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Automated synthesis of colloidal nanoparticles powered by microchip lasers

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Abstract

Energy and health, two topics with continuing high relevance for our society, which require intensive R&D. Nanoparticles, with their unique properties, already make an important contribution to both fields and will play an even more essential role in the future. Access to high-quality nanoparticles for R&D is still difficult, especially when high purity and material diversity are required. Moreover, limited shelf-life, batch-to-batch-variability, and time-consuming ordering or shipping procedures hinder development progress. Pure colloidal nanoparticles of numerous combinations of particle material and dispersion medium become available by pulsed laser ablation, but automation has not been achieved affordably, yet. Compact microchip lasers now enable the transfer of the synthesis method from the laser lab to any R&D lab as a benchtop, easy-to-use machine. The low-power q-switched, cavity-limited lasers impress with unprecedented power-specific ablation efficiency in the laser synthesis of colloids. In addition, innovative solutions in measurement and control technology make full automation of nanoparticle production possible.

Keywords: Benchtop; Infrared; Nanoseconds; Nanomaterials; Productivity

1. Introduction

Nanomaterials and especially nanoparticles established themselves as essential raw materials in the last decades. It is important to distinguish between low-cost powders of aggregated nanoparticles, often metal oxides, from gas-phase synthesis and high-value colloids of dispersed nanoparticles. Both types of nanoparticles have their raison d'être and are used in appropriate applications. The aggregated powder materials are used almost exclusively as additives of mass products such as coatings and building materials, as

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well as food and cosmetics. Colloidal nanoparticles address high-tech applications in biomedicine (Bansal et al., 2020; Elahi et al., 2018; Perumal et., 2021) and energy technology (Astruc, 2020; Huang and Buonsanti, 2019; Losch et al., 2019).

We focus here on the higher quality nanoparticle colloids, which are generally synthesized by wet chemical, bottom-up approaches. Such colloids are generally traded on the market only for a few standard materials and at extremely high prices, which is also related to complex material development. Unfortunately, this leads to a strong slowdown in research and development based on colloidal nanoparticles. In addition, wet chemical methods are operated thermodynamically driven, often limiting access to metastable nanoparticle materials such as high-temperature phases or alloys at compositions that exceed the solid solution miscibility.

Physical, top-down approaches typically allow for the size reduction of many different materials without extensive process development for each material. However, they have not yet been able to establish themselves as an alternative to chemical methods because they either primarily generate irregularly shaped particles with diameters larger than 100 nm or require expensive equipment. Furthermore, mechanical process technology inherently undergoes wear which not only affects operational costs but also causes contamination of the colloids by abrasion. Note that also the material type accessible is limited, e.g. ductile particles cannot be milled down easily to the nanoscale.

The physical method of laser ablation of solids in liquids enables the synthesis of colloidal nanoparticles (Zhang et al., 2017), including alloys (Reichenberger et al., 2019; Löffler et al., 2021) in a scaleable manner (Dittrich et al., 2020; Waag et al., 2021). Also unusual, metastable alloys are accessible by this method (Johny et al., 2021; Liang et al., 2021). With the establishment of pulsed lasers in materials processing, reliable and easy-to-use lasers are now available at comparatively low cost. This makes laser-based colloid synthesis attractive for widespread use. However, system integration is still lacking. The method must be available for operators of different disciplines as an easy-to-use and safe-to-handle system, ideally for non-laser experts, e.g. in a chemical or even medical lab. First efforts in this direction have already been made. Crivellaro et al. built a setup for laser-based nanoparticle synthesis that could be remotely controlled from outside the laser lab with any PC or smartphone (Crivellaro et al., 2019). Freeland et al. succeeded in controlling nanoparticle concentration in laser-based synthesis via integration of inline UV-Vis spectroscopy for concentration determination and pump rate control (Freeland et al., 2021), and Labusch et al. used the acoustic spectrum of laser ablation to continuously readjust the distance between the focusing lens and the target surface, which normally increases successively as the target is consumed (Labusch et al., 2019). This allowed the authors to counteract the reduction in laser energy density and the associated loss in productivity of laser-based nanoparticle synthesis.

We developed a prototype of a fully integrated, operational safe (laser class 1) system, which enables on-demand colloid supply on a laboratory scale. In this paper, we provide an insight into the development of the device, which employs an efficient microchip laser in the automated colloid synthesis.

2. Materials and methods

The laser ablation method was used for automated colloid synthesis similar to the non-automated variant reported before (Dittrich et al., 2021). In brief, a microchip laser (eMOPA1064-500, CryLaS GmbH, Berlin, Germany) with a wavelength of 1,064 nm, a laser pulse duration of 1 ns, a pulse repetition rate of 1 kHz, and average power of 0.5 W was used. The laser beam was expanded to 4 mm in diameter using a telescope. The beam then passed through a custom galvanometer XY-scanner, a lens system with a focal length of 50 mm and an optical window onto metal pieces of Ag (Alfa Aesar, Haverhill, US), Au (Allgemeine Gold- und Silberscheideanstalt, Pforzheim, Germany), and Pt Alfa Aesar, Haverhill, US), which were placed in a custom-made ablation chamber. All metal plates were 0.5 mm thick and had a purity of 99.99 %. Aqueous solutions of

0.1 mM NaCl (Au and Pt) and 0.25 mM sodium citrate (Ag) were continuously flowed through the chamber during the ablation of the metal plates. The liquid flow rate was set individually for each metal to achieve a nanoparticle concentration of about 100 mg/l. The current prototype of the automated synthesis machine is shown in Fig 1a.

