Building Blocks for Nanotechnology from Spark Ablation

Andreas Schmidt-Ott

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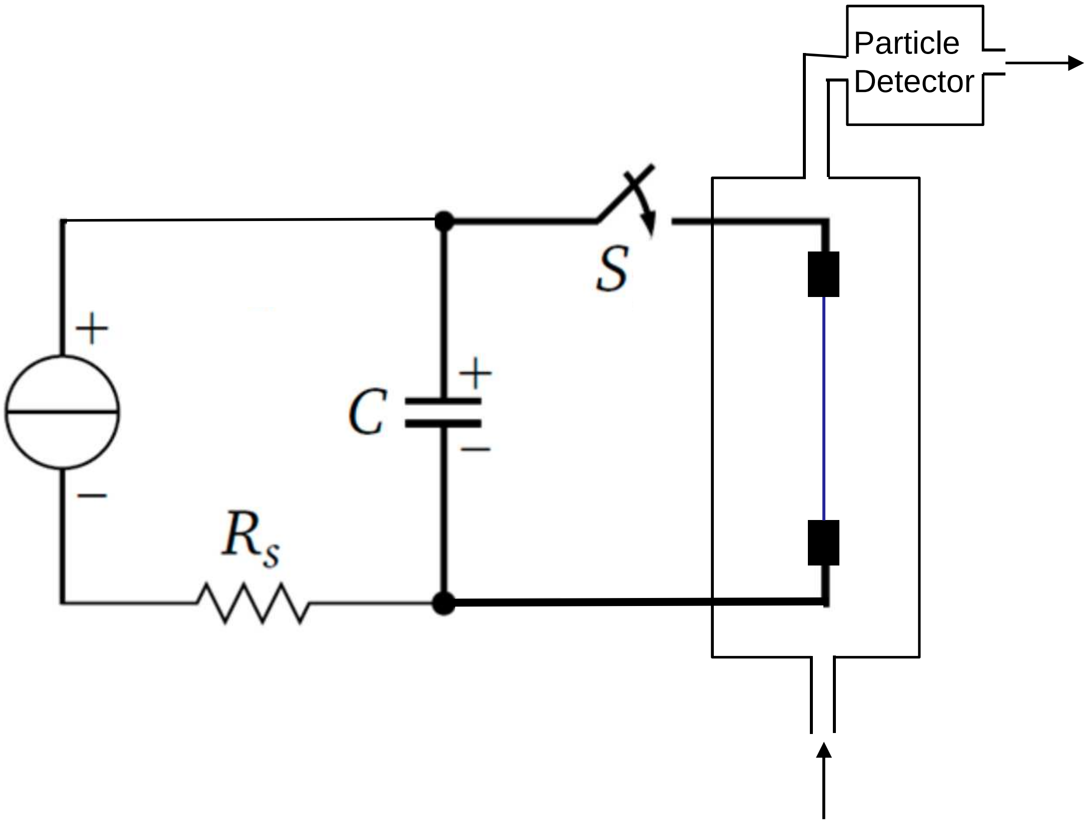
Nanoparticle production by exploding a wire ca. 1975



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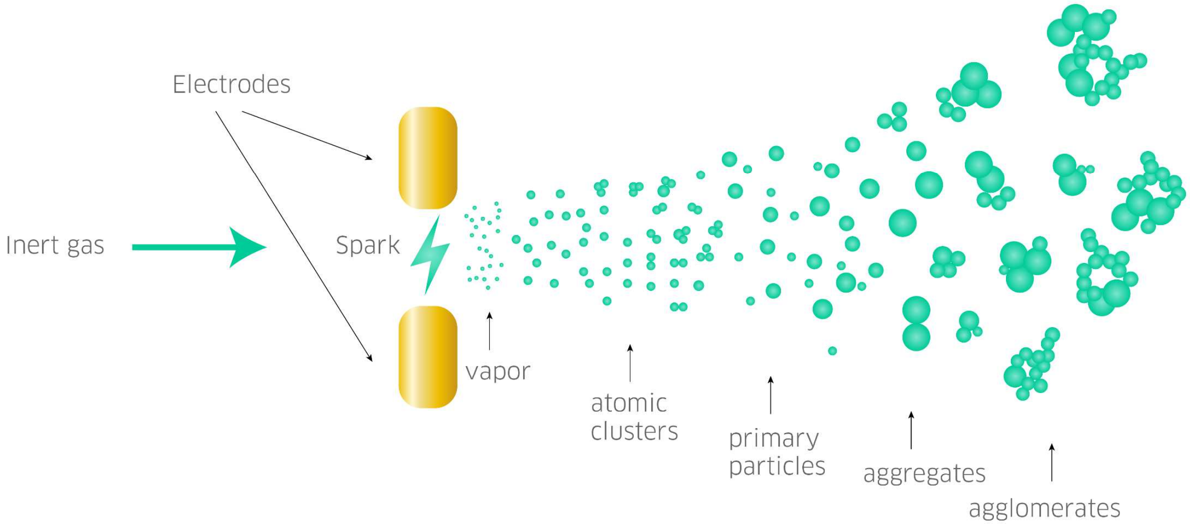
Nanoparticle Production by Spark Ablation (Principle)



Short (1 – 10 µs) repetitive sparks produce strongly quenced vapor (≈ 10^7 K s^{-1})

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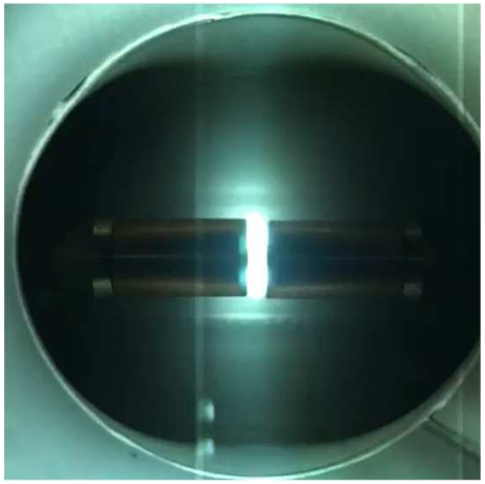
VSP G1 (VSPARTICLE)



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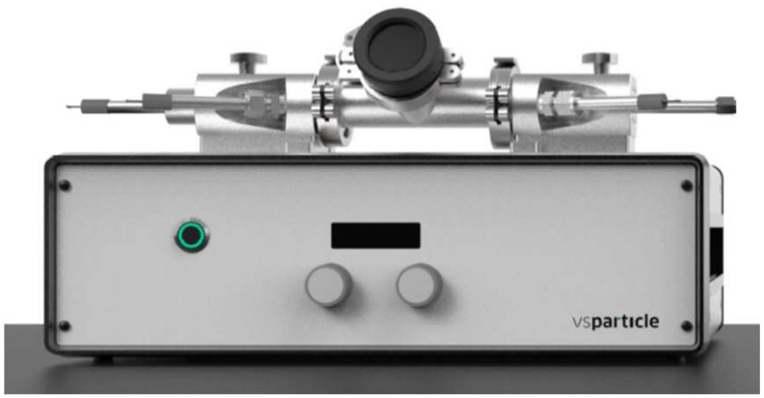
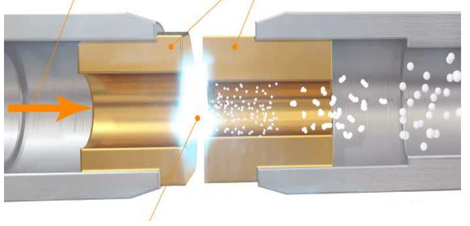
VSP G1 (VSPARTICLE)



Spark Generator
VSP G1 (VSParticle)



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Spark Ablation Features

•Produces particles of high purity

•Requires no precursor

•Works for any conducting or semiconducting material

•<u>Mixes materials</u>

•Particles are partially charged

•Can be scaled up

•Impaction printing is possible

Ideal tool for diameter range <u>below 20 nm</u>

This is where properties are strongly size dependent

→ <u>New materials and new devices</u>

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Size Control

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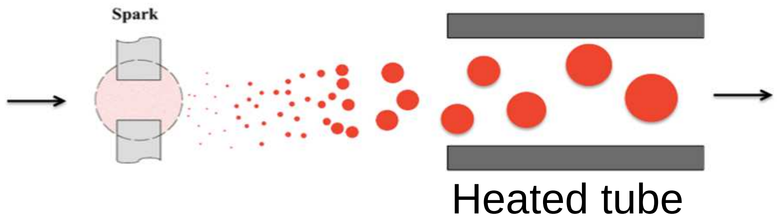
Size Control in Spark ablation



