

# Plasma-in Liquid (PLI) process for the synthesis of silver nanoparticles

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**Abstract:** This work is an experimental study on the reduction of an aqueous silver (Ag) salt to colloidal Ag, by an atmospheric-pressure pulsed electrical discharge. The obtained nanoparticles (NPs) were characterized by UV-Vis absorption spectroscopy, dynamic light scattering (DLS) and scanning electron microscopy (SEM). SEM results showed that non-agglomerated Ag particles of different morphologies were obtained, when synthesized in the presence of a stabilizer, polyvinyl pyrrolidone (PVP).

**Keywords:** pulsed electrical-discharges, plasma-in-liquid, nanoparticles, Ag

## 1. Introduction

Noble metal nanoparticles are widely studied in order to assess their use and applications in very diverse fields, such as sensing<sup>1</sup>, optoelectronics<sup>2</sup>, catalysis<sup>3</sup>, medicine<sup>4</sup>, etc. Considerable attention has been paid to synthesizing a full variety of nanoparticles from a wide range of materials, to targeting the above mentioned applications by tuning their properties. However, little effort has been dedicated to produce them with a method as green as possible. In the context of green chemistry, several key challenges and opportunities have been identified; among them we can cite developing syntheses that reduce solvent use and toxicity of reducing agents<sup>5</sup>. From this perspective, electrical discharges formed directly in aqueous solutions of metal salts present considerable potential as an alternative for nanomaterial's synthesis.

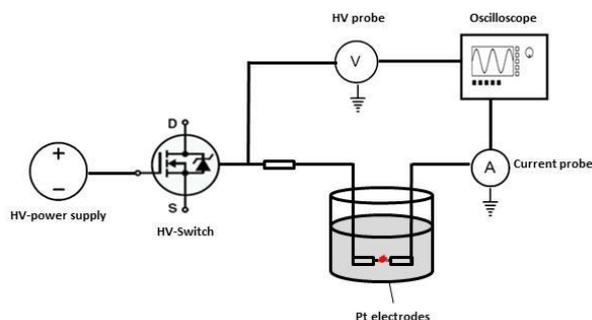
In this work, we studied Ag nanoparticles (Ag NPs) synthesis from aqueous solutions of silver nitrate with the plasma in liquid (PLI) process. The influence of the pulse width, the applied voltage, and the gap distance in the obtained particles, was studied through solution characterization with UV-Vis spectroscopy and DLS measurements. In addition, particles morphology was determined using SEM analysis.

## 2. Experimental set-up

A cylindrical borosilicate glass vessel (I.D. = 90 mm) with a height of 50 mm was used as the plasma reactor. Platinum wires (99% purity) of 200  $\mu\text{m}$  in diameter are used as electrodes, and placed in a horizontal pin-to-pin configuration, with a gap distance of 3 mm. The wires are protected by a capillary tube in order to ensure that only a 0.5mm length of the Pt wires are in contact with the solution. The metal precursor solution is prepared by dissolving a given amount of  $\text{AgNO}_3$  (Acros organics, 99.85%) in filtrated deionized water (Biotechnofix, 18.2  $\text{M}\Omega\cdot\text{cm}$ ) of a conductivity 0.5  $\mu\text{S}/\text{cm}$ , in order to obtain the desired concentration of 2mM. Polyvinyl pyrrolidone (PVP,  $\text{MW}=10000 \text{ g mol}^{-1}$ , Sigma Aldrich) is added to the solution (0.02mM) as a stabilizing agent. The conductivity and pH of the liquid phase were measured before and after the PLI process. During the process the

liquid solution was maintained under gentle magnetic stirring.

