Effective size separation of laser-generated, surfactant-free nanoparticles by continuous centrifugation

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Abstract

High-power, nanosecond, pulsed-laser ablation in liquids enables the continuous synthesis of highly pure colloidal nanoparticles (NPs) at an application-relevant scale. The gained mass-weighted particle size distribution is however often reported to be broad, requiring post treatment like centrifugation to remove undesired particle size fractions. To date, available centrifugation techniques are generally discontinuous, limiting the throughput and hindering economic upscaling. Hence, throughout this paper, a scalable, continuously operating centrifugation of laser-generated platinum NPs in a tubular bowl centrifuge is reported for the first time. To that end, using a 121 W ns-laser, the continuous production of a colloidal suspension of NPs, yet with broad particle size distribution has been employed, yielding productivities of 1–2 g h⁻¹ for gold, silver, and platinum. The power-specific productivities (Au: 18 mg h⁻¹ W⁻¹, Pt: 13 mg h⁻¹ W⁻¹, Ag: 8 mg h⁻¹ W⁻¹, Ni: 6 mg h⁻¹ W⁻¹) are far higher than reported before. Subsequent downstream integration of a continuously operating tubular bowl centrifuge was successfully achieved for Pt NPs allowing the removal of undesired particle size with high throughput. By means of a systematic study of relevant centrifugation parameters involved, effective size optimization and respective size sharpness parameters for a maximum Pt NP diameter of 10 nm are reported. The results of the experimental centrifugation of laser-generated Pt NPs were in excellent agreement with the theoretically calculated cut-off diameter. After centrifugation with optimized parameters (residence time of 5 min; g-force of 38,454 g), the polydispersity indices of the Pt NPs size distributions were reduced by a factor of six, and high monodispersity was observed.

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(Some figures may appear in colour only in the online journal)

1. Introduction

The quality and activity of catalysts, which currently are one of the most important components in the chemical industry
and technology [1, 2], are related to the size of the active material [3–5]. Most (90%) of processes in the chemical industry depend on the use of heterogeneous catalysts, which, in many cases, are constructed of nanoparticles (NPs) immobilized on a carrier material [6]. Due to the particle size-dependence of the performance of the catalyst, optimization is required to determine the best particle size for catalytic applications. Haruta et al [3, 4], in their development of Au/TiO₂-catalysts, showed that the highest catalytic performances in CO conversion were attained by NPs smaller than 5 nm. For the preparation of commercial catalysts, stabilizers, ligands, and reducing agents are used in conventional synthesis methods, such as the chemical reduction of precursors [7] and wet impregnation [8]. The use of reducing agents or stabilizers enables the generation of heterogeneous catalysts that consist of NPs that are less than 10 nm in size and have a monodisperse size distribution [9]. Since additives may poison catalysts [10], the ligands and stabilizers must be removed by calcination or other cleaning methods [11, 12]. Furthermore, during wet impregnation, the increase of the loading of NPs results in an increase in the sizes of the NPs [9].

