

# PREPARATION OF SILVER AND GOLD NANOPARTICLES BY NOVEL PIN-HOLE DC PLASMA SOURCE

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Silver and gold nanoparticles were produced using the pin-hole discharge generated by dc non-pulsing high voltage directly in precursor solution. Silver nitrate solution was used as the precursor for silver nanoparticles, chloroauric acid was used as the precursor for gold nanoparticles. Effects of discharge time, precursor concentration and additives such as reduction agent (ethylene glycol) and capping agent (polyethylene glycol and sucrose) were studied. Nanoparticles were mainly analysed by UV-VIS spectrometry. The size of prepared nanoparticles was determined by dynamic light scattering with backscattering detection. To determine the stability of NPs, Zeta potential was measured by electrophoretic light scattering. Formation of silver and gold nanoparticles was then confirmed by SEM/EDS analysis. Both kinds of particles had spherical shapes.

## 1. Introduction

Nanoparticles (NPs) are defined as particles with size in the range from 1 to 100 nm. Properties of metallic nanoparticles are different from the bulk metals, such as the lower melting point or higher surface area, making them more attractive for different applications [1]. They can be utilized in many different applications, such as biomedical science [2], electronics [3], biotechnology [4] or drug delivery [5]. Various methods can be used to prepare metallic nanoparticles. Recently, a new technique using non-thermal plasma discharge directly in liquids was examined. Metallic nanoparticles can be generated from metallic precursor solution or sputtered from the electrode material. Different setups and plasma reactors were used to prepare metallic nanoparticles, mainly from noble metals such as copper, silver, gold or platinum. Lung et al prepared gold nanoparticles using arc discharge in water [6]. Colloidal copper nanoparticles with gelatine and ascorbic acid as the capping agent were prepared using solution plasma process [7]. Microwave induced plasma in liquid was also used for preparation of gold [8], silver and platinum [9]. This paper deals with synthesis of silver and gold nanoparticles using a special pin-hole electrode system generating plasma directly in liquid solution of a metal precursor by DC high voltage up to 1 kV [10].

## 2. Experimental setup

The plasma reactor, presented in Figure 1 **Error! Reference source not found.**, consisted of two electrodes – the main jet electrode and second (counter) electrode [10–13]. The main jet electrode was constructed by a tungsten wire with diameter of 1.0 mm inserted into a dielectric cylindrical rod made of Macor ceramics with outer diameter of 10 mm. An orifice with the diameter of 1.2 mm was made in the ceramics along its longitudinal axis. A small gap of 1 mm was kept between the end of the wire electrode and the region around the electrode end of the dielectric rod. This configuration substantially increased electric field intensity in the gap of the dielectric rod and thus it allowed plasma ignition at relatively low applied voltage. An outer glass tube served as a holder. The second (counter) electrode was a planar plate made of aluminium with dimensions of 20x100 mm<sup>2</sup> [10]. The system was supplied from the specially designed dc power source giving the non-pulsing high voltage up to 3 kV in the peak. A negative polarity was applied on the main electrode, solution was grounded. Both electrodes were immersed in a vessel containing 200 ml of the precursor solution – AgNO<sub>3</sub> for silver nanoparticles and HAuCl<sub>4</sub> for gold nanoparticles. The treated solutions were sampled every 30 seconds during the discharge operation for the UV-VIS spectrometry. Absorption spectra of sampled solutions were recorded by the Helios Omega (Unicam) spectrometer in the range of 300–600 nm. Dynamic light scattering and Zeta potential measured by the Zetasizer Nano ZS (Malvern Pananalytical Ltd.) were used in order to determine size and stability of nanoparticles. Detailed photos of formed nanoparticles and EDS analysis were taken by the high resolution scanning electron microscope FEI Verios 460L (Thermo Fisher).