Mass production rate =Δm f

Coagulation coefficient

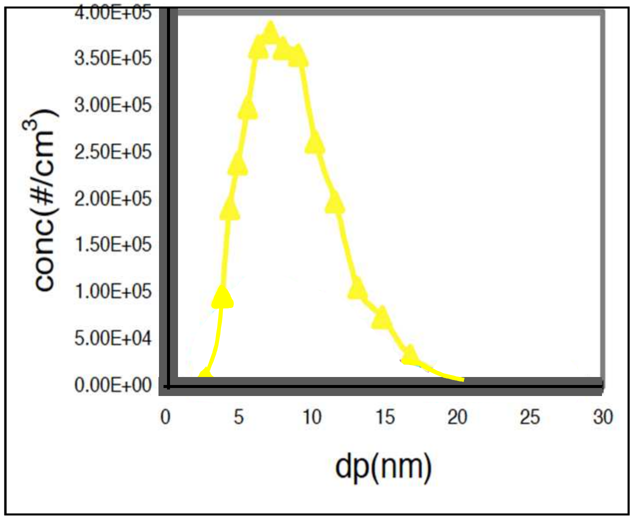
Effective chamber volume

Mean Particle Diameter at outlet

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

Material density

Volume flow rate



Relative Standard Deviation: ca. 1.35-1.40

J. Feng, G. Biskos, A. Schmidt-Ott, *Sci. Reports* 5, 15788 (2015).

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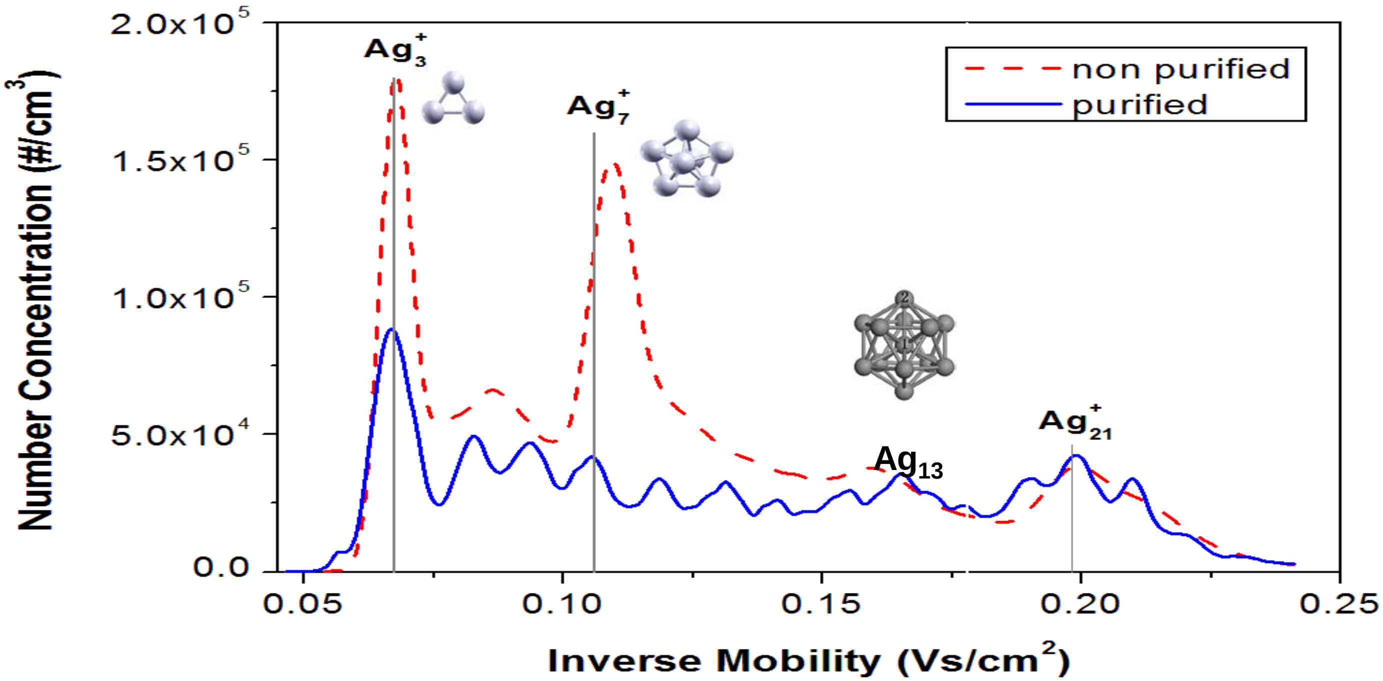
Smallest Sizes: Atomic clusters



Anne Maisser in Spark Ablation: Building Blocks for Nanotechnology, A. Schmidt-Ott, Editor, 2020, Jenny Stanford Publishing

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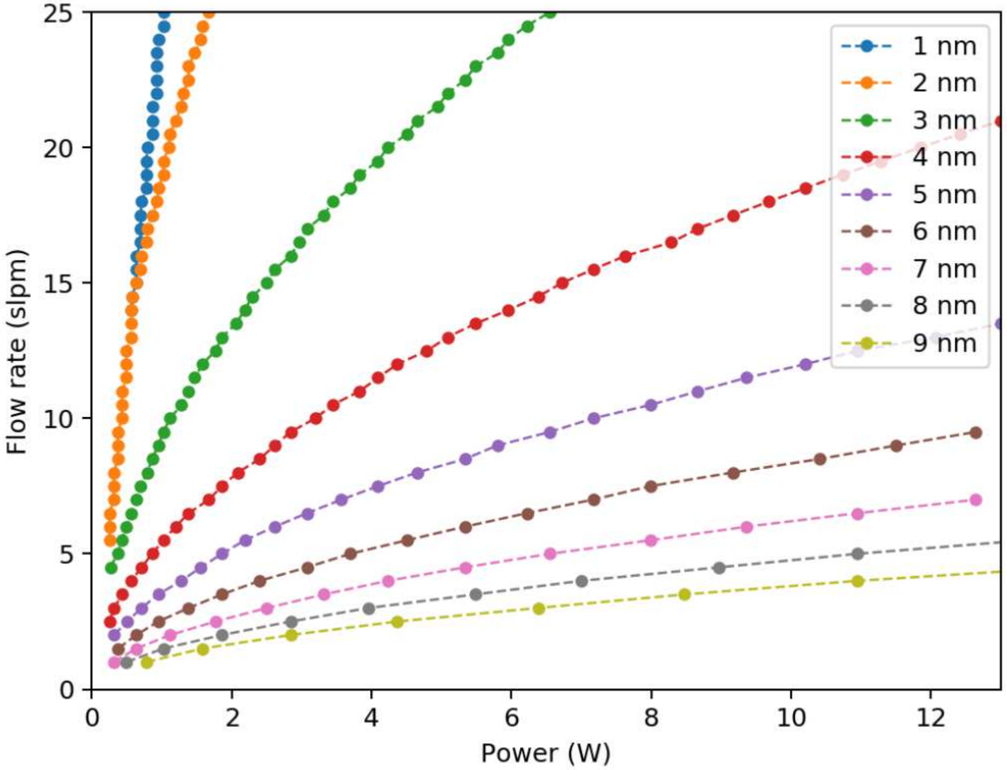
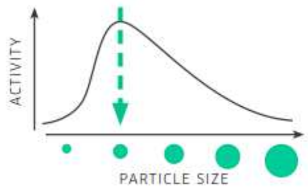
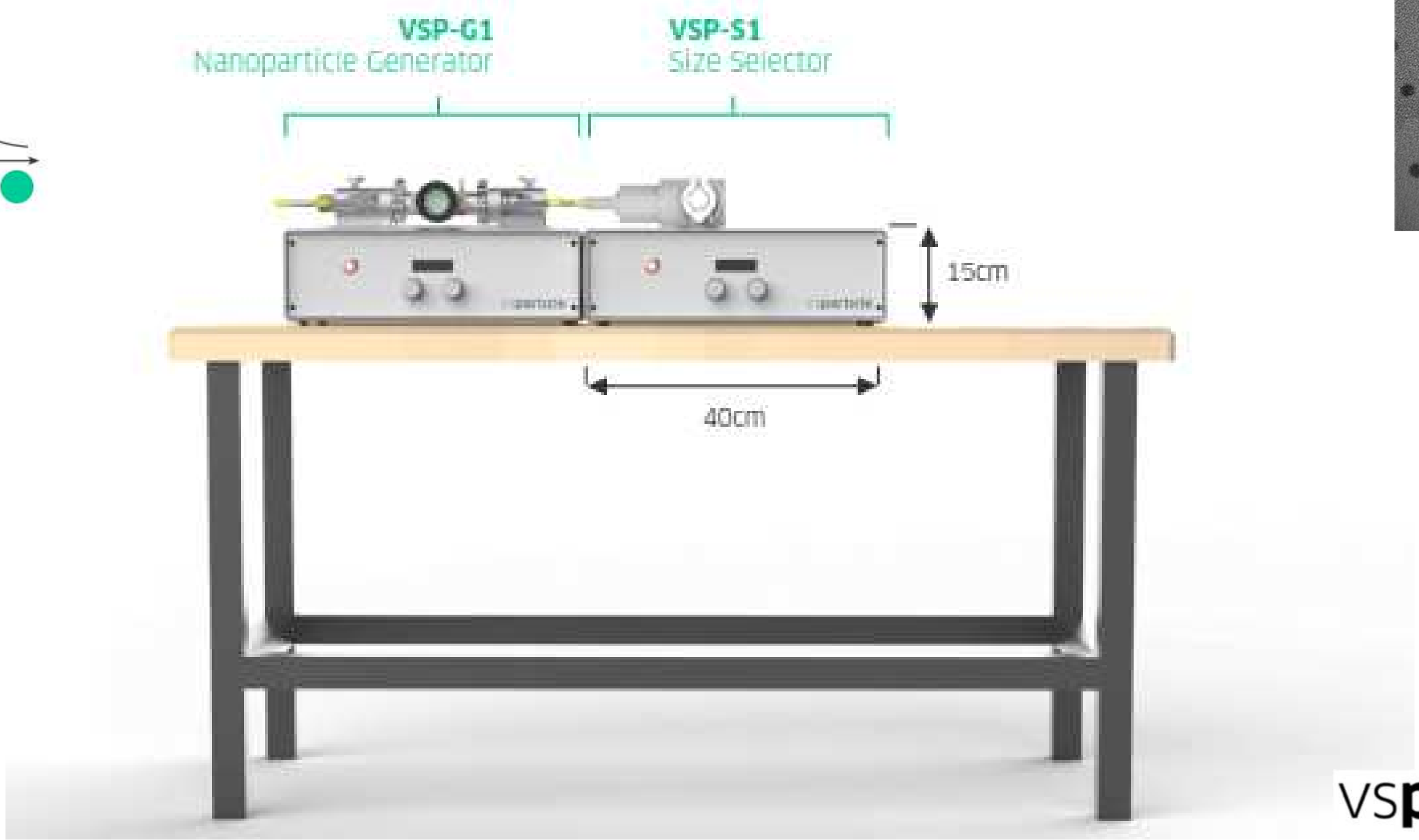
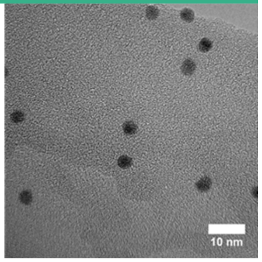
Geometrical Mean Diameter from VSPARTICLE model G1 (model calculation)



Size Selection by Differential Mobility Analyzer (DMA)







