



# INNOVATIVE METAL AND SEMICONDUCTOR NANOSTRUCTURES FOR (BIO)-PHOTONIC APPLICATIONS

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# Outline

1. Self-Organization of Silver and SERS
2. Silicon NanoStructures for Cancer Theranostics

# Philosophy

## Newton's Law of Gravity

$$F_g = G \frac{m_1 m_2}{r^2}$$



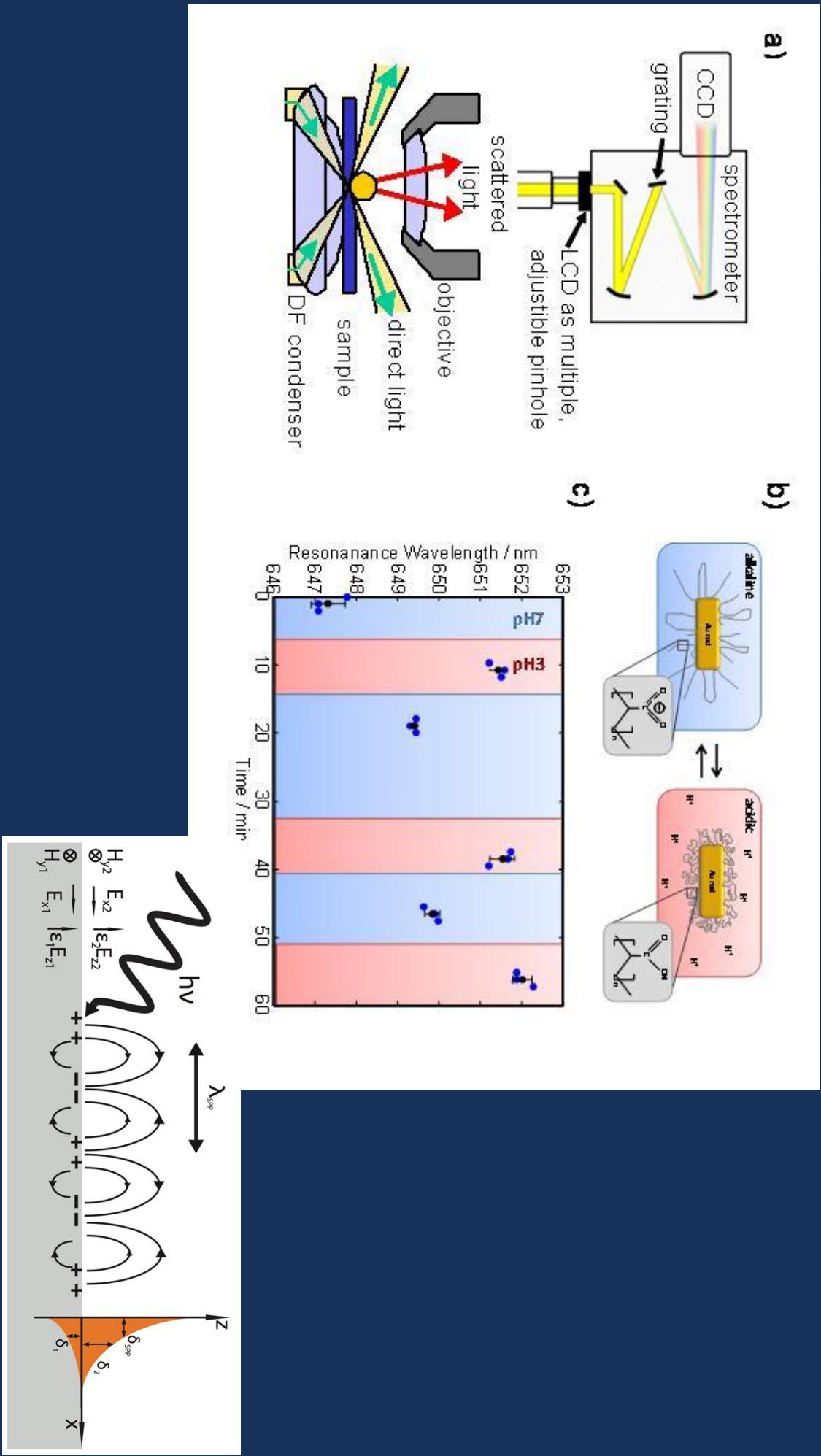
The famous story that Newton came up with the idea for the law of gravity by having an apple fall on his head is not true, although he did begin thinking about the issue on his mother's farm when he saw an apple fall from a tree.



Friedrich August Kekulé said that he had discovered the ring shape of the benzene molecule after having a reverie or day-dream of a snake seizing its own tail (this is a common symbol in many ancient cultures known as the Ouroboros). This vision, he said, came to him after years of studying the nature of carbon-carbon bonds.

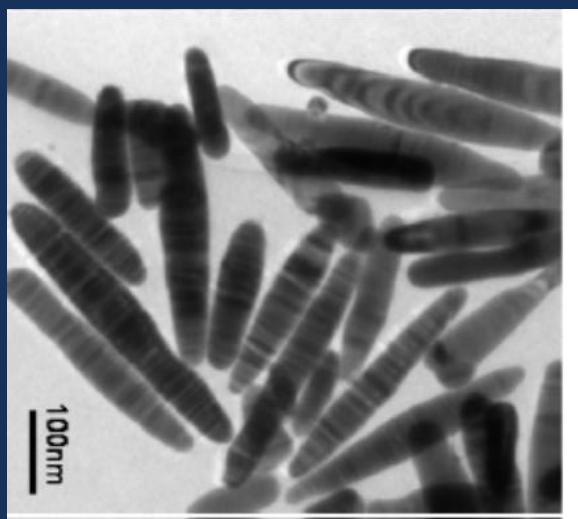
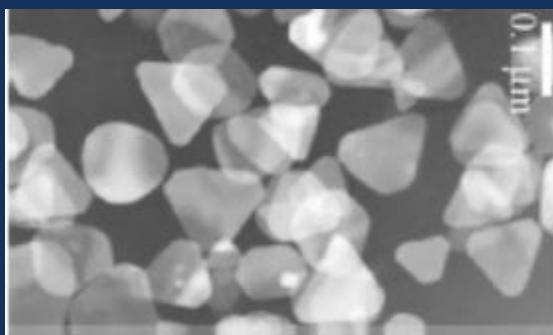
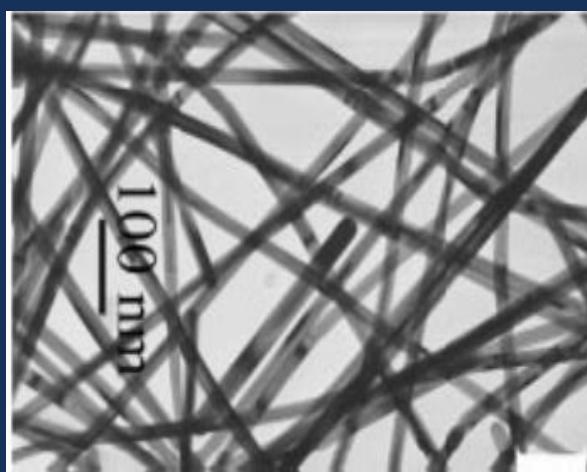
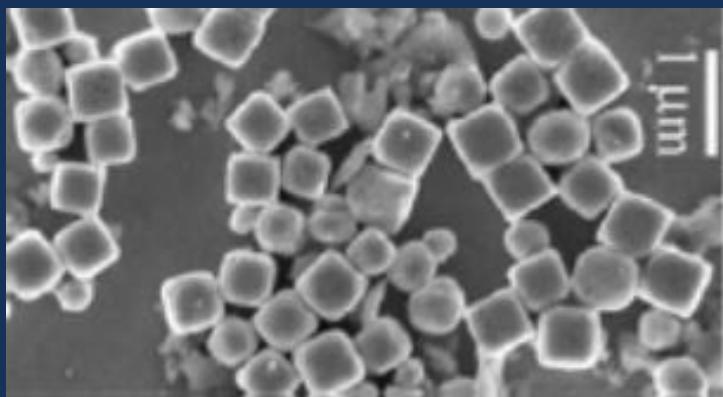
## Observation of NATURE

# SERS Sensoric



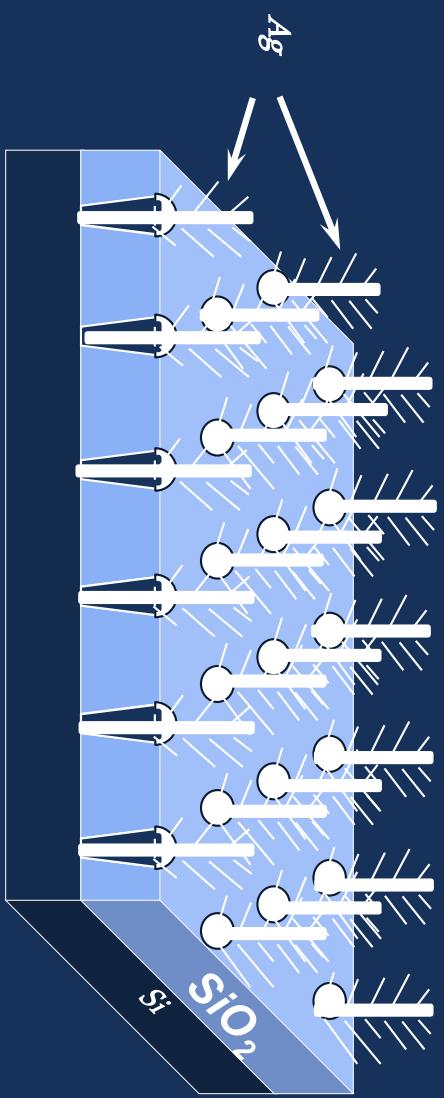
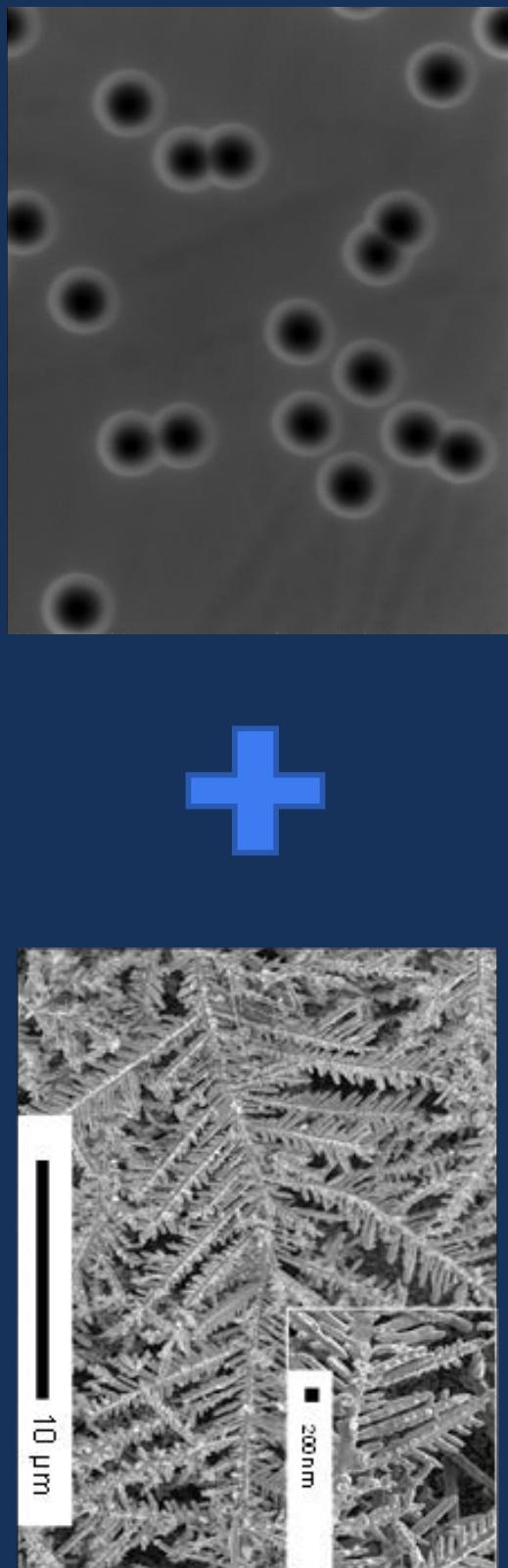
I.Ament, J. Becker, C. Sönnichsen, Molecular Plasmonics 2009,  
Jena/Germany, 14-16.05.2009

