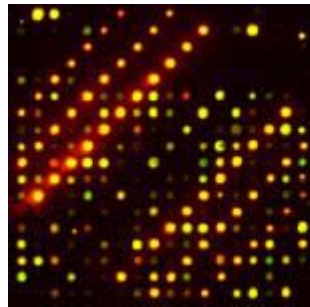
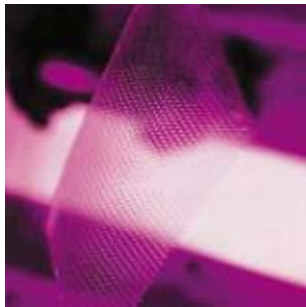

Ink Formulation for the Inkjet Printing of Functional Core-Shell Nanoparticles for Automated Preparation of Multi Feature Biofunctional Surfaces

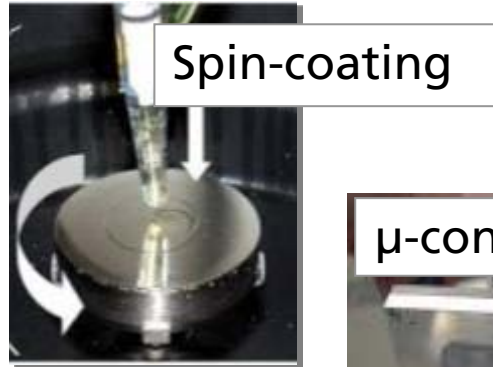
Fraunhofer Institute for
Interfacial Engineering and Biotechnology

K. Borchers, J. Plankalayil, T. Hirth, G.Tovar, Achim Weber
Formula VI & Nanoformulation2010, Stockholm, 10.06.2010



Bio-functionalization of surfaces

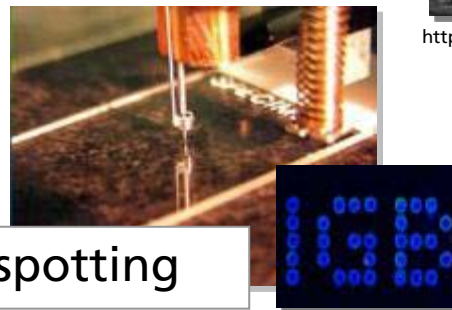
- Biosensors
- Biomaterials
- Cell culture



<http://www.gesim.de>



<http://www.iwt-bremen.de>

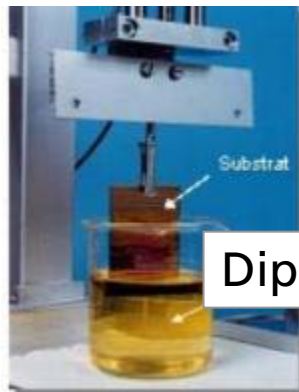


Bio-functionalization of surfaces

- Biosensors
- Biomaterials
- Cell culture



Spin-coating



Dip-coating

<http://www.iwt-bremen.de>



μ-contact printing

<http://www.gesim.de>



Microspotting



Piezo-electric inkjet-printing



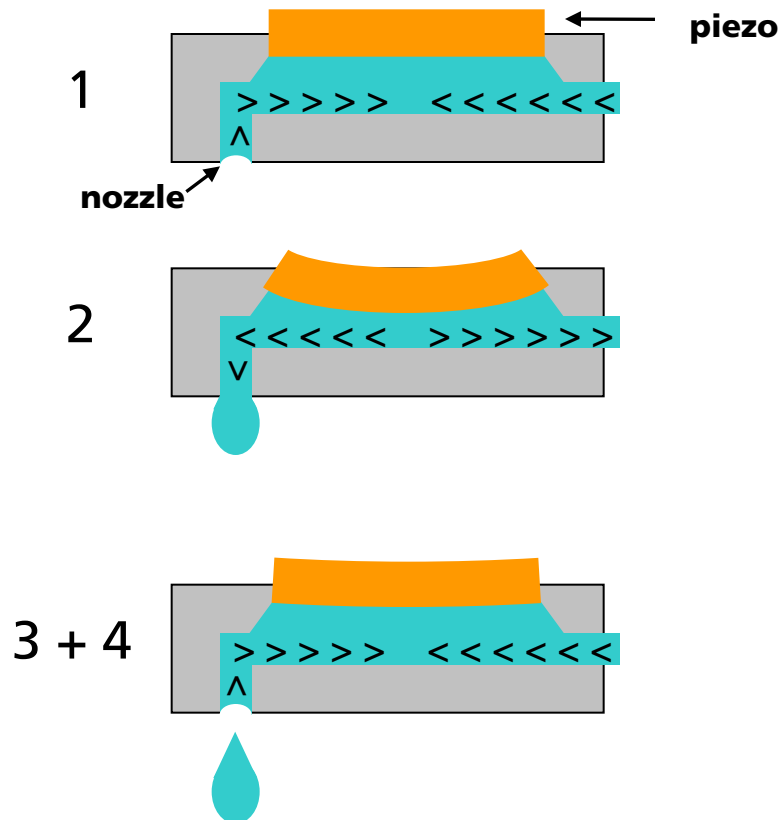
- room temperature process
- digital technique
- scalable
- avoids material spill over

Overview of the talk

- Demands for ink jetting of biological probes
- Ink formulation & protein stability
- Substrate preparation
- (Bio)functional nanoparticles
- Printing
- Evaluation

