Nano-Silver as Interesting Material for Various Applications

Nano and Advanced Materials Workshop and Fair
NAMF 2013
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Building of Mathematics, Pl. Polytechniki 1
Warsaw, Poland
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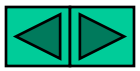

Fraunhofer ICT

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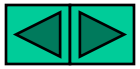
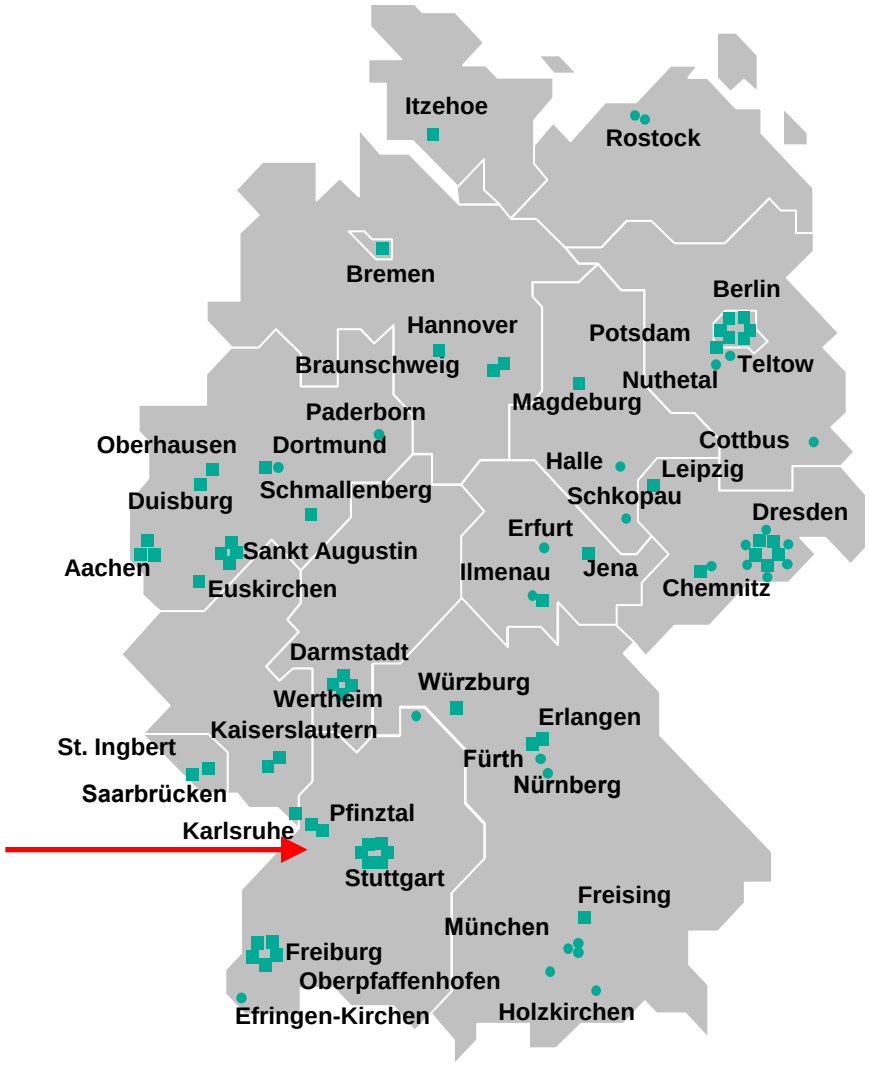


1 Introduction

Fraunhofer-Society
Locations in Germany

- 60 Institutes
- 22 000 Staff
- More than 40 locations in Germany
- International representations



Organigram of Fraunhofer ICT

Institutsleitung (IL)
Prof. Dr. P. Elsner

Stellv. Institutsleitung
Dr. H. Krause, Prof. Dr. F. Henning

Controlling
C. Steuerwald

Querschnittsaufgaben (QA)
Dr. B. Hefer, C. Steuerwald

Zentrales Management (ZM)
Dr. S. Tröster

Energetische Materialien (EM)
Dr. H. Krause
Dr. T. Keicher
Dr. S. Löbbecke

Energetische Systeme (ES)
W. Eckl
G. Langer
Dr. N. Eisenreich

Angewandte Elektrochemie (AE)
Dr. J. Tübke
Dr. K. Pinkwart

Umwelt Engineering (UE)
R. Schweppe

Polymer Engineering (PE)
Prof. Dr. F. Henning
Dr. J. Diemert

Nanotechnologie (ES)
H. Schmid

Projektgruppe Nachhaltige Mobilität FH Braunschweig-Wolfenbüttel Wolfsburg
Dr. J. Tübke

Fraunhofer-Zentrum für Chemisch-Biotechnologische Prozesse CBP Leuna
Prof. Dr. T. Hirth (IGB), Gerd Unkelbach (CBP)

Projektgruppe Funktionsintegrierter Leichtbau FIL Augsburg
Prof. Dr. K. Drechsler (TUM), Prof. Dr. F. Henning

Projektgruppe Neue Antriebssysteme NAS Karlsruhe
Dr. H.-P. Kollmeier
Prof. Dr. P. Elsner, Prof. Dr. P. Gumbsch (IWM)

Fraunhofer Project Center FPC London (Ontario)
Prof. Dr. F. Henning, T. Potyra

Projektgruppe Elektrochemie (im Aufbau) München
Dr. J. Tübke

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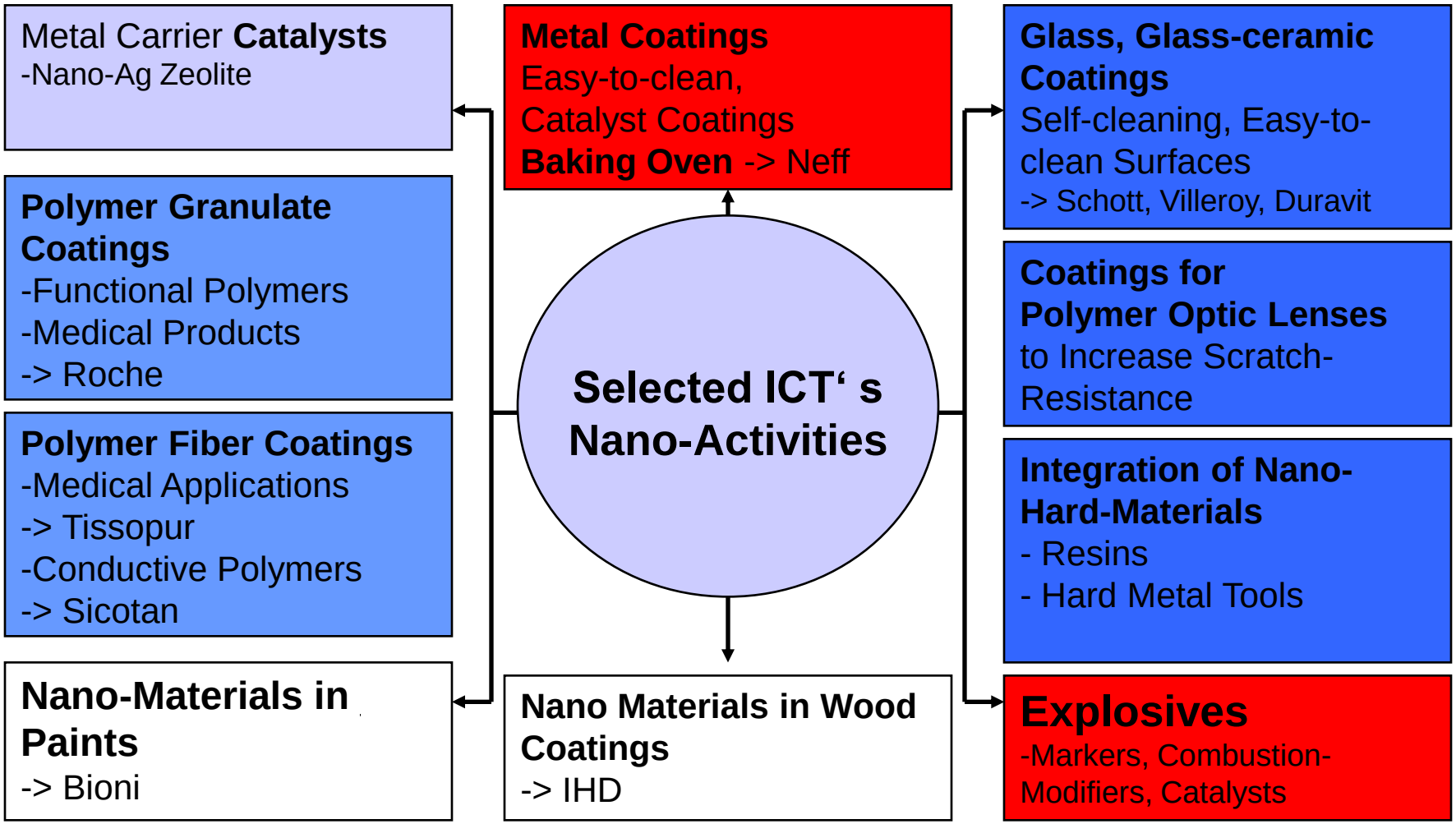
Fields of Application



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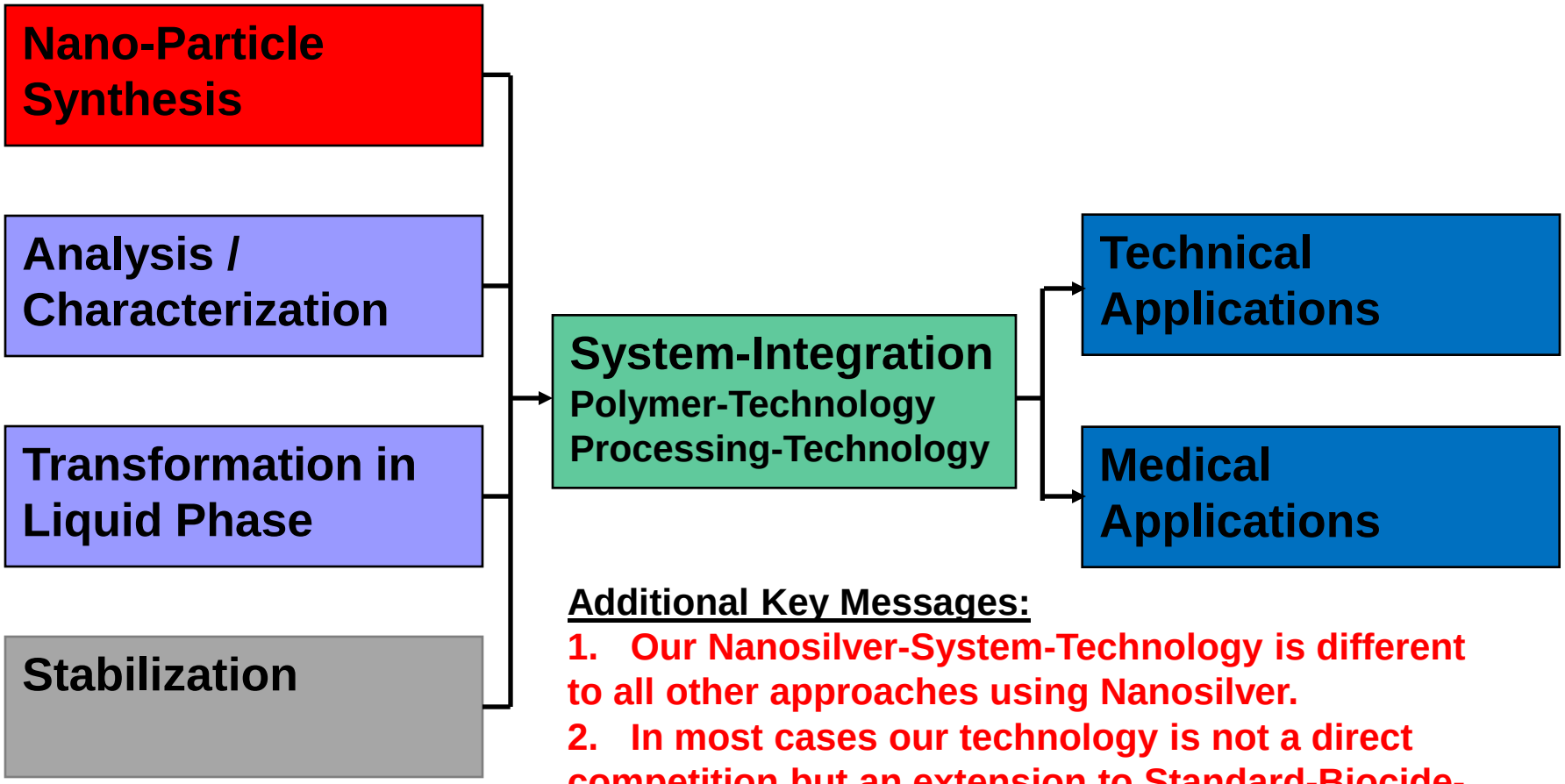
Main Steps from Nano-Particle-Production to Applications



