



Mechanism of nanogold formation by ultrasonic spray pyrolysis

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Abstract

Mechanism of gold nanoparticle synthesis by ultrasonic spray pyrolysis was realized by an investigation of reactions parameters and morphological characteristics. Previous thermochemical analysis of decomposition of HAuCl_4 and subsequent hydrogen reduction of Au_2Cl_3 was performed in order to predict a temperature regime for gold formation. The experimental investigations 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 constant droplet sizes, which depends on the characteristics of the solution and the frequency of the ultrasound. Subsequent thermal decomposition of the aerosol droplets was performed in hydrogen atmosphere between 260 °C and 500 °C. SEM and EDS analysis were used for the characterization of nanoparticles. Different forms of gold nanoparticles were formed after hydrogen reduction: spherical, rod-shaped, triangular particles. The theoretically and experimentally obtained particle sizes were compared. The mechanism of synthesis of nanosized particles was proposed.

1 Introduction

Gold is known to be a noble metal which means that it is inert and shows little reactivity. The resistance of gold to corrosion has been known to the human for millennia and is reflected in the use of gold in jewellery and currency. Also it was found that very small gold particles can catalyze, i.e. accelerate, important chemical reactions (the oxidation of hydrogen and carbon monoxide) [1]. Examination of the published results and especially patents granted before 1978 by Bond [1] reveals frequent observation of the potential of gold a catalyst, some of which may inspire new directions for work on its applications. Qi [2] reported about the production of propylene oxide over nanometer Au catalysts in the presence hydrogen and oxygen.

The release of gold for metallurgical recovery from gold deposits is dependent on the nature and particle size of the gold-bearing mineral, the textural association of gold with gangue and economically recoverable sulfides (e. g. sphalerite, galena, and chalcopyrite), and the gangue mineral [3]. The efficient recovery of scraps and wastes in gold jewellery manufacture is a vital component of a profitable jewellery manufacturing business, irrespective of whether it is a large factory, or small, traditional workshop [4]. Possible techniques for gold purification contain: 1) cupellation, 2) inquir-



tation and parting, 3) Miller chlorination process, Wohlwill electrolytic process, 4) Fizzer cell, 5) Solvent extraction, 6) Aqua regia process and 7) pyrometallurgical process. Which process is selected depends on a number of factors: 1) amount and nature (gold content) of scrap to be processed, b) capital cost of equipment and safety/pollution control installation, c) technical skills available, d) speed and yield of process, which impact overall economics. Process for recovering silver and gold from chloride solution is presented in US Patent 4131454 [5]. It involves adding finely divided activated carbon to the solution for reduction of gold metal and absorption of the gold metal by the carbon.

In last time gold nanoparticles are of high interest because of their potential application of electrochemistry, in medicine and producing nanodevices. Reasons for the high reactivity of these nanoparticles, so-called clusters, are assumed to be hidden in their atomic structure. As the active nanoparticles are smaller than the wavelength of visible light their structure cannot be inspected using an optical microscope. In the recent past, the structure of charged gold clusters had been determined, but that of the neutral clusters, thought to be more relevant for the catalytic activity, remained elusive. Interaction between gold nanoparticles and biological species found in aqueous solution are being used as a basis for the development of biosensors [6]. Many preparation methods of nanometallic particles have been proposed, such as photoreduction, chemical reduction in aqueous medium with or without polymers, chemical reduction in reverse micelles, or thermal decomposition in organic solvents. Aihara et al. [7] reported about a preparation and characterization of gold and silver nanoparticles in layered laponite suspensions. The obtained results lead to a conclusion that bimetallic gold/silver nanoparticles prepared in this study are alloy particles rather than core-shell particles.

Chemical synthesis of gold nanoparticles with well-controlled shapes, sizes and structures is becoming a practical reality. The development of a colloid chemistry route continues to be essential for the synthesis and manipulation of anisotropic gold nanoparticles, with major requirements already demonstrated by Treguer-Delapierre et al. [8], 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 nanospheres, 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. Together with the high degree of biocompatibility of gold, these structures show potential in a wide variety of biological applications. It has also been speculated that they play role in future cancer diagnosis and therapy. To improve early cancer detection, researchers are developing in vivo biomedical imaging techniques with the resolution to distinguish between healthy and malignant tissue.

