

Laser fragmentation of organic microparticles into colloidal nanoparticles in a free liquid jet

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Received: 13 November 2009 / Accepted: 10 May 2010 / Published online: 18 June 2010
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Abstract We present a novel approach for laser fragmentation of melamine cyanurate microcrystals suspended in liquid into colloidal nanoparticles. Laser fragmentation is done by irradiating a liquid jet of melamine cyanurate suspended in water with intense picosecond pulses. The free liquid jet is generated by a nozzle with small diameter and provides a thin liquid filament ($d_{\text{fil}} < 1$ mm) perpendicular to the focused laser beam. This geometry allows tight focusing resulting in high intensities without the danger of damaging an optical element like windows necessary in conventional flow cells or cuvettes. It reduces losses of excitation light by avoiding scattering or absorption in front of the focus. We stabilized the nanoparticles electrosterically in-situ with neutral and polyelectrolytic polymers preventing agglomeration and precipitation. The threshold for sufficient stabilization of laser-fragmented nanoparticles ($d_{\text{hydrodyn}} \approx 200$ nm) is reached at a mass fraction of 0.25 wt% dextrin as a neutral polymer and 0.01 wt% polyacrylic acid as a polyelectrolytic polymer. Hydrodynamic size and zeta-potential of the nanoparticles can be controlled by mass fraction of the stabilization agent.

1 Introduction

Creating colloidal nanocrystals of organic compounds is a promising field of research to design novel substances by combining molecular properties with tailored nanoparticle

characteristics like electronic, optical or solubility properties as a function of particle size. Most research towards organic nanoparticles concentrate on pharmaceutical active substances to enhance water-solubility and bioavailability [1]. Several approaches for the synthesis of organic nanoparticles can be found in literature including precipitation methods [2, 3], milling [4], emulsification [5], expansion of supercritical fluids [6] or homogenization [7, 8]. Unfortunately those methods bear disadvantages like impurities from grinding bodies, chemical precursors or bioincompatible organic solvents. Nanoparticle colloids with high purity can be synthesized by pulsed laser ablation in liquids (PLAL) which is a versatile and simple method applicable to various metals, ceramics or semiconductors [9–11]. However most organic compounds are available as microcrystalline powders instead of solid targets suitable for PLAL. For this purpose Keto et al. [12, 13] showed that laser ablation of microcrystals (LAM) in an aerosol flow is an efficient and universal applicable method for generating nanoparticles in the gas phase. Tamaki et al. [14–16] adopted the LAM-process for the use in liquid media, they irradiated an aqueous suspension of phthalocyanine compounds with intense laser irradiation and generated organic nanoparticles. Schnoor et al. [17] demonstrated laser fragmentation of organic and inorganic microparticles in a counter-current flow through a capillary. An adverse effect of the capillary is the limited throughput and nanoparticle productivity because of limited volume flow. A general drawback of these methods is the limitation of pulse energy by use of optical components like windows or flow cuvettes and the high loss of excitation light by scattering or absorption in case of an opaque suspension.

In this article we report on a novel approach of laser fragmentation of an opaque suspension of organic microcrystals by using a high-throughput liquid jet. The thin liquid

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filament ($d_{fil} < 1$ mm) 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. The use of picosecond pulses prevent increased heating and evaporation of the solvent. For our studies we chose melamine cyanurate as a model compound for a poor water-soluble organic substance with high application potential in nanotechnology (e.g. as a fire retardant).

