Synthesis of Au nanoparticles prepared by ultrasonic spray pyrolysis and hydrogen reduction
Sinteza Au nanodelcev pripravljenih z ultrazvočno razpršilno pirolizo in vodikovo redukcijo

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Abstract

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

Keywords: gold, ultrasonic spray pyrolysis, reduction, nanoparticles

Povzetek

Zlate nanodelce različne velikosti in oblike (sferični, cilindrični, trikotni in okrogli) smo pripravili s sintezo zlata s pomočjo ultrazvočne razpršilne pirolize (USP) in vodikove redukcije. Eksperimentalne raziskave USP metode so bile izvedene z ultrazvočnim izvorom med 0.8 in 2.5 MHz z delovanjem na vodno raztopino $AuCl_4$, kjer je prišlo do formiranja aerosolov z mikro in nano velikostjo 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 naknadno toplotno dekompozicijo kapljic aerosola. Izveden je bil v vodikovi atmosferi med 260 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 resistance to corrosion and it is used mostly in many engineering applications (contacts in micro-electronics), 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 conclusions are that a decrease in the sizes of the 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. Some of such successful praxis are the published results, and especially patents, granted before 1978 by Bond[2] which reveals frequent observations of the potential of gold as a catalyst. Qi[3] reported the production of propylene oxide over nanosized gold catalysts in the presence of hydrogen and oxygen. Polte et al.[4] reported the mechanism of gold nanoparticle formation in the classical citrate synthesis method derived from 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 gold jewellery manufacture 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 possible techniques for gold purification contain: 1) Cupellation, 2) Miller chlorination process, 3) Wohlwill electrolytic process, 4) Fizzer cell, 5) 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 US Patent 4131454 by Piret et al.[6] It involves adding finely divided activated carbon to the solution for reduction of gold metal and subsequent absorption of the gold metal by the carbon.

Prior[7] reported on successful hydrometallurgical refining of gold from the $HAuCl_4$ using SO_2 gas as the selective gold precipitating agent. Gold sponge was produced with a chemical composition better than 99.99 wt % at very uniform particle size. Using an efficient mass transfer gold precipitation was realized by an injection of SO_2-gas, which basically follows the reaction equation:

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

Interaction between gold nanoparticles and biological species found in aqueous solution are being used as a basis for the development of biosensors[8]. Many preparation methods of 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 layered laponite suspensions.

The development of a 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 gold spherical 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 a wavelength or spectral region specific to a particular application.

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

Table 1: Methods for production of 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 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 dissolution	H_2	Spherical, cylindrical,

		of the jewellery scrap in HNO_3/HCl		triangular below 100 nm

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

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

2 EXPERIMENTAL PROCEDURES

2.1 Ultrasonic spray pyrolysis method and hydrogen reduction

Tetrachloroauric acid $HAuCl_4$ (Johnson Matthey Company, Germany) was used as a precursor for the synthesis of gold nanoparticles by 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 an aerosol production in an ultrasonic atomizer. The most important part of the set up contains (**Figure 1**): the ultrasonic atomizer, a small reactor with a quartz tube, a thermostat, two bottles with water and alcohol for nanoparticle collection. 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 and 2.5 MHz.

Figure 1: USP device

Slika 1: USP naprava

Nitrogen was first flushed from the bottle to remove air from the system. Under 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, 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 nano-powder was collected in a 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, a hydrogen atmosphere, flow rate of 1 l/min, concentration of solution 2.5 g Au/l

Tabela 2: Eksperimentalni pogoji za pripravo Au prahu nano - velikost iz vodikove atmosfere, pretok 1 l/min, koncentracija raztopine 2.5 g Au/l

Exp.	Temperature (°C)	Time (hour)	Solution	Ultrasonic Frequency (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 solutions were compared with ones reported for commercial gold nanoparticles (STREM Chemicals, Inc.).

Scanning electron (SEM) and high resolution transmission (HR-TEM) electron microscopy with connected Energy Dispersive Spectroscopy EDS analysis were used for characterization of nanoparticles. SE and TE images visualization have shown the surface morphology of particles formed at different parameter sets.

