Synthesis of gold, platinum, and gold-platinum alloy nanoparticle colloids with high-power megahertz-repetition-rate lasers: the importance of the beam guidance method

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Abstract

Nanoparticles of noble metals and their alloys are of particular interest for biomedicine and catalysis applications. The method of laser ablation of bulk metals in liquids gives facile access to such particles as high-purity colloids and is already used in industrial research. However, the method still lacks sufficient productivity for industrial implementation into series production. The use of innovative laser technology may help to further disseminate this colloid synthesis method in the near future. Ultrashort-pulsed lasers with high powers and megahertz-repetition-rates became available recently, but place high demands on the accurate optical laser pulse delivery on the target. Full lateral pulse separation is necessary to avoid a reduction of nanoparticle productivity due to pulse shielding. In this study, we compare flexible but rather slow galvanometer scanning with much faster but more expensive polygon-wheel scanning in their performance in the production of colloidal nanoparticles by laser ablation in liquid. Both beam guidance technologies are applied in the laser ablation of gold, platinum, and a gold-rich platinum alloy in micromolar saline water. We found that the dimensions of the scan pattern are crucial. A threshold pattern length exists, at which one scan technology becomes more productive than the other one. In addition, a much lower productivity was found for the ablation of gold compared to that of platinum. Alloying gold with only 10 at.% of platinum improved the productivity nearly to the level of platinum, reaching 8.3 g/h.

Keywords Ablation · AuPt · Polygon · Productivity · Galvanometer · Scan

Introduction

Nanoparticles of the noble metals gold and platinum are highly relevant for application in biomedicine (Elahi et al. 2018), (Pedone et al. 2017) and heterogeneous catalysis (Priecel et al. 2016), (Pareek et al. 2017). In both fields, bimetallic nanoparticles even show improved properties compared to single-metal particles (Jang et al. 2015), (He et al. 2017), (Zhang et al. 2020).

Laser synthesis of colloids (LSC) is a method used to produce colloidal nanoparticles by laser ablating the surface of a solid material, which is immersed in a liquid (Zhang et al. 2017), (Amendola et al. 2020). The main advantages

of the method are its straightforward experimental design, a high variety of applicable combinations of solid material and liquid, and the absent need of using ligands to control the nanoparticle formation. Gold (Torres-Mendieta et al. 2016), (Binaymotlagh et al. 2016), (Dittrich et al. 2019) and platinum (Angelov et al. 2016), (Mendivil Palma et al. 2016), (Censabella et al. 2019) are often-used materials for LSC studies due to their high relevance for application.

No less often, LSC studies focus on alloys. The method makes alloy nanoparticles easily accessible, even in compositions difficult to produce by conventional methods, showing particular application potential and superior performance in heterogeneous catalysis (Reichenberger et al. 2019). Recently, kg scale of laser-generated PtPd/Al₂O₃ automotive exhaust gas catalysts were tested in reference reactions of CO and NO oxidation within an industrial test setting where the laser-made catalysts showed a comparable CO oxidation and even higher NO oxidation activity and durability (Dittrich et al. 2020). An important contribution in the field of catalytic applications was made by Canadian

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researchers, who used gold-platinum alloy nanoparticles of various compositions prepared by LSC (Zhang et al. 2012), (Oko et al. 2014), (Oko et al. 2015). Due to the high application potential, we have selected gold, platinum, and a gold-platinum alloy ($\text{Au}_{90}\text{Pt}_{10}$) for this study. The limited miscibility of gold and platinum makes only dilute alloys with gold as the base metal and a maximum platinum content of about 10 at.% accessible by means of conventional melt alloying (Okamoto and Massalski 1985). We chose this platinum content to obtain plasmon damping effect as a proof of the formation of successfully alloyed, bimetal particles (Hodak et al. 2001).

