Stable nano-silver colloid production via Laser Ablation Synthesis in Solution (LASiS) under laminar recirculatory flow

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Abstract. As nanomaterials find applications in an increasingly diverse range of fields such as wastewater treatment, biotechnology and flexible electronics, the demand for nanomaterials with specific properties has increased. This increase is coupled with an increasing emphasis on nanomaterials with highly-specific properties for specialized applications. Industrially, nanomaterials are produced via wet-chemical techniques which employ the use of solvents and reagents which are environmentally harmful. As we move forward with the use of nanomaterials, the ability to produce nanomaterials in a sustainable manner has become a topic of great significance. Towards this end, Laser Ablation Synthesis in Solution (LASiS) is a physical production technique capable of producing tailored nanomaterial colloids in a sustainable manner. These colloids are produced by ablating a solid target immersed in a solvent using a laser. Typically, LASiS is conducted in a batch process and in small volumes limiting commercial viability. To overcome this, there has been a move towards the use of continuous production via LASiS using flow systems. This allows an increase in nanomaterial yield, resulting in colloids concentrations approaching those of commercial colloids. This work investigates a new production technique incorporating a laminar recirculatory flow system to produce stable high concentration nano-silver colloids.

I. Introduction

Silver nanoparticles (AgNps) are among the most widely studied and utilised nanomaterials in the world due to their uptake in applications across fields of electrical engineering, biotechnology and healthcare (1-4). However the established chemical synthesis nanomaterial production technique has a negative environmental impact due in part to its waste by-products. Furthermore, post-production washing steps may be need to remove ligands depending on the surface purity requirements of the application (5). Polymers bound on the nanoparticle surface can also be present post-production and they have been seen to detrimentally effect the conductivity of nano colloid printed circuits (2) . To combat these issues a “green-synthesis” technique has been developed over the past fifteen years. This technique utilises laser irradiation to ablate a solid material target submerged within a liquid, ejecting Nps from the plasma plume into the surrounding liquid, allowing for ligand free Np production and the potential for single step functionalisation. The emergence of LASiS can significantly reduce the amount of post-processing required when compared with chemical production.

However, there are drawbacks with the LASiS technique where high-cost laser systems must be employed to produce colloids of comparable concentrations to those made via commercial wet synthesis (6). Another potential route for LASiS is the focus on applications which are not well supported by chemical synthesis and which require specific Np properties. This avoids the requirement to meet the large-scale production efficiencies of chemical synthesis and can be achieved through the use of low-powered laser systems, reducing the capital costs and allowing bench-scale production of bespoke nanomaterials. One such use for these nanomaterials is the generation of silver thin-films which are gaining applications in various areas such as amplification of light energy in solar panels (7), localized surface plasma response barcodes (8), cell imaging (9), anti-microbial coatings (sub 40 nm peak diameter, concentration > 0.21 mg/L for cytotoxic effectiveness on Yeast (10) & >0.5 mg/L for E. coli cytotoxicity (11),(12)), food packaging (13) and conductive inks (> 15% *wt*.,70-150 mg/ml) (2),(14),(15). Thin-film production requires a narrow Np size dispersion and stable colloids at specific, repeatable concentrations. It is expected that LASiS can meet these demands using low power picosecond and femtosecond lasers systems, at relative low capital costs. However LASiS efficiency problems must be addressed; to-date there has been a transition from "batch" production towards "semi-batch" and "continuous". "Semi-batch" systems have been seen to be advantageous where defined colloid concentrations are required (16), however these system remain sub-optimal as laminar flow at the ablation site is not guaranteed. Near chemical synthesis efficiencies have been reached under certain production conditions (17), but post-production steps to increase the concentration would generally be required in order to obtain useable colloids, when using low power laser systems.

To offer a feasible ink colloid for thin-films printing, colloid quality and stability must be maintained along with increasing LASiS production efficiency. This study examines a new laminar flow semi-batch production process for the production of AgNps in terms of stability and colloid size distribution and the resulting colloid applicability to thin-films printing.

