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SYNTHESIS OF GOLD NANOPARTICLES THROUGH ULTRASONIC SPRAY PYROLYSIS AND ITS APPLICATION IN PRINTED ELECTRONICS

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Abstract: This work presents a review of Ultrasonic Spray Pyrolysis (USP) as a technique for the synthesis of gold nanoparticle (AuNPs). The synthesis mechanism involved the preparation of the precursor solution from Au (III) Acetate and the study of the process parameters. AuNPs were characterized with different techniques, such as DLS, UV-vis and SEM-EDX analyses. In the second step, the AuNPs` ink was prepared with the following procedure: (i) Concentration of the AuNPs through Rotavapor, (ii) Filtration of the concentrated AuNPs through Amicon Ultra 15 Centrifugal Filters. Then, it was used directly for printing on an Ag plate. In the final part, we present some information about AuNPs` future applications, which could be in printed electronics with conducted patterns.

Keywords: ultrasonic spray pyrolysis, gold nanoparticles, characterisation, printing.

1. INTRODUCTION

Nanotechnology is a branch of science and engineering focused on materials with at least one dimension below 100 nm. Nanomaterials could be in the different shapes as nanoparticles (NPs), nanotubes, nano-pyramids and they have different properties compared to materials with ordinary dimensions. Their altered physical and chemical properties come from a large surface-to-volume ratio and a high surface activity. Because of this, they are useful in various fields (electronics, chemistry, biotechnology, medicine) [1].

Especially interesting are gold nanoparticles (AuNPs), as they have an additional property, called Surface Plasmon Resonance (SPR) [2]. This causes the oscillation of conduction electrons on the surface of the NPs, stimulated by incident light. AuNPs have good physical, chemical and optical properties because of plasmon resonance [3–5]. Usually, AuNPs are biologically unreactive and as such are suitable for biomedical imaging and therapy [6,7]. Such AuNPs can be conjugated and functionalized with peptides, medicine and can be used for diagnosis and cancer treatment [8–10].

Different production methods for NPs are known, they are divided into bottom-up and top-down approaches. Bottom-up examples include sol-gel, chemical vapour deposition, flame spray synthesis, various pyrolysis and atomic or molecular condensation [11–14]. Top-down methods include laser ablation, nanolithography and high-energy milling [15,16]. Currently, these methods are suitable for production of small quantities of NPs with major variations in shapes and sizes of the NPs from production of different batches. A bottom-up method, called Ultrasonic Spray Pyrolysis – USP has good potential for removing these technological issues, for a more controlled NPs synthesis [13], [17]. Pyrolysis in general, is a process of chemical decomposition of various compounds at elevated temperatures. With the USP method, we additionally introduce ultrasound for dispersing a precursor solution with our desired material into droplets.

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These droplets are then exposed to high temperature, such that the material inside the droplet is chemically decomposed via pyrolysis and NPs of pure elements are obtained. The advantage of the USP method is the simplicity of setting up individual process segments and changing their configuration, continuous NPs synthesis and the possibility of synthesizing pure NPs from various materials. The disadvantage is a low efficiency of the method when using an unoptimized USP device used for laboratory purposes (currently around 40%), due to losses of the dissolved material on the construction elements of the USP device. The main elements of the standard USP device are the ultrasonic generator, the reactor furnace and a system for NPs collection. There are various raw materials which can be used for preparing precursor solutions for AuNPs synthesis (compounds containing Au: $HAuCl_4$, $AuBr_3$, $HAu(NO_3)_4$, $Au(CH_3COO)_3$ [18], [19]. In our case, Au (III) Acetate ($(Au(CH_3COO)_3$(s) was selected, due to its price availability and chemical stability.

The aim of this research was to present USP as a technique for the synthesis of AuNPs with focus on the successful preparation of the Au (III) acetate precursor solution. In the second step, we performed the characterization of AuNPs. Finally, we started with the introduction of AuNPs for future applications, which could be in printed electronics with conducted patterns. For this purpose, we prepared concentrated AuNPs in the form of ink, and we subsequently performed the first testing of AuNPs ink printing on the Ag plate surface.