Piezoelectric drop-on-demand ink jetting

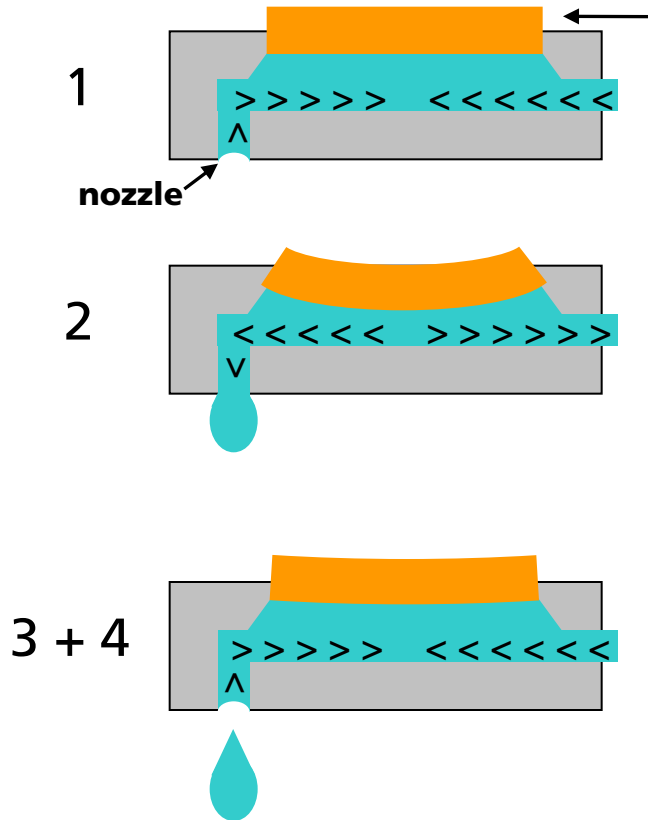
Jetting process



Source: Dimatix

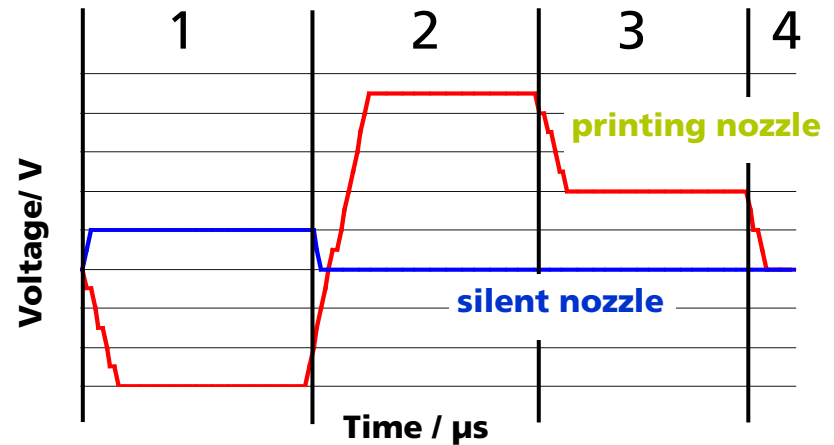
Piezoelectric drop-on-demand ink jetting

Jetting process

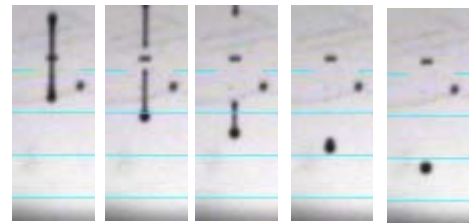


Source: Dimatix

Wave form

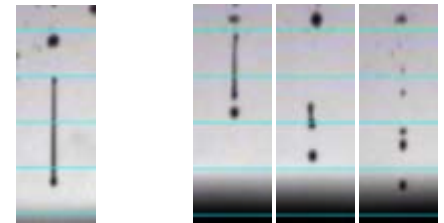


Accurate drop formation



20 μ s 30 μ s 40 μ s 50 μ s 60 μ s

In-accurate drop formation



Distinctive tail

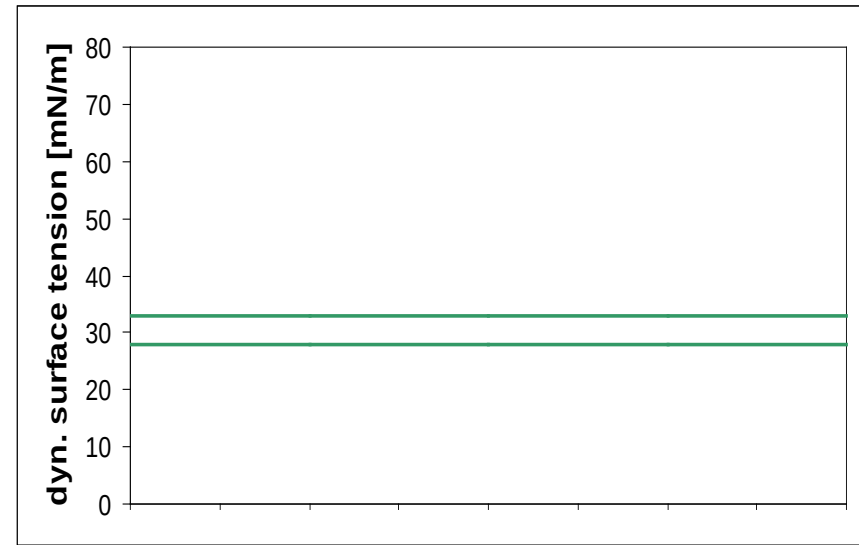
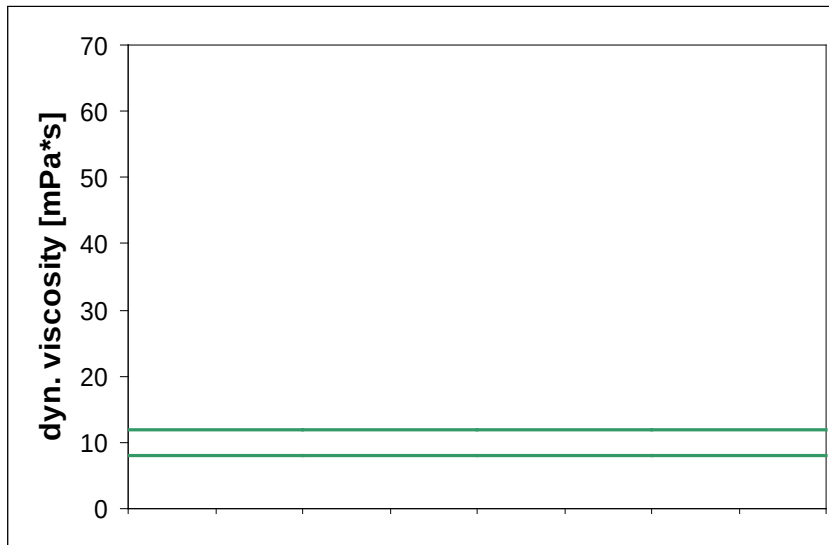
satellites

Ink specification

as indicated for the DMP 2800 Printer by FUJIFILM Dimatix

Dynamic viscosity: 8 – 12 mPa s

Dynamic surface tension: 28 – 33 mN/m

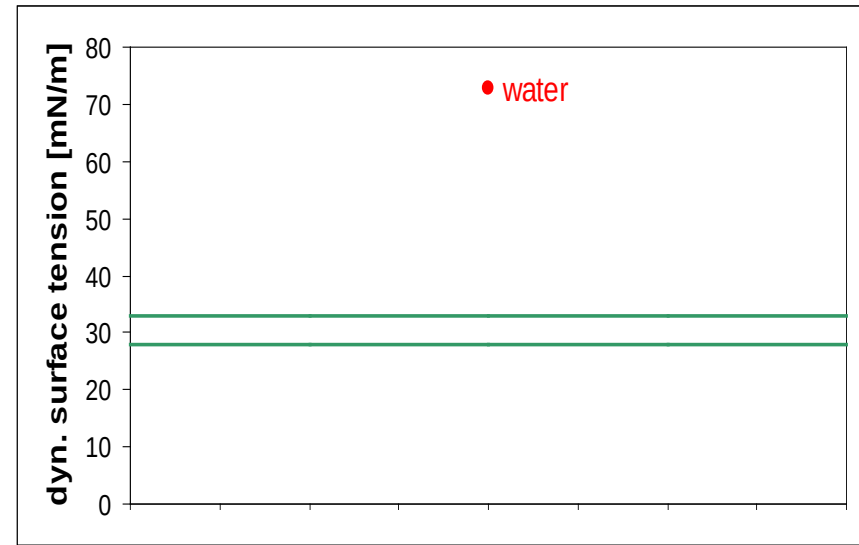
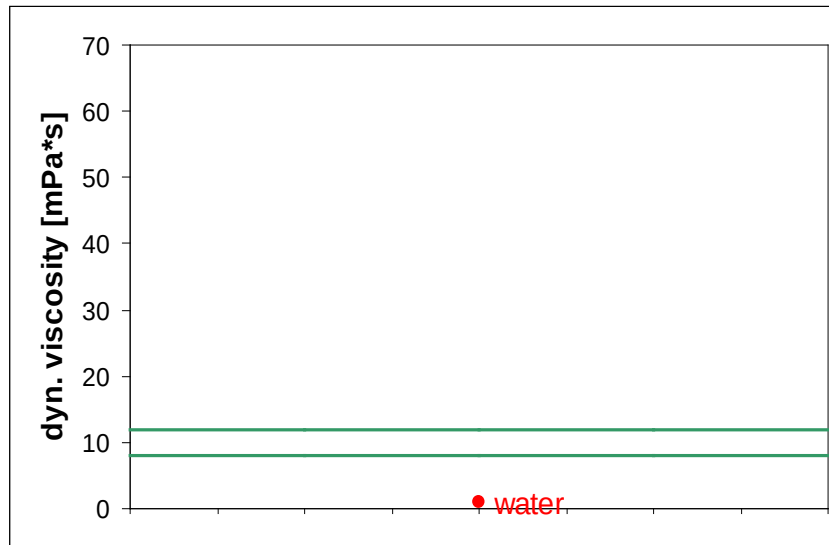