A 30kV/30mA direct current (DC) positive-polarity high-voltage (HV) power supply (TECHNIX CCR-30P450) is used to constantly charge a 1 nF capacitor through a 100k $\Omega$  ballast resistor. The capacitor is then discharged by a fast high voltage solid-state switch (Behlke HTS 301-03-GSM). Positive high voltage pulses with a rise time of about 30 ns, an adjustable duration from 150  $\mu\text{s}$  to 1.5 ms, amplitude from 1 to 12 kV, and a frequency of 50Hz were used. A LeCroy high voltage probe is connected to the HV electrode; the grounded electrode is connected to a Rogowski coil current probe (Pearson Electronics, 1/1 divider). The voltage over the electrodes and the discharge current are simultaneously recorded by a 1GHz oscilloscope (HDO9104 - 1GHz,



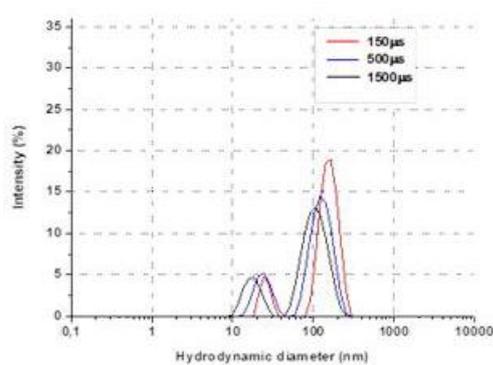
Teledyne LeCroy). A schematic diagram of the experimental set-up is presented in figure 1.

Fig.1. Experimental set-up

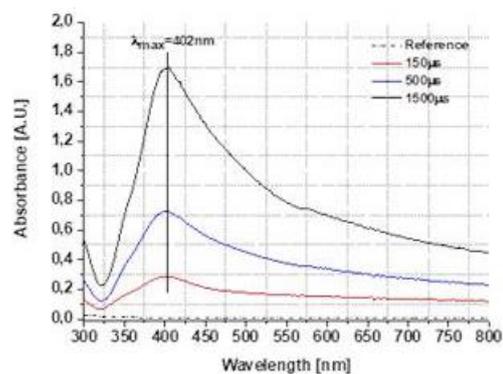
## 3. Influence of the pulse width

Ag nanoparticles synthesis was studied at three different pulse widths - 150, 500 and 1500  $\mu\text{s}$  -, for a 9kV discharge using a 3mm gap between the electrodes. Typical results obtained from DLS and UV-Vis analysis are shown in figure 2.

As can be seen from DLS results, in all the cases, small particles as well as some large agglomerates are present at the end of the process (20 minutes discharge). The smallest particles have a mean size of 20 to 30 nm.



(a)

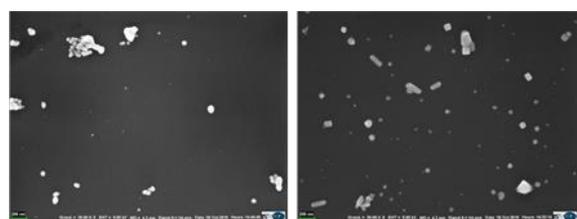


(b)

Fig.2. DLS (a) and UV-Vis (b) analysis of Ag nanoparticles obtained at 9kV - 3mm gap.

UV-Vis analysis is in accordance with this observation. For the three tested pulse lengths, the surface plasmon resonance (SPR) band, characteristic of the formation of silver nanoparticles, is located at the same wavelength ( $\lambda = 402$  nm), meaning that there is no significant variation in the particles size.

SEM images are presented in figure 3. While the longer pulse leads to the formation of rather spherical particles, with the shorter pulse cubic and rod-like particles were also formed.

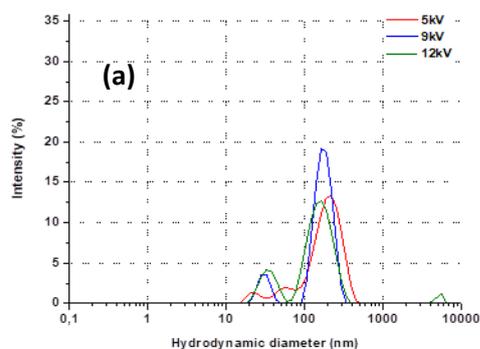


(a)