# Silver Nanostructures



X. Sun, Y. Li, *Adv. Mater.* 17, 2626 (2005); H. Liang, H. Yang, W. Wang, J. Li, H. Xu, *J. Am. Chem. Soc.* 131, 6068 (2009); C. Marchal-Roch, C.M. Mayer, et al., *Chem. Commun.* 36, 3750 (2007); J. Zhang, H. Liu, P. Zhan, Z. Wang, N. Ming, *Adv. Funct. Mater.* 17, 1558 (2007); S.E. Skrabalak, L. Au, X. Li, Y. Xia, *Nature Protocols* 2, 2182 (2007); B.K. Jena, B.K. Mishra, S. Bohidar, *J. Phys. Chem. C* 113, 14753 (2009)

# Silver Plasmonic Nanosructures



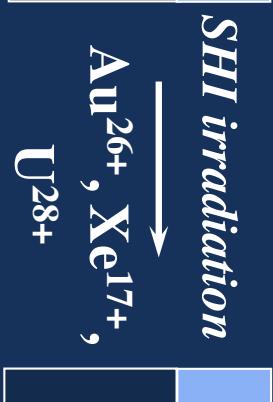
Porous  $\text{SiO}_2$  template on  $\text{Si}$  substrates with  $\text{Ag}$ -dendrites

# Swift Heavy Ion Track Technology

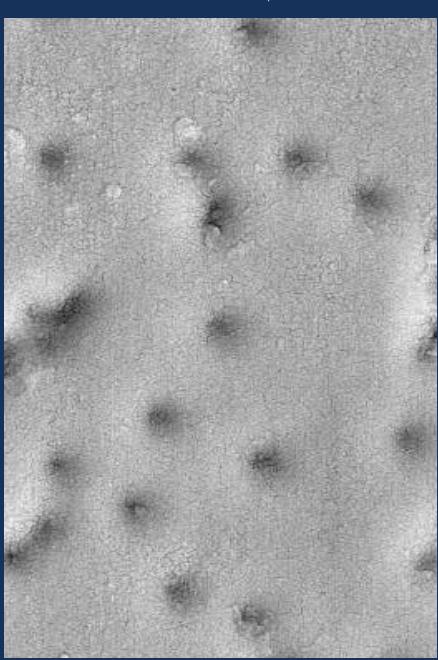
*Si/SiO<sub>2</sub> substrate*



*Latent SHI tracks*



← Au<sup>26+</sup>, Xe<sup>17+</sup> →  
Energy 350 MeV,  
Fluence 5 × 10<sup>8</sup> cm<sup>-2</sup>



Ch. Trautmann, in *Ion Beams in Nanoscience and Technology*, R. Hellborg et al. (eds.),  
2009, Springer, 369.

Dr. Vladimir Sivakov, IPHT

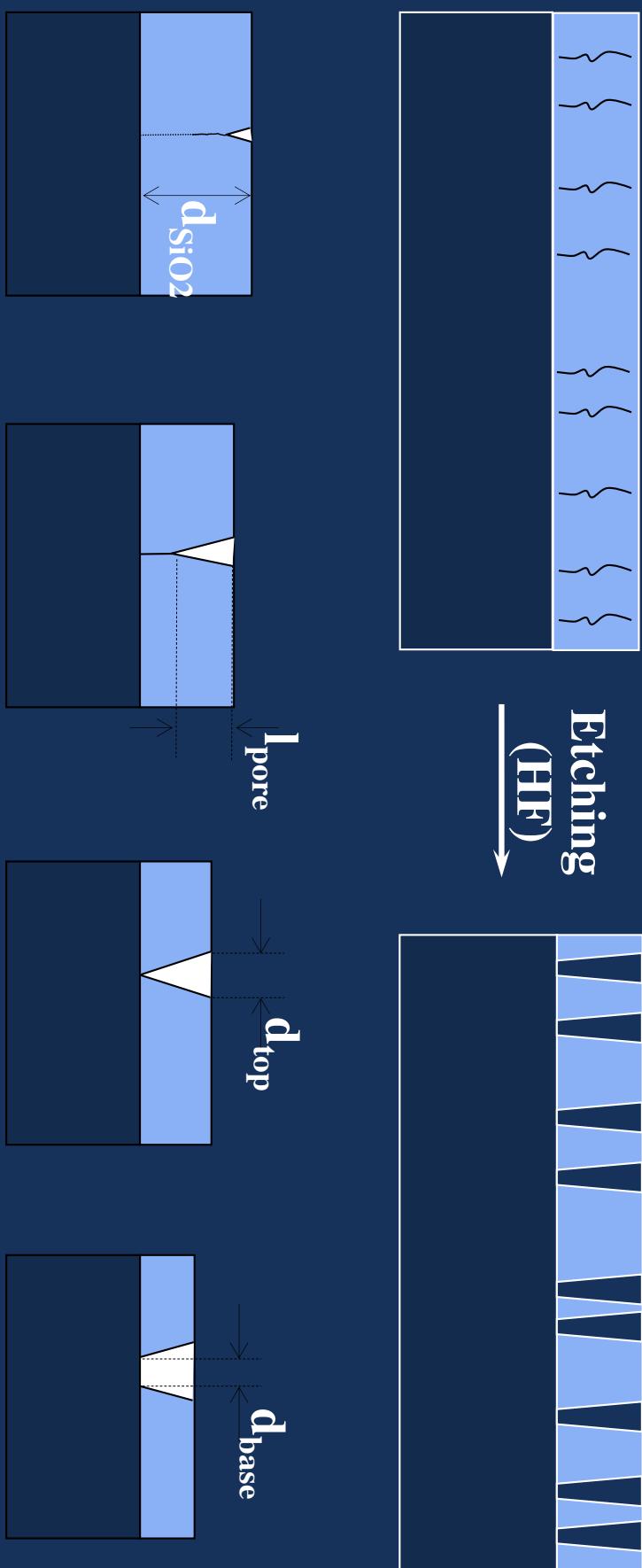
06.03.2014

# Swift Heavy Ion Track Technology

## Latent SHI tracks

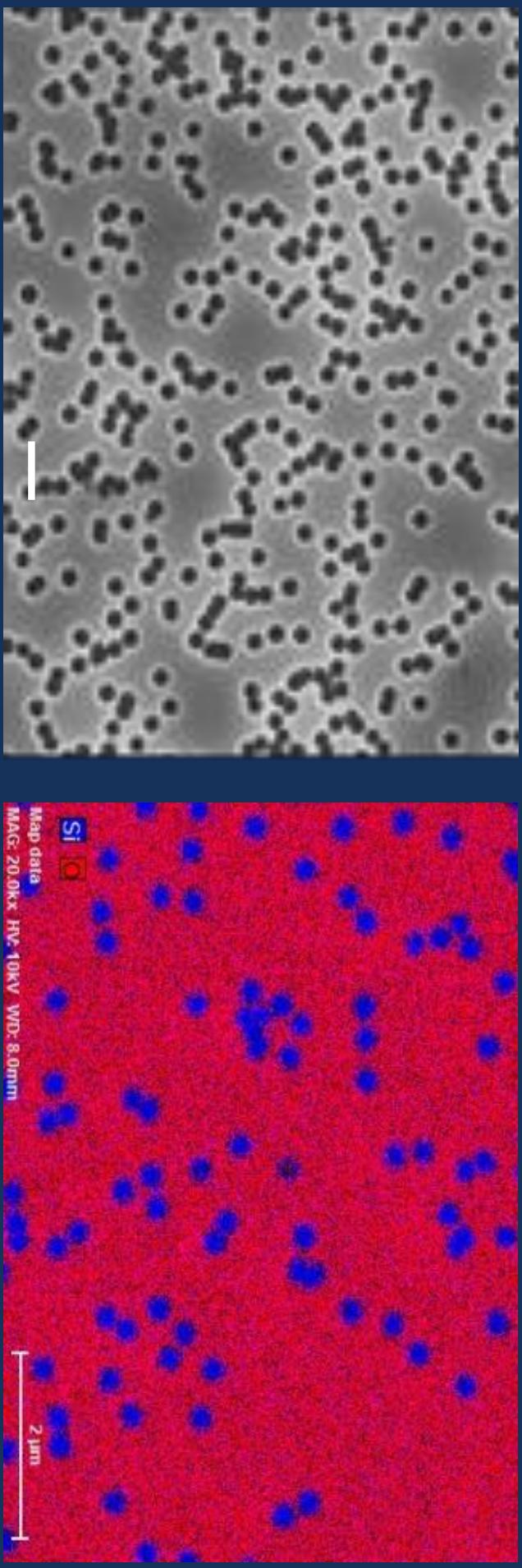
## Etched SHI tracks

Etching  
(HF)