LSC pushes towards industrial application, being already commercialized on three continents (Amans et al. 2019), but still limited nanoparticle productivity is a barrier to overcome. Note that LSC is more economic than wet chemical synthesis, but only if gram scale production can be achieved (Jendrzey et al. 2017). Productivity scales with laser power and thus the attractiveness of the process increases with advancing laser technology (Zhang et al. 2017). Lasers that are more powerful must, therefore, be implemented in LSC, but the challenge is to invest the laser power efficiently in the generation of nanoparticles, i.e., to bring the photons to the target without shielding.

The process of nanoparticle formation in LSC includes a temporal stage, in which a micrometer-scale cavitation bubble forms on the surface of the ablation target during the interaction of the ablation plume and the solvent (Ibrahimkuty et al. 2012; Dell’Aglia et al. 2015; Sasaki et al. 2009; Tiberi et al. 2013). Hence, the interaction of the cavitation bubble and consecutive laser pulses causes a reduction of the overall nanoparticle productivity and must be avoided. This can be achieved by relative displacement between the target surface and the beam, either by very fast target surface agitation via rotational target movement (Nandini et al. 2017; Resano-Garcia et al. 2016) or by beam guidance methods via sufficiently fast laser beam scanning (Wagener et al. 2010), (Zhang et al. 2017). Higher average laser powers are realized today either by increasing the laser pulse energy or the pulse repetition rate. Since high pulse energies cause high peak powers and pose the risk of the occurrence of productivity-reducing effects, e.g., ablation chamber window destruction or optical breakdown of the solvent (Noack and Vogel 1999), the strategy of increasing the pulse repetition rate is often preferred. The deflection speed of the laser scanning system must be increased accordingly to transfer the additional laser power as loss-free as possible to the ablation target. The necessary scanning speeds to achieve full spatial pulse separation can be easily calculated for a known size of the cavitation bubble. Assuming a bubble diameter of about 100 μm (Tomko et al. 2015), a lateral scanning speed of 1 m/s is required for full spatial pulse separation at a pulse repetition rate of 10 kHz. Such speeds can be easily

achieved with galvanometer scanners. But 100-times faster scanning speeds are required for pulse separation at 1 MHz repetition rate. However, these scanning speeds can only be realized with a different technology such as scanners based on polygon-wheels.

We combined a high-power, megahertz laser and a polygon-wheel scanner in the past to achieve the highest productivity in LSC reported so far (Streubel et al. 2016a), however, in that study a comparison with LSC employing galvanometric scanners was not given. In addition, in (Streubel et al. 2016a) only about half of the average power of the laser system was available due to the duty cycle required by the polygon scanner. When working with polygon-wheel scanners, the laser power delivery to the scanner has to be switched off during the transition from one facet mirror to another to avoid uncontrolled deflection at the mirrors’ edges, and the risk of damaging the polygon. The duty cycle describes the time in which the laser power delivery is switched on in relation to the total processing time. While in (Streubel et al. 2016a), the power-specific ablation rate, i.e., the produced nanoparticle mass per hour per Watt, was 16 mg/(h $\times$ W) referring to the output power of 250 W delivered to the polygon, galvanometer scanners can work at full available laser power. Kohnsackowski et al. recently demonstrated that galvanometric-scanned, nanosecond-pulsed LSC can achieve similar power-specific nanoparticle productivities (Kohnsackowski et al. 2017), however, in that study the authors compared two different laser systems (nanosecond- and picosecond-pulsed) at different output powers. A direct comparison of the two scanning methods is still missing, in particular for megahertz LSC. The question arises whether ultrashort-pulsed LSC at megahertz repetition rates is more productive at full average power using a galvanometer scanner or at complete pulse separation using a polygon-wheel scanner.

