Influences on Nanoparticle Production during Pulsed Laser Ablation

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The generation of nanoparticles using pulsed laser ablation has inherent advantages compared to conventional methods, like the purity and stability of the fabricated nanoparticle aerosols and colloids. This study addresses the influence of the pulse energy on the nanoparticle productivity and particle size during femtosecond laser fabrication of nanoparticles in air and liquids (water, hexane). Moreover, in-situ conjugation of nanoparticles in hexane is studied.

The nanoparticle generation rate is 100 times higher in air compared to water. Higher pulse energies lead to higher productivity, but due to shielding effects, the optimum was determined at moderate pulse energies around 200 μJ, measured by the highest absorption intensity of the plasmon resonance of the colloids. In non-polar liquid, the in-situ conjugation of gold nanoparticles to thiol molecules during pulsed laser ablation is studied. At higher concentrations (8 mmol/l) of dodecanethiol in n-hexane solution, significant smaller nanoparticles (30 nm) and less agglomerates are generated.

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1. Introduction

Conventional nanoparticle generation routes such as mechanical milling and grinding, or chemical generation methods like the sol-gel process show drawbacks related to the purity and variety of accessible materials. The use of precursor is often required during the production process so that purification steps to remove the chemical by-products have to be carried out (which are quite complicated in colloids with reactive metal nanoparticles). Gas phase processes give powders, which are often hardly re-disperable into liquids or almost impossible grindable down to the primary particles. Different nanoparticulate materials are already used for a variety of applications such as bioimaging, antiseptic metal ion release, cancer treatment, UV-protection, photo-catalytic effects, scratch-resistance and corrosion protection [1]. But the availability of nanoparticles with high purity is still lacking in particular for biomedical applications [2, 3].

Pulsed laser ablation is an alternative method addressing the deficits of the conventional methods offering the access to an unlimited nanomaterial spectrum, since the nanoparticles may be generated from almost any solid material [4,5,6]. Advantages of this method are the high purity of the nanomaterial, the material variety, and the in-situ dispersion of the nanoparticles in a variety of liquids allowing safe and stable handling of the colloids. However, there is still a lack of data on the influences on the size of the generated nanoparticles and the productivity of the fabrication process. Moreover, adding conjugative organic molecules to the liquid where the ablation is carried out may add value to the colloid if the nanoparticles are selectively coated by functional molecules. These molecules may act as spacer for subsequent conjugations of biomolecules like antigens or RNA.

In this study, the influences of the laser pulse energy and the media (air, water) on the particle size distribution and productivity are investigated. At the example of the organic spacer molecule dodecanethiol, results on the in-situ stabilisation and conjugation of nanoparticles during femtosecond laser ablation in liquid are presented.

2. Experimental

The generation of nanoparticles was carried out using mainly a commercial femtosecond (fs) laser system (Spitfire PRO, Spectra Physics), delivering 120-fs laser pulses at 800 nm. The maximum pulse energy is 1 mJ at a repetition rate of 1 kHz. A four-stage positioning unit for laser micromachining by 3D-Micromac was used. For the ablation of steel, a different laser (Femtopower Compact Pro, Femtolasers) with shorter pulse length (26 fs) was used.

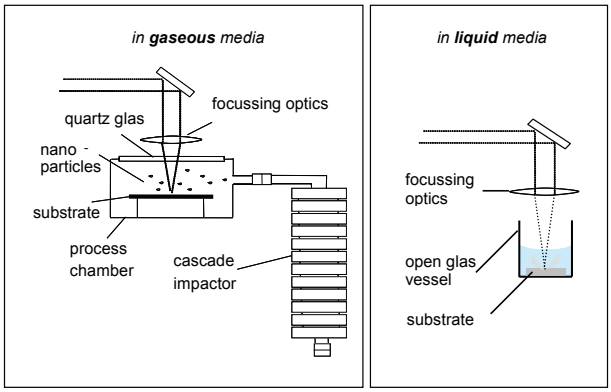

Figure 1. Experimental set-up of pulsed laser ablation in gaseous media (left) and liquid media (right)

The set-up for the experiments carried out in gaseous and liquid media is shown in Fig. 1. Both investigations follow

the same principle. The laser beam is guided through a focussing lens on the surface of the solid material. Laser ablation in gaseous ambience is carried out in a process chamber. The particles are sucked directly after their generation into an electrical low pressure impactor (ELPI, Dekati). The device contains 12 stages and operates in the size of 0.007 to 4 µm. The particles are size-classified by impaction on the respective stage. Here, the number of particles of one aerodynamic equivalent diameter range is counted. The frequency was 1 kHz and the volume flow 10 lpm. The pressure on the lowest stage was 100 mbar. More details on the setup are reported elsewhere [7]. Experiments carried out using liquid were manly carried out in a glass vessel with a diameter of 28 mm.
The investigation on the in-situ stabilisation was carried out in n-hexane as solvent at different concentrations of dodecanethiol. The absorption spectra were measured using UV-VIS-spectrometry. The hydrodynamic diameter of the colloidal nanoparticles have been measured using laser light scattering nanoparticle image velocimetry (Nanosight Halo LM10).