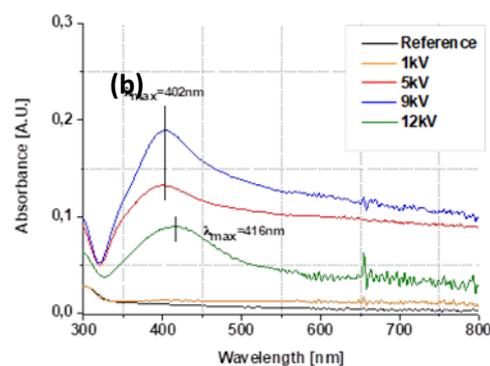
(b)

Fig.3. SEM images of Ag nanoparticles obtained at 9 kV, 3 mm gap and two different pulse widths: (a) 1500  $\mu$ s ; (b) 150  $\mu$ s.

Taking into account that different streamer modes are observed depending on the pulse width<sup>6</sup>, this can certainly have also an impact in the nucleation and/or



(a)



(b)

Fig.4. DLS (a) and UV-Vis (b) analysis of Ag nanoparticles obtained at different applied voltages. Pulse width: 150 $\mu$ s - 3mm gap

growth process during Ag NPs formation. Kim *et al.*<sup>8</sup> have obtained Ag NPs of different shapes by adjusting the pulse width of their bipolar voltage waveform. They concluded that, by changing the physical properties of the discharge, they were able to form different gas bubble conditions, which played a significant role in the nanoparticles formation.

#### 4. Influence of the applied voltage

In order to study the influence of the applied voltage on the formation of Ag NPs, 1, 5, 9 and 12 kV voltages were applied to the liquid solution. DLS and UV-Vis analysis are presented in figure 4. For an applied voltage of 1 kV, it was not possible to obtain a reliable result from the DLS analysis. In addition, the UV-Vis spectra showed no absorbance at the silver SPR wavelength. These two results suggest that no Ag NPs were formed at this applied voltage.

Increasing the applied voltage from 5 to 12kV does not highlight a strong influence in the particle size distribution as shown in Fig.4a; small particles as well as agglomerates are obtained. However, the UV-Vis spectra (fig.4b) show a difference in the maximum of the SPR band, which is red-shifted for the particles obtained at 12kV.

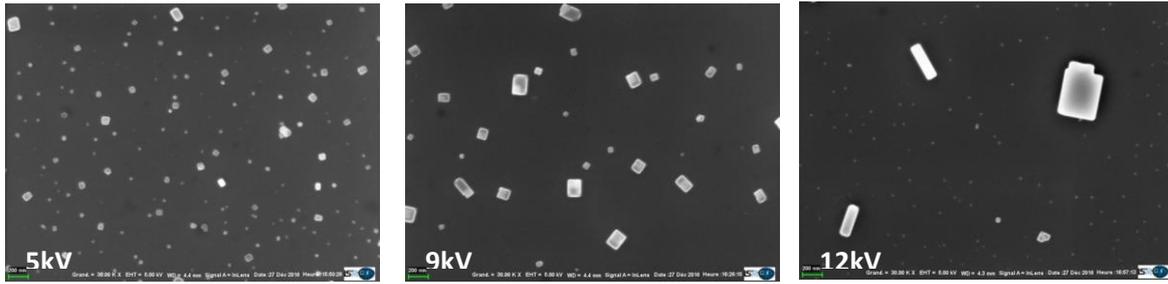


Fig.5. SEM pictures of Ag NPs obtained by increasing the applied voltage from 5 to 12kV. Pulse width: 150 $\mu$ s - 3mm gap

Information on particle morphology is obtained from the SEM pictures presented in figure 5. For the three studied applied voltages, Ag NPs of different shapes were produced. Whereas it seems that there is no significant change in the spherical particles size, the size of the cubic and rod-like particles seems to increase with the applied voltage. This increase in the size of the non-spherical particles could explain the red-shift observed in the SPR band at 12kV.

As the amplitude of the applied voltage pulse can also lead to different streamer modes<sup>6, 7</sup>, the obtained results could point out the influence of the applied voltage on the

growth mechanism of anisotropic Ag NP. Pootawang *et al.*<sup>9</sup> have studied colloidal copper nanoparticles synthesis with a solution plasma process. They have obtained CuNPs with anisotropic shapes and suggest that this could be explained by the crystal growth mechanism.

