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CONTROLLED NANOPARTICLE SYNTHESIS WITH ULTRASONIC SPRAY PYROLYSIS

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Abstract

One form of gold nanoparticle synthesis is a process called Ultrasonic Spray Pyrolysis – USP. USP is a chemical reduction method, where a solution of desired material is atomized by ultrasound, forming an aerosol of the solution, and transported through a tube into a furnace for particle generation. This process can be used to form nanoparticles from different materials (pure metals, oxides, sulfides, core-shell structures, etc.). For gold nanoparticle production we are using a diluted solution of $HAuCl_4$. The formation of particles can be explained with a model following a one particle per droplet mechanism. This model follows a set of stages for the aerosol droplet, when subjecting it to higher temperatures inside the furnace. These are: Evaporation of droplet, reduction of dried particle and particle sintering. Process parameters such as furnace temperatures, solution concentration, ultrasound frequency, etc., control the formation of particles; their selection results in the sizes and shapes of created nanoparticles. However, for gold nanoparticles, a desired outcome has not yet been achieved. So far, we have synthesized non-uniform particle shapes, with variable sizes. Also, when nanoparticles of gold are being synthesized, the efficiency of the process is reduced because of particle deposition on the tube walls and inside the reservoir of the ultrasound generator. This has not occurred in the production of other materials with USP, such as NiTi. With NiTi, the technological problems are with obtaining the desired nanoparticle composition. In order to eliminate these deficiencies, a new USP device must be designed. This presents an opportunity to study further the effect of process parameters on the USP synthesis stages for a better control of particle formation.

Keywords: Ultrasonic Spray Pyrolysis, gold nanoparticle synthesis, model for nanoparticle production

INTRODUCTION

Nanoparticles are an ever expanding field of research. In addition to a higher surface to bulk atom ratio and the increase of material reactivity, nanoparticles also gain properties such as surface plasmon resonance. Ultrasonic Spray Pyrolysis is a relatively simple and cheap method for nanoparticle production [1, 2]. This method

uses a solution (called a precursor) of the diluted material desired for nanoparticles and subverts the surface of this solution to ultrasound. When the ultrasound makes contact with the surface, two physical mechanisms occur: Sonically induced cavitations and capillary surface waves [2–5]. The result is the appearance of droplets of aerosol forming from the solution. The sonically induced cavitation theory states that the aerosol droplets generated are from implosions of cavitation bubbles near the free surface. The theory of the capillary waves states that the ultrasonic generator launches capillary waves parametrically on the liquid/air interface. With increasing power, amplitudes of these waves grow exponentially until droplets break off of the peaks of standing waves. The process of creating aerosol droplets from a solution with ultrasound depends on the surface tension, viscosity, mass density and (by extension of other parameters) the temperature of the solution, as these parameters affect the wavelength of the ultrasound. The frequency of the ultrasound, along with solution parameters, also determines the size of the generated droplets [6]. A well known equation from 1945 by Lang [7] shows a theoretical correlation between the mean diameter of the produced droplet and the ultrasound and solution parameters:

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

The ultrasound does not, however, create equal sized droplets, but instead a distribution of smaller to larger droplets. This is because the droplets are ejected from the solution surface in an erratic fashion, which is intrinsic in the droplet creation mechanism.

Once the aerosol is produced, it is transported through the quartz tubes into the furnace via an inert carrier gas. The high temperature evaporates the solvent and shrinks the initial droplet of the solution while, at the same time, increasing the concentration of the solute inside the droplet. In an ideal situation, the solute diffuses into the core of the droplet until the solvent evaporates completely, and only a dried particle of our desired material precipitates from the solution. This postulates that the evaporation of the droplet solvent is slower than the diffusion of the solute into the droplet center. However, the ultrasound creates a distribution of droplet sizes so that the diffusion and evaporation times vary from droplet to droplet. This causes uneven shapes of the dried particles, since some of the diluted material may precipitate onto the droplet surface, before the solvent has evaporated fully. Conversely, the solute diffusion could be too fast, enclosing the solvent in the center of the dried particle, until the pressure of the evaporated solvent inside the particle causes it to explode. The resulting particles can be spherical, hollow spherical, spherical with holes, shriveled, exploded, etc [8].