II. Experimental setup

Silver nano-colloids were manufactured utilising a "semi-batch" Laser Ablation Synthesis in Solution (LASiS) technique, described in Figure 1. The developed approach is unique in terms of other LASiS "semi-batch" processes, such as the one described by Nachev et al. (18), as it ensures uniform laminar flow at the ablation site. The irradiation source used in this work was a picosecond-pulsed WEDGE HF 1064 (BrightSolutions, Italy) Nd:YAG laser with a wavelength of 1064 nm, maximum output power of 1.2 W, a pulse width of 700 ps and a pulse repetition rate of 10 kHz.

The target material selected was silver plate (>99.999% metals basis, Scottsdale bullion silver) machined and mechanically polished to produce discs of 8 mm outer diameter and 4 mm thickness. The target was placed into a custom designed 3-D printed flow cell. De-gassed, de-ionized water was employed as the base colloid solvent for most of the tests, with the addition of 0.86 mg/L NaCl for additional colloid stability tests. The liquid was recirculated continuously over the surface of the target at a rate of 100 mL/min during the tests. The high flow rate solvent regime ensured that efficient Np production was carried out, enabling the removal of possible masking effects from the laser plume, cavitation bubbles or Nps at the ablation site. The colloid was recirculated within a PTFE piping loop (total volume 100 ml) until the end of the test. This setup allowed the production of colloid under the set processing condtions. The laser beam's spot size was controlled at 140 μm and operational fluence was

maintained at 1.83 J/cm^2. The beam was scanned in an Archimedean spiral across the target surface at a speed of 2 mm/s. Flow control was performed via automatic valve and peristaltic pump actuation via a developed LabVIEW control program. Productions tests were carried out each with a set duration of 15 minutes each.

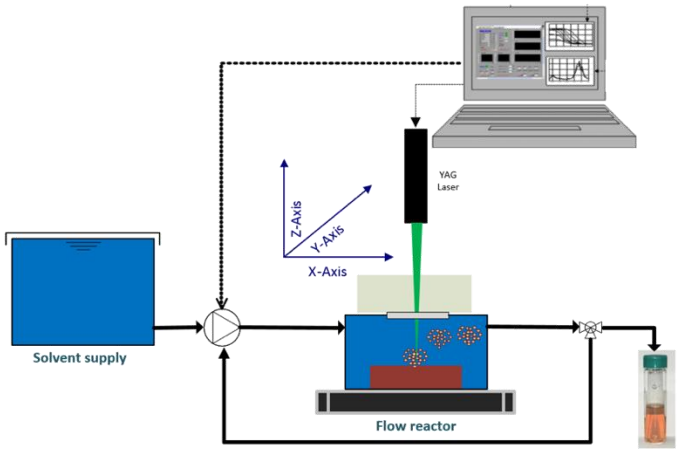


Figure 1: Schematic of the LASiS production setup including flow reactor cell containing the target material, solvent reservoir, laser system and control valves.

Metrology

The colloids size and morphology were determined with various analytical techniques. Np size distribution was determined via 180° backscatter dynamic light scattering (DLS) and transmission election microscopy (TEM). The DLS used was a NanoFlex (Microtrac), with analysis performed on 2 mL samples. A 60 s acquisition time was used averaging over a set of five measurements. Background correction was applied with the base colloid solvent, in this cases DI-water. The TEM used was an FEI Titan with Field Emission Gun and spherical aberration corrector system (Cs-corrector) of the objective lens operated at 300 kV. Analysis was performed using a copper mesh TEM grid with 40 µL of sample applied and allowed to evaporate at room temperature.