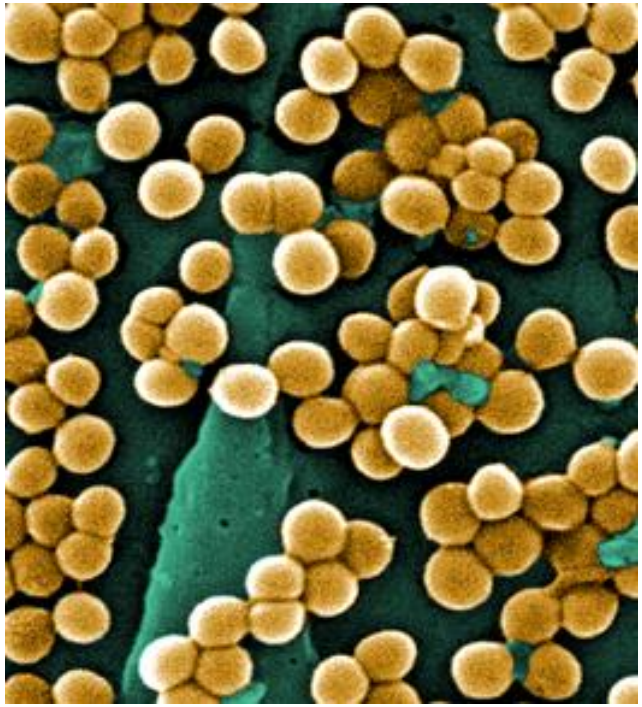
Additional Key Messages:

1. **Our Nanosilver-System-Technology is different to all other approaches using Nanosilver.**
2. **In most cases our technology is not a direct competition but an extension to Standard-Biocide-Applications.**

The Problem

Sources: Simor,

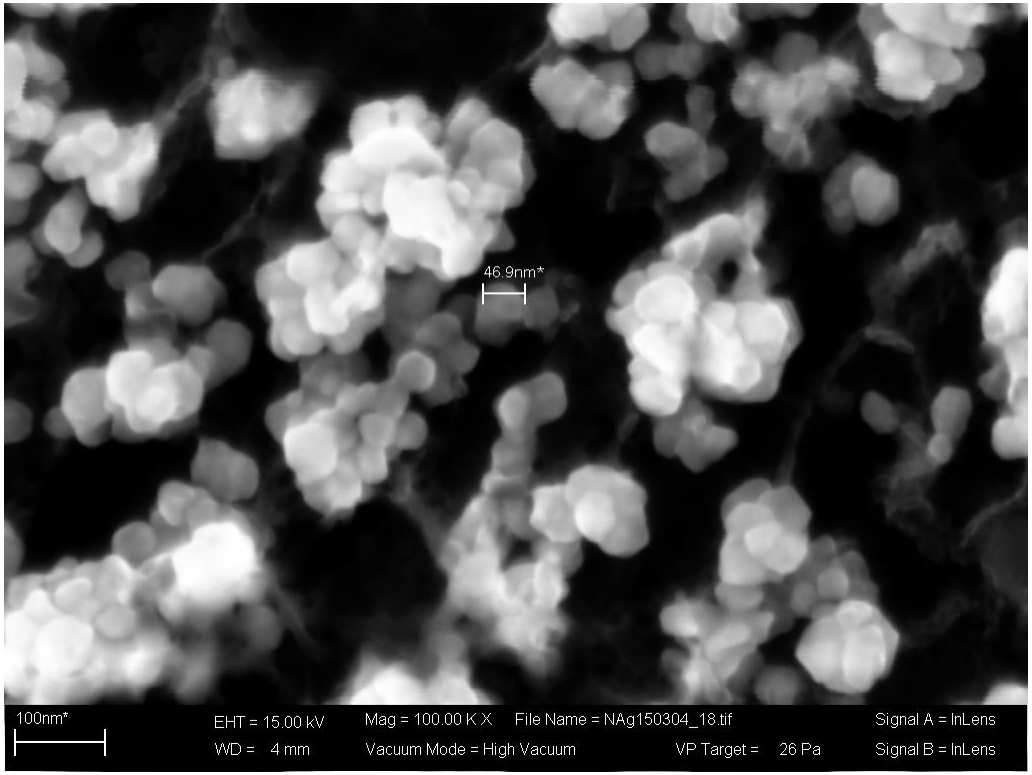
Bacterial Infections	Annual Deaths (USA)	Jahr
MRSA	19000, 1500 (D)	2005[1]
AIDS	14561	2007[2]
TB	644	2006[3]
Viral hepatitis	5793	2002[1]



Staphylococcus aureus MRSA

1.Boucher CID 2008; 46(Suppl 5):S344-9
2. http://www.cdc.gov/hiv/topics/surveillance/basic.htm#ddaids
3 http://www.cdc.gov/TB/publications/factsheets/statistics/TBTrends.htm

The Solution: Nano-Silver with Antimicrobial Functionality



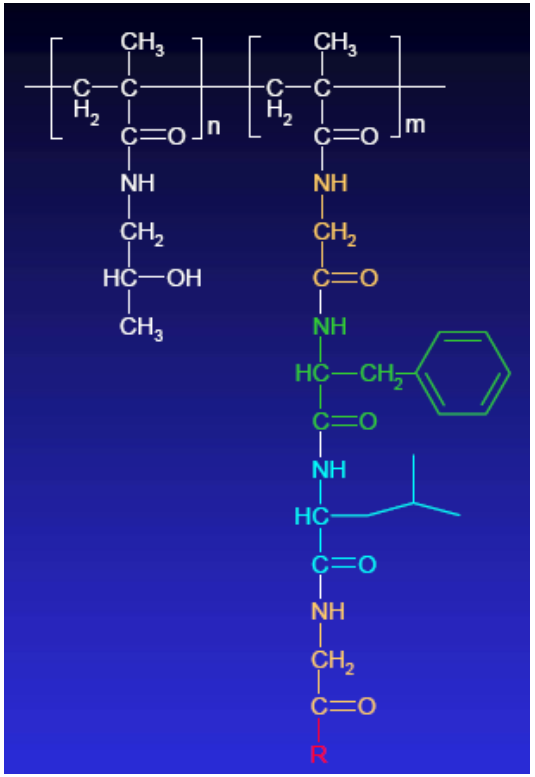
File: NAg150304_18.Tif

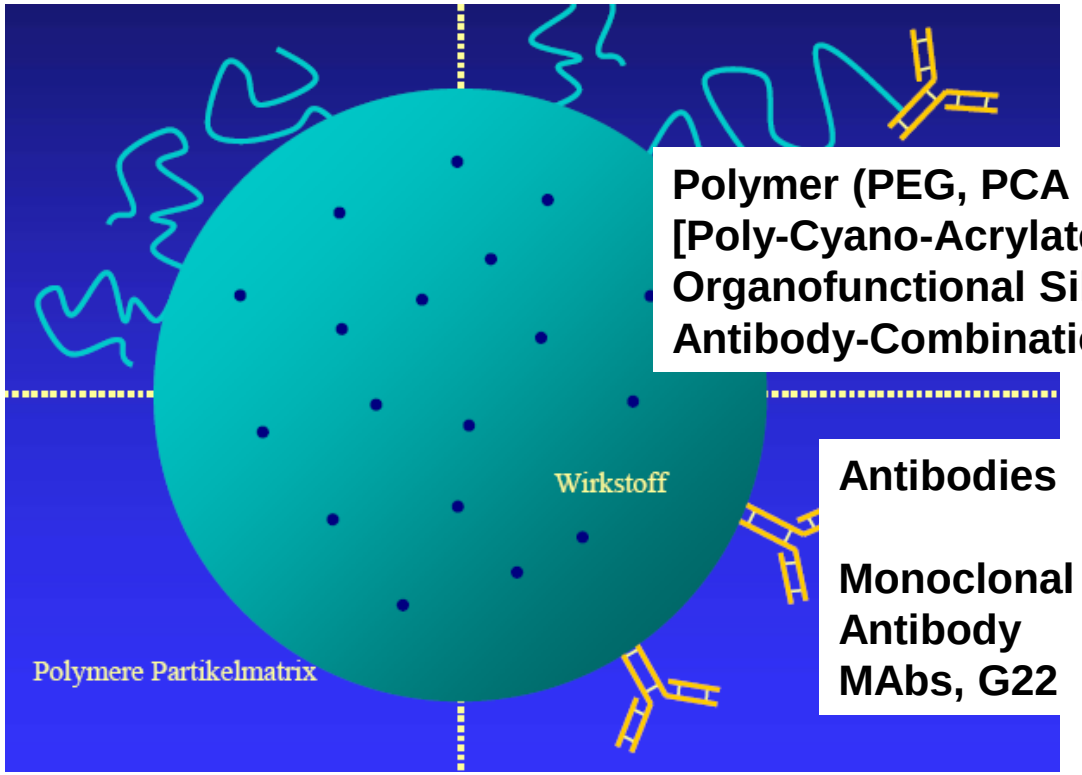
Figure 9.1 SEM-Record of Nano-Ag-Particles. A stable suspension was applied to an Al-plate and investigated after drying. Particle size approx. 50 nm.

