POROUS SILICON TEMPLATING OF METAL NANOSTRUCTURES:

an approach to stable and ultrasensitive SERS substrates

Hanna Bandarenka, Kseniya Girel, Vitaly Bondarenko

Laboratory of Materials and Structures of Nanoelectronics
Belarusian State University of Informatics and Radioelectronics

Andrew Panarin, Sergei Terekhov

Laboratory of Physics of Molecules
B.I. Stepanov Institute of Physics of National Academy of Science of Belarus

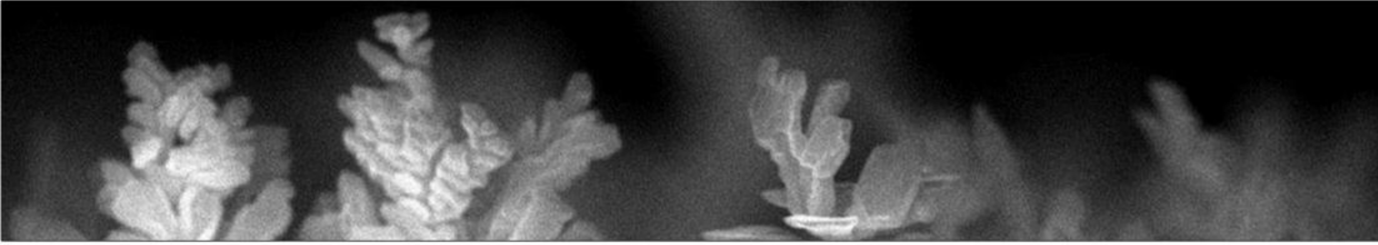
Valery Kopachevsky, Sergej Shashkov

SOL Instruments Ltd.
Minsk, Belarus

2016 E-MRS Fall Meeting • Warsaw University of Technology • September 19 - 22, 2016

TALK LAYOUT

- **Preface**
- **Porous silicon concept to SERS**
- **Fabrication and properties**
  - mesoporous Si
  - microporous Si
  - macroporous Si
- **Application**
- **Concluding remarks**



Preface

Key requirements for SERS substrates

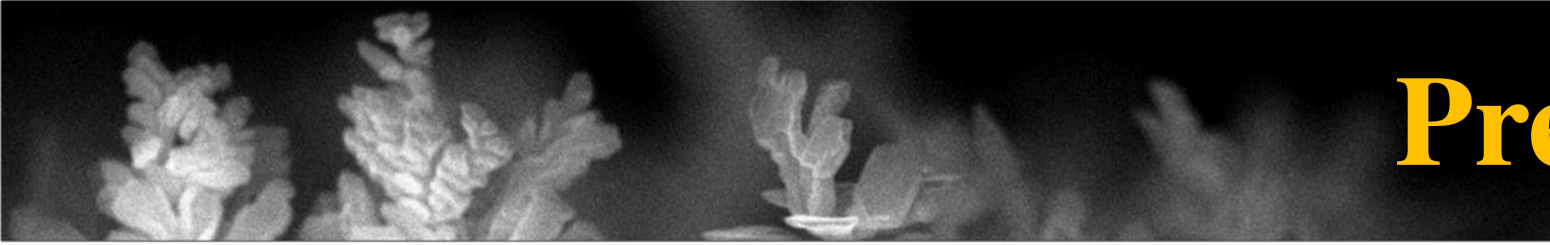
- High SERS-activity (EF > 10^3)
- Good storage stability (< **20%** signal variation, measured weekly over 1 month)
- Sample-to-sample reproducibility (< **20%** signal variation over 10 substrates)
- Spot-to-spot reproducibility (< **20%** signal variation over 10 mm^2)
- Cheap, easy to produce and compact in size

PAPER www.rsc.org/faraday_d | Faraday Discussions

Concluding Remarks
Surface enhanced Raman scattering

Michael J. Natan

Received 31st January 2006, Accepted 31st January 2006
First published as an Advance Article on the web 28th March 2006
DOI: 10.1039/b601494c



Preface

Existing commercial SERS substrates

1. **Thermo Fisher Scientific Inc. (USA)** – **Au** colloid
2. **Agiltron (USA)** – Ag thin film/nanorods on glass
3. **Ocean Optics (USA) –** Au, Ag nanoparticles on paper, Au/Ag sponge
4. **Integrated Optics (Lithuania) –** Au/Ag nanostructures;
5. **Silmeco (Denmark) – Au**, **Ag** lumps on Si nanowires;
6. **Renishaw Diagnostics (UK)** – **Au** thin film on textured Si
7. **EnSpectr (USA) –** Ag nanostructures

…

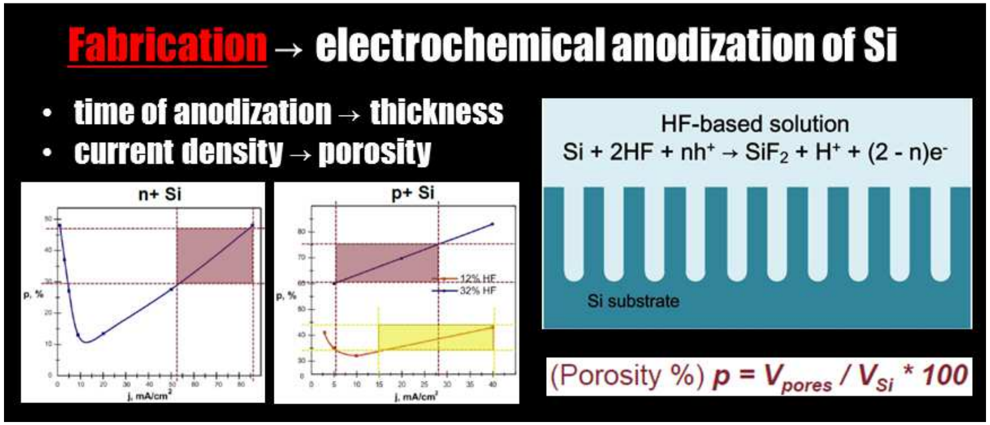
- Detection limit: 10^{-2} – 10^{-9} M
- Enhancement factor: 10^{5} – 10^{7}
- Short shelf life
- Expensive: 15 – 75 €

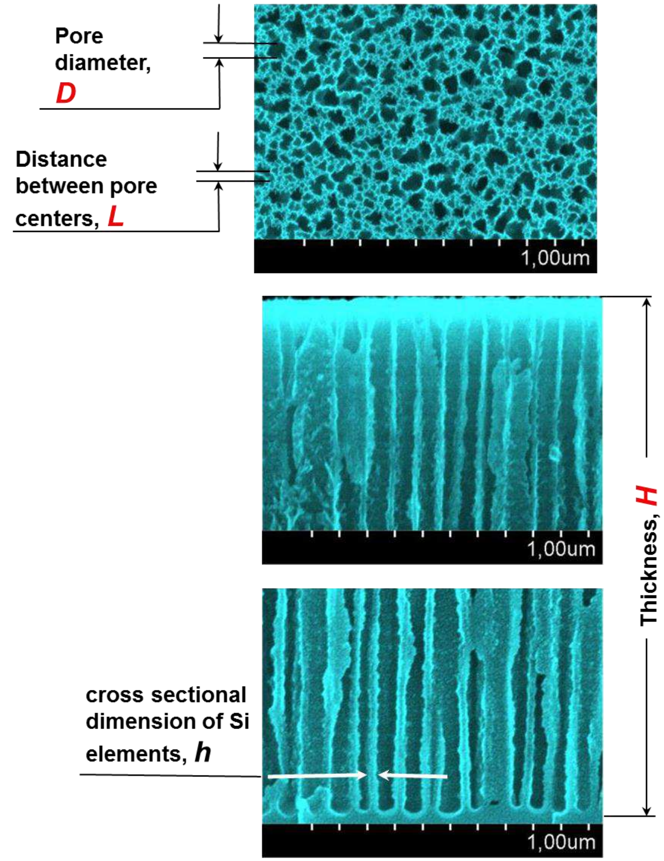
there is a room for improvement of SERS substrates

Porous silicon concept to SERS

Porous silicon (PS)

template for metal nanostructuring
to fabricate SERS substrates

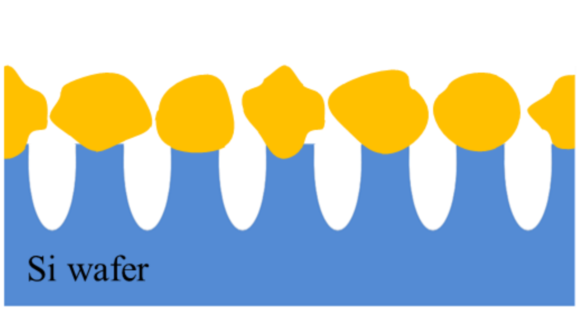




D, L, H, h ⇔ Si type + anodizing regimes → definition of sizes, shape and spacial location of the depositing metal structures

