GENERATION OF BINARY NANOSTRUCTURES VIA SPARK ABLATION

Summary of the PhD thesis

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1. Introduction

The 21st century has seen the rise of nanoscience as one of the most defining scientific and technological fields, fundamentally reshaping materials science, industry, and everyday life. Research and development conducted on the nanometer scale open up new perspectives in electronics, energy, biomedicine, environmental protection, and materials engineering. In recent years, nanoscience has evolved not only into a major area of research but also into an economic driving force. Today, nanotechnology has become a key contributor to sustainability, efficiency, and precision manufacturing.

One of the main advantages of spark discharge nanoparticle generation is that it enables the production of nanoparticles without the need for vacuum systems or chemical precursors, relying solely on metallic or semiconducting electrodes. During the discharge events, material is eroded from the electrode surfaces, and after mixing with the carrier gas, condensation and nucleation processes lead to the formation of pure nanoparticles with well-controlled size distributions and compositions. This method provides the opportunity to produce not only homogeneous but also binary and multicomponent nanostructures, whose properties can be finely tuned by adjusting the electrode materials and discharge parameters.

The present dissertation aims to contribute to the scientific understanding of nanoparticle generation and property control, focusing on the spark discharge–based nanoparticle generation method, which represents one of the most promising approaches among environmentally friendly and industrially scalable nanotechnologies.

2. Objectives

Scientific and industrial interest in binary and multicomponent nanostructures has been steadily increasing, as discussed in detail in the Literature Review chapter of this dissertation. At present, there is no universal and efficient physical or chemical nanoparticle synthesis method that enables the production of binary nanoparticles (BNPs) without costly and time-consuming modifications to the synthesis system, and without contamination or harmful emissions.

Another crucial requirement is the ability to vary the compositional ratio over a wide range while maintaining full control over the morphology, geometric diameter, and size distribution of the generated BNPs during both production and composition tuning. Moreover, many applications require BNPs composed of elements that are immiscible on the macroscopic scale. For instance, gold and cobalt form a typical elemental pair whose BNPs play a crucial catalytic role

in the production of hydrogen from ammonia-borane and are also used in the catalytic oxidation of carbon monoxide (CO).

Therefore, based on my research on spark discharge–generated BNPs, the specific objectives of my doctoral work were as follows:

i) To successfully synthesize binary/two-component nanoparticles using two pure-material electrodes in a spark discharge nanoparticle generator (SDG).

ii) To vary the average composition of the generated BNP population over the widest possible range solely by adjusting the electrical parameters of the generator and by reversing the electrode polarities.

iii) To tune the geometric diameter of BNPs with different compositions such that particles of identical size can be produced across various alloy ratios.

iv) To develop and apply a semi-empirical model capable of predicting the average composition of the generated BNPs.

v) To produce gold–cobalt BNPs in the SDG system, a pairing considered unique since gold and cobalt are immiscible metals at the macroscopic level.

vi) To investigate how, and to what extent, the morphology and chemical structure of BNPs can be modified through post-generation thermal treatment in the aerosol phase.

vii) To examine the effects of anode erosion and cross-contamination phenomena.

3. Instruments and Methods

The experiments were carried out using a spark discharge nanoparticle generator (SDG) developed by the NaMiLab research group. In this setup, microsecond-lifetime spark discharges were generated between two electrodes in an inert argon atmosphere. The system operates with a rod-to-rod electrode geometry, which ensures well-defined and reproducible discharge conditions. The discharge circuit consists of a monolithic capacitor, a high-voltage power supply, and low-inductance conductors.

In the generator, the inter-electrode gap (spark gap) was typically 2.0 mm, and the spark repetition frequency was 100 Hz. Argon was used as the carrier gas, flowing through the chamber at 5 standard liters per minute (slm). The capacitor charging voltage was varied between 1.5 kV and 2.5 kV, resulting in sparks with energies of several microjoules. The electrode materials were gold, silver, and cobalt, enabling the synthesis of Au-Ag and Au-Co binary nanoparticles.

The core of the generator is a gas-tight chamber in which the gas flow was controlled by a mass flow controller. The temporal evolution of the electrical signals was recorded using a high-voltage probe and an oscilloscope. From the measured current and voltage waveforms, dynamic discharge parameters such as amplitude, damping factor, and oscillation frequency were determined.

The resulting aerosol was either passed through a tubular furnace for optional thermal treatment before being deposited onto solid substrates (e.g., copper TEM grids) or collected on micro-fiber glass filters for elemental analysis via inductively coupled plasma mass spectrometry (ICP-MS). The morphology, crystal structure, and composition of the nanoparticles were studied by transmission electron microscopy (TEM). Electrode mass changes were determined using an analytical balance with a precision of 0.01 mg. Time- and space-resolved optical emission spectroscopy was employed for spark plasma characterization.