2. EXPERIMENTAL PART

2.1. USP synthesis of AuNPs

For the precursor solution, Au (III) Acetate ($Au(CH_3COO)_3$, Alfa Aesar, Germany, 99.9%) was used. The in-received Au (III) Acetate powder was dark brown in color containing micron sized particles. The aqueous precursor solution consists of 480 ml of DI water, 20 ml of HCl and 2g of Au (III) Acetate having initial [Au] of 2 g/l. In the next step, this solution was magnetically stirred for 1 hour and a clear yellow solution was obtained. The obtained clear solution was neutralized with sodium hydroxide in the form of solid pellets. This solution is very much similar in color with the gold (III) chloride solution. In the next step, 500 ml of DI water was added. The pH value of the precursor solution now had been achieved in the range of 6-7, while the final concentration of [Au] in precursor solution was 1 g/l.

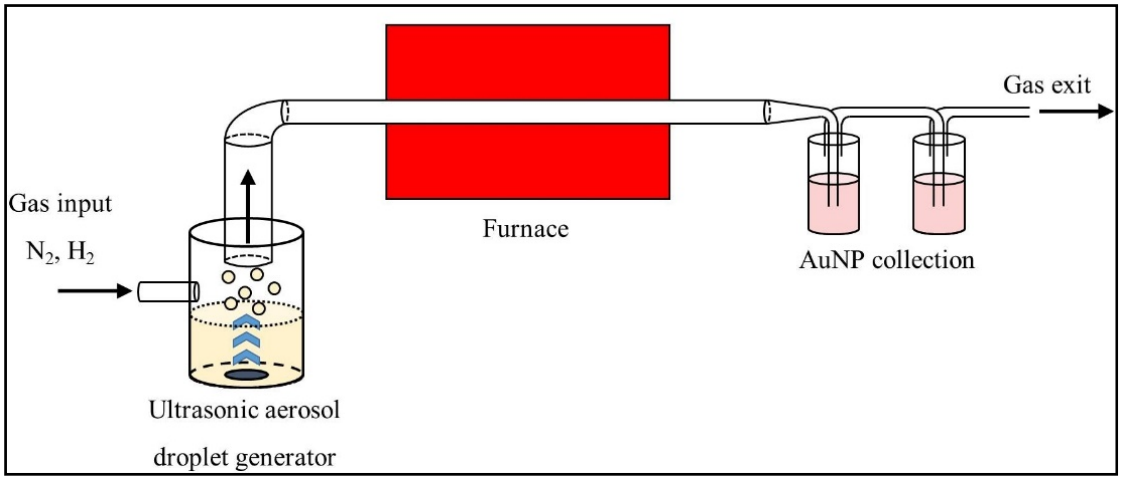


Figure 1. Schematic presentation of USP equipment at Prizma d.o.o. Kragujevac

For AuNPs synthesis, the USP equipment developed at the Prizma d.o.o. Kragujevac Serbia was used (Figure 1) [20,21]. The main elements of the device consist of the ultrasonic atomizer (Prizma Serbia), a tubular reactor furnace, quartz tube (SiO_2, length of 1.0 m, diameter of 25 mm) and quartz connectors, a thermostat, two bottles with collection suspension of De-ionized (DI) water for NPs. The atomizer was set to a frequency of 2.5 MHz and produced aerosol droplets, which were transported by nitrogen gas into the reactor, at a rate of 1.5 l/min. Hydrogen gas was added for reduction at a rate of 1.5 l/min. The reactor was running at a temperature 250°C. When transported to the reactor, the droplets were exposed to drying, droplet shrinkage, solute precipitation, thermal decomposition, hydrogen reduction, densification and final collection in two bottles with suitable