Ink specification

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Overview of the talk

- Demands for ink-jetting of biological probes
- Ink formulation & protein stability
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- (Bio)functional nanoparticles
- Printing
- Evaluation

Ink formulation

Water

(Bio-)functional compound

Viscosity modifier

- Glycerol
- Poly(ethylen glycol) PEG
- Poly(vinyl alcohol) PVA
- Dimethyl sulfoxide DMSO

Surface tension modifier

- surface active compounds
 - detergents
- low surface tension compounds
 - 2-propanol

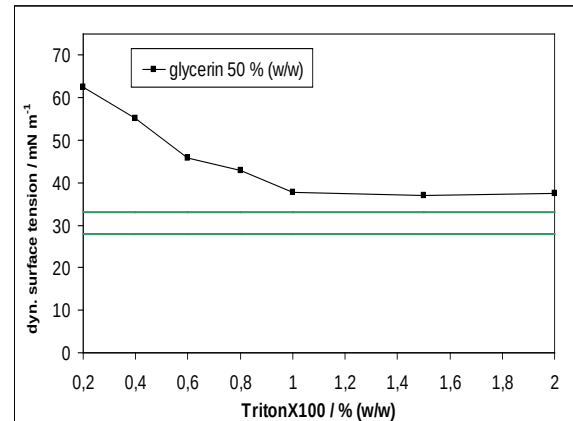
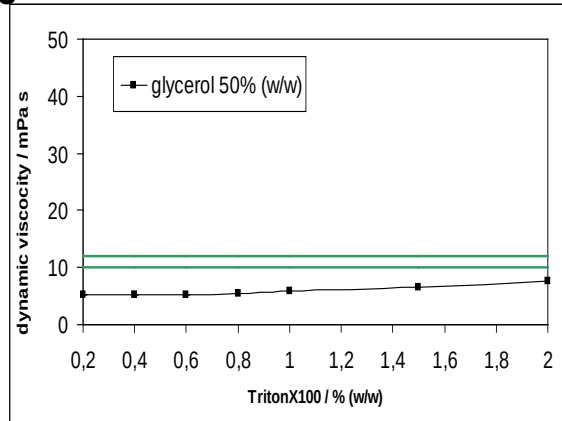
Formulation and characterization of inks

Glycerol / TritonX100

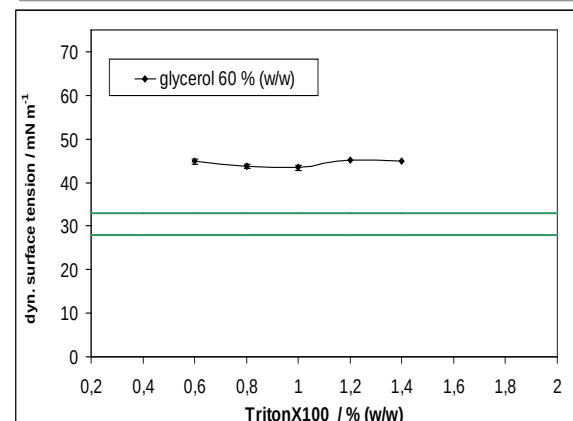
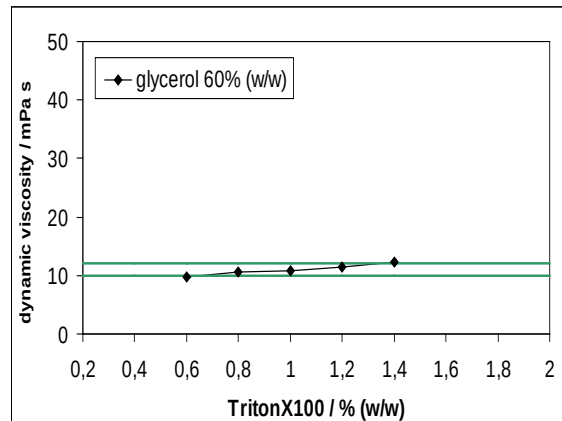
η