After a dried particle has formed from the droplet, further reactions with gases might be needed, depending on the desired nanoparticle material and the gases and precursor type used. In our experiments, we have synthesized nanoparticles of gold from a solution of diluted $HAuCl_4$ and nanoparticles of NiTi from NiTi orthodontic wires dissolved in acid (HNO_3 + 3 HCl) and diluted with water. In both cases, a reduction gas had to be added for particle formation with reduction.

MATERIALS AND METHODS

Figure 1 shows the Ultrasonic Spray Pyrolysis setup that was used for the experiments. The precursor was added inside the ultrasound generator (Gapusol 9001, RBI/France) reservoir. When the furnace had reached the desired temperature nitrogen gas was flooded through the tubes to prevent any problems when the hydrogen would be added. When the hydrogen gas was added and a steady gas flow was reached, the ultrasound generator would be turned on, creating the aerosol droplets from the precursor.

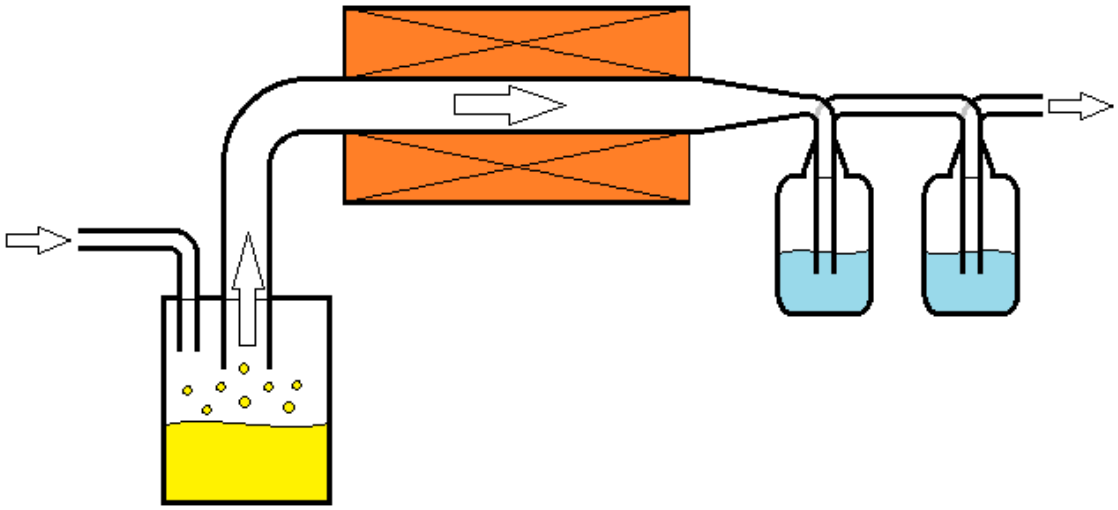

Figure 1: A simple schematic of the USP device used for nanoparticle synthesis experiments

The experiments were carried out with a dissolved tetrachloroauric acid ($HAuCl_4$) in water as the precursor. Different concentrations of $HAuCl_4$ in water were used for nanoparticles of different sizes. We have results for nanoparticle synthesis with the precursor concentration varying from 0,5 g/l up to 10 g/l. An ultrasound frequency of 1,7 and 2,5 MHz was used. The furnace temperature was varied between 260 and 900°C. Different gas flows were used, using nitrogen as the carrier gas and hydrogen as the reaction gas. Recent gold synthesis parameters are presented in Table 1.