4. New scientific results

T1: I have demonstrated that by employing two single-component metallic electrodes and tuning both the total ohmic resistance of the discharge circuit and the polarity of the electrodes in a spark discharge generator, the average composition of the generated nanoparticles can be precisely adjusted (using a 2.0 mm spark gap, 100 Hz discharge frequency, and argon carrier gas flow of 5 slm). The gold content of Au/Ag binary nanoparticles (BNPs) could be varied between 43.7 at.% and 83.7 at.%, while for Au/Co BNPs, the range was 35.8–76.0 at.%, solely by changing the electrode polarity and the total ohmic resistance of the discharge circuit within 1.0–8.5 Ω. **[1, 2]**

T2: Using a spark discharge nanoparticle generator operated at 100 Hz discharge frequency, a 2.0 mm spark gap, 5 slm argon flow rate, and atmospheric pressure with 99.99% pure Au and Ag electrodes, I have shown through systematic experiments and model calculations that the composition of Au/Ag BNPs can be described more accurately than by previously applied models using a newly developed semi-empirical model that also accounts for anode erosion in the generator. This semi-empirical model predicts the ICP-MS–determined average elemental composition of the BNPs with an average relative accuracy of 4.6% over the entire composition range achievable through electrode

polarity reversal and by varying the total circuit resistance between 1.0 and 8.5 Ω. **[2]**

T3: By fitting the semi-empirical model to the experimentally obtained average compositions of Au/Ag BNPs, and calibrating it using the literature value of $U_{Ag^-} = 14$ V for silver, I estimated the effective cathode voltage for gold under the present experimental conditions (argon at atmospheric pressure and 100–200 A discharge current) to be $U_{Au^-} = (60 \pm 4)$ V. Using this value, the model was fitted to the ICP-MS–determined compositions of Au/Co BNPs produced under both polarities and within the same total resistance range (1.0-8.5 Ω), yielding a maximum relative deviation of only 13% between model predictions and measured values. The corresponding effective cathode voltage for cobalt under these conditions was determined to be $U_{Co^-} = (28 \pm 3)$ V. These results confirm that the model can predict the average composition of BNPs for two fundamentally different systems — one macroscopically miscible (Au/Ag) and one macroscopically immiscible (Au/Co). **[1, 2]**

T4: For the Au/Ag system synthesized using the NaMiLab SDG, I have experimentally demonstrated — using ICP-MS–determined elemental ratios — that anode erosion, neglected in the literature, is in fact a significant process. If cathode and anode erosion were identical,

the contribution of the anode could be neglected; however, my measurements clearly show that while gold anode erosion is negligible, silver exhibits a substantial deviation from the ideal $m_{cathode}/m_{anode}$ = 1 ratio. This deviation from ideality provides clear evidence that anode erosion plays a significant role in the spark discharges applied in my study for the Au/Ag material system. **[2]**

T5: By spark ablation of single-component gold and cobalt electrodes (2.0 mm gap, 5.0 slm argon flow, 100 Hz discharge frequency) in a spark discharge nanoparticle generator, I have successfully synthesized Au/Co nanostructures, and demonstrated the following:

- **T5.1:** The macroscopically immiscible elements gold and cobalt can form alloyed nanostructures even without post-synthesis heat treatment. Using SEM, SEM-EDX, and ED analyses on TEM grids, I showed the presence of a crystalline Au/Co solid phase within the nanostructures. Lattice plane analysis of crystalline regions revealed a characteristic gold content of approximately 75 at.%. The crystalline cores were found to be surrounded by amorphous cobalt oxide shells. **[1]**
- **T5.2:** The morphology and crystal structure of the as-synthesized (non-heat-treated) Au/Co/CoO_x nanoparticles did not change when the total ohmic resistance of the discharge circuit was increased from 1.0 Ω to 5.4 Ω. At 5.4 Ω, HR-TEM analysis revealed identical

Au-rich cores (pure Au to ~25 at.% Co alloy) surrounded by amorphous CoO_x structures. However, the particle size distribution changed significantly: the geometric mean diameter of the primary nanoparticles decreased from (4.50 ± 0.13) nm at 1.0 Ω to (3.2 ± 0.21) nm at 5.4 Ω, consistent with the decrease in spark energy. Furthermore, a secondary size-distribution peak appeared around 9 nm for the 5.4 Ω case. The morphology and crystal structure of the as-synthesized (non-heat-treated) $Au/Co/CoO_x$ nanoparticles did not change when the total ohmic resistance of the discharge circuit was increased from 1.0 Ω to 5.4 Ω. At 5.4 Ω, HR-TEM analysis revealed identical Au-rich cores (pure Au to ~25 at.% Co alloy) surrounded by amorphous CoO_x structures. However, the particle size distribution changed significantly: the geometric mean diameter of the primary nanoparticles decreased from (4.50 ± 0.13) nm at 1.0 Ω to (3.2 ± 0.21) nm at 5.4 Ω, consistent with the decrease in spark energy. Furthermore, a secondary size-distribution peak appeared around 9 nm for the 5.4 Ω case. **[1]**