2 Experimental details

The general set-up of the experiment is shown in Fig. 1. The liquid jet is generated by a solid jet nozzle (Lechler 544.320, $d_{nozzle} = 0.8$ mm). The resulting liquid filament is caught by a small funnel before it splits into droplets and is redirected to the reservoir. The suspension is 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 potato starch) and polyacrylic acid was added. For laser irradiation we used a commercial picosecond laser system (Trumpf TruMicro 5250) providing 7 ps pulses with a pulse energy of $125 \mu\text{J}$ at a wavelength of 515 nm. The used repetition rate was 50 kHz. The laser beam was focused by a lens ($f = 40$ mm, best-form shape, anti-reflective coating) into the liquid jet. The experimental parameters used for this study (pulse energy, repetition rate) were determined by highest ablation efficiency (mostly determined by pulse energy [9, 11]) and stability of the liquid jet which will be vaporized at higher laser repetition rates. Fine adjustment of the jet and focusing lens was done by manually controlled micrometer stages. After irradiation for 30 min the residual microparticles were separated by ultracentrifugation (10 min @ 5000 rpm, Hettich Universal 320) and the nanoparticles containing supernatant was used for further analysis by UV/VIS spectroscopy (Shimadzu UV-1650PC), dynamic light scattering (Malvern Zetasizer) and STEM-analysis (Fei Quanta 400 FEG).

3 Results and discussion

Laser ablation of microcrystals is initiated by a focused laser pulse which generates a plasma and a subsequent shock wave within the microparticles. This causes particle breakdown (fragmentation and vaporization) followed by nanoparticle condensation behind the shock wave [12, 13].

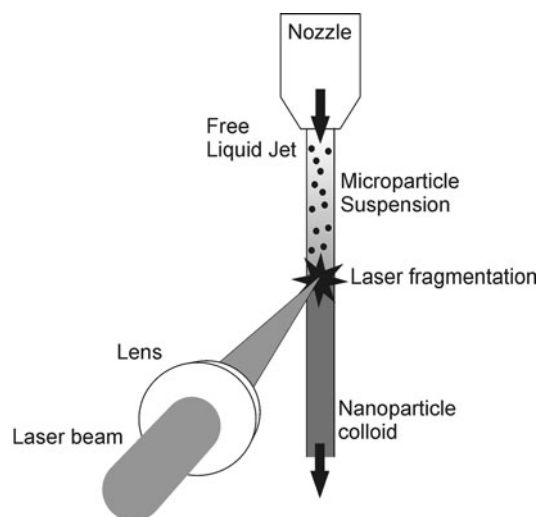


Fig. 1 Schematic view of the experimental set-up of laser fragmentation in liquid flow

Unfortunately, if the stabilization by the solvent is insufficient, the resulting nanoparticles strongly tend to agglomerate with other nanoparticles or residual microparticles. The necessary stabilization of colloidal nanoparticles can be achieved by added stabilization agents, which result in a steric stabilization by forming a protective layer around the nanoparticles [9, 11]. Hence, choosing an appropriate stabilization agent is the essential step towards stable organic nanoparticles.

To compare the raw material and the generated nanoparticles of melamine cyanurate STEM-images of the unirradiated educt and the laser-fragmented suspension are shown in Fig. 2. The educt consists of microcrystalline needles in range of several micrometer lengths (typical length 2–6 μm , Fig. 2a). After irradiation, we can observe spherical nanoparticles with a diameter less than 100 nm (Fig. 2b).

Figure 3 shows UV/VIS absorption spectra of unirradiated and irradiated melamine cyanurate in aqueous solution after centrifugation at different mass fractions of dextrin as a neutral, polymeric stabilization agent. As can be seen, the intensity of the main absorption peak of melamine cyanurate at 205 nm rises after irradiation, indicating that fragmentation of the microcrystalline educt enhances the solubility of the unpolar material in water. Dextrin does not exhibit any significant absorption at a wavelength higher than 200 nm, so the observed absorption band can be assigned exclusively to melamine cyanurate. In case of polyacrylic acid as stabilization agent, the absorption bands of melamine cyanurate and polyacrylic acid overlap around 200 nm. Consequently, quantitative analysis by UV/VIS spectroscopy is just feasible for dextrin as stabilization agent.