Methods

LSC was performed using a ps-pulsed laser (500flex, Amphos GmbH, Herzogenrath, Germany) with up to 450 W average output power. The fundamental wavelength was 1030 nm, the laser pulse duration was 3 ps, and the pulse repetition rate was 5 MHz. A galvanometer scanner (intelSCAN-20, Scanlab AG, Purchheim, Germany) was used at a scanning speed of 5 m/s and a polygon-wheel scanner (Poly 500, Amphos GmbH, Herzogenrath, Germany) was used at a speed of 484 m/s on the fast axis. The polygon-wheel scanner combined a polygon wheel (fast axis, scanned the length of the pattern) and a galvanometer scanner (slow axis, scanned the width of the pattern). The full available laser power of 450 W could be used during LSC with the galvanometer scanner, apart low minor losses at reflective

and refractive optics that were in the range of the measurement accuracy of the power meter. A galvanometer scanner typically has two reflective mirrors to scan the x- and the y-axis of two-dimensional patterns. The reader is referred to Fig. 1a for an illustration of the mirror setup. All laser pulses can be continuously reflected in a controlled manner. In polygon-wheel scanners, one axis of the scan pattern is scanned by one galvanometer mirror but the second axis is scanned by a spinning polygon-mirror-wheel. The reader is referred to Fig. 1b for the setup. The facets of the polygon reflect laser pulses in a controlled way towards the ablation target but not their edges. Reflections from the edges in between two facets would be reflected inside the scanner housing and could damage the system and the mirror bonding. This is avoided by switching off the laser beam whenever it would be reflected by polygon edges. This off-time of the laser limits the delivered power. Typically, the term duty cycle is used in literature which represents the opposite of the off-time, i.e., the on-time. In addition, the length of the scan pattern along the polygon-scanned axis increases the off-time the shorter the length is. At a length of 13 mm, the available laser power of 450 W was reduced to a delivered power of 60 W for our setup. Both scanners have an f-theta lens at their outlet.

Fig. 1 Schematic illustration of the different LSC experimental configuration that uses a galvanometer (**a**) or a polygon-wheel (**b**) scanner. By the beam guidance strategy in **a**, all pulses are delivered to the target, but at the high lateral overlap, whereas in **b** only half of the pulses are delivered but at full lateral separation

All applied scan patterns were rectangular and filled with lines scanned from bottom to top. The distance between single lines was 50 μm . F-theta lenses with focal distances of 212 mm (galvanometer scanner) and 142 mm (polygon-wheel scanner) were used. Note that an ordinary focusing lens would create a laser fluence variation with the angular position of the rotating mirror, which then would affect the ablation rate to deviate between the target center and its edges. F-theta lenses (which are actually a lens system) are employed to minimize these fluence deviations and are widely used in many laser-scanning applications, in particular in precision laser micromachining. Nominal lateral distances between the centers of consecutive pulses were 1 μm (galvanometer scanner) and 97 μm (polygon-wheel scanner), respectively. The working distance between the f-theta lens and the target surface was adjusted for each combination of the scanner and the target material to achieve maximum nanoparticle productivity.

LSC was performed in continuous flow of 0.1 mM aqueous sodium chloride solution having a volume flow rate of 30 L/h. Each LSC run lasted 5 min. Note that in (Streubel et al. 2016a) we showed for the same laser system that the produced nanoparticle mass linearly increases with the ablation duration. Hence, unlike batch chamber setups with unsteady concentrations and back-mixing of volume elements into the beam's cross-section, ultrafast scanning combined with liquid flow allows to extrapolate data from 5 min experiments to g/h statements. In all cases, the delivered power (behind all optical elements) was used to calculate the power-specific ablation rates when evaluating the results.