The Np colloids optical properties were characterized using a Biochrom Libra S22 UV/Vis spectrophotometer, with a scanning range of 200 – 900 nm with DI water background correction applied. For both DLS and UV-Vis measurements, a one-in-ten dilution of the colloid was used to mitigate measurement saturation, no post-filtration was performed, ensuring that the DLS and UV-Vis characterizations were representative of the production process.

A commercial silver Nps colloid (Sigma Aldrich, 10 nm, 25 ml, 0.02 mg/ml, SPR 403 nm, #730785) was compared against the produced colloids. The commercial colloid as measured via the same DLS and UV-Vis method as a calibration concentration reference.

III. Results and Discussion

The nano-colloid produced under continuous re-circulation conditions compares well with commercially available products prepared via wet chemical synthesis in terms of optical response, concentration and size dispersion. The DLS measurement observed a population size distribution peak at 21 nm, with the distribution ranging from 10 - 50 nm, see Fig. 2a. TEM imagining (see result in Fig. 2b) was in agreement with the hydrodynamic size distribution measured via DLS, noted in Fig. 2a.

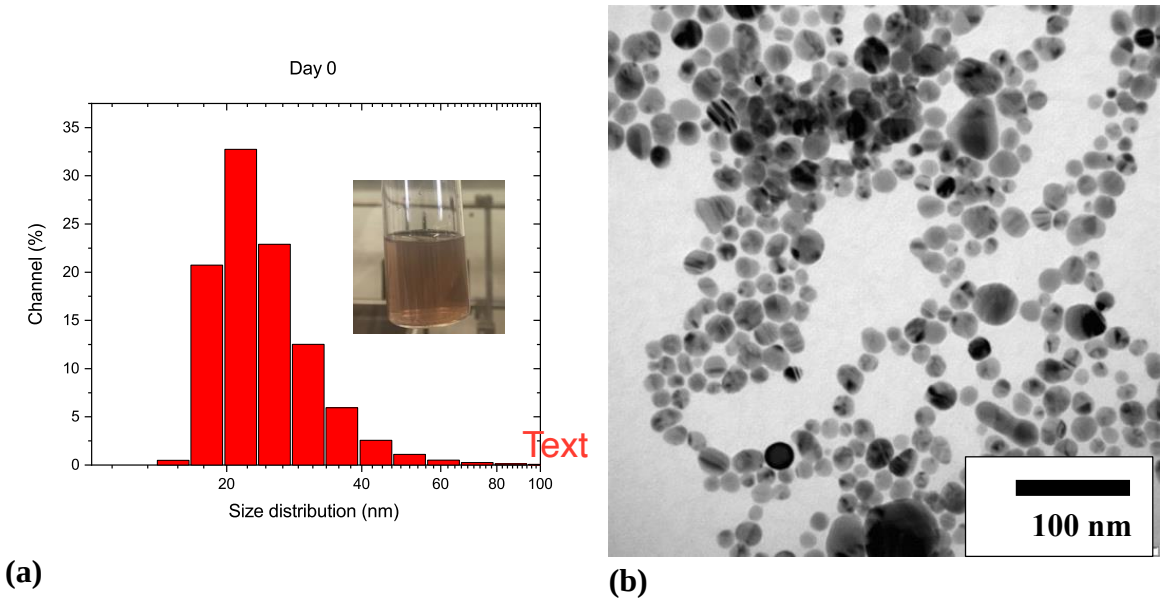


Figure 2: (a) DLS Np size distribution analysis, and (b) TEM image of AgNPs with scale bar of 100 nm.

TEM imagining indicated a small population of larger particles (>50 nm) not observed in the DLS analysis. These particles may be due to aggregation during the TEM grid drop-casting step, or alternatively sedimented during DLS measurement. This alludes to the continuing need for a secondary, direct measurement technique such as TEM when characterizing Nps. The colloids displayed a surface plasmon resonance (SPR) band at 396 nm (Fig. 3) with a red shift to 402 nm after twelve days stored at room temperature. This spectrum compares well with commercial AgNps with an SPR at 403 nm and those reported in literature for laser produced Nps (19), (20).

