Scaling up of Nanopowder Collection in the Process of Ultrasonic Spray Pyrolysis

Gözde Alkan, Fabian Diaz, Greg Matula, Srecko Stopic, Bernd Friedrich

The need of nanostructured materials is increasing owing to their various applications. This is the main motivation to form a platform for increasing production rates by scaling up of ultrasonic spray pyrolysis process. In our previous report, successful scaling up of USP process and initial results had been explained. It was known that the most sensitive part of equipment is electrostatic precipitators which are responsible for particle collection. Therefore, this article is devoted to nanoparticle collection issue and improvements which have been performed to increase collection efficiency.

Keywords:

Nanoparticles – Ultrasonic spray pyrolysis – Scale up

Aufskalierung der Nanopulversammlung im Prozess der Ultraschall-Sprühpyrolyse

Der Bedarf an nanostrukturierten Materialien steigt aufgrund ihrer vielfältigen Anwendungen. Dies ist die Hauptmotivation den Ultraschall-Sprühpyrolyseprozess zu skalieren, um eine Plattform für steigende Produktionsraten zu bilden. In unserem bisherigen Bericht wurde eine erfolgreiche Skalierung des USP-Prozesses und der ersten Ergebnisse erläutert. Es war bekannt, dass elektrostatische Abscheider, welche für die Partikelsammlung verantwortlich sind, die empfindlichsten Teile der Ausrüstung darstellen. Daher widmet sich dieser Artikel dem Nanopartikel-Sammelproblem und Verbesserungen, die durchgeführt wurden, um die Sammeleffizienz zu erhöhen.

Schlüsselworter:

Nanopulver – Ultraschall-Sprühpyrolyse – Aufskalierung

Expansion de la récupération des nanopoudres lors du processus de la pyrolyse d'aérosol pulvérisé par ultrasons

Aumento a escala de la coleccion de nanopolvos en el proceso de pirolisis con atomizador ultrasonico

1 Introduction

Nanopowder synthesis received strong attention in the past ten years, but received production status only for oxides and via chemical routes. When aiming on metallic or metal/oxide compound systems, different approaches has to be used like laser ablation or Ultrasonic Spray Pyrolysis (USP). For both methods scaling up of the lab-scale equipment did never happen so far and the authors took advantage of a German public fund by Deutsche Forschungsgesellschaft (DFG) to build first time a pilot demonstration equipment by transferring scientific achievements from lab scale while keeping the process quality constant. Gas flow and temperature distribution within the equipment were modeled and calculated to yield in optimal geometry. As represented in Figure 1, scale up equipment has been designed with five main parts, consisting of ultrasound generator, gas system, heating/reaction furnace, electrostatic precipitator and vacuum system.

There are five ultrasound generators (2.5 MHz) which are regulated automatically and allow running a continuous process. A gas system with controlled volume resp. mass flow of pure and mixed gases allows for carrying aerosols produced by ultrasound generators to heating zones. Each aerosol generator is connected to an individual reaction