To circumvent this drawback, we used pulsed laser ablation in liquids (PLAL) for the synthesis of ligand-free colloidal NPs [13]. By this method, heterogeneous catalysts are accessible [14] at loadings of up to 60 wt-% with almost quantitative yield [15] via electrostatically [15] or diffusion driven [16] deposition on dispersed supports [15–17]. Furthermore, by ablation of a target made of pressed metal micro-powder mixtures, the laser-based synthesis is applicable not only to yield pure metals but also multi metallic alloy NPs [18–20]. As shown recently, for pure metals a good reproducibility and a linear up-scaling of NP generation were achieved by a continuous flow synthesis using a high-power picosecond laser system consisting of a 500 W ps-laser source and a laser scanner with scanning speeds of up to 500 m s⁻¹. Using this equipment, productivities of up to 4 g h⁻¹ equivalent to 20 L h⁻¹ colloidal NPs were achieved [21, 22]. High productivities have not been investigated for ns-laser ablation, generally thought to come with lower ablation efficiency due to higher thermal energy loss. We will demonstrate in this study that NP productivities in the gram scale can also be realized with a ns-laser. In comparison to commercial catalyst preparation methods, the size distribution of the laser-based NP generation is often polydisperse. Monodisperse gold colloids were gained by laser ablation in micromolar aqueous saline solution [23] with particle size distribution smaller than 10 nm [23, 24]. However, NP by-products in the size range of 10–30 nm are often present in the colloid as reported for different materials such as platinum [15, 25], gold [23, 24], nickel [22, 26] and silver [27, 28]. The main challenge is to up-scale the synthesis while retaining small size, or even narrowing the particle size distribution. Several approaches for size control and control of the monodispersity of laser-synthesized NPs are established (adding salt or adjusting the pH [23], laser fragmentation [29, 30]). It has been shown recently by the molecular dynamic simulations of Zhigilei et al [31] that high laser intensities are the cause of metal layer lift-off and its subsequent instability, jetting large (>10 nm) NPs through the cavitation bubble boundary. Hence, high-intensity PLAL is prone to polydisperse or bimodal particle size distribution. It seems that high productivity was linked to a compromised colloidal quality regarding larger particle by-products. NPs in the range of 10–30 nm, which are often present after PLAL [23, 32], contribute to the mass loading of the catalyst and to a large proportion of the catalyst costs, but the contribution to the catalytic activity is very limited [3, 4]. Therefore a subsequent size optimization and separation step must be integrated into the process chain to synthesize highly active and economically efficient [33] heterogeneous catalysts. State-of-the-art techniques to separate NP size fractions are discontinuous centrifugation [34–36] and laser fragmentation [29, 30, 37], which are limited by a small volume and low throughput. A promising approach to process a high volume of ligand-free colloids, which was less investigated, is the NP centrifugation by tubular bowl centrifuge. Spelter et al [38, 39] have successfully shown the size separation with a cut-off in a hydrodynamic particle size regime of 200–400 nm for poly-styrene (stabilized with sodium dodecyl sulfate) and Aerodil 200 (from Ewonik, dispersed by sonification). However, the investigations of continuous particle separation with these materials were limited to a NP cut-off diameter higher than 100 nm, due to the low material densities. In comparison to previous reports, the targeted cut-off diameter for our laser-generated Pt NPs is 10 nm. This NP size fraction dominates catalytic activities in heterogeneous catalysis. In a first study, Konrath was able to demonstrate that this size range can theoretically be achieved for ligand-stabilized silver NPs [40]. Our aim is to enable the flow-through size separation without using stericly stabilizing ligands, to yield size-optimized Pt NPs free of any organic surface adsorbates.

Therefore, the approach of this study is the high-power nanosecond laser synthesis of colloidal NPs in a gram scale and the optimization of the size of Pt NPs (cut-off: 10 nm) in a continuous process by tubular bowl centrifugation. We study the separation efficiency of the flow rate (variation of residence time) and rotation speed (variation of g-forces) on the size separation process and cut-off particle diameter. Moreover, we correlate the experimental results with theoretical calculations. Altogether, we aim for a continuous process chain of PLAL with downstream size narrowing, yielding ligand-free, mono-disperse Pt NPs with high throughput.

2. Experimental

To generate the colloidal Pt NPs in an application-relevant amount (at least liter scale), we used a ns-laser system (Edge-Wave IS-400-L) and a continuous ablation chamber. The setup is schematically shown in figure 1. For particle generation the laser beam was moved in a rectangular pattern [41] on the platinum bulk target (1 mm thick foil, 99.99% purity, AGOSI) by a galvanometric scanner system (Sunny S-8210D at 2 m s⁻¹ scan speed) equipped with Linos F-Theta lens f=100 mm operating at a working distance between lens (surface) to target...
of 115 mm (optimum in NP productivity for silver and platinum). The pure water (Milli-Q, 18.2 MΩcm, liquid layer height of 6 mm) was pumped with a flow rate of 100 ml min\(^{-1}\) through the chamber yielding about 6 L h\(^{-1}\) colloids with a concentration around 220–250 mg l\(^{-1}\) (see figures 1 and 2).