3. Results

3.1 Nanoparticle generation in gaseous media

During ultrashort pulsed laser micromachining, the emission of aerosols containing nanoparticles cannot be avoided [8]. Despite this unintended generation of ultrafine aerosols, the ablation of a target in gaseous flow gives access to airborne nanoparticles that can be collected and analyzed by an online-coulomb cascade impactor.

In Fig. 2, the influence of the pulse energy on the particle size distribution of titanium and silver is shown. A tenfold increase of the pulse energy from 50 µJ to 500 µJ does not significantly change the size distribution of titanium nanoparticles. Whereas, in the case of silver nanoparticle generation, the increase of the pulse energy causes a shift of the size distribution maximum from 100 nm to 60 nm.

During fs-laser micromachining of steel, a similar shift to smaller sizes was observed at higher pulse energy (and shorter laser pulses of 26 fs) shown in Fig. 3. The pulse energy affects the size distribution of metal nanoparticles generated during femtosecond laser ablation, but this influence is material dependent. We observe the trend that the pulse energy has a stronger effect on materials with a higher reflectivity. However, higher pulse energies might enhance the temperature gradient in the material. A higher temperature gradient results in an higher cooling rate. Former studies found out that higher cooling rates causes smaller particles [9].

In general, for the studied materials, the highest amount of particles are generated using high pulse energy. This tendency is opposite to that observed during fs laser ablation a liquid instead of gas. Results on femtosecond laser ablation in water are characterized by a linear log-normal correlation of the nanoparticle size with the laser fluence [10].

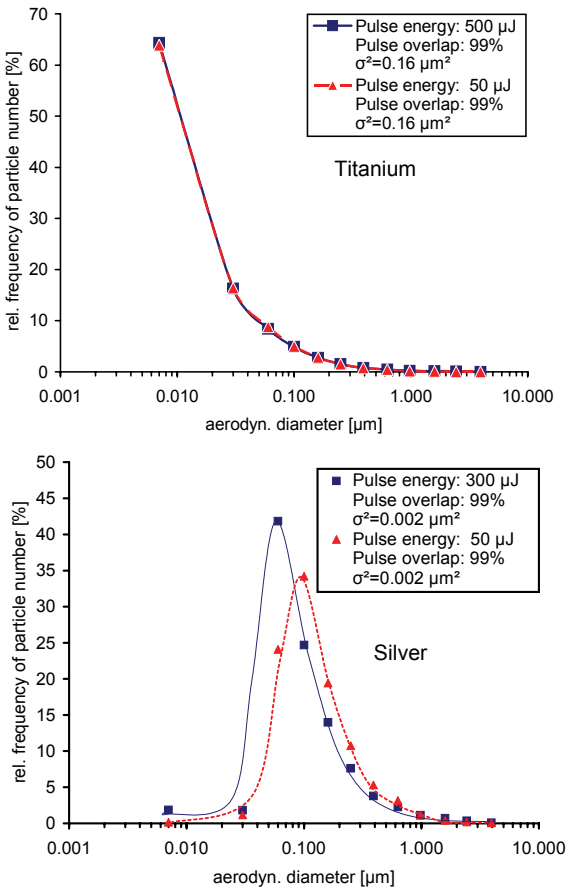

Figure 2. Influence of the pulse energy on the particle size distribution during fs laser ablation of titanium (top) and silver (bottom)

