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SYNTHESIS OF Au NANOPARTICLES PREPARED WITH ULTRASONIC SPRAY PYROLYSIS AND HYDROGEN REDUCTION

SINTEZA Au-NANODELCEV, PRIPRAVLJENIH Z ULTRAZVOČNO RAZPRŠILNO PIROLIZO IN REDUKCIJO Z VODIKOM

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Golden nanoparticles of different sizes and shapes (spherical, cylindrical, triangular and round) were prepared during a synthesis of gold with ultrasonic spray pyrolysis (USP) and hydrogen reduction. The experimental investigations of the USP method were performed with an ultrasonic source of 0.8 MHz and 2.5 MHz, acting on the water solution of $HAuCl_4$ forming aerosols with micron-sized and nanosized droplets. The results of the investigation show that the final shape and size of the Au particles depend on the characteristics of the solution and the frequency of the ultrasound. The second step of synthesizing the Au nanoparticles includes the subsequent thermal decomposition of the aerosol droplets in a hydrogen atmosphere between 260 °C and 500 °C. The investigations showed that the Au nanoparticles prepared in this way are smaller and more homogeneous.

Keywords: gold, ultrasonic spray pyrolysis, reduction, nanoparticles

Zlate nanodelce različnih velikosti in oblik (sferični, cilindrični, trikotni in okrogli) smo pripravili s sintezo zlata z uporabo ultrazvočne razpršilne pirolize (USP) in redukcije. Eksperimentalne raziskave USP-metode so bile izvedene z ultrazvočnim izvirom s frekvenco med 0,8 MHz in 2,5 MHz z delovanjem na vodno raztopino $HAuCl_4$, kjer je prišlo do formiranja aerosolov z mikro- in nanovelikostjo kapljic. Rezultati preiskav kažejo, da je oblika in velikost nastalih Au-delcev odvisna od karakteristik raztopine in od frekvence ultrazvoka. Drugi proces sinteze Au-nanodelcev je vključeval kasnejšo toplotno dekompozicijo kapljic aerosola. Izveden je bil v vodikovi atmosferi med 260 °C in 500 °C. Preiskave so pokazale, da so tako izdelani Au-delci bolj homogeni in manjši.

Ključne besede: zlato, ultrazvočna razpršilna piroliza, redukcija, nanodelci

1 INTRODUCTION

Gold as a noble metal has a resistance to corrosion and it is used mostly in many engineering applications (contacts in microelectronics), medicine (dental alloys, implants) and also in jewellery and currency. When gold is broken into nanoparticles, this form could be highly useful for a wide range of processes, including general nanotechnology, electronics manufacturing and the synthesizing of different functional materials. Schmid and Corain[1] have studied the synthesis, structures, electronics and reactivity of gold nanoparticles. Their main conclusion is that a decrease in the sizes of gold nanoparticles has dramatic consequences on their physical and chemical properties.

Gold nanoparticles can have a better effect than micron-sized ones, because they accelerate the oxidation processes[2] easily. Successful examples of such practice are the published results, and, especially, the patents granted before 1978 (Bond[2]) revealing frequent observations of the potential of gold as a catalyst. Qi[3] reported on the production of propylene oxide over nanosized gold catalysts in the presence of hydrogen and oxygen. Polte et al.[4] reported on the mechanism of gold-nanoparticle formation in the classical citrate-synthesis method derived from a coupled in-situ XANES (X-ray absorption near-edge spectroscopy) and SAXS (small-angle X-ray scattering) evaluation. The efficient recovery of scraps and wastes in the gold-jewellery manufacturing is a vital component of a profitable manufacturing business, irrespective of whether it is a large factory or small, traditional workshop[5]. From the literature it is known that available techniques for gold purification include: 1) the cupellation, 2) the Miller chlorination process, 3) the Wohlwill electrolytic process, 4) the Fizzer cell, 5) the solvent extraction, 6) the aqua regia process and 7) the pyrometallurgical process. On the other hand, the process for recovering gold from a chloride solution is presented in the US Patent 4131454 by Piret et al.[6] It involves adding finely divided, activated carbon to the solution for the reduction of gold metal and its subsequent absorption by the carbon.