After the NPs are continuously generated by PLAL, the colloids are continuously size-separated by a tubular bowl centrifuge (CEPA LE GP) (figure 1). The main advantage of using a tubular bowl centrifuge is that a large volume of the colloid can be processed without interruption. For a 200 ml batch in a discontinuous centrifuge (using a Hettich Universal 320 centrifuge) the time consumption is 210 min. Comparing this discontinuously operated tabletop centrifuge with the continuous tubular bowl centrifuge shows that a time saving of 96% can be realized due to the time reduction for a 200 ml batch in the tubular bowl centrifuge down to only 9 min.

By varying the residence time of the colloid (0.83–10 min | flow rate 25-300 ml min\(^{-1}\)) and g-force (6783–38,454 g | rotation speed 16,800 to 40,000 rpm) of the centrifuge, the correlation of the former with the cut-off particle diameter is studied. To verify these results and to predict the settings, we have compared the correlation of the experimentally determined data with theoretical calculations. To evaluate the separation quality, the colloid concentration and particle size distribution before and after the centrifugation process were measured by UV/Vis extinction spectroscopy (Thermo Scientific Evolution 201, in a glass cuvette with 10 mm path length) and by analytical disc centrifugation (DC24000 from CPS Instrument), respectively. The spectrometer has been calibrated by a certified extinction standard (Helma GmbH, 667.305-UV) so that an absorbance up to 2 could be measured with high linearity. In addition to the hydrodynamic particle size analysis by analytical disc centrifugation the primary particle size of the separated particles is verified by transmission electron microscopy (Zeiss EM 910 at 120 kV). A 10 μl drop of each colloid (before and
after centrifugation with optimized parameters) was cast on lacey carbon film-coated copper grids and dried in air. The particle diameters of at least 498 particles was measured by the software ImageJ and plotted as histograms. Histograms of each sample were generated from this data pool using a step size of 0.5 nm.

### 3. Results and discussion

#### 3.1. Upscaling of NP generation by nanosecond laser ablation

Prior to the investigations of the continuous centrifugation parameters, ligand-free Pt NPs were produced by pulsed laser ablation in water for at least 1 h. Using a continuously operated flow chamber similar to the one previously used by Streubel et al (high-power (500 W) picosecond laser system), the NP productivity was compared [21, 22]. The obtained ns-laser productivities for different materials (Pt, Au, Ag and Ni) are summarized in figure 2(a). Our results show that by means of ns-PLAL a sufficient quantity of Pt NPs can be produced to investigate the continuous centrifugation process. For platinum, a productivity of up to 1.5 g h\(^{-1}\) (approx. 6 L colloid) is reached when operating the laser with a power of 121 W. In comparison, the reported productivities in the literature [21, 22] reach up to 4 g h\(^{-1}\) Pt colloid were produced using a 500 W laser system (measured output power). However, for a reasonable comparison, the laser power-specific productivity must be considered [13] (see figure 2(b)). This value describes the NP productivity related to the used laser power.