Two fundamental LSC experimental series were conducted. In the first series, the nanoparticle productivity of LSC of platinum (99.95%; Allgemeine Gold- und Silberscheideanstalt AG, Pforzheim, Germany) was compared for both scanners in dependence on the delivered laser power. Variation of the delivered laser power was performed by adjusting the average laser power in case of using the galvanometer scanner and by adjusting the length of the fast scan axis, i.e., the duty cycle, using the polygon-wheel scanner. During LSC with the galvanometer scanner, the dimensions of the scan pattern were kept constant at 60 mm $\times$ 15 mm and the laser pulse energy (maximum: 90 μJ) was varied with the delivered laser power. During LSC with the polygon-wheel scanner, the pulse energy was kept constant at 90 μJ and the length of the scan pattern (maximum: 60 mm) was varied. The width of the pattern was kept constant at 15 mm.

In the second experimental series, the nanoparticle productivity of LSC of platinum, gold (99.99%; Allgemeine Gold- und Silberscheideanstalt AG, Pforzheim, Germany), and a gold-platinum alloy ($\text{Au}_{90}\text{Pt}_{10}$; produced by a local goldsmith in Essen, Germany) was compared using both scanners. The dimensions of the scan pattern were kept constant at 13 mm $\times$ 12 mm. This smaller pattern was chosen

because of the dimensions of the alloy target. The laser pulse energy was kept constant at 90 μJ . The delivered laser power was 450 W for using the galvanometer scanner and 60 W for using the polygon-wheel scanner.

Extinction spectra of colloids were determined using an extinction-calibrated UV-Vis spectrometer (Evolution 301, Thermo Fisher Scientific Inc., Waltham, USA). The integration of the spectra was done in the range of 190 to 900 nm for the determination of the relative mass concentration and for identifying the optimum working distance for maximized nanoparticle productivity. Size distributions of nanoparticles were evaluated by transmission electron microscopy (TEM) (EM 910, Carl Zeiss Microscopy GmbH, Jena, Germany). More than 500 particles were analyzed for each sample.

Scanning electron microscopy (SEM) (XL30, Koninklijke Philips N.V., Amsterdam, Netherlands) was used to analyze the surfaces of the ablation targets.

Results and discussion

Effect of beam guidance method on the productivity of platinum LSC

We compared the nanoparticle productivity and power-specific efficiency for LSC of platinum for the two different beam guidance methods using an LSC-setup that utilized a galvanometer and a setup with a polygon-wheel scanner. Figure 1 illustrates the key differences between both experimental approaches. This comparison is of interest because both scanning technologies have different drawbacks, which have not yet been compared in the context of LSC. In MHz-pulsed LSC, the use of galvanometer scanners leads to a strong local overlapping of subsequent laser pulses. It is known that this leads to productivity losses (Wagener et al. 2010), (Streubel et al. 2016a). This problem can be avoided using the faster polygon-wheel scanners. However, the available power of the laser system is significantly reduced. In our case, the delivered power represents only about 50% of the available power at optimum scan conditions. So the question arises to which extend the trade-off between better lateral pulse separation (higher pulse-specific ablation) and 50% less pulses delivered to the target depends on the target length (see also Fig. 3) or the target material (see Fig. 4).

Figure 2 shows the comparison of the absolute and the power-specific ablation rate during LSC of platinum in micromolar saline water using the polygon-wheel (a) and the galvanometer scanner setup (b) at different laser powers. The “laser power” is differentiated into “available laser power” and “delivered laser power” for the comparison. The available laser power represents the full average output power of the laser system. This laser system output power is reduced to the (target-)delivered power due

to power-off switching initiated in the communication of the laser system and the scanner. During galvanometer scanning, power-off switching is related to jumps in the design of the scan pattern and was less than 3% in our study. During polygon-wheel scanning, power-off switching is for component damage protection and process safety reasons and was about 50% here. For the calculation of the power-specific ablation rate, the delivered laser power was used. At the available power maximum of the laser system, an ablation rate of 8.3 g/h could be achieved during LSC of platinum using the polygon-wheel scanner. With the galvanometer scanner, the maximum ablation rate was 60% less (3.4 g). An even larger difference was found in the comparison of the power-specific ablation rate, which was 37.8 mg/(h $\times$ W) using the polygon-wheel scanner at maximum power and reduced by 80% using the galvanometer scanner [7.4 mg/(h $\times$ W)]. Kohsakowski et al. reported a power-specific ablation rate of 12.6 mg/(h $\times$ W) during the LSC of platinum (Kohsakowski et al. 2017) and Streubel et al. reported 16.2 mg/(h $\times$ W) (Streubel et al. 2016a).