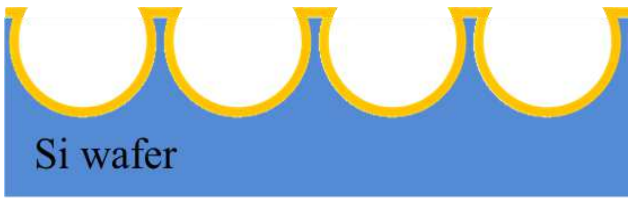
Porous silicon concept to SERS

Family of metallic nanostructures on porous silicon

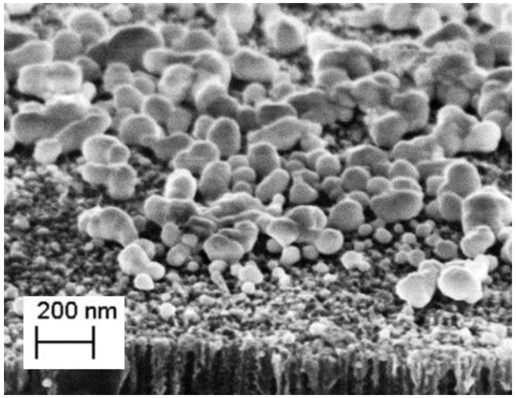


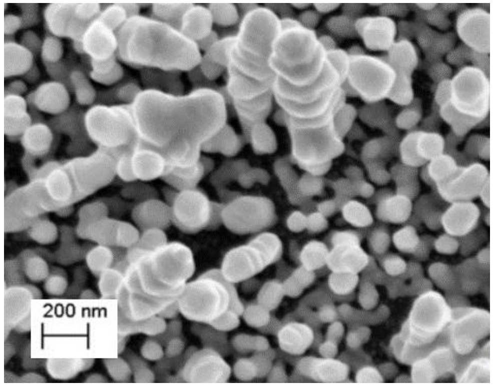
metallic nanoparticles

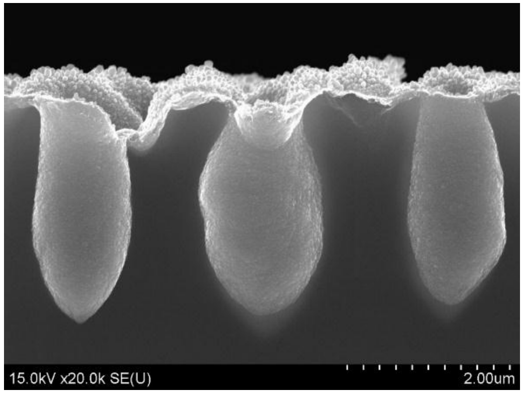
metallic rods/dendrites

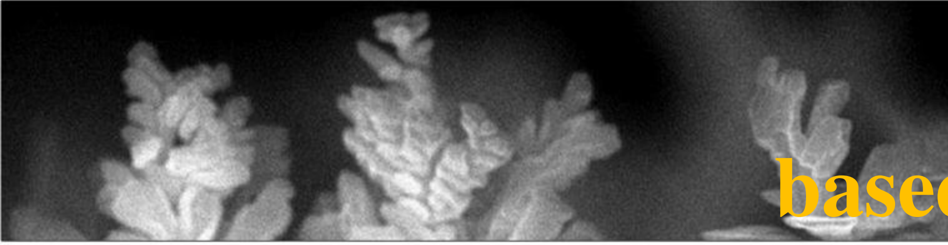


metallic nanovoids





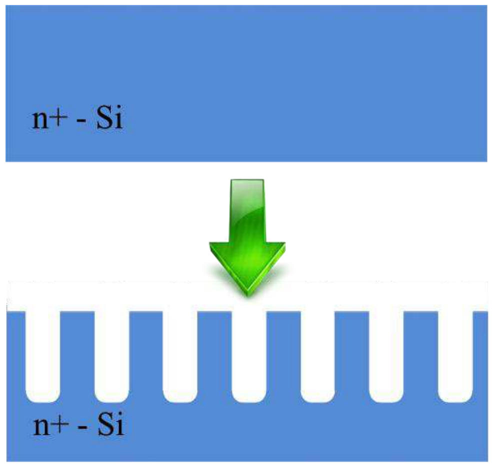


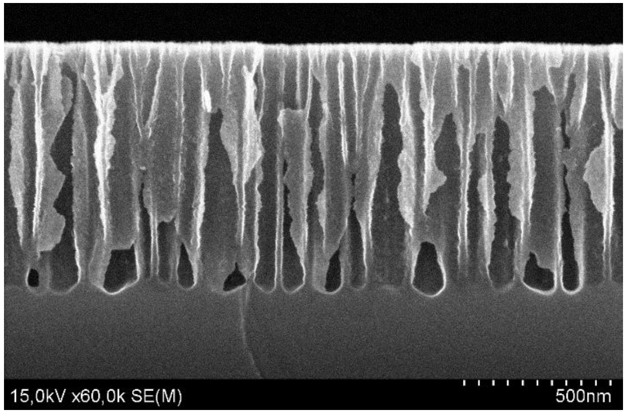


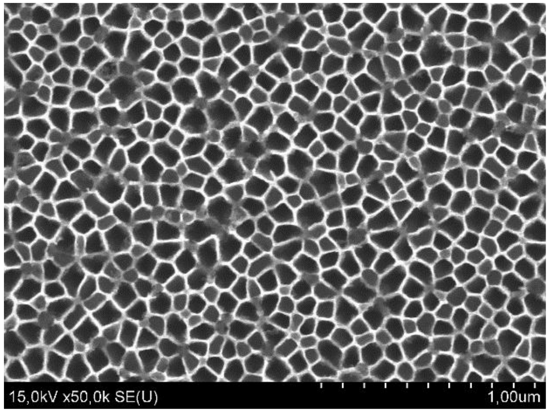
SERS-active substrates based on mesoporous silicon

Structural parameters of porous silicon template

Anodization of n+-Si



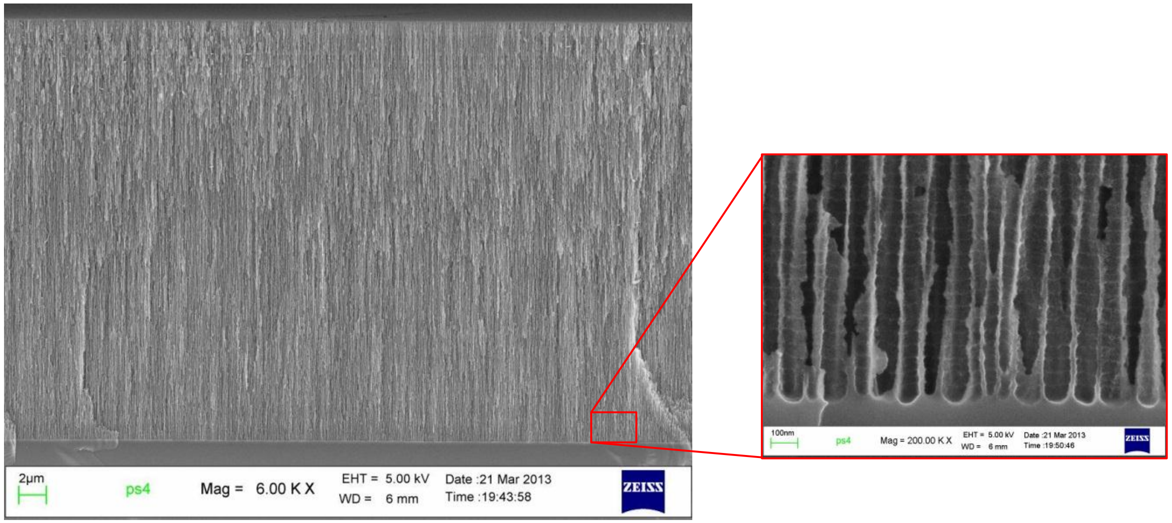


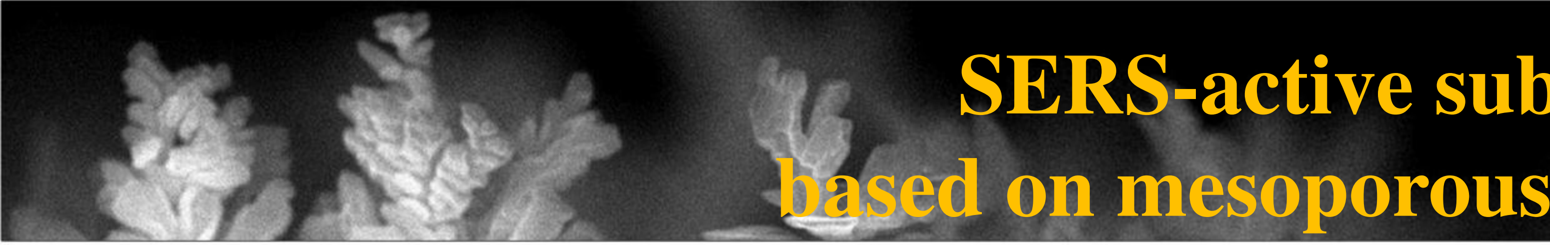


- Porosity, ***p* = 75 %**
- PS thickness, ***h* = 1 – 20 µm**

(was varied to find optimal thickness for the good adhesion of metallic NPs)