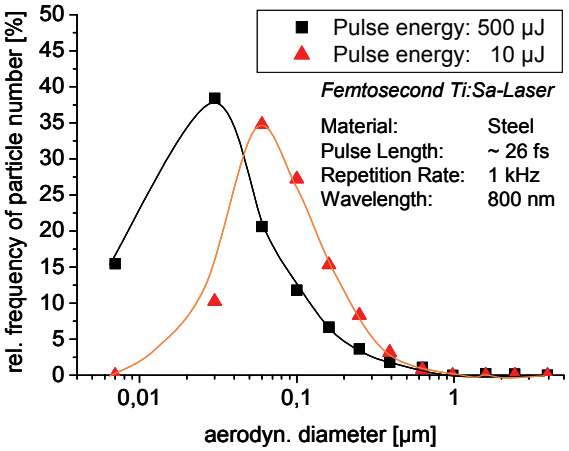

Figure 3. Influence of the pulse energy (500 µJ, $\sigma^2 = 0.01$ µm² /10 µJ, $\sigma^2 = 0.003$ µm²) on the particle size distribution during femtosecond laser ablation of Steel

3.2 Nanoparticle generation in liquid media

If the ablation rate is investigated, another important difference during fs-laser generation of nanoparticles is caused by the media. The ablation mass rates of silver and cobalt in air and water at different pulse energies are shown in Fig. 4.

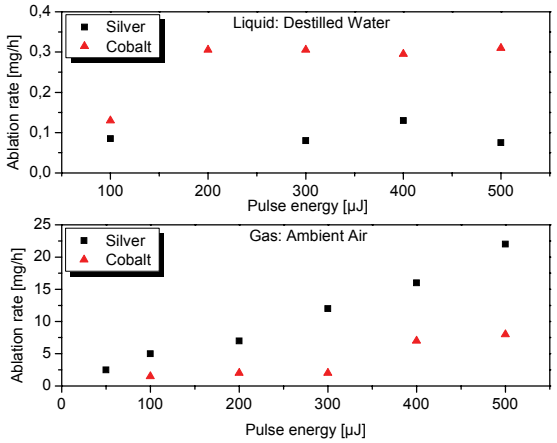

Figure 4. Ablation rates of materials in (a) gaseous and (b) liquid media

In general, the ablation in water appeared to be at least 50-times less mass-efficient. The ablation rate in gas atmosphere increases proportionally to the pulse energy, but the ablation mass rate in water reaches a maximum level at a pulse energy of around 200 µJ. The differences in the tendency may be explained by the energy losses which occur during the ablation process in water. These losses are caused by the generation of bubbles due to the evaporation of the liquid which has been observed during the ablation process. Furthermore, the nanoparticles which stay in the liquid may absorb subsequent laser pulses. Nonlinear effects cause the generation of white light and filamentation of the ultrashort pulsed laser beam in the liquid, which also contribute to energy losses. These three factors lead to an overall lower productivity and shielding phenomena at higher pulse energies.

After only a short time (typically 30 seconds) the ablation process is accompanied by an intensive coloration of the liquid during the production of metal nanoparticles. In particular, the solution becomes red in the case of gold nanoparticles and yellow in the case of silver as ablated target. This coloration is attributed to the plasmon resonance wavelength of the respective metal nanoparticles. The intensity of the absorption peak correlates with the number concentration of the nanoparticles. [11, 12].

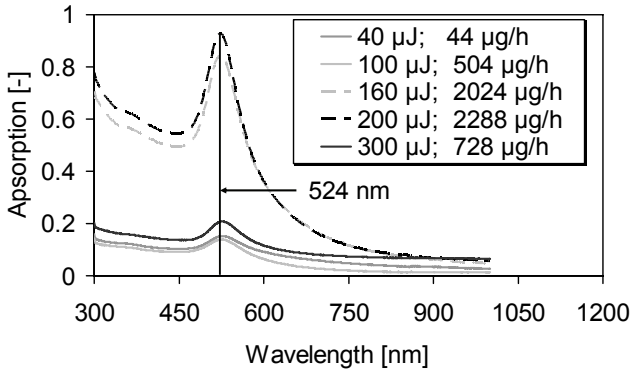

Figure 5. Influence of the pulse energy on the productivity of gold nanoparticles generated by femtosecond laser ablation and optical characteristics (plasmon resonance) of the colloid

Figure 5 shows the absorption peaks (524 nm) of the gold nanoparticles fabricated at different pulse energies. This value correlates with absorption peaks found in literature [11,12,13]. It is remarkable that the peaks with the highest intensity are achieved at moderate pulse energies in the range of 160 to 200 µJ. This result is accompanied with the mass ablation rates which are highest at the same pulse energies. If the pulse energy is further increased, the productivity and the plasmon resonance peak intensity drastically decreases.

The corresponding results on the dependence of the gold nanoparticle absorption peak height from the pulse energy is shown in Fig. 6. Moderate pulse energies results in the highest concentration of nanoparticles and an 80% increase of the absorption is achieved using a pulse energy of around 200 µJ.