Table 1: Gold nanoparticle synthesis experiments with USP

Exp. No.	Precursor concentration	Ultrasound frequency	Furnace temp.	Gas flow	Collection medium	Synthesis time
1	1 g/l $HAuCl_4$	2.5 MHz	900°C	0,8l/min N_2 + 1,7l/min H_2	Ethanol	6 hours
2	0.5 g/l $HAuCl_4$	2.5 MHz	900°C	0,8l/min N_2 + 1,7l/min H_2	Ethanol	6 hours

For synthesis of NiTi nanoparticles, orthodontic NiTi wires were used for the preparation of the precursor. The wires were dissolved using aqua regia (HNO_3 + 3 HCl) and this solution was then diluted with water. The synthesized NiTi nanoparticles were intended for use in electrospinning, thus only precursor concentrations of 0,5 and 0,25 g/l were made. Electrospinning requires small particles (around 30 – 50 nm) to be successful, which is why the precursor concentrations were kept low (higher concentrations produce bigger particles). As the acids dissolved the NiTi wire, chlorides were formed in the solution, requiring hydrogen for reduction during synthesis. The synthesis parameters are presented in Table 2.

Table 2: NiTi nanoparticle synthesis experiments with USP

Exp. No.	Precursor concentration	Ultrasound frequency	Furnace temp.	Gas flow	Collection medium	Synthesis time
1	0,5 g/l NiTi	2.5 MHz	900°C	1l/min N_2 + 1,5l/min H_2	Ethanol	5 hours
2	0.25 g/l NiTi	2.5 MHz	900°C	1l/min N_2 + 1,5l/min H_2	Ethanol	5,5 hours
3	1,5 g/l NiTi	2.5 MHz	900°C	1l/min N_2 + 1,5l/min H_2	Water	6 hours

To prevent agglomeration some samples were collected in alcohol. The resulting nanoparticles of Au and NiTi were analyzed with SEM, TEM and EDS spectroscopy. NiTi nanoparticles were also used in the electrospinning experiments.

RESULTS AND DISCUSSION

The synthesis process model follows a few mechanisms in the sequence shown in Figure 2. As the droplet of initial solution enters the tube furnace, it firstly undergoes droplet evaporation until a dried particle of the solute is precipitated. This particle then reacts with the reaction gases. The resulting reacted particle is then finally sintered, producing a final solid particle.