D. Fink, Fundamentals of Ion-Irradiated Polymers Springer Series in Materials Science 2004, 63,  
Springer, 391.

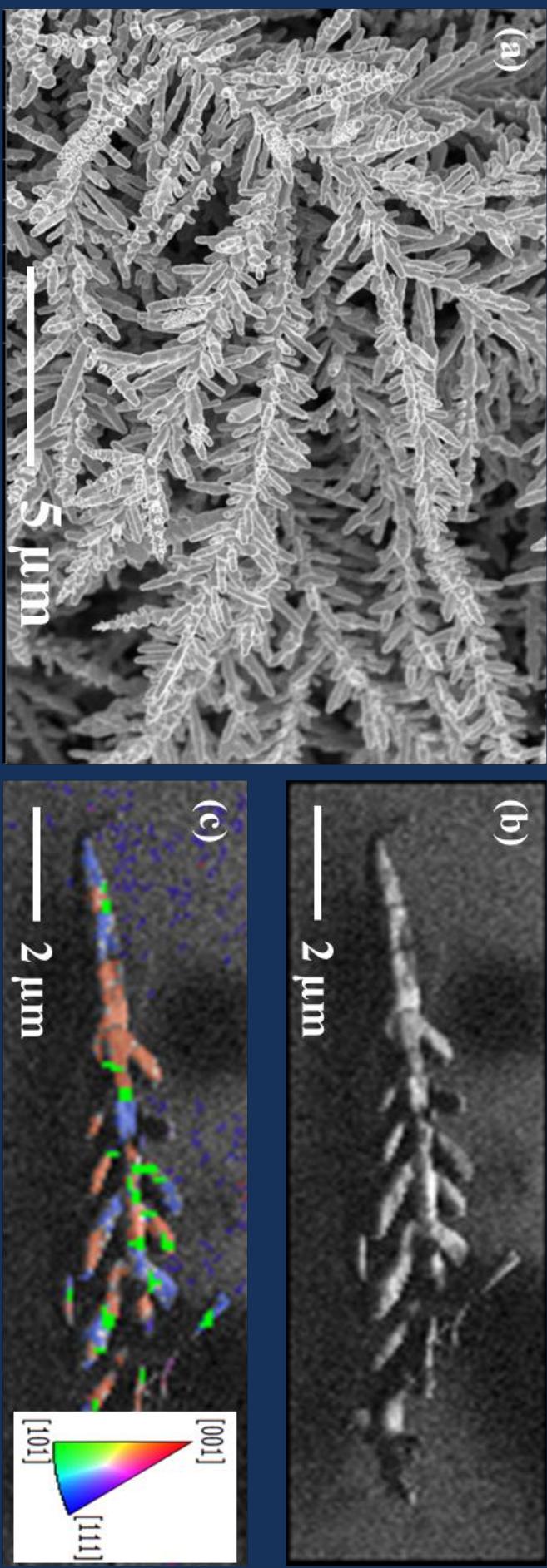
# Swift Heavy Ion Track Technology



planar scanning electron microscopy micrograph and (b) element map (blue: silicon; red: oxygen) from energy dispersive X-ray analysis of a Si/SiO<sub>2</sub> sample irradiated with 350 MeV gold ions and exposed to chemical track etching

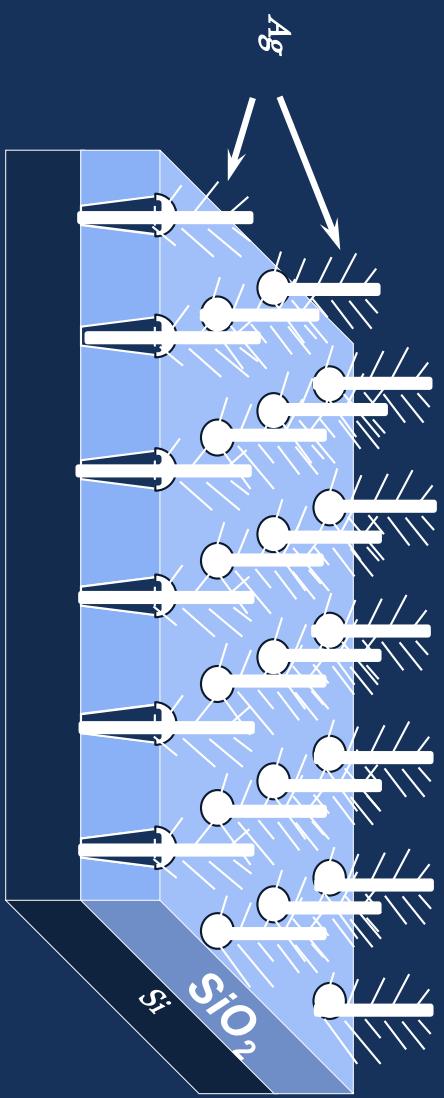
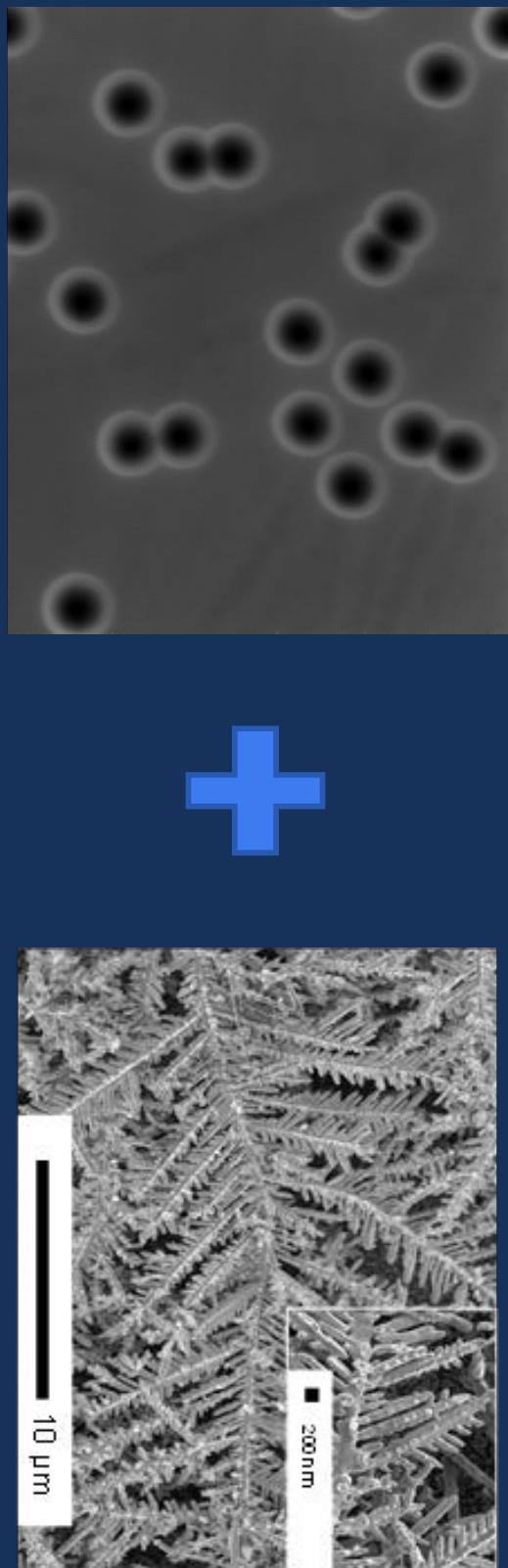
V. Sivakov et al., submitted 2014

# Swift Heavy Ion Track Technology



(a) SEM micrographs of silver dendrite nanostructure on n-Si (100) grown for 30 s at atmospheric conditions; (c) EBSD analysis of single silver dendrite; colour coded inverse pole figure representation.

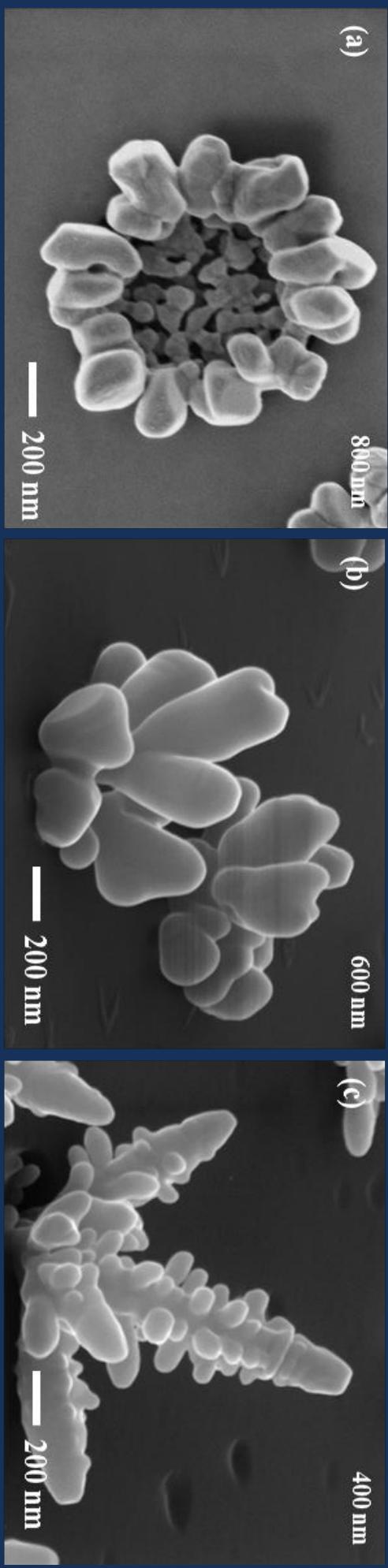
# Silver Plasmonic Nanosructures



Porous  $\text{SiO}_2$  template on  $\text{Si}$  substrates with  $\text{Ag}$ -dendrites

# Silver Plasmonic Nanosrtructures

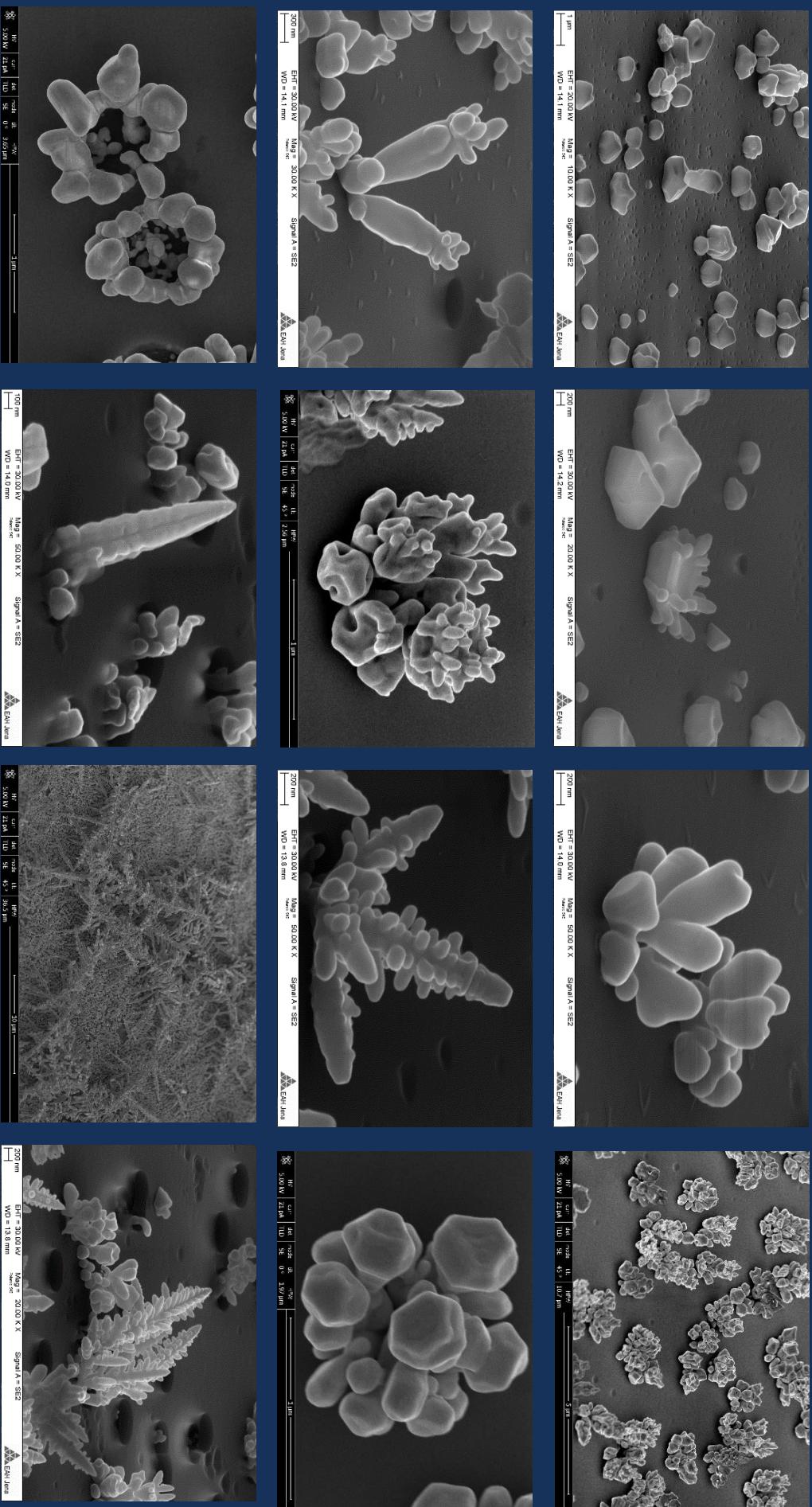
Decreasing of pore top diameter



SEM micrographs of silver nanostructures with (a) “sunflower”, (b) “azalea” and (c) “corn”-like shapes.