In our previous work spherical and cylindric nanosized particles of gold were synthesized by ultrasonic atomization of chloride-nitrate solutions based on gold an alloying element (Cu, Ag, Zn, In and Ni) and a subsequent decomposition of obtained solution at temperatures 300°C and 800°C in hydrogen and nitrogen atmosphere [10]. The produced aerosol by a 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 undergo drying, droplet shrinkage, solute precipitation, thermolysis and sintering to form particles with different forms. Very short residence times, less then one minute are frequently enough to ensure the formation of the desired spherical nanopowder.

Recycled white gold is used as an initial material, that was dissolved by the mixture of chloric and nitric acid. Cytotoxicity of Gold Nanoparticles Prepared by Ultrasonic Spray Pyrolysis was studied in detail. The target cells were rat thymocytes, as a type of non-proliferating cells, and L929 mouse fibroblasts, as a type of continuous proliferating cells. Fractions 1 and 2, composed of pure



nanogold particles, as determined by scanning electron microscopy with a combination of energy dispersive X-ray analysis, were non-toxic for thymocytes, but reduced moderately the proliferative activity of L929 cells. The inhibitory effect of fraction 2, containing particles smaller in size than fraction 1, was stronger. Fraction 3, composed of Au and up to 3% Cu was non-cytotoxic for thymocytes, but was cytotoxic for L929 cells. Fraction 4, composed of Au/Ag and Ag nanoparticles, and fraction 5, composed of Au together with Cu, Ni, Zn, Fe and In were cytotoxic for both thymocytes and L929 cells.

This study provides the newest information regarding to the synthesis of gold nanoparticle from chloroauric acid HAuCl_4 by ultrasonic spray pyrolysis method in order to explain a mechanism of gold formation. In the USP-process, a metal-containing solution is cold atomized forming an aerosol that was transported with hydrogen in to produce nanoparticles of gold between 260 and 500°C.

2 Thermal decomposition of HAuCl_4

Thermalgravimetric analysis was used by Sawada and Ando in order to explain decomposition of HAuCl_4 in neutral atmosphere [11]. They reported that the formation of 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 neutral atmosphere.

The gold formation from HAuCl_4 takes place in two steps:



As shown at Fig. (1) 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, what suggests that this reaction might happen with big probability.

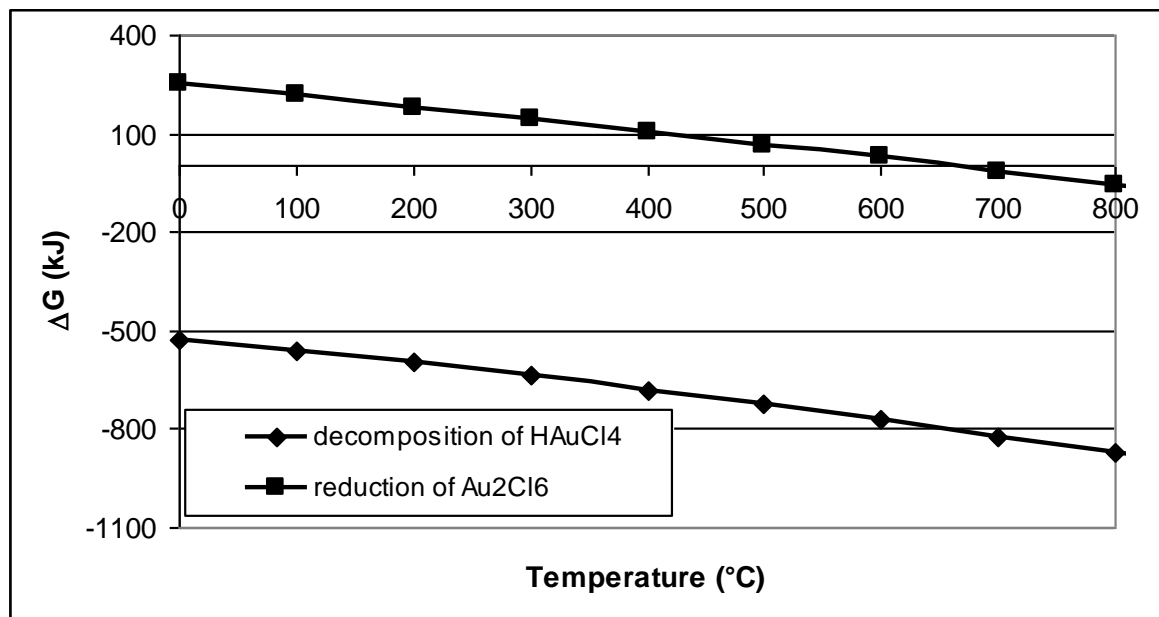


Fig. 1: Thermochemical calculation for decomposition of HAuCl₄ (1) and hydrogen reduction (2)

The positive value of ΔG for thermal decomposition of HAuCl₄ suggests a small possibility for the formation of gold chloride, although theoretical reported decomposition temperature of HAuCl₄ amounts 258°C. Also the previous TGA analysis has confirmed thermal decomposition of HAuCl₄ between 260 and 750 °C.

