Laser ablation of silver in aqueous ambient: effect of laser pulse wavelength and energy on efficiency of the process

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Abstract. Laser ablation (LA) of a Ag target in ultrapure water has been performed with nanosecond laser pulses of 355, 532 and 1064 nm in the range of fluences achievable for the particular wavelength. Efficiency of LA process was quantified in terms of the amount of ablated Ag as determined by atomic absorption spectroscopy (AAS) as well as of the area of the surface plasmon extinction (SPE) band of the resulting Ag nanoparticle hydrosol, and a fairly good agreement between the results produced by the two methods was obtained. Sigmoidally shaped plots of the LA efficiency as a function of laser fluence were obtained for LA with all wavelengths of laser pulses examined. Nevertheless, the maximum amount of Ag transferred from the target into the aqueous medium (yielding Ag nanoparticle hydrosol) is substantially (at least 6.5 x) larger for LA performed with 1064 nm pulses than that with 532 nm and 355 nm pulses. On the other hand, polydispersity of the hydrosol ablated with 1064 nm pulses is higher than that of the sols obtained with 532 and 355 nm pulses, most probably due to a limited extent of Ag nanoparticle fragmentation.

1. Introduction
Laser ablation (LA) of silver (Ag) in liquid ambient is currently explored as a prospective top-down strategy of Ag nanoparticle preparation. Owing to their unique optical properties [1], Ag nanoparticles have found a wide-range of applications, e.g. as components of optical sensors and/or amplifiers of optical processes undergone by molecules located on their surfaces. An important issue in LA of Ag is achievement of a control over the morphological characteristics (such as mean particle size and size distribution) and stability of the resulting Ag nanoparticle hydrosols. The most important of a variety of parameters affecting the outcome of laser ablation are laser pulse duration (fs-ns), wavelength and energy [2,3]. In this contribution, we focus on exploration of the effect of laser fluence on the efficiency of LA of a Ag target in aqueous ambient carried out by pulses of 1064, 532 and/or 355 nm wavelength provided by a nanosecond Nd/YAG laser system. The efficiency of the laser ablation has been expressed in terms of the amount of ablated Ag as determined by atomic absorption spectroscopy (AAS) as well as of the area of the surface plasmon extinction (SPE) band of the resulting Ag nanoparticle hydrosol. For each particular wavelength, the LA efficiency has been measured as a function of laser fluence.
2. Experimental
LA of a 1 mm thick Ag foil (Aldrich, purity 99.999 %) was performed in 40 mL doubly distilled (in a quartz apparatus) deionized water as ablation medium placed in a quartz cell, using the experimental setup described in [3,4] and glassware, accessories and silver foil cleaning procedures reported in [3]. The active, Q-switched Nd/YAG laser system Continuum Surelite I, providing pulses of 1064 nm, 532 nm (frequency doubled) and 355 nm (frequency tripled) wavelength with the maximum energies per pulse of 310 mJ (1064 nm), 180 mJ (532 nm) and 90 mJ (355 nm), pulsewidth (FMHM) of 6 ns, repetition rate of 10 Hz and an effective diameter of 5 mm, was used for LA. The pulse energy was measured by a power detector Gentec PSV 103 equipped with a volume absorber. Optionally, the laser beam was focused using a quartz lens with 200 mm focal length to achieve a higher laser fluence. In each of the LA experiments, the laser impacted area of the Ag foil was determined. At given time of LA process, a batch of Ag nanoparticle hydrosol was withdrawn for AAS and SPE measurements. The efficiency of laser ablation was measured as a function of laser fluence and expressed in terms of total amount of ablated Ag per mm² of laser impacted area (μg/mm²) and in terms of the relative area of SPE band of the resulting Ag nanoparticle hydrosol, respectively. SPE spectra of silver hydrosols were measured with a double beam spectrophotometer Perkin-Elmer Lambda 950, in the transmission mode. For AAS measurements, the AAS spectrometer Perkin-Elmer 3110 was employed.

