STUDY OF THE COMPOSITION AND SIZE DISTRIBUTION OF GOLD-CONTAINING BIMETALLIC NANOPARTICLES SYNTHESIZED IN A SPARK DISCHARGE GENERATOR

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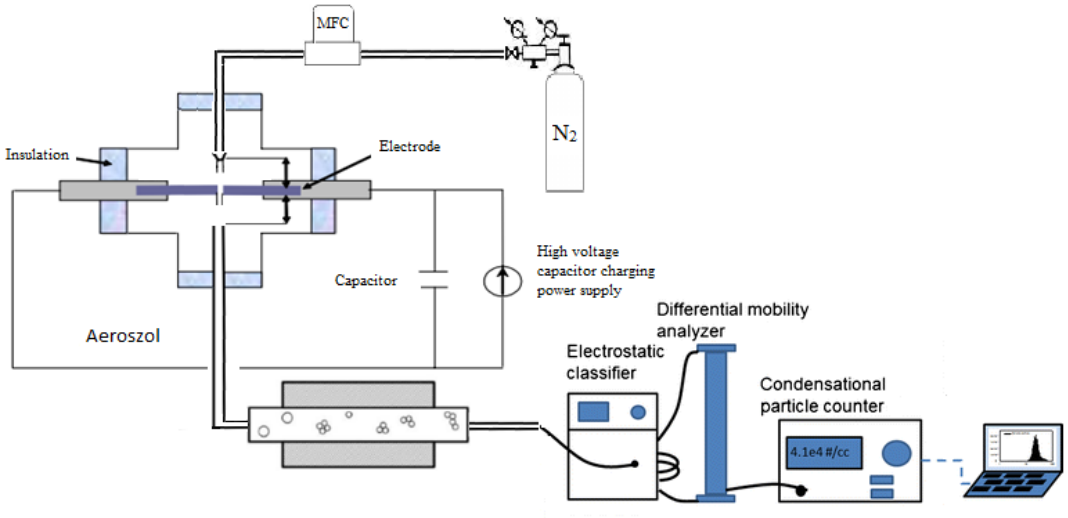
Introduction

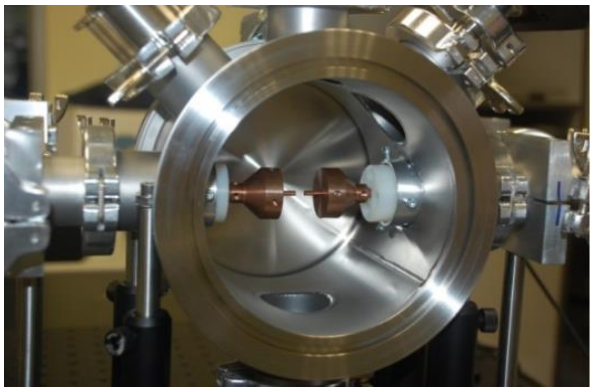
Nanotechnology is one of the most dynamically growing fields of science, which requires the production of engineered nanoparticles (ENP) for various applications. Chemical synthesis procedures were dominating the field for many years, but physical procedures, that are based on laser or discharge ablation, are becoming more and more popular nowadays. One of these ablation-based methods is spark discharge generation, which is a versatile method for the preparation of mono- or bimetallic nanoparticles. In a spark discharge generator (SDG), a high voltage oscillating discharge is produced between two electrodes made of at least moderately conducting material. The erosion of the electrodes produce an atomic vapor in the spark gap, which is carried away by a gas flow. Nucleation and coagulation processes lead to nano-sized aggregates, which are then compacted to form spherical nanoparticles (NP). This method produces high purity NPs. SDGs can also be run continuously, thus industrial rate production is also possible. Control of the particle properties (e.g. concentration and size) can be achieved by tuning the operating conditions of the generator. The SDG method can also be considered cost-efficient and environmentally friendly.