σ

50% glycerol



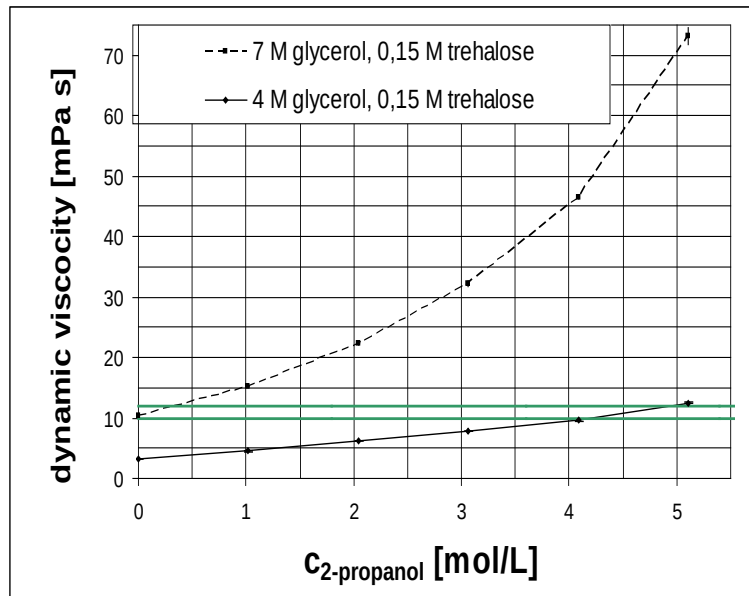
60% glycerol



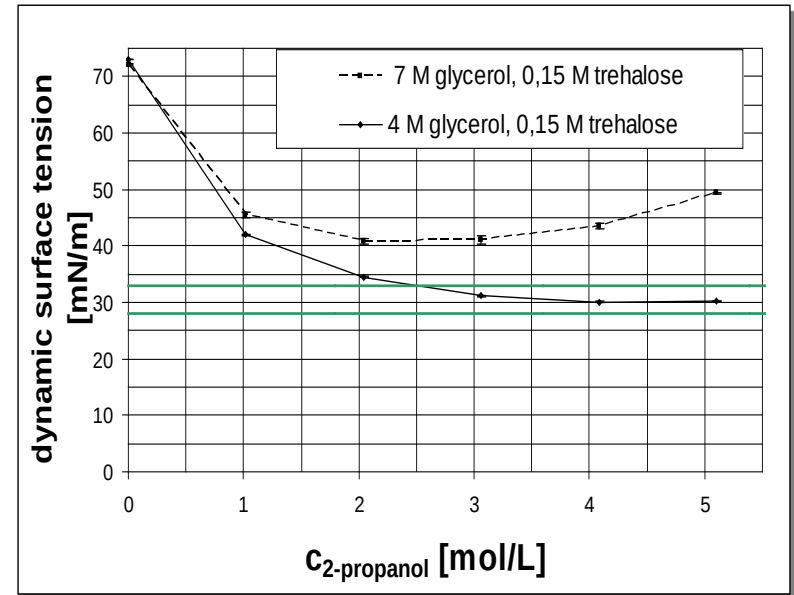
Formulation and characterization of inks