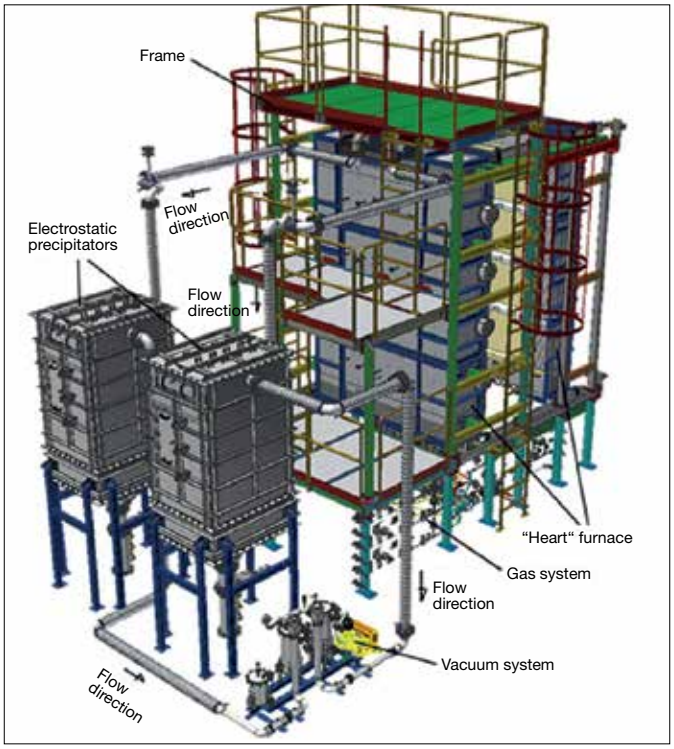

Fig. 1: Schematic drawing of the demo USP equipment at RWTH Aachen University

tube. These five reaction tubes are located in a wall heated furnace with separately regulated four heating zones (max. 1000 °C). At the end of the reaction zones, the stream containing carrier gas and nanoparticles is carried to the powder collection area. There are two electrostatic precipitators (one is connected to three reaction tubes, the other is connected to remaining two tubes) with 12 resp. 8 electrodes and equipped with pneumatic vibration sytems for detaching the powders into containers located below. Finally, a vacuum system is located to suck the stream/carrier gas-mixture through the entire USP device including electrostatic precipitator. More details about equipment can be found in [1].

The demo equipment, which is devoted at the beginning to silver based nano/micro structures was firstly tested with a series of 36 hours continuous experiments. Characterization of products revealed that mono-phase structured and ideally spherical silver particles (a few hundred nanometers) were synthesized, indicating process transfer to demo scale has been successfully synthesized. However, it became obvious that the most sensitive part of the equipment is the electrostatic precipitator which needs to be further optimized. Therefore, further intensive studies focused on improvement of ESP and powder collection efficiency were made and this article presents the main outcome of this research.

2 Nano-powder collection methods

Efficient collection of nanoparticles has been a challenging issue depending on properties of particles. Mainly, collection methods can be categorized into wet and dry collection, respectively.

In terms of wet collection methods, most frequent used are collection devices filled or flushed with compatible liquid media. Here it is important to use fluids that do not react with the nanoparticles nor dissolve them. They should be able to prevent their agglomeration and suitable to be easily separated from the nanoparticles by evaporation. However, for higher amounts of synthesis, feasibility of this method is not sufficient for scaling up.

Dry methods for separation of fine particles from stream or dry gases has various alternatives in industrial applications such as filters, cyclones, settling chambers or electrostatic precipitators. Filtration of nanoparticles with nylone, polysulfone, PC, PP, metal, ceramic, teflon based media has been utilized for large scale applications of particle collection, but never for nano-sized particles. Impaction, interception and diffusion are the main order for powder collection by filtration [2]. Filtration is more efficient for smaller particles owing to their higher diffusion coefficient. However, particles can penetrate to the top of the filter surface and enter into filter body. When materials like silver with a sticky nature of their nano/submicron silver nanoparticles are aimed for, this system is not promising. Another technique frequently used is based on cyclones, which utilizes artificial gravity by spiraling an aerosol gas through cylinders or cones very similar to a centrifuge [3]. However, it was reported that this technique is most efficient at particle size bigger than 5 µm, while our target particle size is of maximum 500 nm. Considering such product, cyclones are also not promising. One more common technique is based on simple chambers where gravitational forces are used for particle settling [4]. In this method, upward flowing gas velocity is adjusted to be slower than settling velocity of solid particles. However, this technique is efficient where settling velocities are fast which corresponds to particle sizes bigger than 25 to 50 µm, which is also out of scope of this study.

Above drawbacks of current methods induced the development of an electrostatic precipitator as collection component of the prototype nano-particle equipment. Coulomb's inverse-square is the basic theoretical law in construction and operation for any electrostatic precipitator (ESP). The magnitude of the electrostatic force of interaction between two point charges is directly proportional to the scalar multiplication of the magnitudes of charges and inversely proportional to the square of the distance between them, which is known as Coulomb's law. Coulomb's law or Coulomb's inverse-square law, is a law of physics that describes the force interacting between static electrically charged particles. In its scalar form the law is:

$$F = k_c \frac{q_1 \cdot q_2}{r^2} \quad (1)$$

where k_c is Coulomb's constant ($k_c = 8.99 \cdot 10^9\ Nm^2C^{-2}$), q_1 and q_2 are the signed magnitudes of the charges, and the scalar r is the distance between the charges. The force of interaction between the charges is attractive if the charges have opposite signs (i.e. F is negative) and repulsive if like-signed (i.e. F is positive). This law was first published in 1784 by French physicist Charles Augustin de Coulomb and was essential to the development of the theory of electromagnetism.