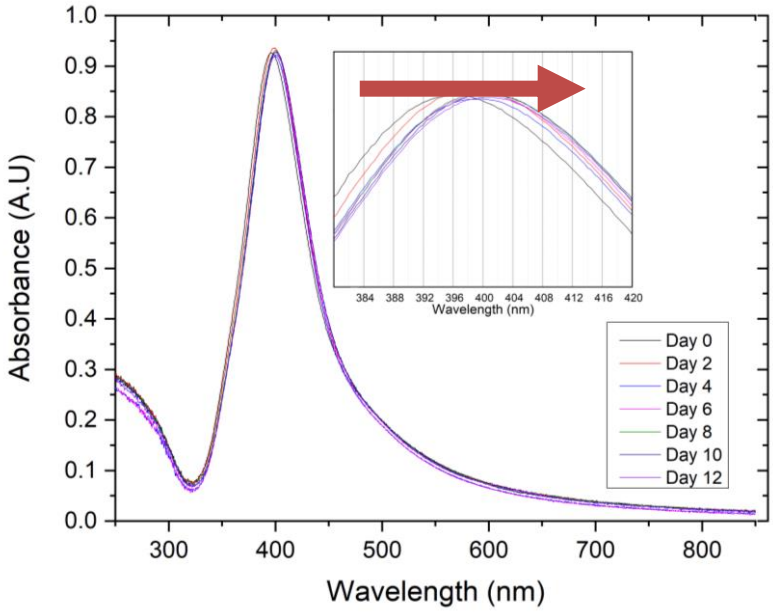
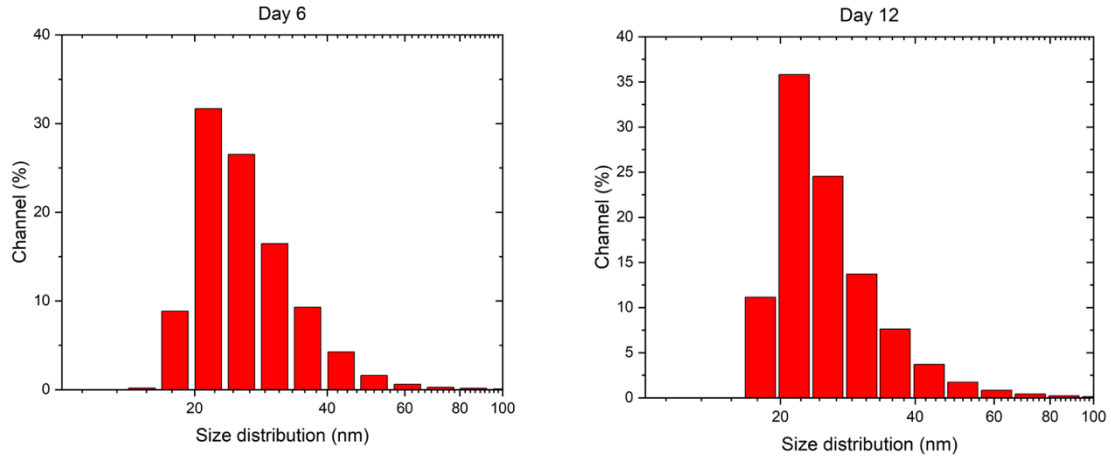


Figure 3: Absorption spectrum of AgNps produced, with a plasmonic peak at 396 nm at day 0, and red shifting towards 402 nm at day 12 while showing a small intensity drop.