Glycerol / 2-Propanol

η



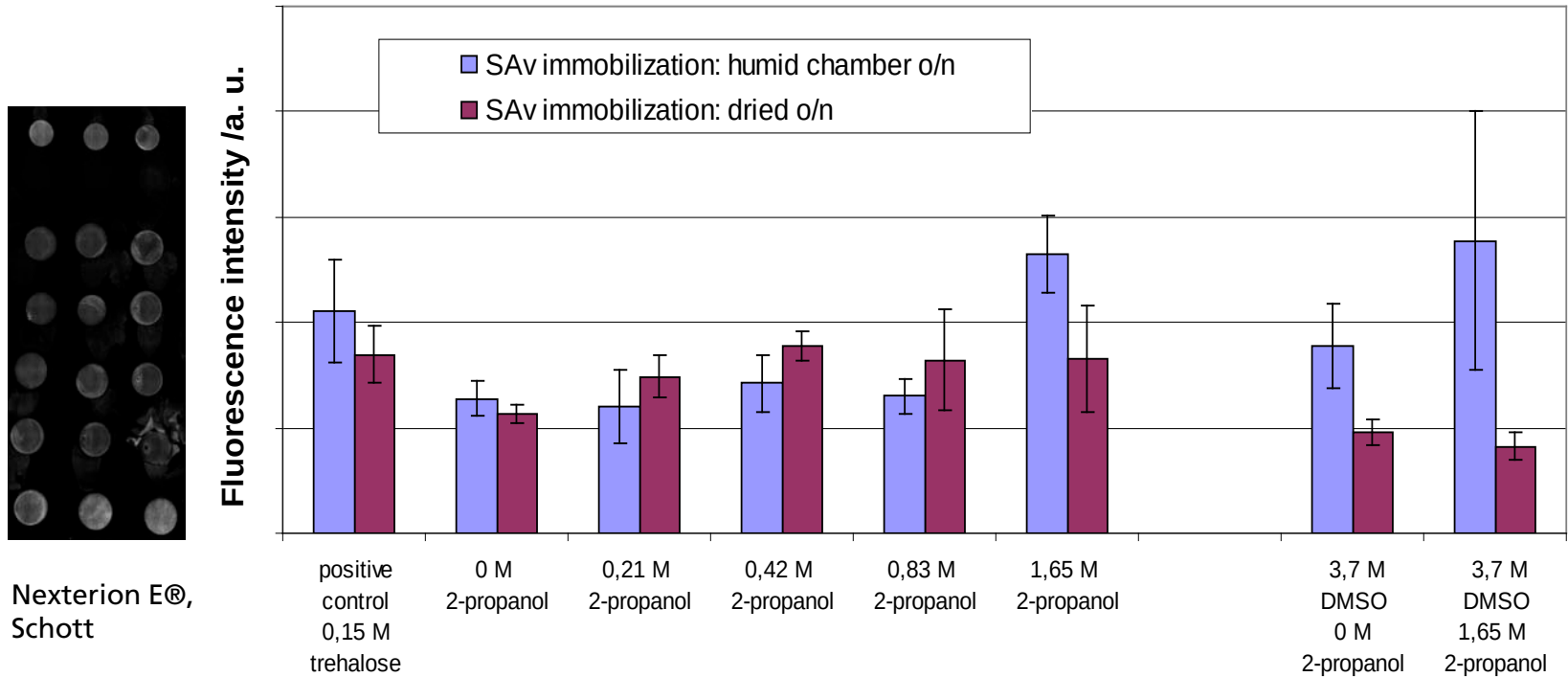
σ



→ 4 M glycerol, 4 -5 M 2-propanol

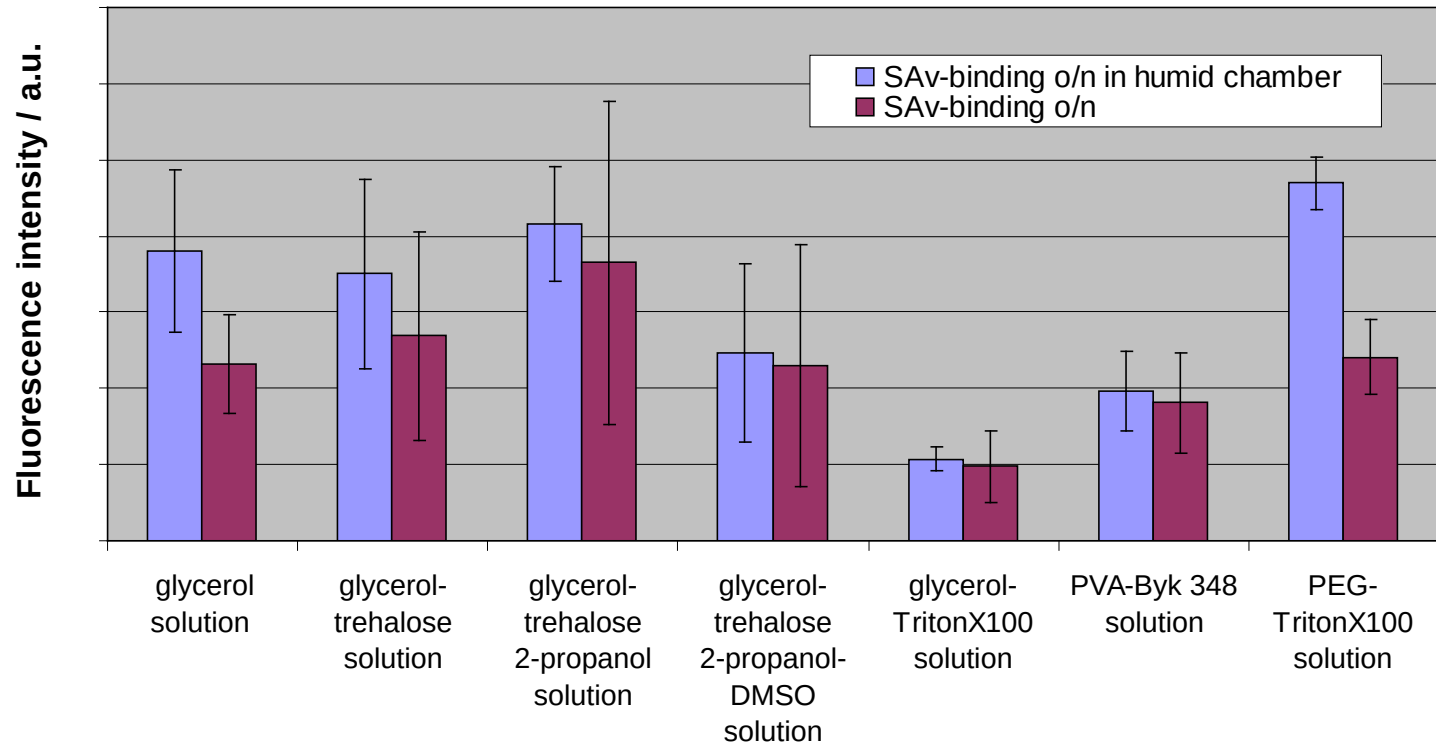
Protein compatibility of ink

Effect of **increasing 2-propanol concentration** on **biotin binding-capability of streptavidin**



Protein compatibility of ink

Biotin binding-capability of streptavidin after deposition in **various ink-compositions**



Substrate wetting: Impact of ink-composition

Nexterion® E surface ($\theta_{\text{water}} = 50^\circ$)

$$\theta_{\text{water/glycerol}} = 52^\circ$$



$$\theta_{\text{water/glycerol/DMSO}} = 38^\circ$$



$$\theta_{\text{water/glycerol/DMSO/alcohol/additive}} = 12^\circ$$

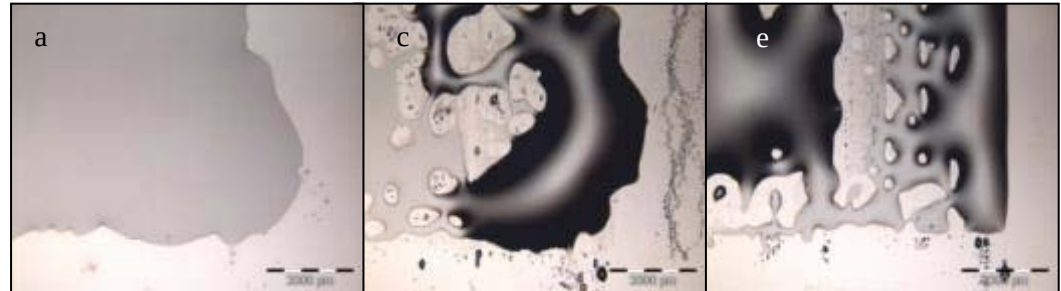


Preparation and characterization of substrates

Ink: 5 M glycerol, 0,15 M trehalose, 3 M 2-propanol

Substrate: TiO_x coated glass slides

drop
spacing
5 μm



drop spacing
10 μm



TiO_x coated glass
cleaned

TiO_x coated glass
polykation (PDADMAC) coated

epoxy-silan (GPTS)
pre-treatment

Pattern generation:

→ **surface-ink interaction (contact-angle)**

→ **volume-deposition per area**

Preparation and characterization of substrates

Wetting behaviour

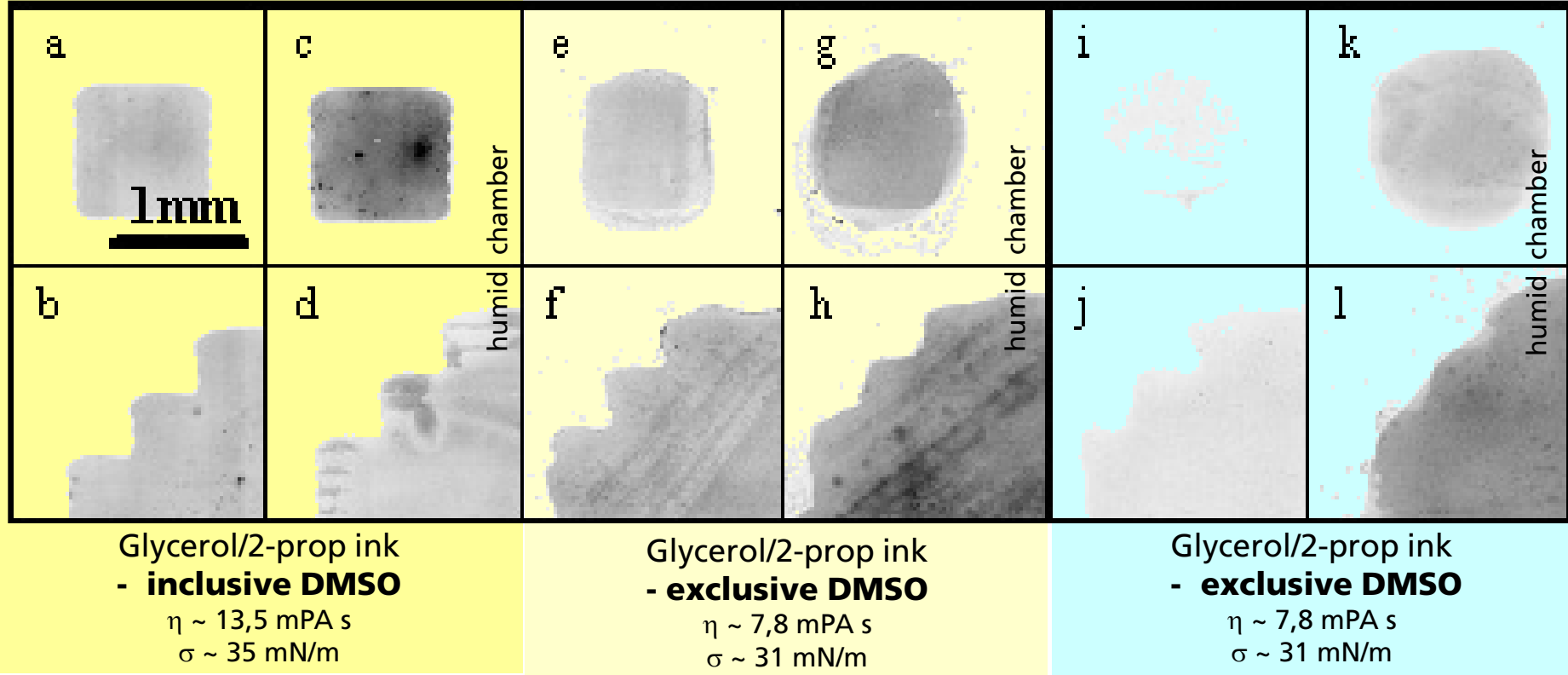
	ddH ₂ O	4 M glycerol, 150 mM trehalose, 3 M 2-propanol	4 M glycerol, 3 M DMSO, 150 mM trehalose, 3 M 2-propanol
interface	contact angle θ		
Nexterion E	$53^\circ \pm 2^\circ$	$23^\circ \pm 3^\circ (+)$	$20^\circ \pm 4^\circ (+)$
glass_PDADMAC	$17^\circ \pm 5^\circ$	$4^\circ \pm 6^\circ (+)$	$14^\circ \pm 14^\circ$
TiO _x _Hellmanex	$21^\circ \pm 4^\circ$	wetting (+)	wetting (+)
TiO _x _PDADMAC	$28^\circ \pm 3^\circ$	$24^\circ \pm 5^\circ (-)$	$25^\circ \pm 9^\circ (-)$
TiO _x _GPTS	$63^\circ \pm 4^\circ$	$35^\circ \pm 6^\circ (-)$	$36^\circ \pm 3^\circ (-)$