V. Sivakov et al., submitted 2014

# The diversity of the Ag-structures

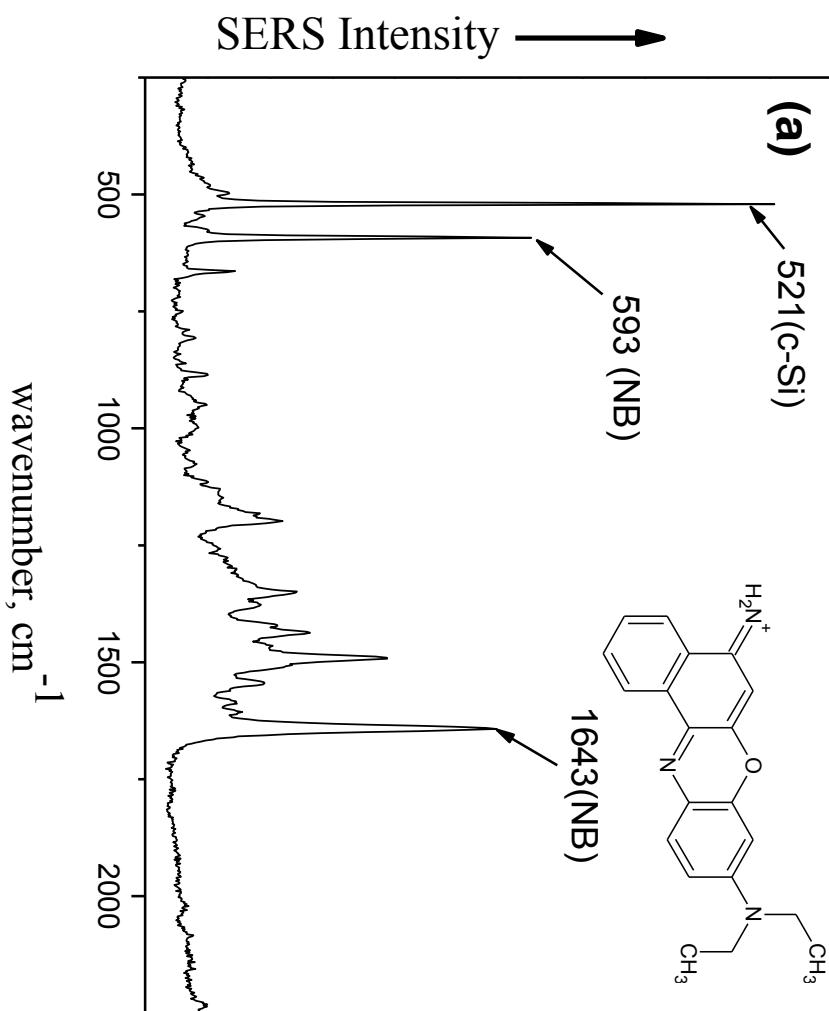


# Silver Plasmonic Nanosructures

(b)



(a)



# Outline

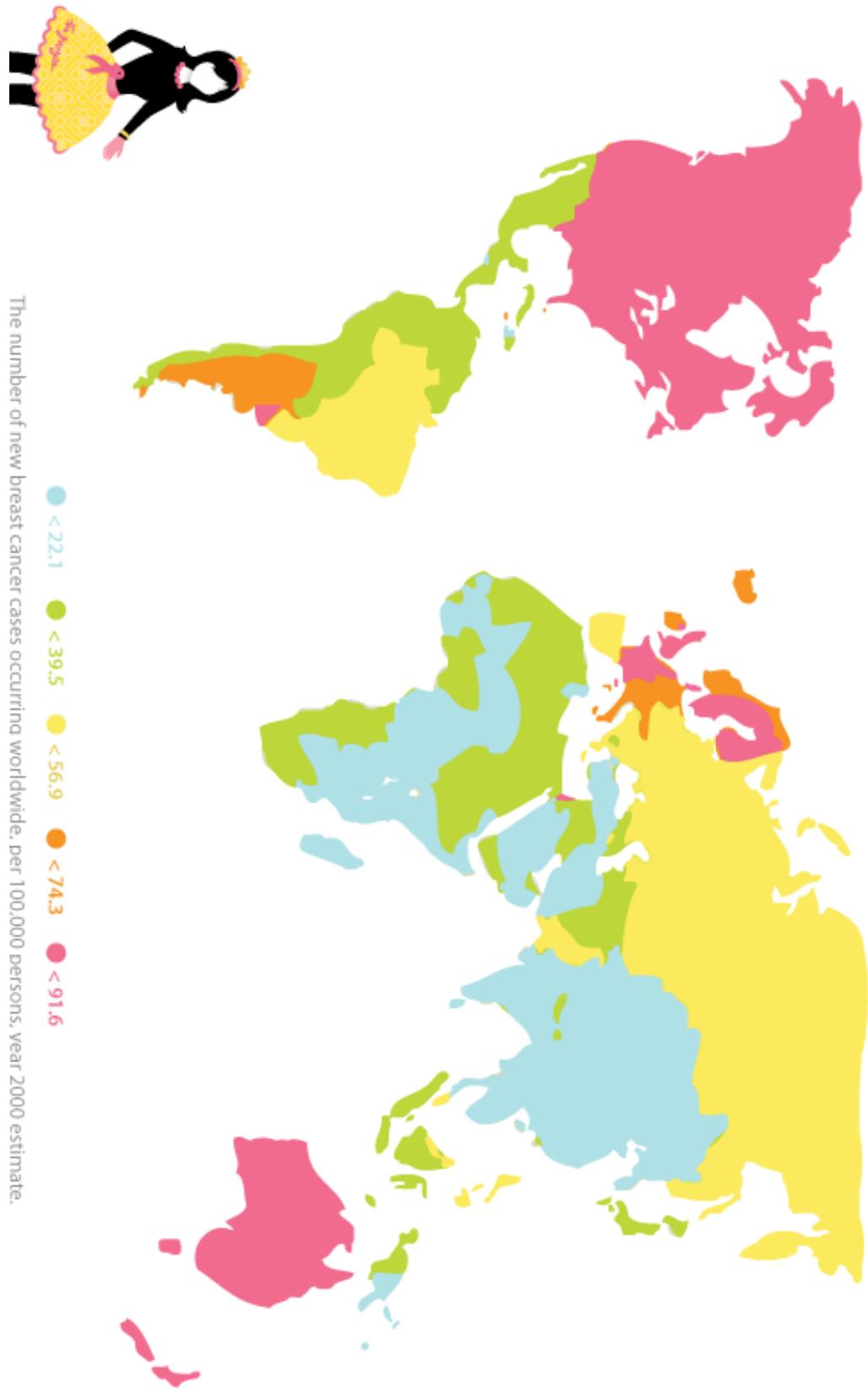
1. Self-Organization of Silver and SERS
2. Silicon NanoStructures for Cancer Theranostics

# Introduction



- Silicon (**Si**) is the 1-st element for semiconductor microelectronics and solar cells
- Si constitutes above 27 % of the mass of Earth crust (the 2-nd element after oxygen)
- Si content in a normal healthy adult body (70 kg) is about 0.5-1 g, which makes this element to be the 3rd most abundant trace mineral (after Fe and Zn)

# Breast Cancer

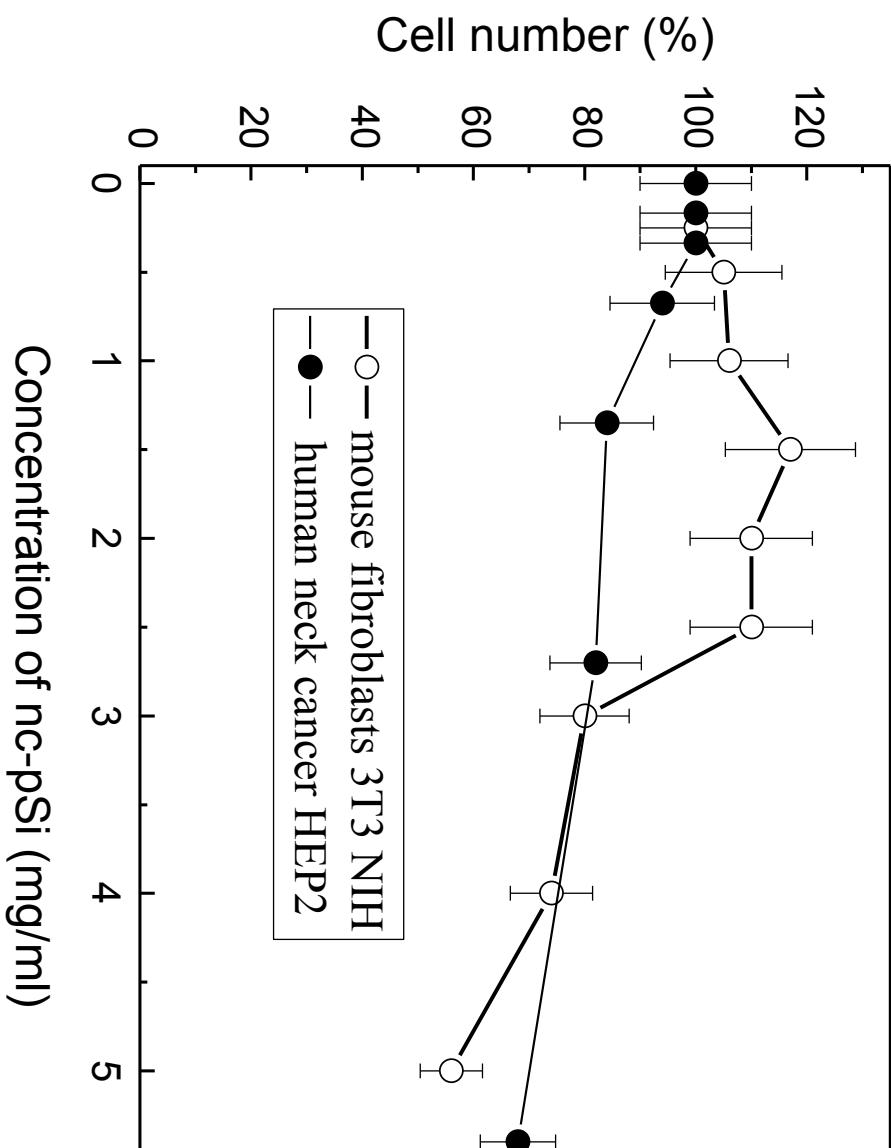


The number of new breast cancer cases occurring worldwide, per 100,000 persons, year 2000 estimate.

