OPERATOR RISK ASSESSMENT DURING DISMOUNTING AND CLEANING OF A GAS AGGREGATION NANOCOMPOSITE DEPOSITION SOURCE

Harry Nizard[1,2], Eleonore Fröhlich[3], Carsten Kykal[4], Sigrun Klinkenberg[2], Dominic Hecker[2], Daniel Glöß[2]

1 TU Dresden, IFE, Dresden, Germany
2 Fraunhofer FEP, Dresden, Germany
3 Medizinische Universität Graz, Austria
4 TSI GmbH, Aachen, Germany

13.09.2023 Nanoworkshop Plön

© Fraunhofer FEP

Experimental setup for direct nano-particle synthesis

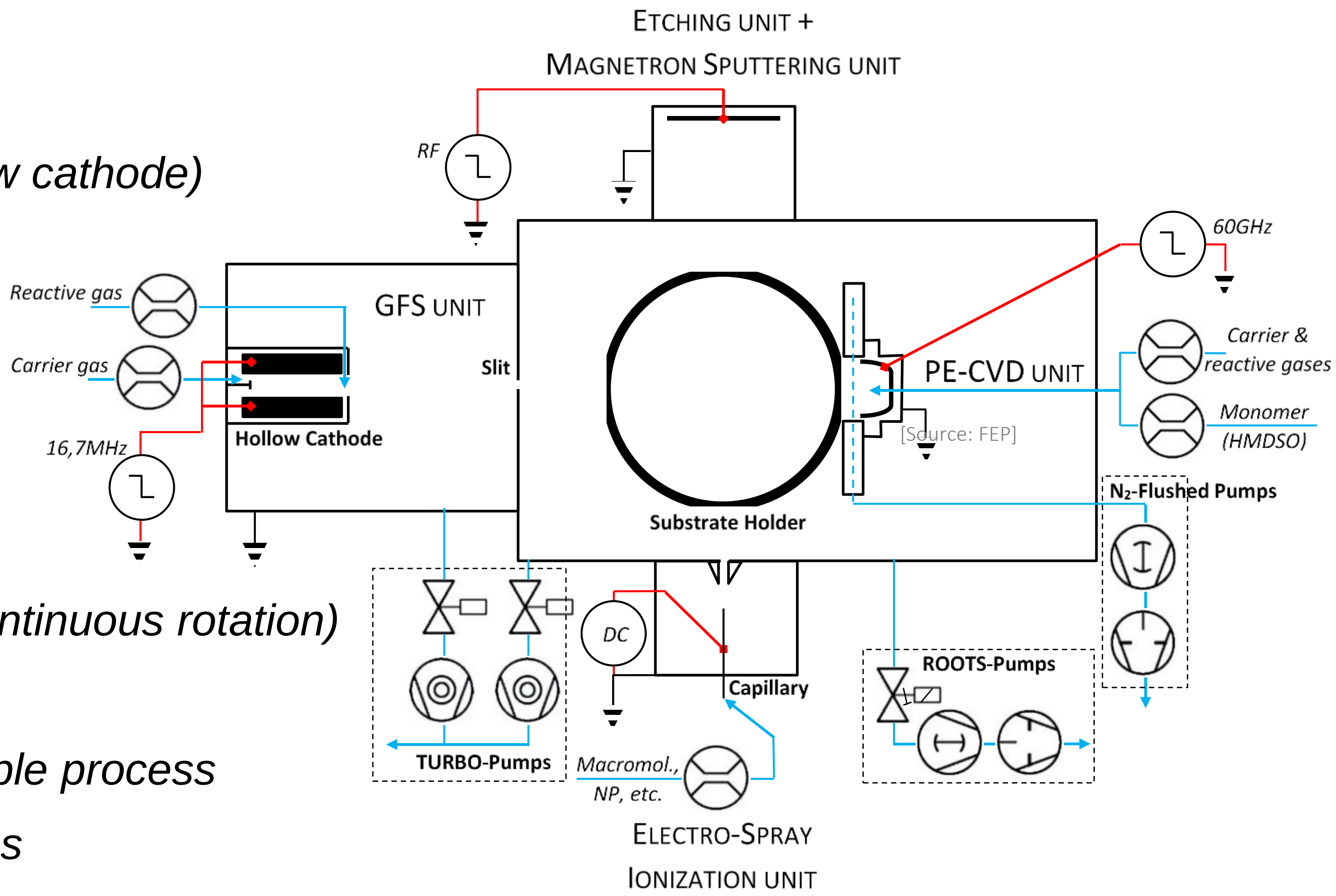
In vacuo synthesis of ultra pure nano particles for catalysis with or without matrix material

Gas aggregation setup :

- *NPs: Gas flow sputtering source (Hollow cathode)*
- *Matrix deposition: PECVD source*
- *Matrix deposition: Sputtering source*

Sample holder

- *Rotating between 4 positions*
- *4x flat Sample holders 200x100mm*
- *Or 200x1200mm flexible substrates (continuous rotation)*



Objectives:

- *Scalable, in-line and roll-to-roll compatible process*
- *Wide materials choice and morphologies*
- *contamination free, and safe-by-design*

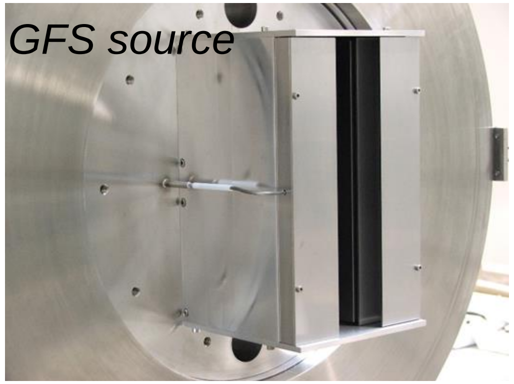
© Fraunhofer FEP

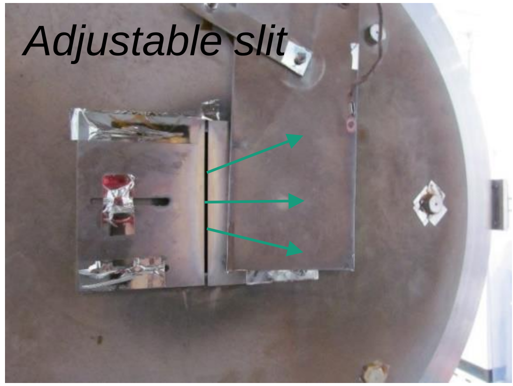
Vertraulich / Confidential

Fraunhofer FEP

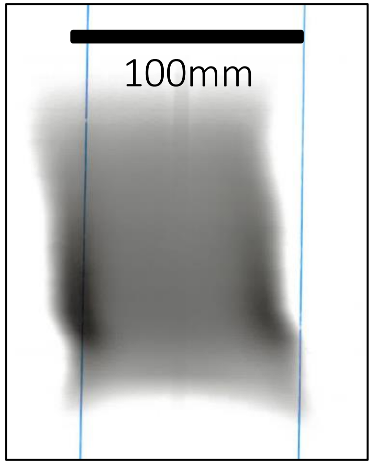
Gas Flow Sputtering source and nanoparticle synthesis

Gas Flow Sputtering (GFS): combination of a hollow cathode glow discharge and a high gas flow





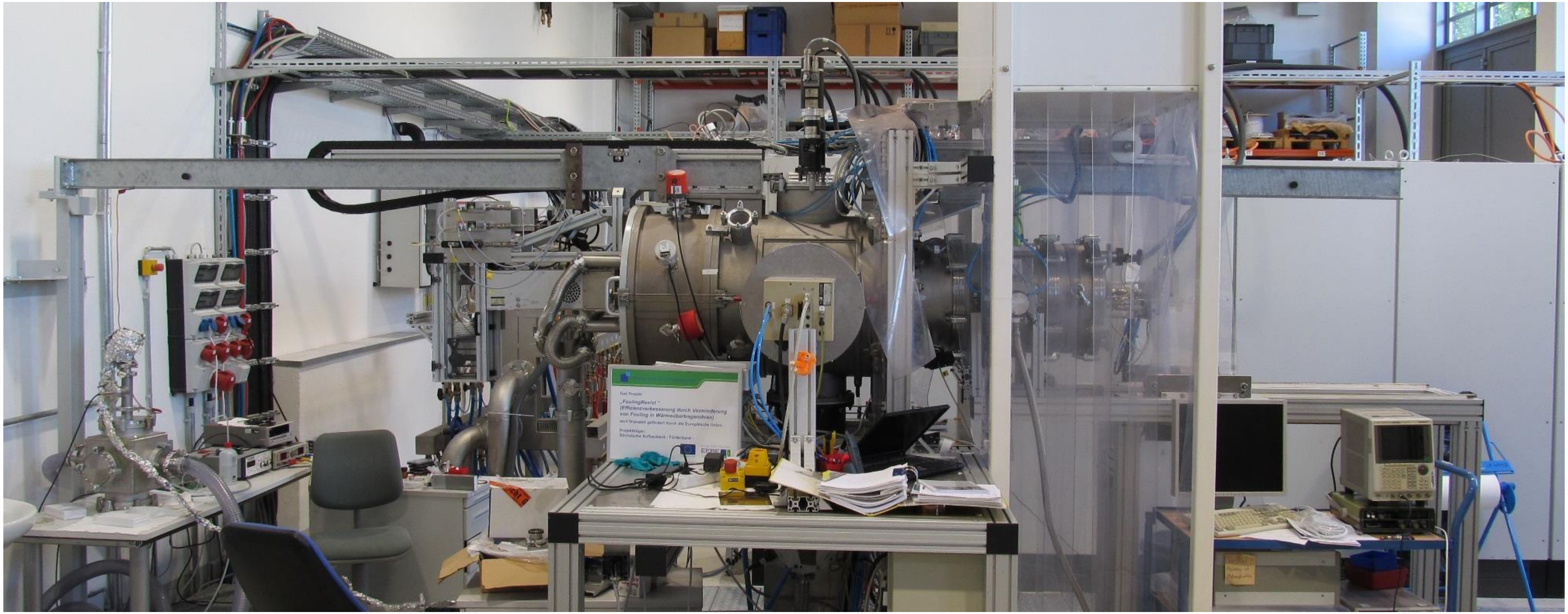
- Hollow cathode effect: High plasma density
  → high ionization efficiency and high sputter rate
- Target geometry: 250 mm x 80 mm, no magnets
  → coating of magnetic nanoparticles possible
- Low temperature process
  → coating of thermally sensitive substrates possible
- Low kinetic energy of NPs → very low damage of substrates/growing layers
- Point aperture is replaced by a 120mm adjustable slit, resulting in up to 100 x 200 mm deposition area (vs classically 10 to 20mm wide deposition area with round aperture)
- Flexible substrates can be rotated under NP plane jet resulting in up to 200 x 1300 mm deposition area