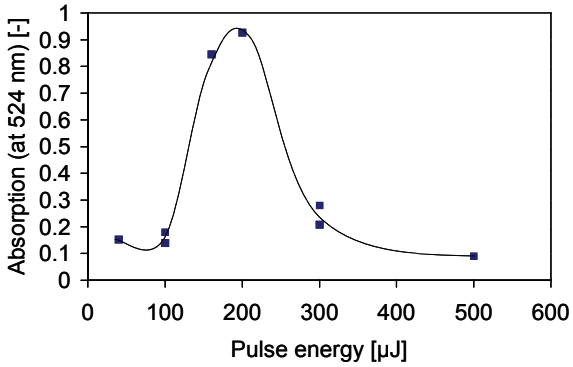

Figure 6. Influence of the pulse energy on the peak height of the optical characteristic of gold nanoparticles

These results correlate with those from the mass rate comparison for silver and copper. This emphasises the presence of effects which directly influence the gold nanoparticle generation in water and which leads to a loss of energy at higher pulse energies. An effective tool to minimize of these losses can be the realization of a continuous liquid flow, which removes the bubbles and nanoparticles directly after their generation [14]. In stationary liquid, moderate pulse energies should be applied for highest nanoparticle productivity.

3.3 In situ coating

One of the main advantages of the ablation process carried out in liquids is the possibility of an in-situ stabilization of nanoparticles by their conjugation to organic molecules. Since the thiol group has a high affinity to gold, an effect on the gold nanoparticle size and stability is expected. These effects are studied at the example of dodecanethiol added to n-hexane before fs laser ablation.

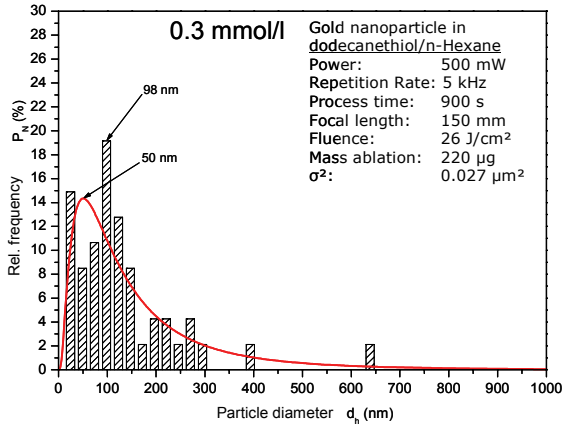

Figure 7. Particle size distribution of gold nanoparticles generated in n-hexan with 0.3 mmol/l dodecanethiol

Like ablation of gold in pure n-hexane, the laser ablation of gold in n-hexane with 0.3 mmol/l dodecanethiol gives a relatively broad particle size distribution (Fig. 7). An increase of the concentration of dodecanethiol up to threshold of 8 mmol/l results in a particle distribution which is remarkably more narrow (Fig. 8).

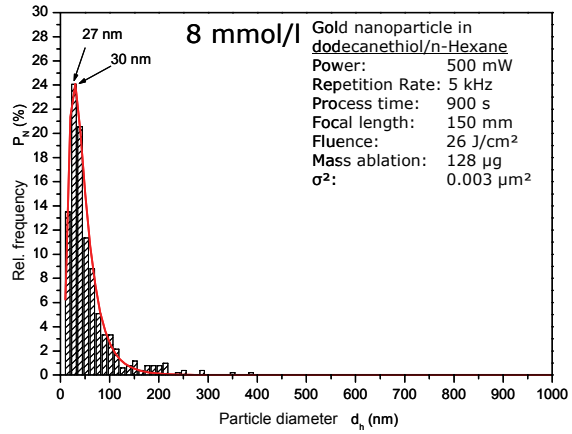

Figure 8. Particle size distribution of gold nanoparticles generated in n-hexan with 8 mmol/l dodecanethiol

A further increase of the concentration does not significantly affect the size distribution. This lets assume that dodecanethiol quenches the nanoparticle growth. Furthermore, we observed that dodecanethiol stabilizes the gold nanoparticles (which are in water stabilized by surface charge [14]) against agglomeration in non-polar liquid.

A closer look and more detailed investigation was carried out with respect to the optical characteristic of gold nanoparticles and the influence of the pulse energy on the required amount of thiol. The wavelength and intensity of the absorption peak maximum of the gold nanoparticles depend on the concentration of dodecanethiol. Both diagrams in Fig. 9 show that the intensity of absorption of gold nanoparticles is higher at higher concentrations of dodecanethiol in n-hexane. In the case of laser generated gold nanoparticles, a blue color of the colloid (corresponding to red-shift of the absorption spectrum) generally indicate the presence of agglomerates. The shift of this maximum towards smaller wavelength with increased thiol concentration indicates the change in the size distribution of the gold nanoparticles. At higher thiol concentration, less agglomerates and smaller particles are formed.