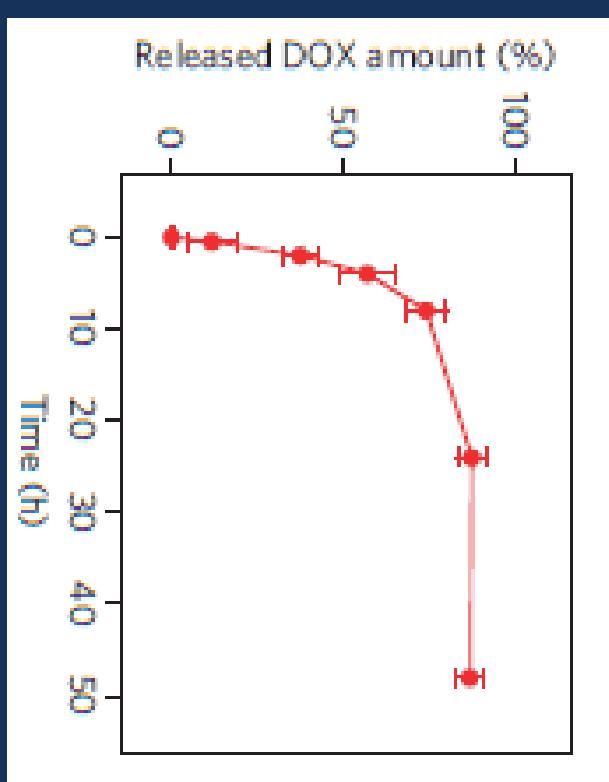
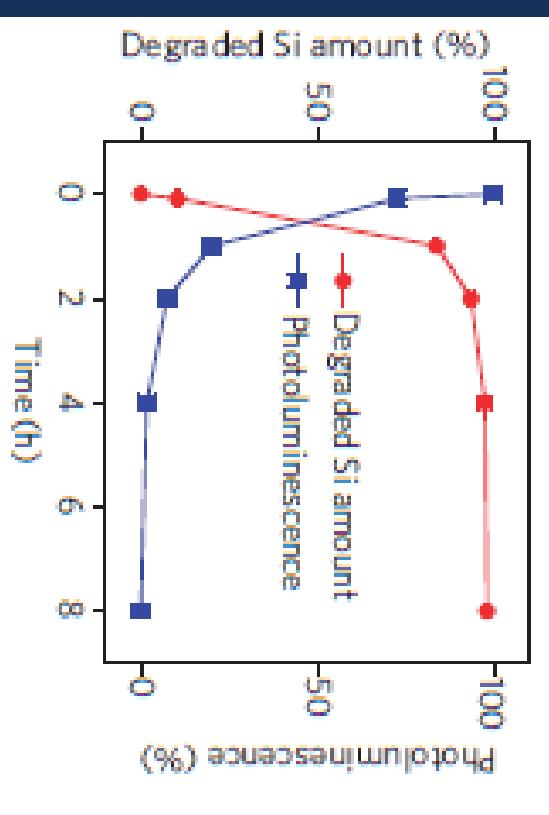
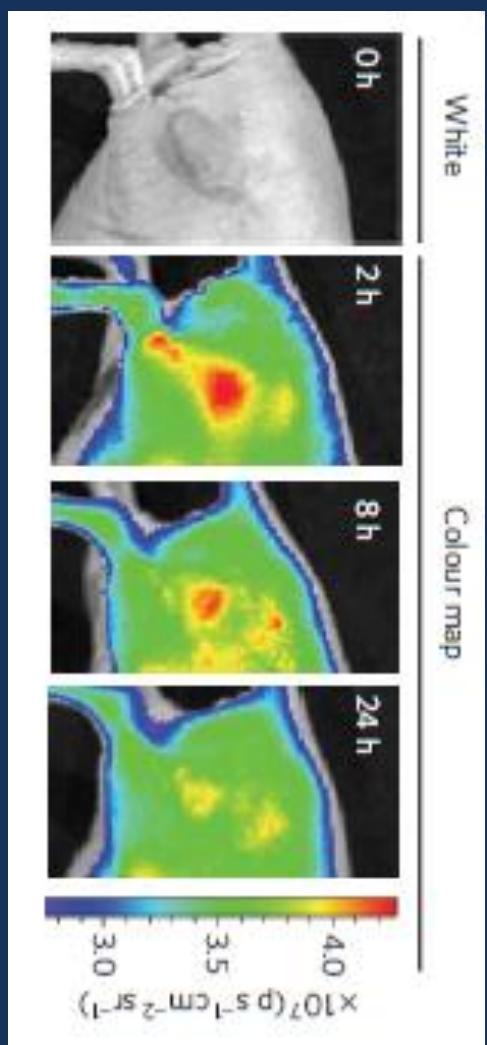
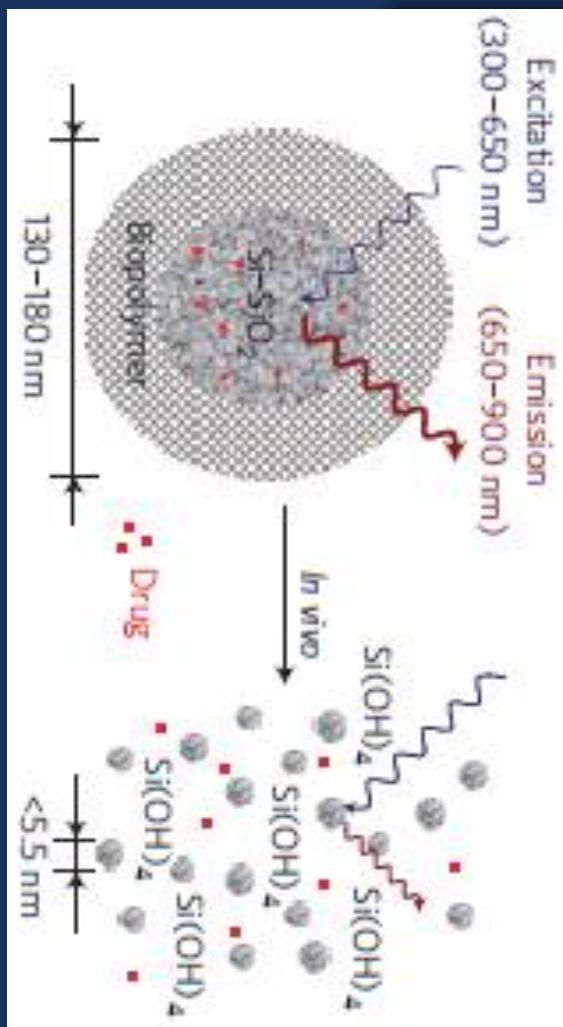
**World Health Organization, Breast Cancer Facts & Figures 2011-2012,**  
<http://www.cancer.org/acs/groups/content/@epidemiologysurveillance/document/acspc-030975.pdf>

# Concentration dependence of citotoxicity of Si nanoparticles

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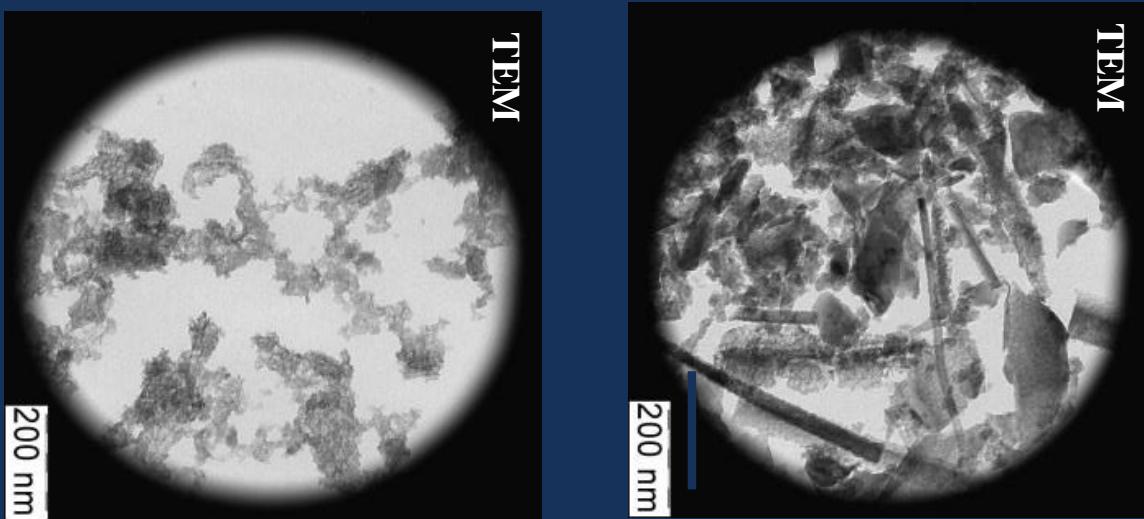
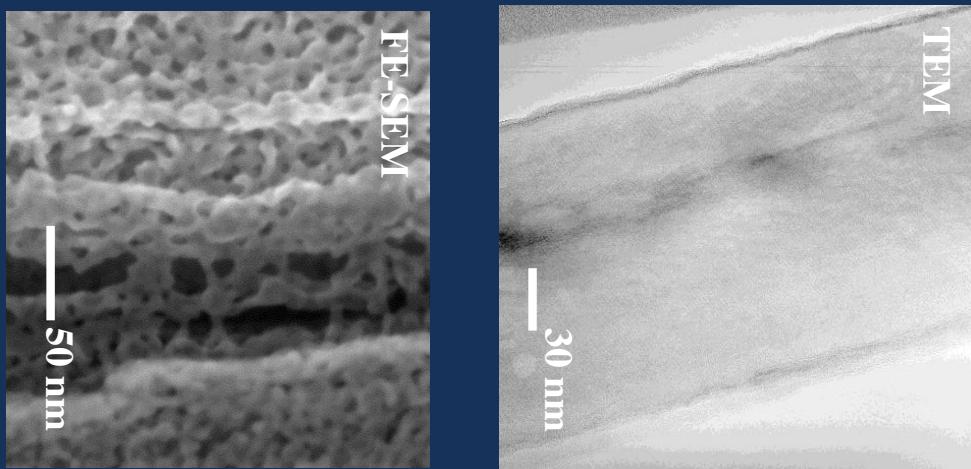
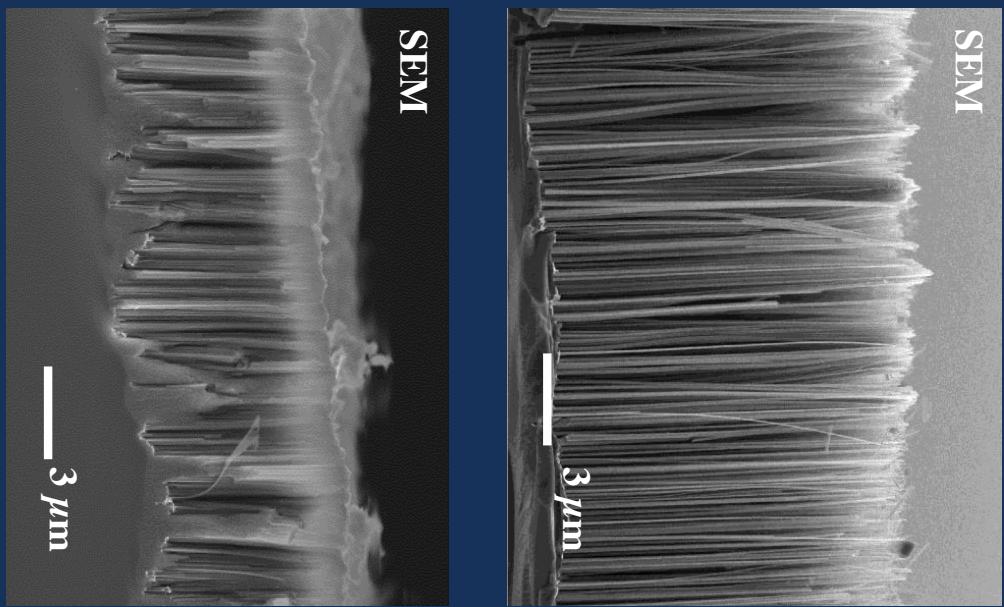