The goal of the present work was to study how the operating parameters of SDGs influence the composition and size distribution NPs in the case of certain bimetallic particles (BNPs). In particular, we intended to study the influence of the electrode polarity, gap size and compaction on Au-Ag and Au-W particles.

Experimental

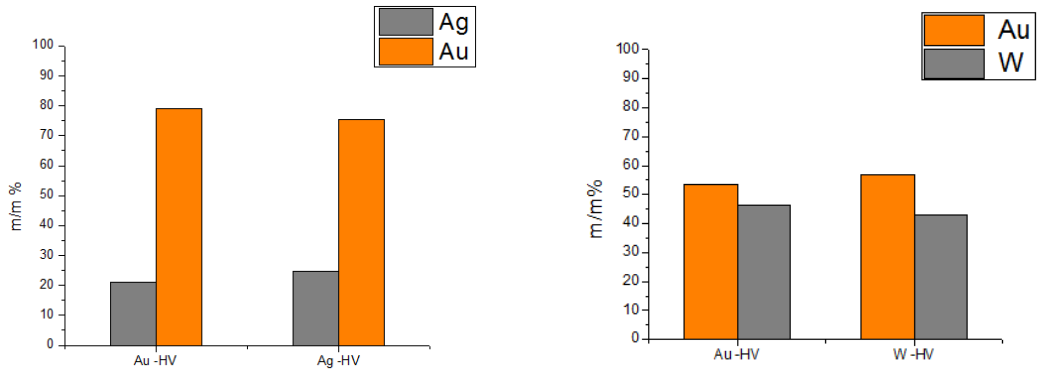
Our SDG system is built around a gastight stainless steel chamber (DN 160). The two, 3 mm diameter, cylindrical electrodes (99.9% purity, Goodfellow Inc.) are uniaxial and positioned horizontally. The electrode gap can be controlled by two microadjusters. The carrier gas, 99.995% purity nitrogen, entered the chamber ca. 5 mm above the electrodes and flowed downwards. The flow rate was set at 5 l/min using a mass flow controller (Modell GFC16, Aalbor Inc.). All experiments were performed at atmospheric pressure (~1015 mbar). Evacuation of the chamber was done using a membrane pump (UN726TTP, KNF Neuberger Inc.). The discharge circuit consisted of an 8 nF, monolithic, high voltage capacitor (Modell 450PM980 , General Atomics) and a high voltage capacitor charging power supply (HCK 800-12500, FuG GmbH). The discharge current was adjusted to keep the spark repetition rate at 100 Hz. The size distribution was monitored by an SMPS (SMPS-C, Grimm Aerosol Technik GmbH). The generated NPs were collected on glass fiber filter and then dissolved in aqua regia prior to their composition determination by ICP-MS analysis. The produced solution was then filtered on a 0.22 μm PTFE membrane syringe filter. The solution was finally measured on an Agilent 7700X ICP-MS instrument.