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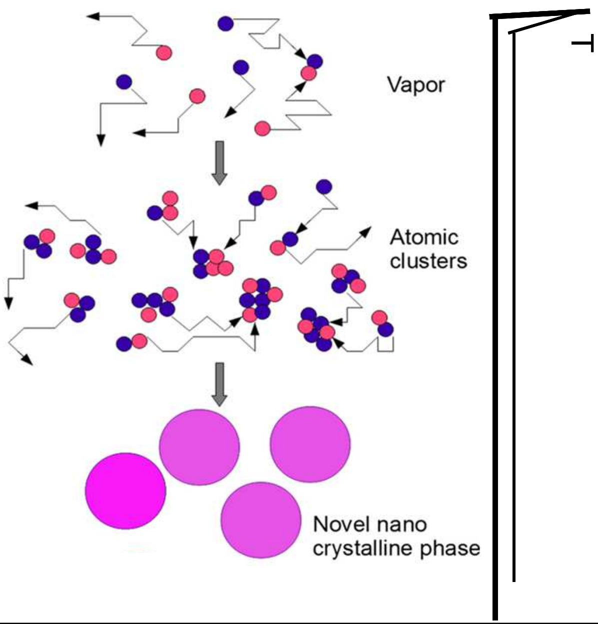
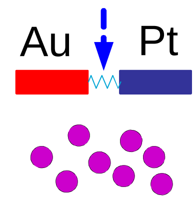
Mixing

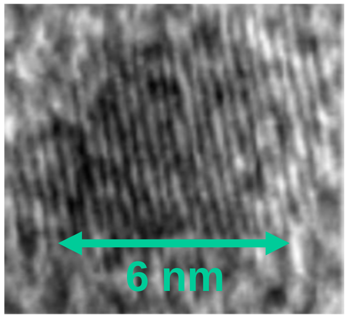
Mixed (Alloyed) Nanoparticle Formation



The sparks have to be short enough to produce atomically mixed particles

→ Mixing of materials immiscible in the bulk!





A. Muntean et al. in Spark Ablation – Building Blocks for Nanotechnology, ed. by A.Schmidt-Ott, Jenny Stanford Publishing, 2020, ISBN 978-981-4800-82-2

Tabrizi, N. S., Xu, Q., Van Der Pers, N. M. and Schmidt-Ott, A. (2010). Generation of mixed metallic nanoparticles from immiscible metals by spark discharge, *J. Nanopart. Res.*, **12**, pp. 247–259.

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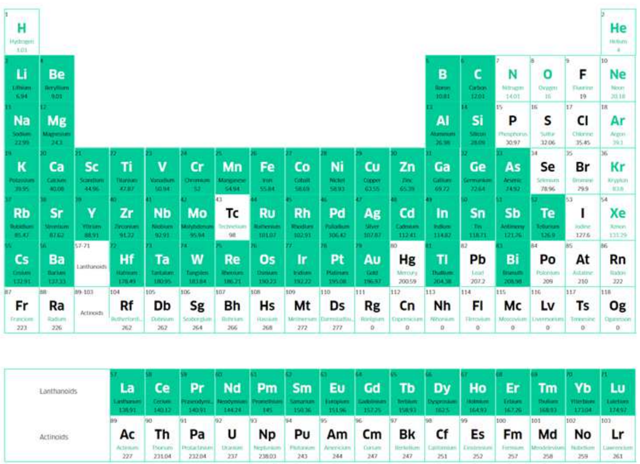
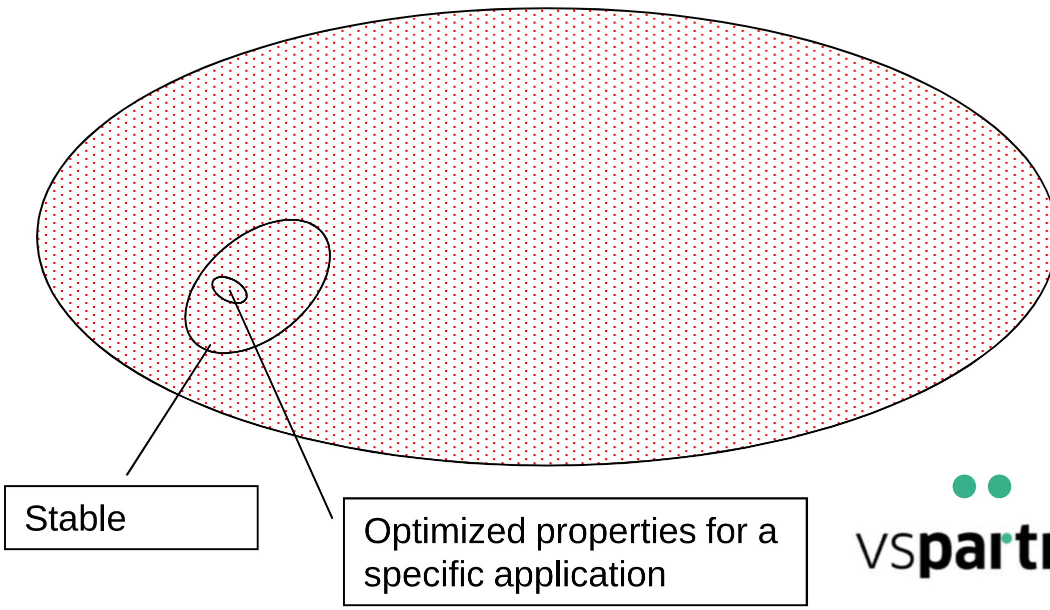
Material discovery is all about mixing!



About 80 elements can be converted to nanoparticles by spark ablation

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



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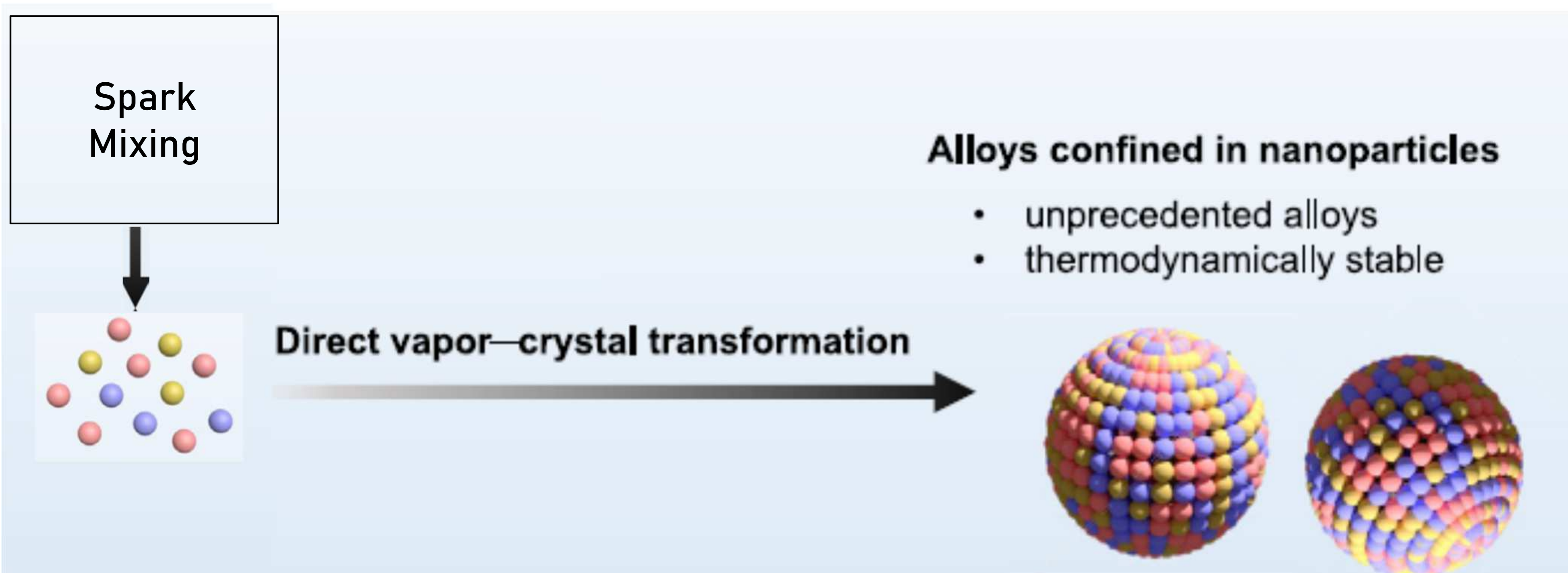
High-Entropy Alloy Nanoparticles



Crystalline, but distribution of the elements is disordered!

J. Feng, D. Chen, P.V. Pikhitsa, Y. Jung, J. Yang, M. Choi, Unconventional Alloys Confined in Nanoparticles: Building Blocks for New Matter, Matter 3, 1646–1663 (2020).

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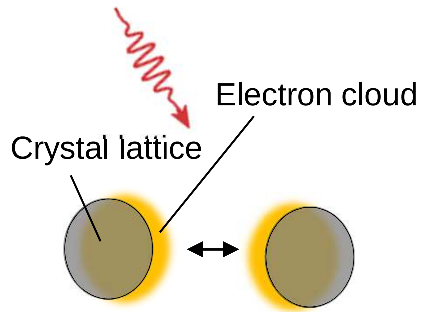
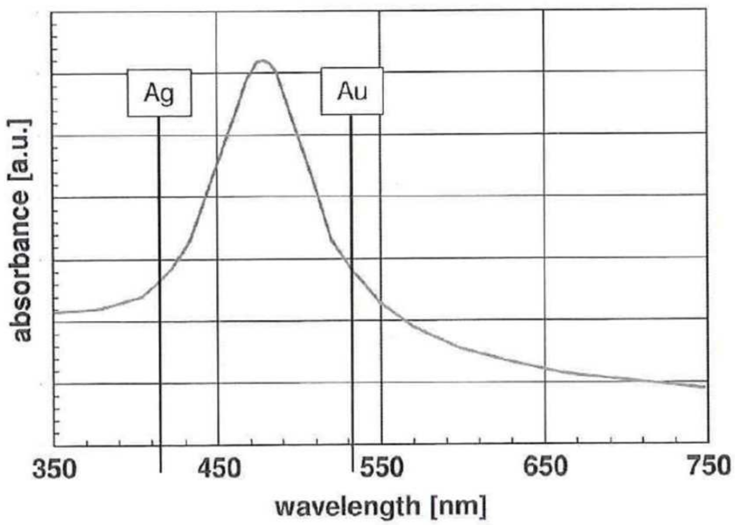
By mixing, many properties can be tuned!
Example: The plasmon resonance