# Bio-degradation Porous nc-Si

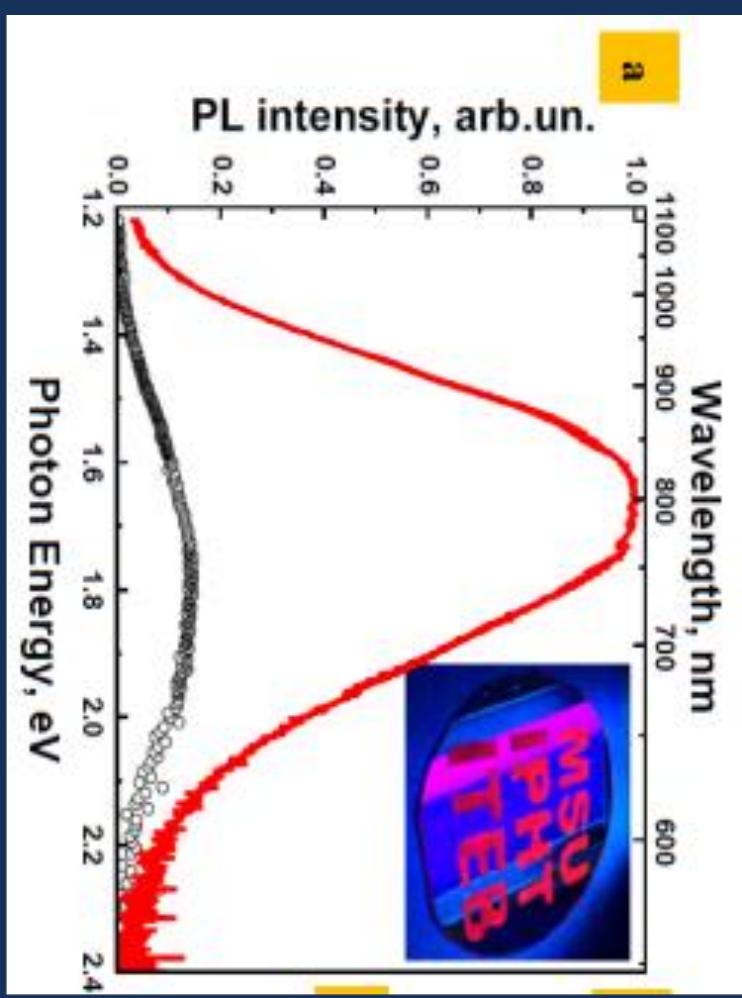


# How to visualize *Si nanoparticles?*

# Top-Down Silicon Nanostuctures

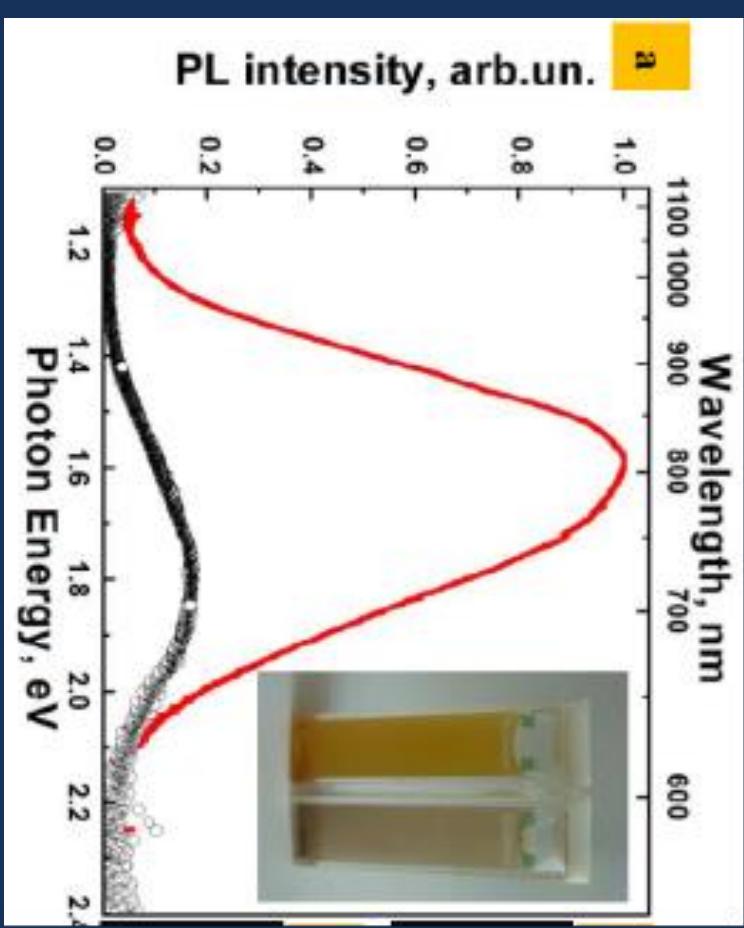


# Top-down: Wet-Chemical Etching

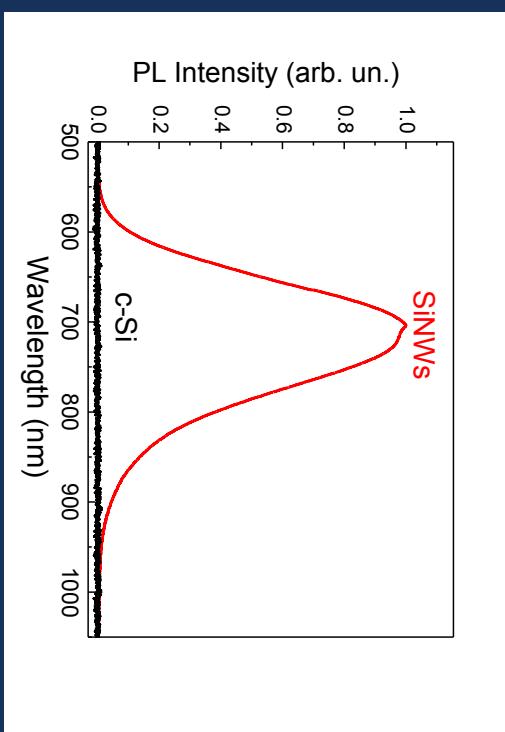
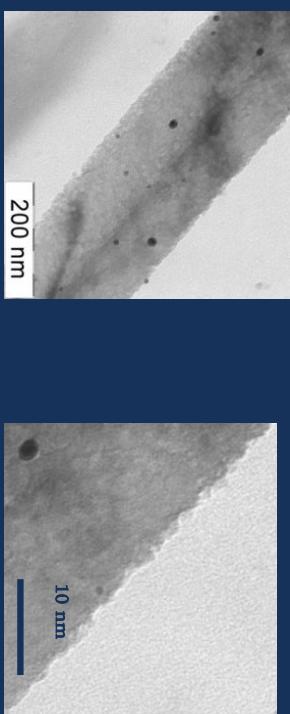


V.A. Sivakov et al. Phys. Rev. B 82, 125446(2010)

K. A. Gonchar et al., J. Nanoelectr. Optoelectr. 7(6), 602 (2012)



SiNW Length < 200 nm



Photoluminescent images of CF2Th (dog thymus) cells with SiNWs. Green, blue, and red colors correspond to the PL of cell membrane, cell nucleus, and SiNWs, respectively.

V.A. Sivakov et al., *Phys. Rev. B* 82, 125446 (2010)

K. Gonchar et al., *Journal of Nanoelectronics and Optoelectronics* 6(4), 519-524 (2011)

Dr. Vladimir Sivakov, IPHT

L.A. Osminkina et al., *Nanoscale Research Letters* 7, 524 (2012)

# Bioimaging with SiNWs

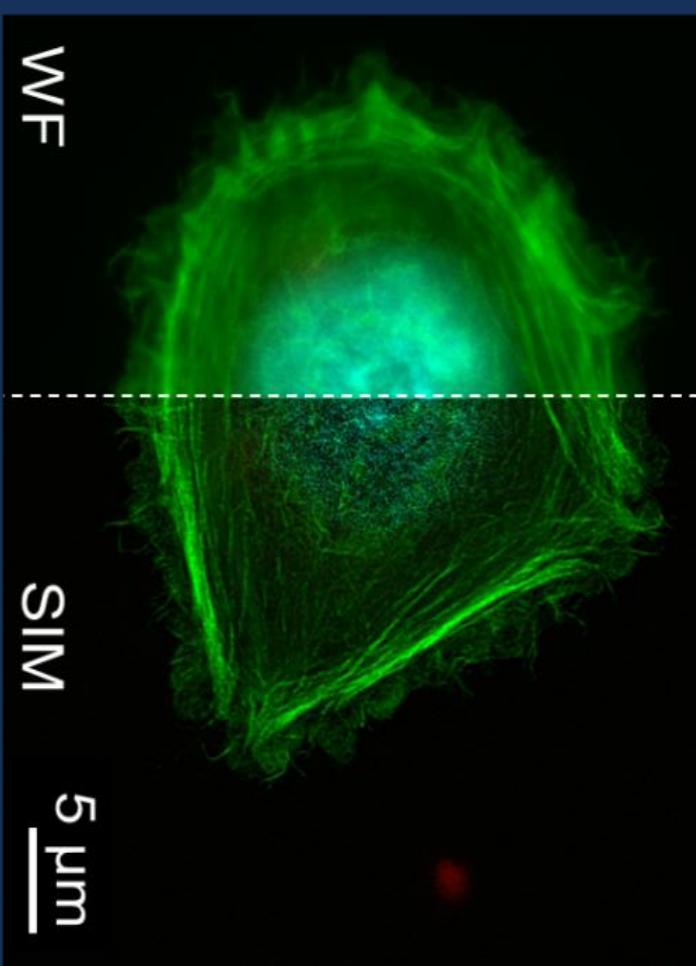
- Cell line: **MCF-7** (*Michigan Cancer Foundation - 7*)  
a breast cancer cell line