- Pore diameter, ***D* = 50 nm**





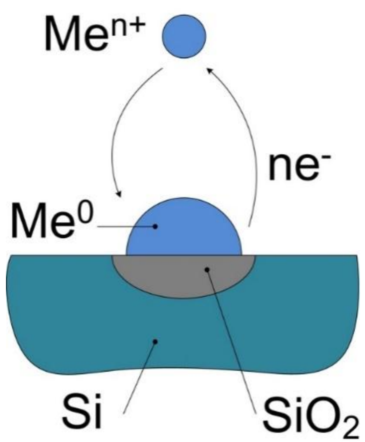
SERS-active substrates based on mesoporous silicon

Fabrication of Me nanostructures: **immersion deposition**

Negative redox potential ← | → Positive redox potential

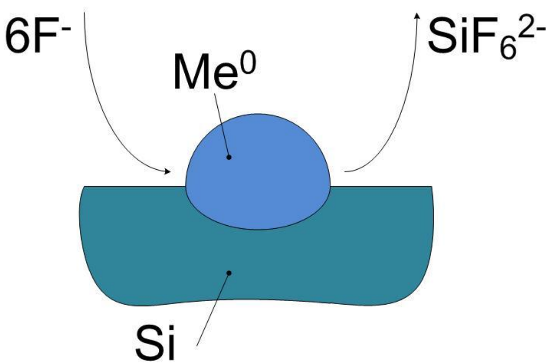
...	H	Sb	Bi	As	Cu	Hg	Ag	Pd	Pt	Au

Me salt+H_2O: Si oxidation + Me reduction

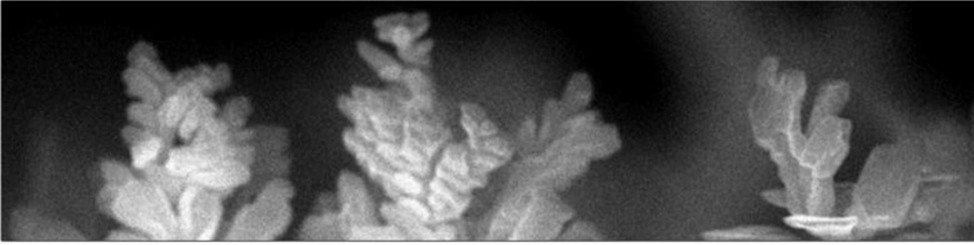


$$Me^{n+} + ne^- \rightarrow Me^0$$
$$Si^{n-} + 2H_2O \rightarrow Si0_2 + 4H^+$$

Me salt+H_2O+HF: ...+ Si dissolution



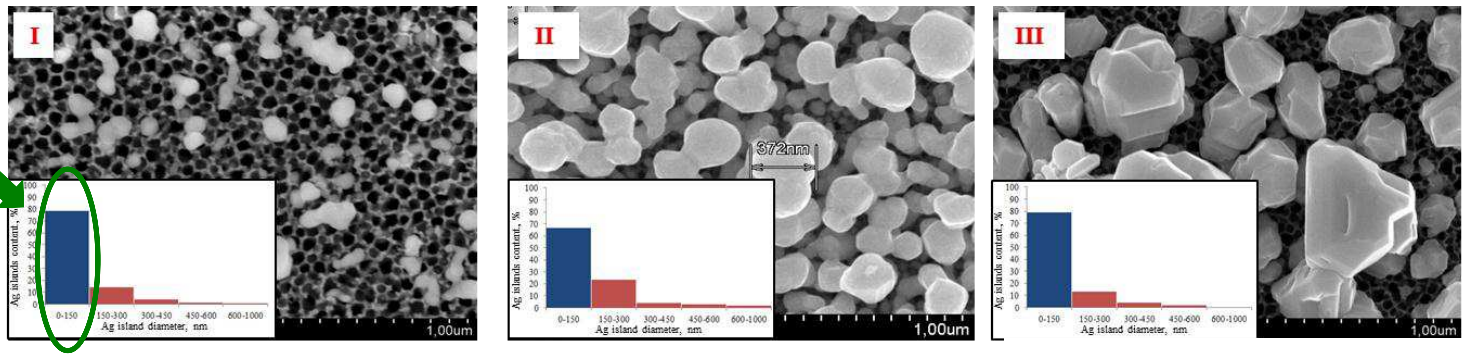
$$SiO_2 + 6HF \rightarrow 2H^+ + SiF_6^{2-} + 2H_2O$$

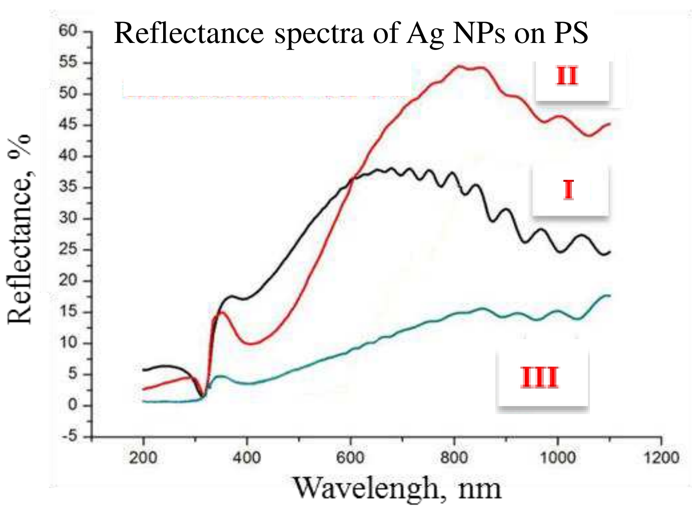


SILVER nanoparticles on mesoporous silicon

Structure and reflectance

NPs of sizes favorable for SPR





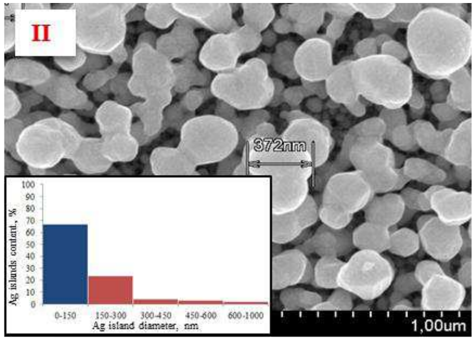
[A.Yu. Panarin et al. Physics, chemistry and application of nanostructures, 2013]