Suggested Combination of Principles for Drug-Functionalization

Polymer-Protein-Conjugates
Hydrolyzed-Polymaleic-Anhydride (HPMA)-Copolymer-Gly-Phe (Phenylalanine)-Leu-Gly-R

Source: Uni Frankfurt





R: Doxorubicin -> Apoptosis, Programmed Cell Death (PCD), Galactosamin

Mathematical Modeling of Cumulative Drug-Realease

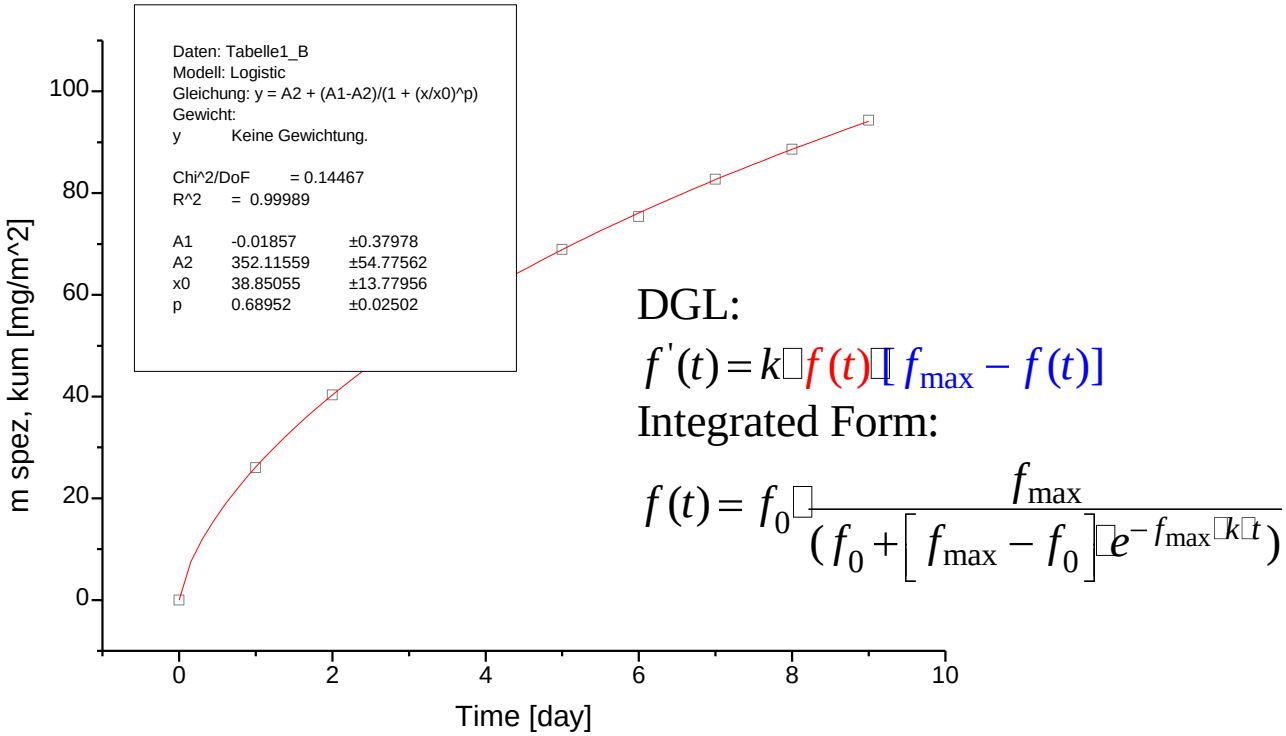
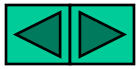


Figure 11.1 Example for Mathematical Modeling of Drug-Release under Consideration of a Superimposed Solution and Diffusion Process using an Exponential-Function representing „Logistic Growth“.



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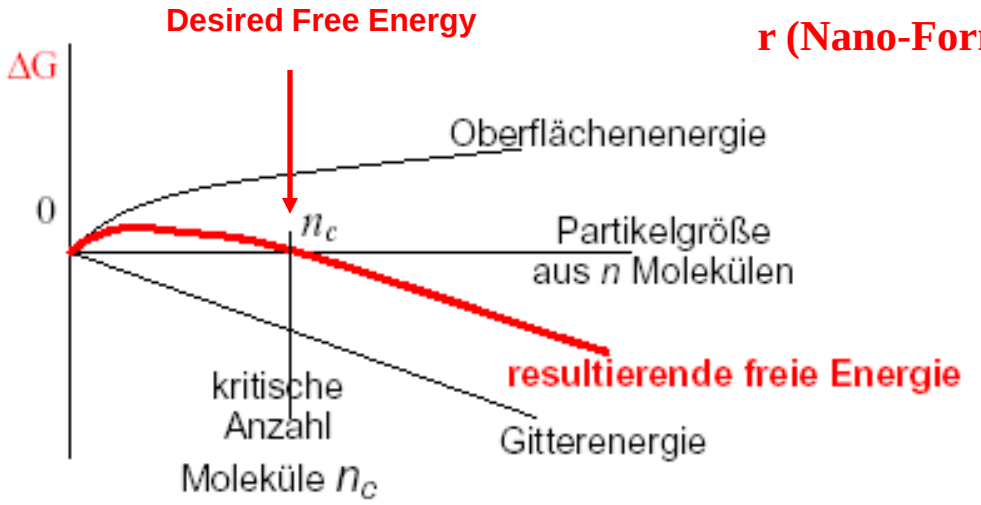
Source: Penth

Thermodynamic Effect

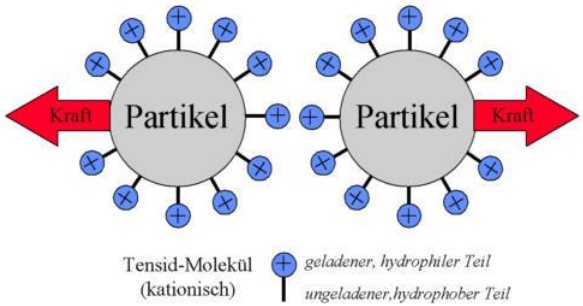


Kinetic Aspect

r (Nano-Formation) >> r (Growth, Agglomeration)

Necessity for Stabilization ->

Surface Treatment



Theorectical Aspects – Potential and Field-Theory

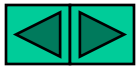
$$\nabla^2 U(\eta,\theta) = \frac{(\cosh\eta - \cos\theta)^2}{B^2}\frac{\partial^2 U}{\partial \eta^2} + \frac{(\cosh\eta - \cos\theta)^2}{B^2}\frac{\partial^2 U}{\partial \theta^2} - \frac{\sinh\eta\,(\cos\eta - \cos\theta)}{B^2}\frac{\partial U}{\partial \eta} +$$

$$\left(\frac{(\cosh\eta - \cos\theta)^2}{\tan\theta} - (\cosh\eta - \cos\theta)\sin\theta\right)\frac{1}{B^2}\frac{\partial U}{\partial \theta} = \sinh(U(\eta,\theta)) \qquad (1)$$

U: Reduced Electrostatic Potential, B: Constant in Bispheric System of Coordinates

Equation 1

Calculation of Surface Potential U according to Poisson-Boltzmann-Equation (1) in order to make a suitable selection of chemical additives enabling stabilization and preventing from reagglomeration. B correlates with k_H (Hamaker Constant) of Van der Waals Interaction. This type of interaction has to be reduced.



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Theorectical Aspects – Potential and Field-Theory

Source: TU-Darmstadt

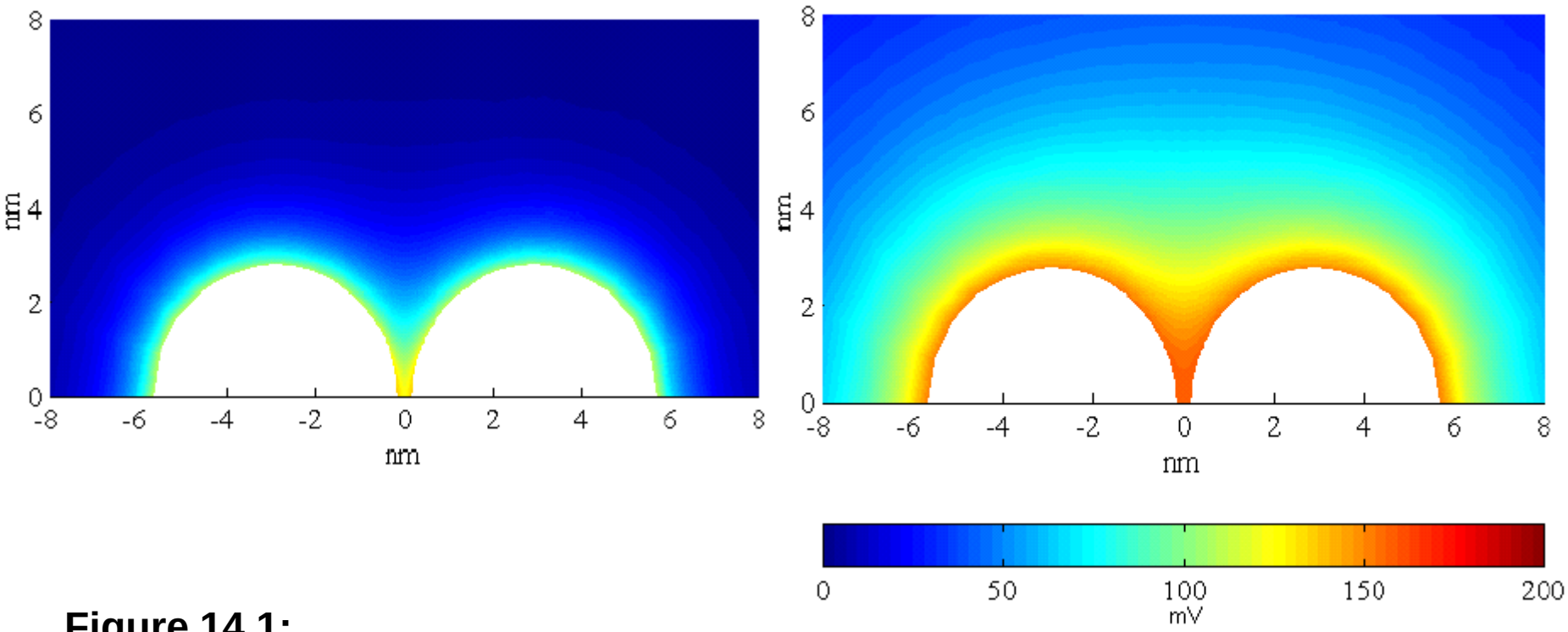
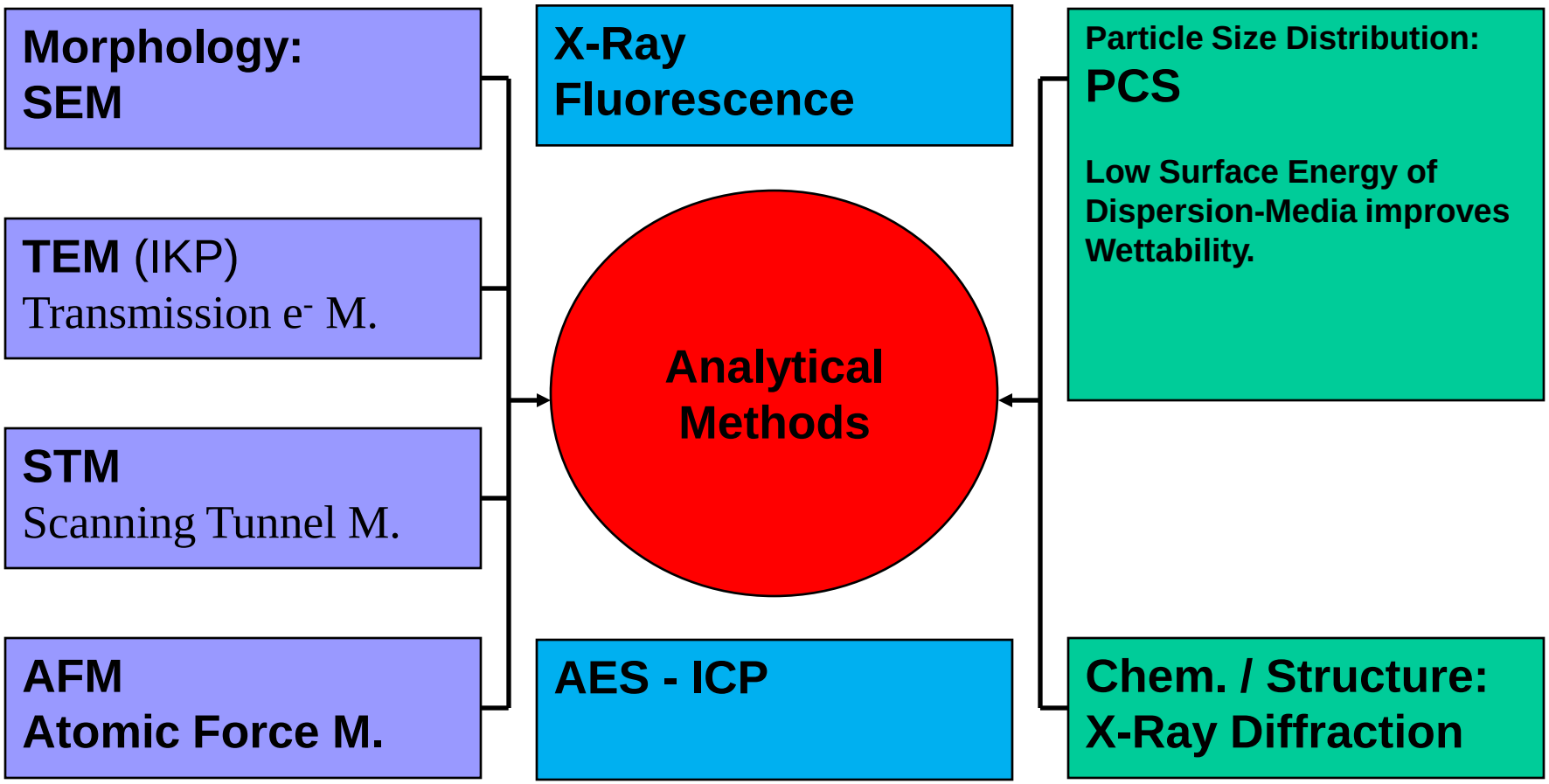