- Labeling:

405nm – cell nucleus: DAPI

488nm – cell body: Calcein AM

561 nm / 642nm – Si

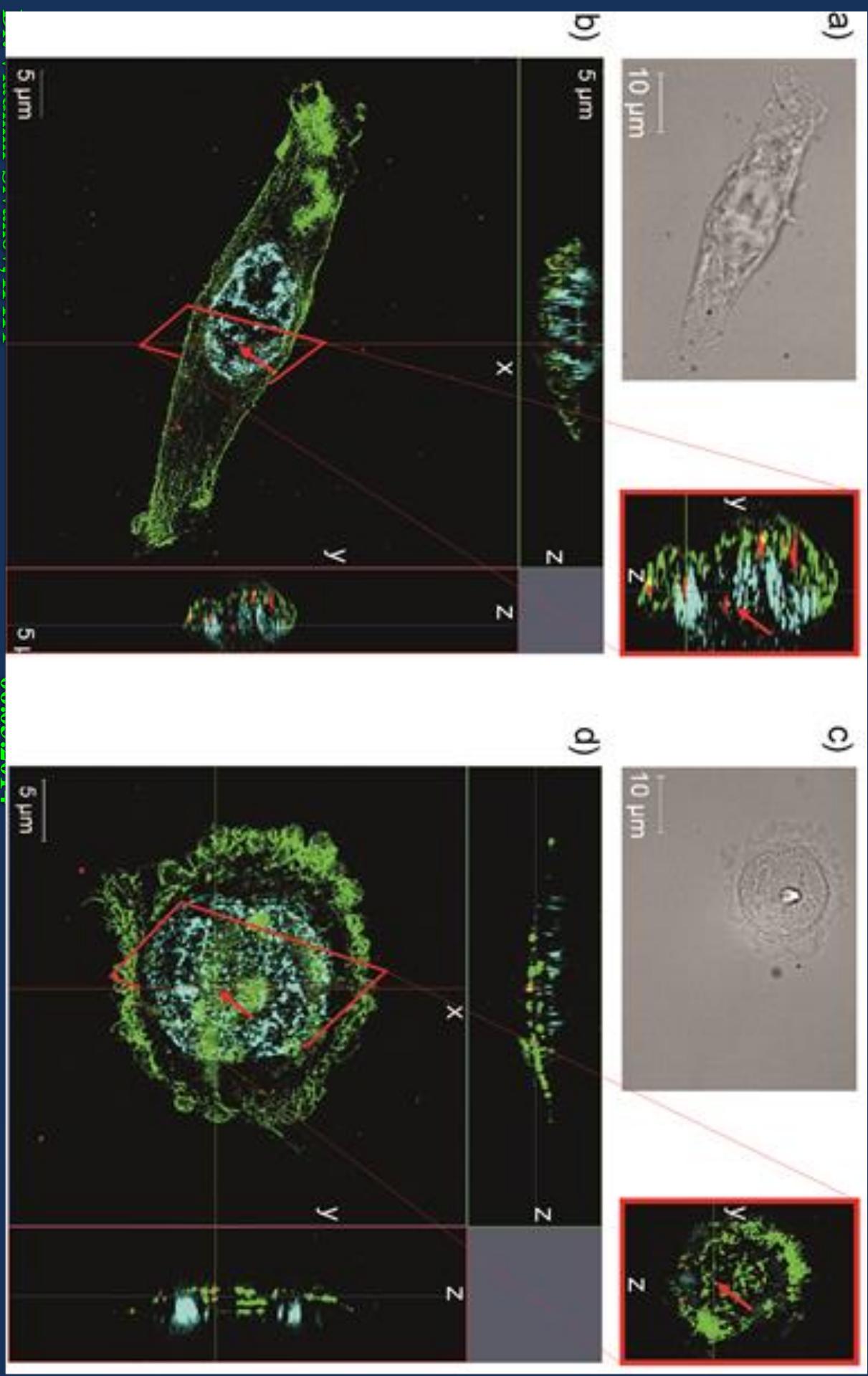


Wide-field (WF, left) and SIM (right) imaging of MCF-7 cells transfected with Cy5-coupled siRNA-peptide complexes

- A. Jost und R. Heintzmann, *Annu. Rev. Mater. Res.*, Bd. 43(1), 261, 2013.  
L. Schermelleh, R. Heintzmann, und H. Leonhardt, *J. Cell Biol.*, 190( 2), 165, 010.  
Dr. Vladimir Sivakov, IPHT  
06.03.2014

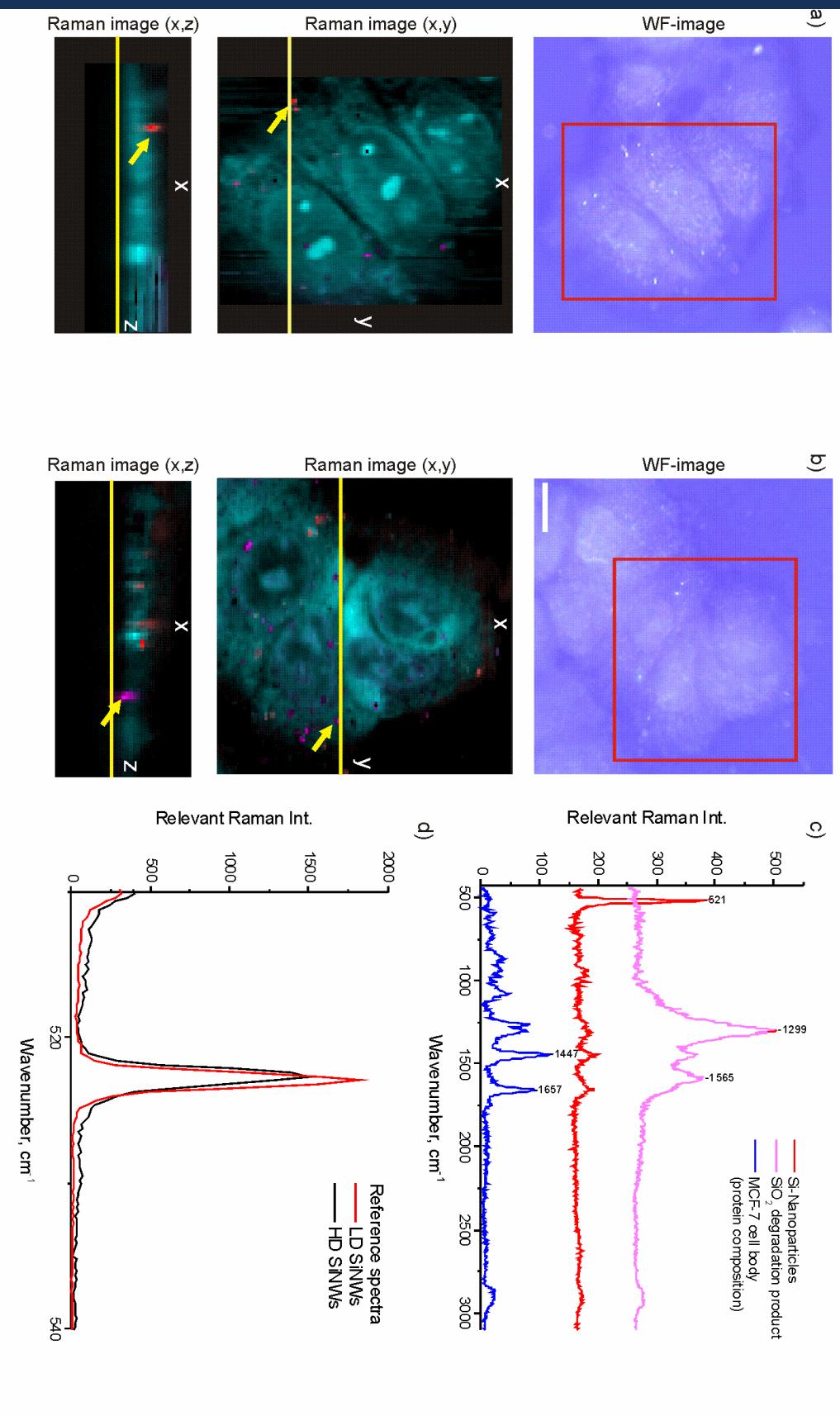
# Bioimaging with SiNWs

SIM image of MCF 7 cells (green) +Si HD (red)  
(24h incub. + Calcein AM)



