

Organic Nanoparticles Generated by Combination of Laser Fragmentation and Ultrasonication in Liquid

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Melaminocyanurate microcrystals suspended in water were converted into colloidal nanoparticles by a novel approach of ultrasound-assisted laser fragmentation in a free liquid jet. A crucial step within the laser-based synthesis is the sufficient stabilization of nascent nanoparticles with an adequate stabilization agent. Electron microscopy of stabilized and unstabilized nanoparticle colloids revealed that insufficiently stabilized colloids contain a huge fraction of agglomerates consisting of nanoparticles adsorbed on microparticles. Those agglomerates could be destroyed by ultrasound sonication. Therefore, an implementation of ultrasonication into the laser fragmentation process enhances efficiency which was quantified by absorption spectra. By using a high-power nanosecond laser we demonstrated that the technique of laser-fragmentation in free liquid jet could be suitable for scale-up because nanoparticle properties like hydrodynamic size or zeta potential did not depend on laser power or process time and laser-fabricated nanoparticle yield continuously increases during process duration.

Keywords: Laser ablation of microcrystals, ultrasonication, nanocrystals, flame retardant, scale-up,

1. Introduction

The fascinating idea behind the synthesis of colloidal organic nanoparticles is the combination of unique nanoparticle properties with the enormous opportunities of classical organic synthesis. A current topic in this field of research is the enhancing of water-solubility of pharmaceutical relevant agents to raise bioavailability [1]. Further, organic nanoparticles can be used as biosensors, optical devices, inks, cosmetics or even fire retardants. In future, broad application in all fields of chemistry, material science and medicine will be imaginable.

Nevertheless, most conventional synthesis methods like precipitation [2], milling [3] or homogenization [4] are limited by diverse factors like process impurities (by co-solvent or grinding bodies) or the choice of feasible solvents, minimum achievable particle size and process time. Because of the demand of a more versatile and simple method to generate organic nanoparticle colloids, Asahi et al. showed that laser-fragmentation of microparticles in liquid could be an alternative route [5-7]. Exposing microparticles to intense laser pulses leads to absorption and subsequent fragmentation into nanoparticles [8,9]. The mechanism of this process and its dependency on pulse duration was studied by Zhigilei et al. using classical molecular dynamics (MD) calculations [10]. In general, ultrashort pulses induce a pressure buildup and the focusing of the pressure wave within the irradiated particle leads to low ablation thresholds. Laser pulses in the regime of nanoseconds leads to explosive thermal decomposition due to overheating.

Although laser fragmentation of microcrystals in liquids is a very energy-efficient process, most experimental studies report a low productivity [5-7, 11]. There are sev-

eral limiting factors which lower productivity like losses of excitation light by opaque microparticle suspensions or limitation of pulse energy by damage threshold of optical components. To avoid those limitations we introduced a novel technique based on laser ablation of microcrystals in a free liquid jet [12]. For that purpose, a thin liquid filament ($d_{fil} < 1$ mm) is generated via a fine nozzle and irradiated by focused laser beam. This set-up provides a short optical path length within the suspension minimizing excitation light losses by scattering or absorption. Furthermore, no additional optical components like windows are needed which allows very tight focusing without the danger of damaging those components.

Laser-fragmentation of melamine cyanurate as a model compound for organic microparticles showed that the resulting nanoparticles have to be stabilized, otherwise they strongly tend to agglomerate with other nanoparticles or residual microparticles [12]. At low concentration of stabilization agent, laser fragmentation leads to micrometer-sized particles that precipitate as voluminous flocculent precipitate. In that case, the laser-generated nanoparticles are insufficiently stabilized by solvent and strongly tend to adsorb to the residual microparticles. By exceeding a specific threshold of stabilization agent (0.25 wt% for dextrin, 0.01 wt% for polyacrylic acid), laser fragmentation results in stable colloidal nanoparticles with hydrodynamic diameters below 200 nm. In this article, we studied the structure of picosecond laser-generated organic nanoparticles and agglomerates by electron microscopy and how to improve nanoparticle yield by ultrasound-assisted laser fragmentation in a liquid jet. Furthermore, for scale-up purposes we studied the application of a nanosecond high-power laser with an output power up to 450 W.