Maximum intensity of the absorption peak (see insert figure in Fig. 3) is reached at a mass fraction of 0.25 wt% dextrin. Higher concentrations lead to smaller absorption peaks

Fig. 2 STEM-images of unirradiated microcrystalline melamine cyanurate **a** and laser-fragmented melamine cyanurate **b** stabilized with dextrin (mass fraction 0.25 wt%) after irradiation ($E_{\text{Pulse}} = 125 \mu\text{J}$, 50 kHz, 30 min)

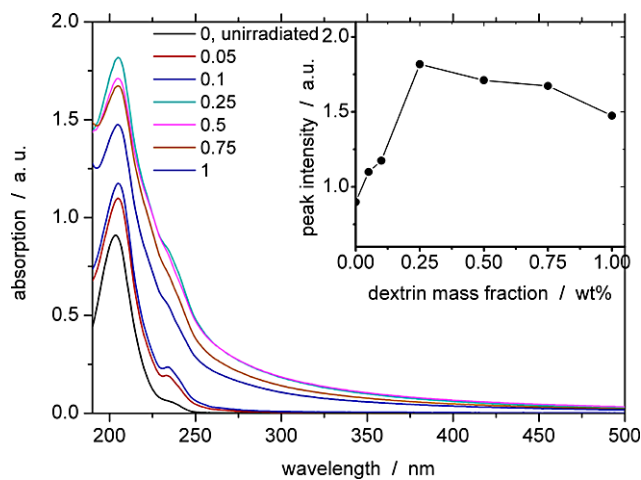
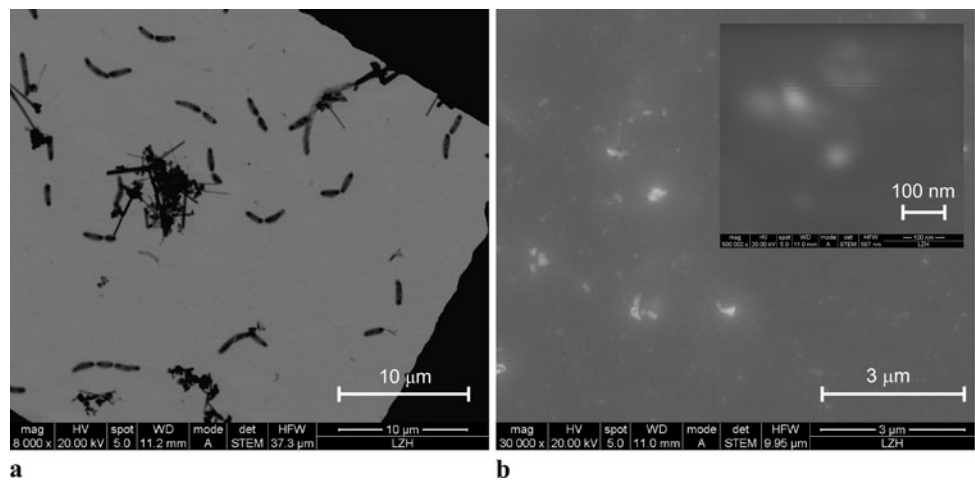


Fig. 3 UV/VIS absorption spectra of laser-fragmented melamine cyanurate. The main plot shows the spectra of melamine cyanurate at different dextrin mass fractions (in wt%) after centrifugation. The absorption spectra of unirradiated and irradiated melamine cyanurate without stabilization agent did differ significantly. The *insert plot* shows the intensity of the absorption peak at 205 nm in dependence of dextrin mass fraction

indicating that efficiency of laser fragmentation is lower. Furthermore, the absorption peak broadens with rising concentration of dextrin. This can be interpreted in terms of enhanced scattering due to higher concentration of nanoparticles after laser fragmentation. Light scattering at small particles can be described by Mie's solution to Maxwell's equations or in terms of Rayleigh scattering if the particle size is smaller than the scattered wavelength. The latter is appropriate for nanoparticle colloids. The intensity of Rayleigh-scattered light is inversely proportional to the fourth power of the wavelength. Consequently, more light is scattered at shorter wavelengths. So the measured UV/VIS spectra in Fig. 3 are composed of two attributes: The absorption of melamine cyanurat centered at 205 nm and Rayleigh scattering. The more nanoparticles are produced, the higher the