Prior[7] reported on successful hydrometallurgical refining of gold from the $HAuCl_4$ using the SO_2 gas as

the selective gold-precipitating agent. A gold sponge was produced with a chemical composition better than mass fraction 99.99 % and a uniform particle size. Using an efficient mass transfer, gold precipitation was realized with an injection of the SO_2 gas, based on the following reaction equation:

$$3\ SO_2 + 2\ HAuCl_4 + 6\ H_2O = \\ = 2\ Au + 3\ H_2SO_4 + 8\ HCl \quad (1)$$

The interactions between the gold nanoparticles and biological species found in an aqueous solution are being used as the basis for developing biosensors[8]. Many preparation methods for nanometallic particles have been proposed, such as photo reduction, chemical reduction in an aqueous medium with sodium citrate, chemical reduction in reverse micelles, or thermal decomposition in organic solvents. Aihara et al.[9] have reported on the preparation and characterization of gold and silver nanoparticles in the layered laponite suspensions.

The development of the colloid chemistry route continues to be essential for the synthesis and manipulation of anisotropic gold nanoparticles, with the major requirements already demonstrated by Treguer-Delapierre[10], such as the control of the nuclei shape and the growth on specific facets. A key feature of the non-spherical nanoparticles is that their optical properties vary dramatically with their physical dimensions. In contrast to the spherical gold nanoparticles, their resonance frequency is tuneable over a wide range from blue to near infrared and enables one to set the surface plasmon resonance to the wavelength or the spectral region specific to a particular application.

The most commonly used methods for synthesizing the gold powder are presented in **Table 1**.

In our previous research[11] spherical, round and cylindrical nanosized particles of gold were synthesized with the ultrasonic atomization of chloride-nitrate solutions based on the gold from a jeweller's scrap and an alloying element (Cu, Ag, Zn, In and Ni). A subsequent decomposition of the obtained solution at the temperatures of 300 °C and 800 °C in hydrogen and nitrogen atmospheres was performed. The aerosol produced by the resulting frequencies of 2.5 MHz and 0.8 MHz was transported by a carrier, mostly a reduction gas, into a hot reactor, where the aerosol droplets underwent drying, droplet shrinkage, solute precipitation, thermolysis and sintering to form the particles with different forms.

This study provides the latest information regarding the synthesis of different gold nanoparticles from a chloroauric acid using the USP method and the subsequent hydrogen reduction. Our main aim was to identify the influence of the reaction parameters on the particle size in order to obtain a better control of the particle nanosize and its morphology.

2 EXPERIMENTAL PROCEDURES

2.1 Ultrasonic spray pyrolysis method and hydrogen reduction

Tetrachloroauric acid $HAuCl_4$ (Johnson Matthey Company, Germany) was used as the precursor for the synthesis of gold nanoparticles with ultrasonic spray pyrolysis using the equipment developed at the IME, RWTH Aachen University.[12] The precursor was dissolved in water in order to prepare the solution for the aerosol production in an ultrasonic atomizer. The most

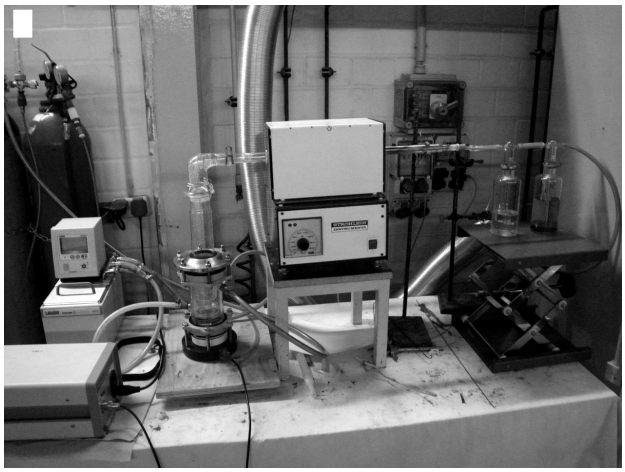

Figure 1: USP device
Slika 1: USP-naprava

Table 1: Methods for producing Au nanoparticles
Tabela 1: Metode izdelave Au-nanodelcev