© Fraunhofer FEP

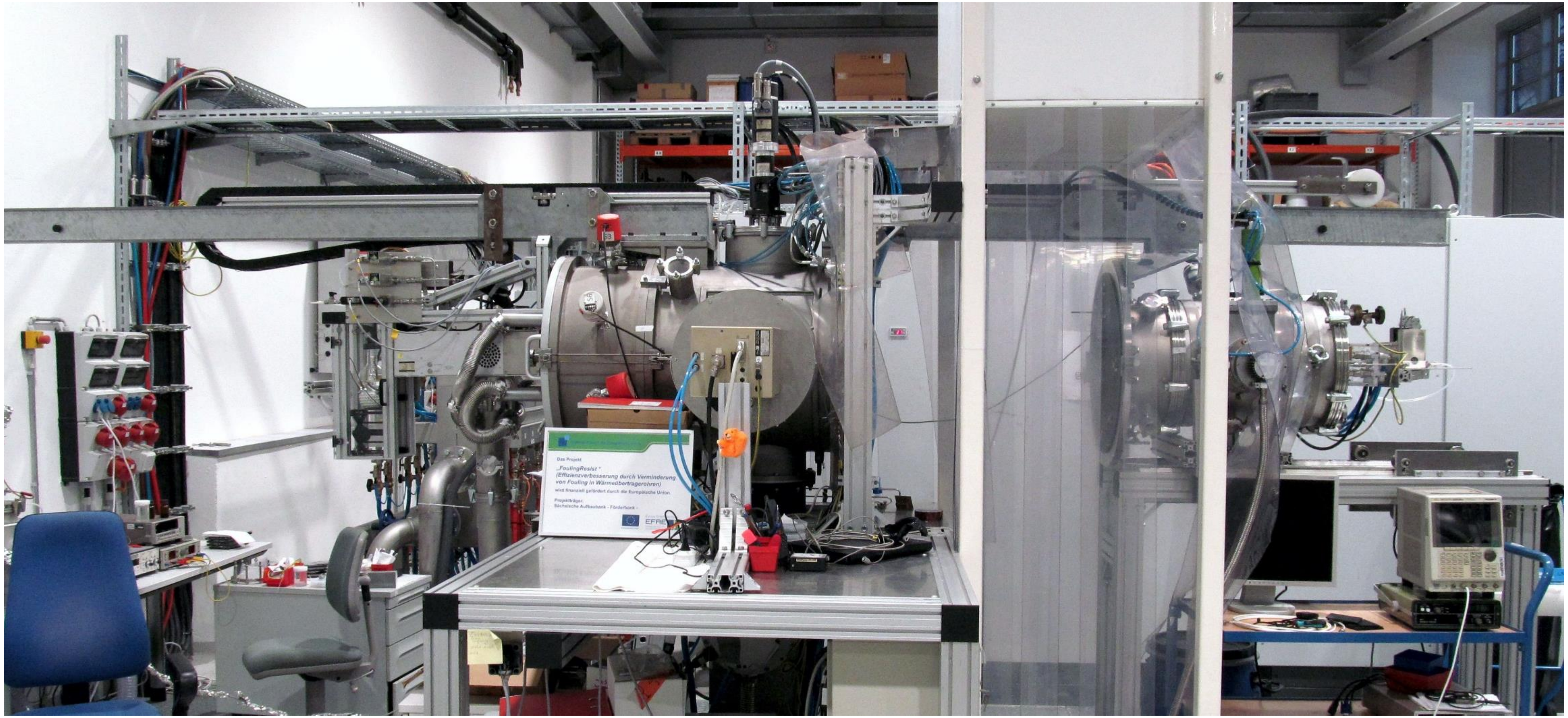
Fraunhofer FEP

Experimental setup (overview)



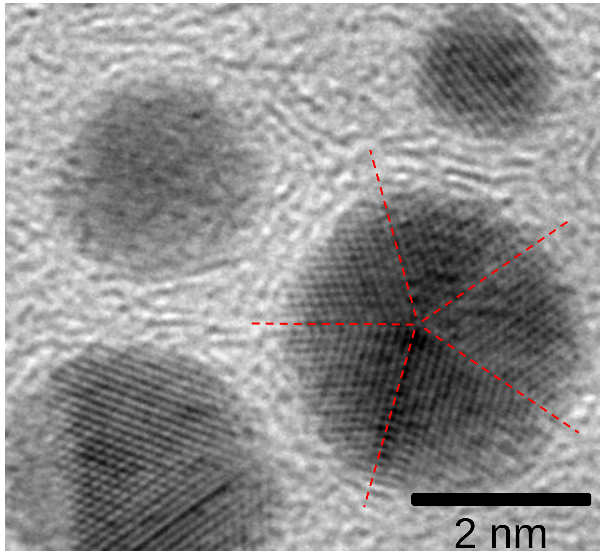
© Fraunhofer FEP

Experimental setup (open)

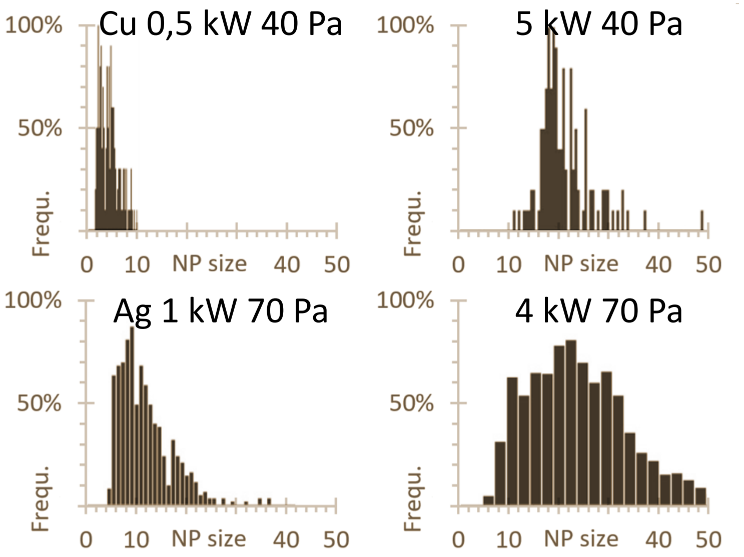


© Fraunhofer FEP

Introduction – 1: Synthesized nanoparticles



Single Ag nanoparticles (TEM image) with lattice parameter a=237 pm in (110) orientation corresponding to that of 99.999% pure silver [1]



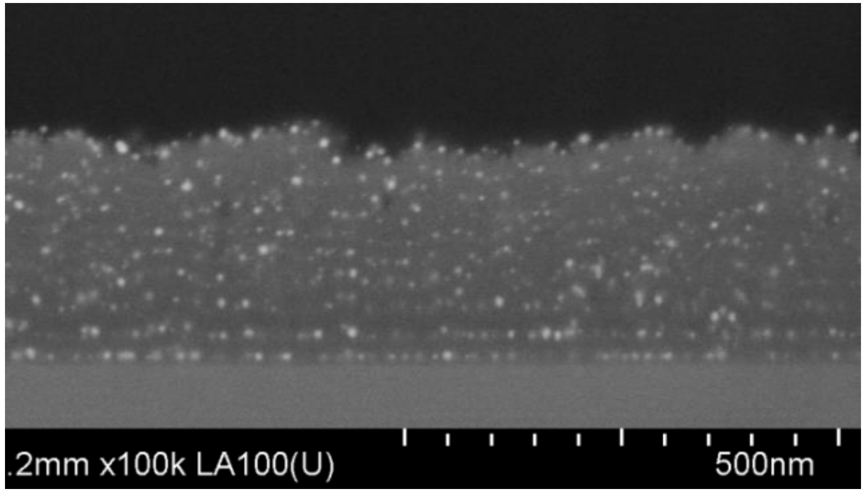
NP size distribution for Cu and Ag nanoparticles (as estimated on SEM image of layer surface)

→ Clusters and NPs are generated with sizes ranging from a few nm to 50nm.

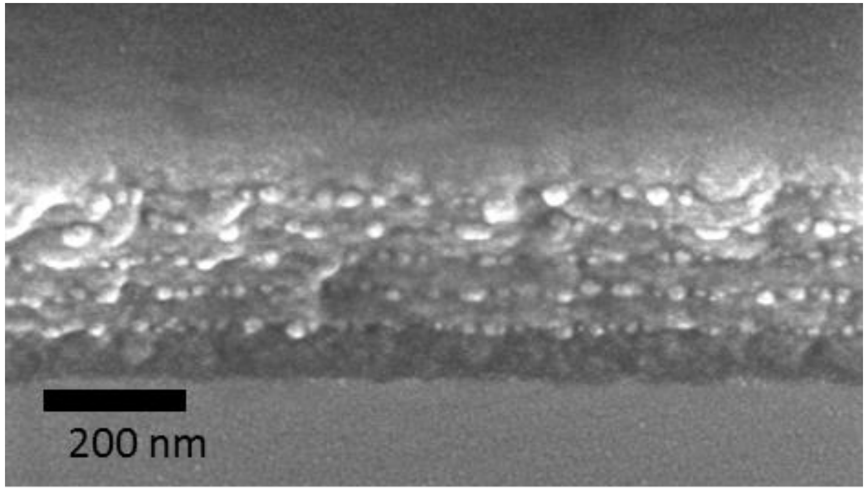
[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

Introduction – 2: Nanoparticles fixation (deposition side)



Cross-section SEM-image, multi-layer (10 x 1min) Ag NPs + SiC_xO_y (250nm).



Multilayer Nano-composite, Ag NP (15nm) & SiC_xO_y matrix. Thickness 50nm

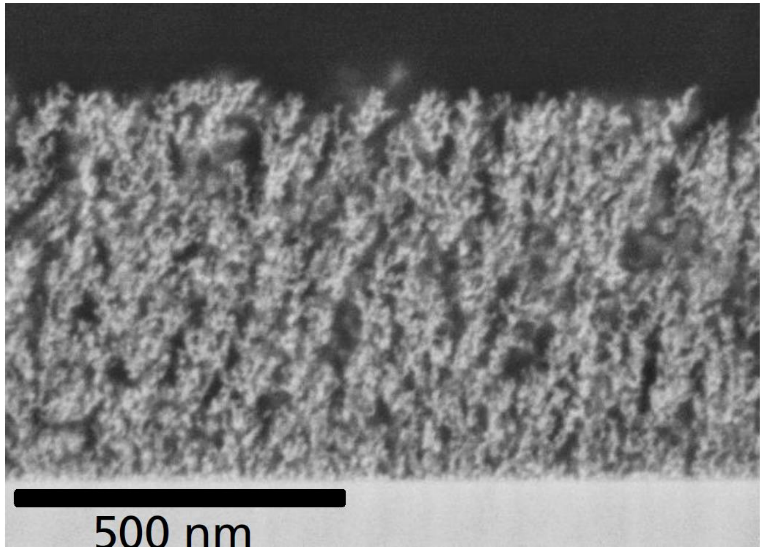
→ NPs are generally included in a solid matrix attached to substrate. Nanocomposites are obtained by alternating NPs and filler material depositions.