3. Experimental

3.1 Material and procedure

Chloroauric acid HAuCl₄ was used as precursor for the synthesis of gold nanoparticles by ultrasonic spray pyrolysis using the equipment shown schematically in Figure 1. 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 contain: the ultrasonic atomizer, a small reactor, two bottles with water and alcohol for nanoparticle collection. Atomization of the obtained solution based on water solution of gold chloride took place in an ultrasonic atomizer (Gapusol 9001, RBI/ France) with one transducer to create the aerosol. Regarding to our previous results the resonant frequency was selected to be between 0.8 and 2.5 MHz.



Fig. 2 Experimental setup for the USP-synthesis of gold nanoparticles at IME, RWTH Aachen

The most important components: ultrasonic generator, thermostat, reaction tube, furnace, a bottle with water and alcohol, bottle with hydrogen. Nitrogen was firstly flushed from bottle to remove air from the system. Under spray pyrolysis conditions hydrogen overpassed continuously through the quartz tube ($l= 1.0$ m, $b= 20$ mm) at a flow rate of the 1 l/min. Then atomized droplets of the solution based on gold were further transported by hydrogen to the furnace for hydrogen reduction at different reaction temperature. After thermal decomposition and reduction transported aerosol in furnace the formed nanopowder of gold was collected in a reaction tube and a bottle. The performed experiments are shown in Table 1:

Table 1: 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

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



In order to stabilize the collected gold nanoparticle different solution were used in bottles. The obtained colors of solutions were compared with ones reported for commercial gold nanoparticles.

A scanning electron microscope with connected EDS analysis were used for characterization of nanoparticles. SEM images have shown the surface morphology of particles formed at different parameter sets.

3.2. Results

3.2.1 Morphological characteristics of particles

Different morphology of nanoparticles is obtained by ultrasonic spray pyrolysis method at 260°C. The presence of triangular, rounded and irregular particles revealed that the synthesis of gold nanoparticles is possible at small temperatures, but this structure is different in comparison to ideally spherically metallic nanoparticles (copper, cobalt, nickel) prepared in our previous work [12]. The presence of similar triangular and rounded morphology was reported by the synthesis of silver nanoparticles from silver nitrate at 300°C.

The increase of temperature at 280°C has revealed the presence of cylindric particles (Figure 4). Also the ratio of rounded particles is more available at 280°C than at 260°C. It seems that nanoparticles grow together.

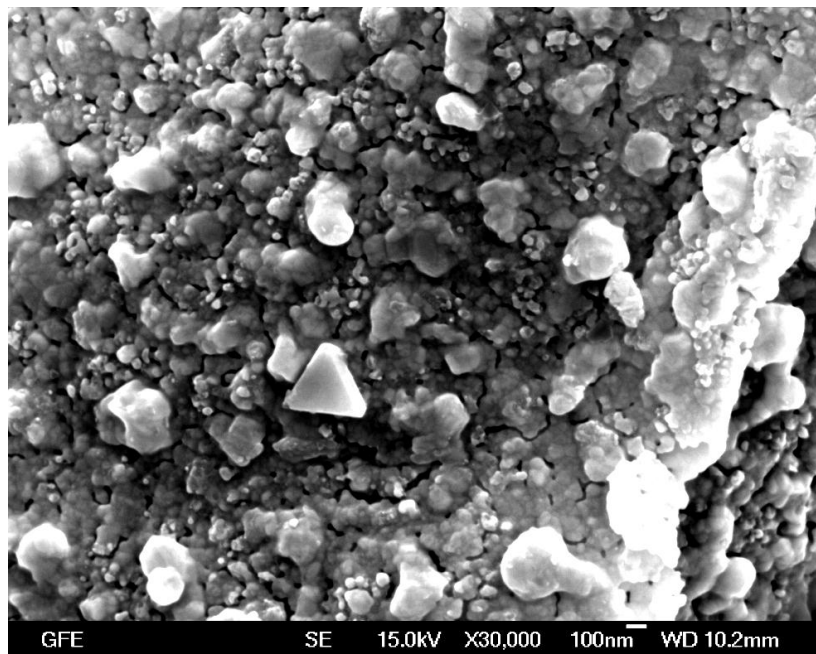


Figure 3 SEM analysis of Gold- nanoparticles (Exp.1, f=0.8 MHz)