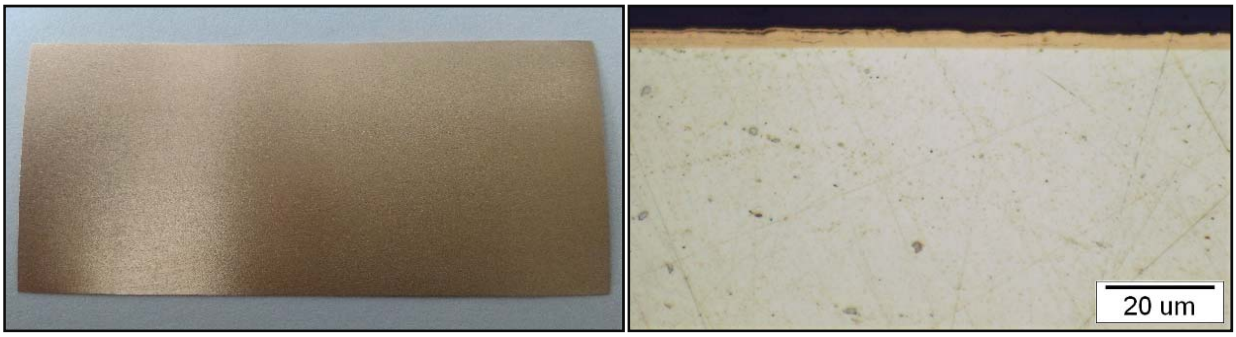
collection medium. 0.1 wt.% of PVP dissolved in 250 ml of DI water was used as a stabilizing collection medium to prevent the possible agglomeration of the synthesized AuNPs. The Table 1 shows the parameters selected for experiment.

2.2. Ink Jet Printing of AuNPs

To test the ink-jet printing on the metal surface, the appropriate Ag plate was prepared. This Ag-surface was first mechanically treated with diamond point with the aim to achieve appropriate surface roughness, which is necessary for AuNPs embedding. The treated rough Ag surface was after that coated with rose Au (see Figure 2).

Table 1. Experiments in the USP for synthesising AuNPs from Au (III) Acetate with the following parameters

Precursor Solution	[Au] (g/l)	T (ºC)	N_2 (l/min)	H_2 (l/min)	Time (h)	Collection Medium
Au (III) Acetate	1	250	1.5	1.5	3	DI water + PVP



a) b)

Figure 2. a) Schematic presentation of Ag plate for AuNPs printing b) cross-section of Ag plate with coating

For ink preparation, AuNPs solution were concentrated through Rotavapour. Initially, 100 ml of the AuNPs were rotavaporized to the final volume of 10 ml. The initial parameters for the rotavapour were: Vacuum Pressure = 25 millibar, Water Bath temperature = 50ºC, RPM = 60.The concentrated AuNPs were filtered through these centrifugal filter membranes "Amicon Ultra-15 with 100,000 NMWL" in order to remove the content of PVP stabilizer. Each step of 1.5 ml had been filtrated with the following parameters: Speed: 5000 rpm and Time: 5 minutes.

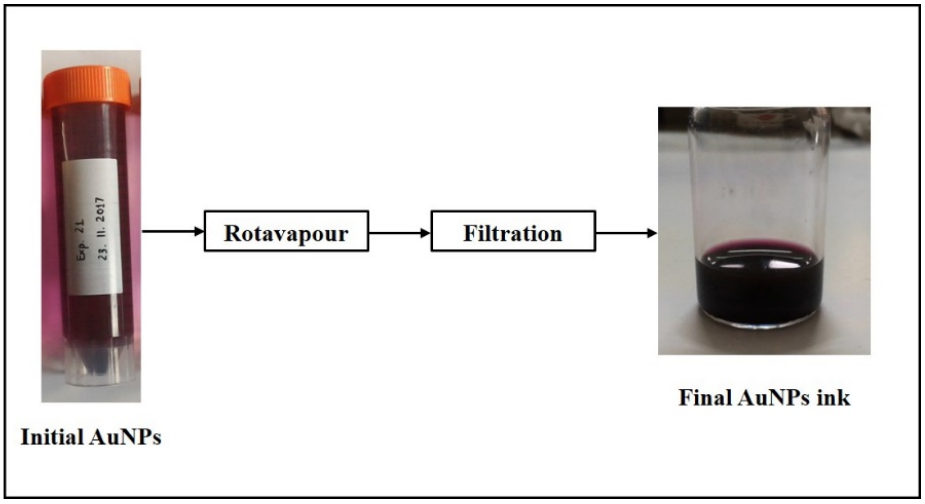


Figure 3. Flow chart representation of the preparation of AuNPs ink

The ink jet printer used in the printing of AuNPs is Fujifilm Dimatix DMP-2831 with