1. Experimental Section

Details of the experimental set-up can be found elsewhere [12]. In brief, we generate a fine liquid jet by a solid jet nozzle (Lechler 544.320, $d_{\text{nozzle}} = 0.8$ mm). Laser fragmentation is done by focusing the laser beam into the liquid filament through a lens (best-form shape, $f = 40$ mm, anti-reflective coating). Two different laser system were used: A picosecond laser (Trumpf TruMicro 5250, 515 nm wavelength, pulse width 7 ps, pulse energy 125 μJ , repetition rate up to 200 kHz) and a high-power nanosecond laser system to up-scale the process (Coherent Mamba-IR, 1064 nm wavelength, pulse width 60 ns, pulse energy up to 90 mJ, repetition rate 5 kHz). The irradiated suspension was caught by a small funnel, redirected into a reservoir and cycled by a geared pump; the resulting flow (350 ml min^{-1}) is strong enough to prevent sedimentation of the suspended microparticles in the reservoir. For all experiments an amount of 0.5104 g melamine cyanurate was suspended in 100 ml deionized water (20 mmol l^{-1} , approx. mass fraction 0.5 wt%) and dedicated amount of stabilization agents (dextrin (from potatoe starch) and polyacrylic acid) was added. After irradiation for a designated time interval, the residual suspension was worked up by ultracentrifugation (10 min @ 1,845 RCF, Hettich Universal 320). Ultrasonication of selected samples was done by an ultrasound homogenizator (Hielscher UP400S, incoupled power 40 W) for 5 minutes. Analysis of the resulting colloids was done by UV/VIS spectroscopy (Shimadzu UV-1650PC), dynamic light scattering (Malvern Zetasizer) and electron microscopy which was done by Sachtleben Chemie GmbH.

2. Results and Discussion

2.1 Picosecond Laser Fragmentation in Suspension: Controlling Agglomeration by Stabilization Agent Concentration

Laser fragmentation of melamine cyanurate using the picosecond laser system and dextrin as stabilization agent in various concentrations resulted in nanoparticle colloids with different agglomeration status as reported before [12]. To gain further information, we performed transmission electron microscopy (TEM) of those samples which reveals some interesting details on nanoparticle agglomerates and stabilization mechanism. Figure 1 shows TEM-images of laser-processed samples with different concentration of stabilization agent. Without stabilization agent all produced nanoparticles adsorb to residual microparticles (microcrystalline needles of about 5 μm length) and form agglomerates. This also might be an artefact resulting from the drying process during sample preparation. Nevertheless, all insufficient stabilized samples result in a flocculent precipitate [12] which hydrodynamic diameter is even bigger than the hydrodynamic diameter of the educt. This gives evidence that the agglomeration process takes part already within the nanoparticle colloid. By increasing the stabilization agent concentration, the laser-generated nanoparticles get more and more stabilized resulting in lower tendency to adsorb to microparticles and agglomerates are found significantly less frequently. At concentrations > 0.25 wt% dextrin, stabilized nanoparticles are fabricated which are not in contact with microparticles. Residual microparticles can be found at any dextrin concentration (not shown in

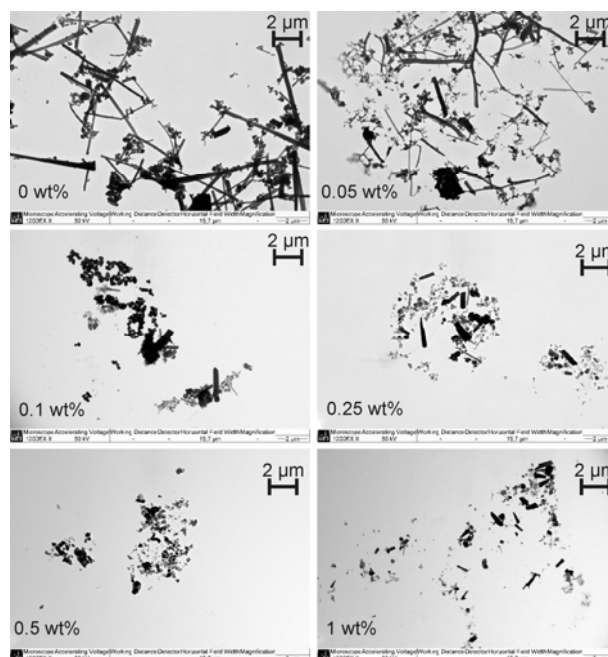


Fig. 1 TEM-images of laser-processed melamine cyanurate at different concentrations of dextrin as stabilization agent (laser-irradiated for 30 min with picosecond laser system)

every electron micrograph in Figure 1) which indicates that fragmentation efficiency does not depend on stabilization agent concentration. Thus, the productivity of nanoparticles is not limited by the fragmentation process but by subsequent agglomeration which results in micrometer-sized agglomerates. Consequently, the crucial step to fabricate laser-fragmented nanoparticles is to stabilize nascent particles.

