Building Blocks for Nanotechnology from Spark Ablation

Andreas Schmidt-Ott
Nanoparticle production by exploding a wire ca. 1975
Nanoparticle Production by Spark Ablation (Principle)

Short (1 – 10 µs) repetitive sparks produce strongly quenched vapor ($\approx 10^7$ K s$^{-1}$)
VSP G1 (VSPARTICLE)
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Spark Generator
VSP G1 (VSParticle)

Inert carrier gas
Desired material

Electric spark ablation (ca. 20000K)
Spark Ablation Features

- Produces particles of high purity
- Requires no precursor
- Works for any conducting or semiconducting material
- Mixes materials
- Particles are partially charged
- Can be scaled up
- Impaction printing is possible

Ideal tool for diameter range below 20 nm
This is where properties are strongly size dependent
→ New materials and new devices
Size Control
Size Control in Spark ablation

\[ d_p \approx \left( \frac{\dot{m} \beta V}{\rho \frac{\pi}{3} Q^2} \right)^{1/3} \]

- Mass production rate = \( \Delta m f \)
- Coagulation coefficient
- Effective chamber volume
- Mean Particle Diameter at outlet
- Material density
- Volume flow rate


Relative Standard Deviation: ca. 1.35-1.40
Smallest Sizes: Atomic clusters

Anne Maisser in Spark Ablation: Building Blocks for Nanotechnology, A. Schmidt-Ott, Editor, 2020, Jenny Stanford Publishing
Geometrical Mean Diameter from VSPARTICLE model G1 (model calculation)
Size Selection by Differential Mobility Analyzer (DMA)
Mixing
Mixed (Alloyed) Nanoparticle Formation

The sparks have to be short enough to produce atomically mixed particles
→ Mixing of materials immiscible in the bulk!


Material discovery is all about mixing!

About 80 elements can be converted to nanoparticles by spark ablation.

There are myriads of possible combinations of elements with different mixing ratios!

Stable

Optimized properties for a specific application
Spark Mixing

Alloys confined in nanoparticles
- unprecedented alloys
- thermodynamically stable

Direct vapor–crystal transformation

Crystalline, but distribution of the elements is disordered!

By mixing, many properties can be tuned!

**Example: The plasmon resonance**

- Plasmon resonance is made use of for
  - Catalysis
  - Photovoltaics
  - Sensors
  - Photoelectrochemical water splitting
  - Photoelectrochemical CO$_2$ reduction
  - Surface enhanced Raman scattering

Absorption spectrum of a Au-Ag alloy, ratio 1:1. (Cattaruzza et al., 2003)

Mixing Possibilities Using Spark Ablation: Spark Mixing

Mixing on a nanoscale
Generic approach for catalyst production, unique in its flexibility

Coating
"Spark Coating"

Spark Coating of PSL Spheres by Gold

\[ \gamma_{\text{coat}} > \gamma_{\text{subs}} \]

decoration

Deposition
**Different Ways of Depositing Nanoparticles from Spark Ablation onto Surfaces**

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
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| Aerosol | • Deposition possible when for example combined with cell culture exposure systems  
          • For calibration                                                              |
| Filtration | • Porous substrates  
               • High deposition efficiency                                                      |
| Diffusion | • Low impact, no particle deformation  
              • Ideal for low surface coverages of nanoparticles                             |
| Impaction | • High surface coverages  
                • Production of porous material                                                |
| Printing | • Patterning and impact sintering  
               • High surface coverages  
               • Production of porous material                                                |
Components for Nanofabrication (VSPARTICLE)
Nanoparticle collection on filter

Estimate of void fraction: 80%
Printing of catalyst layers by impaction (VSPARTICLE)
Lines of porous ZnO and Au printed with P1

Void fraction ca. 30%

Joost van Ginkel, European Aerosol Conference, 2020
Printing Nanoparticles from Spark Ablation by Electrostatic Focussing (Mansoo Choi Group, Korea)

Resolution < 1 μm
Applications
Application Domains as Summarized in Spark Ablation Book

Applications:

Chemical sensors
Chemiresistive Gas Sensor: NO$_2$ – detection by WO$_3$ Nanoparticles

Changes in the resistance of nanoparticulate WO$_3$ films exposed to 0 and 10 ppm NO$_2$ in air at 200ºC. Inset: Normalized sensitivity of the nanoparticulate films as a function of temperature.

Electronic Nose

Polluted air

Example 3: Higher speed of chemical reactions: Tarnishing

Layer of silver VSParticles

Colorimetrical Sensor to Predict Tarnishing of Objects

$\textit{SLOW!}$ (takes months)

Color change indicates concentration of corroding gases in the air.

$\textit{FAST!}$ (takes minutes)

Optical signal $\rightarrow$ **Corrosiveness of ambient air**
Applications:

Surface Enhanced Raman Scattering (SERS)
Surface Enhanced Raman Scattering (SERS)

Specific molecules can be detected with single molecule sensitivity, if the laser frequency is in resonance with the plasmon frequency.

**Possible applications:**
- Medical: Trace components in human breath
- Explosives
- Drugs
- Viruses


**Pure** Plasmonic particle layer with optimized
- Composition
- Particle size
- Structure
Applications:

Catalysis
Particles from Spark Ablation for Catalysis
“Aerosol Catalysis”

Ni catalyst

\[ \text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \]

SHINERS uses SERS to test catalysts.

Spark Ablation (VSP G1) -> Catalyst particles -> Diffusional deposition (VSP catalyst sampler) -> Coated plasmonic particles

2 nm Ni particles are deposited on plasmonic particles by diffusional deposition

**Conclusions**

Spark ablation offers great opportunities for discovery and development of new materials. Examples have been shown for the domains of

- Catalysis
- Chemical sensors
- Surface Enhanced Raman Spectroscopy
  (explosives, medical diagnosis, viruses, …)

Breakthroughs in these domains are to be expected due to the unique features of spark ablation regarding

- Flexibility in composition; unlimited mixing capability!
- Particle size control
- Size range < 20 nm, where size effects occur
- Purity

For more details: Book Ed. by A. Schmidt-Ott, 2020:
Spark Ablation – Building Blocks for Nanotechnology (450 pages)