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

During an aerosol formation gold nanoparticles appeared in the ultrasonic generator, which was not 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 some optimal parameters for the synthesis (ultrasonic frequency, hydrogen flow rate, concentration of solution). We hope that an ultrasonic frequency (0.8 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 by filtration. Collected gold nanopowders from the ultrasonic generator were analysed by SEM and EDS (Fig. 2)

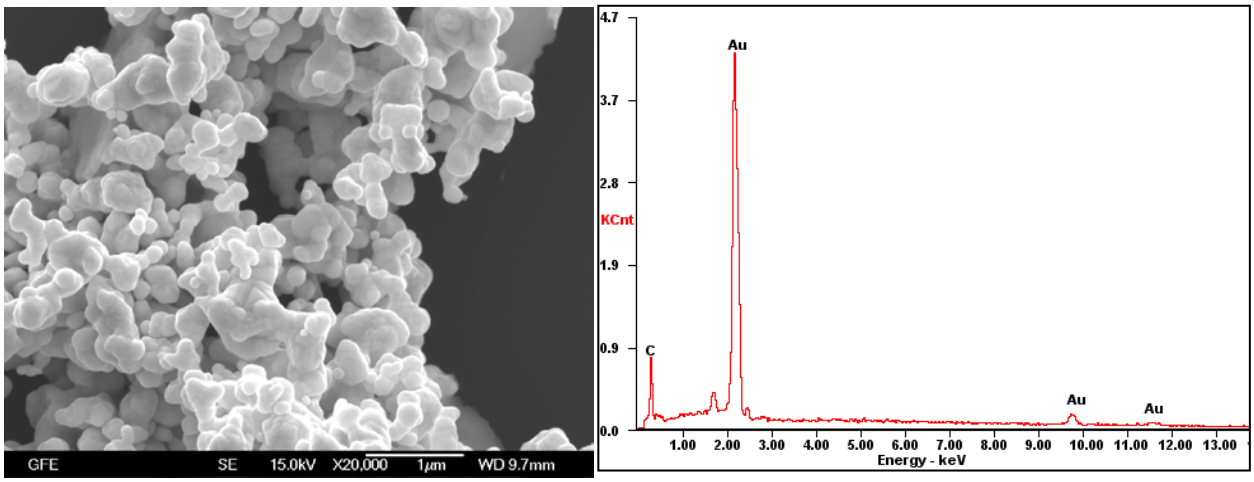


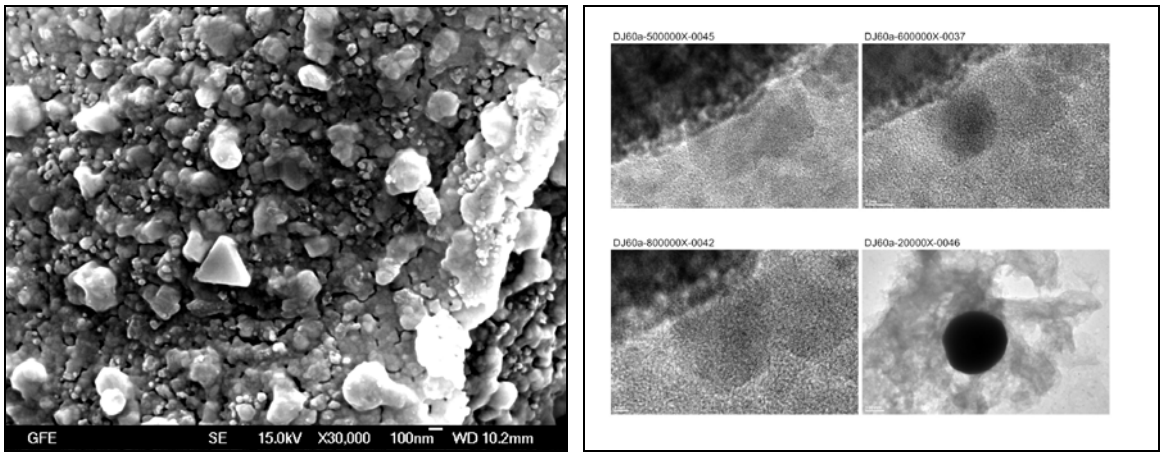
Figure 2: SE image and EDS analysis of Au nanoparticles obtained in an ultrasonic generator