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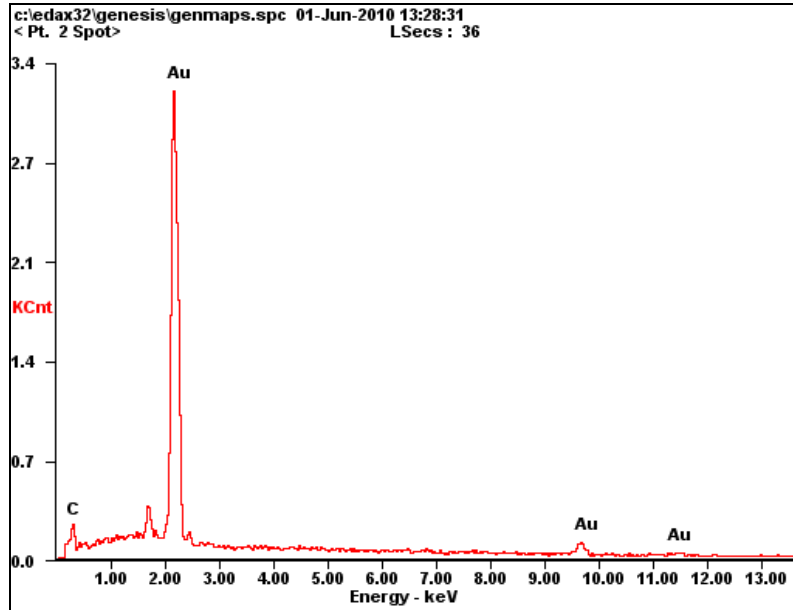


Figure 4: EDS analysis of Gold- Nanoparticles (Exp.1)

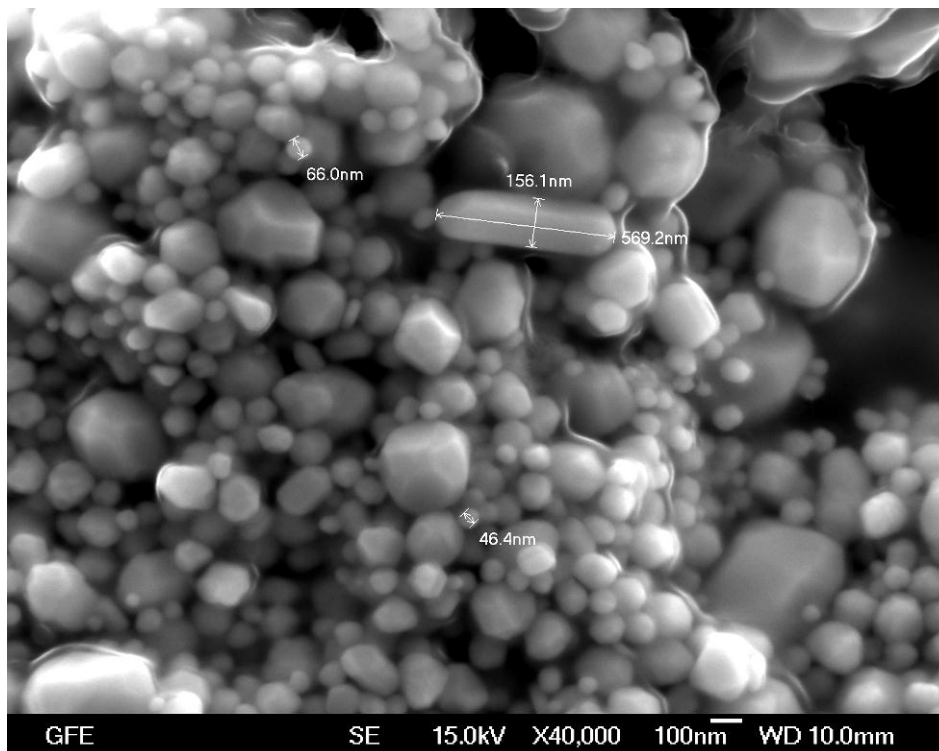


Figure 5: SEM analysis of Gold- Nanoparticles (Exp.8)