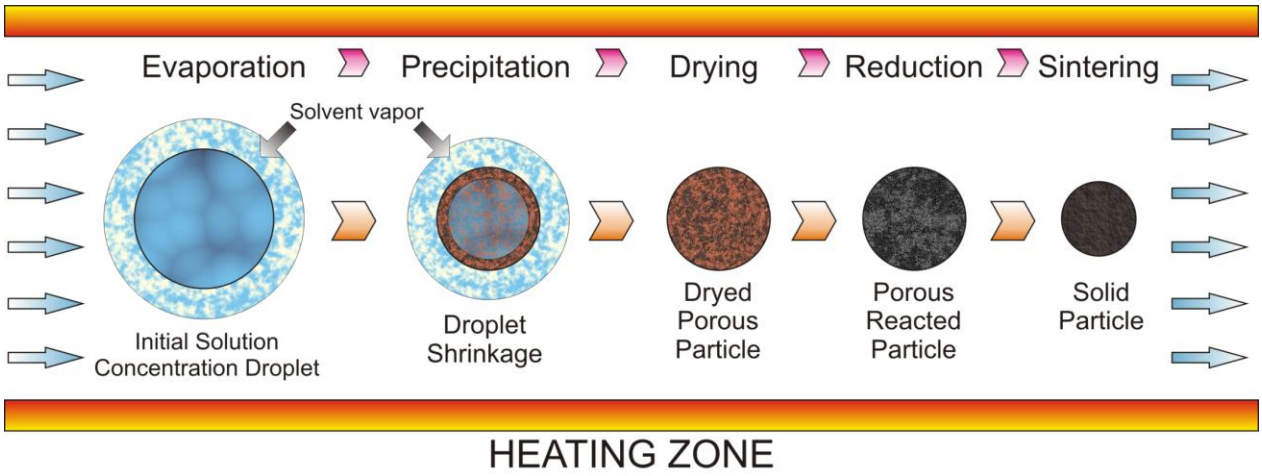

Figure 2: Model of nanoparticle synthesis mechanisms with USP

The sizes and shapes of synthesized nanoparticles are dependent upon the initial precursor concentration and the sizes of the generated droplets. Increasing the ultrasonic frequency reduces the sizes of droplets and results in smaller final particles. Turbulent effects and droplet coagulation also have an effect on final sizes of nanoparticles. When synthesizing gold nanoparticles this issue has proven to have a stronger effect on final particle properties than with other materials [1]. Changing the furnace temperature from 260°C to 500°C has shown an emergence of triangular shapes at 260°C and cylindrical shapes at 500°C (Figure 3). With higher temperatures, more agglomeration between particles and a higher ratio of irregular shapes was present.

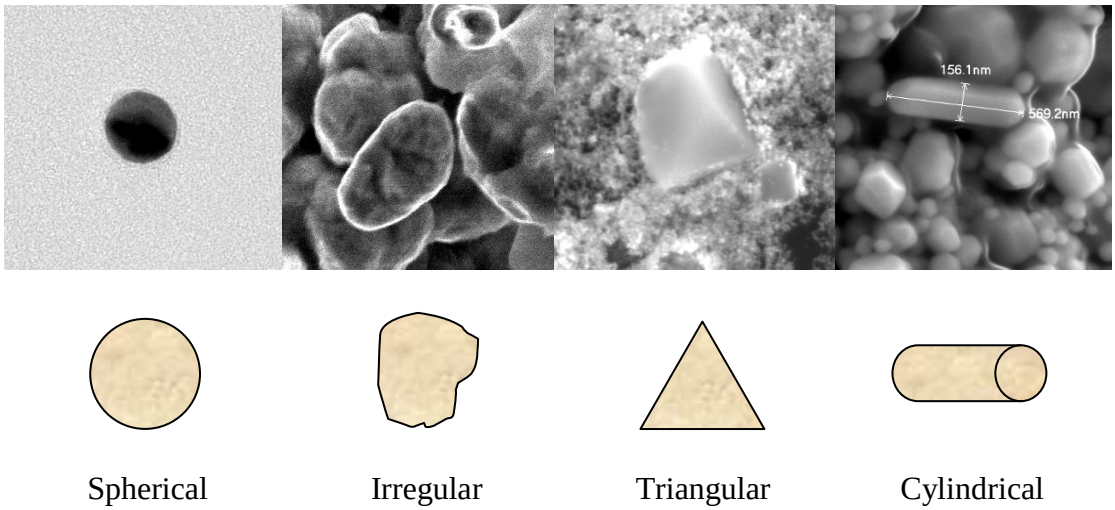

Figure 3: Collection of SEM and TEM images of different shapes of produced gold nanoparticles with simple representation of the shapes

It seems that gold nanoparticles produced from tetrachloroauric acid need a more controlled environment for production of uniform shapes than other materials that were experimented on with the USP process. A steadier flow of gases, without turns

and turbulent effects in the pipeline, could reduce the amount of droplet coagulation and produce more uniform final particle shapes. In addition to this, synthesizing gold nanoparticles has some inefficiency in the current process. During the experiments, gold nanoparticles were being synthesized inside the reservoir of the ultrasonic generator [1]. The cause for this may be the physical effects of atomizing the input solution with ultrasound and reactions of the generated droplets with the reduction gas. The solution to a lot of the problems will be introduced in our future work, where we will facilitate more control in the USP process with a separate hydrogen gas intake and divided process mechanisms. The goal is to produce uniform particle shapes of controlled sizes and, since a mixture of particle shapes is hard to characterize and utilize successfully in an application, we will be focusing on spherical particles, as depicted in figure 4, which are useful for many applications (from catalysis to medicinal use).