Slika 2: SE posnetek in EDS analiza Au nanodelcev izdelanih v ultrazvočnem generatorju

3 RESULTS AND DISCUSION

3.1 Characterisation of obtained gold nanoparticles

Different morphology of nanoparticles was obtained by 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 the synthesis of gold nanoparticles is possible at low temperatures, but this structure is different in comparison to the ideally spherical metallic nanoparticles (copper, cobalt, nickel) prepared in our previous work[12]. The presence of similar triangular and rounded morphology was only reported by the synthesis of silver nanoparticles from silver nitrate at 300°C in our previous work.



A) **B)**

Figure 3: A) SE image of Au- nanoparticles (synthesis parameters: 260°C, f=0.8 MHz), B) TE image of Au- nanoparticles (synthesis parameters: 260°C, f=0.8 MHz).

Slika 3: A) SE posnetek Au - nanodelcev (parametri sinteze: 260°C, f=0.8 MHz)

B) TE posnetek Au - nanodelcev (parametri sinteze: 260°C, f=0.8 MHz)

The Au particles which are produced by USP experiment are high purity what could be seen also from spectrum on the **Figure 4**.

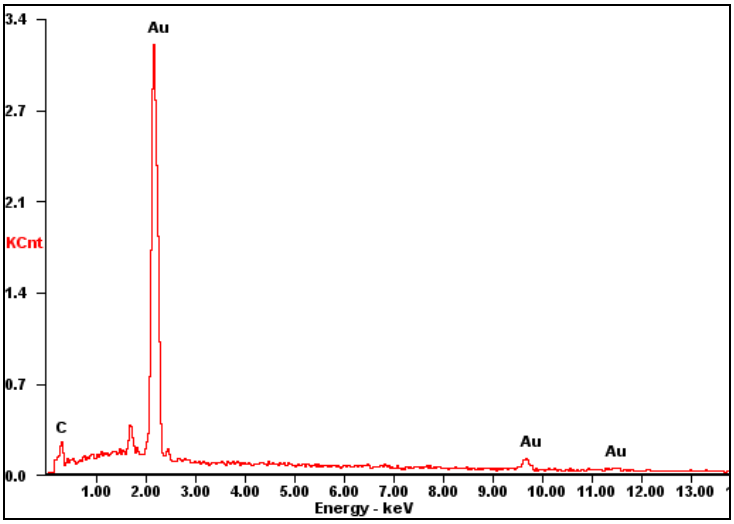


Figure 4: EDS analysis spectrum of Au- nanoparticles from experiment (1)

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

The increase of temperature to 280°C has revealed the presence of cylindrical particles (**Figure 5**). Also the ratio of rounded particles is more available at 280°C than at 260°C. It seems that nanoparticles grow together.

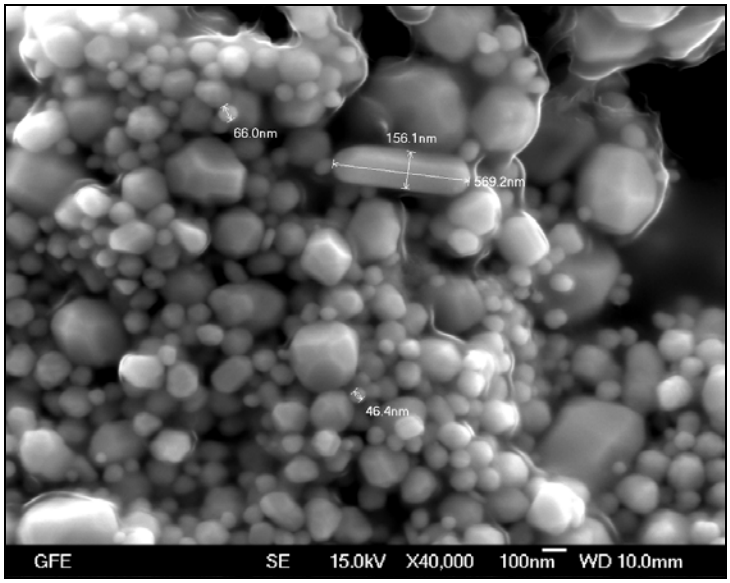


Figure 5: SE image of Au- nanoparticles (synthesis parameters: 280°C, 2.5 MHz)