### 5. Influence of the gap distance

While keeping the applied voltage at 12kV, the gap distance between the electrodes was increased from 3 to 4mm. The results obtained from Ag NPs characterization are shown in figures 6 and 7.

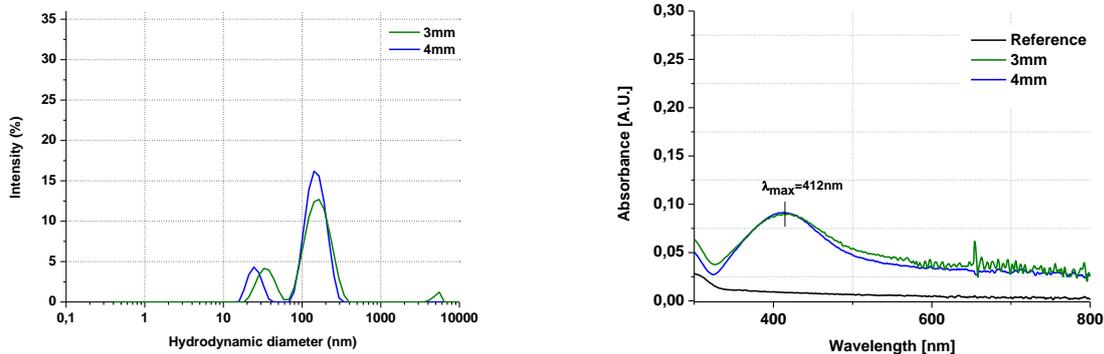


Fig.6. DLS (a) and UV-Vis absorption (b) analysis of Ag NPs obtained at different electrode gap distances. Pulse width : 150 $\mu$ s; applied voltage : 12kV.

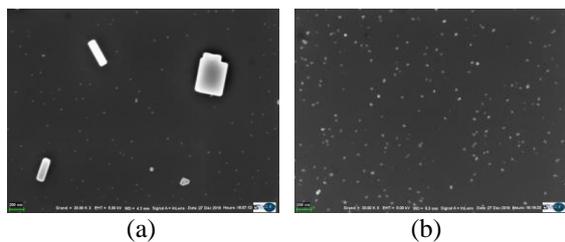


Fig.7. SEM images of Ag NPs obtained at 12kV and electrode gap of (a) 3mm, (b) 4mm. Pulse width: 150 $\mu$ s.

Increasing the gap distance doesn't seem to have a significant impact on the particle size Ag NPs. As for the other experimental conditions studied, small particles and agglomerates are produced. The mean diameter of the small particles obtained from the DLS measurements decrease from 40 to 30nm (fig.6a) when increasing the gap. In addition, UV-Vis absorption spectra are very similar, with no difference in the SPR maximum band (fig.6b).

Figure 7 present the SEM images for 3 and 4 mm gaps. Two main remarks can be made from these images: (i) the small spherical particles have very similar size, (ii) the absence of anisotropic particles in the sample obtained at

4mm. Given the fact that the UV-Vis absorption spectra does not show any particular difference between these two samples, and considering that only a small representation of the sample is being observed during the SEM analysis, there is a possibility that even if anisotropic particles were formed during the synthesis, none was present in the SEM sample.

Heo and Lee<sup>10</sup> synthesized gold nanoparticles using a solution plasma process. Their results demonstrate that the distances between electrodes have a strong effect on the formation of Au nanoparticles. In their experimental conditions, increasing the gap distance lead to the formation of bigger particles.

## 6. Conclusions

Ag NPs were formed from an aqueous solution of the silver precursor, using the PLI process. The particles were characterized using DLS, UV-Vis absorbance and SEM techniques. The obtained results showed that it is possible to obtain Ag NPs of different shapes by changing the physical properties of the discharge. Indeed, the pulse length, applied voltage and electrode gap distance play a significant role in the mechanism of nucleation and growth of silver nanoparticles.

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