Figure 14.1:

Theory of Nano-Particle-Stabilization:

FE-Calculation of Electrostatic-potential-gradient between two Al_2O_3-Particles (5 nm) as a Function of pH and Electrolyte-concentration (left pH2, 0.1 M NaCl, right pH4, 0.001 M NaCl)

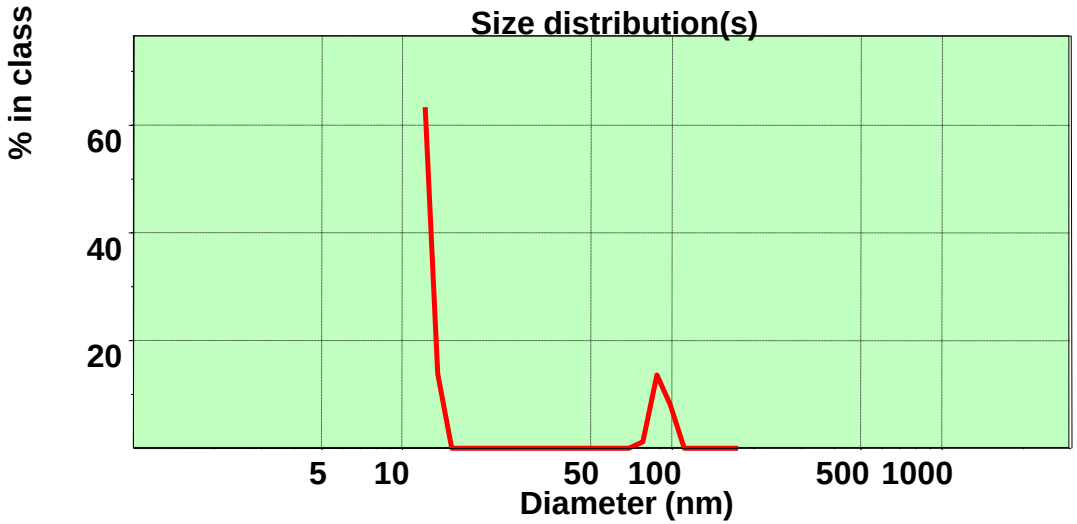
Nano-Analysis, Characterization



AAg00103

Zetasizer 3000
Data taken on 22/07/04 at 17:07:06
Temperature 25.0 Viscosity 0.890 cP Angle 90.0 deg
RI medium 1.33 RI particle 1.92 + Abs. 1.00

Cumulant Z Ave 46.3 nm Polydispersity 0.599



Size (nm)	% Intensity	Size (nm)	% Intensity	Size (nm)	% Intensity
12.1	63.3	30.8	0.0	78.2	1.2
13.6	13.8	34.6	0.0	87.8	13.6
15.3	0.0	38.9	0.0	98.7	8.1
17.2	0.0	43.7	0.0	110.9	0.0
19.3	0.0	49.0	0.0	124.6	0.0
21.7	0.0	55.1	0.0	140.0	0.0
24.4	0.0	61.9	0.0	157.3	0.0
27.4	0.0	69.6	0.0	176.8	0.0

Peak : Mean 12.4 width 0.5

Figure 16.1
Particle Size Distribution
Results of **PCS-Analysis** of Nano-Ag, 1 Vol.-% Suspension in H_2O (CAg00103).

Temperature-resolved X-Ray Diffraction

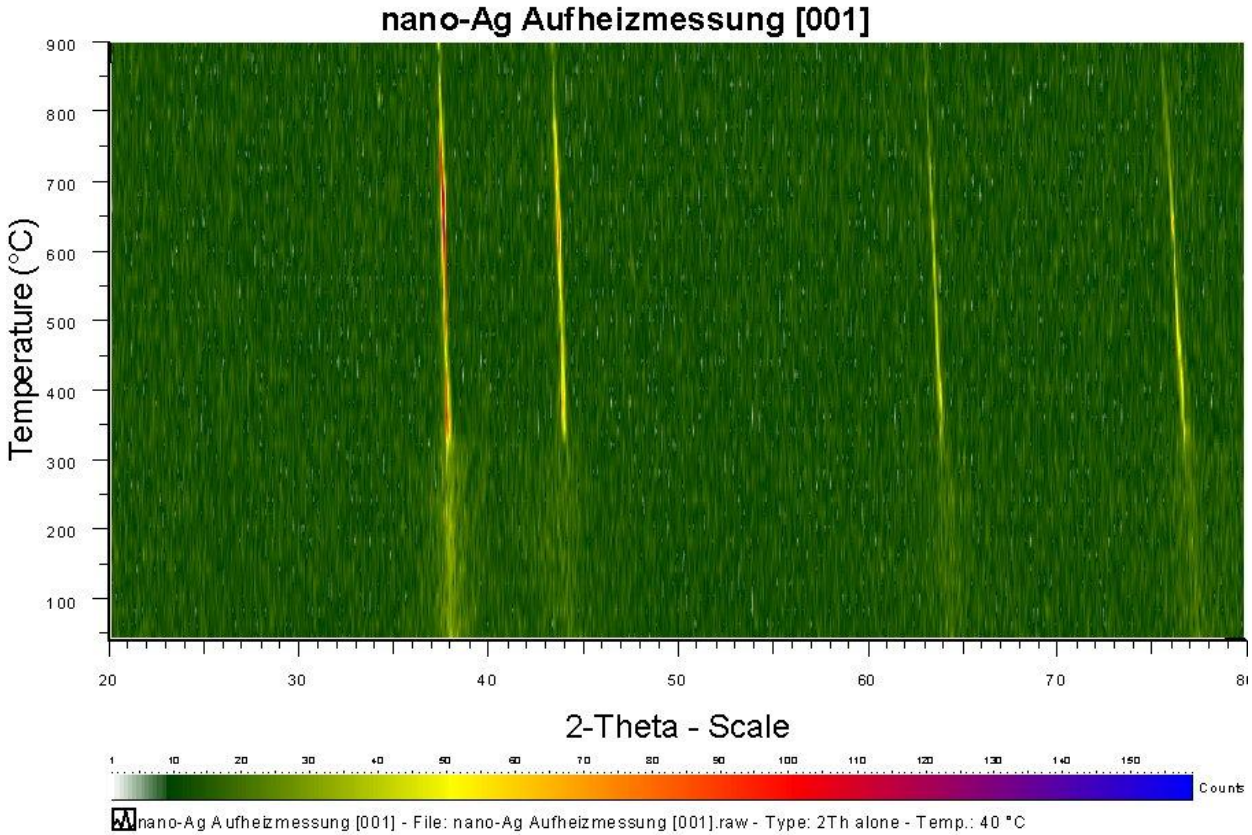


Figure 17.1 Temperature-resolved **X-Ray Diffraction** Diagrams of a Nano-Ag sample in air in a temperature-range from 40 – 900 ^{0}C, χ = 10 K/min (Fp Ag: 961.9 ^{0}C) [Nano-Ag Aufheizmessung_02.jpg]. Peaks represent Ag-reflexes in different phases.

Temperature-resolved X-Ray Diffraction

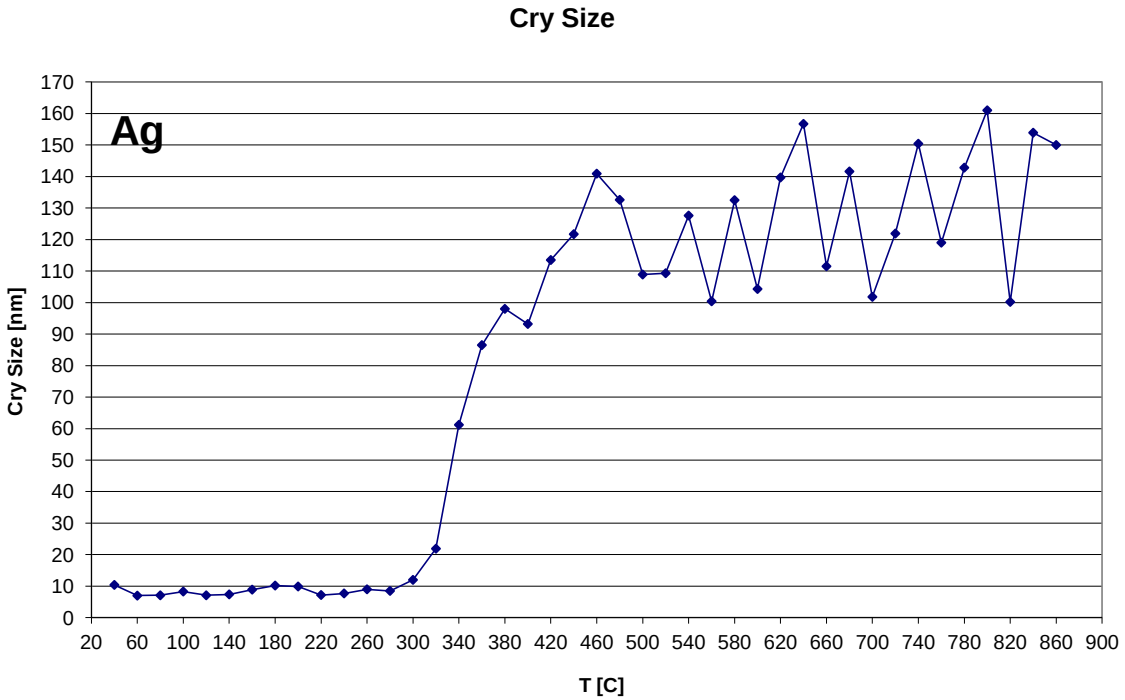
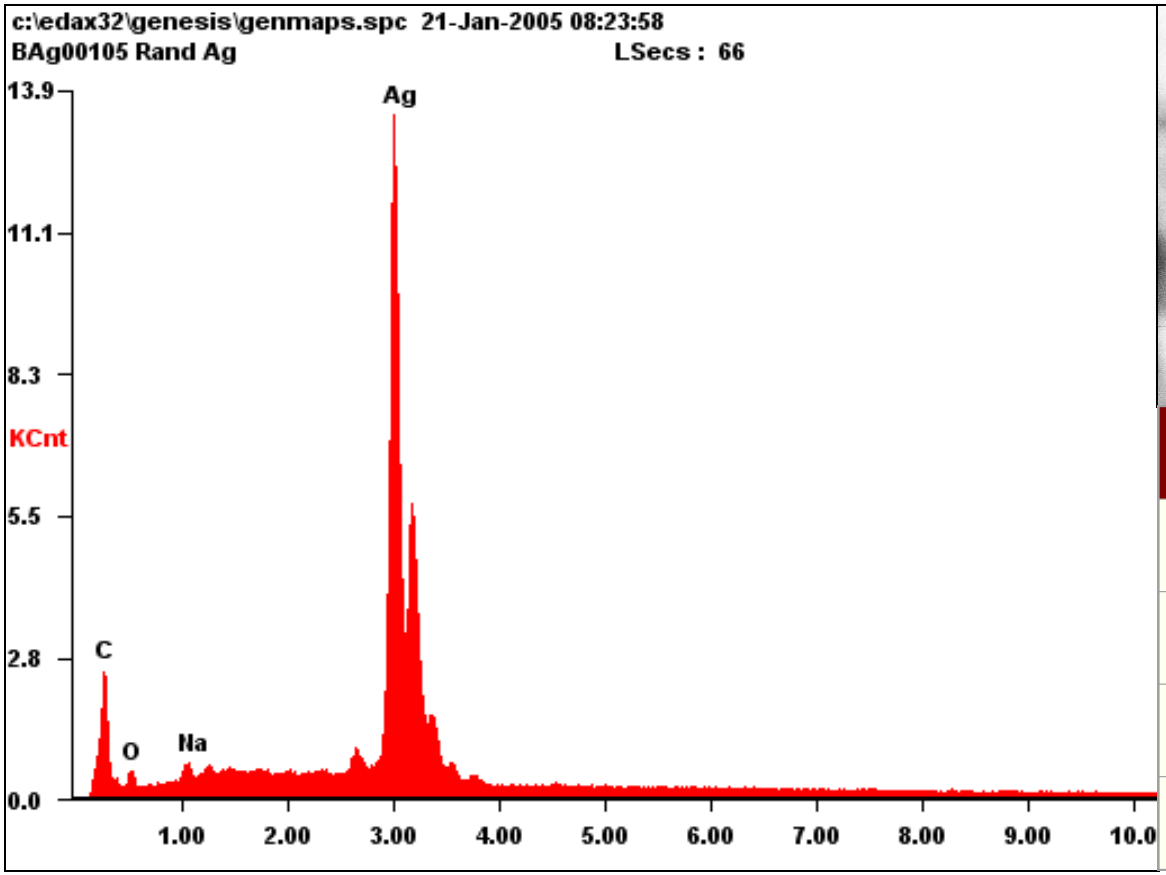
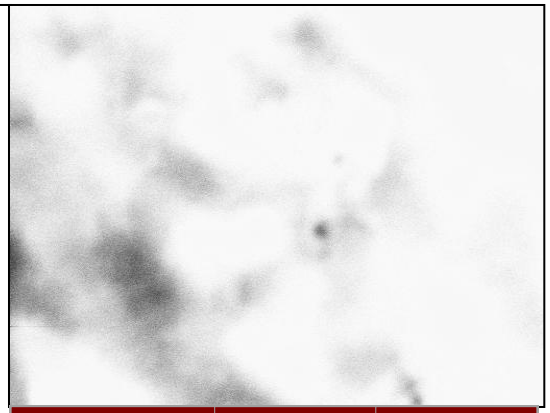


