Synthesis and characterization of silver nanorods using water coupled atmospheric pressure dc plasma

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Abstract. Non-thermal microplasmas are gaining attention of research community due to their unique physical, chemical, optical and catalytic properties. Due to these remarkable properties, microplasmas are being used in medicine, electronics, material processing and biotechnology. In this study, silver nanorods (AgNRs) were synthesized by coupling dc plasma with aqueous solution of silver nitrate (AgNO₃). Sucrose was added in the solution as a stabilizing agent. AgNRs were produced in aqueous solution by reducing AgNO₃ with dc plasma jet of argon at atmospheric pressure. No additional reducing agent was added used during production of AgNRs. Different molar ratios of AgNO₃ were used to control the size and dispersion of nanorods. Chemical composition and surface morphology of AgNRs were examined by using different techniques, such as scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The EDX spectrum confirmed that nanorods are AgNRs metallic silver with atomic weight of 16.86%. SEM micrographs revealed the formation of AgNRs. The rod length varied from 5 nm to 100 nm, depending on the molarity of solute.

1. Introduction

Synthesis of metal nanoparticles of extremely small dimensions, large surface area, controlled shapes and narrow size distribution is imperatively required for their use in cutting-edge technologies, such as optical sensing, catalysis, electronics and energy production devices [1-3]. Different methods for synthesis of silver nanoparticles (AgNPs) have been adopted, such as conventional biological, physical, photochemical and chemical methods. Each technique has benefits and drawbacks with cost, functionality, particle size and size distribution, etc [2, 3]. Among the available methods, chemical approach is regarded as simple and cost-effective method of synthesis of nanomaterials. Pure AgNPs can be produced through this method under mild conditions [4]. On the other hand, green synthesis method consists of photosynthesis and biosynthesis processes, which are usually carried out at high temperatures for longer periods under highly cleaning conditions [3, 5-8]. The chemical reduction approach is used to synthesize AgNPs with colloidal dispersions in water or organic solvents. Reducing silver ions in solvents produces distinct particle diameters of colloidal silver nanoparticles. Mostly, saccharides that include glucose, sucrose, soluble starch, lactose and fructose are used as reducing agents. Huang et al. [9] synthesized AgNPs by using an atmospheric pressure dc plasma jet and AgNO₃. A stabilizing agent was used to prevent aggregation of nanorods. Morphological features of synthesized AgNPs strongly depended on the parameters, such as process temperature, metal...
precursor, molar ratio of AgNO₃, reducing agents and stabilizing agents [9]. Bisht et al. [10] prepared AgNPs by using sucrose as a stabilizing agent. Filippo et al. [7] produced AgNPs under mild conditions by using sucrose and maltose as stabilizing agents and found the dramatic effect on the formation of nanoparticles. Water coupled atmospheric pressure dc plasma showed great authority on parameters of nanostructures [11, 12].

Microplasma is a cost-effective single step procedure, which works at room temperature, low current, high voltage and low gas flow rate. Morphology and configuration of nanorods depends on the parameters, such as processing time, current, voltage, precursor and flow rate of plasma source. [9, 11-14]. Richmonds and Sankaran [15] explained the microplasma-assisted production of AgNPs by combining fructose with AgNO₃ in molar ratio of 0.1-1 M. In this study, AgNRs were synthesized by impinging dc plasma jet on a solution of AgNO₃ and sucrose. The distance of plasma jet, gas flow rate and amount of stabilizer were varied to control the nanorod properties.

2. Materials and methods

Argon gas, AgNO₃ and sucrose (C₁₂H₂₂O₁₁) were used as plasma source, precursor and stabilizing agent, respectively. Molar concentration of 0.06 M of AgNO₃ was made and sucrose was added to the solution to prevent agglomeration of AgNRs. 20 ml of solution was exposed to argon plasma jet under ambient conditions for synthesis of AgNRs. The experimental setup, used in the presented work, is shown schematically in figure 1.

![Figure 1. Schematic of experimental setup used for synthesis of AgNRs.](image)

Two electrodes were used in this experiment. One electrode acted as cathode, which was a stainless-steel needle with outer diameter of 2 cm and inner diameter of 1 mm. The length of the needle electrode was 7 cm. The needle was placed just above the solution with 1 cm page. Second electrode was a tungsten electrode, which acted as anode. It was dipped in the solution to make a direct contact with the solution. The distance between electrodes was about 3 cm. Argon gas was coupled with cathode and gas was flowing through the capillary. An argon gas flowmeter was used to monitor and control the gas flow rate. Cathode was connected with negative terminal of dc power source and copper electrode was connected with the positive terminal. High dc voltage (2 to 10 kV, 20 to 40 mA)
was provided to the electrodes. A 100 kΩ blast resistor was connected between the power supply and the cathode to avoid the breakdown. The argon flow rate was fixed to 1200 sccm. Figure 2 shows all the steps and materials used in this work are shown in figure 2. The final product was centrifuged to get AgNRs. These nanorods were dried in an oven for 6 h at 80 °C.

![Figure 2](image1.png)

**Figure 2.** Different steps involved in synthesis of AgNPs.

### 3. Results and discussion

The chemical composition of AgNRs was analysed using energy dispersive X-ray spectroscopy (EDX). EDX analysis gives the information on elements present in the sample, but the exact content of each element in the sample cannot be determined through this technique because the elemental composition depends highly on the scan area. Figure 3 shows EDX pattern of the nanorods. The peaks around 3 keV, 1.8 keV, 0.5 keV and 0.3 keV correspond to Ag, Si, O and C, respectively. It was revealed that the nanorods are metallic silver. The weight of Ag was 16.86%, carbon 36.40% and oxygen 45.59%, as shown in table 1. Another peak, found in EDX spectrum, corresponds to Si. The Si peak in EDX appeared to the substrate on which AgNRs were deposited for characterization.

![Figure 3](image2.png)

**Figure 3.** Typical EDX spectrum of AgNRs.
SEM micrographs were generated to study the size and surface morphology of AgNRs. SEM micrographs in figure 4 confirmed the formation of Ag nanorods rather than Ag nanoparticles. These rods were more likely to appear in the form of nanostrips. The size and shape of the nanorods depended on the distance between solution and cathode needle. For a gap of 0.5 mm between cathode and solution, the shape of nanorods was more spherical at 60% molar ratio of sucrose to AgNO$_3$ [10, 16].

Table 1. Chemical composition of as-grown AgNRs.

| Element | Weight % | Atomic % |
|---------|----------|----------|
| C K     | 0.06     | 36.40    |
| O K     | 0.11     | 45.59    |
| Si K    | 0.00     | 1.15     |
| Ag L    | 0.26     | 16.86    |
| Total   | 44       | 100      |

![Figure 4. SEM micrographs of as-synthesized AgNRs using 20% molar ratio.](image)

4. Conclusion
Silver nanorods were successfully synthesized through atmospheric pressure DC plasma jet of argon gas. The rod diameter remained between 5 nm and 100 nm, depending on the nozzle distance and solution molar ratio. Therefore, different molar ratios of AgNO$_3$ were used to control the size and dispersion of nanorods. The presented synthesis technique is cost-effective and environment friendly for synthesis of nanomaterials of different types.

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