Author	Method	Precursor	Reducing agent	Form and particle size (nm)
Schmid[1]	Reduction	$HAuCl_4$	Phosphor	Spherical
Polte[4]	Reduction	$HAuCl_4$	$Na_3C_6H_5O_7$	Spherical, below 100 nm
Piret[6]	Reduction, precipitation	Precious metal containing chloride leach	Zn, Fe	Above 1000 nm
Prior[7]	Reduction	$HAuCl_4$	$S0_2$	No information about the particle form (above 1000 nm)
M. Treguer-Delapierre[10]	Reduction	$HAuCl_4$	$NaBH_4$	Non-spherical, below 100 nm
Rudolf[11]	Ultrasonic spray pyrolysis/reduction	Water solution after a dissolution of jewellery scrap in HNO_3/HCl	H_2	Spherical, cylindrical, triangular, below 100 nm

important part of the set up contains the following (**Figure 1**): an ultrasonic atomizer, a small reactor with a quartz tube, a thermostat, two bottles with water and alcohol for the nanoparticle collection. The atomization of the obtained solution based on a water solution of gold chloride took place in an ultrasonic atomizer (Gapusol 9001, RBI/ France) with one transducer to create the aerosol. With regard to our previous results, the resonant frequency was selected to be between 0.8 MHz and 2.5 MHz.

Nitrogen was first flushed from the bottle to remove the air from the system. Under the spray-pyrolysis conditions hydrogen was passed continuously through the quartz tube (l = 1.0 m, b = 20 mm) at a flow rate of 1 L/min. Then, the atomized droplets of the solution based on gold were transported further by hydrogen to the furnace for the subsequent reduction of gold chloride at a different reaction temperature. After the completed reduction process, the obtained gold nanopowder was collected in the reaction tube and in two bottles with ethanol and water. In order to stabilize the collected gold nanoparticles, different solutions were used in the bottles. The performed experiments are shown in **Table 2**.

Table 2: Experimental conditions for the preparation of nanosized Au powder in hydrogen atmosphere, flow rate of 1 L/min, solution concentration of Au 2.5 g/L

Tabela 2: Eksperimentalni pogoji za pripravo Au-prahu nanovelikosti v vodikovi atmosferi; pretok 1 L/min, koncentracija raztopine Au 2,5 g/L

Exp.	Temperature, T/°C	Time, t/h	Solution	Ultrasonic frequency, f/MHz
1	260	5	Ethanol/Water	0.8
2	300	5	Ethanol/Water	0.8
3	280	5	Ethanol/Ethanol	0.8
4	400	5	Water/Water	0.8
5	500	6	Ethanol/Ethanol	0.8
6	300	5	Ethanol/Ethanol	2.5
7	260	5	Ethanol/Ethanol	2.5
8	280	6	Ethanol/Ethanol	2.5
9	260	4	Ethanol/Ethanol	2.5
10	260	4	Ethanol/Water	2.5

The obtained colours of the solutions were compared with the ones reported for the commercial gold nanoparticles (STREM Chemicals, Inc.).

Scanning electron (SEM) and high-resolution transmission (HR-TEM) electron microscopy with the connected energy-dispersive-spectroscopy (EDS) analysis were used for characterizing the nanoparticles. The SEM and TEM images have shown the surface morphologies of the particles formed at different parameter sets.