absorption peak at 205 nm grows by enhancing the water-solubility. Further, scattering occurs which broadens the red edge of the absorption peak. This can be clearly seen in Fig. 3 for mass fractions of dextrin higher than 0.25 wt%. UV/VIS spectra of irradiated melamine cyanurate with mass fraction of dextrin lower than 0.25 wt% just show a marginal broadening by Rayleigh scattering. Below this threshold only small amounts of nanoparticles are produced (Fig. 3). The significant absorption peak of unirradiated and irradiated melamine cyanurate without using dextrin (Fig. 3) can be assigned to physically solved melamine cyanurate which has a poor water-solubility but a very high absorption coefficient. Because of this, the broadening of the absorption peak is much more sensitive to the occurrence of nanoparticles.

The hydrodynamic size of the resulting nanoparticles was measured by dynamic light scattering shown in Fig. 4a. The size decays exponentially from several micrometers down to 200 nm at a minimum mass fraction of 0.25 wt% dextrin and is nearly constant for higher mass fractions. This is in good agreement with the UV/VIS absorption spectra. Images of the samples taken 5 days after laser fragmentation (see inbox figure in Fig. 4a) demonstrate as well that below the threshold mass fraction of 0.25 wt% the irradiated suspensions precipitate completely. The irradiation of a suspension without any stabilization agent leads (left images of sample in Fig. 4a) to a flocculent voluminous precipitate. This indicates that laser-fragmented nanoparticles without in-situ stabilization strongly tend to agglomerate and a certain threshold of concentration of the stabilization agent has to be exceeded to produce stable nanoparticles. The difference in particle size determined by dynamic light scattering (200 nm) and TEM-analysis (<100 nm) is due to the solvation shell in liquid and the layer of stabilization agent which may have a lower TEM-contrast.

The use of a polyacrylic acid as a polyelectrolytic stabilization agent in contrast to the neutral dextrin leads to comparable results. Figure 4b shows the hydrodynamic diame-

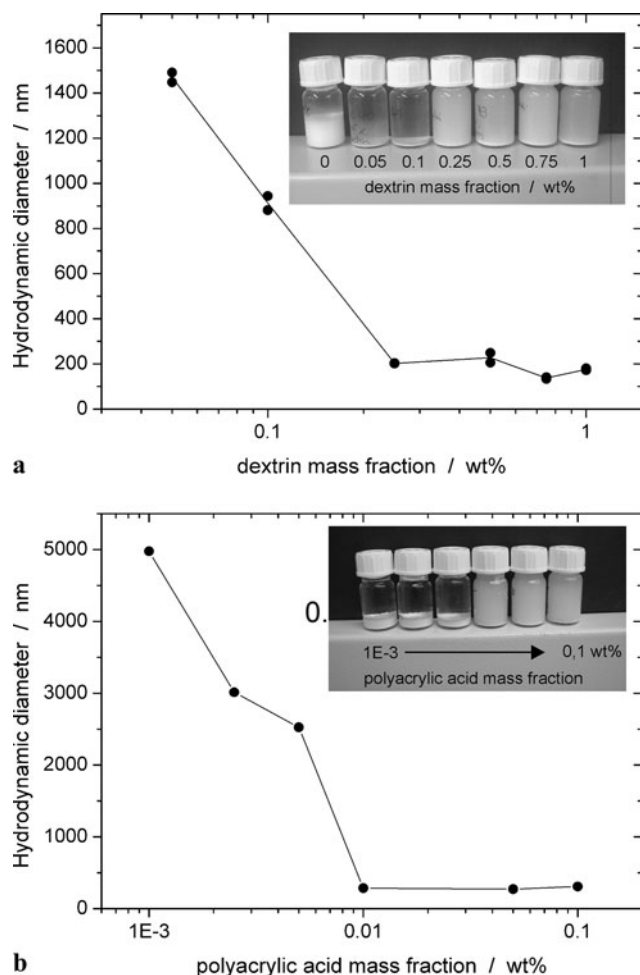


Fig. 4 In-situ stabilization: Hydrodynamic diameter of laser-fragmented melamine cyanurate in dependence of mass fraction of the used stabilization agent (**a**: dextrin, **b**: polyacrylic acid). The *insert images* show samples of the irradiated suspensions 5 days after laser fragmentation