This leads to the electrostatic precipitator (ESP), which is a separation device that removes fine particles, like dust and smoke, from a flowing gas using the force of an induced electrostatic charge minimally impeding the flow of gases through the unit [5]. In contrast to wet scrubbers which apply energy directly to the flowing fluid medium, an ESP applies energy only to the particulate matter being collected and therefore is very efficient in its consumption of energy (in the form of electricity). Furthermore, as the area of gas flow is not reduced, ESPs show very low pressure drops and such pump energy needs. The precipitator performance is very sensitive to two particulate properties: electrical resistivity/conductivity and particle size distribution. respectively. Resistivity can be determined as a function of temperature. In an ESP, where particle charging and discharging are key functions, resistivity is an important factor that significantly affects collection efficiency. While resistivity is an important phenomenon in the inter-electrode region where most particle charging takes place, it has a particularly important effect on the dust layer at the collection electrode where discharging occurs. Particles that exhibit high resistivity are difficult to charge, particles with high conductivity are difficult to keep attached to the polarized electrodes.

In order to create an optimal design of ESP, a design model according to the technical idea, followed by a 3D simple model for FEM/CFD simulations were made to confirm temperature uniformity and particle flow insidean ESP. After receiving satisfactory information, a lab-scale device was built and tested, followed by construction, manufacturing and full scale operation of the pilot device, including analyses of the temperature and flow patterns in order to assure temperature uniformity inside ESP.

3 Lab-scale results – prove of principle for ESP of nano-scale particles

In smaller scale, an electrostatic filter has been established utilizing electrostatic field to charge and collect particles. After thermal decomposition of an aquous solution of silver nitrate, the silver nanoparticles which have been formed after thermal decomposition were collected in this new collection system developed at the IME, RWTH Aachen University (Figure 2). A particle collection efficiency up to 42 % has been achieved with a voltage value of 27 kV and current intensity between 0.08 and 0.14 mA. Details of this equipment and study can be found in [6].

4 Technical challenges when upscaling the ESP to pilot dimensions

The main design of ESP and CFD simulation is found in Figures 3 and 4; respectively.

While running this device it became apparent (presented in Figure 5), that due to inhomogeneous temperature distribution inside the EGR cabinet and due to a too low output temperature from ESP to vacuum pump, strong condensation and short cut problems occurred. So it was decided to redesign some parts of the ESP.

In order to increase and regulate/homogenize the temperature, heating elements were inserted inside the bottom walls of the ESP. the advanced configuration can be seen in Figure 6.

In the following experimental series after eight hours run of the equipments, it was observed, that temperature distribution has become homogenous throughout the cabinet and reached around 140 °C which is high enough to prevent condensation inside the collection box, as shown in Figure 7. After assessing the ESP working efficiently, continuous runs of 30 hours aiming for bulk production has been performed with 0.1 M of silver nitrate precursor using nitrogen as carrier gas. The experiments were set with heating zone temperatures in the pyrolysis reactors at 500–1000–1000–800 °C respectively. During reaction, tem-

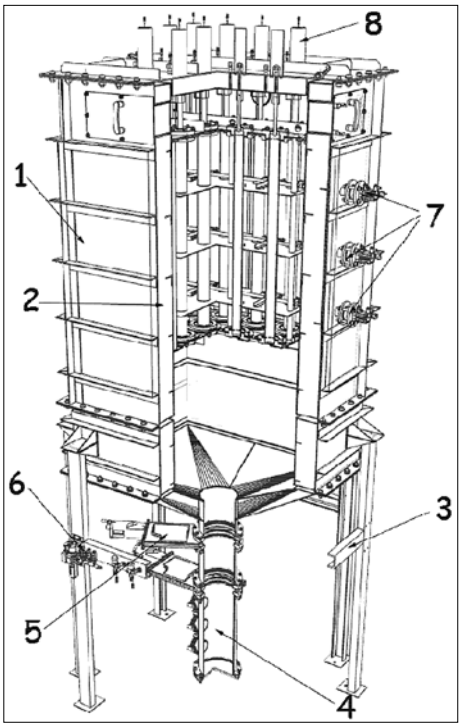

Fig. 3:
Design of the ESP as part of the DFG large equipment project aiming for nano-particle synthesis and collection, consisting of: 1 – body, 2 – isolation, 3 – frame, 4 – container for powder, 5 – vacuum tight valves, 6 – pneumatic system for cylinder in hammer system, 7 – hammer system, 8 – electrodes and reaction pipes