Figure 18.1 By means of **temperature-resolved** X-Ray Diffraction evaluated primary crystallite dimension of Nano-Ag as a function of temperature. Grain growth starting from 300 ^{0}C.

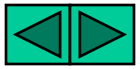
Energy Dispersive X-Ray Spectroscopy (EDX)





Element	*Wt%*	*At%*
C K	41.08	78.57
O K	06.71	09.64
NaK	00.86	00.85
AgL	51.35	10.94

Figure 19.1 Quantitative Ag-Analysis in Sample BAg00105 with X-Ray Fluorescence



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Processing-Technology

Figure 20.1 **Mini-Twin-screw-extruder** for sample-production in lager scale (500 g / h)

Nano-Strukturing / Coating of Polymer-Granulate to Achieve System Functionality

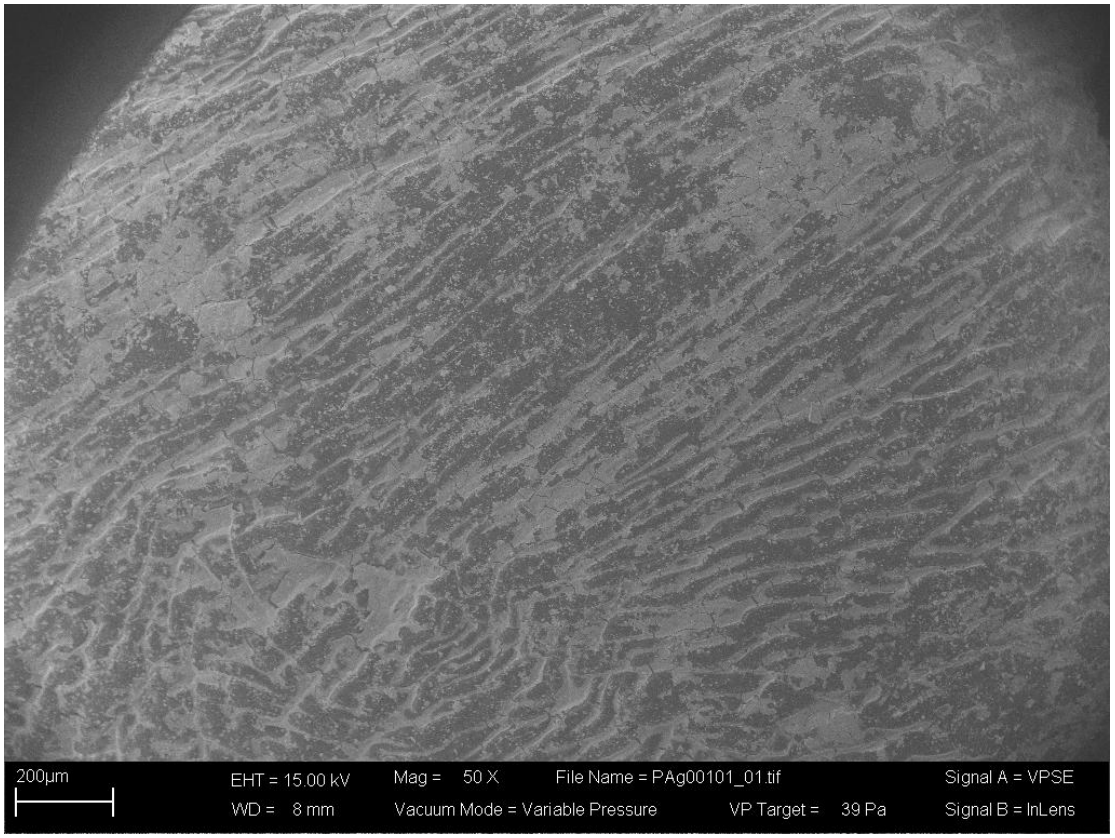
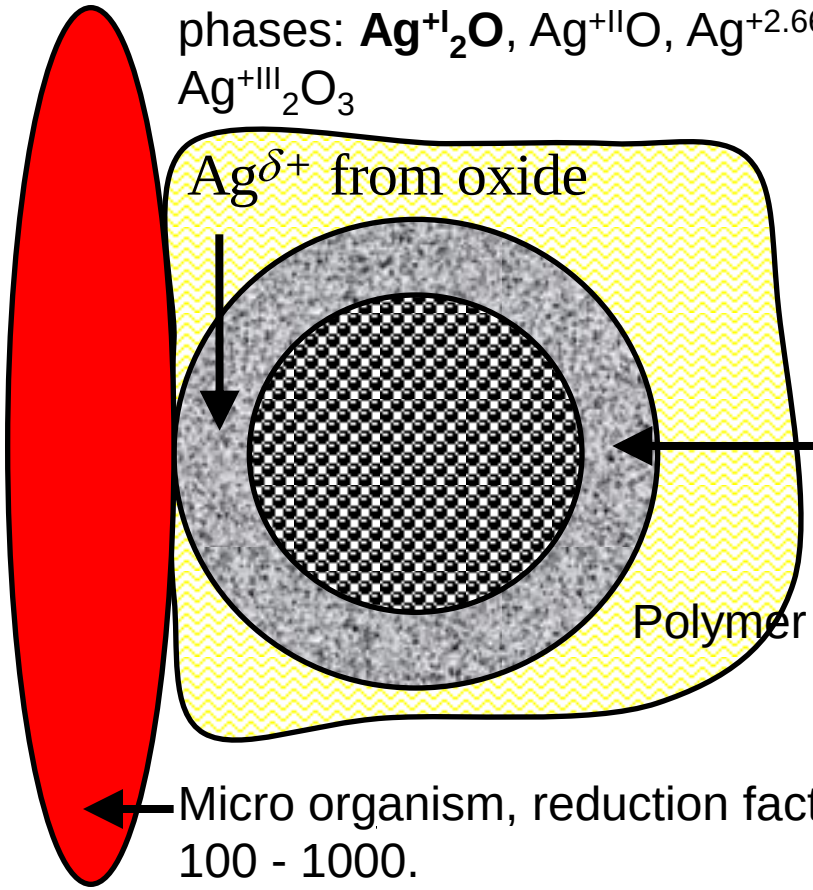


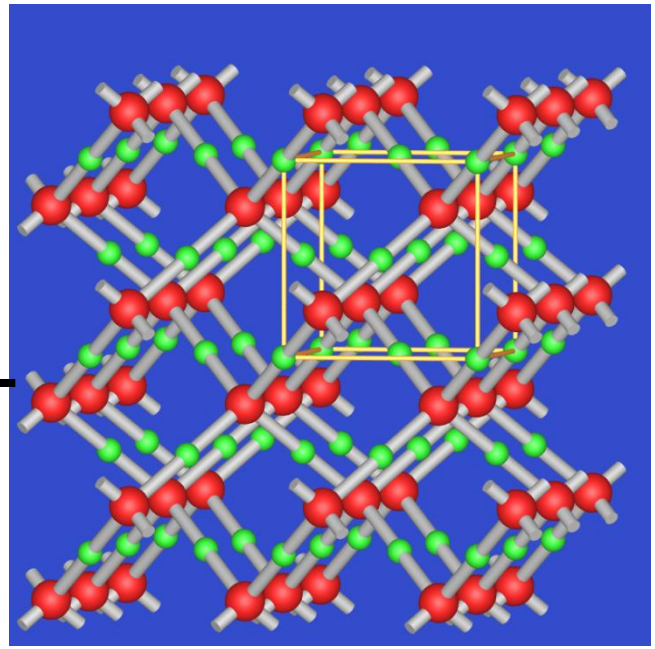
Figure 21.1 SEM-Data of Nano-Ag-Particles on PP-Granulate (PAg00101).

3 Results / Discussion, Selected Applications, Nano-Silver-Technology

Approx. 25-30 mass-% as porous oxide-phases: **Ag^{+I}_2O**, $Ag^{+II}O$, $Ag^{+2.66}_3O_4$, $Ag^{+III}_2O_3$

Source: Uni Freiburg





Micro organism, reduction factor 100 - 1000.

Crystal structure Ag_2O:
Cubic closest packed **Ag^+**,
O^{2-} occupy ¼ of tetrahedral gaps.