ter of irradiated melamine cyanurate stabilized with polyacrylic acid. The particle size decreases from several micrometers below 200 nm at a minimum mass fraction of 0.01 wt% polyacrylic acid. The lower threshold of stabilization agent concentration of polyacrylic acid (0.01 wt%) compared to dextrin (0.25 wt%) implies that stabilization with polyacrylic acid is much more efficient. Polyacrylic acid is a polyelectrolyte. Every monomer unit (acrylic acid, $pK_a = 4.26$) contains a carboxylic acid moiety which is capable to dissociate into anion and proton. The resulting charge of the stabilization agent layer causes higher electrostatic stability of the nanoparticles.

The electrostatic stability of nanoparticle colloids stabilized with dextrin was determined by measuring the zeta-potential. Figure 5 shows the zeta-potential of nanoparticle colloids in dependence of mass fraction of dextrin. The zeta-potential decreases linearly with rising dextrin concentration. Under the assumption that stabilization of nanoparti-

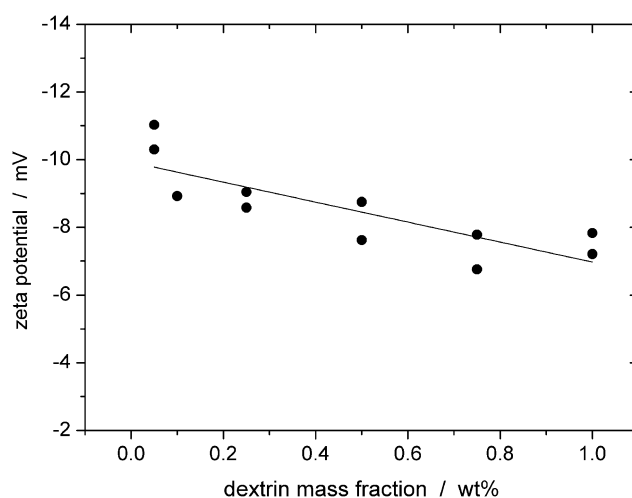


Fig. 5 Colloidal electrostatic stability: Zeta-potential of laser-fragmented melamine cyanurate particles in dependency to dextrin mass fraction after centrifugation

cles after fragmentation is a diffusion-controlled process of absorption of stabilization agent on the nanoparticle surface, higher initial concentration of stabilization agent results in a higher rate constant of adsorption. Furthermore the equilibrium of adsorbed and desorbed stabilization agent is shifted towards adsorption at higher concentration of stabilization agent. In consequence the stabilization layer around the nanoparticles is more pronounced and shields the nanoparticles charge, which lowers the zeta-potential. In this case the electrostatic stabilization is weaker but higher steric stabilization by more bulky stabilization agent layer may compensate for this.

4 Conclusion

We demonstrated the laser fragmentation of microcrystalline melamine cyanurate in aqueous suspension into charged, colloidal nanoparticles using a free liquid jet which is a scaleable, continuous flow technique.

The resulting nanoparticles can be stabilized in-situ electrostatically by a stabilization agent. The threshold concentration for sufficient stabilization depends on the electrostatic properties of the stabilization agent. The minimum mass fraction of dextrin as a neutral stabilization agent is 0.25 wt%, while the use of polyelectrolytic polyacrylic acid results in lower threshold concentration of 0.01 wt% because of better electrostatic stabilization due to the charged stabilization agent layer. Furthermore, nanoparticle properties like size and zeta-potential can be controlled by adjusting the concentration of the stabilization agent.

Acknowledgements The work was supported by the German federal ministry of education and research (BMBF) within the project EnGeL (FKZ 03X0064D).

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