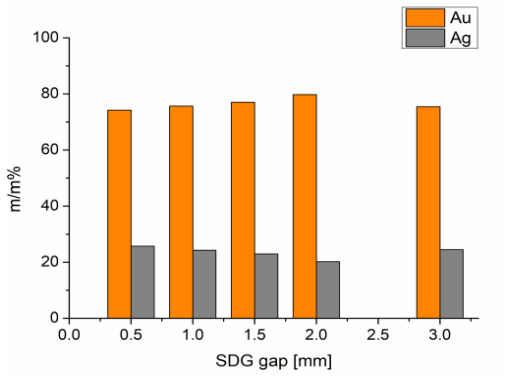


Results and discussion

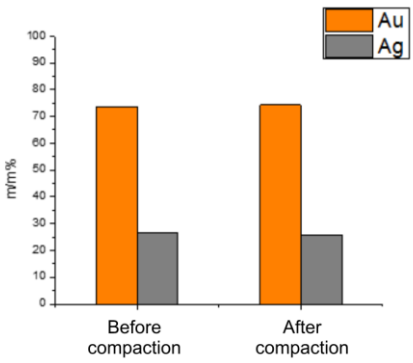
Effect of initial electrode polarity on NP composition. This parameter is expected to have only a minor influence on NP composition, since it has little impact on the extent of electrode erosion. The oscillating current will ablate always the cathode, which one of electrodes in one half-cycle and then in the next half-cycle, the other electrode gets to be the cathode and so ablated, and so on. Erosion rate is porportional to the square root of the electrical current, and since the current dampends with about a couple of percents in every half-cycle, therefore the rate of erosion will slightly (5-10%) higher for the electrode that was initially the cathode (HV). If the quality of the electrodes is different, then the erosion rate can also be different, thus this polarity-driven contribution only perturbs the already existing erosion rate difference. This translates to a slightly differing composition of NPs, as is illustrated by the graph below, which shows the case of Au/Ag and Au/W electrodes. The concentration of particles does not change significantly.



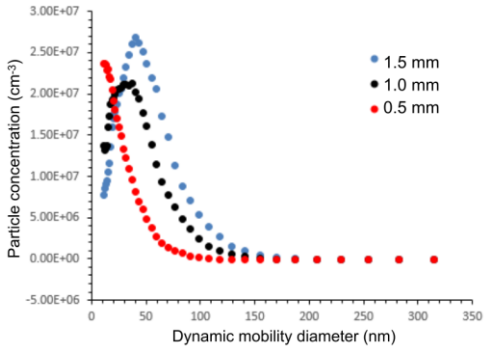
Effect of gap size on NP composition. The gap size influences the breakdown voltage, which in turn proportionally changes the spark energy. Hence, a larger gap size produces a higher energy spark, which causes more erosion. The effect of this on NP composition is such that the softer component will become slightly overrepresented in, as its erosion will increase more. Along with this, the particle concentration will typically decrease, because spark repetition rate, which primarily influences the particle yield, decreases with an increase in the breakdown voltage (assuming a constant charging current). The figure below shows the observed effect of the gap size on the NP composition for Au and Ag electrodes. It should also be added, that using extreme gap sizes, can shift the character of the discharge too – for example, at around ca. 0.5 mm gap size, a spark-to-glow transition occurs, which slightly also influences the erosion processes. As it can be seen, the total change in composition is only a few percents in the range of 0.5 to 3 mm.



Effect of compaction on NP composition. Compaction (sintering) of the particle aggregates by leading the NPs through a tube furnace is often advantageous in NP production, as it makes the particles more spherical, more uniform. The control of the process needs the optimization of the carrier gas flow rate and the furnace temperature. In the present case, we worked with a 900°C temperature, which is the highest value that can be set in our furnace. The process may result in some loss of the more volatile metal of the two, thus NP composition may be affected. In the case of Ag/Au BNPs, where there is no significant difference in the melting point (Au 1064°C, Ag 962°C), the process caused no change in the composition of particles.



Effect of gap size on NP size distribution. It is probably needless to say that the size distribution of only compacted particles can be meaningfully determined, thus we also studied this effect on compacted particles. As it turned out, the size distribution of Au-Ag BNPs shifted with an increase of gap size in such a way that the modus increased.



Conclusions

It was established that neither the initial electrode polarity, nor compaction or gap size does not significantly change the composition of the generated Au-Ag BNPs in an SDG. The effect was only a few percent. This is advantageous, since it allows the production of different concentration or size of particles of the same composition with the same set of electrodes. At the same time, the few percents change in composition caused by the polarity change can be considered as a simple and elegant means of fine-tuning the NP composition. It was also observed that the gap size strongly influences the size distribution of NPs.

At present, work is being carried out in our laboratories to extend the experiments over to other BNPs. We are also currently making attempts to assess the performance of electrode erosion models (e.g. Lwellyn-Jones and Feng et al.) in estimating the composition of BNPs.

Acknowledgments

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