[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

Fraunhofer FEP

Introduction – 3: Nanoparticles fixation (aggregation side)



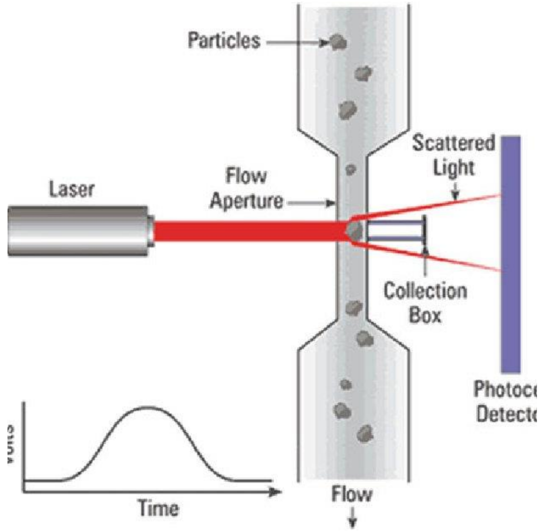
Continuous deposition of NPs results in a highly porous aggregate with low adhesion, here: Ti NP, deposition rate ≈15 nm/min (SEM cross-section)

→ NPs aggregates are produced in vacuum, carrying electric charges and tend to (weakly) adhere to surfaces thanks to electrostatic forces. As the system is put back to atmospheric pressure, they may be expected to mostly remain fixated on solid surfaces.

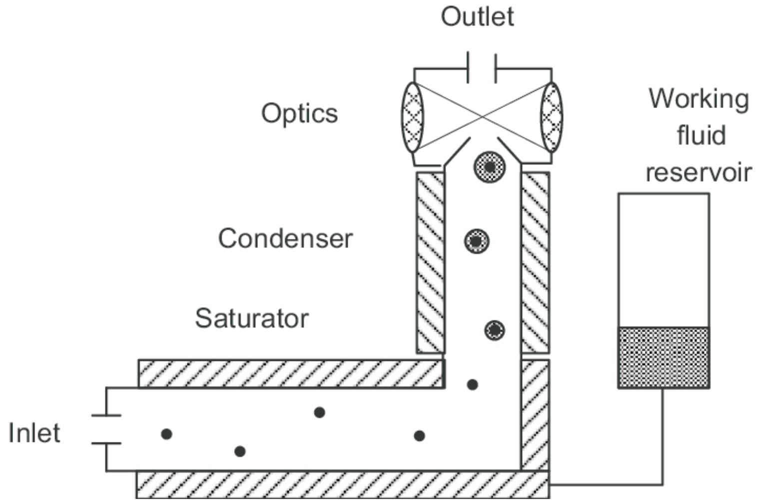
[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

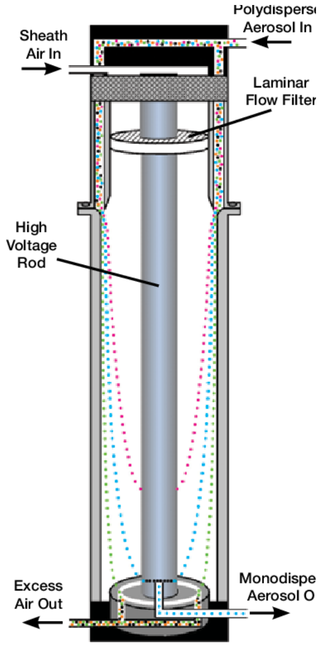
Particle concentration measures – 1: Principle



[Pollutant Diseases, Remediation and Recycling pp 1–44]



[Journal of Aerosol Science 67(Part T):48 – 86]



[Source: TSI]

Optical particle sizer (OPS):

- Particles illuminated by a thin sheath-shaped laser beam.
- Laser light scattered by particles and collected on a 120° light detector
- Pulses get counted and sized.

Detection range 300 nm – 10 µm

Condensation particle counter (CPC):

- Sample stream + alcohol vapor in heated saturator.
- Vapor reaches super-saturation into a cooled condenser.
- Particles = condensation sites.
- Alcohol droplets counted using an optical detector.

Detection range 10 nm – 3 µm.

Electrostatic classifier :

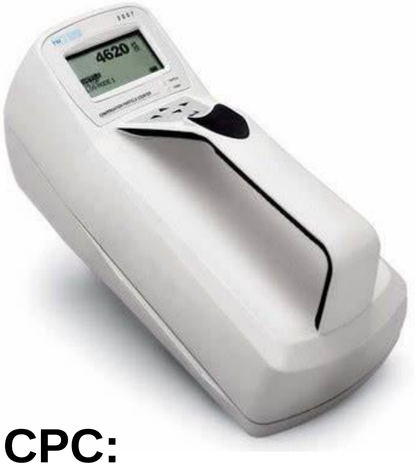
- Bipolar neutralizer gives stream a std. equilibrium charge-distribution
- Differential mobility ana-lyzer selects particles based on electrical mobility
- Filtered sample streams counted by CPCs

© Fraunhofer FEP
Fraunhofer FEP

Particle concentration measures – 2: Setups

TSI 3330 OPS:

- Optical particle sizer (OPS)
- Detection range: 300 nm – 10 µm
- Concentration range: 1.10^6 - 3.10^9 part./m^3
- Sample flow rate: 1 L/min.



TSI 3007 CPC:

- Handheld condensation particle counter (CPC)
- Detection range: 10 nm – 3 µm
- Concentration range: 1.10^6 – 1.10^9 part./m^3
- Concentration Accuracy: ±20%
- Inlet / sample flow rates: 0.7 / 0.1 L/min

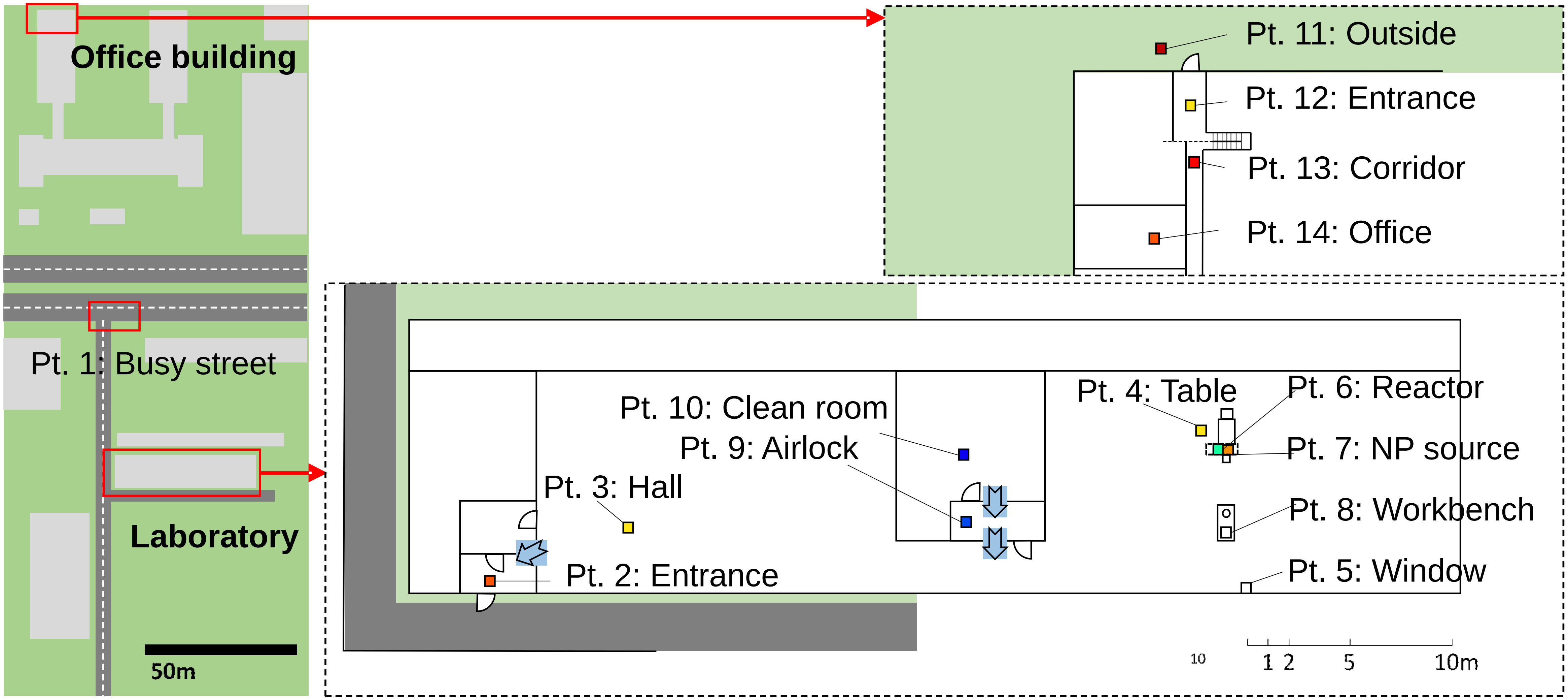
TSI 3910 Nanoscan:

- Portable particle sizer: electrostatic classifier + CPC to count the sorted particles.
- Detection range: 10 - 420 nm
- Concentration range: 1.10^8 to 1.10^{12} part./m^3
- Measurement time: 60s

[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

Particle concentration measures – 3: Sampling points

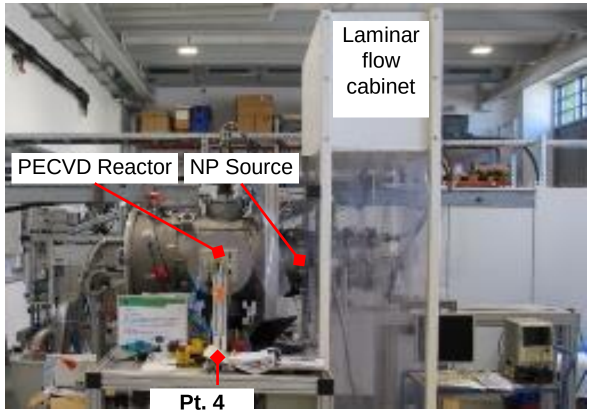


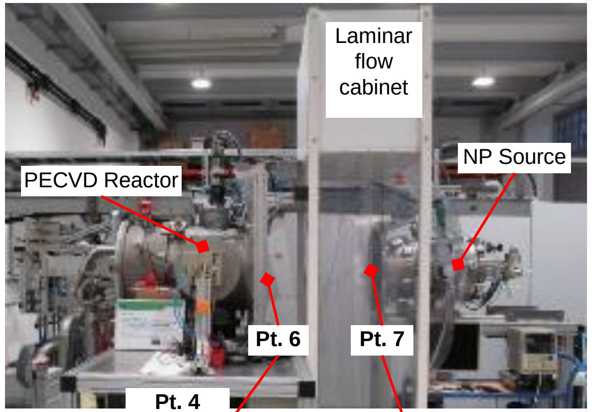
[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