2.2 Formation of Au nanoparticles with hydrogen reduction in an ultrasonic generator

During the aerosol formation, the gold nanoparticles appeared in the ultrasonic generator, which was not

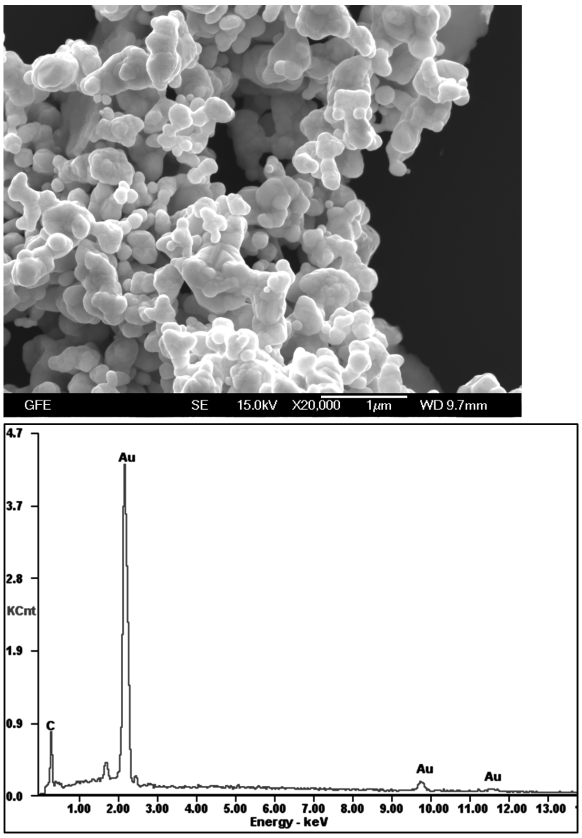

Figure 2: SEM image and EDS analysis of the Au nanoparticles obtained in an ultrasonic generator

Slika 2: SEM-posnetek in EDS-analiza Au-nanodelcev, izdelanih v ultrazvočnem generatorju

expected. The formed particles were agglomerated and round, as shown in **Figure 2**. This phenomenon has to be investigated further and discussed in order to find the optimum parameters for the synthesis (ultrasonic frequency, hydrogen flow rate, concentration of the solution). We hope that the ultrasonic frequency (0.8 MHz and 2.5 MHz) can initiate the formation of nanosized gold particles at room temperature. In the absence of hydrogen the formation of gold nanoparticles was not seen. After the experiments, the gold nanoparticles were separated with the filtration. The collected gold nanopowders from the ultrasonic generator were analysed with SEM and EDS (**Figure 2**).

3 RESULTS AND DISCUSSION

3.1 Characterisation of the obtained gold nanoparticles

A different morphology of the nanoparticles was obtained with the USP method at 260 °C using an ultrasonic frequency of 0.8 MHz (**Figure 3**). The presence of triangular, rounded and irregular particles revealed that a synthesis of gold nanoparticles is possible at low temperatures, but this structure is different from the ideally spherical metallic nanoparticles (copper, cobalt, nickel)