Electron cloud oscillates =
Local Surface Plasmon
Resonance (LSPR)



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

Plasmon resonance is made use of for
- Catalysis
- Photovoltaics
- Sensors
- Photoelectrochemical water splitting
- Photoelectrochemical CO_2 reduction
- Surface enhanced Raman scattering

M.F.J. Boeije et al. in Spark Ablation – Building Blocks for Nanotechnology, ed. by A.Schmidt-Ott, Jenny Stanford Publishing, 2020, ISBN 978-981-4800-82-2

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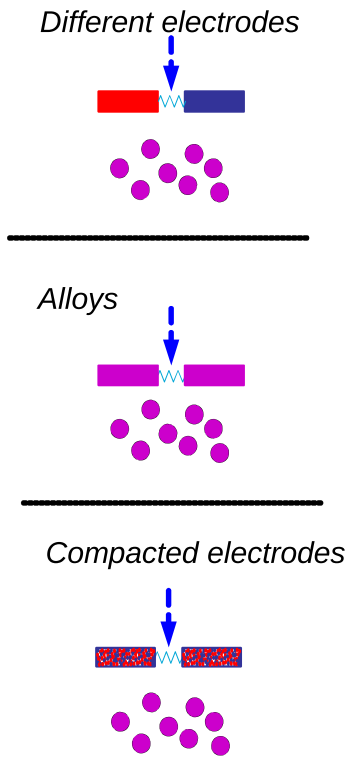
Mixing Possibilities Using Spark Ablation: Spark Mixing



Pfeiffer, T. V., Feng, J. and Schmidt-Ott, A. (2014). New developments in spark production of nanoparticles, *Adv*. *Powder Technol*., **25**, pp. 56–70.

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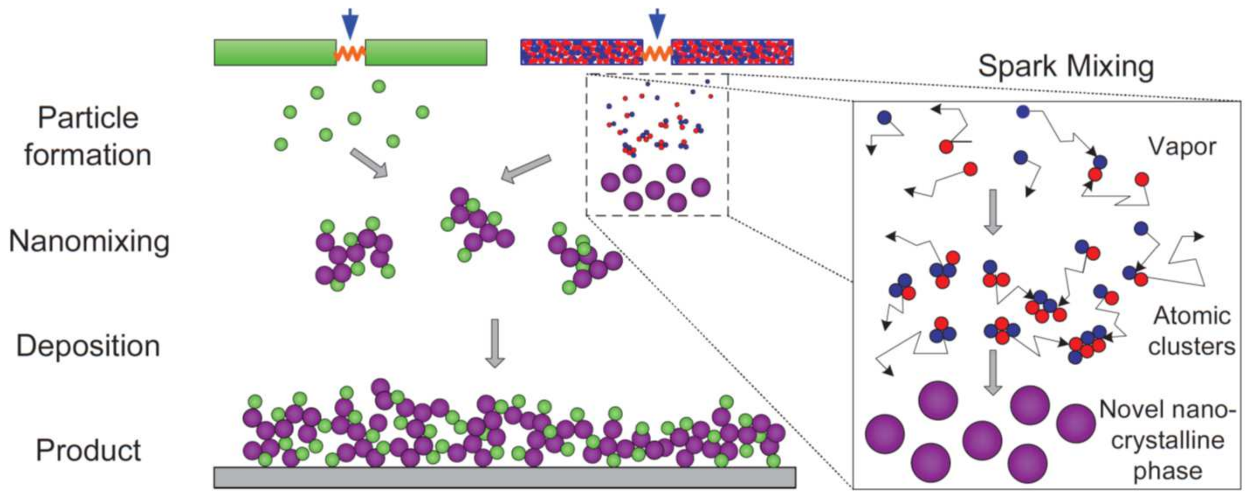
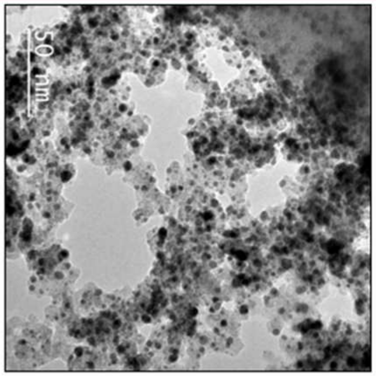
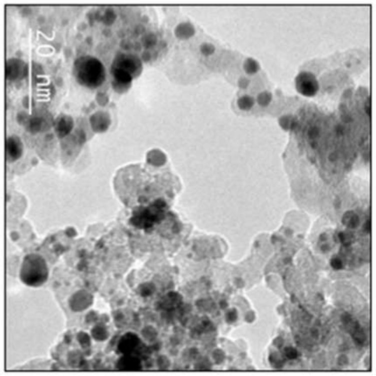
Mixing on a nanoscale
Generic approach for catalyst production, unique in its flexibility







M.F.J. Boeije et al. in Spark Ablation – Building Blocks for Nanotechnology, ed. by A.Schmidt-Ott, Jenny Stanford Publishing, 2020, ISBN 978-981-4800-82-2

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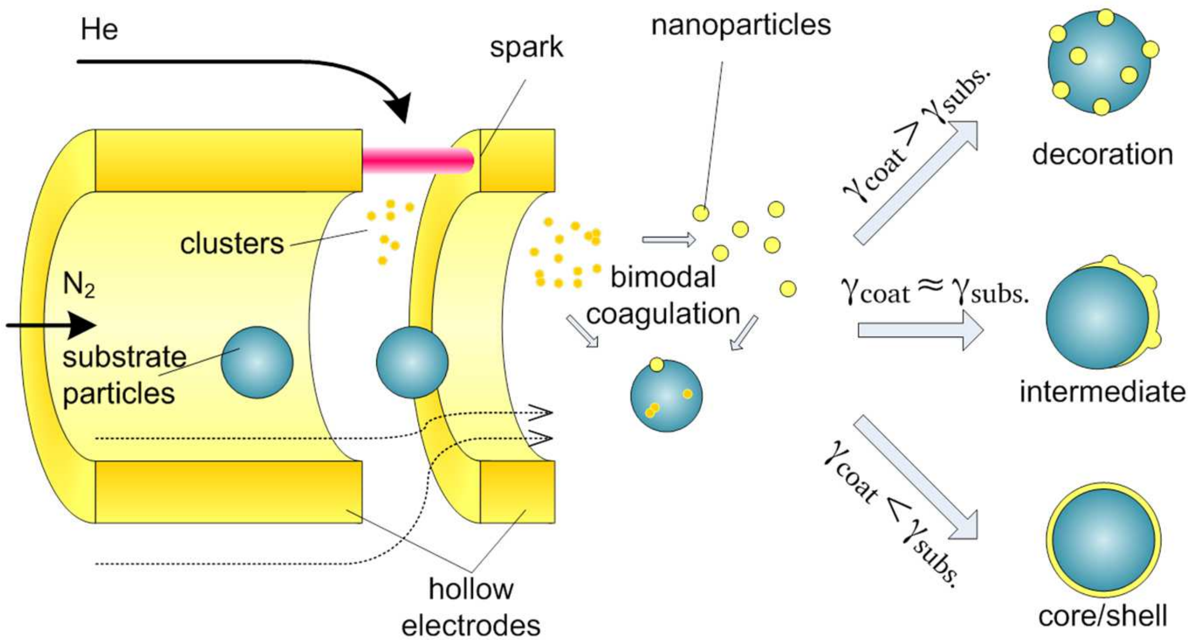
Coating

“Spark Coating”



T.V. Pfeiffer, P. Kedia, M.E. Messing, M. Valvo, A. Schmidt-Ott, Precursor-Less Coating of Nanoparticles in the Gas Phase, Materials 8 (2015) 1027-1042 ,

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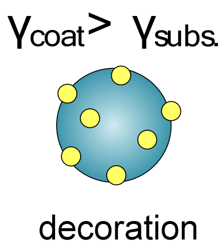
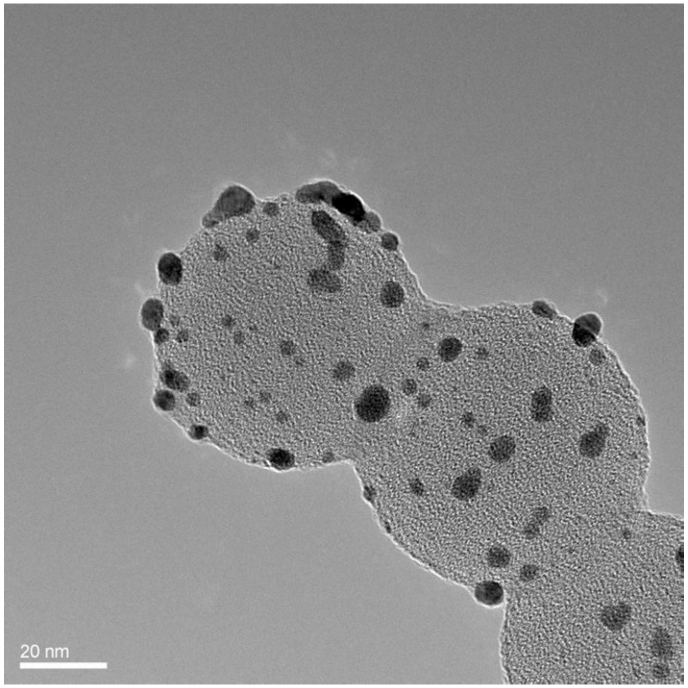
Spark Coating of PSL Spheres by Gold





T.V. Pfeiffer, P. Kedia, M.E. Messing, M. Valvo, A. Schmidt-Ott, Precursor-Less Coating of Nanoparticles in the Gas Phase, Materials 8 (2015) 1027-1042 ,

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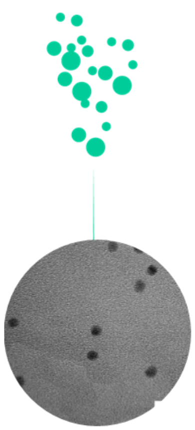
Deposition

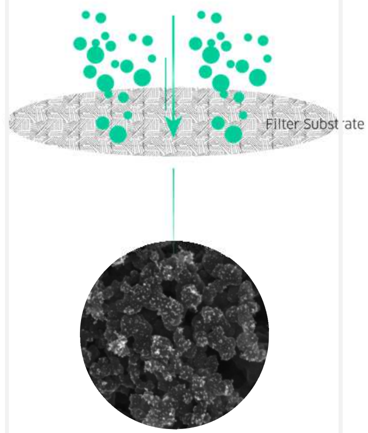
Different Ways of Depositing Nanoparticles from Spark Ablation onto Surfaces