Biocides, Sub-group Micro-Biocides – Working Mechanism

Source/Autorization: Wortundbildverlag, 08.02.06

Golgi-Apparatus
Last modification of proteins produced by Endoplasmic Reticulum

Endoplasmic Reticulum
Protein production guided by nucleus in order to control metabolism

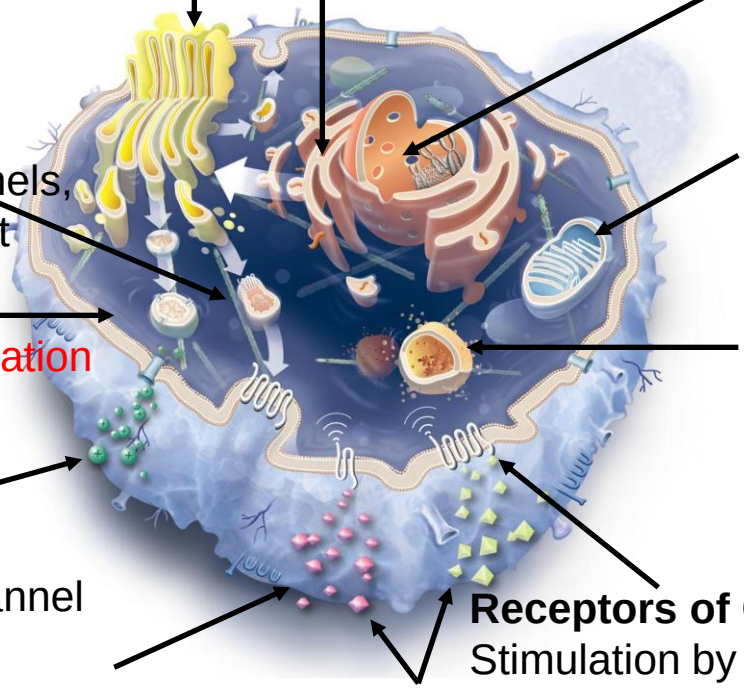
Nucleus
Location of genetic informations and control center

Microtubuli
Internal transport channels, mechanic reinforcement

Mitochondrium
Energy delivery by glucose degradation

Peroxisom
Waste disposal, degradation of internal pollutants (RCOOH, ROH)

Lysosom
Waste disposal, acid degradation of foreign substances

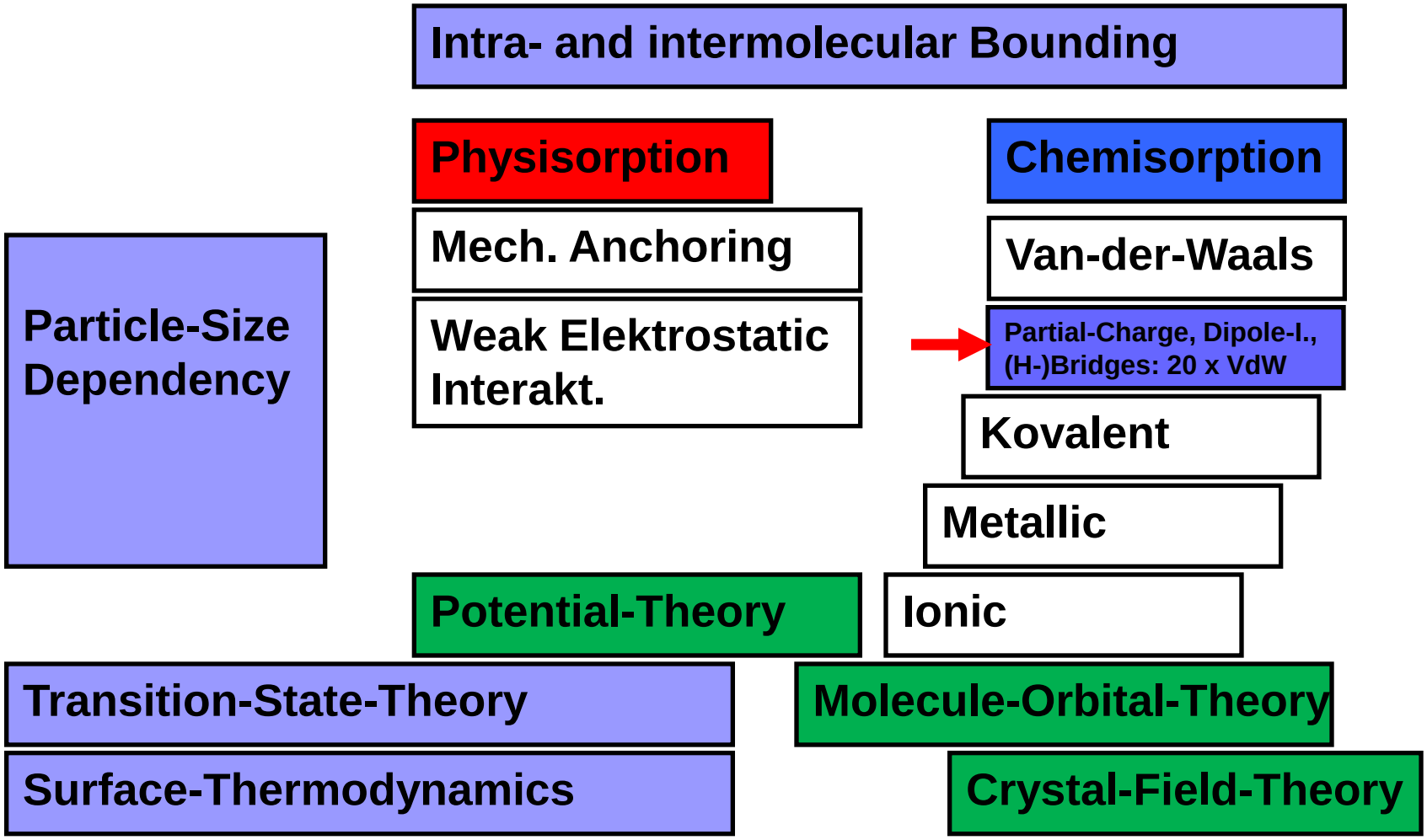


Ion Channel
Two-directional Na^+ channel
50 – 99 pm

External Hormons

Receptors of Cell Membrane
Stimulation by external hormons, signal generation and transmission in to the cell, protein production, action

Theoretical Aspects – Safety Concept



Result of Biocide Treatment

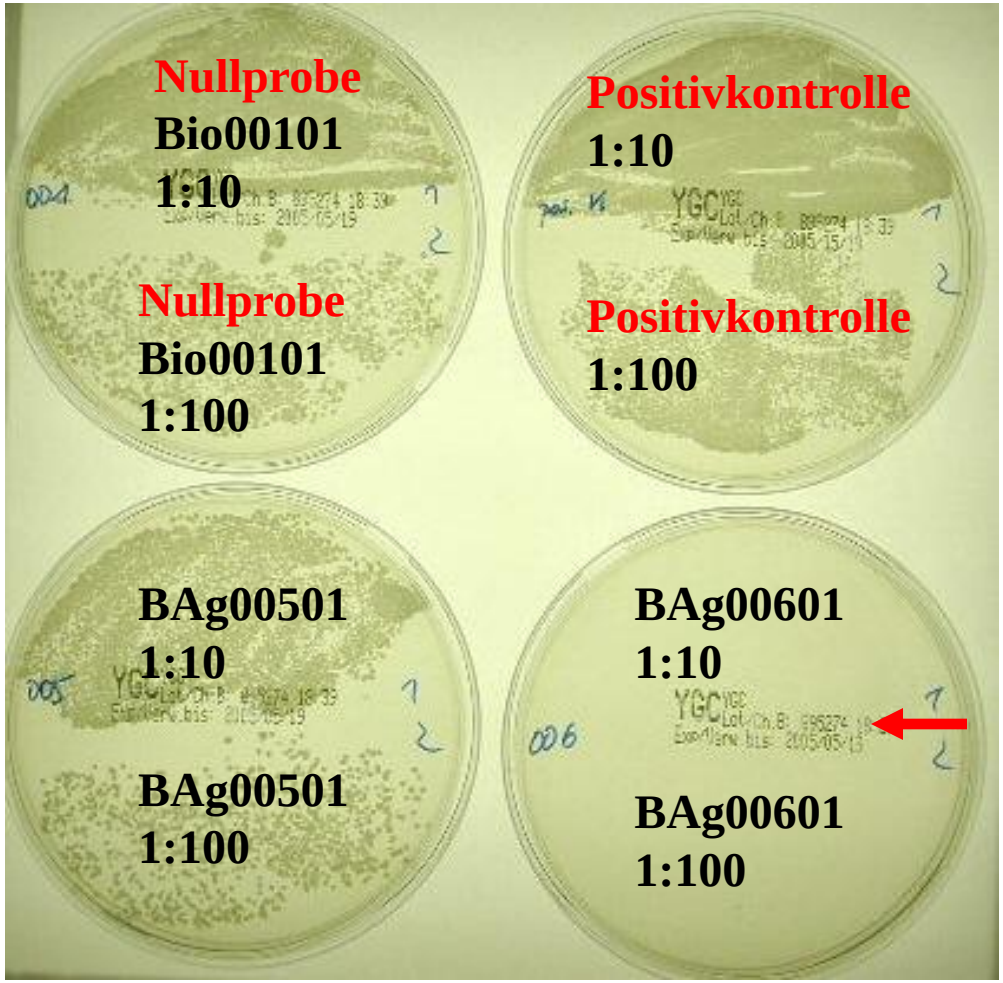


Figure 25.1 Result of breeded diluted crop-out of the samples (mP/mNL=const.)

Antimicrobial Coatings

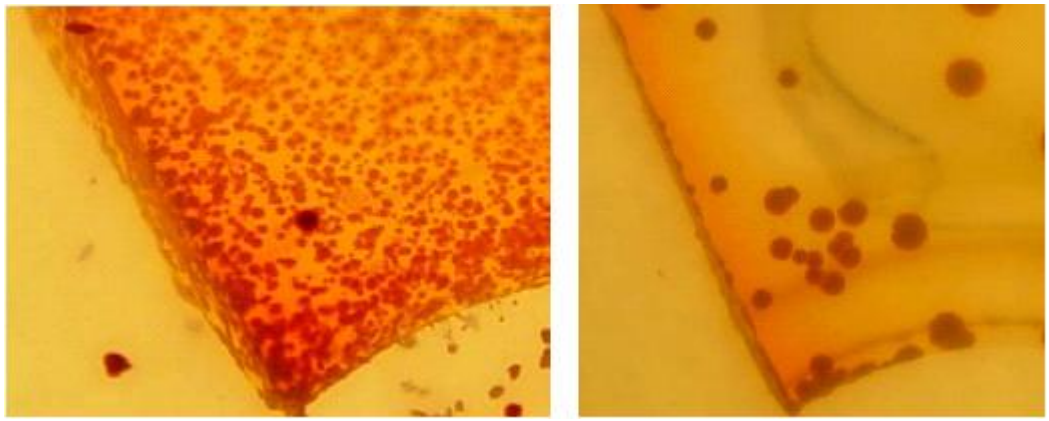


Figure 26.1 Example of a Nano-Ag-coated Silicon-Polymer (on the right) compared to a untreated sample (on the left) with colonies of **Staphylococcus Aureus**.

A reduction rate of factor 100 was detected based on the applied Nano-Ag-content (Test-setup: Spray-test).

Depending on Nano-Ag-content reduction rates of 99,999 % (5 log-levels) are possible.