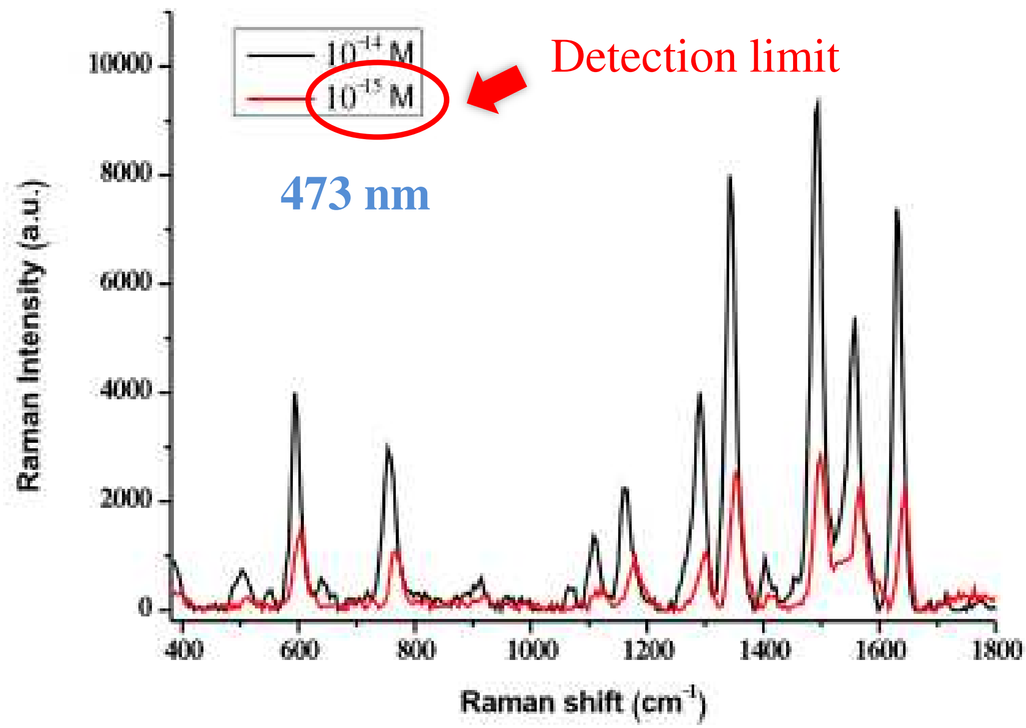
SILVER nanoparticles on mesoporous silicon

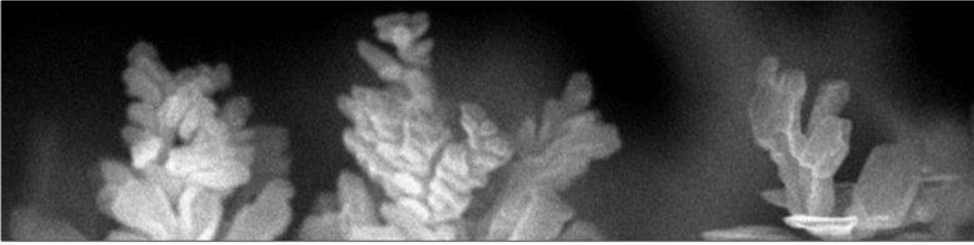
SERS-activity

Test analyte: **R6G**

- organic dye
- well-studied Raman spectrum
- easy to compare with other results

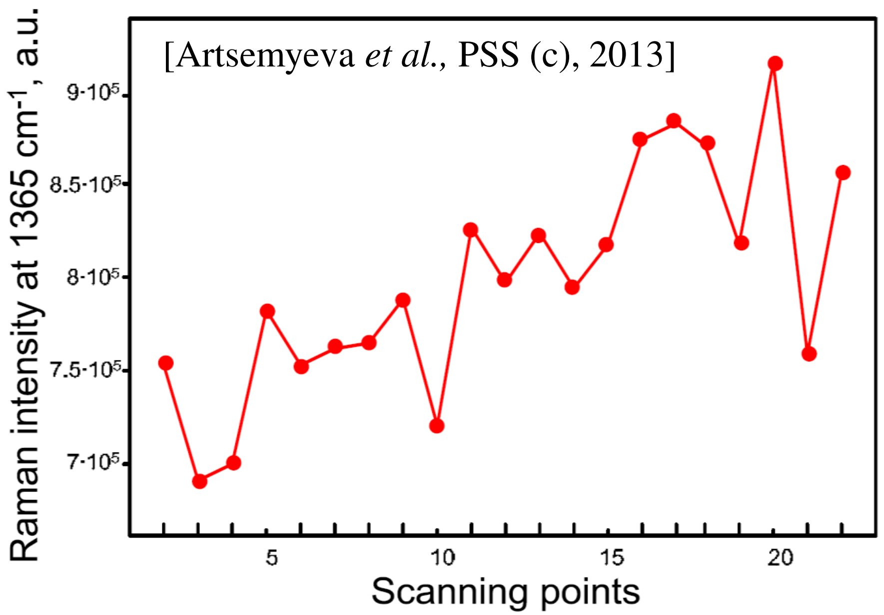


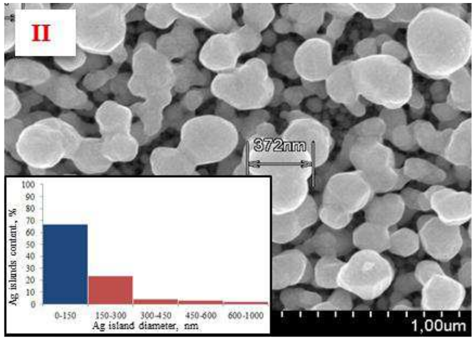




SILVER nanoparticles on mesoporous silicon

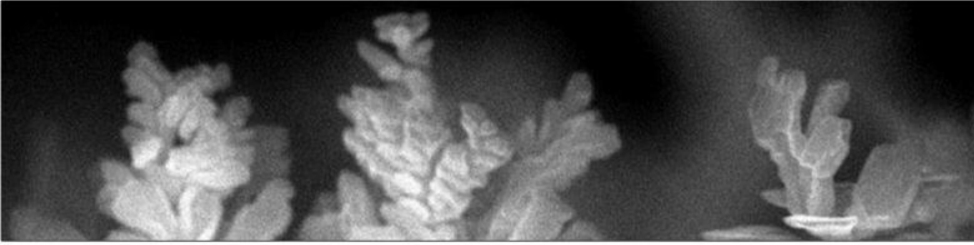
Stability of SERS-signal





- Spot-to-spot, sample-to-sample variation of SERS intensity: **7 – 10 %**
- Storage stability of SERS intensity: **7 – 10 %, > 6 months**

meet requirements for commercial SERS substrates



SILVER nanoparticles on mesoporous silicon

SERS-activity

Test analyte: fatty acids → control of fatty acids concentration in a human waste – a part of early colorectal cancer diagnostics*

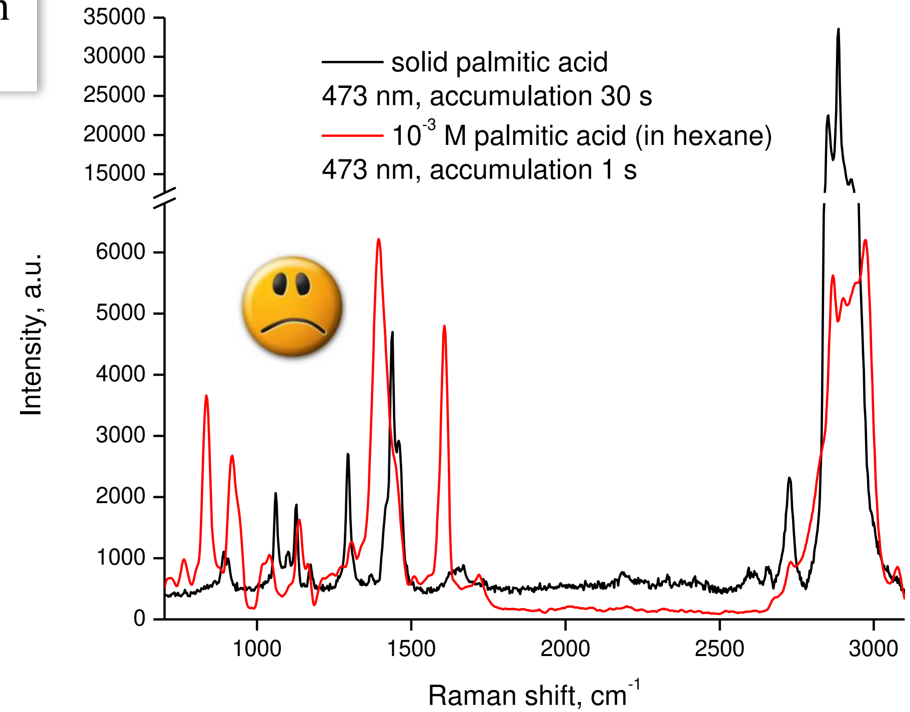
bioorganic molecules + d-metal + excitation wavelength close to UV