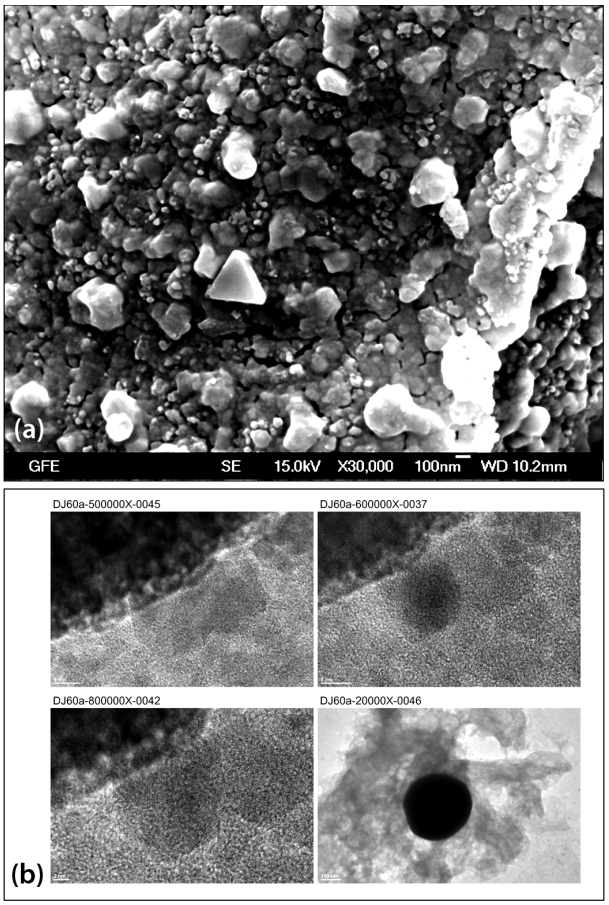

Figure 3: a) SEM image of Au nanoparticles (synthesis parameters: 260 °C, f = 0.8 MHz), b) TEM image of Au nanoparticles (synthesis parameters: 260 °C, f = 0.8 MHz)

Slika 3: a) SEM-posnetek Au-nanodelcev (parametri sinteze: 260 °C, f = 0,8 MHz), b) TEM-posnetek Au-nanodelcev (parametri sinteze: 260 °C, f = 0,8 MHz)

prepared during our previous research[12]. The presence of a similar, triangular and rounded, morphology was only reported for the synthesis of silver nanoparticles from silver nitrate at 300 °C in our previous work.

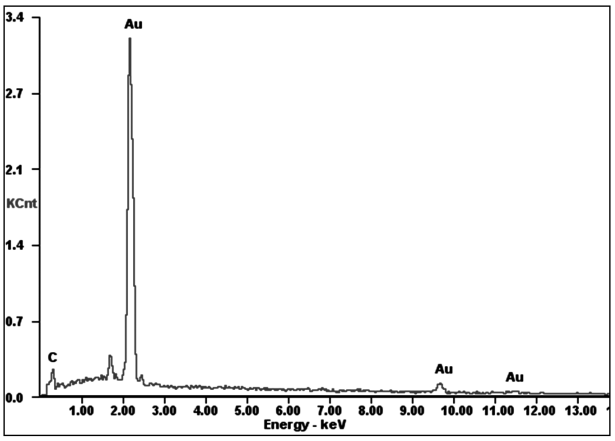

Figure 4: EDS analysis spectrum of the Au nanoparticles from the experiment (1)

Slika 4: EDS analizni spekter Au-nanodelcev iz eksperimenta (1)

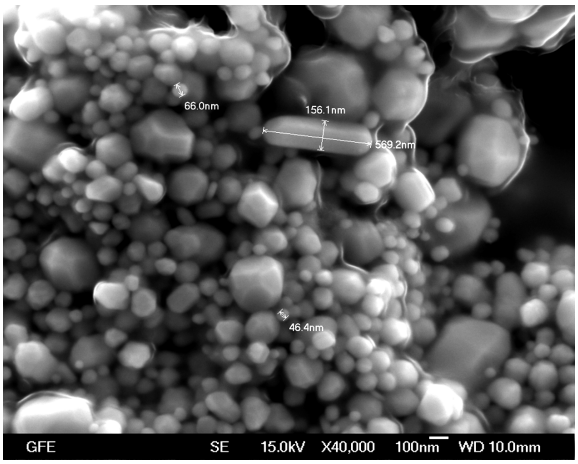

Figure 5: SEM image of Au nanoparticles (synthesis parameters: 280 °C, 2.5 MHz)

Slika 5: SEM-posnetek Au-nanodelcev (parametri sinteze: 280 °C, 2,5 MHz)

The Au particles produced during the USP experiment are of high purity as seen also from the spectrum on **Figure 4**.

The increase in the temperature to 280 °C revealed a presence of cylindrical particles (**Figure 5**). In addition, the proportion of the rounded particles is larger at 280 °C than at 260 °C. It seems that the nanoparticles grow together.