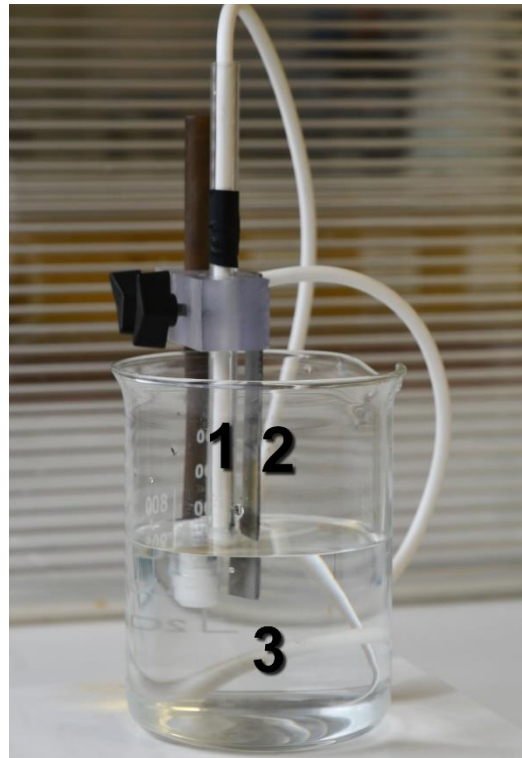
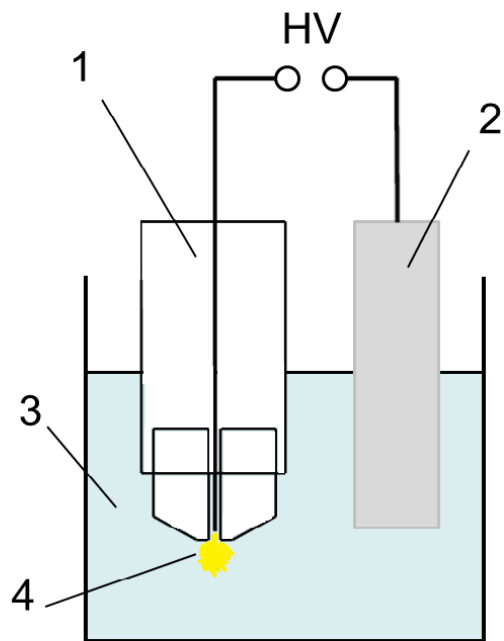


Figure 1 Experimental setup (left: scheme, right: photograph): 1 - main jet electrode, 2 - counter electrode, 3 - precursor solution, 4 - active plasma region

### 3. Results

Silver nitrate in the concentration of  $25\text{--}200\text{ mg l}^{-1}$  was used as a precursor for silver nanoparticles formation. Solutions were sampled every 30 seconds during the discharge operation to determine nanoparticle formation in time. Nanoparticles were formed in the plasma region near the main jet electrode and spread into the solution. The absorbance of silver nitrate solution increased during the discharge treatment with the maximal absorption at  $410\text{ nm}$  (Figure 2 left). The same increase of absorbance was observed while examining the effect of precursor concentration. Experiments were carried out at the mean input power of  $60\text{ W}$  for silver nanoparticles and the discharge lasted for 2 minutes. After 2 minutes of the discharge, Ag nanoparticles had Zeta potential over  $30\text{ mV}$  and were stable. The size of Ag NPs ranged from  $10$  to  $1000\text{ nm}$ . On the SEM photograph in Figure 3 (left) we can see that nanoparticles had mainly spherical shapes.

Gold nanoparticles were prepared from the solution of chloroauric acid at the mean input power of  $100\text{ W}$ . The time and concentration effect was also observed. According to the absorption spectra shown in Figure 2 (right), Au NPs were formed in the solution after 3 minutes of the discharge treatment. In order to determine the effect of concentration, solutions with concentration from  $25$  to  $100\text{ mg l}^{-1}$  were prepared. According to data from DLS, the size of Au NPs was  $10\text{ nm}$  on average. Au NPs prepared from the solution with the concentration of  $100\text{ mg l}^{-1}$  had average size of  $100\text{ nm}$ . In Figure 3 (right) we can see SEM photograph of gold nanoparticles with spherical shapes. Their Zeta potential was over  $30\text{ mV}$ , which means that nanoparticles were stable. To stimulate the reduction process of Au NPs, ethylene glycol in the concentration of  $1\text{mM}$  was added. Its addition decreased the mean input of power needed for the stable discharge operation to  $80\text{ W}$ . However, ethylene glycol destabilized NPs (Zeta potential was lower than  $30\text{ mV}$ ) and they started to form larger structures and sediment. Even after the addition of the capping agent into the solution of  $\text{HAuCl}_4$  and ethylene glycol ( $50\text{ mg l}^{-1}$  of sucrose or  $50\text{ mg l}^{-1}$  of polyethylene glycol), NPs still had Zeta potential lower than  $30\text{ mV}$ . To conclude the effect of additives, it is the best to prepare NPs from their precursor solution only, even if the power consumption is higher. With this method, only few milligrams of chemicals are needed, nanoparticles are stable on their own, and it is time efficient as it only takes  $2\text{--}4$  minutes to prepare them.