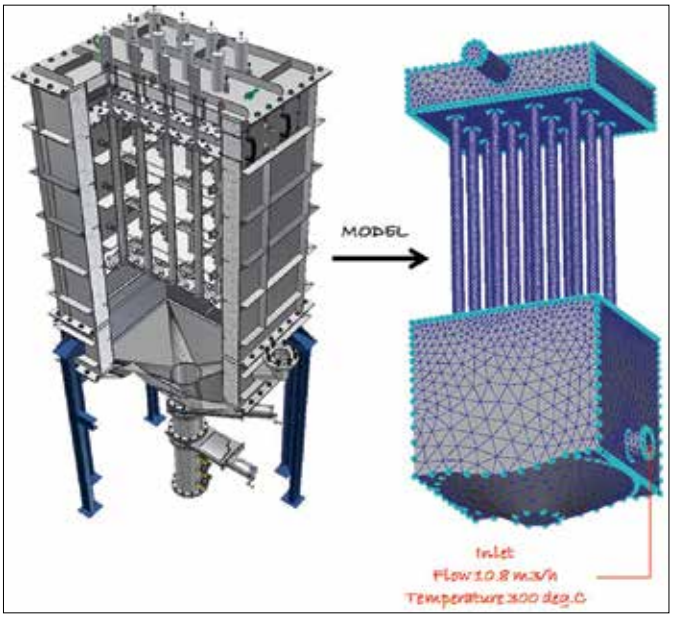

Fig. 4: Deriving a simple model from real device for CFD simulations

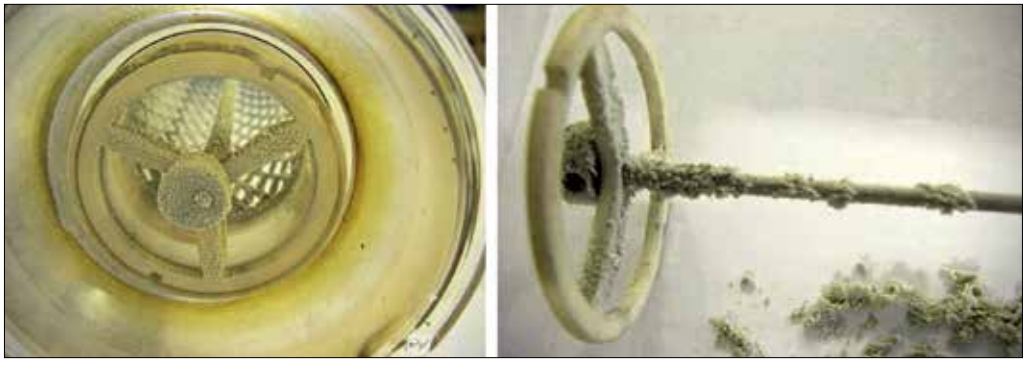

Fig. 2:
Silver nanoparticle collection with lab scale ESP

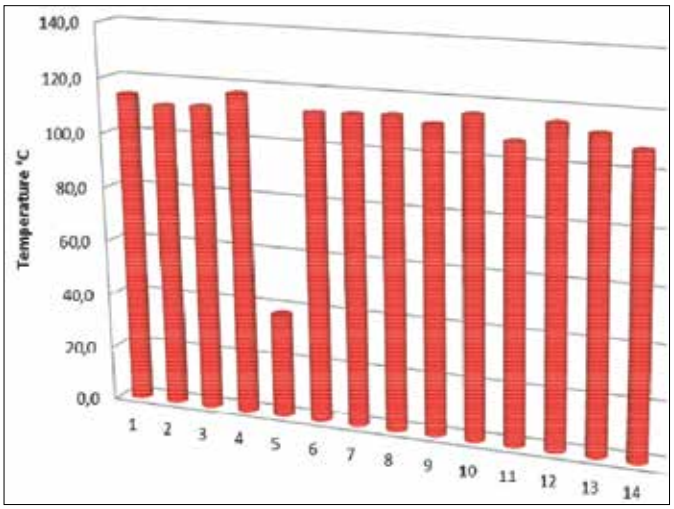

Fig. 5: First temperature distribution throughout ESP (1 – entry area, 2-14 – exit points of tubes, 14 – exit area)