PROBLEM

photodegradation of analyte

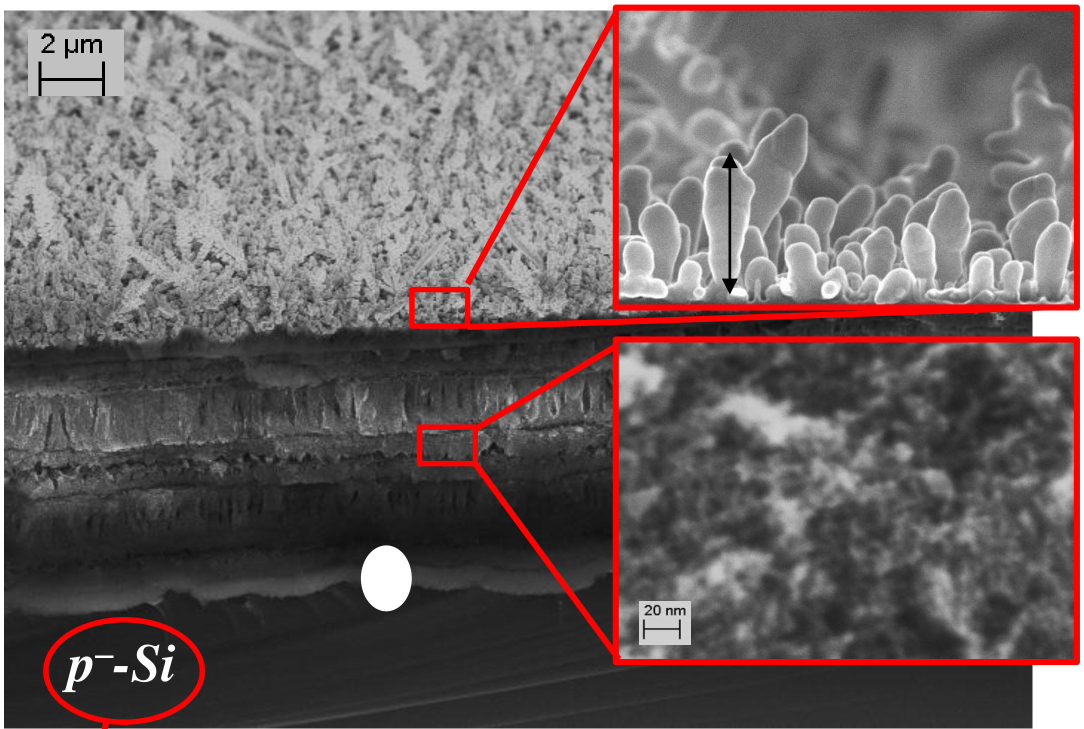
SOLUTION?

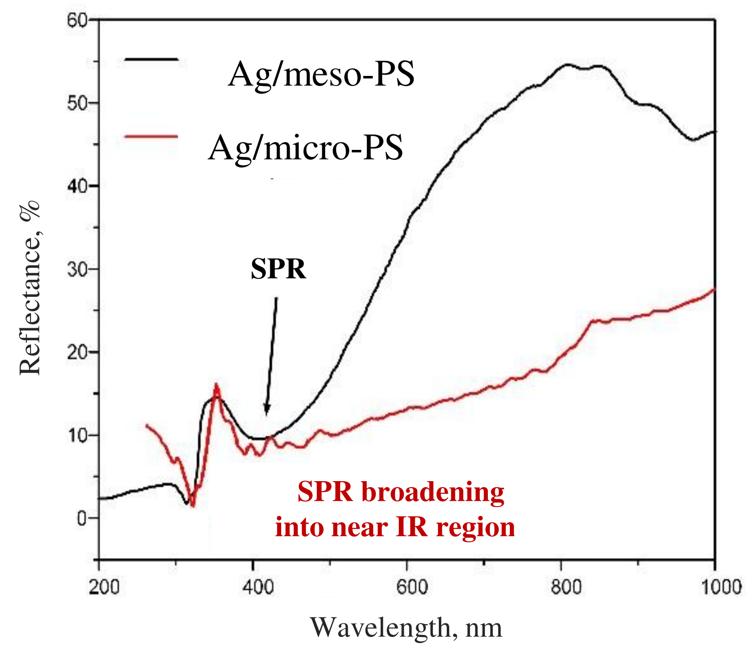
to move SPR into IR region by changing structural parameters of porous silicon and metallic nanostructures



SERS-active substrates based on microporous silicon

Structure and reflectance





transverse and multiple **longitudinal** SPR modes in elongated Ag structures

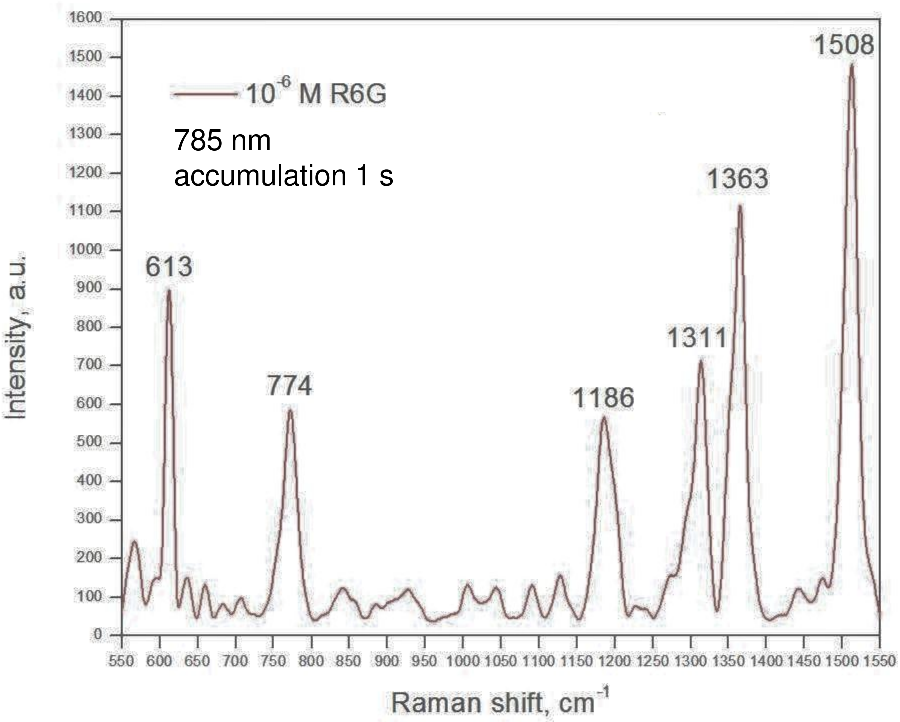
limited supplying of Ag^{+} with e^{-} of Si atoms
(not e^{-} of dopant atoms in contrast to n^{+}-Si)

Favorable for prolong NPs growth

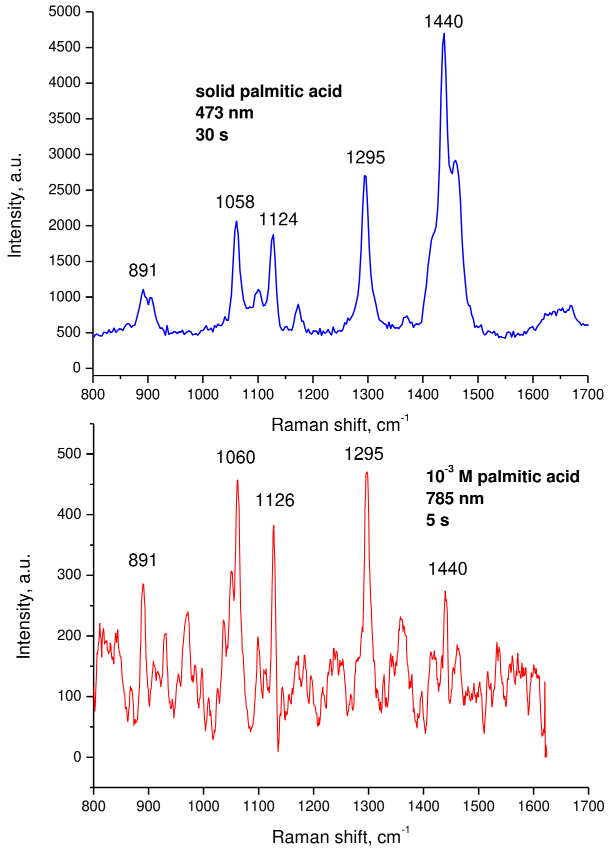
SERS-active substrates based on microporous silicon