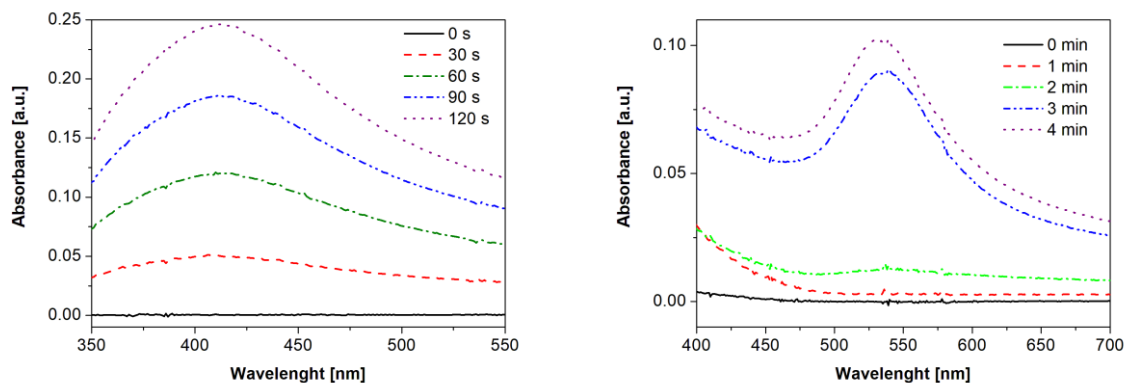


Figure 2 Left: Absorption spectra of  $\text{AgNO}_3$  solution ( $100 \text{ mg l}^{-1}$ ) during the discharge treatment (mean input power of 60 W). Right: Absorption spectra of  $\text{HAuCl}_4$  solution ( $100 \text{ mg l}^{-1}$ ) during the discharge treatment (mean input power of 100 W).

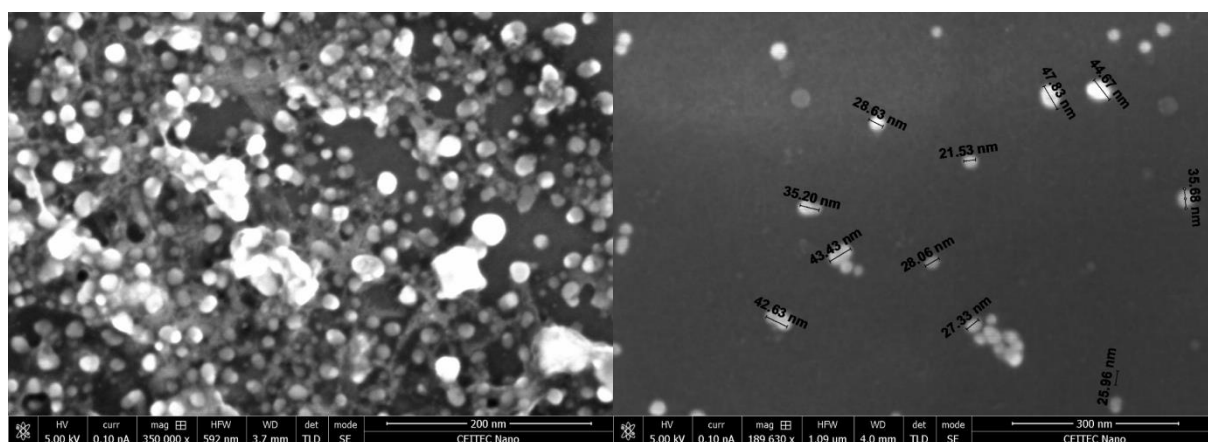


Figure 3 Left: SEM photograph of silver nanoparticles formed after the 2-minute discharge treatment (mean input power of 60 W) in  $\text{AgNO}_3$  solution ( $100 \text{ mg l}^{-1}$ ), magnification: 350 000x. Right: SEM photograph of gold nanoparticles formed after the 4-minute discharge treatment (mean input power of 100 W) in  $\text{HAuCl}_4$  solution ( $100 \text{ mg l}^{-1}$ ), magnification: 190 000x.

## 4. References

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