2.2 De-Agglomeration by Ultrasonication

The tendency of nanoparticles to agglomerate with microparticles reduces the yield of laser fragmentation. Even by adding a stabilization agent, a certain amount of nanoparticles will adsorb to microparticles and lower the productivity. Primarily, the adsorption process is dominated by physisorption of nanoparticles onto microparticles. Regarding Figure 1, no sintered particles can be seen. This indicates that nano-microparticle interactions are dominated by relatively small adhesion forces. Because of this, the agglomeration process should be reversible. Consequently, we tried to de-agglomerate nanoparticles adsorbed to unprocessed microparticles by ultrasound. For that purpose, we laser-fragmented suspensions with two different concentrations of stabilization agent (0.25 and 0.5 wt% dextrin) using the picosecond laser and ultrasonicated these samples for 5 minutes after laser-processing. Figure 2 shows the UV/VIS absorption spectra of ultrasonicated and unsonicated melamine cyanurate suspended in water after ultracentrifugation. It can be seen that ultrasonication strongly enhances the absorption peak of melamine cyanurate at 205 nm. The used stabilization agent dextrin does not exhibit any significant absorption at a wavelength higher than 200 nm, so all observed absorption bands in Figure 2 can be exclusively assigned to melamine cyanurate nanoparticles. Further, the absorption band is significantly broadened after ultrasonication because of

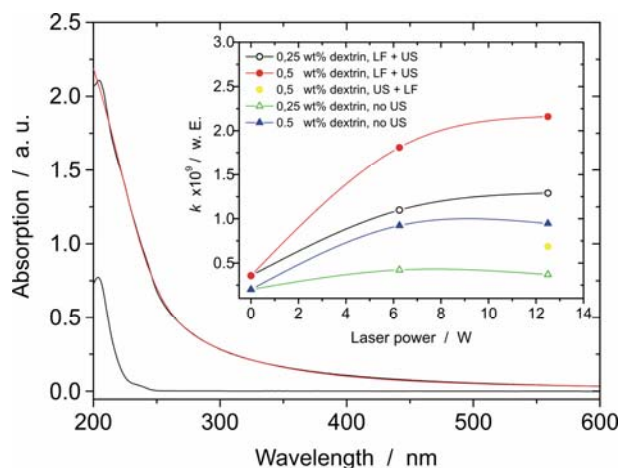


Fig. 2 UV/VIS spectra of melamine cyanurate solved in water (black line); after picosecond laser fragmentation (30 min.) and subsequent ultrasonication (black line: exp. data, red line: fit due to eq. 1).

Inserted Figure: k -factors depending on laser power, stabilization agent concentration, laser-fragmentation (LF) and ultrasonication (US).

enhanced Rayleigh-scattering due to higher nanoparticle concentration.

For a quantitative analysis, we fitted the measured absorption spectra by a model function. This model function (see equation 1) is constructed of two different functions: A Gaussian function representing the absorption band of melamine cyanurate centred at 205 nm and a function that represents the Rayleigh-scattering which is inversely proportional to the fourth power of the wavelength [13]:

$$f(\lambda) = y_0 + \frac{A}{w\sqrt{\pi/2}} \exp\left(-2\left(\frac{x-x_c}{w}\right)^2\right) + k \cdot \lambda^{-4} \quad (1)$$

As can be seen in Figure 2 the model function (red line) coincides quite well with the experimental data. Furthermore, in equation 1, the proportionality factor k is a measure for the total number of scattering particles and can be used to quantify the produced nanoparticles. Figure 2 (inserted figure) shows this coefficient k in dependency on laser power, ultrasonication and stabilization agent concentration. It can be seen that ultrasonicated samples show a significantly higher k which is equal to higher nanoparticle concentration. This indicates that ultrasonication can destroy agglomerates and produce non-agglomerated nanoparticles. As expected, this process is more efficient at higher concentration of stabilization agent.

