase rate was not very significant for the low dispersed population with ranges of variations for the mean size from 6 to 12 for Ag and from 4 to 15 nm for Au. In contrast, the broad distribution showed much stronger and almost linear increase of the mean size as the fluence increased. Similar changes of the mean size and size dispersion of nanoparticles related to two populations were observed under the shift of the target position with respect of the focal point position [18]. In the later case, the mean size of nanoparticles associated with the highly dispersed population rapidly decreased as the target was removed from the focal point toward the focusing lens or in the opposite
direction, whereas the size of the low dispersed population changed only slightly. We reason that it was the decrease of radiation intensity on the target surface, induced either by the decrease of laser fluence or by the increase of the radiation spot surface, that caused changes of size distributions in these two cases.

Figure 1. TEM micrograph images and corresponding size distributions of Ag nanoparticles prepared by the fs ablation in water at 160 J/cm².

It is interesting that in the case of gold we were able to completely avoid the production of nanoparticles associated with the highly dispersed population. This phenomenon could be realized at F < 30 J/cm², as one can see from Fig. 2 (b). One can see that very small (3-4 nm) and almost monodispersed nanoparticles were produced in this case without any chemical reducing agent [14]. The fabrication of such samples required a significant number of laser shots corresponding to several hours of the experiments. It should be noted that the ablation of Ag even at very low fluences was accompanied by the presence of a certain fraction of nanoparticles associated with the highly dispersed population.

Figure 2. Mean size for the low (1) and highly (2) dispersed populations as a function of laser fluence for laser-synthesized Ag (a) and Au (b) nanoparticles.
The presence of two populations, revealed in our experiments, suggest an involvement of two different mechanisms of nanoparticle growth. To understand the nature of these mechanisms, we performed a detailed analysis of craters produced on the target surface as a result of the femtosecond laser ablation. SEM images of typical craters for a silver and gold target are shown in Fig. 3 and 4, respectively. One can see that the craters prepared at high fluences $F > 100 \text{ J/cm}^2$ were very broad and had irregular profiles, while their walls and bottom contained traces of molten material. In addition, these craters were surrounded by a significant heat-affected zone. In contrast, craters formed at low fluences were such smoother. Nevertheless, we were able to completely avoid melting effects only for the gold target. An example of such a crater is shown in Fig 4 (b).

**Figure 3.** SEM images of typical craters on Ag after the ablation by 5000 laser pulses at $F = 1000 \text{ J/cm}^2$ (a) and $F = 30 \text{ J/cm}^2$ (b) in water.

**Figure 4.** SEM images of typical craters on Au after the ablation by 5000 laser pulses at $F = 1000 \text{ J/cm}^2$ (a) and $F = 60 \text{ J/cm}^2$ (b) in water.

4. Discussion
Our experiments clearly show the presence of two populations of nanoparticles produced by femtosecond laser ablation. The first, less dispersed, population was characterized by a relatively small mean nanoparticle size, which varied only slightly as the radiation intensity decreased through a decrease of laser fluence or a removal of the target from the focal point. Since the ablation in this region is characterized by a significant reduction or a complete absence of target melting effects (Fig. 3(b), 4(b)), it can be attributed to pure photon-based ablation of nanoclusters and their subsequent coalescence in a water environment. Indeed, the absence of the melting effects is consistent with a significant reduction, or the complete removal of, the heat-affected zone, as a direct consequence of the femtosecond laser pulse being much shorter than the heat diffusion time [21]. In contrast, the
fabrication of the second highly dispersed population of nanoparticles was efficient only under the production of intense plasma in a liquid environment. Here, the ablation was accompanied by the formation of craters containing traces of molten material, as shown in Fig. 3(a) and 4(a). Taking into account the absence of melting effects under the femtosecond laser ablation, the appearance of these craters can be explained by the involvement of plasma-related processes. Potential mechanisms include plasma-caused thermal evaporation of the target and its erosion as a result of the collapse of the cavitation bubble [22]. Note that this supposition is confirmed by a recent study of the dynamic of plume formation in liquid during nanosecond laser ablation of a target [23]. In this study, two phenomena were clearly identified. The first one is a formation of a plasma jet at the first moments after the laser action (before 50 μs), which was attributed to photon-related ablation of material. The second one is the formation of the cavitation bubble, which grows until 150-250 μs and then collapses. It was concluded that the collapse of the bubble released a significant amount of mechanical energy and could be an additional source of the material ablation. Although the efficiency of conversion of the radiation energy to a cavitation bubble is much lower for femtosecond pulses compared to nanosecond ones (as measured in [22], the decrease of the pulse length from 76 ns to 100 fs leads to a decrease of the efficiency from 22-25% to 1-2%), the energy of the bubble can however become sufficient to melt and evaporate the target. We reason that this explosive process can lead to an ejection of a large number of nanoparticles within a small volume near the target surface, increasing the efficiency of the coagulation process and thus leading to a relatively large mean size of nanoparticles produced. In our experiments, we were able to avoid this secondary ablation of material only in the case of Au target at low fluences, while the ablation of Au was always accompanied by the presence of highly dispersed population. This difference of results for Ag and Au is probably explained by a much lower thermal conductivity and higher threshold of ablation of gold compared to silver [24]. It should be noted that our experiments at high fluences were accompanied by the generation of white continuum due to self-focusing effects. However, these phenomena could hardly influence the nanofabrication process. Indeed, these phenomena should lead to different profiles of formed craters from pulse to pulse due to a casual focusing of light to different points, which was not the case in our studies.

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