Mathematical Modeling of Microbial Growth

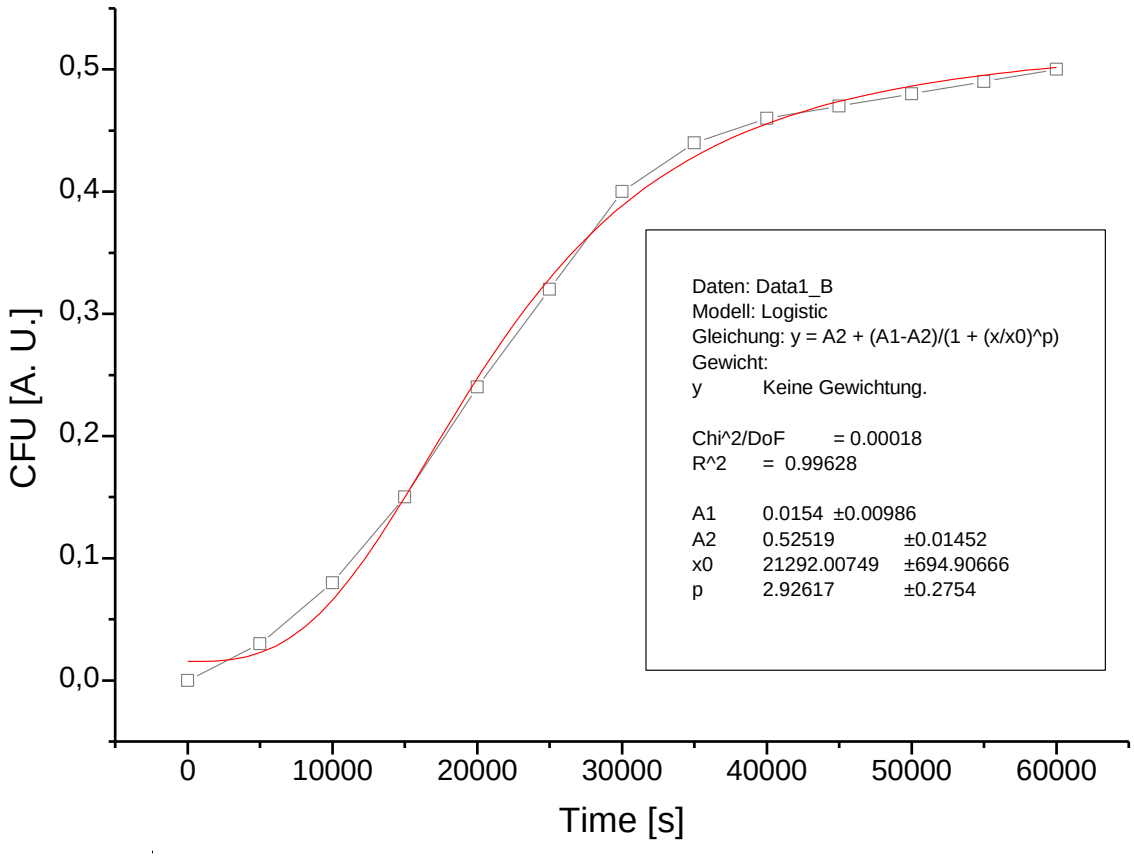
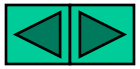


Figure 27.1 Example for Mathematical Modeling of Microbial Growth (Exp. Data) with an Exponential-Function representing „Logistic Growth“.



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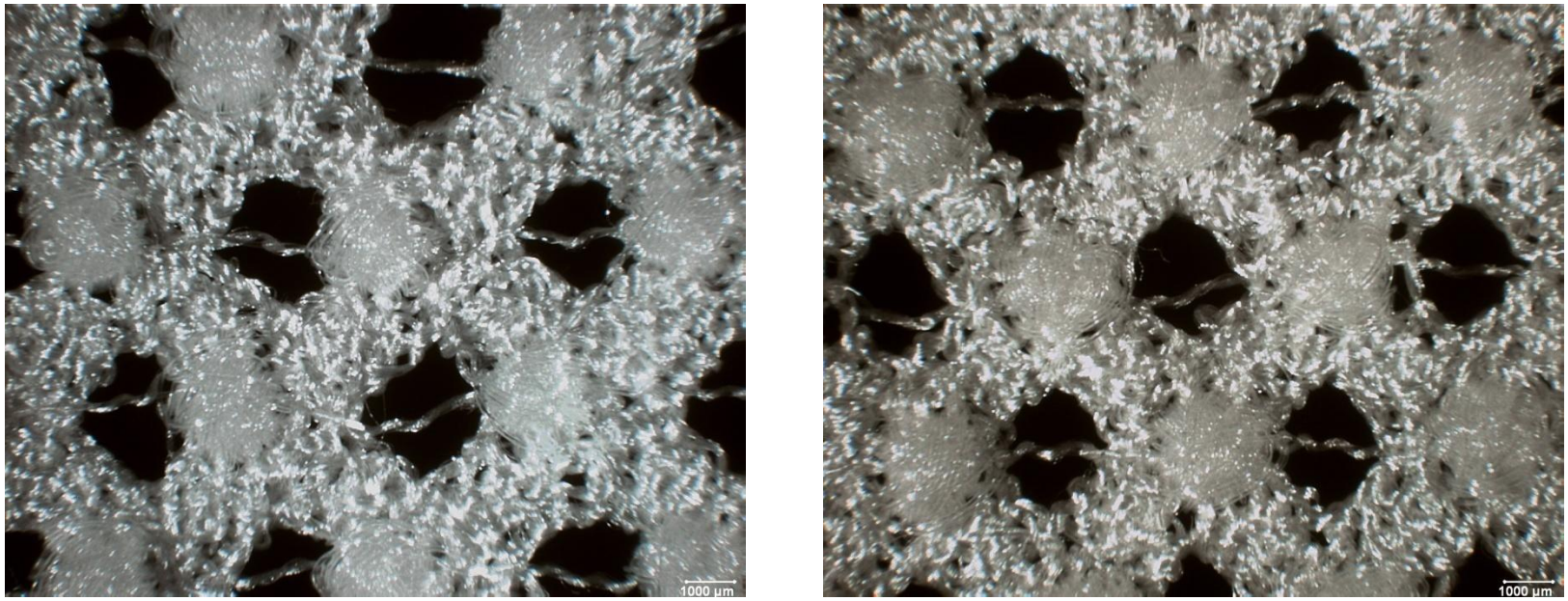
Wound-Pad Application



<u>Figure 28.1</u> Macroscopic Image of a PE-Biopad NURPES-001 (Wound-Pad). Left sample uncoated, right sample Nano-Ag-coated, x < 100 ppm (GAg00001, GAg00101).
Goal: Medical Device Class 2b.

Product Example: Antimicrobial Nano-Silver-Dispersion-Paint

Product Safety by Life Cycle Analysis

Production	Transport	Application	Utilisation, Disposal
•Waste water •Factory wasts	•Emission in case of accidents	•Abrasion •Aging •Wash out	•Recycling •Therm. untilization •Dumping

Product Example: Antimicrobial Nano-Silver-Dispersion-Paint

Figure 30.1 Al Wasl Hospital, Dubai, U.A.E.

Product Example: Antimicrobial Nano-Silver-Dispersion-Paint

Figure 31.1 Al Wasl Hospital (Building 2), Dubai, U.A.E.

Product Example: Antimicrobial Nano-Silver-Dispersion-Paint

Figure 32.1 Hospital in Moscow which was equipped with the developed Nano-Silver-Dispersion-Color as a protection against Staphylococcus Aureus (MRSA).

Electrically Conductive Surfaces

Source: N.N

Surface Resistance [Ohm]

10^{12}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}

Static Dissipation

Polymers

Antistatic

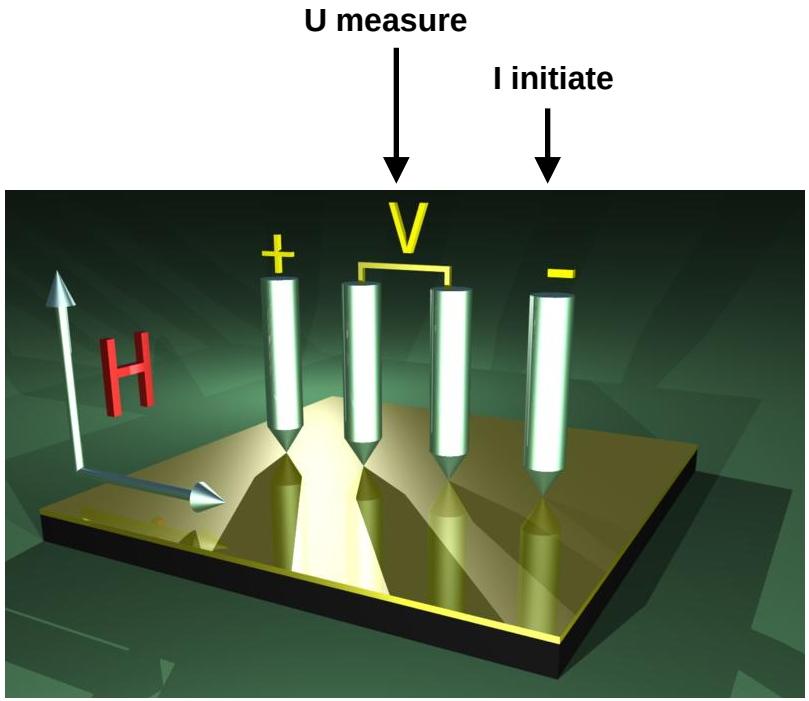
Conductive

Fibers,
EMV-Products

Metals

Spezifischer Flächen-Widerstand
bei quadratischem Meßfeld (vgl. Bild)
Specific Surface Resistance

$$R_O = \rho_\square \left[\Omega\right] = \frac{\pi}{\ln 2} \frac{U\left[V\right]}{I\left[A\right]}$$



Nano-Structuring / Coating of Fibers

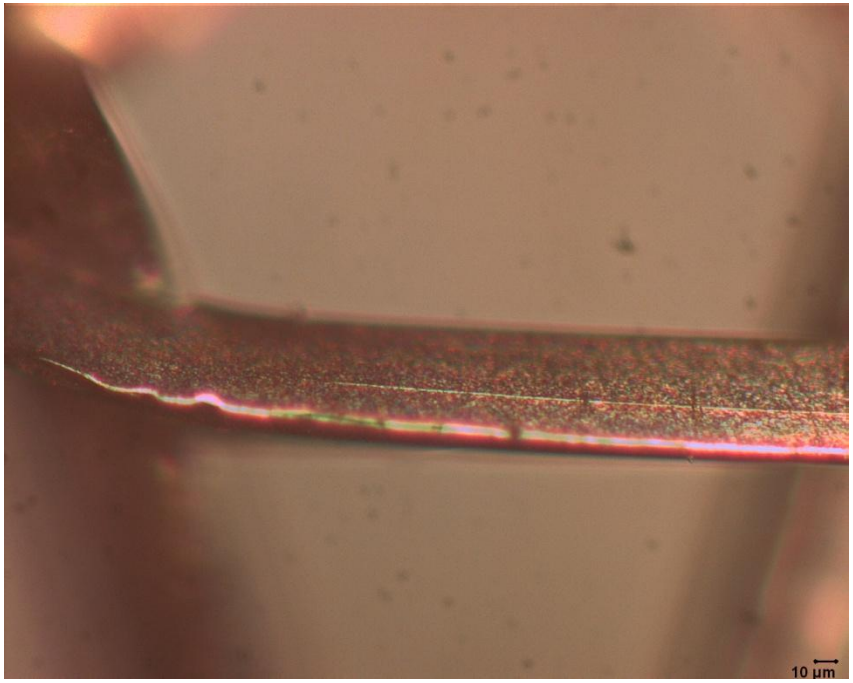


Figure 34.1
Microscopic image (incident-microscopy) of a metal-coated PA-fiber
(File: TüllA.Jpg, 33%)