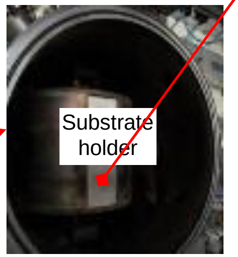
© Fraunhofer FEP

Fraunhofer FEP

Particle concentration measures – 3: Sampling points



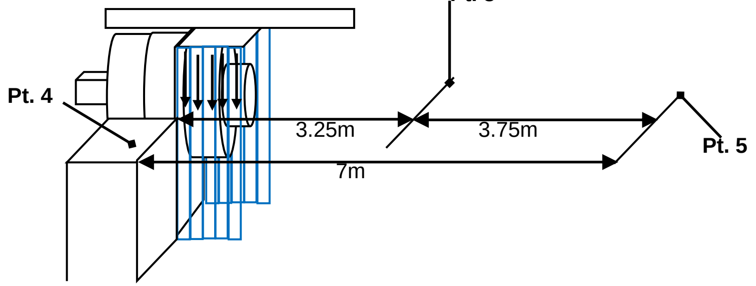




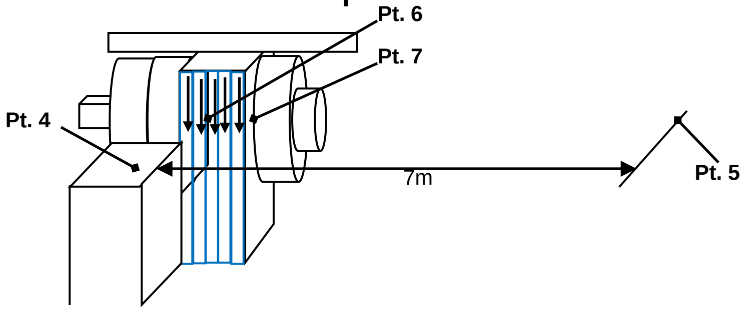
Reactor entrance

NP source entrance

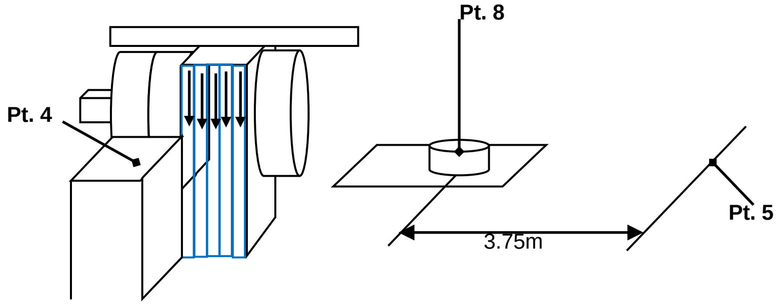
Closed Reactor



Open reactor



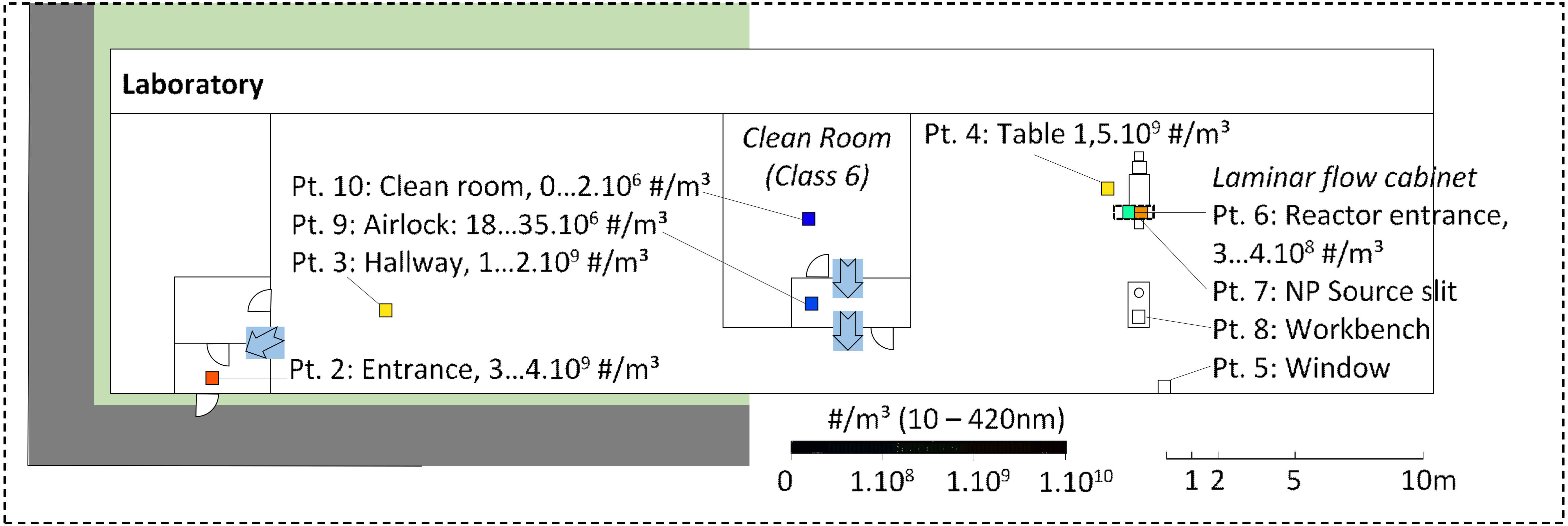
Dismounting of NP source for maintenance



[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

Results – 1: particle concentration measures in Lab



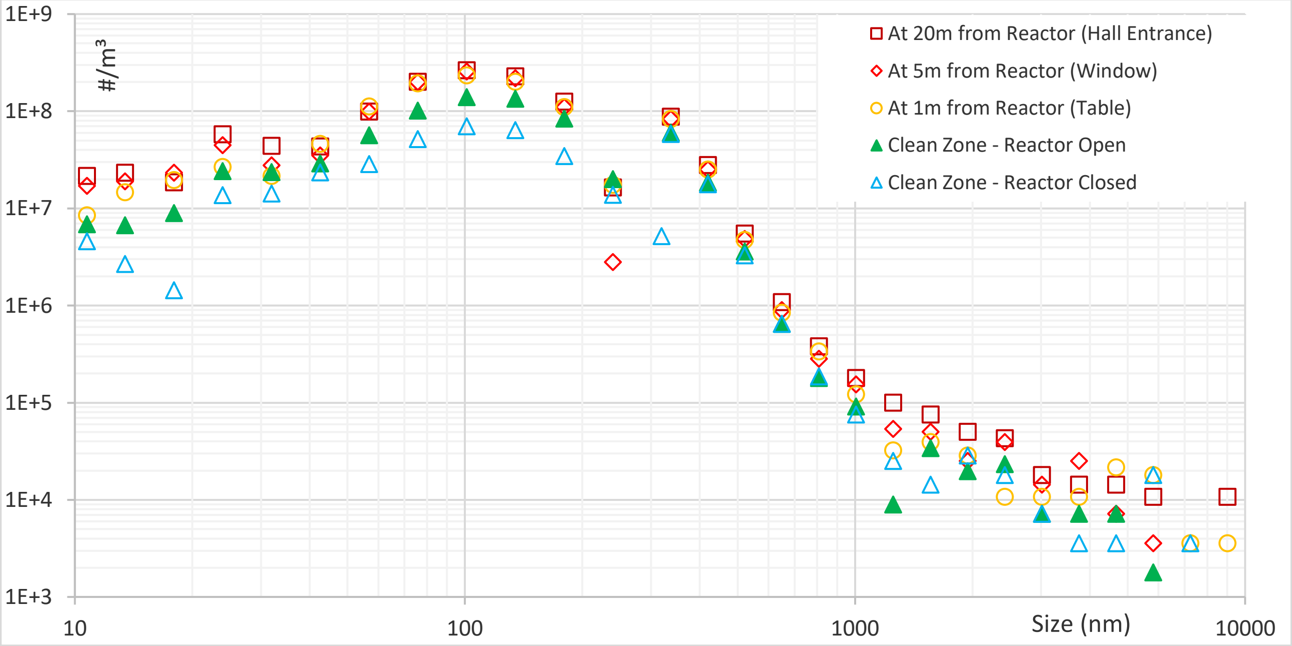
Additional measures:
Busy street Pt.4: 0,9-1,3.10^{10} #/m³
Outside office building Pt. 11: 7-8.10^{9} #/m³
Office building Pts 12-14: 1-6.10^{9} #/m³

→ Particle count in laboratory particularly low due to the neighboring clean room, which circulates the air of the whole laboratory through particle filters.

[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196
© Fraunhofer FEP

Results – 2: Measures near reactor

Table 1: Particle counts obtained at various points.		
Device	3330 + 3910	3007
(Size range)	(10 nm – 10 µm)	(10 - 3 µm)
Pt. 3 (hallway, 30m from reactor)	$1{,}27.10^9$ #/m³	$1\ldots2.10^9$ #/m³
Pt.4 (table, 1m from reactor)	$1{,}12.10^9$ #/m³	$1{,}5.10^9$ #/m³
Pt.5 (window, 7m from reactor)	$1{,}17.10^9$ #/m³	
Pt.6 (reactor closed)	$4{,}09.10^8$ #/m³	$3\ldots4.10^8$ #/m³
Pt.6 (reactor open)	$7{,}22.10^8$ #/m³	5.10^8 #/m³



→ An increase of particle counts from 4,09 to $7{,}22.10^8$ #/m³ is observed in the immediate surrounding, when the reactor is opened.

At least part of this increase is due to external air ($1{,}1\ldots1{,}2.10^9$ #/m³) leaking in.