UV-Vis extinction spectra of nanoparticle colloids were recorded offline or inline using a benchtop spectrometer (Evolution 201, Thermo Fisher Scientific, Waltham, US) or compact USB spectrometer (Red Tide USB650UV, Ocean Optics, Dunedin, US) and a quartz cuvette with 10 mm optical path.

Size distributions of colloidal nanoparticles were analyzed using an analytical disc centrifuge (DC2400, CPS Instruments, Prairieville, US) in a sucrose gradient at 24,000 rpm and a laser wavelength of 405 nm. PVP particles with an average particle diameter of 237 nm (FWHM: 23 nm) were used as a calibration standard.

3. Results and discussion

Our development of a compact automated laboratory system for the laser-based synthesis of colloidal nanoparticles primarily involved two aspects: the qualification of monolithic microchip laser systems for the synthesis process and the integration of measurement and control technology. The small size of microchip lasers and their passive cooling made it possible to implement our machine as a compact benchtop device that fits into any laboratory (Fig 1a).

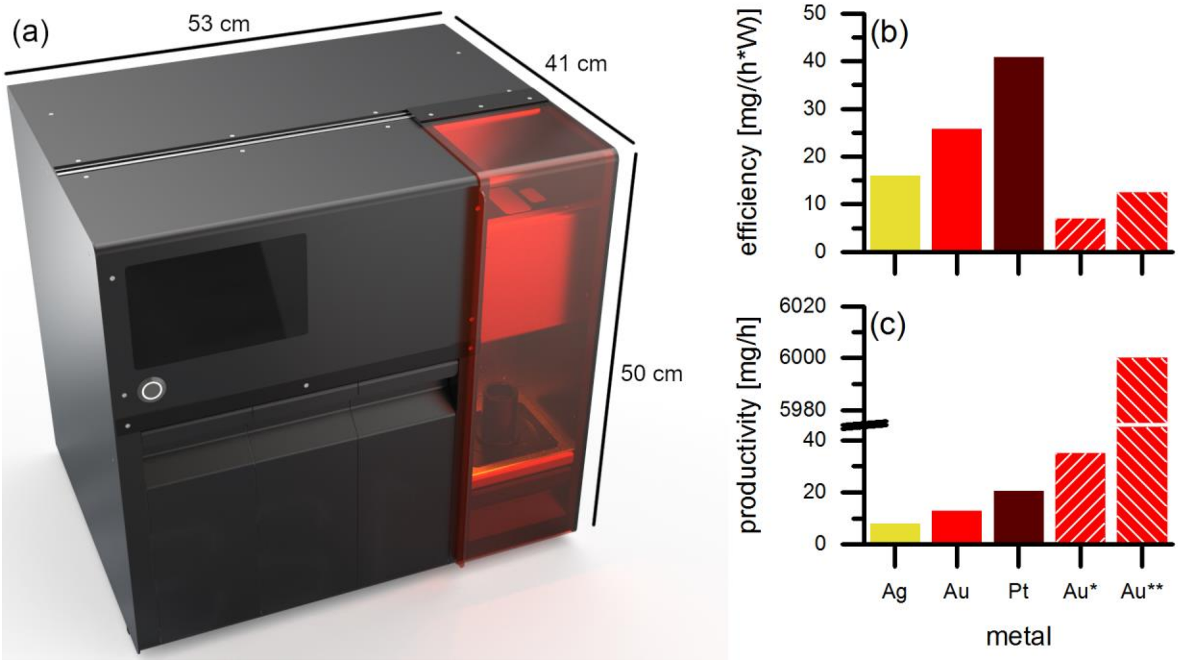

Fig. 1. (a) 3D model of the automated laser-based colloid synthesis machine. (b) power efficiency and (c) productivity of nanoparticle generation achieved by laser ablation of Ag, Au, and Pt with a 0.5 W microchip laser system. Data of * and ** from (Dittrich et al., 2019). *: standard laser system (5 ns, 5 W), **: optimized, high-tech laser system (3 ps, 480 W).

We first tested the productivity and power efficiency of the automated machine in the synthesis of colloidal nanoparticles of Ag, Au, and Pt. Fig 1b shows the achieved nanoparticle productivity as well as power efficiency at the optimum preset working distance between the focusing optics and the target surface. The power efficiency depended on the respective metal and was 16 mg/(W*h) (Ag), 26 mg/(W*h) (Au), and 41 mg/(W*h) (Pt). The respective productivity value is half of the efficiency in mg/h due to the average laser power of 0.5 W. As a comparison, power efficiency of 7 mg/(W*h) with a maximum productivity of 35 mg/h was recently found for a standard marking laser (5 ns, 5 W) which represents the most used type of laser for colloid synthesis (Dittrich et al., 2019). A high-end, ultrashort-pulsed laser system (3 ps, 480 W), which had been optimized for colloid synthesis, achieved an efficiency of 12.5 mg/(W*h) with a maximum productivity of 6,000 mg/h (Dittrich et al., 2019). Thus, the automated synthesis machine showed significantly better power-specific efficiencies in nanoparticle generation than the benchmark systems.