The presence of the triangular, rounded and irregular particles revealed that a synthesis of gold nanoparticles is possible at low temperatures, but their structure is different from the ideally spherical metallic particles (silver, nickel) prepared during our previous research.[12,13] The increase in the temperature from 260 °C to 280 °C revealed a presence of cylindrical particles. Also, the proportion of the rounded particles is more prevalent at higher temperatures. It seems that nanoparticles grow together. The particle size of the finally obtained Au powder especially depends on the droplet diameter and the initial concentration of the solution. The increase in the ultrasonic frequency from 0.8 MHz to 2.5 MHz, at a constant precursor concentration, leads to a decrease in the the droplet size and, finally, to a higher amount of smaller nanoparticles in the final product.

The experiments showed that the increase in the reaction temperature to 500 °C, at the same frequency, leads to a different form of the particles and an increased agglomeration of the particles.

Based on the capillary theory, the diameter of nanoparticles was predicted from equation (2), formed by combining the Kelvin equation and the equation reported by Messing at al.[14]:

$$D_{\mathrm{Au}} = 0.34 \cdot \left(\frac{8\pi\gamma}{\rho_{\mathrm{sol}} f^2} \right)^{\frac{1}{3}} \cdot \left(\frac{C_{\mathrm{sol}} M_{\mathrm{Au}}}{\rho_{\mathrm{Au}} M_{\mathrm{sol}}} \right)^{\frac{1}{3}} \qquad (2)$$

where D_{Au} is the diameter of a nanoparticle (m), γ is the surface tension (N/m), f is the ultrasonic frequency (s^{-1}),

C_{sol} is the concentration of the starting solution (g/cm^3), M_{sol} is the molar mass of the starting solution of $HAuCl_4$ (g/mol), M_{Au} is the molar mass of gold (g/mol), ρ_{sol} is the density of the atomized solution and ρ_{Au} is the density of gold (g/cm^3).

Assuming that the characteristics of water are close to those of the used diluted precursor solution, the parameters of our experiments amounted to: $\gamma = 72.9 \times 10^{-3}$ N/m, $\rho = 1.0$ g/cm^3, $f = 0.8 \times 10^6$ s^{-1} leading to the calculated value of the ultrasonically dispersed droplet diameter of $D = 4.79 \times 10^{-6}$ m. An increase in the operating frequency from $f = 0.8 \times 10^6$ s^{-1} to $f = 2.5 \times 10^6$ s^{-1} decreased the aerosol droplet size from $D = 4.79 \times 10^{-6}$ m to 2.26×10^{-6} m.

The expected mean diameter of a particle in the finally obtained Au-powder, after the hydrogen reduction, depends, especially, on the droplet diameter and the initial concentration of the solution. Assuming that each droplet is transformed into one particle and that during the atomization no coalescence occurs, the final particle diameter can be calculated using equation (2).

Using the parameters of our experiments – the droplet mean diameter $D = 4.79$ μm, $M_{Au} = 196.97$ g/mol, $M_{HAuCl4} = 339.8$ g/mol, $\rho_{Au} = 19.3$ g/cm^3, the concentration of gold between 1 g/dm^3 and 10 g/dm^3 – the calculated mean particle diameter of gold amounts to between 60 nm and 150 nm. Under the same conditions and for the frequency of $f = 2.5 \times 10^6$ s^{-1} the calculated mean particle diameter of gold amounted to between 150 nm and 300 nm (**Figure 6**). The particle size of gold was decreased as a result of the reaction in a smaller droplet with the same concentration. In contrast to the water solution, the stabilization of gold nanoparticles was performed successfully using ethanol in the second bottle in order to prevent a possible agglomeration.