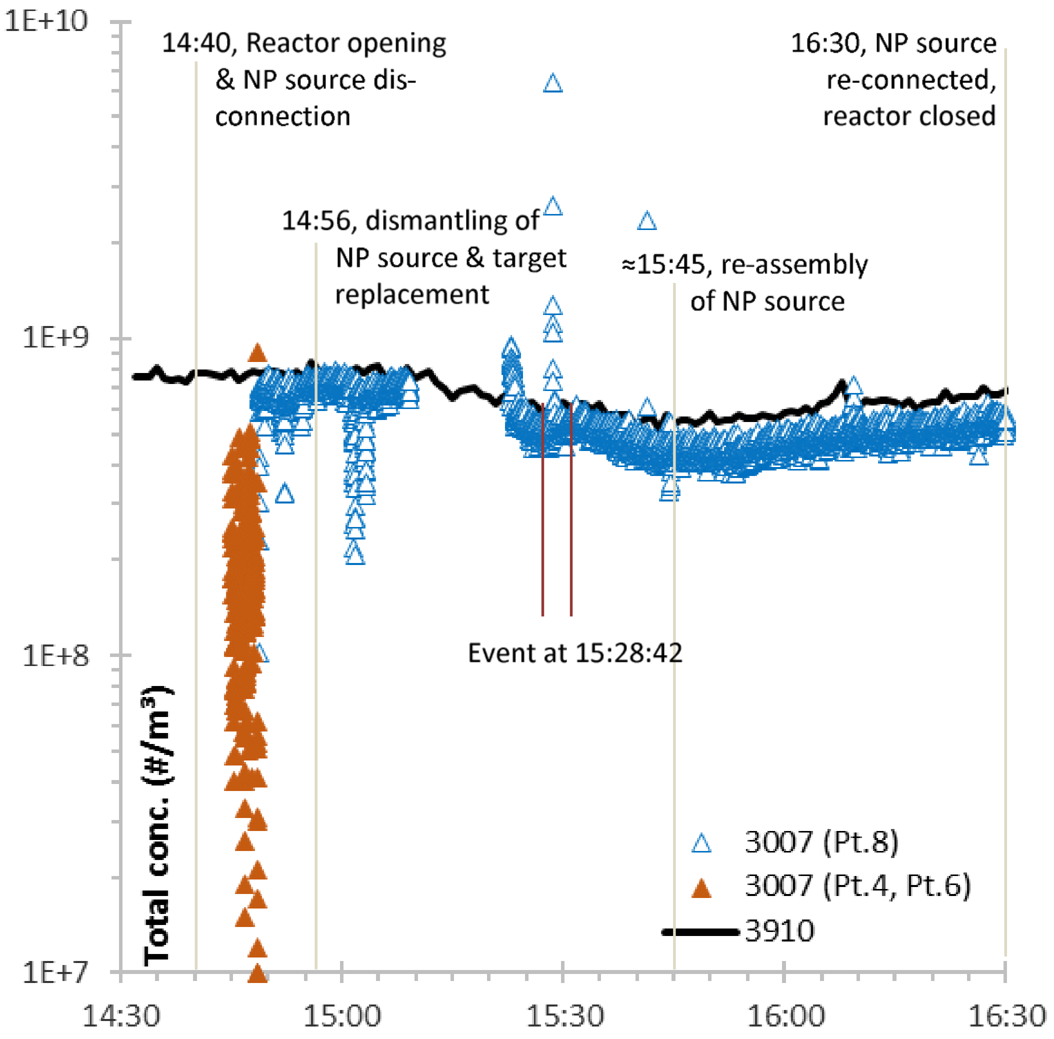
This is confirmed by the particle size distributions for Pt. 6 (laminar flow cabinet near the Nanoparticle source), which do not differ significantly from Pt. 3 (hallway, 30m from reactor) Pt.4 (table, 1m from reactor) and Pt.5 (window, 7m from reactor).

Particle size distributions collected in (□) Pt.3, (◊) Pt.5, (○) Pt.4, (▲) Pt.6 reactor open, and (△) Pt.6 reactor closed.

[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

Results – 3: Measures during maintenance operations



In typical maintenance operation, operators disconnected NP gas aggregation source, dismounted it and changed targets on the workbench. Particle count was acquired at Window (Pt.5, 3.75 m away, solid line) and from the handheld 3007 moved in and out laminar flow cabinet (Pt.4 and 6, ▲) and workbench (Pt. 8, △)

→ *Results confirm a ≈ factor 10 reduction in NP count between laboratory hallway (Pts. 3, 4, 5, 8) and laminar flow cabinet (Pt. 6)*

→ *No general increase of the airborne NP count is observed during the operation (6 to 8.10^8 #/m³)*

→ *Handheld 3007 continually sampled <1 cm away from dismounted parts, with mostly stable NP count*

→ *In 3 occurrences, sampling tube had direct contact (<1 mm away) with powder residues. Peak events were observed with up to 8.10^9 #/m³.*

[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

Operator Risk Assessment – 1: Mask efficiency

(a)

(b)

(c)

Permeability K and Absorption rate A were evaluated over the nanoparticle size range:

$A = 1 - K$ and $K = \frac{P_f}{P_m}$, with

P_f filtered particle concentration (2x2min measurements for each mask), and

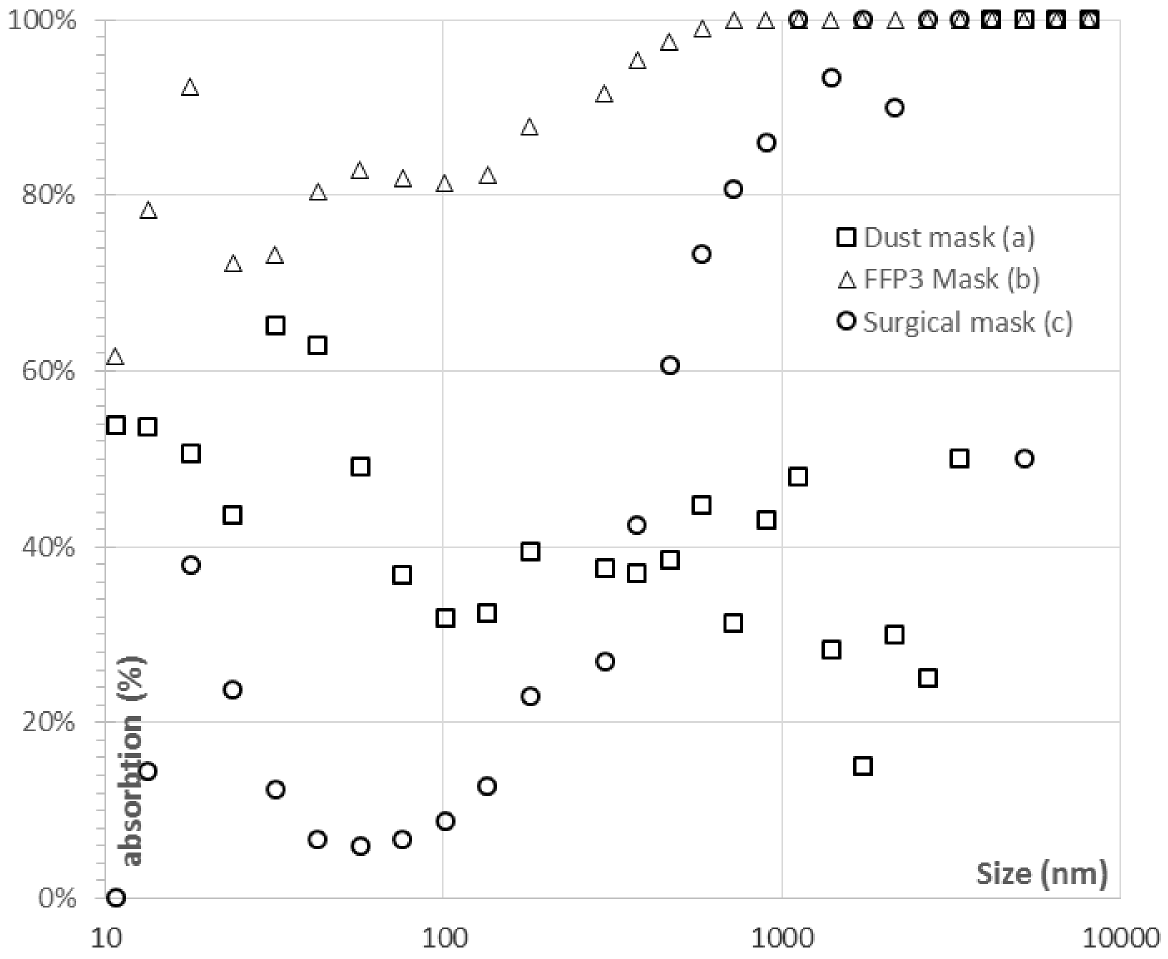
P_m non-filtered particle concentration (average of 6 measurements).

Absorption rate was evaluated for reusable dust mask respirator (□, a), FFP3-rated face mask (△, b) and surgical mask (○, c) as functions of nanoparticle size., average of 6 measurements for the non-filtered particle concentration.

[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

Operator Risk Assessment – 1: Mask efficiency



→ FFP3-rated masks appear to be the best recommendation for the operator protection with permeability of 20% is observed in the 10…100nm range

→ conservative estimation: 40% exposure at lower end of particle size range

→ estimated exposure of operator to NP:

$$P_{Op.} = K \cdot P_T \approx 0.4 * 2.5 \cdot P_m \approx \cdot P_m$$

[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

Fraunhofer FEP

Operator Risk Assessment – 2: Total particle count

Increase particle count:

- **1.10^8 #/m³** (10 nm – 420 nm) at open reactor,
- very localized peaks up to 8.10^9 #/m³.

In experimental conditions 96% to 44% of particles have measurable sizes > 10 nm.

Total particle count P_T corrected using $P_T = (1 + R).P_m \approx 2.5 \cdot P_m$: up to **$0{,}75.10^9$ #/m³**

Using averaged nanoparticle unit weight and normal breathing (24,1 L/min) operators exposure rates of 7.10^6 #/min or **2.10^{-2} µg/min** in the normal conditions can be estimated.

By comparison:

- measured exposure in a busy street translates into a **8.10^8 #/min** exposure (**x100**).
- Workplace peak concentrations of 1.35 µg/m³ (**x1,4**) and 5 to 289 µg/m³ (**x5** to **x289**) have been measured in consumer products and silver manufacturing [J.H. Lee et al., Nanotoxicology **6**:6 (2012) pp.667-9]

[1] W.P. Davey, Phys. Rev. 25 (1925) p. 753; [2] Marks & Howie, Nature 282 (1979) p. 196

© Fraunhofer FEP

Fraunhofer FEP

CONCLUSIONS

This work establishes a NP exposure in the range of 0.5 to 2 µg/m^3 in normal conditions

Results present the relative safety of GFS deposition process for the operators during normal operation, as well as maintenance

Maximal daily exposure for workers on the described setup should be set as follows:

- Normal use (under laminar flow box, with FFP3 mask): not over 1H 36 min next to the open reactor. Usual operation of the reactor requires opening for 5 to 15 minutes for each experiment. This would lead to a lung deposition dose (LDD) of 0.616 µg in this situation.