Aerosol



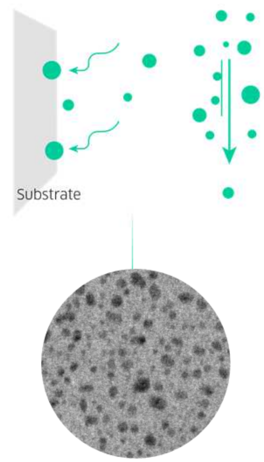
- Deposition possible when for example combined with cell culture exposure systems
- For calibration

Filtration



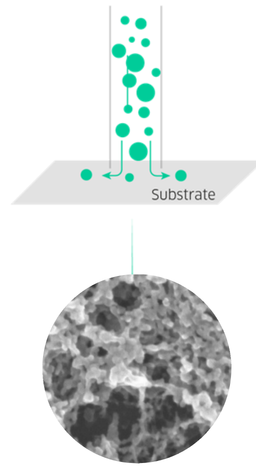
- Porous substrates
- High deposition efficiency

Diffusion



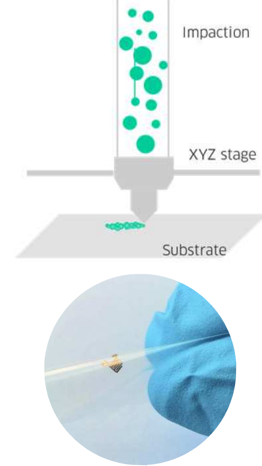
- Low impact, no particle deformation
- Ideal for low surface coverages of nanoparticles

Impaction



- High surface coverages
- Production of porous material

Printing



- Patterning and impact sintering
- High surface coverages
- Production of porous material

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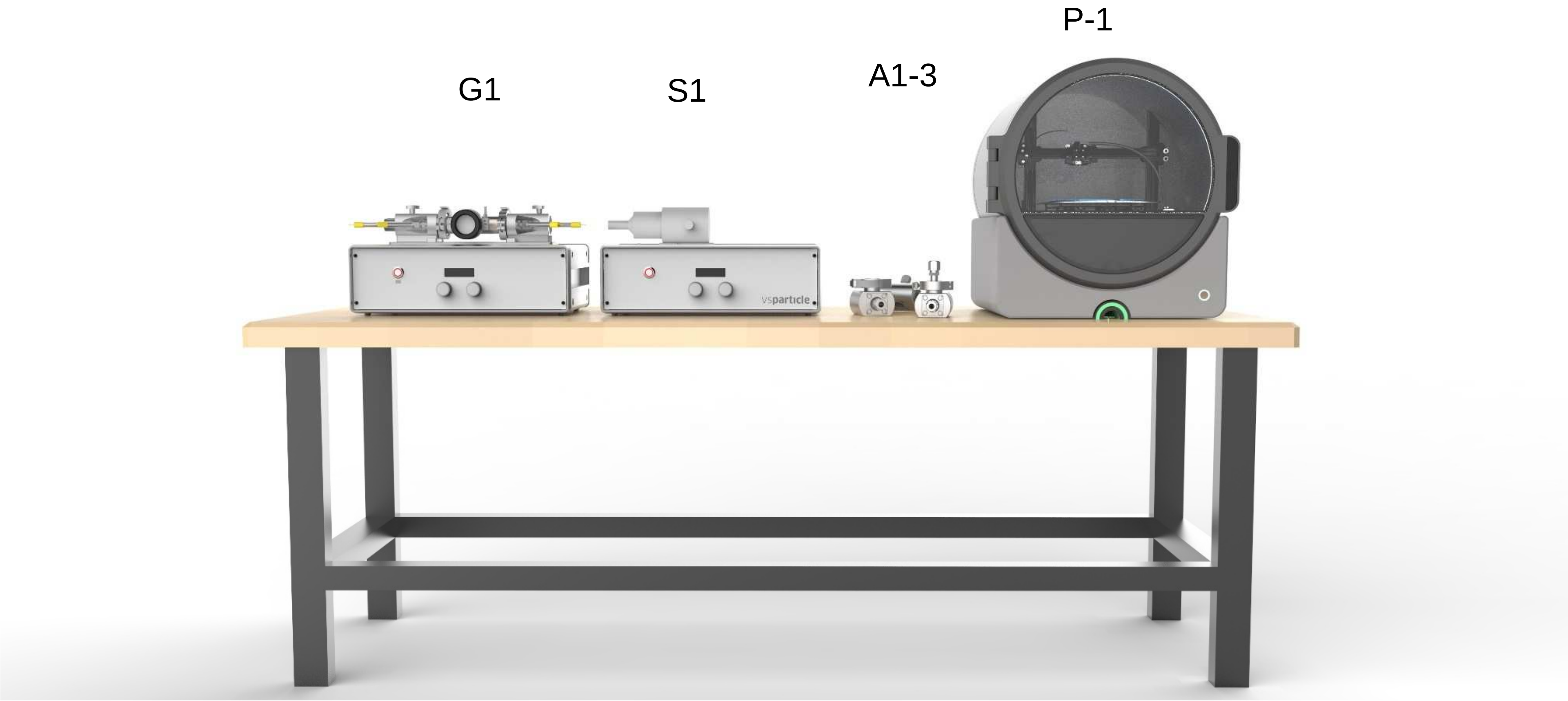
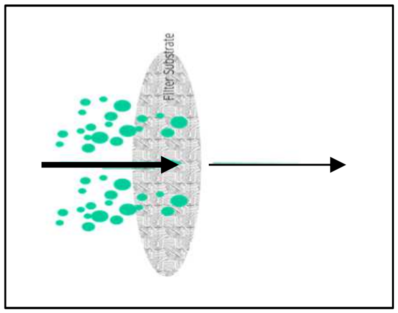
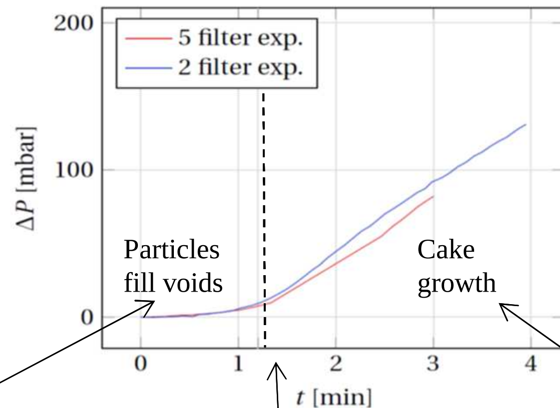
Components for Nanofabrication (VSPARTICLE)

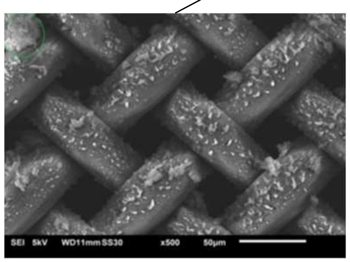


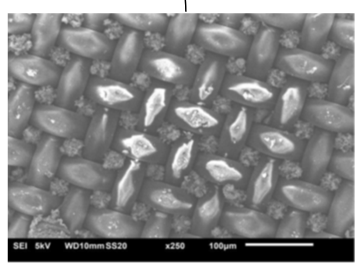
Nanoparticle collection on filter

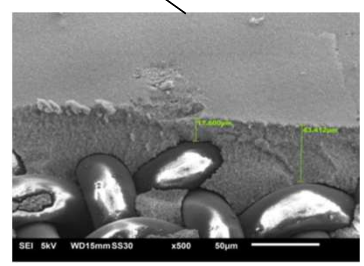




Tijmen Kroesen, Master's Thesis







Zhouping Zhou, Bachelor's thesis

<u>Estimate of void fraction: 80%</u>

(G.J. Lindquist, D.Y. H. Pui, C.J. Hogan, J. Aerosol Sci. 74 (2014) 42–51.)

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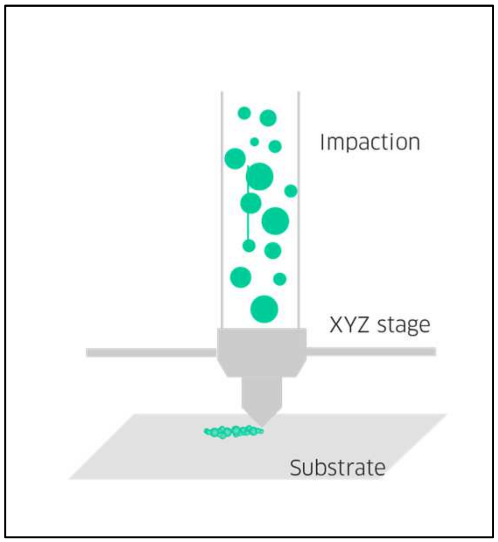
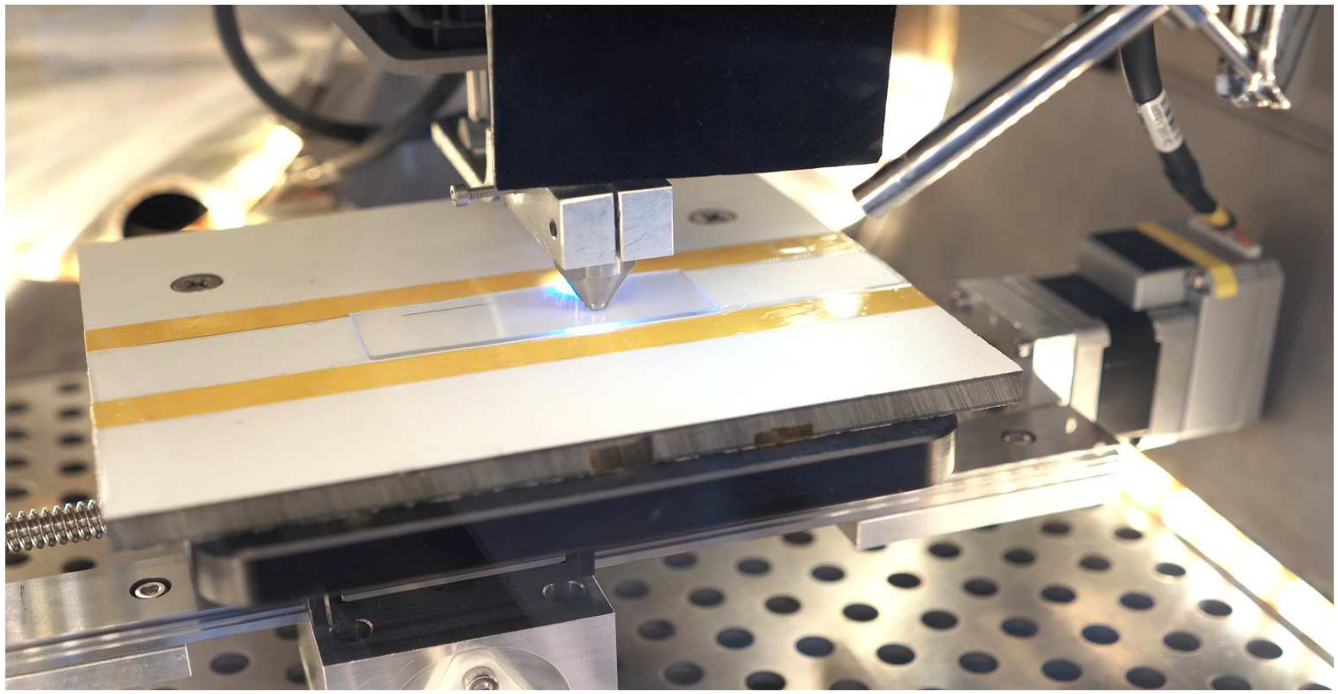
VSPARTICLE P1 printer