Slika 5: SE posnetek Au nanodelcev (parametri sinteze: 280°C, 2.5 MHz)

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

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

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

$$D_{Au} = 0{,}34 \cdot \left(\frac{8 \cdot \pi \cdot \gamma}{\rho_{sol} \cdot f^2} \right)^{\frac{1}{3}} \cdot \left(\frac{C_{sol} \cdot M_{Au}}{\rho_{Au} \cdot M_{sol}} \right)^{\frac{1}{3}} \qquad (2)$$

where D_{Au} is the diameter of the nanoparticle (m), γ- surface tension (N/m) , f- ultrasonic frequency (s^{-1}), C_{sol}- concentration of the starting solution (g/cm^3), M_{sol}- molar mass of the starting solution of $HAuCl_4$ (g/mol), M_{Au}- molar mass of gold (g/mol), ρ_{sol}- density of the atomized solution, and ρ_{Au}- 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: $\gamma = 72.9 \cdot 10^{-3}$ N/m, $\rho = 1.0$ g/cm^3, $f = 0.8 \times 10^6$ s^{-1} and led to a calculated value of the ultrasonically dispersed droplet diameter of $D = 4.79 \times 10^{-6}$ m. An increase of 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 particle diameter of the finally obtained Au-powder after hydrogen reduction depends especially on droplet diameter and the initial concentration of the solution, assuming that each droplet is transformed into one particle and that during atomization no coalescence occurs, the final particle diameter can be calculated using equation (2).

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

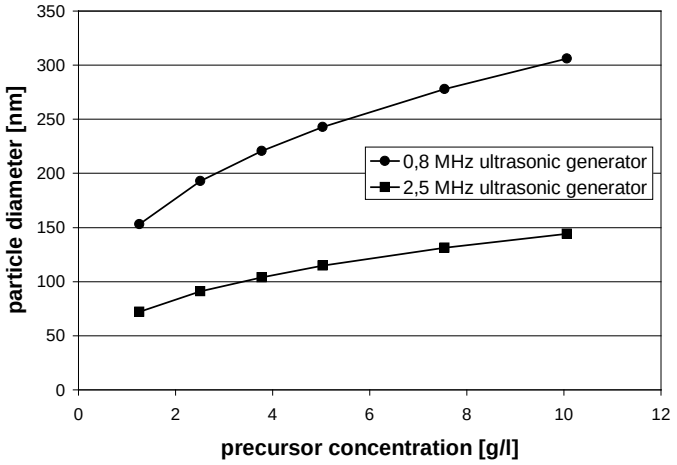


Figure 6: Calculated size of Au nanoparticles

Slika 6: Izračunana velikost Au nanodelcev

Present differences between 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, micro-porosity of particles and, especially, due to the coalescence/agglomeration of aerosol droplets at a high flow rate for the carrier gas (turbulence effects). Also in the equation (2), based on the assumption of one particle per one droplet, the influence of temperature on the mean particle size was not taken into account. In order to decrease this difference of the calculated and experimentally obtained values of gold nanoparticles the aerosol droplet size obtained from gold based solution should be measured precisely by laser diffraction and used in the above-mentioned calculations (**Table 3**). Additionally, in contrast to our previous 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.

Table 3: Comparison of experimental and calculated particle size diameter

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 The influence of different parameters

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

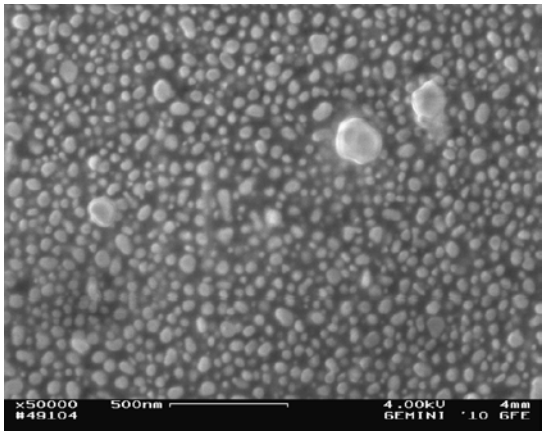


Figure 7: SE image of Au –nanoparticles (synthesis parameters: 260°C, 2.5 MHz)