But the amount of dodecanethiol required for stabilisation depends on the pulse energy applied during fs laser ablation in hexane. The minimum thiol concentration at which the absorption peak maximum can be stabilized is higher at higher pulse energy. At lower pulse energy a concentration of 3 mmol/l is enough to conjugate the gold nanoparticles present in the liquid to the thiol. Whereas at higher pulse energy (300 µJ), the required thiol concentration is higher (6 mmol/l). This may be mainly due to the higher productivity at higher pulse energies during fs laser ablation in hexane. Of course, the required concentration of the stabilizing agent has to correlate with the concentration of the fabricated nanoparticles.

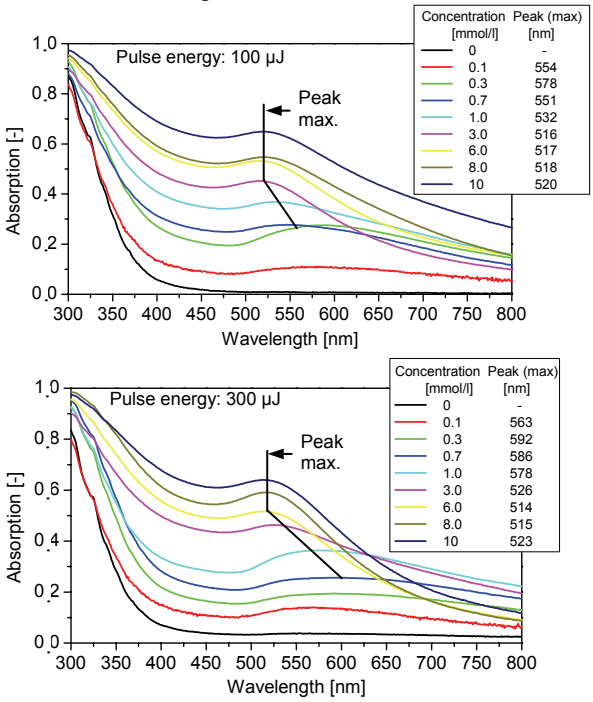

Figure 9. Optical characteristic of gold nanoparticles in different concentrations of dodecanthiol added to n-hexane prior to fs laser ablation at (a) 100 µJ and (b) 300µJ pulse energy

4. Summary and Conclusion

Pulsed laser ablation in gas and liquids is a tool for the fabrication of ultrapure nanomaterials, even if data on the influences of the laser parameters and the media on the particle productivity, size and stability are still lacking.

The influence of pulse energy on the size distribution of airborne nanoparticles generated during fs laser micromachining of silver, titanium and steel depends on the ma-

terial. This is confirmed by former results during fs-laser ablation of graphite [15]. For all investigated materials, smaller sizes are generated at higher pulse energies, but this size shift moderates for materials with lower reflectivity.

The nanoparticle generation mass rate in air (aerosol) compared to the nanoparticle generation in water (colloid) is up to 100 times higher. During the fs-pulsed laser ablation in a vessel with stationary liquid media, disturbing effects like bubbles and filamentation are observed which cause energy losses. This results in an asymptotic production rate progression at pulse energies higher than 200 μJ.

The high stability of metal nanoparticles generated during laser ablation in de-ionised water is reported to be related to the surface charge of the particles causing a zeta-potential and electrostatic repulsion of the particles. But if nanoparticles are fabricated in non-polar liquid like hexane, more care has to be taken to avoid agglomeration of the particles. The in-situ conjugation of gold nanoparticles to an organic compound with thiol group results in the stabilization of the colloid, as demonstrated during fs laser ablation in hexane with dissolved 3-8 mmol dodecanethiol. This novel approach for in-situ conjugation of nanoparticles implies two advantages. First, less agglomerates and smaller particles are formed. Second, this route is the first step to achieve bio-conjugated nanoparticles. If thiol spacers with carboxylic or NH_2–group are used for in situ conjugation during laser ablation, subsequent coupling of antigens can easily be achieved.

In future, this method can be used for the rapid generation of ultrapure bio-conjugated metal nanoparticles for drug targeting, drug delivery and bio-response studies.

5. Acknowledgments and Appendixes

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