The peak intensity changed by 1.7% within twelve days, this is well within the general range of 5% UV-Vis absorption reduction typically recorded post production for a stable colloid (21). Typically a red shift would indicate aggregation, however this would usually be linked with a higher drop in intensity. The short optical tail corresponds to a red tint in the colloid (22), and supports the assumption of low particle size dispersion present in the colloid. A change of Nps diameter of 1.7 nm after six days (Fig. 4a) was measured, this is less than the 2 nm resolution of the measurement device. No change was observed at day twelve. These results indicate that a highly stable colloid was produced, with similar size and SPR characteristics to the commercial colloid. Due to Np similarities, it allowed for a calibration curve of colloid concentration to absorption to be developed from a series of dilutions of the commercial colloid, starting with a known concentration. From this, it was estimated that LASiS produced colloid possessed a concentration of 0.091 mg/mL after the 15 minute ablation period, this yielded a colloid concentration higher than an example commercially available colloid (0.02 mg/ml).



(a) **(b)**

Figure 4: DLS analysis of AgNps colloid (a) after six days resting at room temperature, the peak diameter is 22.7 nm and distribution width (instrument defined variable, 2σ) is 11nm. After twelve days (b) the indicated distribution change is within the accuracy of the measurement device; with a peak diameter of 22 nm and width of 12 nm, (n=3,).

Electrolytes to aid size reduction

It has been well established that the presence of electrolytes in the ablation liquid can have a size quenching effect on particle formation (23). The NaCl acts as a stabiliser on initial particles formed within the cavitation bubble. These "primary-particles" are smaller than the general colloid population (sub-10 nm) (24), as they can act as "seeding particles' for Np growth. Therefore if the "primary-particles" are stabilized, the colloid size distribution should exhibit a higher proportion of smaller Nps while lowering the possibility of agglomeration (5). Other studies have suggested that at low concentrations, NaCl addition can aid Np long-term stability (25), but at higher concentrations act as a destabilizer. In these tests, AgNps formation was tested in the presence of a low concentration ionic liquid environment.

In Fig.5 a 3 nm red-shift on the SPR can be observed from day 0 to day 12 however the intensity dropped by a higher proportion (4.3%) than the salt free AgNps. As this drop is

approaching the limit of 5% allowed deviation of absorbance, it would be expected that the colloid would be unstable over a period of 5 or more weeks (26). However size quenching did occur as the peak diameter has reduced from 22 nm when DI water was used to 11 nm when the weak ionic fluid was used. Therefore the application of ionic fluids allowed the fabrication of AgNps with equal Nps peak diameters to a commercially available example (10 nm). A smaller size distribution of only 5 nm at day 0 was recorded using the weak ionic solution compared to a main peak size distribution of about 12nm when DI water was used . These results indicate that the AgNps size remained constant over the testing period but some colloid may have fallen out of suspension, leading to the drop in absorption intensity. This work shows promising results for using varying salts concentrations to adjust AgNps size distribution.