piezoelectric ink jet cartridge. The following initial parameters were used: Head Angle: 4.5°, Substrate Temperature: 30°C, Substrate Thickness: 300 microns, Voltage: 40 V, Increment in volt: 1.0 V, Temperature (cartridge): 30.0°C, Jets in Use: 16 Nozzles, Cartridge Print Height: 1.000 mm, Substrate Pattern – X (width): 75.58 mm, Y (height): 101.00 mm, Drop Spacing 64 μm (397 DPI). For substrate Ag Plate as presented before was used with repetition of 8× printing.

2. 3. Characterisation

ICP-OES Measurements

An ICP-OES was used for the Au3+ quantification (i.e. concentration of Au in AuNPs). Prior to the analysis, samples were diluted 10-fold with de-ionised Milli-Q water (purity 18 MΩ cm) and acidified with aqua regia (5% v/v). For calibration, single element standard solutions were used (Merck, Darmstadt, Germany). Analysis was carried out using an ICP MS spectrometer (Agilent, 7500 ce, equipped with collision cell) under the operating conditions: RF power - 1.5 kW, Sample depth 8 mm, Nebulizer - Meinhard, Plasma gas flow (L/min) – 15, Nebulizer gas flow (L/min) - 0.85, Make up gas flow (L/min) - 0.28, Reaction gas flow (mL/min) - 4.0.

DLS Measurements

The AuNPs` size and zeta-potential were obtained using a Malvern (Multipurpose Titrator) Zetasizer Nano ZS. During the automatic measurements (10–30 runs), the initial parameters for absorption (0.01), refractive index (1.59), dispersant properties (water), temperature (25°C), equilibration time (25 s), measurement angle (173° backscatter), and cell type (Dip Cell) were set for zeta-potential measurements.

UV-Vis Spectrometry

It was measured in a colloidal solution of AuNPs by using quartz cells, with a Varian Cary 100 Scan – UV- Vis spectrophotometer.

SEM-EDX

Scanning Electron Microscopy (SEM) with Sirion 400NC (FEI, USA) was equipped with Energy-Dispersive X-ray spectroscopy (EDX), which was used for determination of the chemical analysis. A small sample of the synthesized AuNPs from colloidal solution and concentrated AuNPs` ink was deposited/stuck onto carbon film. It was done in STEM mode due to the required high magnification.

Statistics and Diagrams

Data were presented as a representative experiment, or as a mean ± Standard Deviation (SD) of at least 3 independent experiments. The differences between control experimental samples were analysed using the Kruskal-Wallis test, with Bonferoni post test, and values at $p < 0.05$ or less were considered to be statistically significant. Origin Pro 8 was used for plotting the graphs and Figures were made with the help of Microsoft Office Tools.

3. RESULTS AND DISCUSSION

AuNPs

The concentration of AuNPs after USP synthesis was about 180 ppm. The higher concentration, with a value of more than 1000 ppm, was achieved via rotavapour technology for further use in the preparation of the ink.

The hydrodynamic size distribution of AuNPs was measured by DLS. The average diameter was 42±21.75 nm, having a much broader peak, signifying the larger variation in the sizes. The size density varied from 20 nm to 80 nm. The zeta potential measured for AuNPs was -33.8±1.2 mV respectively. This value shows that AuNPs will inhibit stability for at least up to 4 months without the phenomena of agglomeration.

The UV-vis spectra of AuNPs had the maximum absorbance wavelength at 528 nm signifying the peculiar characteristic of AuNPs.

The shape and morphology and some dimensions of AuNPs were visible in Figure 4, while chemical composition was detected by EDX analysis. The shape appeared to be much more ellipsoidal, with the measured circularity of 60%. AuNPs were agglomerated in nature. This agglomeration occurred due to the collision and partial sintering of the particles in the gas phase. There were no visible defects on the surfaces of AuNPs. EDX analysis showed about 92 wt.% of Au, 6 wt.% of O and 2 wt.% Cl. O and Cl could be attrib uted as a residues of the USP process.

