

# Synthesis of Nanoparticles using Atmospheric Microplasma Discharge

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## 1. Abstract

Silver nanoparticles have been synthesized by the reduction of aqueous AgNO<sub>3</sub> solution, with sucrose as a stabilizing agent, using Atmospheric Microplasma discharge (AMP). The microplasma caused the aqueous metal ions present in the solution to reduce and nucleate into nanoparticles at ambient conditions (room temperature and atmospheric pressure) without presence of any chemical reducing agents. Highly mono-dispersed silver nanoparticles were obtained and analyzed using FESEM, UV/Visible absorption and DLS (Dynamic Light Scattering). This AMP based nanofabrication offers a simple, fast, cost effective and an environment friendly technique for the fabrication of silver nanoparticles which in principle can be extended to the reduction of any cationic species through plasma-liquid coupling.

## 2. Introduction

There has been an increasing interest in creating electrical discharges under atmospheric conditions (here referred to as atmospheric plasmas) both inside and on the surfaces of liquids. This has been done for technological utilization and scientific understanding of the plasma-liquid interactions which are not very well understood. Stable plasmas interfaced with liquids are envisaged to influence environmental [1], medical [2] and analytical applications [3]. Most popular mode of nanoparticle synthesis is through wet chemical techniques causing nucleation with the help of reducing agents in solution [4, 5]. In comparison, plasma assisted synthesis provides for nucleation without reducing and capping agents (hence clean), and is rapid and simple. Though various types of plasma sources exist, the ones which operate at high pressures (near atmospheric pressure) and room temperatures are particularly useful as they will not cause the liquid to evaporate during the process.

Ag being one of the important plasmonic materials offers plethora of application especially from nanophotonics viewpoint. Control over their shape, size and dielectric environment leads to wide variety of nanophotonic devices ranging from nanosensors [6] to waveguides [7] as well as application in biotechnology [8].

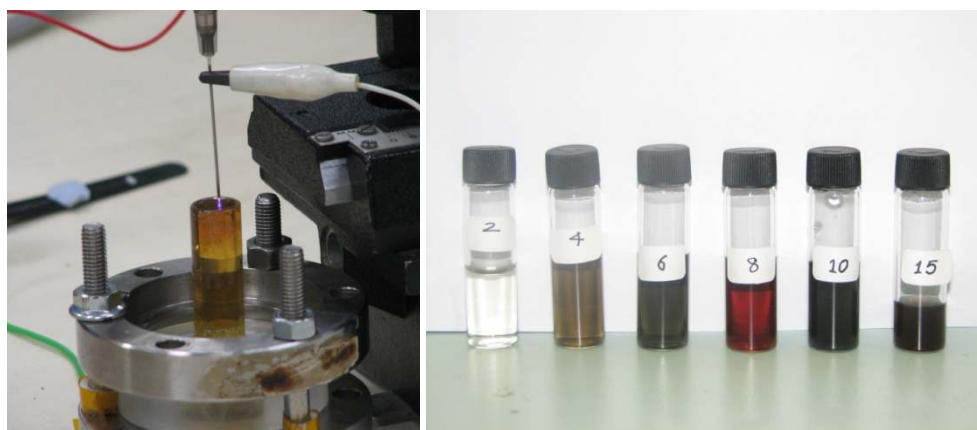
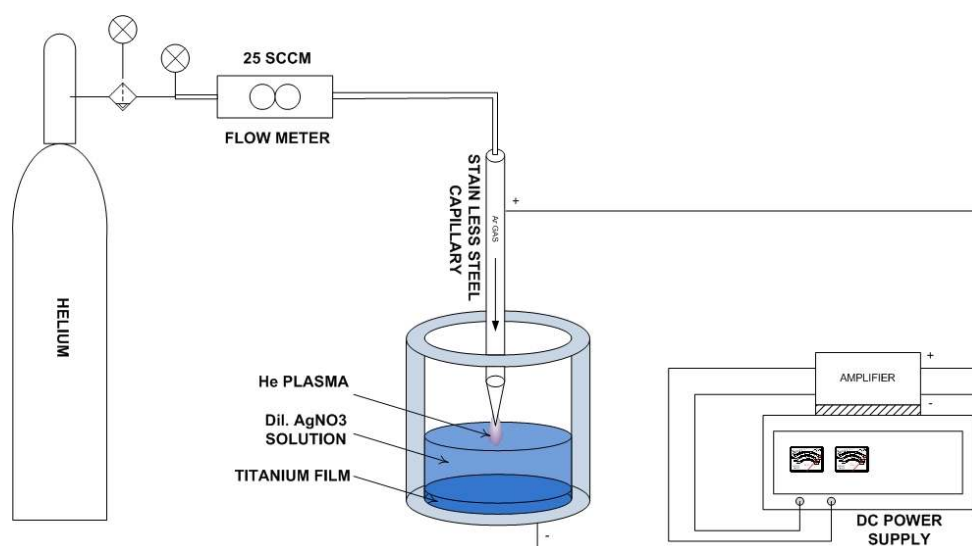
Here we present a home designed gas-liquid atmospheric plasma based electrochemical cell which allows for coupling between the non-thermal gaseous discharge operating at atmospheric pressure and the liquid [9].