Consequently, less power was transferred to the ablation process of platinum using the galvanometer scanner, the laser energy was probably dissipated as heat in the ablation target (Waag et al. 2019). The origin of energy dissipation most likely was due to scattering of incident laser light by the cavitation bubble induced by the previous laser pulse (Wagener et al. 2010), (Streubel et al. 2016a). The lateral distance of the spot centers of two consecutive laser pulses was only 1 μm for the applied galvanometer scanning resulting in a pulse overlap greater than 98% for a calculated spot diameter of 61 μm (calculated based on the used optics, the applied experimental LSC setup, and the laser beam properties).

Increasing the laser power led to a reduction of the power-specific ablation rate for both scanning strategies. In the case of the galvanometer scanner, this effect can be explained by an increasing amount of scattered laser pulse energy at higher laser powers keeping power-off time or duty cycle constant. Increasing the pulse energy from 25 μJ (125 W) to about 90 μJ (450 W) also is known to lead to a larger size of the cavitation bubble (Tomko et al. 2015), (Reich et al. 2017) and thus to a larger overlap of the bubble with subsequent laser pulses. Variation of the laser power was achieved by variation of the duty cycle during LSC using the polygon-wheel scanner. The decreasing power-specific ablation rate, which was observed at higher laser powers (Fig. 2a), indicated that persistent products of LSC, like nanoparticles and microbubbles, also contributed to the loss of power efficiency (Kalus et al. 2017). The fast scanning speed fully prevented lateral pulse overlap, but longer duty cycles led to longer interaction intervals of the delivered laser pulse trains and persistent LSC products in the beam path.

Fig. 2 Ablation rate and power-specific ablation rate determined for the LSC of platinum at different laser powers using the polygon-wheel (a) and the galvanometer scanner (b). The delivered power

(behind all optical elements) was used to calculate the power-specific ablation rate. Exponential functions were fitted to the data. *Poly* polygon-wheel scanner, *Galvo* galvanometer scanner

Fig. 3 Ablation rate determined for the LSC of platinum at different lengths of the scan pattern using the polygon-wheel (a) and illustration of on- and off time during polygon-wheel scanning of targets with larger (b) and smaller (c) scan patterns. The red line in a marks the expected maximal ablation rate achievable using the galvanometer scanner, which represents the break-even target length of ≥ 15 mm

Effect of scan pattern length on the productivity of LSC with polygon-wheel scanner

The length of the scan pattern along the fast scan axis of a polygon-wheel scanner has a significant impact on the duty cycle, i.e., the delivered laser power. Figure 3a demonstrates the effect of the variation of the length of the scan pattern on the ablation rate for our LSC setup with the polygon-wheel scanner. The red line shows a scan-pattern-independent, constant ablation rate for galvanometer scanning. In addition, a blue arrow marks the critical length (15 mm) of the scan pattern along the fast scan axis, which is necessary to deliver enough laser power for a more productive synthesis of platinum with the polygon scanner. The effect of the

where polygon is more effective. All power values represent the delivered laser power. Exponential functions were fitted to the data. The blue arrow marks the critical length of the scan pattern, at which LSC of platinum with both scanners is equally productive. *Poly* polygon-wheel scanner, *Galvo* galvanometer scanner

length of the scan pattern along the fast scan axis on the off- and on-time of the laser, i.e., the duty cycle and delivered power, is sketched in Fig. 3b and c. Overall, there has to be a break-even point of the galvanometric and polygon-based beam guidance methods in LCS, where the polygon wins with increased target length. For platinum, this break-even is found at a minimal target length of 15 mm. The upper target size limit is defined by the flat-field image plane's dimensional accuracy set by the f-theta lens. At a maximal tolerable focal distance deviation along with the target of ± 1 mm (Streubel et al. 2016b), this upper target length is 60 mm.