- Accidental “sniffing” accidents during the maintenance of the dismounted NP source must not exceed 3min and 40sec in order to avoid reaching the INEL threshold, and should be prevented by FFP3 masks and by operational procedure ensuring >10cm to NP source during maintenance. This would lead to a LDD of 0.462 µg per accident.

K. Aschberger et al., Environ Int **37** (2011) pp. 1143–1156. doi : 10.1016/j.envint.2011.02.005

© Fraunhofer FEP

Vertraulich / Confidential

Thank you very much for your attention!

Acknowledgements:

Project FlexFunction2Sustain
www.flexfunction2sustain.eu
(DT-NMBP-03-2019, Nr. 862156)

Project Nano-LAPS
(MSCA-IF-2014, Nr. 655628).

Contact:

Dr. Harry Nizard

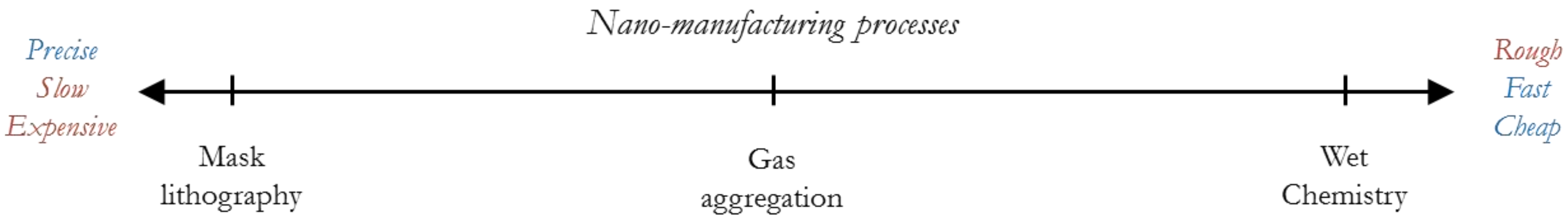
PrecisionLab - Fraunhofer FEP

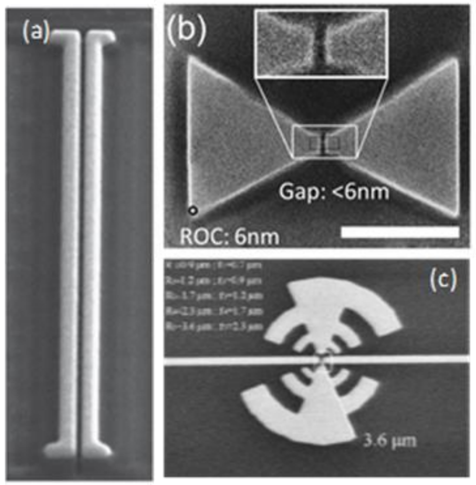
Harry.Nizard@fep.fraunhofer.de

© Fraunhofer FEP

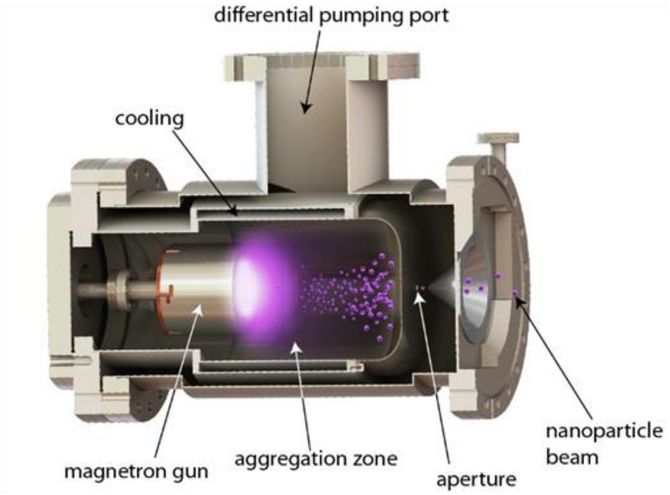
Fraunhofer FEP

Motivation – Nano-manufacturing Processes

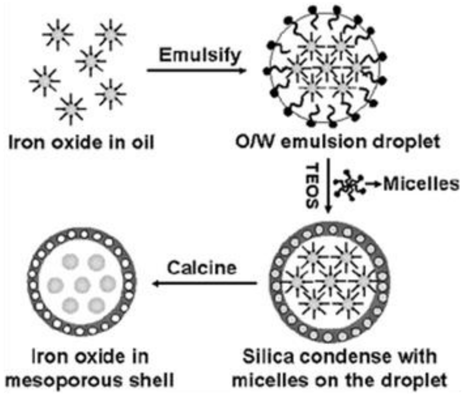




[Source: Nano Letters **14**:8 (2014) p. 4778]



[Source: Mantis]



[Source: J. Mater. Chem. **19** (2009) p.1811]

Mask lithography

⊕ Control of NP Shape & position
⊕ Std. µ-electronic Process Equipment
⊕ Well-known technology
⊖ Small deposition aera
⊖ Slow, expensive & complex (numerous steps)

Gas aggregation

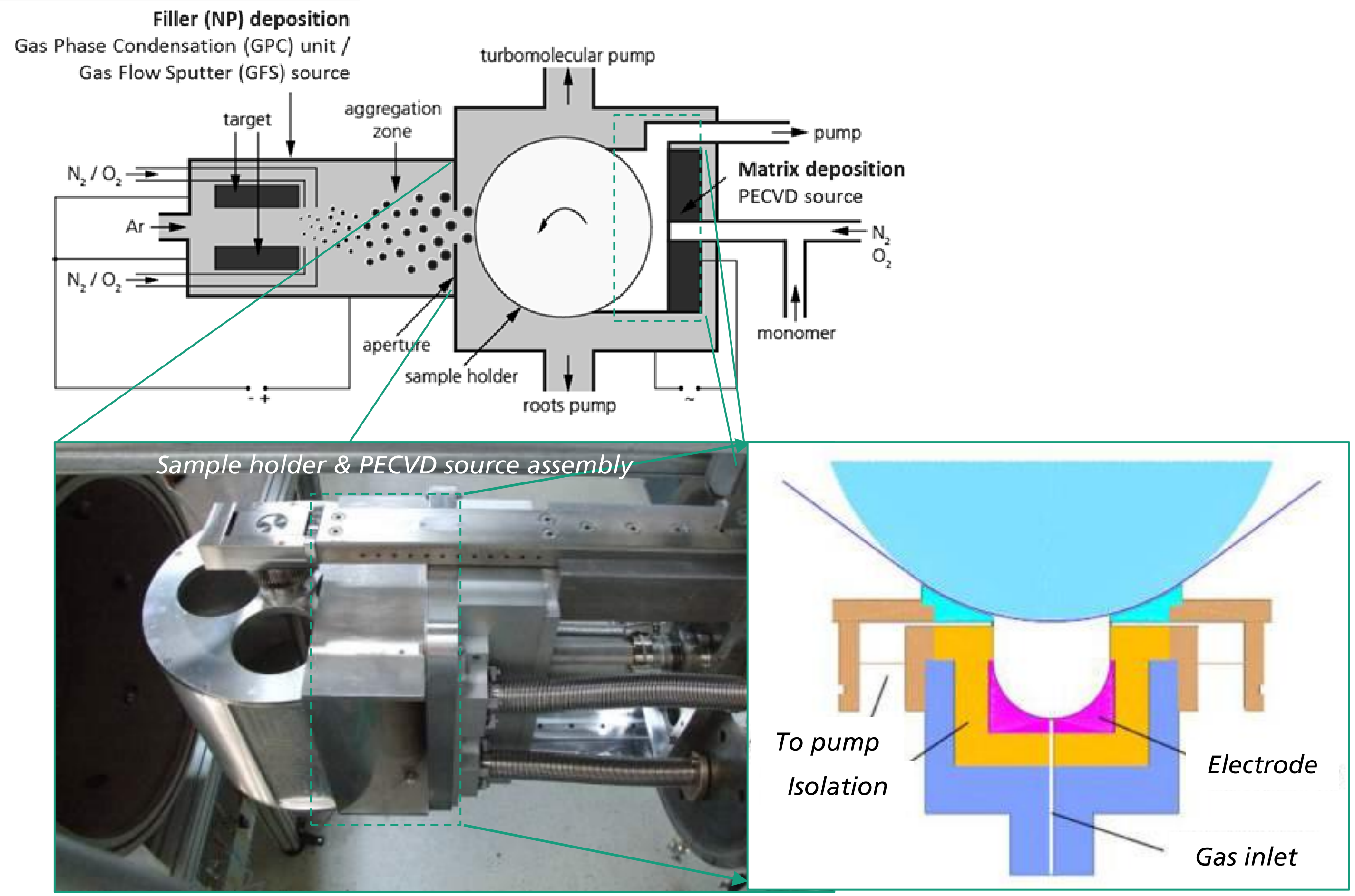
⊕ µ-electronic Process Equipment
⊕ Large deposition area
⊕ Cheap & Fast
⊕ High purity – Oxidation free
⊖ Random NP position
⊖ Newer technology

Wet Chemistry

⊕ Cheap & simple
⊕ Large deposition area
⊖ Random NP position
⊖ Impurities (surfactants, emulsifiers, catalysts, etc.) & oxidation
⊖ Complex interfacing with µ-electronic equipment