SERS-activity

Test analyte: R6G

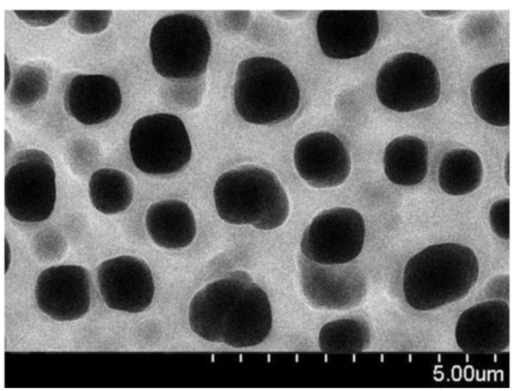


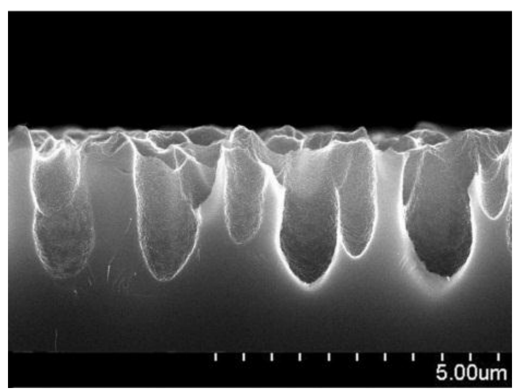
Test analyte: palmitic acid



SERS-active substrates based on macroporous silicon

Structural parameters of macroporous silicon



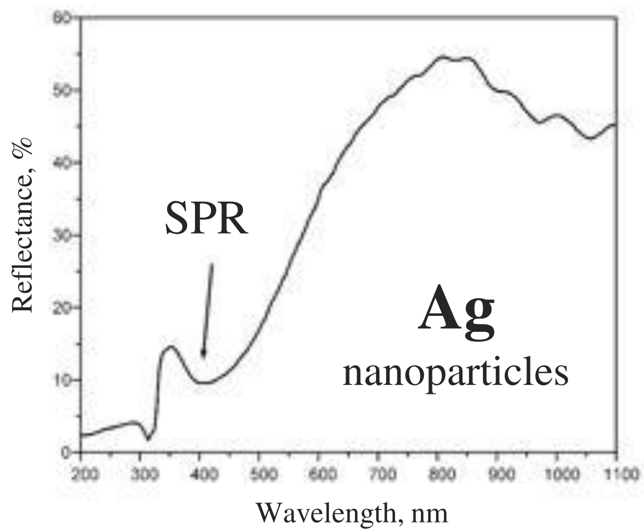


Pore diameter ~ 1 – 1.5 μm
PS thickness ~ 1.5 – 2.5 μm

Dimensions typical for **plasmonic nanovoids**

SERS-active substrates based on macroporous silicon

BIMETAL nanovoids on macroporous silicon



SPR in UV region ← **Ni** + **Ag** → the strongest plasmonic metal ← **Ag** + **Cu** → SPR in red region

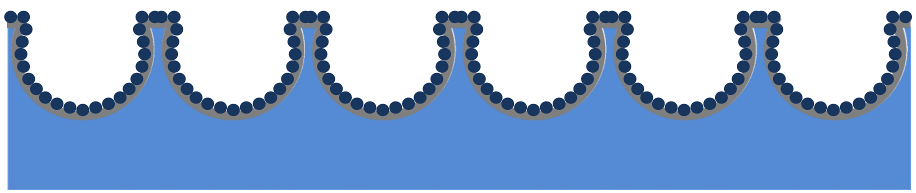
Controllable SPR + great enhancement in nanovoid

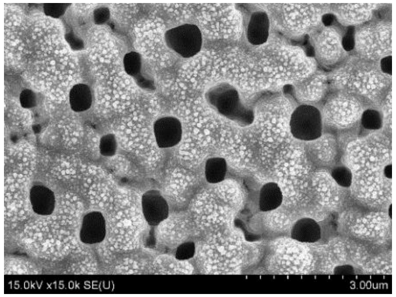
SERS-active substrates based on macroporous silicon

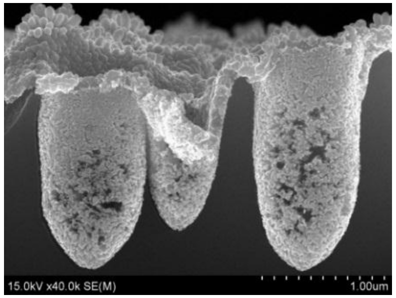
Fabrication and structure of bimetallic nanostructures:

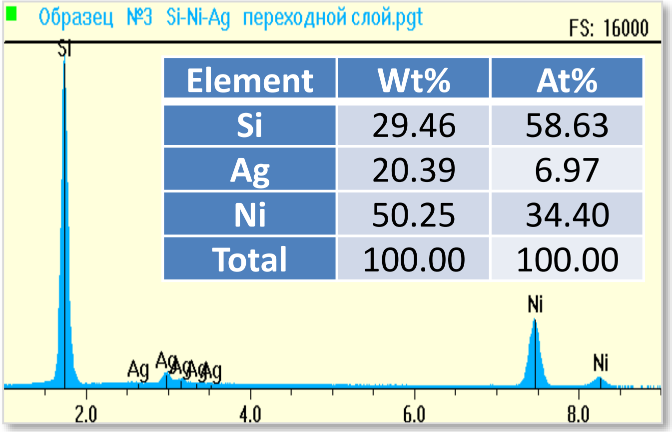
1) **Ni (Cu) electrodeposition**

2) **Ag immersion deposition**





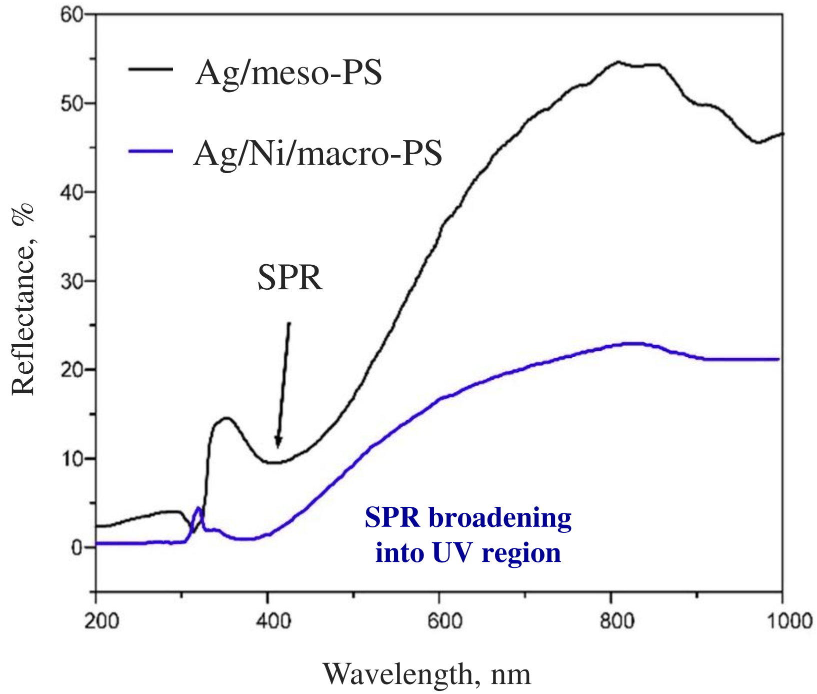


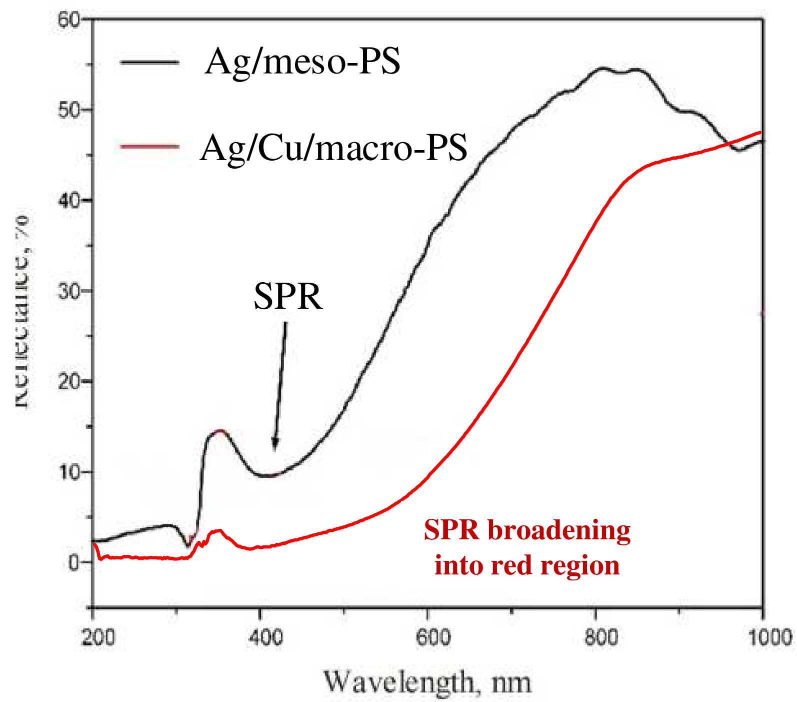


Element	Wt%	At%
Si	29.46	58.63
Ag	20.39	6.97
Ni	50.25	34.40
Total	100.00	100.00

SERS-active substrates based on macroporous silicon

Reflectance

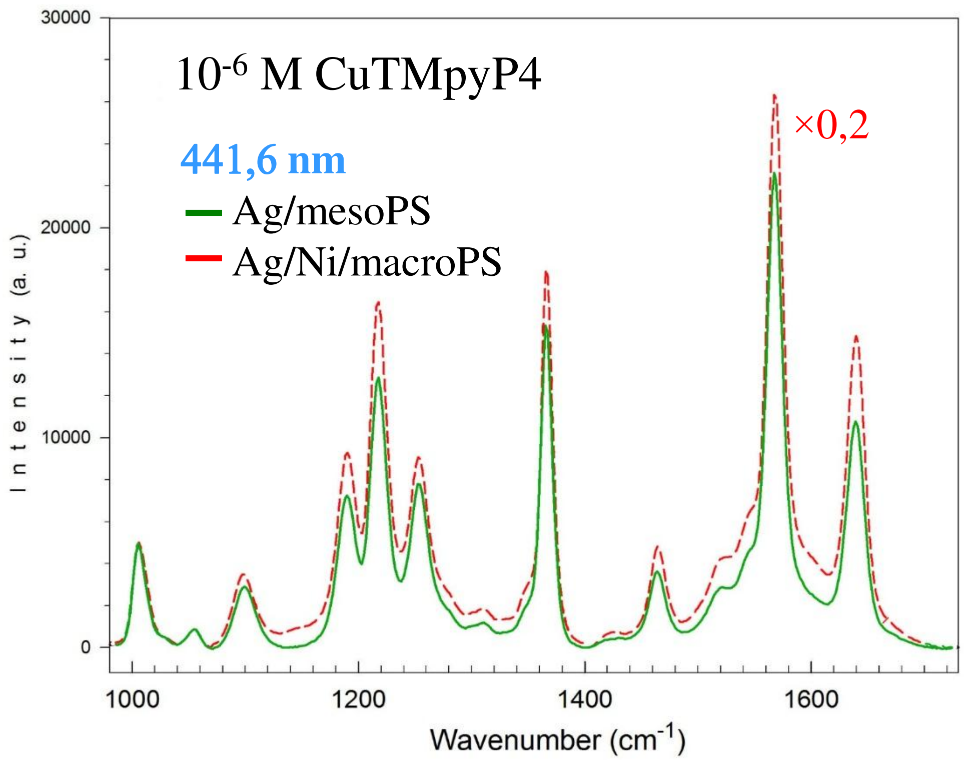


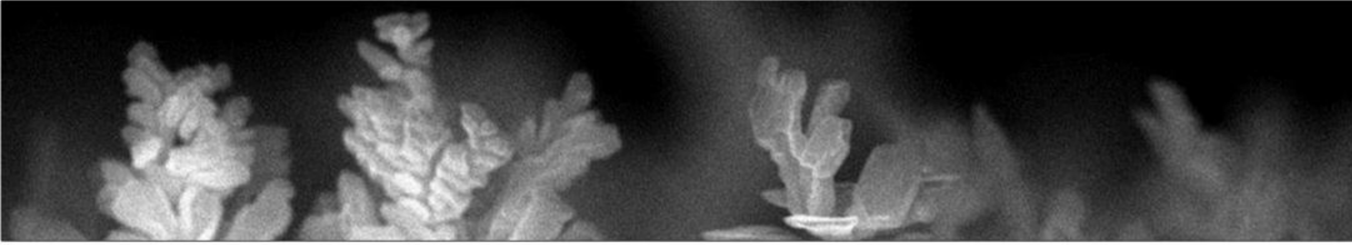


Fabrication of substrates demonstrating SERS-activity in the required region of excitation wavelength

SERS-active substrates based on macroporous silicon

SERS-activity





Application

reveal all secrets BelSERS

2015 The project on the SERS substrates based on porous silicon was a winner of the Innovation Projects Competition for young researchers in Belarus

Small scale manufacturing started

BelSERS substrates are under medical certification

Characteristics of SERS-active substrates

- Active material:
silver nanovoids, dendrites, nanoparticles
- Detection limit:
$10^{-3} – 10^{-15}$ M*
- ~~Graphene protection~~*
- Excitation wavelength:
visible and near-IR ranges**
- Shelf life:
6 month***

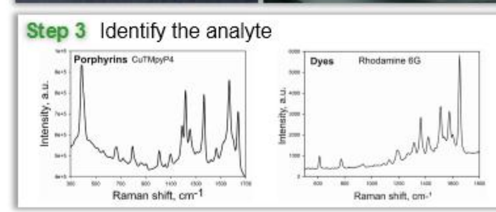
* depending on analyte
** depending on substrates type
*** rinse with HCl before use

Analytes:

- porphyrins,
- proteins,
- fatty acids,
- DNA,
- organic dyes,
- cytochromes,
- chlorin e6,
- heavy metals compounds, etc.

Price:
5 – 7 Euro/substrate

How to use?

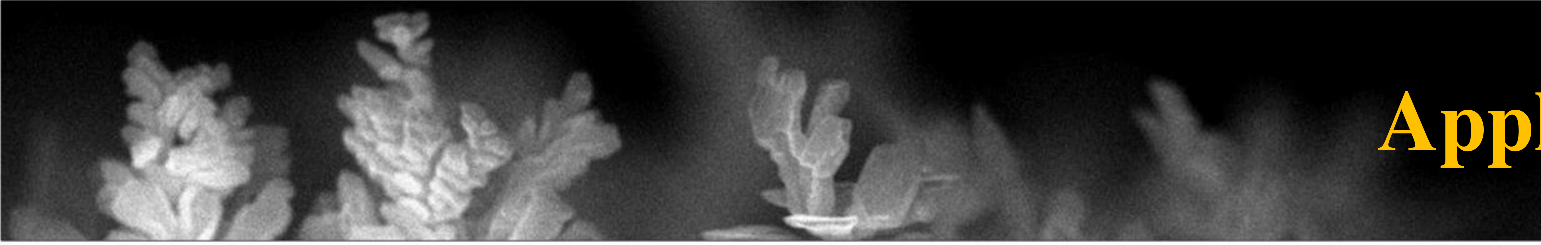


Package variants

Glass slide with SERS chip
→ active area: 100 mm²

Plastic bag with SERS chip
→ active area: 50 mm²

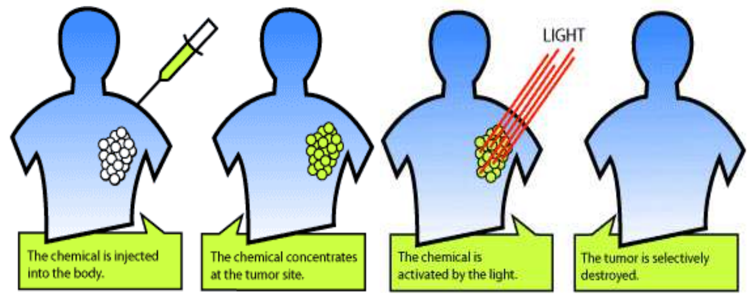
Eppendorf tube with SERS chip
→ active area: 35 mm²