## 3. Experiment

Silver Nitrate ( MW 169.87 gmol<sup>-1</sup> supplied by Sigma-Aldrich) and Sucrose (MW 342.30 gmol<sup>-1</sup> supplied by Sigma-Aldrich) were used as received. Deionized ultra-filtered water prepared from

Milli-Q water purification system was used at all times during the experiment. The sucrose was added as a stabilizing agent to prevent the agglomeration of Ag nanoparticles. The solution was kept in a home designed electrochemical cell (Fig 1) coupled to AMP, supported on 1cm × 1cm square piece of annealed titanium foil (12.5 μm thick, 99.6% purity obtained from Goodfellow LS228840LC). The Ti foil acts as the cathode in our setup. A stainless steel capillary (700 μm in diameter and 3.8 cm in length, obtained from Terumo) was used to deliver Helium gas towards the liquid surface. The capillary is connected to the positive terminal of a high voltage power supply. This power supply is made by using flyback transformer, which can produce voltages in the range of 0-15kV depending on the input DC voltage applied.

The gas flow was controlled using a (Alicat Scientific model no.MC-200SCCM-D) mass flow meter and was adjusted to 25 SCCM (cubic centimeters per minute) for our experiments. The morphology of the resulting nanoparticles was characterized using a Joel JSM 6700 Field Emission Scanning Electron Microscope (FESEM), and Carry UV-50 Spectrophotometer was used to obtain UV/Visible absorption spectrum from a colloidal solution of the nanoparticles.



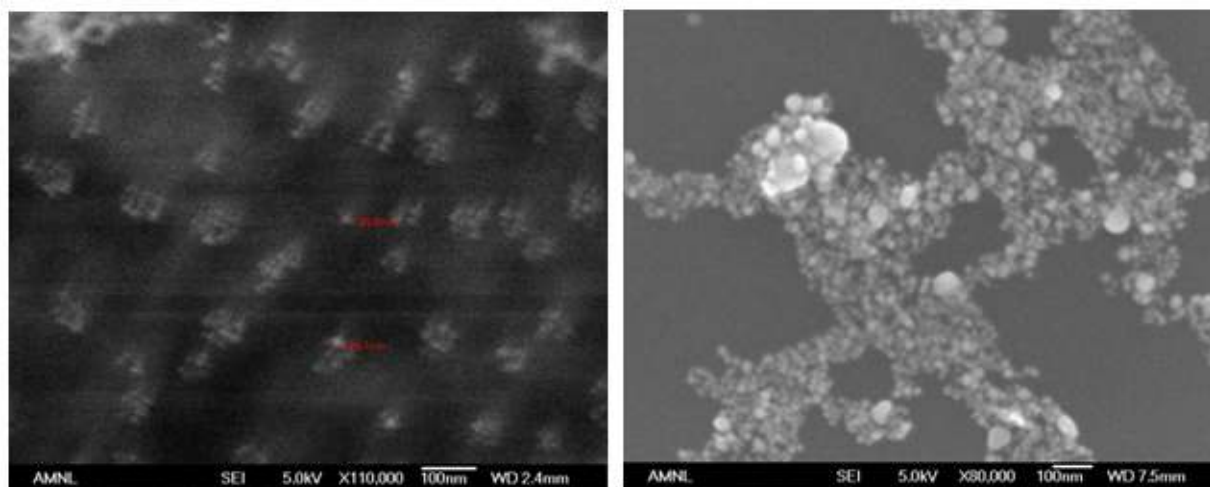
*Figure 1. Schematic of the experimental setup (top) showing the plasma-liquid electrochemical cell, picture of the actual setup (bottom left) and coloured solutions corresponding to different AMP exposure times (bottom right).*