© Fraunhofer FEP
Vertraulich / Confidential
Fraunhofer FEP

PECVD Plasma Polymerization

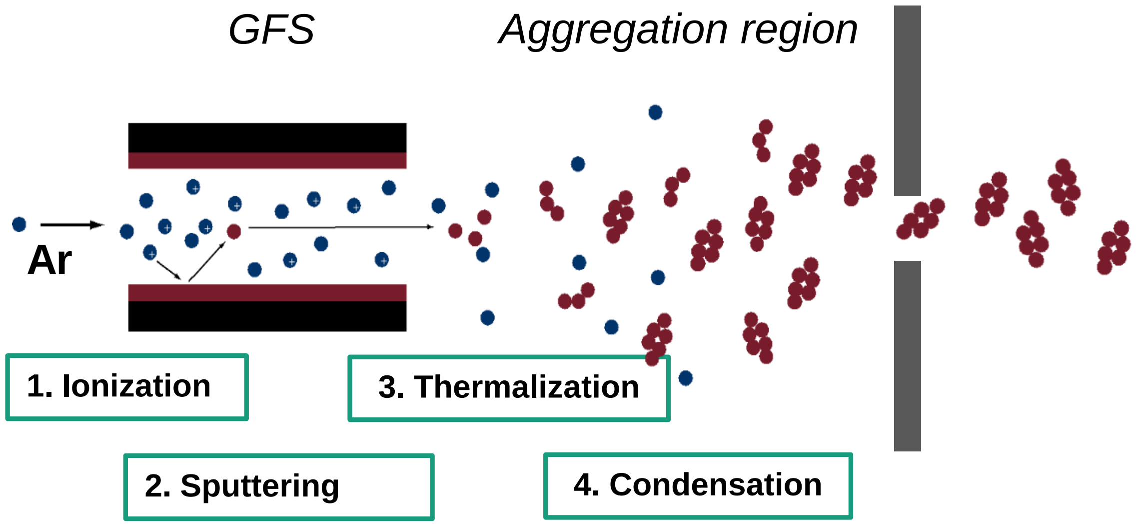


- Matrix source (PECVD):
  - Coating area 340x100mm
  - Working pressure 1...15 Pa
  - Process gase Ar, N_2, O_2, Precursors
  - Typicaly: amorphous SiO_x (1.4<x<1.9)
  - Deposited monomers: HMDSO, Isopren, Styrol, MMA, NFH, HFB
- RF Linear source (capacity coupled):
  - Excitation frequency: 60 MHz (VHF)
    → high degree of ionization
    → high deposition rate
  - $T^e \sim 5…10$eV, $n^e \sim 10^{11}$ /cm³
  - Coating rate ~5...200 nm/min

© Fraunhofer FEP

Gas Flow Sputtering source and nanoparticle synthesis

Gas Flow Sputtering (GFS): combination of a hollow cathode glow discharge and a high gas flow



- Process parameters:
  - Base vacuum: 5×10^{-6} mbar
  - Up to 3slm gas flow
  - High process pressure (10-100 Pa)
  - DC power supply: Typ. 2 kW, max. 10 kW
    Pulsed DC operation at 1…50 kHz
    $T_e \sim 2$ eV, $n_e \sim 10^{11} \ldots 10^{12}$ /cm³
  - NP Deposition rate 15…60 nm/min (~10mg/hour)
  - Reactive sputtering by reactive gas introduction
- Particle size can be adjusted by the gas flow and the discharge power

© Fraunhofer FEP

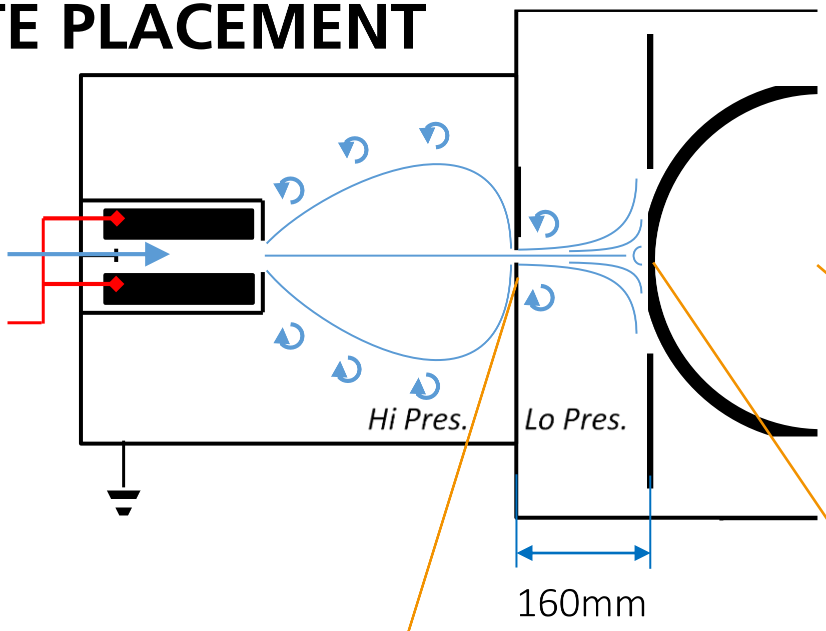
Fraunhofer FEP

NP target materials available at FEP and potential applications

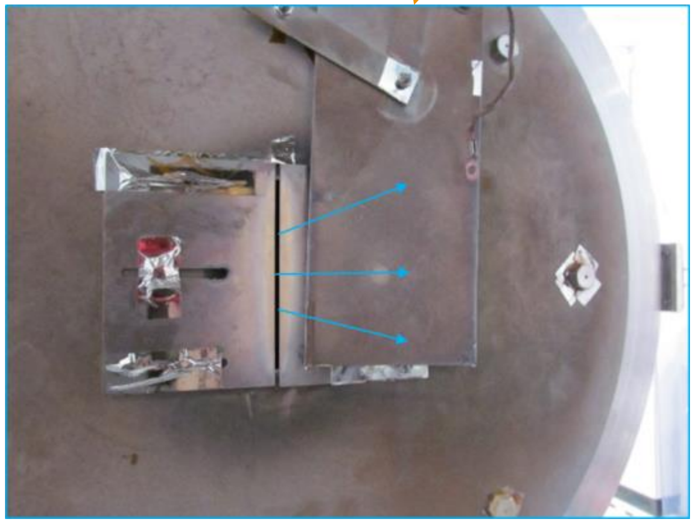
Metal	Applications (**investigated** / not investigated at FEP so far)
Ag	**Plasmonics for e.g. color filters (decorative applications), antibacterial applications,** photosensitive, security applications with TiO_2
Cu	Plasmonics for e.g. color filters (decorative applications), **Reinforcement in carbon-fiber reinforced composites**
Au	**Plasmonics for e.g. color filters (decorative applications),** Plasmonic-applications, no oxidations barrier required
Pt	**Charge separation for improved photocatalytic efficiency of TiO_2**
V	Thermochromic and electrochromic applications, antibacterial applications
W	Doping of thermochromic V-oxides, electrodes, catalysis, antibacterial applications
Mg	Antifouling, antibacterial applications
Ti	Photocatalysis (TiO_2-NP)
Te	Semiconductor properties, X-Ray absorber, electrocatalysis
ITO	IR-Plasmonics, Transparent conductive oxides
Sn	Transparent conductive oxides, antibacterial applications, photodetectors

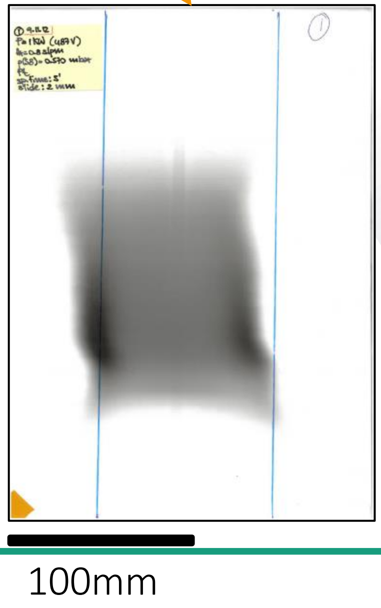
© Fraunhofer FEP
Fraunhofer FEP

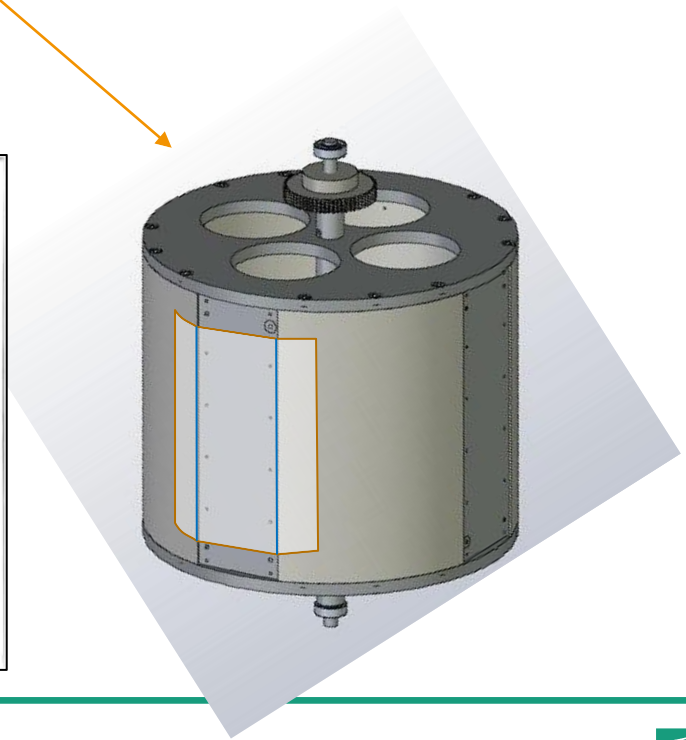
SUBSTRATE PLACEMENT



In order to display the deposition area, nano-particles are deposited on A4 paper sheets. Paper is attached on the substrate holder. After deposition, the NP-coated paper are sealed in plastic envelope and scanned. The 2 blue lines show the limits of the flat deposition area