For platinum, a far higher value of 13.0 mg h W\(^{-1}\) is observed in this study, while the reported ps-laser productivities [21, 22] correspond to 8.1 mg h W\(^{-1}\). As can be seen, the achieved laser power-specific productivity for platinum is 37.7% higher than by Streubel et al [21, 22], although a cost-effective (76% less laser power) laser system has been used here. Note that Streubel et al [21, 22] optimized their laser-focusing conditions for copper, so their productivity data may not present the upper limit of what may be possible with their laser system for platinum and the other metals. Also for gold (18 mg h W\(^{-1}\)), platinum (13 mg h W\(^{-1}\)), silver (8 mg h W\(^{-1}\)) and nickel (6 mg h W\(^{-1}\)), the laser power-specific mass ablation rate was systematically higher than reported before. On the one hand, ns-PLAL may be cost-effective for Pt NP production. But on the other hand, often the peak-diameter of the first particle size distribution mode is larger in (compared to ps-PLAL), demanding size-narrowing efforts. In terms of a catalyst production, the more important aspect is the production of the small NP fraction (<10 nm). In addition to the total NP productivity, the productivity of the relevant size regime was measured by analyzing the initial particle size (figure 3(b)). Hence, the particle diameter distribution defines the mass loss if centrifugation steps are taken. To maximize the mass concentration of small NPs during the laser process, a salt (in mM-concentration range) can be added to the water before the ablation process [23, 32]. Thus, we generated the Pt NPs in an aqueous 0.1 mM KOH electrolyte, since in comparison to other ions like chlorides and sulfates, the catalytic activity in fuel cell reactions (ORR) is not negatively influenced by hydroxide ions [42, 43]. Another advantage of the electrolyte or salt is the increased electrostatic stability (pronounced surface charge) during centrifugation. Note that particle agglomeration cannot be totally avoided during centrifugation (see SI figure S4). For the pure Pt colloid in water, a size shift of the peak maximum from 7.5 nm to 9.0 nm due to slight agglomeration (decrease in catalytic activity) during centrifugation driven by the acting g-forces [44] is observed, as can be seen in figure S4 (SI). The Pt NPs in pure water are not stable enough for the centrifugation process. The addition of salt in micromolar concentration avoids this problem (figure 3(a)). The size-quenching effect by the dissolved hydroxy anions and the associated increase of the mass concentration of NPs smaller than 10 nm are depicted in figure 3(b).

The average hydrodynamic particle diameter \(x_{\text{mean}}\) of the Pt NPs is reduced by 39% from 14.9 nm down to 9.1 nm due to the size-quenching of the base, as can be seen in the mass-weighted size distribution in figure 3(a). Moreover, the size-quenching effect is also reflected in the 29% reduction of the...
polydispersity index from 0.55 to 0.39. To determine the mass concentration of NPs smaller than 10 nm, and to assess the maximum particles separation capability, the relative mass distribution can be converted into a cumulative size distribution. From the cumulative mass-weighted size distribution an increase of the mass concentration of NPs smaller than 10 nm of 31.5% is determined as can be seen in figure 3(b).

For this reason, the starting colloid for the investigation of the centrifugation parameters was generated in 0.1 mM KOH to reduce the mass loss during the centrifugation process. In the following experiments, the influence of the g-force of the centrifuge and the residence time of the colloid is investigated with the colloid in 0.1 mM KOH.

3.2. Investigation of the influence of g-force

After the size separation in the tubular bowl centrifuge at varied rotation speeds, the centrifuge supernatants were analyzed by analytical disc centrifugation. The cut-off can be determined from the size distributions. The measured size distributions and extracted average particle diameters, $x_{\text{mean}}$, (from LogNormal fitting) are summarized in figure 4.

As can be seen in figure 4(a), the normalized mass-weighted size distribution is shifted to smaller particle diameters with increasing g-force. Obviously, the NPs are stable also after centrifugation at high centrifugal forces. The aimed particle size cut-off at 10 nm is reached for g-forces higher than 31,000 g (at 5 min residence time with a throughput of NPs with diameters of less than 10 nm of 0.46 g h$^{-1}$). The downshift of the size with higher g-force can be seen in the reduction of the average particle diameter, $x_{\text{mean}}$, of the mass- and surface-weighted size distribution (figures 4(b) and (d)). In comparison to the raw colloid directly after particle synthesis, the mass-weighted average particle diameter is reduced from 8.6 nm to 5.1 nm, which represents a reduction of 35 %. The narrowing of the size distribution and the efficiency of the particle separation of the NPs bigger than 10 nm becomes more apparent if the polydispersity index (PDI) is considered. The PDI is calculated by $\text{PDI} = \frac{\text{variance}}{\text{average particle diameter}}$. The monodispersity of the Pt NPs
increases with higher g-forces. Here, a reduction of the PDI by about 81% is observed, which is highly desired in the field of catalysis. The same trend can be seen in the surface-weighted size distributions, where a reduction of 22% of the average particle diameter, $\bar{x}_{\text{mean}}$, and a decrease of the PDI of around 69% is determined with increasing g-force. Overall, a surface-weighted particle diameter of 4.6 nm with a high monodispersity (PDI 0.05) can be achieved by downstream centrifugation. As reported in the introduction, the NPs smaller than 10 nm are the most responsible active sites in catalyst application [4, 45]. Thus, the fraction and concentration of the NPs smaller than 10 nm must be considered and is depicted as a function of the g-force in figure 5.