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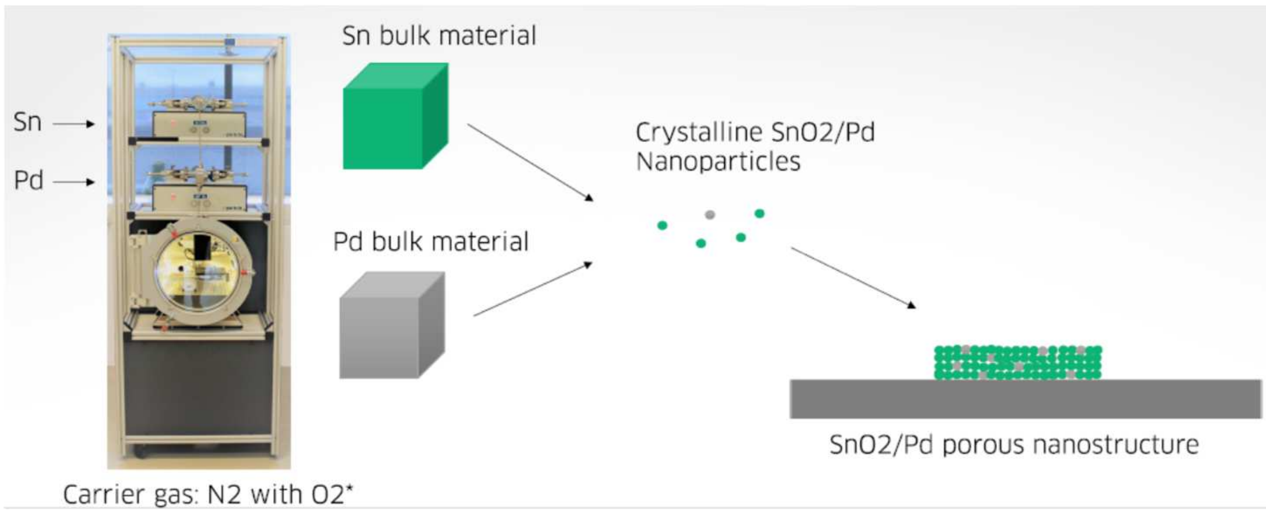
Printing of catalyst layers by impaction (VSPARTICLE)



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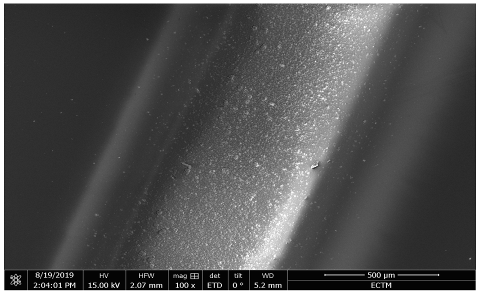
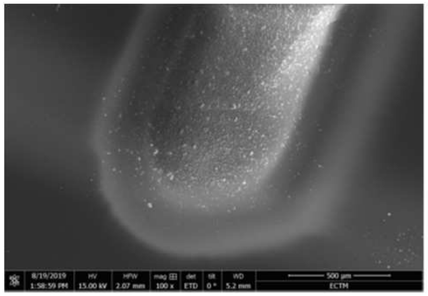
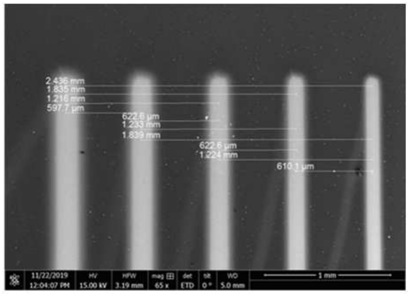
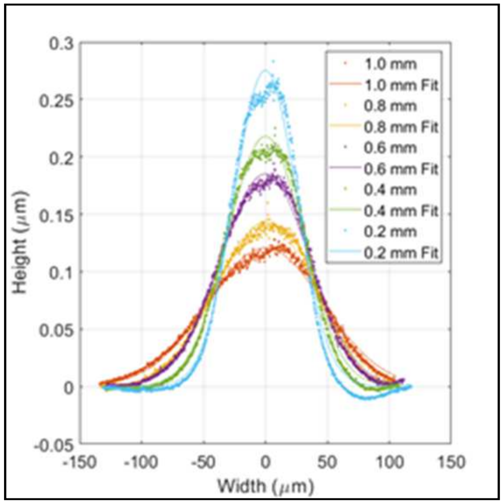
Lines of porous ZnO and Au printed with P1









ZnO

Au

<u>Void fraction ca. 30%</u>

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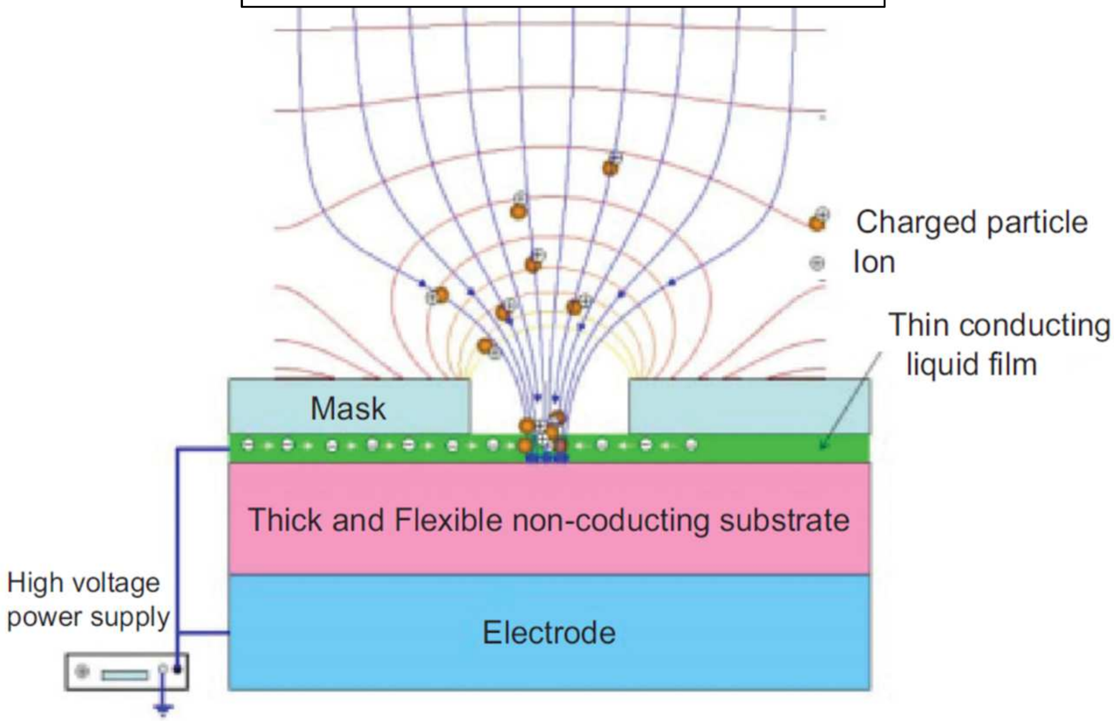
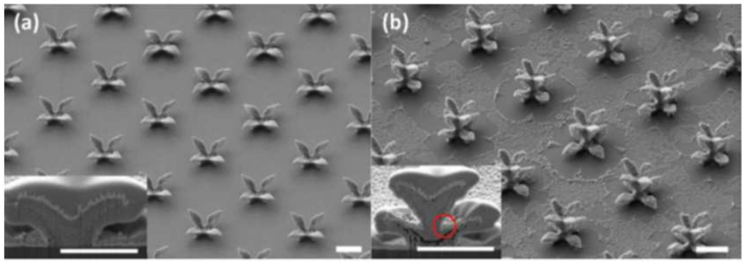
Joost van Ginkel, European Aerosol Conference, 2020

Printing Nanoparticles from Spark Ablation by Electrostatic Focussing (Mansoo Choi Group, Korea)

Electric Field Assisted Aerosol Lithography



Resolution < 1 µm



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Applications

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Application Domains as Summarized in Spark Ablation Book