Based on capillary theory the diameter of nanoparticles was predicted from the eq. 1, formed by combination of Kelvin's equation and an equation reported by Messing et al. [14]:



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

where D_{Au} is the diameter of nanoparticle (m), γ -surface tension ($\text{N} \times \text{m}^{-1}$), f - frequency ultrasound (s^{-1}), C_{sol} - concentration of the starting solution ($\text{g} \times \text{cm}^{-3}$), M_{sol} - molar mass of the starting solution of HAuCl_4 ($\text{g} \times \text{mol}^{-1}$), M_{Au} - molar mass of gold ($\text{g} \times \text{mol}^{-1}$), ρ_{sol} - density of the atomized solution and ρ_{Au} - density of gold ($\text{g} \times \text{cm}^{-3}$).

Assuming that the characteristics of water are close to those of the used diluted precursor solution, the parameters of our experiments amount: $\gamma = 72.9 \cdot 10^{-3} \text{ Nm}^{-1}$, $\rho = 1.0 \text{ g cm}^{-3}$, $f = 0.8 \times 10^6 \text{ s}^{-1}$ and lead to a calculated value of the ultrasonically dispersed droplet diameter of $D = 4.79 \times 10^{-6} \text{ m}$. An increase of the operating frequency from $f = 0.8 \times 10^6 \text{ s}^{-1}$ to $f = 2.5 \times 10^6 \text{ s}^{-1}$ decreases the aerosol droplet size from $D = 4.79 \times 10^{-6} \text{ m}$ to $2.26 \times 10^{-6} \text{ m}$.

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 formula (1).

Using the parameters of our experiments: droplet mean diameter D : $4.79 \text{ }\mu\text{m}$, M_{Au} : 196.97 g/mol , M_{HAuCl_4} : 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 amount between 60 and 150 nm . Under same conditions for the frequency $f = 2.5 \times 10^6 \text{ s}^{-1}$ the calculated mean particle diameter of gold amounts between 150 and 300 nm . The particle size of gold was decreased as a result of the reaction in a smaller droplet for same concentration.

In contrast to water solution (Figure 6) the stabilization of gold nanoparticles was successfully performed using ethanol in the second bottle in order to prevent a possible agglomeration.



Figure 6: Precipitation of gold nanoparticles in water solution (Exp. 1)

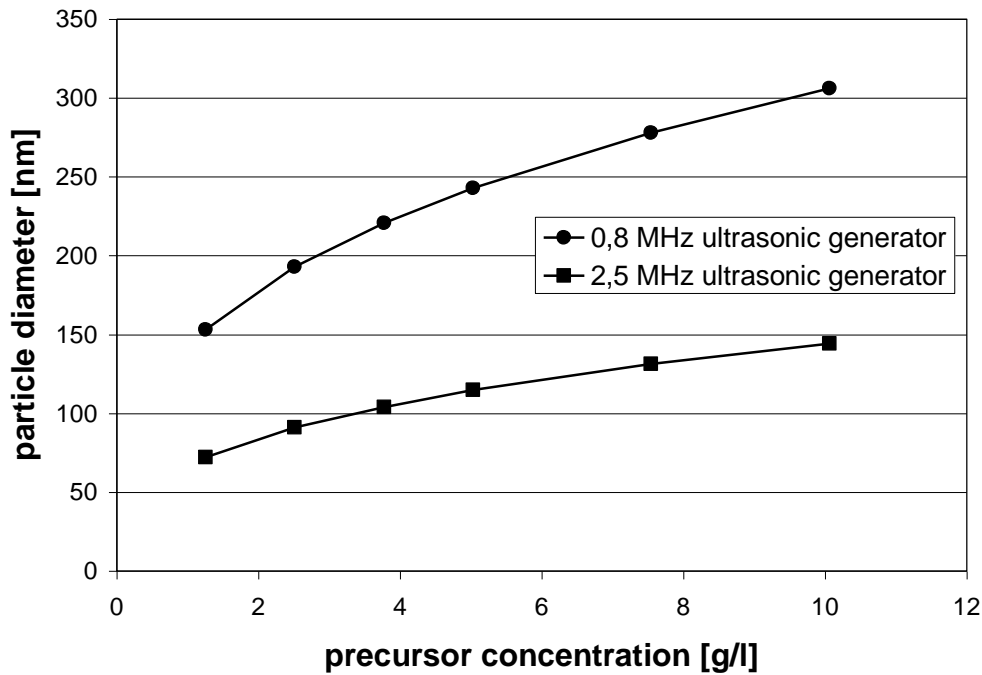


Figure 7: Theoretical calculated values of gold nanoparticles

Table 2: Comparison of experimental and calculated particle size diameter

Concentration of Au in H _{Au} Cl ₄ : 2.5 (g/l)	Particle size (nm)	
	f= 0,8 MHz	f= 2,5 MHz
Experimental	38-200	10-250
Theory	193	91