Effect of scan pattern length on the productivity of LSC with polygon-wheel scanner

Figure 4 shows the results of a comparison of the power efficiency during LSC of gold, platinum and $\text{Au}_{90}\text{Pt}_{10}$. Both previously introduced scanners were used. LSC was performed with a scan length of 13 mm, which is close to the critical scan length found for platinum (Fig. 3a). Much higher power-specific ablation rates were found for LSC with polygon-wheel scanning compared to galvanometer scanning. The specific ablation rate was found to be the highest for platinum with 47 mg/(h × W) followed by $\text{Au}_{90}\text{Pt}_{10}$ [44 mg/(h × W)] and gold [21 mg/(h × W)]. Interestingly, the low amount of platinum in the gold-rich alloy increased the ablation yield to a comparable level of pure platinum. Switching from polygon-wheel scanning with full pulse separation to galvanometer scanning with huge lateral pulse overlap reduced the power-specific ablation rate by factors of 16 (gold), 7 (platinum), and 11 ($\text{Au}_{90}\text{Pt}_{10}$), respectively. Surprisingly, the similarity of platinum and $\text{Au}_{90}\text{Pt}_{10}$ seemed to be weakened at strong pulse overlapping.

We analyzed the surface topographies of the targets after laser ablation for further investigation of the different changes in the power-specific ablation rates found for the three metals. The SEM images in Fig. 5 show patterns of microscale segments on the ablated surfaces of all targets, but with much higher similarity for gold and the gold-rich alloy. While an elongated pattern was found on gold and the gold-rich alloy, more randomly shaped structures appeared on platinum. In the case of $\text{Au}_{90}\text{Pt}_{10}$, a tendency to randomness existed for the topography. On closer inspection of the topographies, finer periodic structures could also be identified on all targets, which can be classified as laser-induced periodic surface structures (LIPSS) (Bonse et al. 2017).

The coexistence of regular microstructures and LIPSS on surfaces ablated by ultrashort laser pulses has been observed before (Tsukamoto et al. 2007), (Li et al. 2015), (Zhang and Sugioka 2019). Li et al. observed periodic mounds covered with concentric ripples after femtosecond-pulsed laser ablation of stainless steel in air (Li et al. 2015). The authors classified the formation of mounds, when increasing the number of laser pulses, in four stages: (1) formation of LIPSS, (2) generation of mound precursors from LIPSS, (3) formation of isolated mounds, and (4) linking of isolated mounds to a periodic mound network. Local differences in the laser fluence and the ablation rate are the main driving force. The microstructures found in our experiments resemble the as-described mound network but also differ in morphology in the case of gold and $\text{Au}_{90}\text{Pt}_{10}$. Interestingly, the elongation of the patterns on gold and $\text{Au}_{90}\text{Pt}_{10}$ took place along the direction of the fast scan axis of the polygon-wheel scanner. The elongation may have been induced by heat accumulation. It is a common effect during high-repetition-rate laser

Fig. 4 Power-specific ablation rate determined for the LSC of gold, platinum and $\text{Au}_{90}\text{Pt}_{10}$. Blue arrows symbolize the increase of the power-specific ablation rate when switching from galvanometer to polygon-wheel scanning. *Poly* polygon-wheel scanner, *Galvo* galvanometer scanner

material processing, which also affects the topography of the processed target surface (Eaton et al. 2005), (Di Niso et al. 2014), (Weber et al. 2014). This indication for a contribution of thermal energy to the pattern formation may be a link to the observed convergence of gold and $\text{Au}_{90}\text{Pt}_{10}$ in their ablation yield in LSC with the galvanometer scanner, i.e., with quasi full pulse overlap.