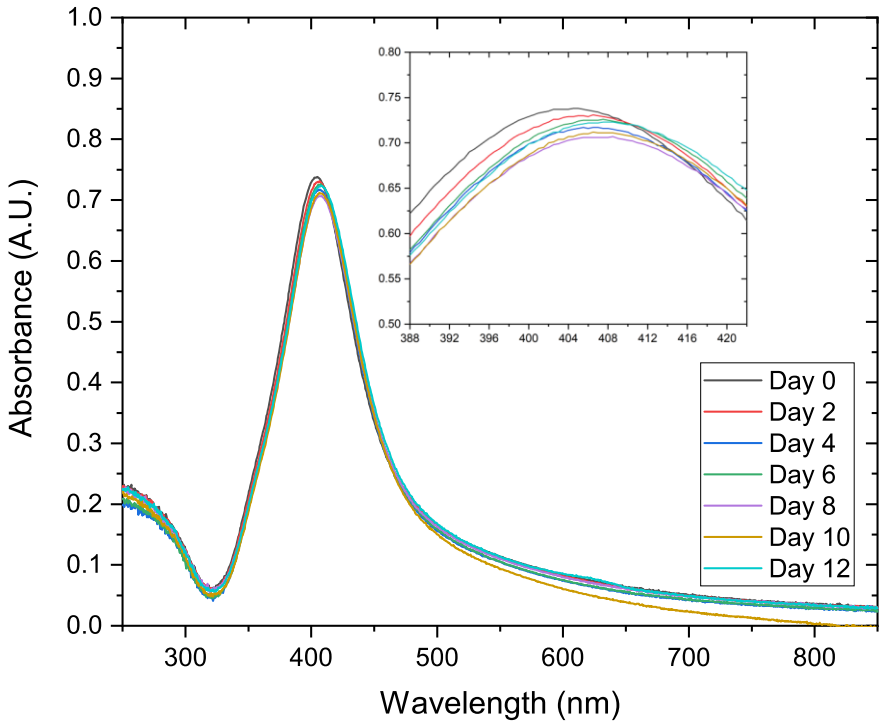
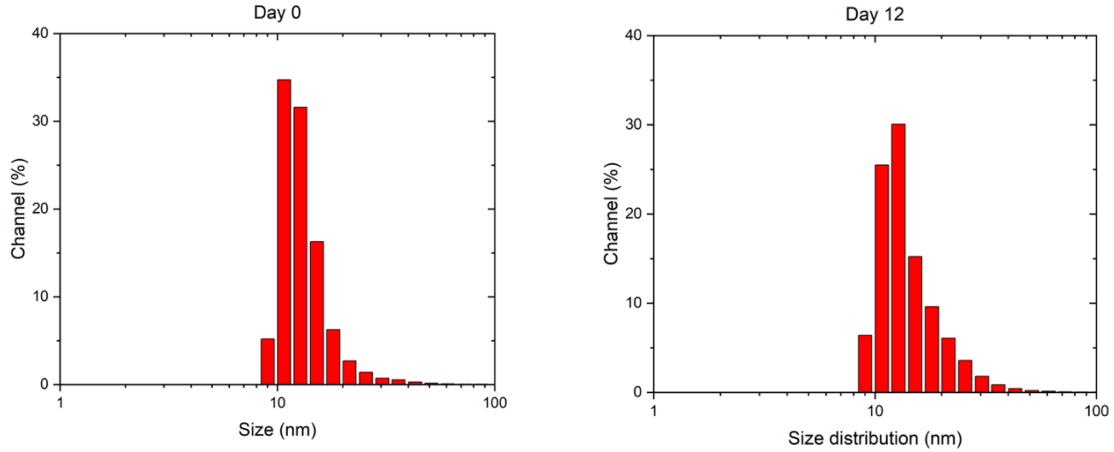


Figure 5: Absorption spectrum of AgNps produced in a weak NaCl ionic solvent of 0.86 mg/L. The plasmonic peak was at 404 nm at day 0, and red shifted to 407 nm at day 12. The signal intensity also dropped by 4.3%.



(a) **(b)**

Figure 6: DLS measurement of AgNps produced in the presence of 0.86 mg/L NaCl/DI water solution showing (a) the peak diameter of 11.3 nm and a width of 5 nm at day 0, and (b) a peak diameter of 11.9 nm and an increased width of 7 nm at day 12.

IV. Conclusions

Silver nanoparticles were produced utilising a new laminar flow "semi-batch" production method. The colloids were seen to be comparable with commercially available colloids in terms of optical response, size and stability. The colloids were produced within a 15 minute period and could be directly applied to thin-film printing of anti-microbial surfaces. If applied for the printing of conductive circuits, post colloid production processing would be required to increase their concentration. Using a weak ionic liquid for Nps production was found to provide size quenching during providing a pathway towards increased size control during the production process. However, it was seen to have a more variable effect on colloid stability than when DI water alone was used as the solvent. Electrolyte addition along with its interaction with Nps concentration at the ablation site needs to be studied in more detail to gain a better understanding of maintaining high density, stable colloids. This work confirms that LASiS is a feasible technique towards commercial low-powered laser based nano-colloid production for thin-films manufacture.

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VI. References

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