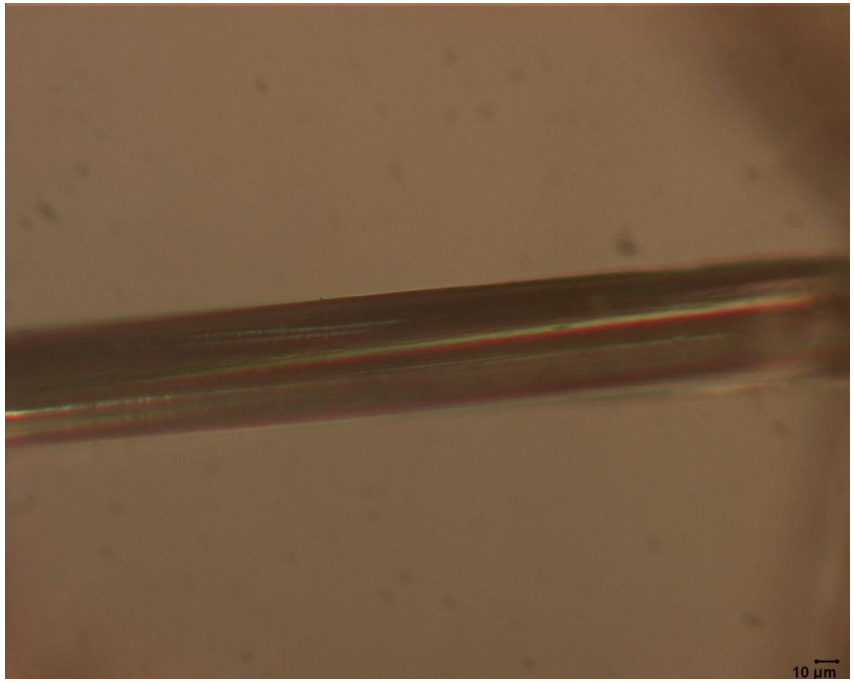
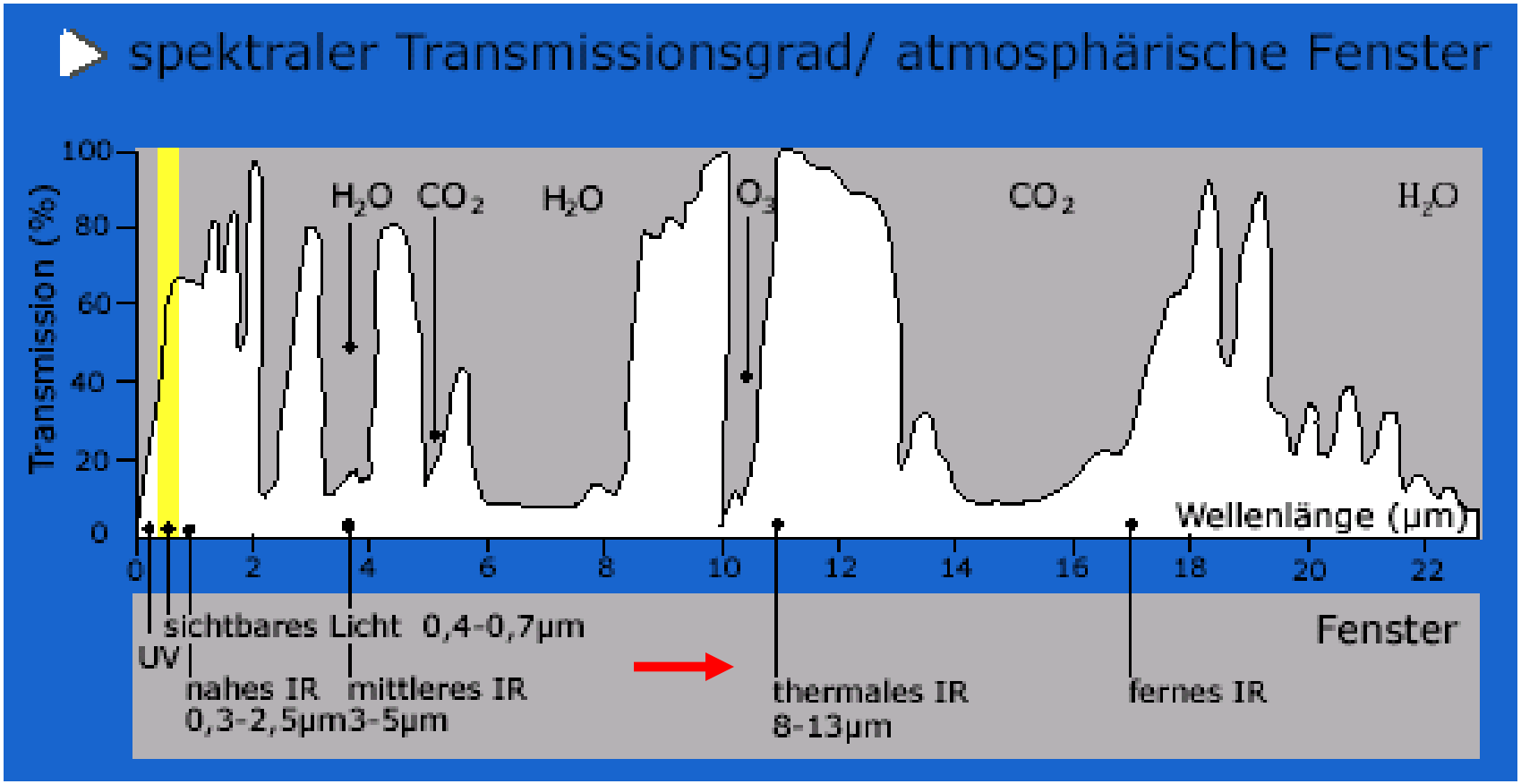


Figure 34.2
Microscopic image (incident-microscopy) of a **nano**-metal-coated PA-fiber
(File: TüllRohA.Jpg, 33%)

Functional Surfaces for Heat Reflection
Spectral Range of Thermal Infrared

Source: Uni Potsdam



λ = 10 [µm] = 10 * 10^{-4} = 10^{-3} [cm]

$\tilde{\nu}$ = 1/ λ = 10^{3} = 1 000 [1/cm]

IR-Reflection -> Improvement of Thermal Insulation and „Comfort“

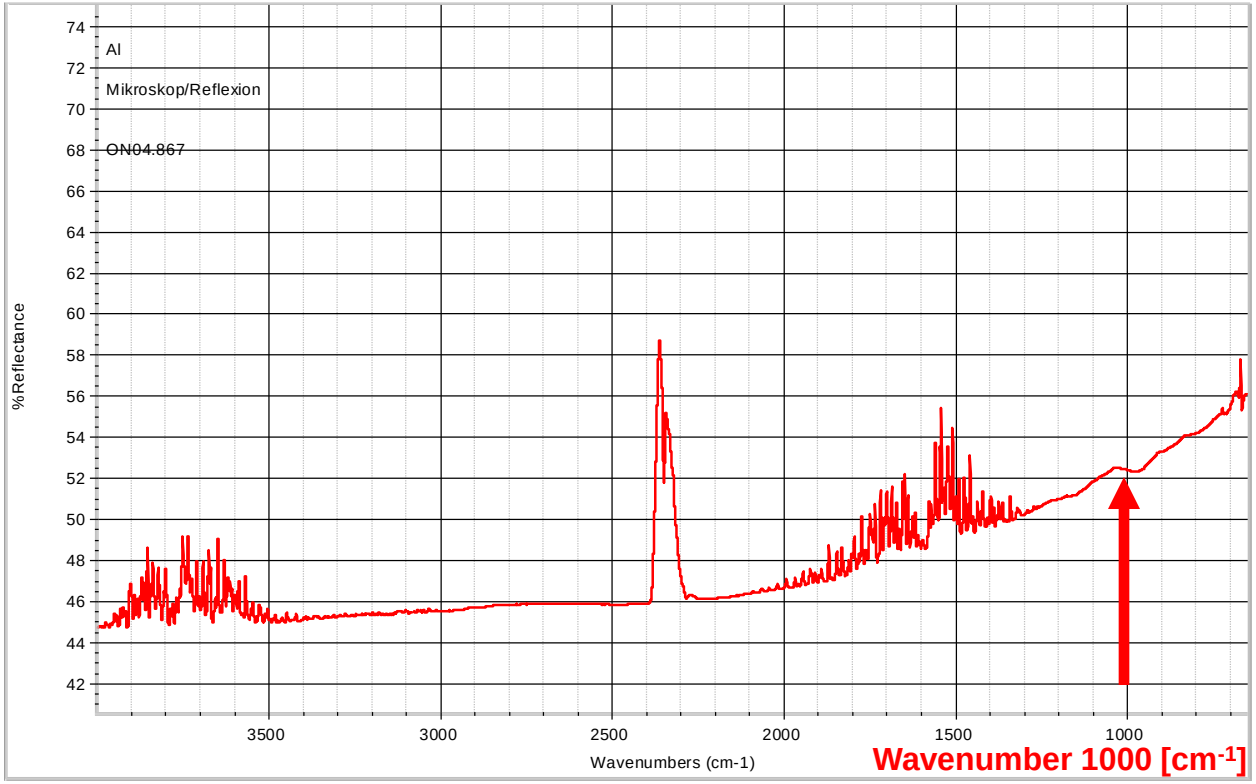


Figure 36.1 IR spectrum of a mixture to increase the average reflection rate. For example, by increasing the average reflection rate from 2,5 to 11 % - energy in an order of magnitude of 4,5 % could be saved (File: Al.Wmf, 65%).

IR Reflection as a Contribution to Fire Protection

Source: N.N.

Chemisch-technische und physikalische Aspekte
(Flächenspezifische) Wärmefluss-Dichte der Reaktionszone

$$\dot{q}_{rz} = \dot{q}_{ext} + \dot{q}_{fl} - \varepsilon \cdot \sigma \cdot \left(T_s^4 - T_u^4 \right) - k \cdot \left(T_s - T_u \right) \qquad (10)$$

$\dot{q}_{ext}$: Surface-specific heatflux-density from external source

$\dot{q}_{fl}$: Surface-specific heatflux-density from flame

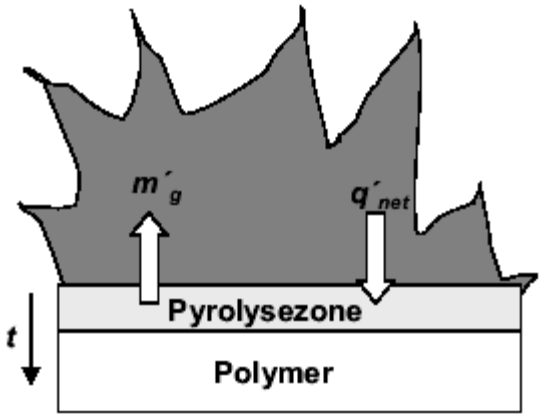
σ : Boltzmann-constant

ε : Emission-constant

k : Convection-constant

T_s : Surface-temperature

T_u : Ambient-temperature

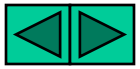


4 Abstract / Summary

[38] Nano-silver has many beneficial properties that enable a high number of different applications.

1. **The antimicrobial properties can be used for product applications in medicine, the construction and sanitary sector, coating of handles, controls and worktops up to antifouling coatings for ships – to name just a few.**
2. **Excellent electrical conductivity predestinate to applications for conductor pathways and printed electronic circuits. This effect can be even further improved in combination with CNT´s.**
3. **A high reflection rate in the range of thermal-IR is suitable for indoor as well as for outdoor applications. Heat insulation surfaces can help to save energy and improve indoor comfort. External applications help to avoid excessing heating of facades which leads to cool buildings.**

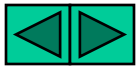
The paper is focussed to product applications in the described areas showing research and development activities of FhG-ICT and covers all steps from nano-particle-synthesis, stabilization, analysis and system-integration under special consideration of nano-safety throughout the entire product life-cycle.



Fraunhofer ICT

5 Prospective

- **Further Nano-Products with additional antimicrobial effect, will be put to market soon**
- **Numerous promising systems are still under development**
- **Nanomedicine is identified as an outstanding field of application**
- **Recognizing the overall benefit, investments in this technology makes sense. Fraunhofer-ICT is looking for further cooperations and product applications especially in Poland**



Nano-Technologies

Спасибо за ваше внимание!

Dziekuje za uwage!

Děkuji za pozornost!

Σας ευχαριστώ για την προσοχή σας!

非常感谢您的关注

ご清聴ありがとうございました

Danke für die Aufmerksamkeit!

Danko pro via atento!

Tak for din opmærksomhed!

Takk for oppmerksomheten!

Tack för er uppmärksamhet!

Dank u voor uw aandacht!

Terima kasih atas perhatian Anda

Cảm ơn bạn đã quan tâm của bạn

Tibi gratias ago pro attentio!

Obrigado pela vossa atenção!

Gracias por su atención!

Grazie per l'attenzione!

Merci pour votre attention!

Thanks for your attention!