Film-formation:

$\theta \ll 25^\circ$

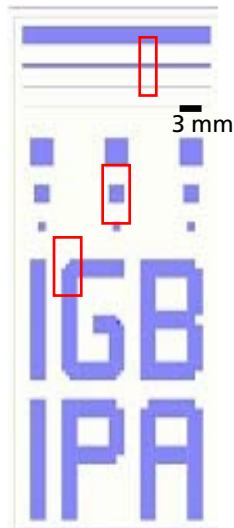
Inkjet printing

← Nexterion E® → PDADMAC (+) →



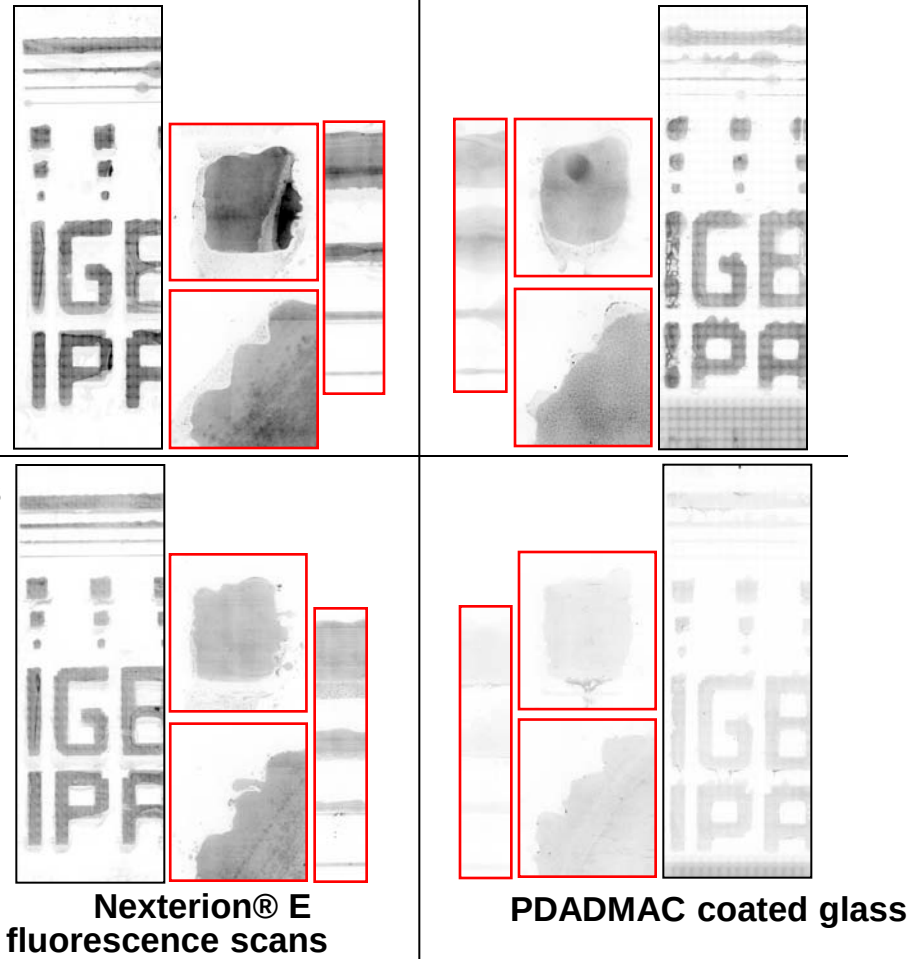
Inkjet printing of streptavidin

$c_{SAV} = 660 \mu\text{g/mL}$
4 M Gly, 2,7 M 2-Prop, 0,15 M Tre
Nexterion® E



humid chamber

ambient conditions



Overview of the talk

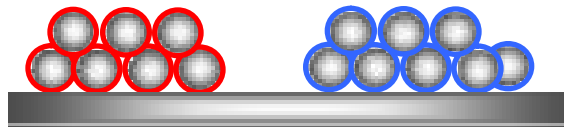
- Demands for ink-jetting of biological probes
- Ink formulation & protein stability
- Substrate preparation
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- Evaluation

NANOCYTES[®]-based Microarrays

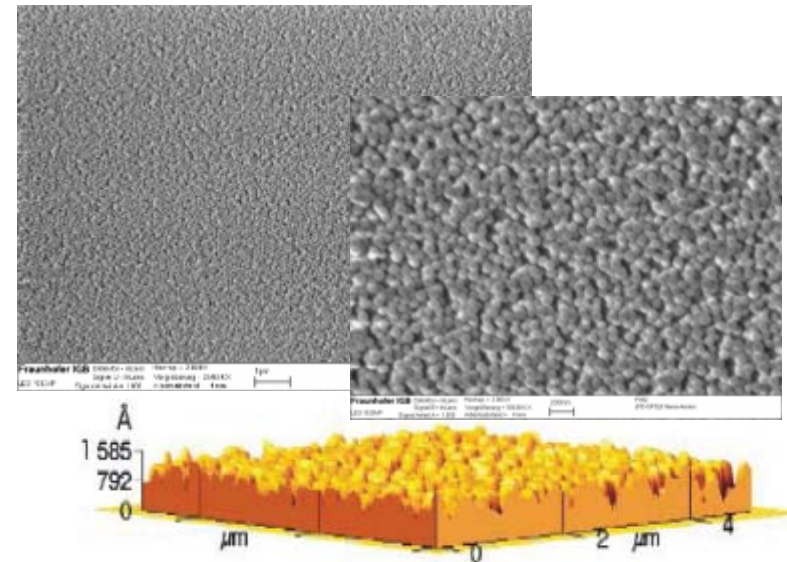
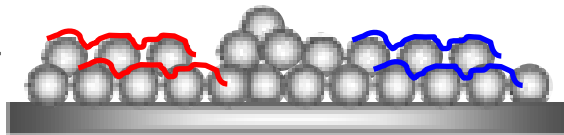
State of the art