In contrast to the topographies on the laser-ablated targets, the colloids of platinum and $\text{Au}_{90}\text{Pt}_{10}$ share a more similar appearance than those of gold and $\text{Au}_{90}\text{Pt}_{10}$ (Fig. 6a). This is also expressed by the UV-Vis extinction spectra (Fig. 6b). The surface plasmon resonance (SPR) peak can be clearly seen for the gold colloid. The SPR peak is also present in the spectrum recorded for the $\text{Au}_{90}\text{Pt}_{10}$ colloid, but strongly reduced compared to gold. The presence of platinum at the surface of gold-rich particles strongly damps the plasmon band of gold and thus the extent of the non-linear optical response (Hodak et al. 2001). This strong damping of the plasmon resonance at comparable mass concentrations of the colloids and at similar particle size distributions (Fig. 6c) indicates the bimetallic character of the particles. Zhang et al. already found that solid-solution alloy nanoparticles of gold and platinum can be synthesized by LSC (Zhang et al. 2012). The observed similarity in the electronic structure of platinum and $\text{Au}_{90}\text{Pt}_{10}$ colloids may also be connected to the similar ablation behavior found during LSC with the polygon-wheel scanner, i.e., with no pulse overlap. The transfer of laser energy absorbed by electrons of the conduction band to the lattice of the metals could take place on a comparable time scale for bulk platinum and $\text{Au}_{90}\text{Pt}_{10}$.

The results of the analysis of the ablation targets and the produced nanoparticles suggest that differences in the electronic structure of the conduction bands of the investigated metals play the main role in the origin of their ablation

Fig. 5 Representative SEM images of the surfaces of gold (a), platinum (b), and $\text{Au}_{90}\text{Pt}_{10}$ (c) targets after LSC using the polygon-wheel scanner

behaviors. Both absorption and thermal conduction properties of the metals are affected. Platinum absorbs light of the laser wavelength of 1030 nm by a factor of 0.3 more efficiently than gold (Werner et al. 2009) and couples energy almost by a factor of two faster from electrons to phonons (Norris et al. 2003). Both properties are favorable for an increased ablation per pulse, which agrees with our results found using the polygon-wheel scanner (Fig. 4). The absorption properties of $\text{Au}_{90}\text{Pt}_{10}$ are closer to those of gold as indicated by its reflectivity in the near IR (Shiraishi and Tilley 2014). On the other hand, the electron–phonon coupling of the alloy is more comparable to that of platinum (Hodak et al. 2001), (Hartland 2004). Point defects in crystals, such as substitutional atoms in diluted alloys, have a direct effect on the local electron band structure and thus may scatter lattice oscillations (Maradudin 1966). Hence, platinum atoms in the gold lattice also reduce the heat conduction of the alloy compared to pure gold. In fact, the total heat conductivity of pure gold is by a factor of 4.4 higher than for platinum (Cook and van der Meer 1970), (Powell and Tye 1963) and presumably by a factor of 2.7 higher than for $\text{Au}_{90}\text{Pt}_{10}$ (Singh and Yadawa 2010). Faster energy coupling

into the lattice and reduced energy dissipation could be the cause of the beneficial effect of adding a comparably low amount (only 10%) of platinum to the gold lattice towards more productive LSC at full lateral pulse separation.

Switching the LSC-setup from a setup with polygon-wheel to a setup with galvanometer scanning, i.e., causing quasi full pulse overlapping, led to a much stronger reduction of the power-specific ablation rate of gold compared to platinum (Fig. 4). The reduction of the power-specific ablation rate for $\text{Au}_{90}\text{Pt}_{10}$ was found to be in between those of the pure metals. We assume that the heat conductivity of the ablation target contributed more strongly to LSC using galvanometer scanning compared to polygon-wheel scanning. In addition, Wagener et al. observed decreasing ablation rates at increasing inter-pulse distances above full pulse separation during picosecond-pulsed LSC of zinc in tetrahydrofuran (Wagener et al. 2010). The authors assumed that heat of previous laser pulses affected the target volume around the crater and reduced its fluence threshold for ablation. Thus, a contribution of dissipating heat of previous laser pulses to the overall ablation can be assumed also in our experiments, in particular at full pulse overlap.