The present differences between the calculated and experimentally obtained values of gold particles may be due to the approximate values used for the surface tension and density of the aqueous solution, the microporosity of the particles and, especially, due to the coalescence/agglomeration of the aerosol droplets at a high flow rate of the carrier gas (the turbulence effects). Also, in equation (2), based on the assumption of one particle per one droplet, the influence of the temperature on the mean particle size was not taken into account. In order to decrease this difference between the calculated and experimentally obtained values of gold nanoparticles, the aerosol droplet size obtained from the gold-based solution should be measured precisely with the laser diffraction and used in the above-mentioned calculations (**Table 3**). Additionally, in contrast to our previously prepared spherical particles of Cu, Co and Ni, the presence of rods and discs in the gold structure represents news of interest for an application.

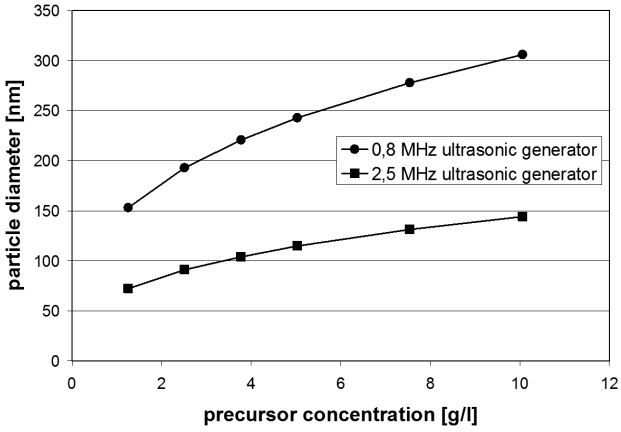

Figure 6: Calculated size of Au nanoparticles
Slika 6: Izračunana velikost Au-nanodelcev

Table 3: Comparison of the experimental and calculated particle diameters
Tabela 3: Primerjava eksperimentalno dobljenih ter izračunanih vrednosti premera delcev

Concentration of Au in $HAuCl_4$: 2.5 (g/L)	Particle size (nm)	
	$f = 0.8$ MHz	$f = 2.5$ MHz
Experimental	38–200	10–250
Calculated	193	91

3.2 Influence of different parameters

The influence of the reaction temperature and type of the carrier gas on the size and shape was studied. Because of the very fast kinetics of the thermal decomposition of $HAuCl_4$ and a short retention time of the aerosol in the reactor, causing a fast particle formation and growth of gold nanoparticles, it is very difficult to separately obtain only one ideal form of the nanoparticles (a sphere or a triangle) by changing different reaction parameters (**Figure 7**).

Treguer-Delapierre et al.[10] maintained that further efforts should focus on a better understanding of the growth mechanism to find the best shape.

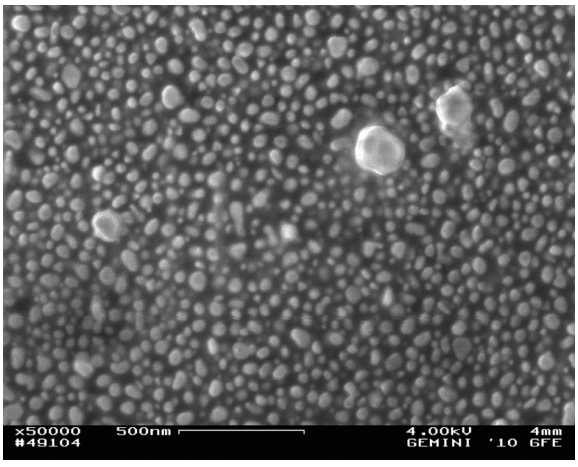

Figure 7: SEM image of Au nanoparticles (synthesis parameters: 260 °C, 2.5 MHz)
Slika 7: SEM-slika Au-nanodelcev (parametri sinteze: 260 °C, 2,5 MHz)