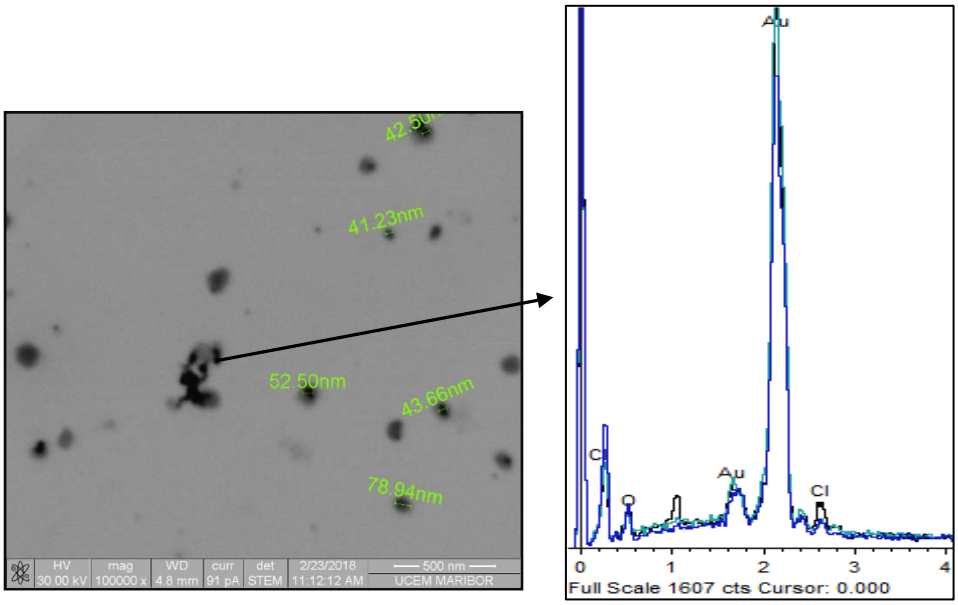


Figure 4. STEM micrograph of AuNPs with corresponding EDX analysis

It was known from the literature [13,17,18,22] that the sizes of the synthesized AuNPs depend on the ultrasound frequency, which determines the sizes of the aerosol droplets, and the concentration of the dissolved Au in the droplets. Due to vibrations of the ultrasound below the solution surface, the kinetic energy of the solutions molecules was rapidly increased. This had caused the small droplets to overcome surface tension and broke away from it. With a high-frequency ultrasound (0.5-3 MHz), droplets in a size distribution from 1 to 15 micrometers were created [23]. By using low concentrations of dissolved gold (1.0 g/l) in the precursor solution, each droplet contained such an amount of material. It was known that after evaporation and drying, the following particle sizes are formed: i) with diameters of a few 10 nm at 0.5 g/l Au and ii) with diameters of more than 100 nm at 5.0 g/l Au in the precursor solution. Droplets of the starting solution were transported into the furnace with a carrier gas. Inside the furnace, the AuNPs were formed according to the following synthesis stages: Evaporation and droplet shrinkage, Thermal decomposition, Reduction with hydrogen and formation of Au, Densification. The listed synthesis stages were taking place at the same time with the conventional USP. With smaller diameters of the aerosol droplets ($2r>1$ μm), NPs were formed much sooner then with larger droplets ($2r<10$ μm). Therefore, NPs of different sizes and shapes can be synthesized, due to droplet collisions and coagulation. This was not suitable for synthesizing the targeted AuNPs. More detailed studies [20,24] had shown that the shapes of the synthesized AuNPs depend on the rate of droplet evaporation and the rate of ion diffusion $[CH_3COO]^-$ and Au^{3+} inside the droplet. These rates with USP synthesis depend on several factors: precursor solution concentration, droplet sizes, number of droplets and relative humidity in the system, velocity of droplet transportation into the furnace with the carrier gas, pressure in the system, dimensions of the transport pipes, and temperature inside the furnace. For setting up suitable parameters (precursor solution concentration, gas flow, furnace temperature), information was needed for the starting solution properties, such as density and surface tension, and characteristics of the dissolved $[CH_3COO]^-$ and Au^{3+}, ion diffusion inside the solution and AuNP growth.