In comparison to the starting colloid, the mass concentration of NPs smaller than 10 nm is increased with higher g-force and an increase from 60% to about 90% NP yield with diameters of less than 10 nm is reached, as can be seen in figure 5. Considering the surface- and number-weighted cumulative size distribution the fraction of NPs smaller than 10 nm reach even 95%–100%.

In summary, a g-force higher than 31,000 g is necessary to adjust the cut-off at a particle diameter of 10 nm. The NPs inside the centrifuge are exposed to higher g-forces due to the increase in the rotation speed of the centrifuge. With the maximum adjustable g-force of 38,454 g (for 40,000 rpm), the most effective separation could be implemented. The table 1 in the supporting information is available online at stacks.iop.org/NANO/31/095603/mmedia and summarizes the g-forces for the different rotation speeds. Since the flow rate of the liquid affects the residence time of the NPs inside the centrifuge, this parameter is a further degree of freedom to optimize the size separation by centrifugation. After a variation of the residence time, the NPs from the centrifuge centrate were analyzed and the results are shown in the following paragraph.

3.3. Investigation of residence time variation

By variation of the flow rate, the residence time inside the centrifuge cylinder (volume of 250 ml) can be adjusted.

Therefore the cut-off diameter and separated particle diameter is decreased by increasing the residence time within the centrifuge. The measured average particle diameters, $\bar{x}_{\text{mean}}$, and PDIs of the mass- and surface-weighted size distributions are summarized in figures 6(a) and (b), respectively.
Figure 6(a) shows the decrease of the mass-weighted average particle diameter with increasing residence time. The NPs reside longer in the cylinder (separation volume) at lower flow rates, which results in a more efficient separation of the size fractions. The lowest mass-weighted average particle diameters are achieved by centrifugation with g-force of 38,454 g and residence times higher than 2 min. The minimum in average particle diameter, $x_{\text{mean}}$, is observed for a residence time of 5 min due to a reduction of the diameter by 39% in comparison to the Pt colloid before centrifugation (see dashed line in figure 6(a)). With decreasing residence time the average particle diameter, $x_{\text{mean}}$, approaches the $x_{\text{mean}}$-value (8.3 nm) of the raw colloid, which means that no significant size separation takes place at low residence time. The same trend and effect can be observed for the PDI. Here a reduction of around 90% is observed with a residence time of 10 min due to the narrowing and separation of all NPs bigger than 10 nm. For the surface-weighted size distribution, the maximal observed reduction of the average particle diameter, $x_c$, and PDI is 15% and 78%, respectively. Analogous to the investigation of the influence of the g-force, the mass concentration of NPs smaller than 10 nm can be extracted from the cumulative size distributions. As can be seen in figure 6(c) the fraction of NPs smaller than 10 nm is increased to 90% with the increase of the residence time. The most efficient separation is observed with residence times higher than 3 min with a maximum mass fraction of 90% of NPs with diameters of less than 10 nm. The efficiency of the separation process and the success of the separation of the particles bigger than 10 nm with a g-force of 38,454 and a residence time of 5 min is confirmed by TEM particle size analysis.

The associated size histogram and a representative image depicted in figures 7(a) and (b). The average particle diameter of the colloid before centrifugation is 7.4 nm with a significant number of NPs $> 10$ nm. After the centrifugation process with a residence time of 5 min and 38,454 g, an average particle diameter of 3.8 nm was determined and most of the NPs bigger than 10 nm were removed. The observed average particle diameter is in good correlation with the analytical centrifuge results ($x_{\text{mean}}$: 5.1 nm).