Fig. 6 Photographs (a), UV-Vis extinction spectra (b), and particle size distributions (c) of Au, Pt, and $\text{Au}_{90}\text{Pt}_{10}$ nanoparticles and nanoparticle colloids produced by LSC using the polygon-wheel scanner. Spectra in b were factorized by 2.3 (Au), 1.1 ($\text{Au}_{90}\text{Pt}_{10}$), and 1.0 (Pt)

to normalize the extinction by mass concentration. In c, characteristic parameters (x_c : center value, σ : standard deviation) of lognormal fits are given. For single size distributions in c, more than 500 particles were counted

Dissipated heat is also most likely responsible for the different behavior of the power-specific ablation rates between gold, platinum and Au₉₀Pt₁₀ during LSC with the galvanometer and the polygon-wheel scanner.

The primary particle diameters reported in Fig. 6c are quite typical for LSC of noble metals in water if micromolar saline is used for in-situ size quenching caused by the presence of anions (Sylvestre et al. 2004), (Marzun et al. 2015). At high power MHz LSC, in-process fragmentation also contributes to a narrowed particle size distribution. Recently, it has been shown with the same polygon system that the mass fraction selectivity towards small particles is adjustable between 5 and 40% by balancing between the in-process fragmentation (downsizing) and ablation (overall productivity) particle formation pathway (Dittrich et al. 2020).

Conclusion

New, more powerful lasers may increase the relevance of LSC for the industrial production of colloidal noble-metal nanoparticles for application in biomedicine or catalysis. However, higher laser powers also bring challenges. The additional power must be efficiently transferred into nanoparticle generation. When using high-power lasers with megahertz repetition rates in LSC, beam guidance plays a key role in this context.

We compared two beam guidance technologies, i.e., galvanometer and polygon-wheel, in picosecond-pulsed LSC of noble metals and found that polygon-wheel scanners allow a more efficient invest of the delivered laser power in the nanoparticle generation. However, the delivered power depends on the length of the scan pattern, which typically equals the maximum length of the target to be ablated. At short pattern length, galvanometer scanners can lead to more productive LSC even though their power efficiency is lower. We found a threshold pattern length of 15 mm for LSC of platinum with our setup. Hence, high-throughput colloid production requires large target dimensions, to minimize laser downtime during target exchange after its mass is ablated.

We also found a 2-times higher picosecond-LSC productivity for platinum compared to gold at individually optimized conditions for high productivity. Interestingly, LSC of the dilute alloy of both metals with only 10 at.% of platinum (7.8 g/h) was as productive as LSC of elemental platinum (8.3 g/h) due to the inference of the electronic structure of gold by platinum atoms. The interference causes faster energy coupling and lower heat conductivity, which seemed to improve LSC productivity.

In conclusion, polygon-wheel scanners enable more power-efficient LSC than galvanometer scanners and are, therefore, better suited for the industrial production of

colloidal nanoparticles despite the loss of power caused by the optical duty cycle. Only for low target dimensions, i.e. below 15 mm for LSC of platinum with our setup, galvanometric scanners become a feasible alternative. In addition, for dilute alloys, a significantly higher LSC productivity may be possible to achieve than for the base metal. As dilute alloying may have no large or sometimes even a beneficial effect on some alloy properties, e.g., for catalysis applications, it could provide an alternative to pure metals in LSC.

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Data availability All available data is presented in the manuscript and can be requested as raw data from the corresponding author.

Compliance with ethical standards

Conflict of interest There are no conflicts of interest to declare.

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