Surface-enlargement, flexible surface chemistry

(Bio-)functional
nanoparticles

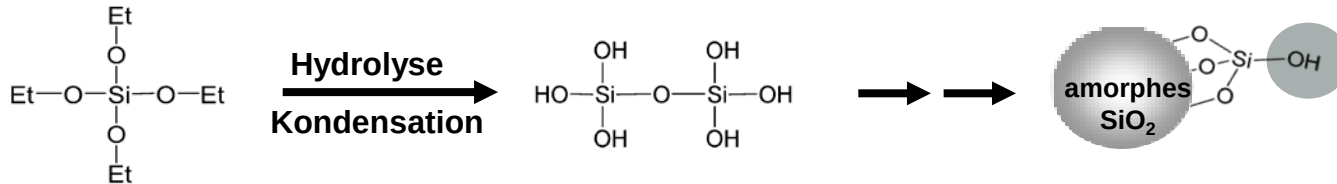


Functional nano-
particle films

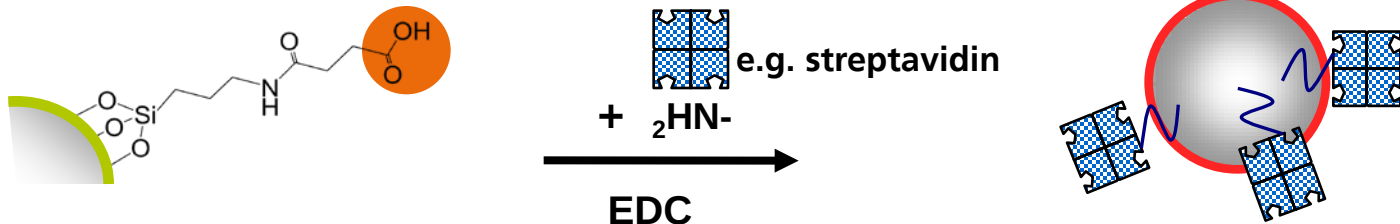
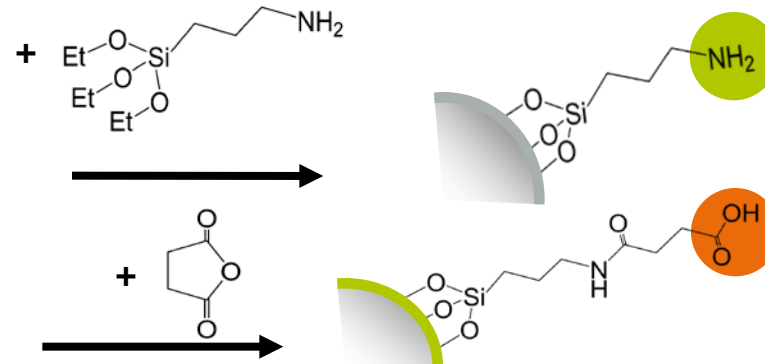
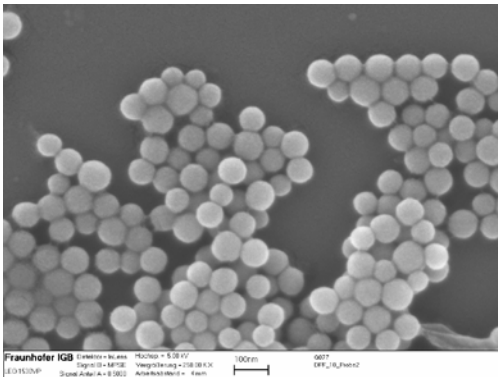


NANOCYTES®: Silica Cores and Functionalization

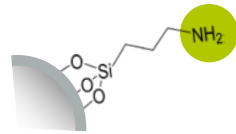
■ Synthesis by Stöber



- Some functionalization



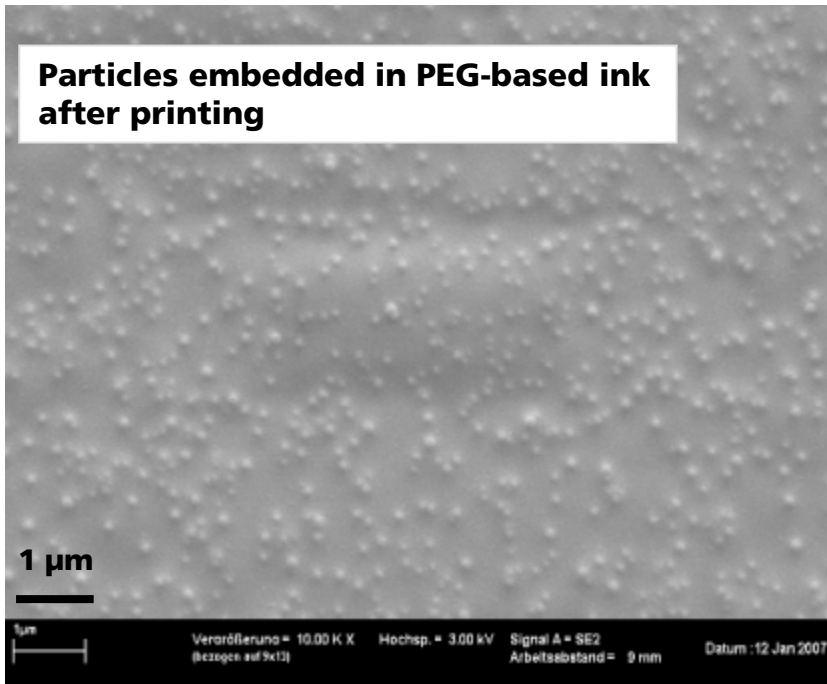
Inkjet printing of functional nanoparticles



$\text{NH}_2 \leftrightarrow \text{NH}_3^+$ modified nanoparticles

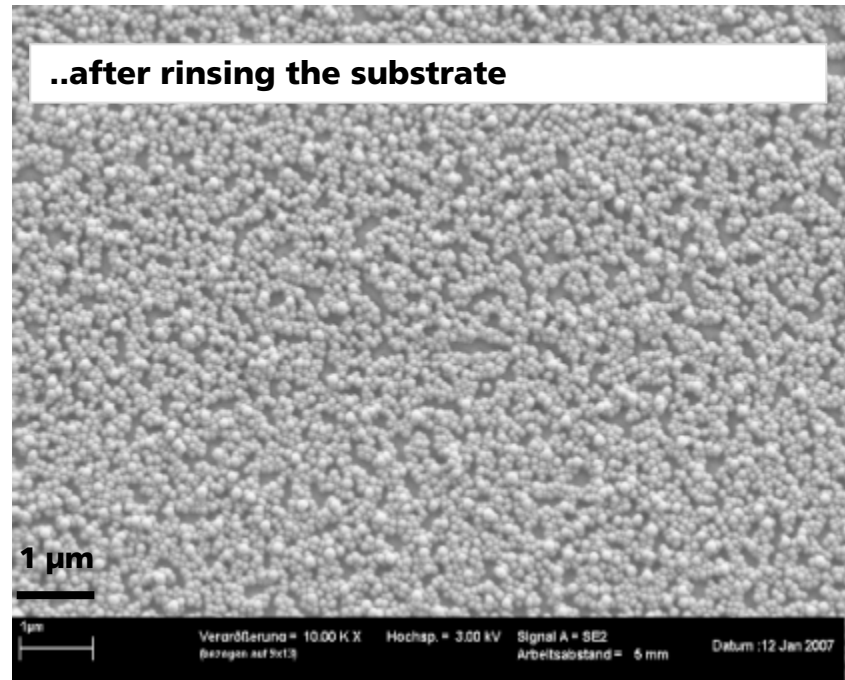
Substrate: SPS (sodium poly(styrene sulfonate)) coated glass