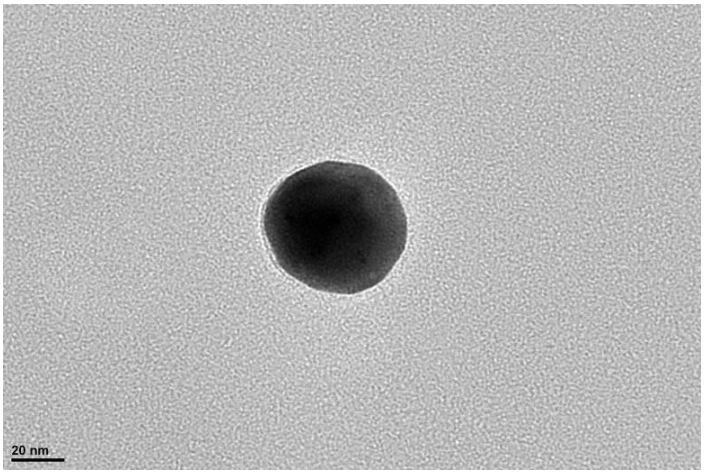

Figure 4: A spherical gold nanoparticle

The synthesis process is the same for any material desired to be made into nanoparticles; however the nanoparticle formation is not. Depending on the different properties, reactiveness, affinities for bonding of the input material, morphologically different nanoparticles are synthesized. When using a gold precursor, nanoparticles of spherical irregular, triangular and cylindrical shapes were synthesized. However, using a NiTi precursor created only spherical particles (Figure 5), but with a different composition than was expected [9].

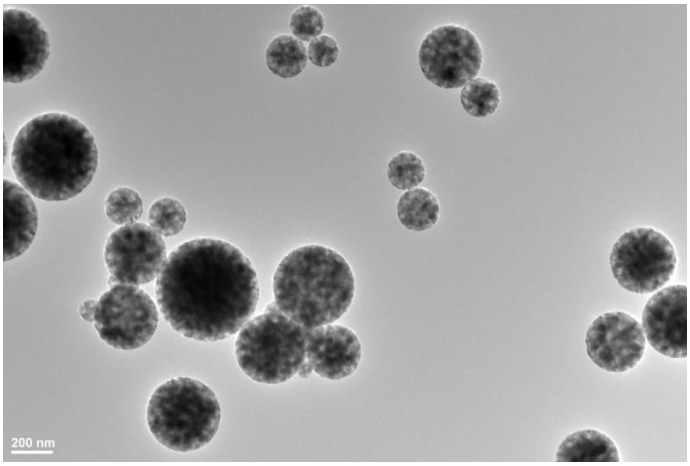

Figure 5: TEM image of nanoparticles synthesized from NiTi wires

Because of the high reactivity of titanium, a titanium oxide has formed on the surfaces of these nanoparticles. This created a structure similar to core-shell structures, where the titanium dioxide encapsulated the Ni content inside the cores of the particles (Figure 6). The titanium oxide does not exhibit the shape memory and superelasticity properties inherent in the NiTi alloy used for synthesis. For these properties to be present in the nanoparticles there should be no oxygen content, or it should be kept at a minimum. Here, we face a different issue, where we are not required to change the conditions of synthesis drastically, such as with gold nanoparticles, but rather the input materials along with collection and handling methods for the NiTi nanoparticles. Since titanium has an affinity to react with oxygen and form an oxide, the amount of oxygen should be reduced, preventing these reactions.