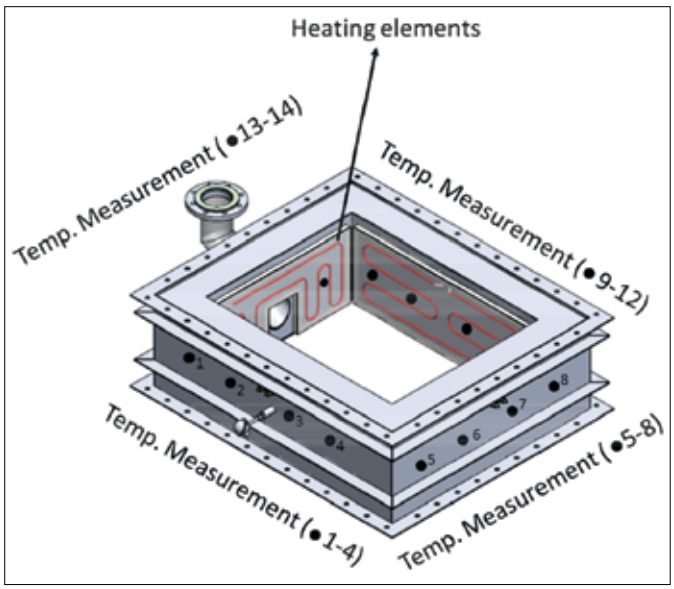

Fig. 6: Installation of heating elements to homogenize and increase temperature inside the ESP chamber for nano-sized particle collection

perature distribution and voltage value inside EGR were continuously recorded as indicated in Figure 8.

In the EGR, 20 kV of voltage was used (max. installation value 100 kV) during the experiment and current was constant at 0.77 mA. Moreover, temperature distribution was stable and good controlled as shown in Figure 8. According to the recorded temperatures, it a slightly increased temperature can be observed in the first five hours after reaching the set point of 200 °C in the heating system. This might be due to increased proportional parameter (P-value) in the temperature controller dedicated for the EGR. An increased P-value increases the heating rate of the unit presenting a small overshoot in the temperature profile. From this result and after visual analysis of the EGR after the experiment, it can be concluded that the temperature in the EGR is found within optimum levels (190 to 210 °C). Therefore, no water condensate has been detected in the cabinet nor malfunction of the ESP was observed (voltage and current constant and stable).

The temperature of the ongoing carrier gas was monitored after the EGR during the whole experiment. The gas temperature can be seen in Figure 9. The gas temperature is found around 130 °C, which is considered high enough to avoid any condensation in the EGR.

The gas after the EGR is transferred through a water cooled pipe to the vacuum pump system. In previous long term experiments, it was observed that the water amount condensed in the vacuum system was high, thus, considerable amount of water flowed through the vacuum pump, which effects its efficiency and is strongly undesired since life time of the unit is highly diminished. Therefore, a special system was designed and built between the EGR and the vacuum system to periodically remove the condensed

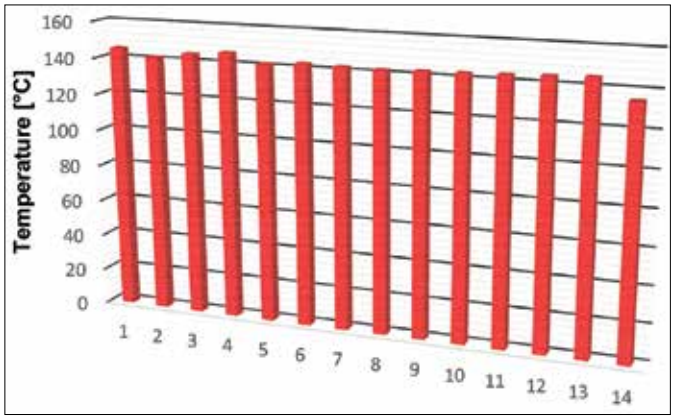

Fig. 7: Homogeneous and target temperature distribution throughout ESP while running multi-day experiments in the prototype USP device with silver-system after 8 h run