The reverse process, i. e. ultrasonication and subsequent laser-fragmentation did not enhance the nanoparticle productivity significantly (see Figure 2, yellow point). That indicates that the incoupled energy of ultrasound is not high enough to fragmentize the microcrystalline educt.

2.3 High-Power Nanosecond Laser Fragmentation

The use of picosecond laser pulses to fragment microparticles in free liquid jet is advantageous because it prevents raised heating and evaporation of the solvent. This is mandatory to ensure a stable liquid jet. If heating of the jet by incoupled laser energy is too high, instantaneous

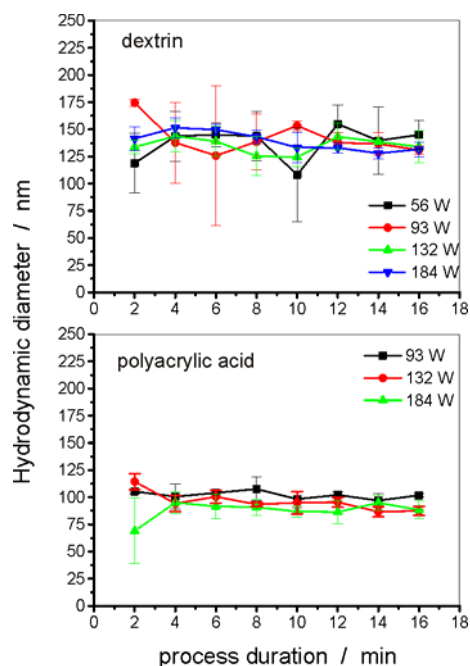


Fig. 3 Hydrodynamic size of nanosecond laser fragmentation-derived melamine cyanurate particles depending on laser power and process duration for different stabilization agent (used mass fraction: 0.25 wt% dextrin or 0.05 wt% polyacrylic acid)

evaporation of the fine liquid jet could occur and end the process. Furthermore, thermal decomposition of the educt might occur. Very recently, Sylvestre et al. investigated the decomposition of megestrol acetate by laser fragmentation in aqueous milieu using femtosecond and nanosecond laser systems [14]. To judge whether the educt is decomposed by laser irradiation we have chosen melamine cyanurate in particular because of its thermolability. Melamine cyanurate is known to decompose at moderate temperature (320 °C) under vigorous release of nitrogen and ammonia gas. Neither in use of picosecond pulses nor the use of more intense nanosecond pulses any considerable gas formation could be observed during irradiation. Furthermore, the UV/VIS and IR spectra before and after picosecond irradiation (not shown here) showed no significant changes. Therefore, we conclude that there is just a minor thermal decomposition especially for the use of picosecond laser pulses.

However, scale-up of pulsed laser ablation in liquid showed that high-power nanosecond pulsed laser systems are quite useful to fabricate nanoparticles in large quantities [15]. Consequently, we used a nanosecond-pulsed laser system with an output power of several hundred watt and pulse energy up to 90 μ J (Coherent Mamba-IR). Laser fragmentation followed the procedure as described in the experimental section, the concentration of stabilization agent was 0.25 wt% for dextrin and 0.05 wt% for polyacrylic acid. The stability of the liquid jet was surprisingly high, even at laser power up to 200 W there was just a minor evaporation. To prevent condensation and contamination of optical components like lenses the resulting vapor was exhausted.

Figure 3 shows the hydrodynamic diameter of produced nanoparticles depending on process time and laser power. It

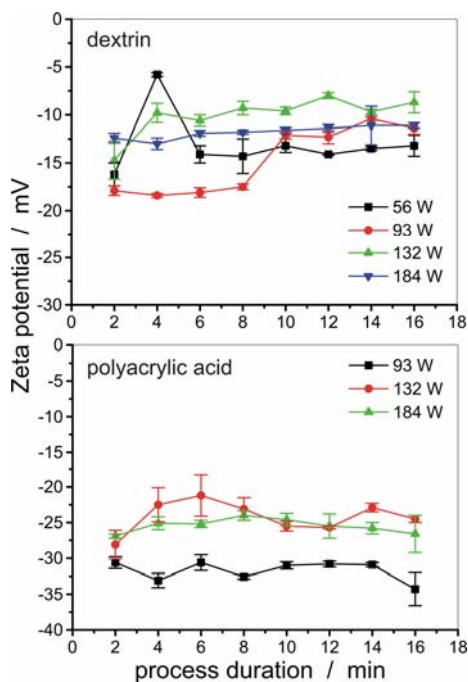


Fig. 4 Zeta potential of nanosecond laser-fragmented melamine cyanurate in dependency to laser power and process duration for different stabilization agents (used mass fraction: 0.25 wt% dextrin or 0.05 wt% polyacrylic acid)