3. Results and Discussion
LA of a Ag target in ultrapure water was performed with nanosecond laser pulses of 355 nm wavelength with fluences within the range 0 - 15.5 mJ/mm² and 30 min. ablation time, of 532 nm with 0 - 21 mJ/mm² fluences and 20 min. ablation time, and of 1064 nm with 0 - 27.5 mJ/mm² fluences and 5, 10 and 20 min. ablation time, respectively. The Ag content and the SPE band area of samples of the resulting Ag nanoparticle hydrosols were determined and mutually correlated (Figure 1). A fairly good linear correlation between the results yielded by these two diverse methods of LA efficiency evaluation has been observed. Furthermore, when the amount of Ag and the SPE band area, respectively, are plotted as a function of fluence for a particular set of Ag hydrosol samples (obtained by LA at the same wavelength and for the same time period), such as those obtained by 10 min. of LA at 1064 nm (Figure 2A and 2B, respectively), a fairly good match of the resulting sigmoidally shaped plots was observed. The two methods tested thus provide comparable results in evaluation of LA efficiency.

Sigmoidal plots of LA efficiency as a function of increasing fluence were obtained for LA with all three wavelengths of laser pulses, as demonstrated in Figure 3. Sigmoidal shapes of the plots indicate that there is a certain value of fluence required for initiation of the LA process, however, its exact determination is limited by the sensitivity of AAS as well as SPE measurements at extremely low concentrations. Above this fluence threshold, efficiency of LA increases up to the saturation value (Figure 3). Comparison of the maximal values of amount of Ag produced by LA with the 355, 532 and/or 1064 nm pulses (i.e. those determined at saturation) (Table 1) indicates that the efficiency of LA with 1064 nm largely exceeds that of LA with 355 and 532 nm pulses. In particular, the maximum amount of Ag ablated by 1064 nm pulses in 20 min. time is 6.5x higher than that obtained by the same time of LA with the 532 nm pulses, and 6.5x higher than that ablated with 355 nm pulses during a 1.5 times longer ablation time (Table 1). At least two factors can contribute to the very high efficiency of LA with 1064 nm pulses. At this wavelength, the value of the absorption coefficient \( k \) of bulk
Table 1. Total amount of ablated Ag per unit area impacted by laser pulses at saturation fluences for LA performed with pulses of 1064 nm (20 min.), 532 nm (20 min.) and 355 nm (30 min.) wavelength

| Ablation wavelength | Ablated Ag (μg/mm²) |
|---------------------|---------------------|
| 1064 nm             | 230                 |
| 532 nm              | 34                  |
| 355 nm              | 33                  |
silver is about 2x higher than at 532 nm and about 6x higher than at 355 nm. In addition to that, absorption of laser pulses by the resulting Ag hydrosol is substantially lower at 1064 nm than at the other two wavelengths, which manifests itself by a substantially less efficient fragmentation of Ag nanoparticles in the course of the ablation/fragmentation process, and, consequently, by a larger polydispersity of the resulting Ag hydrosol. This polydispersity is responsible for broadening of the SPE band of the 1064 nm-ablated Ag hydrosol, and its extension towards longer wavelengths, in comparison to the substantially more narrow and symmetric SPE bands of the hydrosols ablated with 532 and 355 nm pulses (Figure 4).

4. Conclusions
Efficiency of LA can be quantified both by the amount of Ag transferred from the Ag target into the liquid ambient as determined by AAS and by the area of the SPE band of the resulting Ag nanoparticle hydrosol. Advantages of the latter method are its speed and simplicity, together with the possibility to perform the SPE measurements directly in situ, as demonstrated e.g. in ref. [5].

The efficiency of LA with 355 nm, 532 nm as well as 1064 nm laser pulses increases sigmoidally with the increasing laser fluence. Nevertheless, the maximum amount of ablated Ag is substantially (at least 6.5 x) higher for LA with 1064 nm pulses than that obtained by LA with 355 nm and 532 nm laser pulses.

Laser ablation with 1064 nm pulses and the value of fluence corresponding to the saturation value is proposed as a fast and efficient way of production of highly concentrated Ag nanoparticle hydrosols. Concentration of Ag in the resulting hydrosol can be varied by both the value of laser fluence (up to saturation) and by ablation time. At laser pulse energies providing fluences exceeding the saturation value, efficiency of LA can be increased only by increasing of the laser beam-impacted area via defocusation of the laser beam. The resulting Ag hydrosol displays a considerable polydispersity, which, however, has been found to be advantageous for certain types of applications, namely SERS (surface-enhanced Raman scattering) spectral measurements [4]. For applications requiring monodisperse sols, such as nanoparticle assembling [6], polydispersity of the sol can be reduced by a subsequent Ag nanoparticle fragmentation using 532 nm and/or 355 nm laser pulses, as has been demonstrated in [3,4,5].

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