- **T5.3:** Post-heattreatment of $Au/Co/CoO_x$ nanoparticles generated by the spark discharge at 900 °C in the aerosol phase resulted in significant morphological and structural transformations. The amorphous CoO_x shells crystallized, forming phase-segregated $Au/Co/CoO_x$ nanoparticles that assembled into “clustered” or “fused” aggregates. **[1]**

6. Publications

Publications Forming the Basis of the Theses

[1] **Lajos Péter Villy,** Attila Kohut, Albert Kéri, Ádám Bélteki, György Radnóczi, Zsolt Fogarassy, György Zoltán Radnóczi, Gábor Galbács & Zsolt Geretovszky: „*Continuous spark plasma synthesis of Au/Co binary nanoparticles with tunable properties*", Scientific Reports, **12,** 18560 (2022), MTMT: 33208918, **IF: 4,600 [T1, T3, T5]**

[2] Attila Kohut, **Lajos Péter Villy**, Albert Kéri, Ádám Bélteki, Dániel Megyeri, Béla Hopp, Gábor Galbács & Zsolt Geretovszky: „*Full range tuning of the composition of Au/Ag binary nanoparticles by spark discharge generation*", Scientific Reports, **11,** 5117 (2021), MTMT: 31879425, **IF: 4,996 [T1, T2, T3, T4]**

Additional Publications

[K1] Attila Kohut, **Lajos Péter Villy**, Linnéa Jönsson, Dániel Megyeri, Gábor Galbács, Maria E. Messing, Zsolt Geretovszky: „*Gold–silver alloy nanoparticle formation via spark ablation: the dynamics of material mixing*", Nanoscale Advances, **7,** 3322-3330, (2025), MTMT: 36100289, **IF: 4,700**

[K2] Attila Kohut, **Lajos Péter Villy**, Gergely Kohut, Gábor Galbács, and Zsolt Geretovszky: „*A Calibration-Free Optical Emission Spectroscopic Method to Determine the Composition of a Spark Discharge Plasma Used for AuAg Binary Nanoparticle Synthesis*", Applied Spectroscopy, **77,** 12, (2023), MTMT: 34393015, **IF: 2,200**

[K3] Dávid J. Palásti, **Lajos Péter Villy**, Bálint Leits, Albert Kéri, Attila Kohut, Ádám Bélteki, Gyula Kajner, Fernando A. Casian Plaza, Éva Kovács-Széles, Tibor Ajtai, Miklós Veres, Zsolt Geretovszky, Gábor Galbács: „*Detection and characterization of mono- and bimetallic nanoparticles produced by electrical discharge plasma generators using laser-induced breakdown spectroscopy*", Spectrochimica Acta Part B: Atomic Spectroscopy, **209,** 106804, (2023), MTMT: 34536295, **IF: 3,200**

[K4] Dávid J. Palásti, **Lajos Péter Villy**, Attila Kohut, Tibor Ajtai, Zsolt Geretovszky, Gábor Galbács: „*Laser-induced breakdown spectroscopy signal enhancement effect for argon caused by the presence of gold nanoparticles*", Spectrochimica Acta Part B: Atomic Spectroscopy, **193,** 106435, (2022), MTMT: 32836484, **IF: 3,300**

[K5] Attila Kohut, **Lajos Péter Villy**, Tibor Ajtai, Zsolt Geretovszky, Gábor Galbács: „*The effect of circuit resistance on the particle output of a spark discharge nanoparticle generator*", Journal of Aerosol Science, **118,** pp. 59-63., (2018), MTMT: 3326631, **IF: 2,240**

Conference Presentations and Posters

Oral Presentations

[S1] XVI. Hungarian Aerosol Conference, Szarvas, 2024
Presentation title: Investigation of the mixing of gold–cobalt nanoparticles produced by spark ablation
Villy Lajos Péter, Kohut Attila, Geretovszky Zsolt
MTMT: 36378622

[S2] XV. Hungarian Aerosol Conference, Hévíz, 2022
Presentation title: Effect of hydrogen on the spark plasma and the resulting nanoaerosol during spark ablation production
Villy Lajos Péter, Kohut Attila, Márton Zsuzsanna, Geretovszky Zsolt
MTMT: 36378628

[S3] Spring Wind Conferenc 2022, Pécs, 2022
Presentation title: Investigation of the mixing dynamics of electrode materials by emission spectroscopy during nanoparticle production via spark ablation
Villy Lajos Péter, Kohut Attila, Márton Zsuzsanna és Geretovszky Zsolt
MTMT: 36378646