# Bioimaging with SiNWs

## Non-invasive Raman Imaging



E. Tolstik et al., in press (2014).

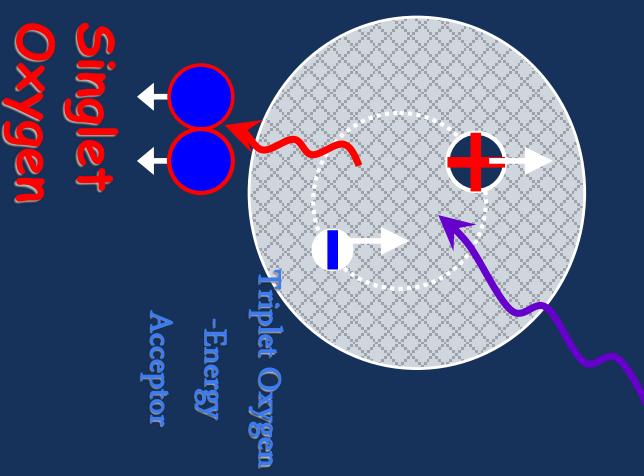
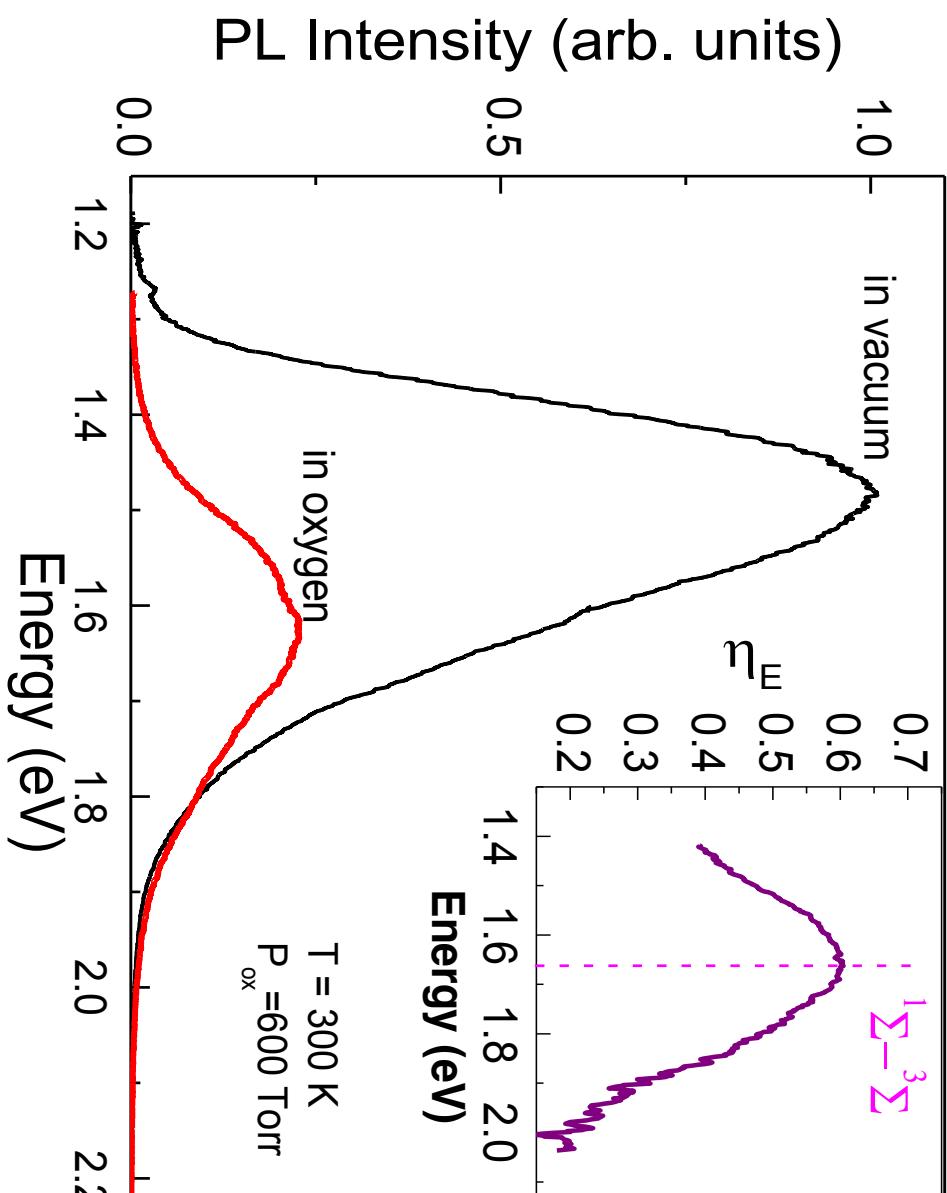
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# Singlet Oxygen Photosensitization by microporous Si at Room Temperature

$$\eta_E = 1 - I_{PL}^{oxygen}/I_{PL}^{vac}$$

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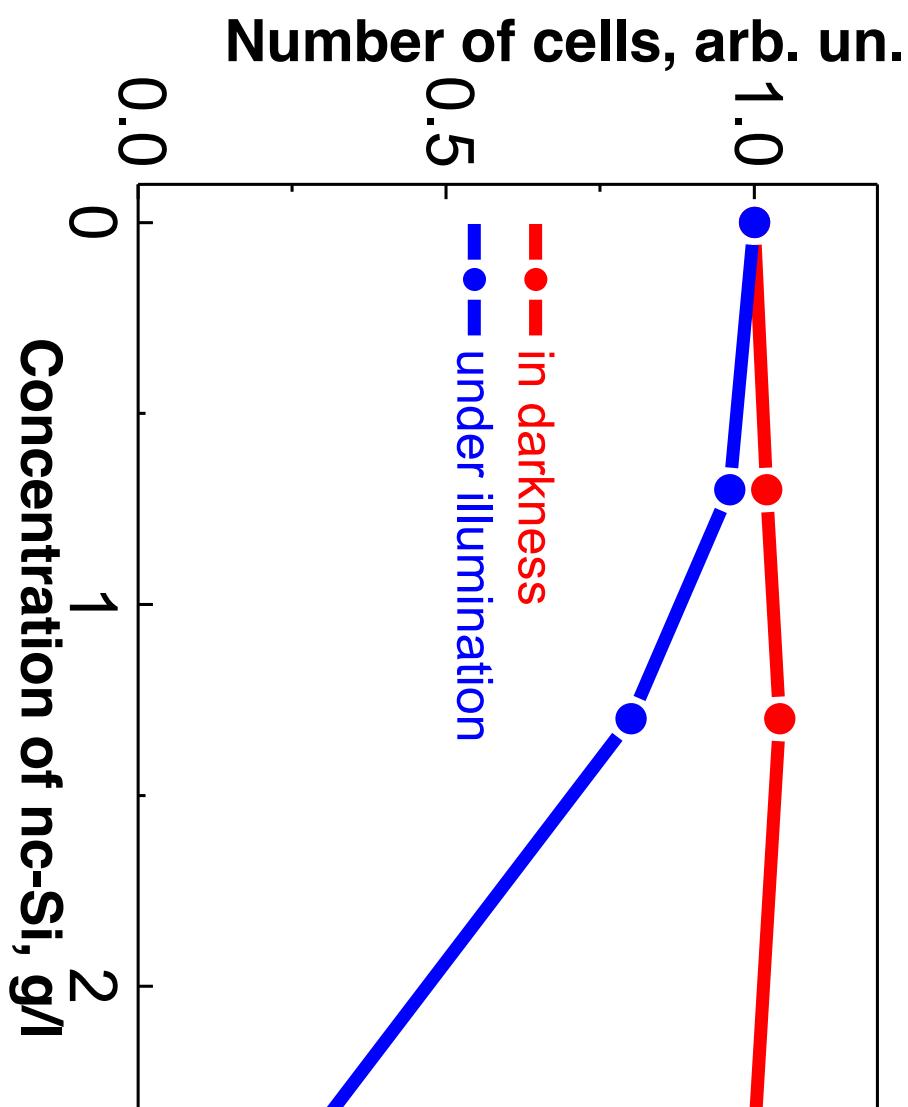
- Quantum efficiency of the SO generation:  $\eta_{SO} = \eta_E h_E \approx 5\%$

# Suppression of the cancer cell proliferation by photo-excited nc-Si

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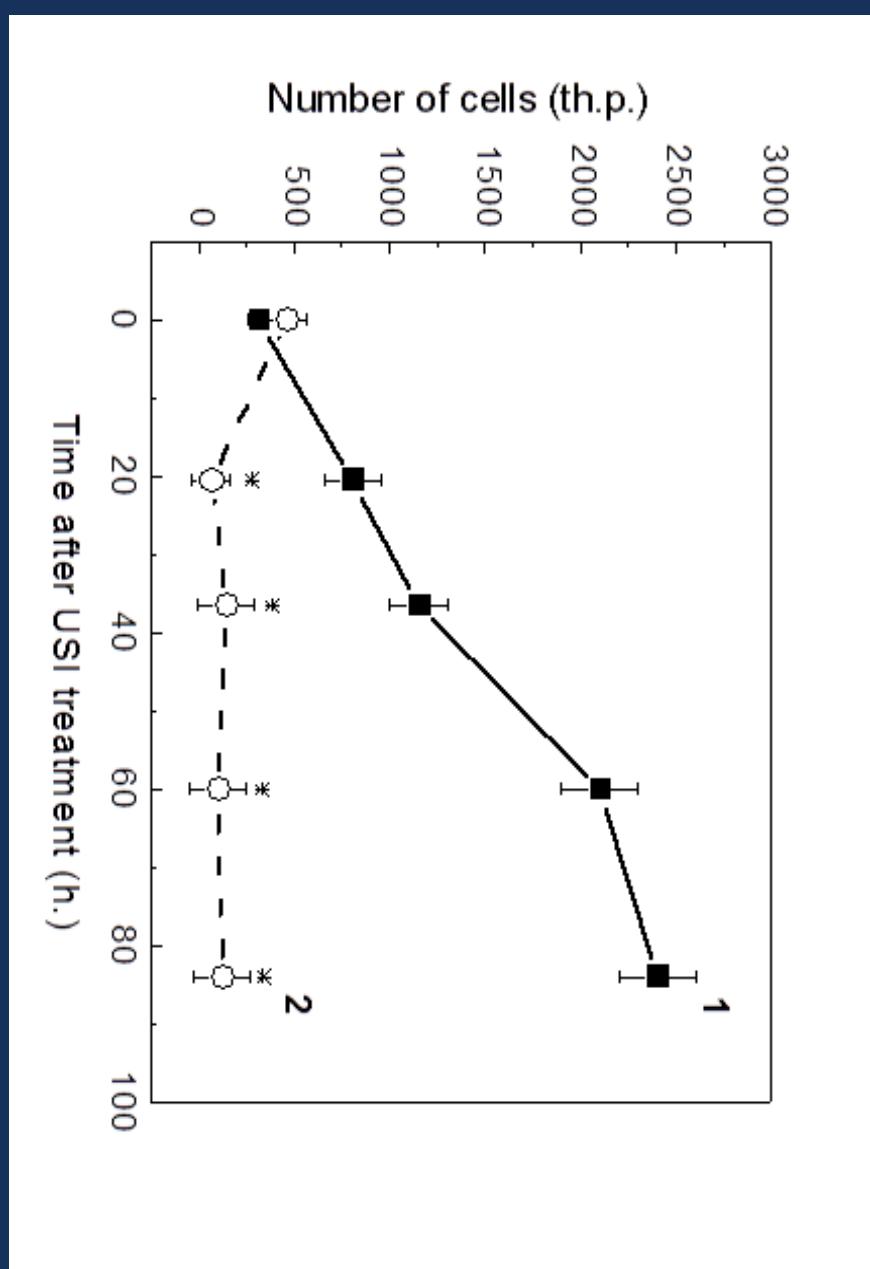
V.Yu. Timoshenko et all.,  
JETP Lett. 83 (9), 423  
(2006).



The decrease of cancer cells (mouse fibroblasts) number was observed in suspensions of silicon nanocrystals under illumination. This decrease is explained by the effect of singlet oxygen photosensitized by nc-Si.

# Effect of Low Intensity Ultrasound

Min USI ~0.2 W/cm<sup>2</sup>



2 – USI+ nano-por-Si  
*Bull. Exper. Biol. & Med.*  
(2011)

USI-treatment with minimal power in the presence of nc-Si nanoparticles did not destruct instantly the cancer cells, but they lost their proliferation properties and died within 20-80 h after the treatment.



# With Silicon Nanowires/Nanoparticles From Optoelectronic to Powerful Drugs@Therapy!

Prof. Victor Timoshenko

Dr. Liubov Osminkina

Prof. Jürgen Popp

Prof. Sergey Demyanov

Dr. Alexander Petrov

Prof. Steffen Teichert

Dr. Olga Korolik

Dr. Christian Mazanik

Dr. Elena Matthäus

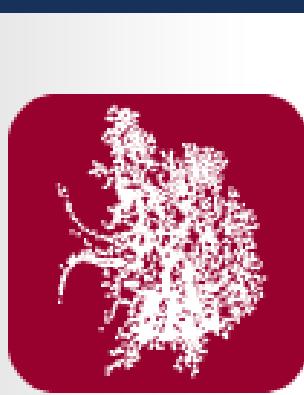
Dr. Bela Pecz

Dr. György Radnoci

Dr. Felix Voigt.....



**Династия**



Bundesministerium  
für Bildung  
und Forschung



Thanks for your  
attention!

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