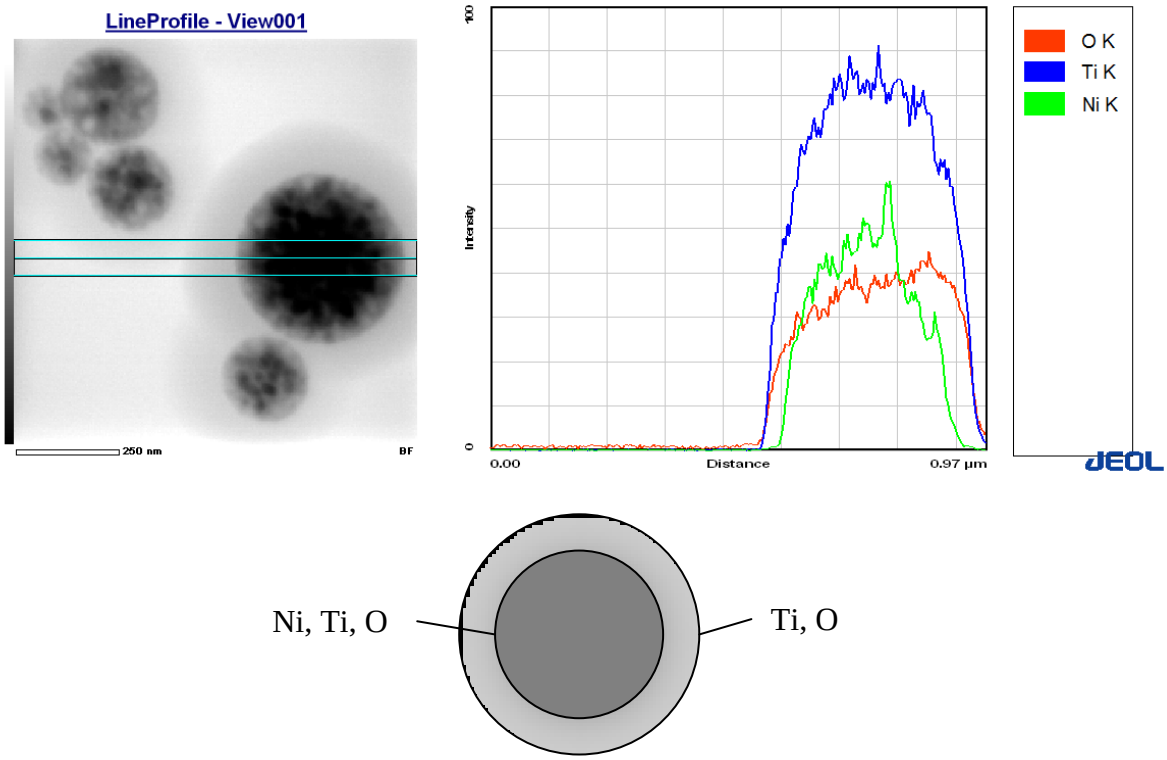

Figure 6: EDS line profile and a schematic representation of a particle synthesized from a precursor made from NiTi wires

CONCLUSIONS

Ultrasonic Spray Pyrolysis is useful for synthesizing nanoparticles of various materials. In our experiments we have tried to produce nanoparticles of gold and of NiTi shape memory alloy with varying success. The gold nanoparticles produced were of non-uniform shapes and sizes and thus require better synthesis conditions for complete control over particle morphology. A steadier gas flow and controlled droplet evaporation could reduce these issues. Regarding NiTi nanoparticles, the high content of titanium oxide reduced the amount of the NiTi crystal lattice in the particles and most likely reduced the shape memory and superelasticity properties of the material. A better form of collection methods and precursor materials is required in order to reduce the amount of oxygen that can be bound to titanium.
The particle morphology is dependent upon precursor concentration, furnace temperature, consistency and type of gas flow, ultrasound frequency, droplet evaporation rate and solute diffusion rate. The droplet evaporation and solute diffusion mechanisms need to be studied in order to obtain a better understanding of nanoparticle creation.

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