Slika 7: SE slika Au nanodelcev (parametri sinteze: 260°C, 2.5 MHz)

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

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 $HAuCl_4$ to $AuCl_3$, because the residual weight between 260 and 750°C (75%) was close to the weight of $AuCl_3$ (77%). Subsequent decomposition began at 750°C and did not terminate at 900°C. This indicates that $HAuCl_4$ was not reduced to gold by 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 at **Figure 8,** an increase of temperature up to 800°C increases changes of Gibbs free energies ΔG between -527 and -872 kJ for hydrogen reduction and from 251 and -54 kJ for thermal decomposition of $HAuCl_4$. In contrast to thermal decomposition (positive values of ΔG) until 600°C the hydrogen reduction of gold chloride was always characterized with negative values, which suggests that this reaction might happen with a high possibility. Thermal decomposition of $HAuCl_4$ is reported by Kumar[16] in the reduction of tetrachloroauric acid with trisodium citrate. Trisodiumcitrate is both the reducing agent and the stabilizer. In the 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.

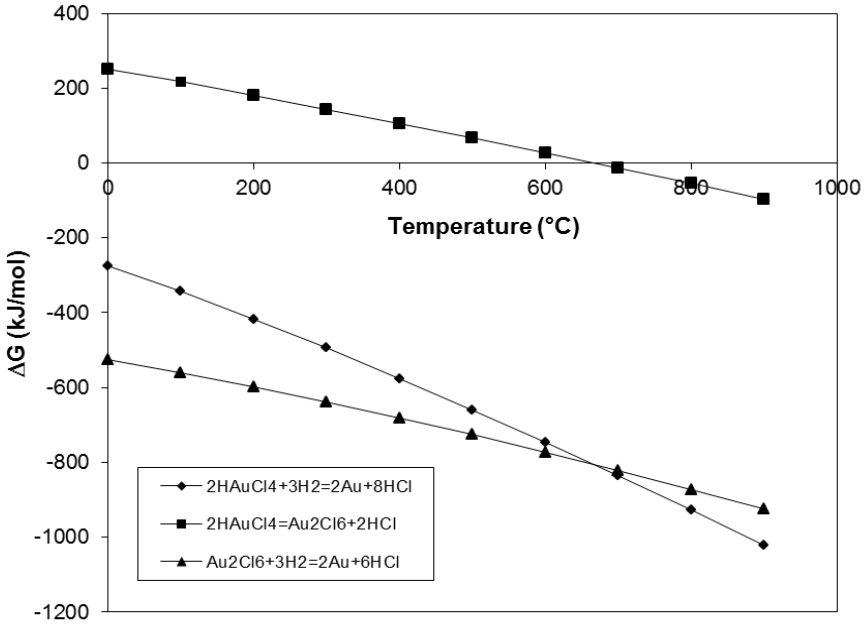


Figure 8: Thermochemical calculation for decomposition of $HAuCl_4$ and hydrogen reduction

Slika 8: Termokemijski izračun za razgradnjo $HAuCl_4$ in redukcijo vodika

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

4 Conclusions

Gold nanoparticles were prepared by USP and subsequent hydrogen reduction between 260 °C and 500 °C. Using the ultrasonic frequencies between 0.8 and 2.5 MHz the formed aerosols with constant droplet sizes between 2.2 and 4.8 µm were thermally decomposed in a hydrogen atmosphere in a reactor. SEM and EDS analysis have 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 prepare separately only one ideal form of nanoparticles (sphere or triangle) by changing the different reaction parameters during USP synthesis and a subsequent hydrogen reduction. The controlled morphology of gold nanoparticles prepared by USP and other

methods (precipitation, reduction in autoclave) will be studied in our future work investigating the influence of other important reaction parameters (reducing agent, gas flow rate, pressure).

5 Acknowledgment

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