Table 1.2 Application examples of particles below 20 nm in diameter

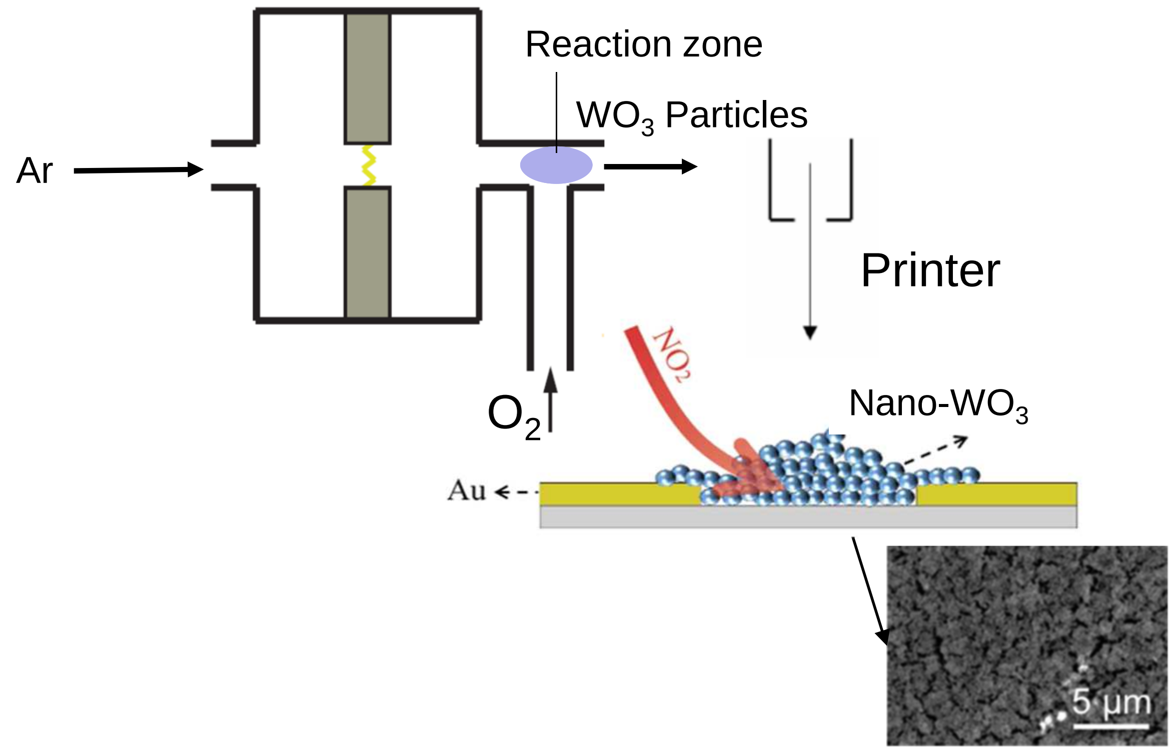
Broad application domain	Specific application examples	Relation to size effect in Table 1.1	Chapter/ Section
A1 Heterogeneous catalysis	A1.1 Improved catalyst discovery by optimizing • Size (down to atomic cluster range) • Composition (atomic scale) • Composition (nanoscale, co-catalysts) A1.2 Photocatalytic degradation of airborne contaminants A1.2.1 Preserving ancient artifacts A1.2.2 Fighting the sick building syndrome A1.3 Microfluidic catalysts A1.4 Aerosol catalysis	B1 B2.5 B2.6 B2.7 B3	2 **10** 1.4.1 1.4.3 1.4.4
A2 Solar energy conversion	A2.1 Photoelectrochemical reaction acceleration A2.1.1 Water splitting A2.1.2 CO_2 reduction (artificial leaf) A2.2 Fuel cells A2.3 Photovoltaic efficiency enhancement	B1.1 B3.3	**12** 1.4.3 1.4.7 1.4.8
A3 Chemical sensors	A3.1 Metal oxide sensors A3.1.1 E-nose A3.1.2 Humidity sensing A3.2 Inert metal sensors A3.3 Plasmonic (bio)sensors A3.4 SERS-based (bio) sensors	B1.1 B1.2 B1.4 B2.5 B2.6 B3.1 B3.2 B3.7	9 **11** **12** 13 1.4.1 1.4.2 1.4.6 8.3
A4 Low-temperature welding	A4.1 Printed circuits A4.1.1 Contact lens	B2.1	1.4.2 1.4.5
A5 Antimicrobial, antifungal, antiviral, and cytotoxic agents	A5.1 Toxicity research A5.1.1 Inhalation toxicity A5.1.2 Organ-on-a-chip A5.2 Antibacterial surfaces A5.2.1 Medical implants	B1.3	**13** 1.4.10
A6 Magnetic materials	A6.1 Magnetic cooling A6.2 Water pollution treatment A6.3 Magnetic oil filtering A6.4 Magnetic cell separation	B3.4	1.4.15
A7. Diagnostics and drug delivery	A7.1 Diagnostics A7.1.1 Lab-on-a-chip A7.1.2 Imaging A7.2 Cancer treatment A7.2.1 Hypothermia A7.2.2 Photothermal (quantum dots)	B1.3 B3.4	**13** 1.4.10.3
A8 Atomic clusters	A8.1 Self-organized particle growth A8.2 Nanodevices A8.3 New materials composed of "superatoms"	B2.1 B3.5	**7** **1.4.4.4**
A9 Energy storage	A9.1 Batteries A9.2 Supercapacitors A9.3 Hydrogen storage materials	B1.1 B1.2 B1.4	1.4.9 1.4.14
A10. Electronics	A10.1 Magnetic cooling A10.2 LED's A10.3 Conductive paths A10.4 Welding with nanopowders	B2.1 B3.2 B3.4	8 1.4.2 1.4.5
A11. Model aerosol production	A11.1 Filter testing A11.2 Measurement device calibration		**14** 1.4.13
A12. Lithography and printing	A12.1 Multimaterial printing A12.2 All-carbon electronic devices A12.3 Hybrid metal-carbon-polymer nanosystems A12.4 Soft robotics	B2.1 B3.2	2 8 **9** 1.4.2
A13 Lubricants		B2.9	8.3 1.4.11
A14 Tracers for high-speed flows		B1	1.4.12
A15 Carbon nanotube production		B2.4 B2.5	13 1.4.4.3

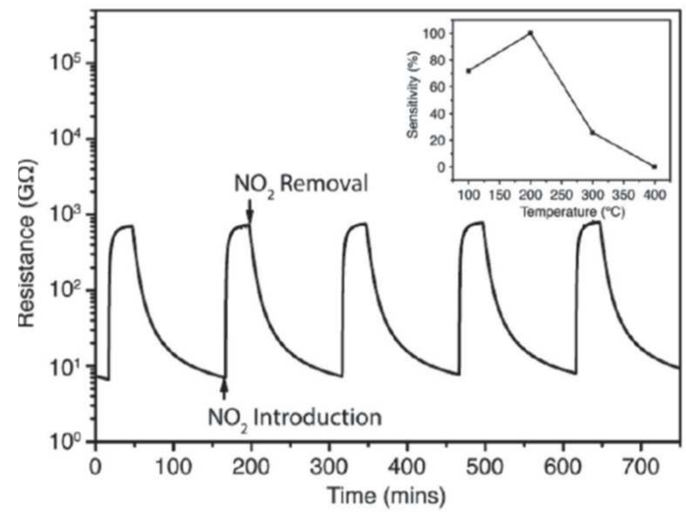
E.A.J. Rennen, Spark Ablation – Building Blocks for Nanotechnology, ed. by A.Schmidt-Ott, Jenny Stanford Publishing Co., 2020

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.

Isaac, N. A., Valenti, M., Schmidt-Ott, A. and Biskos, G. (2016). Characterization of tungsten oxide thin films produced by spark ablation for NO^2 gas sensing, *Appl. Mater.*, **8**(6), pp. 3933–3939.

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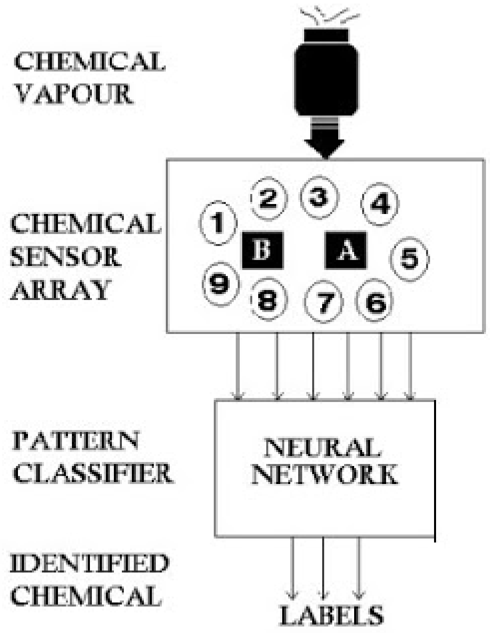
Electronic Nose



https://www.elprocus.com/electronic-nose-work/

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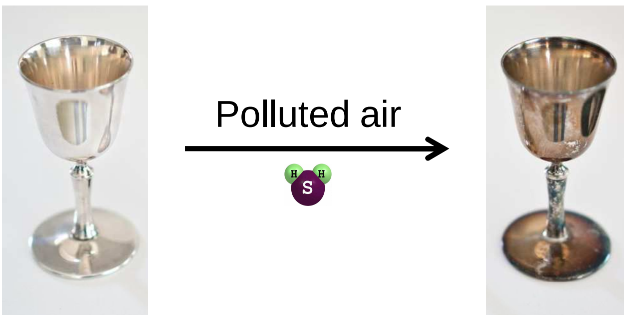
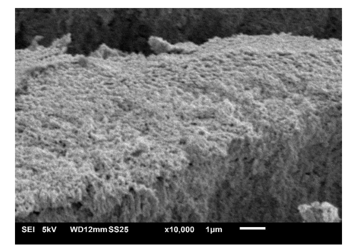
Colorimetrical Sensor to Predict Tarnishing of Objects

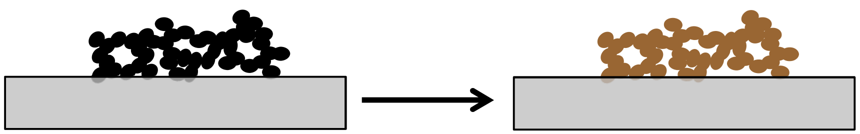
Example 3: Higher speed of chemical reactions: Tarnishing



SLOW! (takes months)

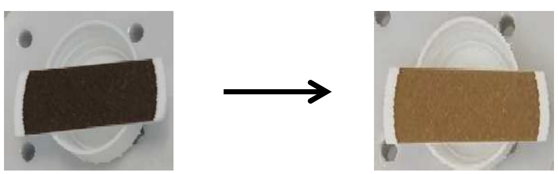
Color change indicates concentration of corroding gases in the air.