Comparing the influence of the g-force and the residence time of the colloid, the parameter studies show that for the separation of ligand-free Pt NPs bigger than 10 nm a residence time between 3–10 min and a g-force higher than 31,000 g is most effective. Another parameter to validate the efficiency of the separation is the degree of separation and separation sharpness, thereby comparing the experimental results with theoretical calculation.

### 3.4. Correlation to theoretical calculations

In order to evaluate the experimental data and to describe the success of centrifugation process, the degree of separation $T(x)$ is determined. This value characterizes the separation probability depending on the particle size. The degree of separation is determined by equation (1) which is based on the contexts reported in the literature [40, 46].

$$T(x) = \left(1 - \frac{q_{\text{supernatant}}}{q_{\text{colloid}}}\right)*100\%$$

Thus, the degree of separation $T(x)$ is calculated by the ratio of the measured size distribution of the centrifuge supernatant (colloid after centrifugation) $q_{\text{supernatant}}$ and the starting colloid $q_{\text{colloid}}$. The following applies to the course of the degree of separation: the steeper the degree of separation curve, the better the separation result. From the calculated curves, different particle diameter values with different separation probabilities can be extracted (see figures S5 and S6). Another important parameter to assess the centrifugation results and separation efficiency is the sharpness factor $\kappa$, which is determined from the quotient of the particle sizes with 25 percent ($x_{\text{75},25\%}$) and 75 percent ($x_{\text{75},75\%}$) separation probability [47, 48].

$$\kappa = \frac{x_{\text{75},25\%}}{x_{\text{75},75\%}}$$

For an ideal separation, the sharpness factor is 1, which is usually not achievable in practice due to several reasons. A value between 0.3 and 0.6 is observed for technical separation and a sharp technical separation is reached with values...
between 0.6 and 0.8. In literature, values of 0.8-0.9 are mentioned as analytical separation [48].

To validate the determined separation efficiencies and separated particle diameters the results are correlated to the theoretical separated grain size \( x \) which is calculated by equation (3) [40]:

\[
x = \frac{18 \ast \eta \ast V \ast \ln \left( \frac{r_{cylinder}}{r_{weir}} \right)}{\pi^3 \ast (p_{Particle} - p_{Fluid}) \ast (1 - c_V)^{1.2} \ast (r_{cylinder}^2 + r_{weir}^2) \ast (l \ast (0.8)) \ast \frac{1}{n}}
\]

(3)

with \( V \) for the flow rate and \( n \) for the rotation speed, which can be varied during the operation process. Moreover, \( \eta \) for the viscosity of the fluid \((0.001 \text{ kg m}^{-1} \text{s}^{-1})\), \( p_{Particle} \) \((21,450 \text{ kg m}^{-3})\) and \( p_{Fluid} \) \((1,000 \text{ kg m}^{-3})\) for the particle and fluid density respectively, \( c_V \) for the particle volume concentration in the liquid concentration \((0.01)\) and the dimensions of the centrifuge \((\text{radius of the cylinder } r_{cylinder} = (0.0215 \text{ m})\) and \( r_{weir} = (0.00725 \text{ m})\), \( l \) for the length of the cylinder \((0.187 \text{ m})\) are needed to calculate the theoretical separated grain size. In comparison to Konrath, we integrated a correction term, \((1 - c_v)^{1.2}\) for the particle concentration, which involves the particle interaction and particle size distribution. Moreover, a correction factor \((0.8)\) for the inlet and outlet geometry of the cylinder (empirically determined by CEPA) is integrated in this equation.

With equation (1) the degrees of separation for a probability of 25, 75 and 99% in case of the different g-forces are calculated and summarized in figure 8.