Particles embedded in PEG-based ink
after printing

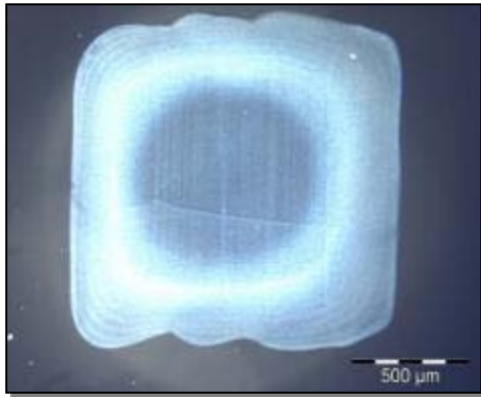
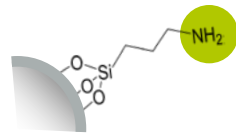


SEM

..after rinsing the substrate



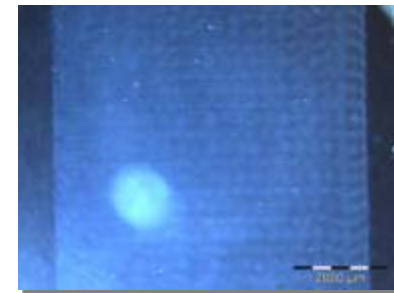
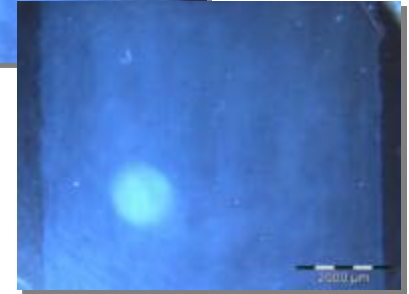
Generating homogeneous particle films



"coffee-ring-"effekt

LM (darkfield modus)

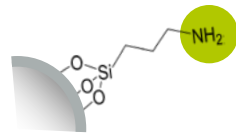
The diagram shows a cross-section of a grey, curved surface representing a substrate. Three oxygen atoms (O) are bonded to the surface, each connected to a central silicon atom (Si). The silicon atom is further bonded to a propyl chain (three carbon atoms in a zig-zag) which terminates in an amino group (NH₂) represented by a green circle.



Overview of the talk

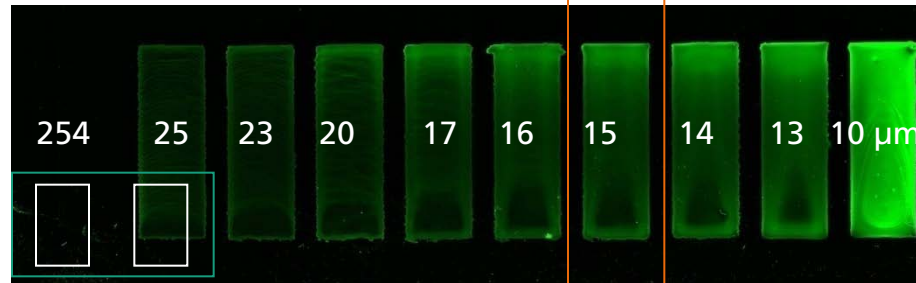
- Demands for ink-jetting of biological probes
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Inkjet printed nanoparticle-silane coatings



532 nm background signal

Silane + nanoparticles



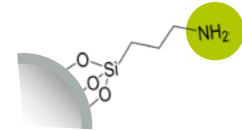
Filter: 532 nm
PMT 400

Pure silane



Variation of drop-spacing (= coating thickness)



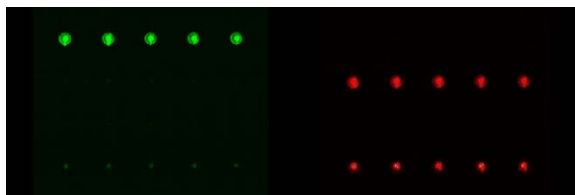
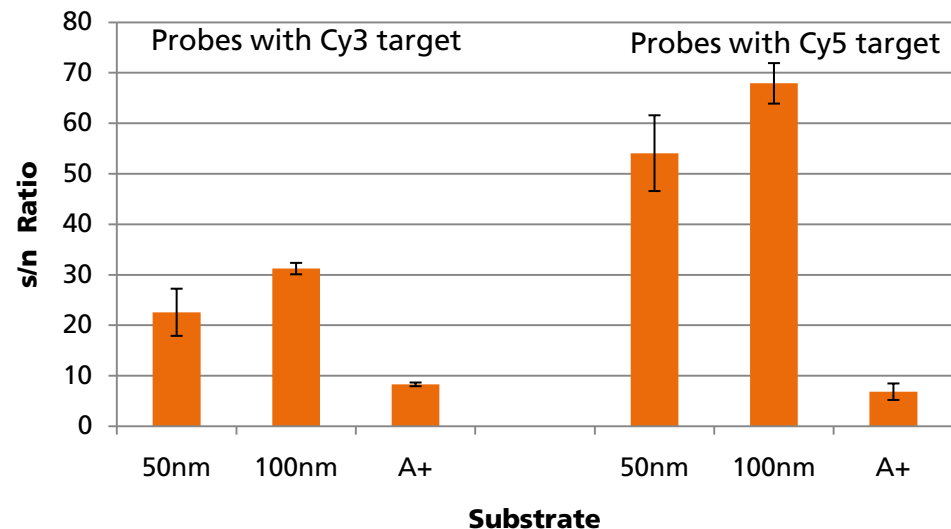


DNA Microarray onto printed particle layers

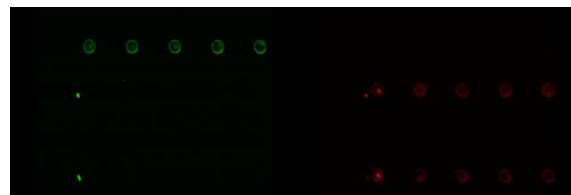
Signal to noise ratio

- Model DNA Microarray with 2 probes, one spotting- and negative control with specific targets at 66°C oN hybridization
- 100 nm und 50 nm nanoparticle layers
- Comparison to Schott Nexterion A+

DNA Microarray (70mere) onto printed amino nanoparticle layers (50 nm and 100 nm)



Slide: 50 nm amino particle



Slide: Schott Nexterion A+

Scan with Axon Genepix 4300A
PMT300, 100% Laserpower

Conclusion

- **Ink formulation**
 - ✓ Inkjet compatible
 - ✓ Bio compatible (SAv)

- **Pattern generation**
 - ✓ Substrate preparation ($\theta \ll 25^\circ$)
 - ✓ Printing parameters
(volume/area, sequential ink deposition)

- **Inkjet printing (bio)functional components**
 - ✓ Amino modified nanoparticle suspension
 - ✓ DNA array
 - ✓ Protein solution

Acknowledgements



Money

BMBF

Fraunhofer Gesellschaft

Collaborations

Dr. Stefan Güttler (Fraunhofer IPA)

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(all University of Stuttgart)

