Synthesis of ultra-small gold nanoparticles by ns-pulsed laser fragmentation in liquids - Impact of laser intensity and electrolytes on particle size

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Pulsed laser fragmentation in liquids (LFL) is a useful tool to tune the particle size of laser-fabricated nanoparticles (NP) [1], yielding ultra-small NP (USNP) with mean diameters < 3 nm. However, adequate process control requires an understanding of the PLFL mechanisms, which could be affected by the laser parameters, the size of the educt NP, and the composition of the medium. Typically, the pulse duration is discussed as a decisive criterion ruling the fragmentation process. Commonly, distinctions are made between electronically induced Coulomb explosion for high laser peak powers (ultrashort pulses) and thermally induced evaporation for low laser peak powers [2]. Immediately after the laser pulse, the USNPs must be stabilized to prevent coalescence processes. In case NP are synthesized without organic ligands, electrostatic stabilization by ions, similar to that previously reported for laser ablation in liquids [3], is anticipated.

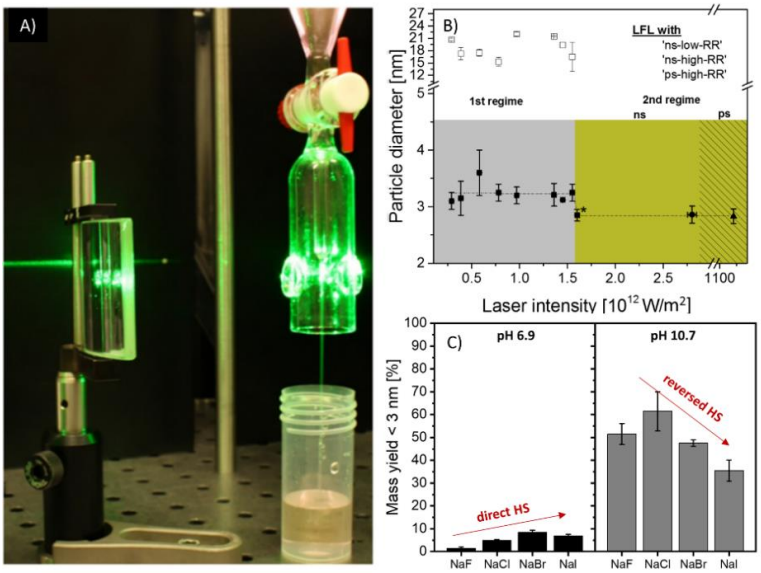

Figure 1: A) Illustration of the fragmentation process [1]. B) Plot of the resulting particle sizes after fragmentation with different laser intensities. Squares show the results after fragmentation with a 9 ns laser with 0.1 kHz ('ns-low-RR'), circles show the result after fragmentation with a 2 kHz, 7 ns laser ('ns-high-RR') and triangles the results after PLFL

In this work, we systematically examined the LFL of AuNP with high-intensity nanosecond pulses and aimed to differentiate effects associated to physical parameters (laser intensity) and chemical effectors (medium composition). All experiments were carried out in a liquid flow passage reactor, which allows a precise control of the energy input per volume (Figure 1A). In an initial study we examined to what extent the laser intensity and the educt particle size affect the size distribution of the resulting USNP. These findings indicate that the fragmentation process is a one pulse and one step event, yielding monomodal AuNPs in case a pulse peak power of 1.62×10^{12} W/m^2 is exceeded and all educt particles are larger than 13.4 ± 2.1 (Figure 1B). In a second study we examined whether the pH and ionic strength of the aqueous fragmentation medium influences the resulting particle size distributions and mass yield of NP < 3 nm. We could verify a significant synergism between pH and specific ion effects, yielding the highest mass yield of USNPs at pH = 10 and at micromolar sodium chloride concentrations. Furthermore, our findings indicate that the influence is anion specific, following a direct Hofmeister series (HS) of anions at neutral pH and an inverse HS in the alkaline regime (Figure 1C).

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