As can be seen in figure 8(a), the separated particle diameter (cut-off diameter) is reduced with increasing g-force due to a more efficient separation of the bigger particles. The observed reduction of the \( X_{T,25\%} \) and \( X_{T,75\%} \) diameters is also reflected in the increase in the separation sharpness from 0.35 to 0.75 with an increase of the g-force from 6,783 to 38,454 g correlation with the theoretical calculations. As expected, with smaller g-forces the deviation between theory and experiment increases due to the deterioration of the separation process in the centrifuge. The deviation to the theoretical calculations and the pronounced error bar for the lowest g-force could be an indication for a non-stable state (no steady-state) in the centrifuge. However, for the relevant and significant workspace (g-forces higher than 31,000 g, see section 3.2) the theoretical line agrees well with the measured particle diameters. For these g-forces a cut-off diameter around 10 nm can be efficiently realized. It follows that for the efficient separation of Pt NPs at a 10 nm cut-off diameter, a g-force higher than 31,000 g is required. On the other hand, the separation productivity and throughput is dominated by the residence time. Thus, theoretical calculations and comparison to the experimental results are investigated for this parameter as well. Figure 6(a) has shown that the average particle diameter, \( x_c \), is reduced by an increase of the residence time. Consequently, in analogy to the g-force investigation, the degree of separation \( T(x) \) and the separation sharpness are extracted from the determined size distributions. The influence of the residence time (for a constant maximum g-force of 38,454 g) on the particle separation is examined in figure 9.

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**Figure 8.** Correlation of the experimental centrifugation with theoretical results for the rotation speed variation. (a) Cut-off diameter extracted from equation (1) for several probabilities of the degree of separation as a function of the g-force of the centrifuge. The dashed green line shows the theoretically cut-off diameter \( (x_{T,99\%}) \) (equation (3)). (b) The separation sharpness by Eder [47] (equation (2)) as a function of the g-force of the centrifuge (residence time: 5 min).

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With the highest g-force a sharp technical separation is observed.

To compare the experimental results (green dots in figure 8(a)) with theoretical calculations (green dashed line in figure 8(a)) the \( X_{T,99\%} \) was compared. The experimental \( X_{T,99\%} \) values for g-forces higher than 18,842 g are in good agreement with the theoretical calculations.
The observed $X_{T,25\%}$ and $X_{T,75\%}$ diameters decrease from 9.5 nm and 19.3 nm to 5.7 nm and 6.7 nm when increasing the residence time from 0.83 to 10 min, respectively. Thus, an decrease of the cut-off size by 66.7% ($X_{T,25\%}$) and 188% ($X_{T,75\%}$) is observed. This decrease is also reflected in the separation sharpness. The sharpness factor shifts from a sharp technical separation (0.6-0.8) to a technical separation with values around 0.5 [47, 48]. However, for the application of the colloids, a sharp separation at a cut-off at 10 nm is more important than the separation sharpness. Thus, a sharp separation of the NP size fractions at 10 nm can be realized by the optimization of the residence time during the centrifugation process.