can be clearly seen, that the hydrodynamic size does not change during the irradiation process. This indicates that the incoupled laser power is mainly used to fragment microparticles. The generated nanoparticles interact much less with the focused laser beam so re-irradiation processes do not change the nanoparticle properties or lower the efficiency of the generation process. This is a quite important characteristic for up-scaling. If re-irradiation of laser-generated nanoparticles do not change its properties or lower the efficiency a continuous process is much easier to realize. Furthermore, enhancing the laser-power does not effect the nanoparticle size as well.

Analysis of the zeta potential (see Figure 4) shows quite similar results. The measured zeta potential for all samples is nearly constant within the process duration of 16 minutes. The use of polyacrylic acid as stabilization agent yielded in more electrostatic-stabilized nanoparticles represented by the higher zeta potential (up to -35mV).

Quantification of the laser-generated nanoparticles was done by analysis of UV/VIS spectra. Melamine cyanurate shows an intense absorption band centered at 205 nm. As reported before [12], the peak intensity of this band can be considered as a measure to quantity of colloidal laser-generated nanoparticles. Since the nanoparticles have a hydrodynamic diameter of about 100 nm (see Figure 3) no significant Rayleigh-scattering occurs and the peak intensity of the absorption spectra is a sufficient parameter to estimate the concentration of nanoparticles. Figure 5 shows the dependency of the peak intensity on process duration using different laser power. The increase of absorption during laser processing indicates continuous fabrication of organic nanoparticles with defined particle properties as discussed in section 2.3. By increase of laser power, there

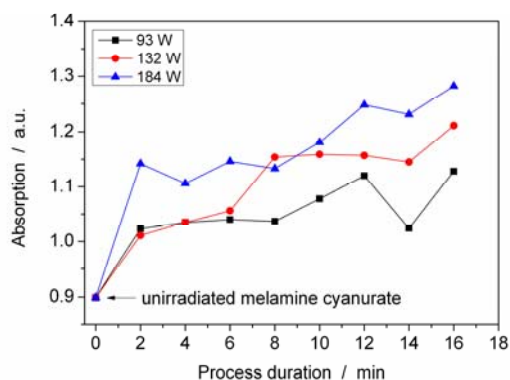


Fig. 5 Peak intensity of optical absorption spectra as a measure of fabricated nanoparticles and its dependency on process duration (polyacrylic acid as stabilizer with used mass fraction of 0.05 wt%)

is just a slight increase in absorption and nanoparticles. Compared to the results of picosecond laser fragmentation [12], the nanoparticle productivity represented by the final peak intensity is comparable. Thus, further investigations are necessary to exploit the whole potential of high-power nanosecond laser systems for laser fragmentation of microparticle suspensions.

3. Conclusions

In general, laser fragmentation of microparticles in a poor solvent is a fast and convenient method to fabricate various organic nanoparticles. This is of special interest for organic nanoparticles which synthesis by conventional methods is often limited. Using a free liquid jet to irradiate a microparticle suspension enables the use of high-power lasers because no optical components like entrance windows limit the maximum pulse intensity. Furthermore, this set-up enables a continuous process not limited by disadvantages of batch processes. During laser-fragmentation of microcrystalline melamine cyanurate in water the resulting nanoparticles have to be stabilized by an adequate stabilization agent, otherwise it agglomerates with the residual microparticles. The adhesion forces between nano- and microparticle within the agglomerates are weak enough to be destroyed by ultrasonication. This ultrasonication significantly enhances the nanoparticle productivity. Because of this, the combination of laser-fragmentation and ultrasonication seems to be a promising way to enhance the efficiency of nanoparticle production.

By use of a high-power nanosecond laser we took the first step towards a further up-scaling. Nanoparticle properties like hydrodynamic size or zeta potential did not depend on laser power or process duration. Prolonged laser fragmentation allows continuous fabrication of nanoparticles indicated by constant increase of nanoparticle-specific absorption.

Acknowledgments

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