A thermal-gravimetric analysis was used by Sawada and Ando[15] in order to explain the decomposition of $HAuCl_4$ in a neutral atmosphere. They reported that the formation of the first peak below 120 °C was caused by the evaporation of the crystal water and the decomposition of $HAuCl_4$ into $AuCl_3$, because the residual weight between 260 °C and 750 °C (75 %) was close to the weight of $AuCl_3$ (77 %). The subsequent decomposition began at 750 °C and did not stop at 900 °C. This indicates that $HAuCl_4$ was not reduced to gold by the thermal treatment below 900 °C in a neutral atmosphere. The gold formation from $HAuCl_4$ takes place in two steps:

$$2\ HAuCl_4 \Leftrightarrow Au_2Cl_6 + 2\ HCl \quad (3)$$

$$Au_2Cl_6 + 3\ H_2 \Leftrightarrow 2Au + 6\ HCl \quad (4)$$

As shown in **Figure 8**, an increase in the temperature up to 800 °C increases the changes in the Gibbs-free energies ΔG between –527 kJ and –872 kJ for the hydrogen reduction and between 251 kJ and –54 kJ for the thermal decomposition of $HAuCl_4$. In contrast to the thermal decomposition (positive values of ΔG), up to 600 °C the hydrogen reduction of gold chloride was always characterized with negative values, which suggests that there is a high possibility that this reaction happens. The thermal decomposition of $HAuCl_4$ is reported by Kumar[16] for a reduction of a tetrachloroauric acid with trisodium citrate. Trisodiumcitrate is both the reducing agent and the stabilizer. In this multiple-step process, the most important steps are:

$$AuCl_3 + 2\ e^- \rightarrow AuCl + 2\ Cl^- \quad (5)$$

$$3\ AuCl \rightarrow 2\ Au^o + AuCl_3 \quad (6)$$

The disproportion step requires three aurous species to gold atoms.

The positive value of ΔG for the thermal decomposition of $HAuCl_4$ suggests a small possibility for a formation of gold chloride, although the reported theoretical decomposition temperature of $HAuCl_4$ amounts to 258 °C. Also, our previous TGA analysis[13] confirmed that the thermal decomposition of $HAuCl_4$ takes place between 260 °C and 750 °C.

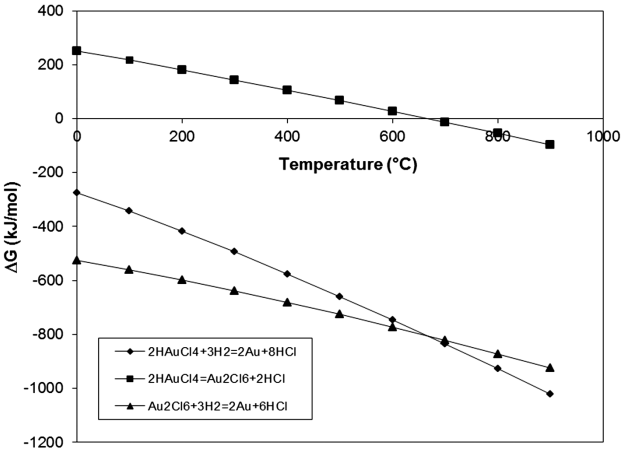

Figure 8: Thermochemical calculation for a decomposition of $HAuCl_4$ and hydrogen reduction

Slika 8: Termokemijski izračun za razgradnjo $HAuCl_4$ z redukcijo v vodiku

4 CONCLUSIONS

Gold nanoparticles were prepared with USP and the subsequent hydrogen reduction between 260 °C and 500 °C. Using the ultrasonic frequencies between 0.8 MHz and 2.5 MHz, the formed aerosols with constant droplet sizes between 2.2 μm and 4.8 μm were thermally decomposed in a hydrogen atmosphere in a reactor. The SEM and EDS analyses confirmed the presence of gold with different morphological forms (spherical, cylindrical and triangular), which is of great importance for some medical applications. It was very difficult to separately prepare only one ideal form of nanoparticles (a sphere or a triangle) by changing different reaction parameters during the USP synthesis and the subsequent hydrogen reduction. The controlled morphology of the gold nanoparticles prepared with USP and other methods (precipitation, reduction in autoclave) will be studied in our future research investigating the influence of the other important reaction parameters (reducing agent, gas flow rate, pressure).

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