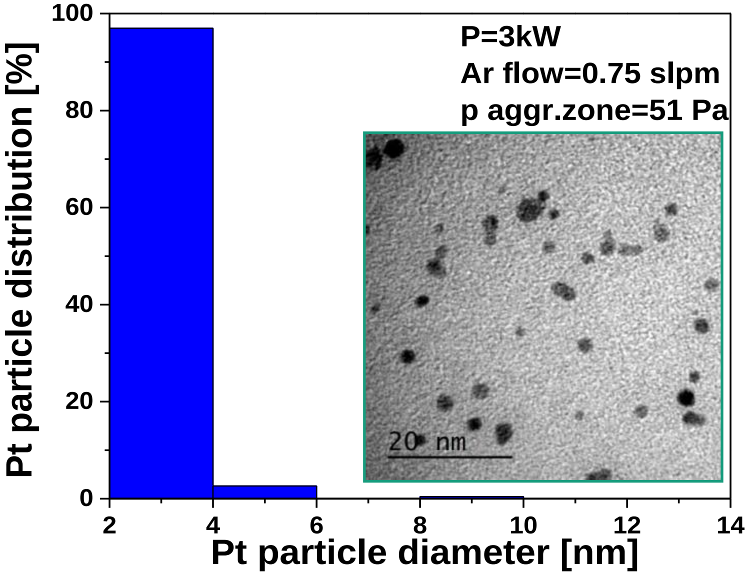




© Fraunhofer FEP

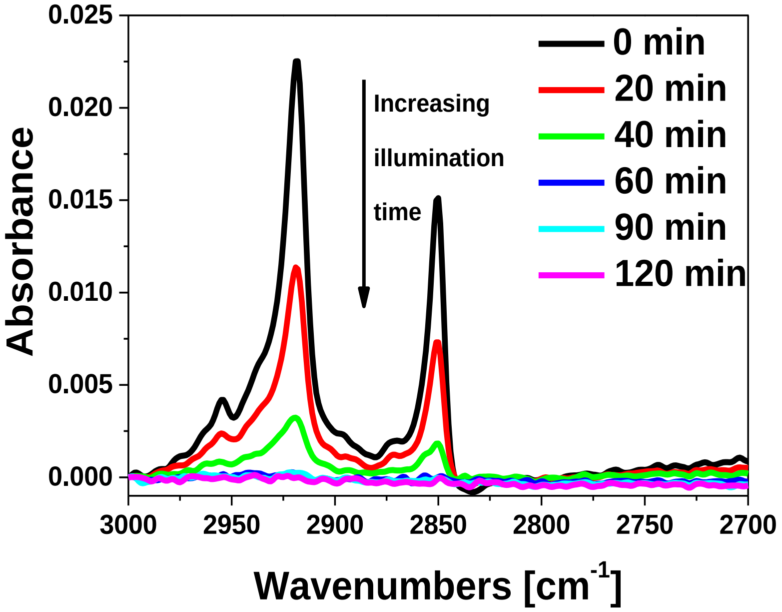
Fraunhofer FEP

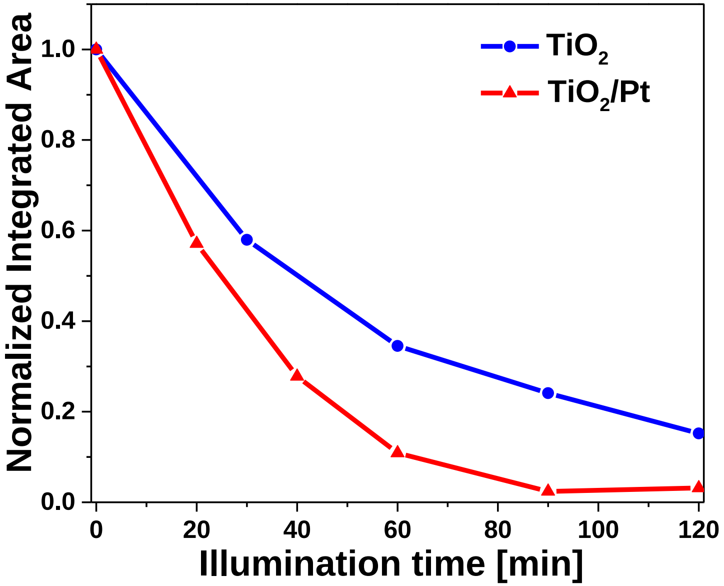
Example: Improved photocatalytic activity with nanoparticle top layer



Pt NPs with narrow size and size distribution can be deposited by Gas Flow Sputtering

Stearic acid decomposition on Pt/TiO_2 layers





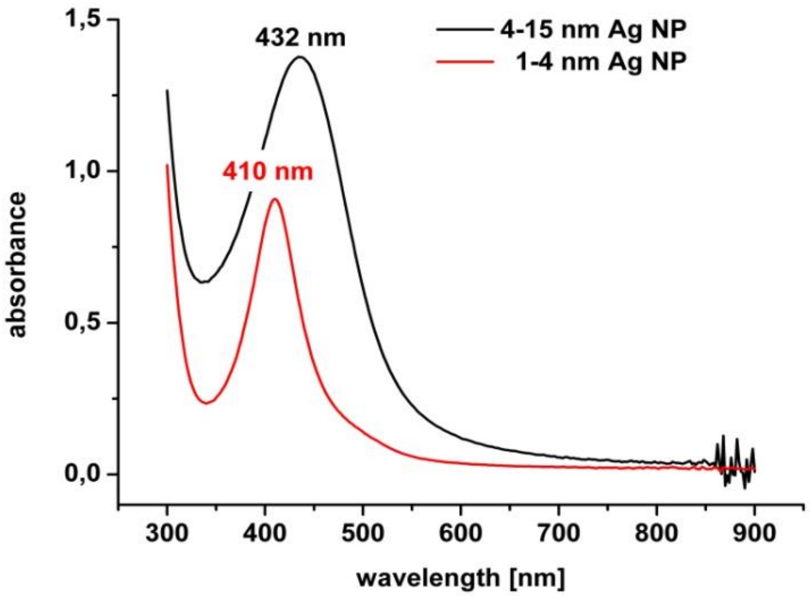
The deposition of Pt NPs enhance the stearic acid decomposition of TiO_2 photoactive layers by approx. factor 2

© Fraunhofer FEP

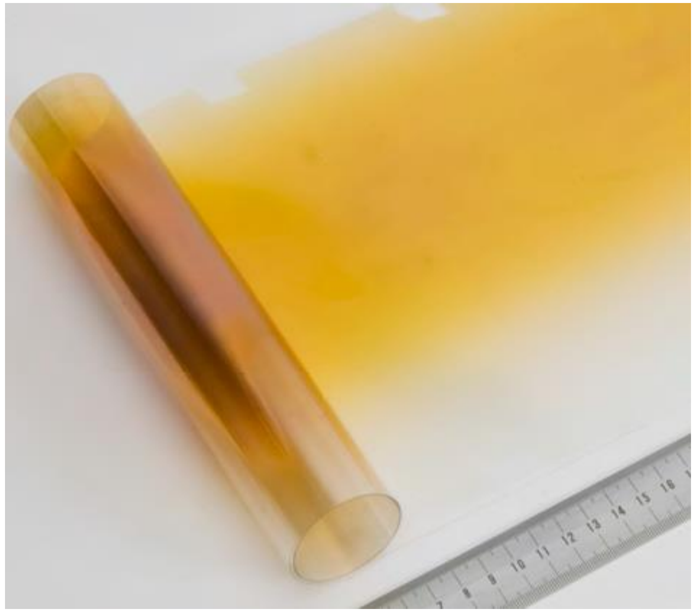
[D. Gloess et al., SVC Bulletin Summer 2014, page 36-40]

Example: Plasmonic coatings for color filters

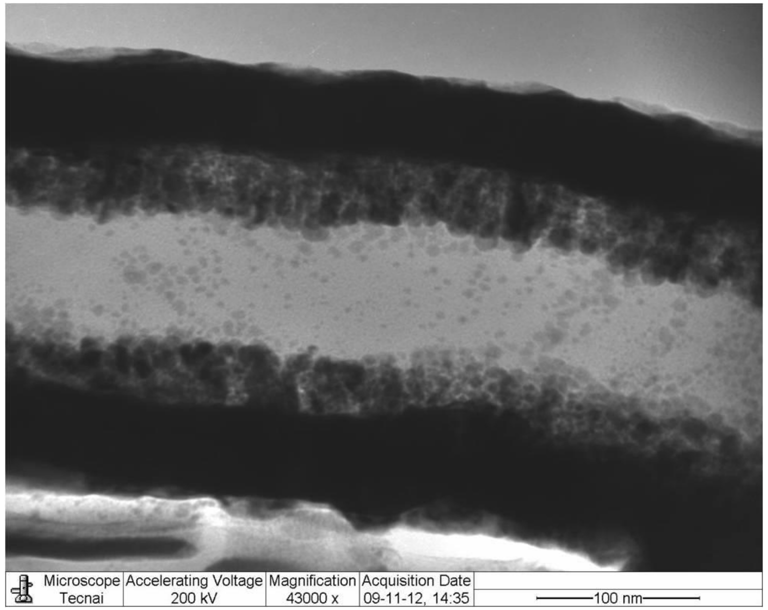
Ag nanoparticles (NPs) embedded in a dielectric matrix exhibit Surface Plasmon Resonance (SPR) effect



Absorption wavelength can be adjusted by tuning NPs size and NP distribution
(Increase of particle size: red-shift of the SPR peak)



Plasmonic coating on flexible substrate (200x1200mm),
Ag NP in isoprene matrix deposited during continuous rotation of the sample holder

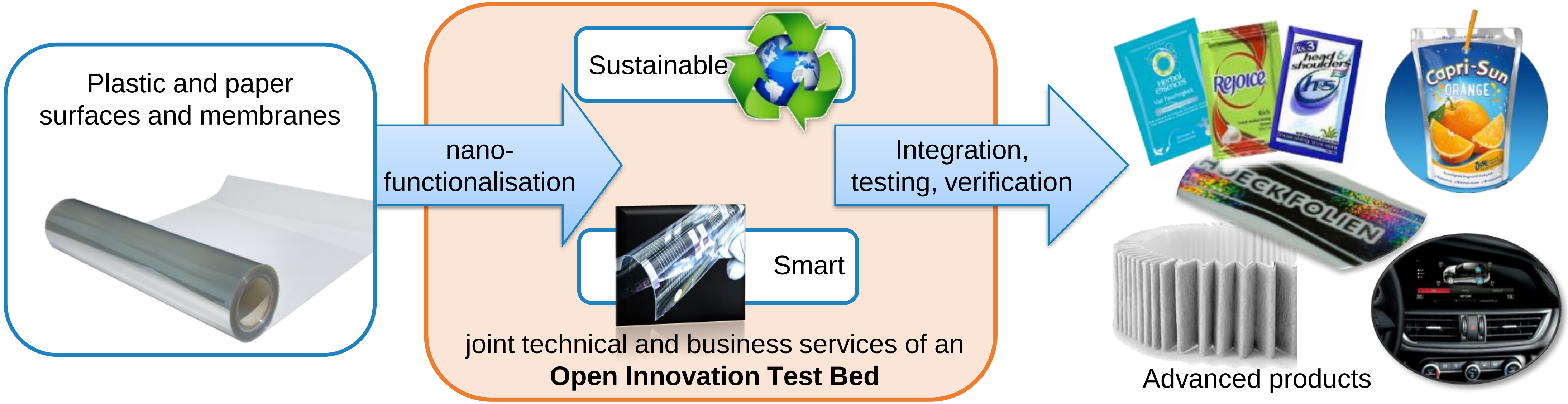


Complete intermixture of NPs in the matrix by fast sample holder rotation (TEM image)

© Fraunhofer FEP

Fraunhofer FEP

Project: Open Innovation Test Bed (OITB) "Flex Function 2 Sustain"



- **Open Innovation Test Bed:** Network of Experts and Innovation Service Providers to Industry
- **Single Entry Point:** Research, Development, Business Consulting, IP Services offered from one hand
- **FlexFunction2Sustain:** OITB on Nanotechnology for sustainable and smart plastic and paper technology
- **Save the Date:** Open Call for SME driven innovation projects funded by EU in 01 / 2022 and 01 / 2023

COMING SOON

www.flexfunction2sustain.eu
Horizon 2020 Grant Agreement: 862156

© Fraunhofer FEP
Fraunhofer FEP