#### 4. Results and Discussion

On applying the appropriate potential (few kV's) across the needle and the liquid surface a stable glow discharge plasma is formed at atmospheric pressure between the stainless steel capillary and the electrolyte surface. The distance between the needle and the liquid surface is kept within 3-4 mm. The high energy electrons and charged ionic species (He, N and O ions) in the plasma help in completing the circuit and a current (order of few mA) starts flowing in the system. The AMP forms a 'contact-less' electrode for our setup, meaning that it allows for the circuit to be completed without interfering with the electrolyte. Few seconds after the discharge is started the solutions starts turning brown from the liquid surface and slowly diffuses towards the centre of the cell. This is a clear indication of the formation of Ag nanoparticles. The nanoparticle nucleation depends on a lot of factors including the concentration of the electrolyte, time of discharge, discharge current, distance between the capillary and the electrode, capillary diameter and gas flow rates.

A part of the colored solution was extracted and drop-casted on a clean silicon substrate. The sample was then kept in an oven at 60 °C for 4 hrs. The agglomeration/assembly evident from Fig 2. is not intrinsic but is the result of the drying, causing increasing interaction between individual nanoparticles as the solution evaporates. It can be noticed from the figure that the nanoparticles are quite uniform and small in size, though there are some occasional chunks of big nanoclusters. The particles are also well separated.

Fig 3. shows the UV/Visible absorption spectrum for solutions exposed with AMP for different times. The peak at 400 nm corresponds to the localized surface plasmon resonance of silver nanoparticles while the smaller peak at 550 nm comes from the contribution of anisotropic nanoparticles in the solution.



*Figure 2. FESEM images of the Ag nanoparticles drop casted on a clean Si substrate. The diameter of these nanoparticles falls is around 25 nm.*

Using DLS we were able to obtain the sizes of the nanoparticles with radius in the range of 7-13nm which corroborates the sizes extracted from FESEM images.

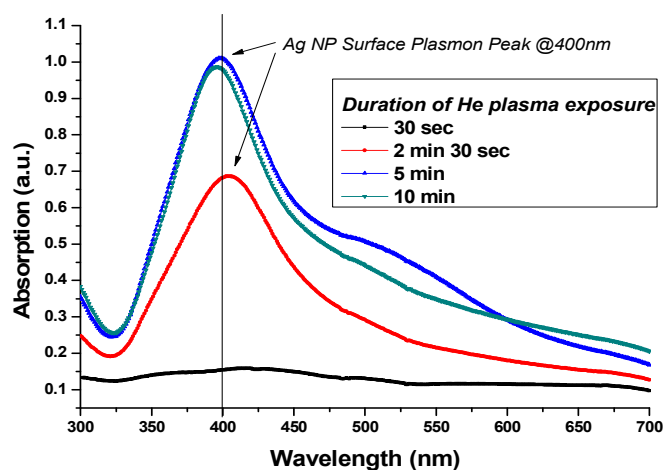


Figure 3: UV/Visible absorption spectrum for 0.8mM aq. soln.

## 5. Conclusion

Using an Atmospheric Microplasma discharge we have been able to successfully synthesize Ag nanoparticles. Uniform nanoparticles with radii in the range 7-13 nm were obtained. This technique offers a simple, fast, cost effective and an environment friendly technique for the fabrication of large amount of silver nanoparticles in relatively short time. In the future, it is envisaged that playing with experimental parameters should offer a way to tune the size of obtained nanoparticles.

## 6. References

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