Present differences between calculated and experimentally obtained values of gold particles may be due to the approximate values used for surface tension and density of aqueous solution, microporosity of particles, and especially due to coalescence/agglomeration of aerosol droplets at a high flow rate for the carrier gas (turbulence effects). Also in the equation (1), 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 precisely measured by laser diffraction and used in above mentioned calculations.

Additionally in contrast to our previous prepared spherical metal particles (copper, cobalt, nickel) the presence of rods and discs in gold structure represents news interesting for an application, what makes this calculation and comparison more difficult as usually.

3.2.2. Mechanism of formation of nanoparticles

The formation of nanoparticles contains different steps starting from an initial solution of HAuCl_4 . The formed aerosol droplets from HAuCl_4 solution undergo drying, droplet shrinkage, solute precipitation, thermolysis and hydrogen reduction. The last step is sintering in order to form gold particles with different forms.

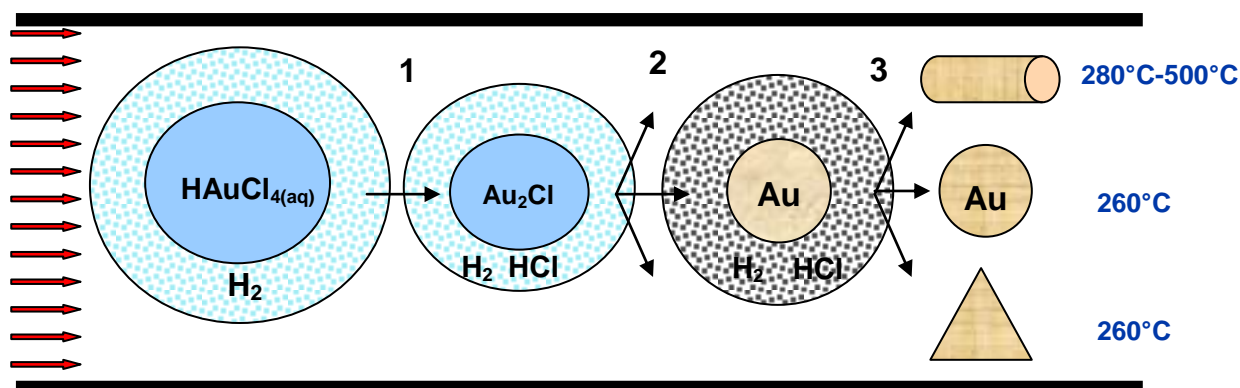


Figure 8: The formation of gold nanoparticles

4. Conclusion

Gold nanoparticles were prepared by ultrasonic spray pyrolysis changing of the reaction temperature and ultrasonic frequency. Two ultrasonic sources of 0.8 and 2.5 MHz, acting on the water solution of the HAuCl_4 forming aerosols with constant droplet sizes between 2.26 and 4.79 μm . The real size of droplet depends on the characteristics of the solution (surface tension, viscosity, and density) and the frequency of the ultrasound. In order to produce gold nanoparticles a subsequent thermal decomposition of the aerosol droplets was performed in hydrogen atmosphere between 260 $^\circ\text{C}$ and 500 $^\circ\text{C}$. SEM and EDS analysis have confirmed the presence of gold with different morphological forms (spherical, cylindrical and triangular), what is of big importance for some medical application. The mechanism of synthesis of nanosized particles was proposed from aerosol droplet via a solution precipitation and hydrogen reduction of formed gold chloride and sintering of formed nanoparticle. Thermochemical investigations have confirmed high value of negative Gibbs free energy for the hydrogen reduction of gold chloride up to 800 $^\circ\text{C}$ in contrast to calculated positive values for the thermal decomposition of HAuCl_4 . Thermalgravimetric analysis of HAuCl_4 by Sawada and Ando was confirmed a decomposition of HAuCl_4 to AuCl_3 between 250 $^\circ\text{C}$, what is agreed with our presented thermochemical analysis. In order explain the formation of gold nanoparticles the kinetic of thermal decomposition of HAuCl_4 shall be investigated by DTA, TGA, DSC analysis in future.



5. References:

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