Layer of silver VSParticles

FAST! (takes minutes)



Optical signal → **Corrosiveness of ambient air**

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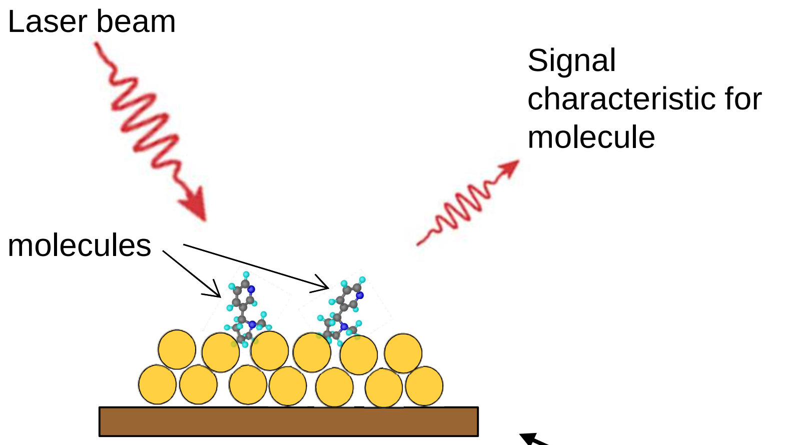
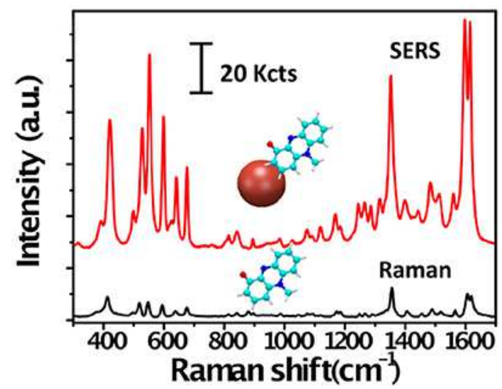
Applications:

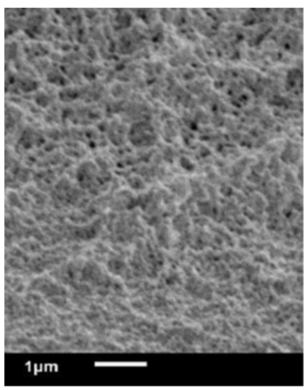
Surface Enhanced Raman Scattering (SERS)

Surface Enhanced Raman Scattering (SERS)





G. Bodelón, V. Montes-García, J. Pérez-Juste I. Pastoriza-Santos, Front. Cell. Infect. Microbiol., 11 May 2018 | https://doi.org/10.3389/fcimb.2018.00143



Pure Plasmonic particle layer with optimized

- *Composition*
- *Particle size*
- *Structure*

Specific molecules can be detected with <u>single molecule sensitivity</u>, if the laser frequency is in resonance with the plasmon frequency

Possible applications:

- Medical: Trace components in human breath
- Explosives
- Drugs
- Viruses

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Applications:

Catalysis

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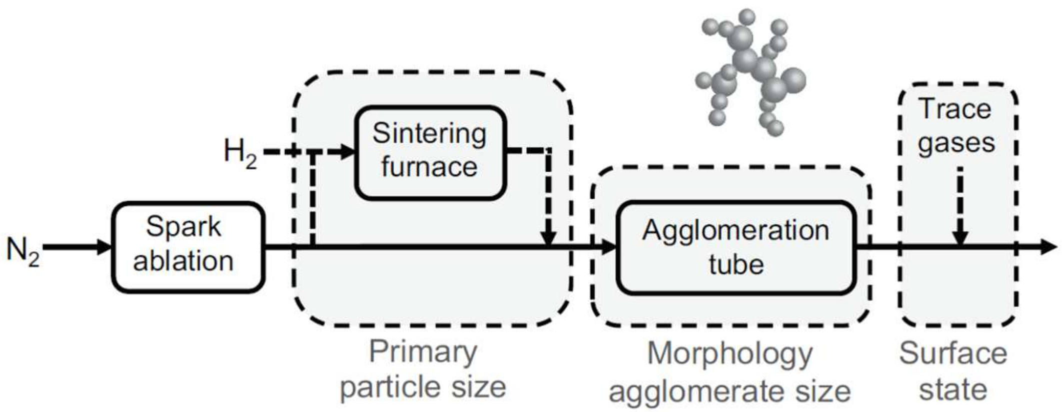
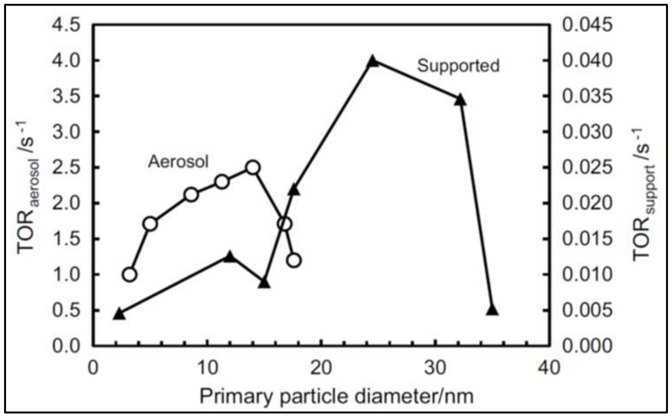
Particles from Spark Ablation for Catalysis
"Aerosol Catalysis"



Ni catalyst

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$



Alfred P. Weber in Spark Ablation: Building Blocks for Nanotechnology, A. Schmidt-Ott, Editor, 2020, Jenny Stanford Publishing

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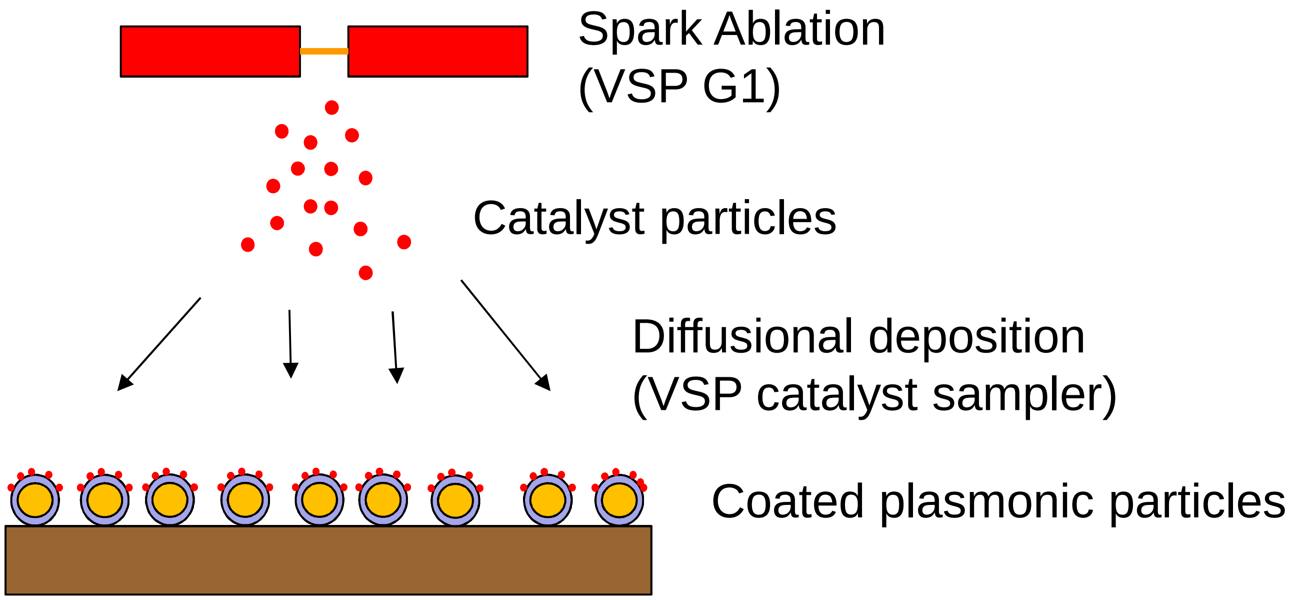
SHINERS uses SERS to test catalysts.



C.S. Wondergem, J.J.G. Kromwijk, M. Slagter, W.L. Vrijburg, E.J.M. Hensen, M. Monai, C. Vogt, B.M. Weckhuysen, *In Situ* Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy of Nickel-Catalyzed Hydrogenation Reactions, ChemPhysChem 2020, 21, 625 –632

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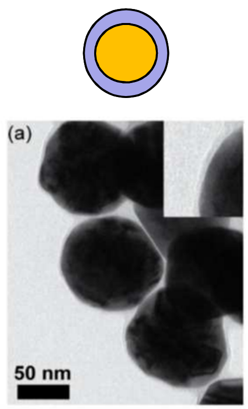
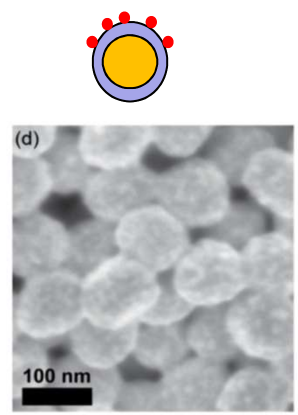
2 nm Ni particles are deposited on plasmonic particles by diffusional deposition



$Au@SiO_2$
(TEM)

Diffusional deposition of 2 nm Ni catalyst particles



$Ni/Au@SiO_2$
(SEM)

C.S. Wondergem, J.J.G. Kromwijk, M. Slagter, W.L. Vrijburg, E.J.M. Hensen, M. Monai, C. Vogt, B.M. Weckhuysen, *In Situ* Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy of Nickel-Catalyzed Hydrogenation Reactions, ChemPhysChem 2020, 21, 625 –632

Conclusions

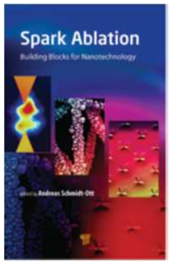
Spark ablation offers great opportunities for discovery and development of new materials. Examples have been shown for the domains of

- 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)



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