[S4] Conference of Young Hungarian Researchers in the Carpathian Basin (Kárpát-medencei Fiatal Magyar Kutatók Konferenciája), Online ZOOM, 2021
Presentation title: Szikra ablációs módszerrel előállított arany-kobalt binér nanorészecskék morfológiájának és összetételének vizsgálata
Villy Lajos Péter, Kohut Attila, Kéri Albert, Bélteki Ádám, Galbács Gábor, és Geretovszky Zsolt
MTMT: 36378653

[S5] XIV. Hungarian Aerosol Conference, Visegrád, 2019
Presentation title: Kétkomponensű nanorészecskék előállítása és összetételük változtatása szikrakisüléses nanorészecske generátorban
Villy Lajos Péter, Kohut Attila, Kéri Albert, Bélteki Ádám, Galbács Gábor, és Geretovszky Zsolt
MTMT: 36378702

Poster presentation

[P1] Quantum Electronics 2025: Symposium on the Results of Hungarian Research in Quantum Electronics (Kvantumelektronika 2025: Szimpózium a hazai kvantumelektronikai kutatások eredményeiből), Szeged, 2025
Mixing dynamics of gold and silver atomic plumes during the spark ablation synthesis of alloy nanoparticles
Attila Kohut, **Lajos Péter Villy**, Linnéa Jönsson, Dániel Megyeri, Gábor Galbács, Maria E. Messing, Zsolt Geretovszky
MTMT: 36329522

[P2] European Aerosol Conference, Malaga, Spain, 2023
The effect of hydrogen on the spark plasma and generated nanoparticles produced in a spark discharge generator
Lajos Péter Villy, Zsuzsanna Márton,Attila Kohut, Zsolt Geretovszky
MTMT: 36378751

[P3] 11th International Aerosol Conference, Athen, Greece, 2022
On the mixing dynamics of the electrodes' material during the formation of multicomponent nanoparticles in a spark discharge generator
Lajos Péter Villy, Gábor Galbács, Zsuzsanna Márton, Zsolt Geretovszky, Attila Kohut
MTMT: 36388699
[P4] International Workshop on LIBS, Szeged, 2020
On-line and off-line libs detection of nanoaerosols generated by electrical discharges
Ádám Bélteki, Tira Biros, Dávid J. Palásti, **Lajos P. Villy**, Bálint Leits, Albert Kéri, Attila Kohut, Éva Kovács-Széles, Tibor Ajtai, Zsolt Geretovszky, Gábor Galbács
MTMT: 31817889

[P5] International Workshop on LIBS, Szeged, 2020
Signal enhancement of gaseous samples in the presence of nanoaerosols generated by a spark discharge
Lajos Péter Villy, Dávid J. Palásti, Gábor Skoda, Attila Kohut, Zsolt Geretovszky, Éva Kovács-Széles, Gábor Galbács
MTMT: 3181791

[P6] 10th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy, EMSLIBS, Praha,Czech Republic, 2019
Nanoparticle analysis by LIBS and ICP-MS in industrial and environmental samples
Palásti Dávid, Kéri Albert, **Villy Lajos Péter**, Biros Tyra, Bélteki Ádám, Leits Bálint, Janovszky Patrick, Kohut Attila, Kovács-Széles Éva, Geretovszky Zsolt, Galbács Zoltán, Galbács Gábor
MTMT: 32151550

[P7] 25th International Symposium on Analytical and Environmental Problems, Szeged, 2019
Assessment of the usefulness of libs and icp-ms for the characterization of nanoparticles in industrial and environmental samples
Dávid Palásti, Albert Kéri, **Lajos Péter Villy**, Tíria Biros, Ádám Bélteki, Bálint Leits, Patrick Janovszky, Attila Kohut, Zoltán Galbács, Éva Kovács-Széles, Zsolt Geretovszky, Gábor Galbács
MTMT: 32151520

[P8] European Winter Conferenceon Plasma Spectrochemistry, Pau, France, 2019
Composition and morphology analysis of bimetallic nanoparticules generated in a spark discharge plasma
Albert Keri, Henrik Bali, **Lajos Péter Villy**, Attila Kohut, Tibor Ajtai, Zsolt Geretovszky, Gabor Galbács
MTMT: 31903065

[P9] 24th International Symposium on Analytical and Environmental Problems, Szeged, 2018
Study of the composition and size distribution of gold-containing bimetallic nanoparticles synthesized in a spark discharge generator
Bali Henrik, Kéri Albert, Kohut Attila, **Villy Lajos Péter,** Bélteki Ádám, Geretovszky Zsolt, Galbács Gábor
MTMT: 31604464

MTMT identifier: 10077115