Second, we investigated the reproducibility of the colloid synthesis with the automated machine. Fig 2 shows UV-Vis extinction spectra (a) as well as size distributions (b) and extracted size indices (c) for five aqueous colloids of Pt nanoparticles. The colloids were produced with the automated synthesis machine at the same parameter sets. The UV-Vis spectra of the five colloids show almost no deviations from each other (Fig 2a). There are negligible fluctuations in the extinction, which can be seen in the almost constant peak maximum in the UV range. This points to minor concentration fluctuations of the colloids. The size distributions of the different colloids are also almost on top of each other (Fig 2b), which is naturally reflected in the extracted size indices (Fig 2c). A slight deviation from the rest of the series can be observed for the first sample, whose size peak is slightly shifted to larger diameters.

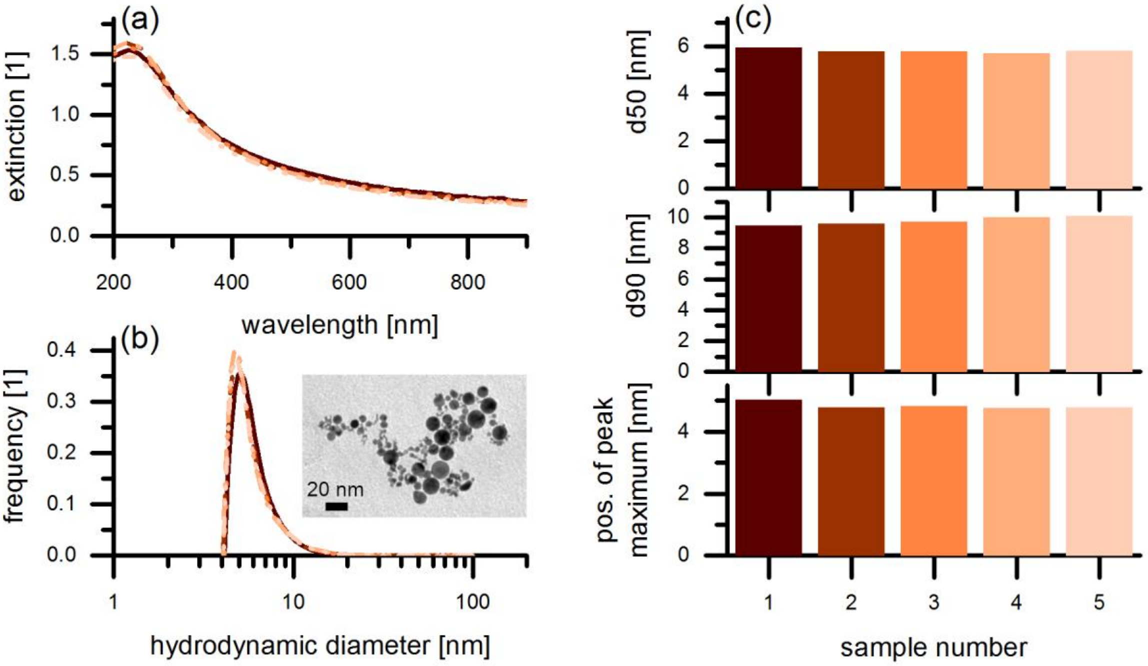

Fig. 2. Reproducibility and robustness of the automated colloid production system. (a) UV-Vis extinction spectra, (b) number-weighted size distributions measured with analytical disc centrifugation, and (c) extracted size indices of five aqueous Pt colloids. All colloids were produced at the same parameters of the automated synthesis machine. In (b), an exemplary TEM image of Pt nanoparticles of one of the samples is shown.

4. Conclusions

We conclude that the developed automated laser synthesis machine generates colloidal nanoparticles of consistently high quality with great power efficiency. The monolithic microchip laser built into the machine produces nanoparticles with significantly higher efficiency than typical lasers for the synthesis method. Furthermore, the small size of the microchip laser allowed us to realize a compact, laser-safe, laboratory machine. Our machine enables on-demand access to colloidal nanoparticles of a wide variety of materials to research and development laboratories of different disciplines. This may boost research and development based on colloidal nanoparticles and provides convenience in the daily lab work.

The laser ablation method can be used to produce a wide variety of solids as colloidal nanoparticles. We are currently expanding the range of qualified materials to include base metals and their alloys. For this purpose, we are integrating organic dispersants into the automated operation to avoid oxidation of ignoble elements, such as non-precious alloys, e.g. for catalysis research. In addition, we want to take advantage of the scalability of the synthesis method in the future to develop automated machines for use in pilot and industrial production.

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