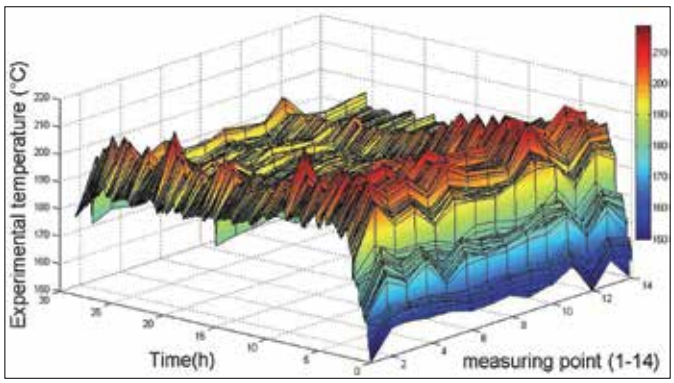

Fig. 8: Temperature distribution in the EGR during one of the 30 h experiments

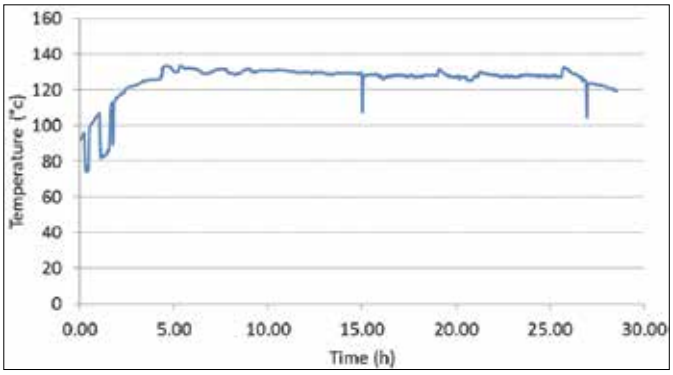

Fig. 9: Temperature of the separated carrier gas/water vapour monitored after the EGR

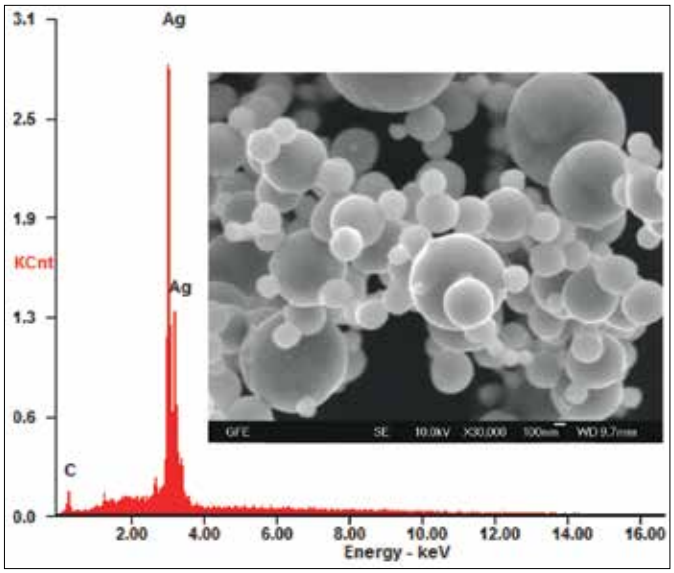

Fig. 10: SEM analyses of the 30 h synthesis products Ag nanoparticles

water from the off-gas pipe in such a way that a very limited amount of water could enter the vacuum system. This adapted setup has also been tested in many 30 h experiments as well. From the observed results, at least 70 % of the condensed water was successfully removed from the system directly. The rest of the condensed water was collected in a special cooled absorber (first part of the vacuum system). Such, during the experiments no water was detected inside the vacuum pump. In addition, the removed condensed water was analyzed for super-fine nanoparticles and later safely disposed.

Of cause, synthesized particles have been always investigated by SEM/EDX to reveal microstructure and chemistry as revealed in Figure 10. Despite this article is not aiming on the USP synthesis and product characteristics, it should be shown here as well, that EDX revealed a phase pure structure of the Ag nanoparticles and ICP proved that this was realized without any contamination and unreacted precursor. Moreover, ideally spherical and dense silver particles with a range between 100 nm up to submicron were observed in these tests, which were targeted for applications in catalysts and active electrodes.

5 Conclusion and existing challenges for the collection stage

In brief, reproducible, spherical and dense nano/submicron silver nanoparticles have been succesfully synthesized and collected with this scale up USP equipment. From a general point of view, the performance of the scaled up Ultrasonic Spray Pyrolysis device is satisfactory. However, the dried form of the nano powder is still difficult to collect by volume just by vibrating the electrodes. Considerable amount of material was still found on the inclined surfaces and not an the bottom of the ESP's collection chamber, which indicates the need of future improvements in the design of the electrode cleaning and the collection chamber for instance through use of advanced vibration systems or optimization of the geometry of the inclined surfaces. We will report in due time about the progress of this work.

Acknowledgements

This work was financed by the DFG Deutsche Forschungsgemeinschaft and Land NRW in frame of the program "Forschungsgeräte" (INST 222/874-1 FUGG), Equipment for Nanopowder production. We gratefully acknowledge the support of Dipl.-Ing. Dieter Schäufler, General Manager of Elino GmbH, and furthermore Amir Khamoushkoo for his continuous help in debugging the equipment with creative ideas and design work.

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