To evaluate the influence of the residence time, the $X_{T,99\%}$ and theoretical line (dashed green line) are depicted in figure 9(a). As can be seen in figure 9(a), the measured diameters $X_{T,99\%}$ from a residence time of 1.48 min onwards can be described quite well with the theoretical model. For lower residence times the deviation increases as it was observed for g-forces smaller than 18,840 g. These deviations are caused by the limited residence time of the NPs in the centrifuge and a non-reproducible separation occurred. But for the region with a cut-off around 10 nm, the theoretical calculation can be used to predict the cut-off diameter and separation diameter. We aim to remove virtually all >10 nm NPs to achieve a high-quality catalyst. Thus, a residence time higher than 2.91 min should be used to generate an efficient heterogeneous catalyst. In summary, a g-force higher than 31,000 g and a minimal residence time of 5 min have to be used to remove all Pt NPs bigger than 10 nm if a degree of separation of 99% is desired. These parameters enable a reproducible and stable separation process (NPs < 10 nm) in the tubular bowl centrifuge. But also cut-off diameters higher than 10 nm can be adjusted by the residence time during the centrifugation. The separation productivity for Pt NP with diameters of less than 10 nm can be calculated from the product of the colloidal concentration, the flow rate and the associated mass loss (60%). For the optimized centrifugation parameters $\text{(38,454 g, 5 min)}$ and a Pt NP colloid concentration of $\text{261 mg l}^{-1}$, a maximal Pt NP ($<10 \text{ nm}$) productivity of $\text{0.46 g h}^{-1}$ is calculated. Outlooking, these NPs can be electrostatically deposited on carrier materials (catalyst supports) as described by Marzun et al [15], and can be used as a heterogeneous catalyst [14]. Furthermore, was shown by the theoretical calculations and their correlation with the experiments, the centrifugation parameters can be easily pre-determined, facilitating the planning of experiments. Contrary to the investigation of Spelter et al [38], we could show that a size classification for NPs much smaller than 100 nm can be realized in the tubular bowl centrifuge. The efficient centrifugation process can be transferred to other NP materials as is shown for Au- and Ag-NPs in figure S8 (SI). In future, the optimization of the cumulative mass of NPs smaller than 10 nm will be investigated to reduce the centrifugation losses. This can be done by using ps-lasers or different size-quenching anion types and concentration. Alternatively, the separated bigger particles can also be recycled in the process chain, which is a great advantage in using centrifugation in particular for precious metals. In this context, these re-dispersed NPs may also be recycled to produce laser ablation targets. The fraction of small NPs (<10 nm) can be deposited on carrier materials in the next step to fabricate heterogeneous catalysts. Hence, efficient laser-based heterogeneous catalyst production at application-relevant scale is feasible since contamination-free NPs with diameters smaller than 10 nm were shown to be continuously produced by this process.

4. Conclusion

High-power, ns-laser ablation in liquids provides a continuous, cost-effective production of ligand-free colloidal NPs that is unparalleled by other techniques. The power-specific mass-productivity of gold ($\text{18 mg h}^{-1} \text{ W}^{-1}$), platinum ($\text{13 mg h}^{-1} \text{ W}^{-1}$), silver ($\text{8 mg h}^{-1} \text{ W}^{-1}$) and nickel ($\text{6 mg h}^{-1} \text{ W}^{-1}$), was systematically higher than reported
previously by Streubel et al [21]. But the particle diameters that have been attained so far, were not yet optimized for catalytic applications. In this work, we demonstrated that the particle size of laser-generated Pt NPs can be optimized by a continuously operated, tubular bowl centrifuge for economic laser-based catalyst synthesis. With such a centrifuge, a sharp separation of the NPs was achieved with a cut-off at 10 nm. The centrifuged colloids had high monodispersity (down to 0.05), and their size distribution was narrowed significantly. By varying the g-force of the centrifuge and the residence time of the colloid, we were able to shift the cut-off to smaller diameters. Thus, an increase of the g-force from 6,783 to 38,454 g resulted in a decrease of the average diameter, xmean, from 7.4 to 5.1 nm with a simultaneous increase in the cumulative mass fraction of NPs smaller than 10 nm from 75% to 90%. In comparison to the colloid after the synthesis, the average particle diameter, xmean, for an optimal g-force (38,454 g) was reduced by 41% (from 8.6 to 5 nm), and the cumulative mass fraction of NPs with diameters less than 10 nm was increased from 60% to about 90%. An analogous decrease of the average particle diameter, xmean, of the Pt colloids decreased to 5 nm and 90% of the cumulative mass of NPs had diameters smaller than 10 nm. In addition, a satisfactory correlation between the theory and the experimental results was observed, as validated for the separation diameters and degree of separation, XTR,99%. Note that the NPs generated by laser ablation in water had properties similar to those of a ‘hard sphere’, which is a basic assumption of Stokes’ law facilitated by basic correlations of the theoretical and experimental assessments of particle movement [49, 50]. Thus, laser-generated aqueous NP colloids may be considered as a good model material to investigate the centrifugation process in a tubular bowl centrifuge. Practically, the application of the bowl centrifuge allowed to transfer the process chain of laser-based NP synthesis to a continuously continuous level important for economic laser-based synthesis of heterogenous catalysts.

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