Ink jet printing of AuNPs

In the trial of the ink-jet printing of AuNPs on the Au coated Ag plate, the ink was prepared in the same procedure as compared with previous trials. The ink was concentrated and filtered up to the concentration value of 1000 ppm. The water content had been reduced and thereby achieving the high concentration of Au in ink solution. The analysis showed the large presence of a bunch of clusters of AuNPs without much distortion in the morphology. EDX analysis confirmed the corresponding peaks of Au with 99.9%.

The printing of AuNPs with 8× repetition on Ag plate was successful. This could be attributed to the ellipsoidal shape of AuNPs that eases the flow behaviour of the concentrated ink through the nozzles of the cartridge The SEM analysis of the AuNPs printed pattern on Ag surface (Figure 5) showed clusters and non-homogenously distribution of the

formed nano-coating.

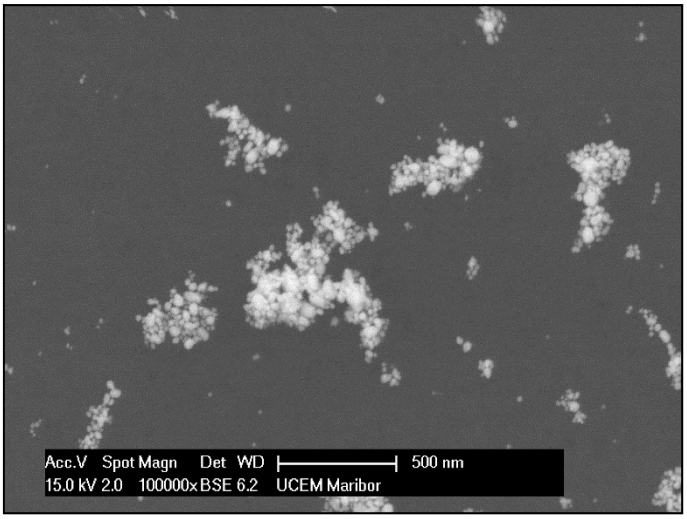


Figure 5. SEM micrograph of the AuNPs printed pattern on Ag plate

4. CONCLUSIONS

USP had been shown as a promising technique for the synthesis of AuNPs from Au (III) Acetate. AuNPs produced through USP were ellipsoidal in shape with a circularity of 60%, average diameter of 42±21.75 nm, having a zeta potential value of -33.8±1.2 mV and maximum absorbance wavelength of 528 nm.

Concentrated and stable customised ink was prepared from AuNPs. The ink jet printing was demonstrated successfully on an Ag plate. The ellipsoidal shaped AuNPs in the mentioned size range were appropriate for printing due to their smooth flow behaviour through the nozzle. These printed patterns showed the feasibility of printing on a metal surface. In the future, it is necessary to solve the technical problems of the non-uniformity and dispersibility of AuNPs.

5. ACKNOWLEDGEMENT

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СИНТЕЗА НАНОЧЕСТИЦА ЗЛАТА КРОЗ УЛТРАСОНИЧНУ СПРЕЈ ПИРОЛИЗУ И ЊЕНА ПРИМЈЕНА У ШТАМПАНОЈ ЕЛЕКТРОНИЦИ

Сажетак: Овај рад представља преглед ултрасоничне спреј пиролизе (УСП) као технике за синтезу наночестица злата (AuNPs). Механизам синтезе је обухватио припрему раствора прекурсора од Au(III) ацетате и проучавање процесних параметара. AuNPs су карактерисане различитим техникама, као што су DLS, UV-вис и CEM-EDX анализе. У наредном кораку, AuNPs мастило је припремљено сљедећом процедуром: (i) концентрација AuNPs кроз Ротавапор, (ii) филтрација концентрисаних AuNPs кроз Amicon Ultra 15 центрифугалне филтере. Затим је коришћена директно за штампање на Ag плочици. У завршном дијелу, представљамо неке информације о будућим примјенама AuNPs, које могу бити у штампаној електроници са вођеним обрасцима.

Кључне ријечи: ултрасонична спреј пиролиза, наночестице злата, карактеризација, штампање.

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