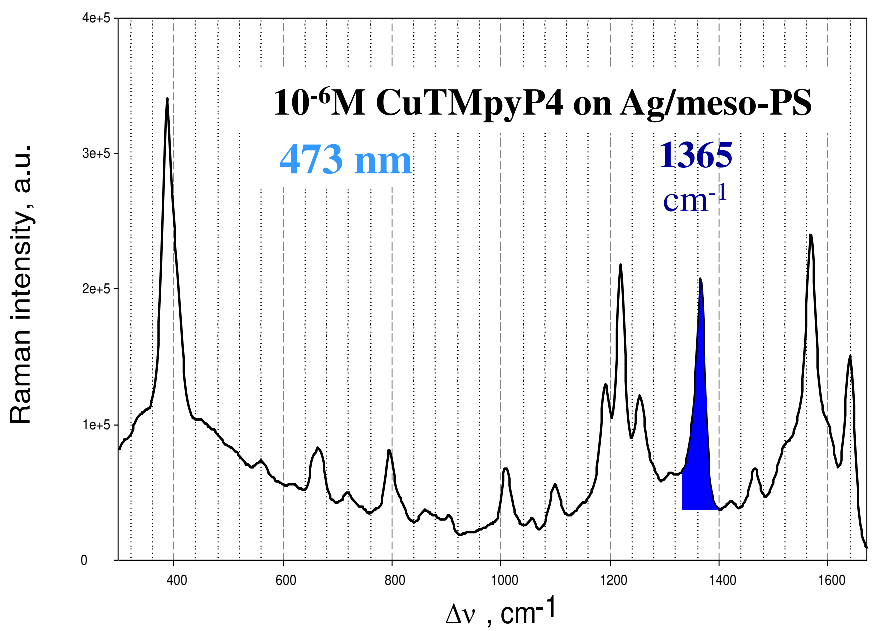


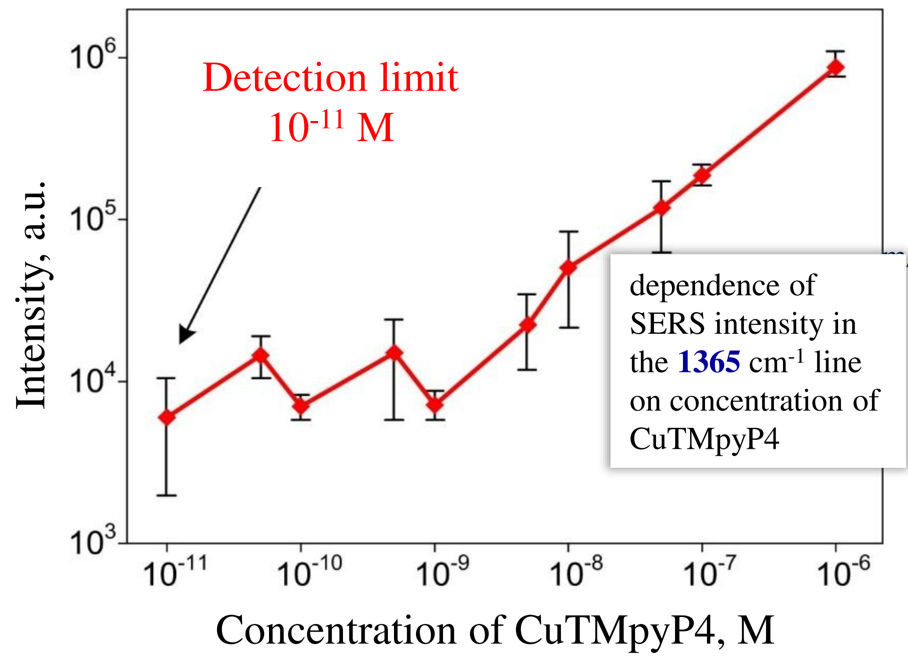
Application

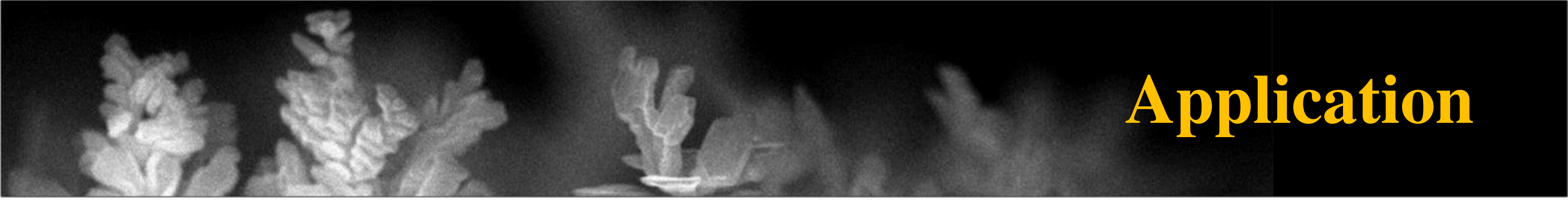
Test analytes: metallic porphyrines

porphyrin derivatives – **photosensibilizators** in photodynamic therapy of cancer







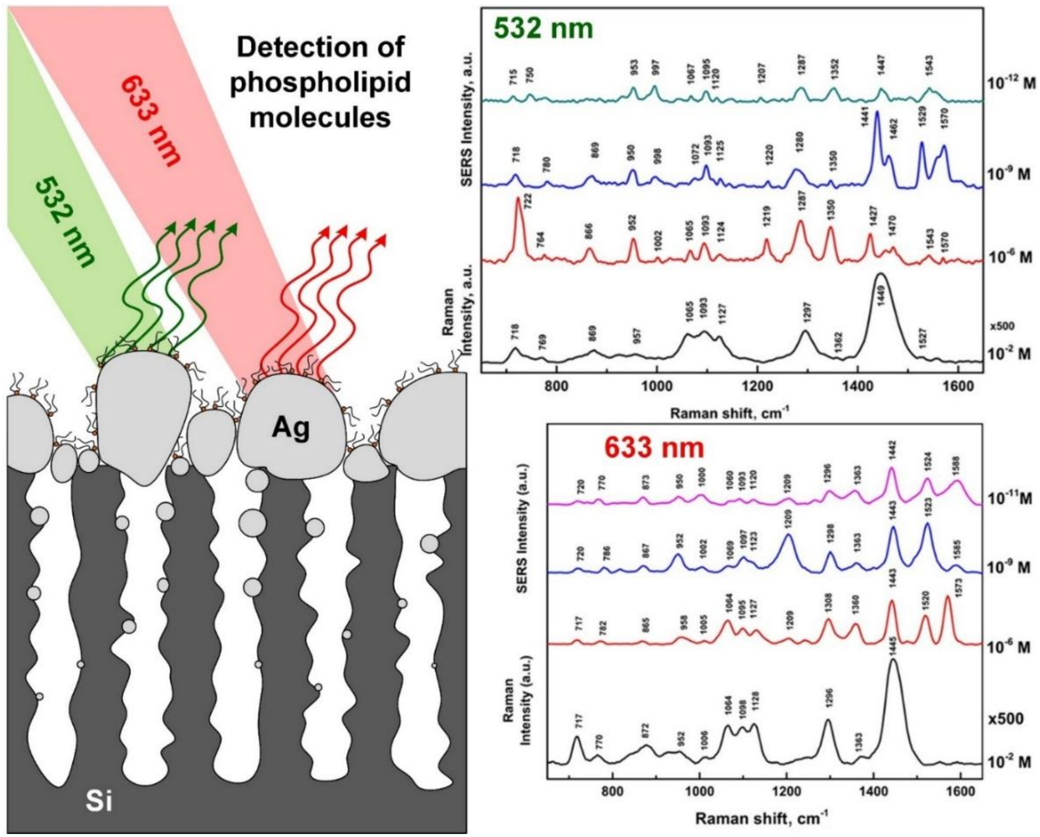


Application

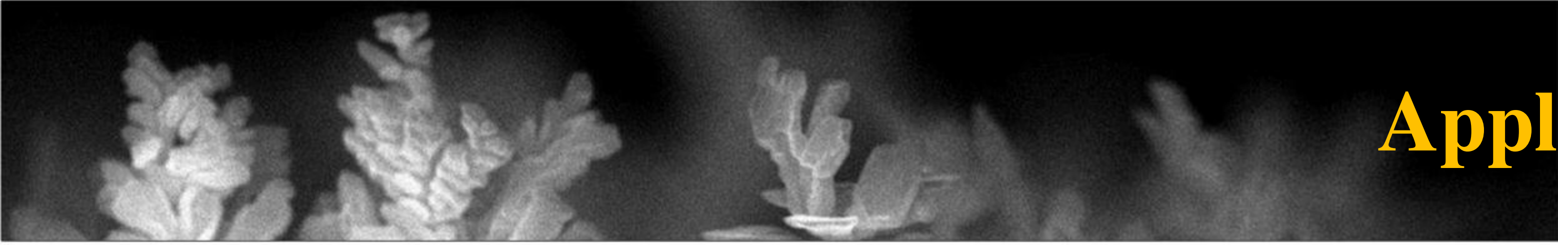
Detection of phospholipids

Test analytes:
phospholipids

part of early diagnostics of pulmonary, hepatic, sclerotic diseases

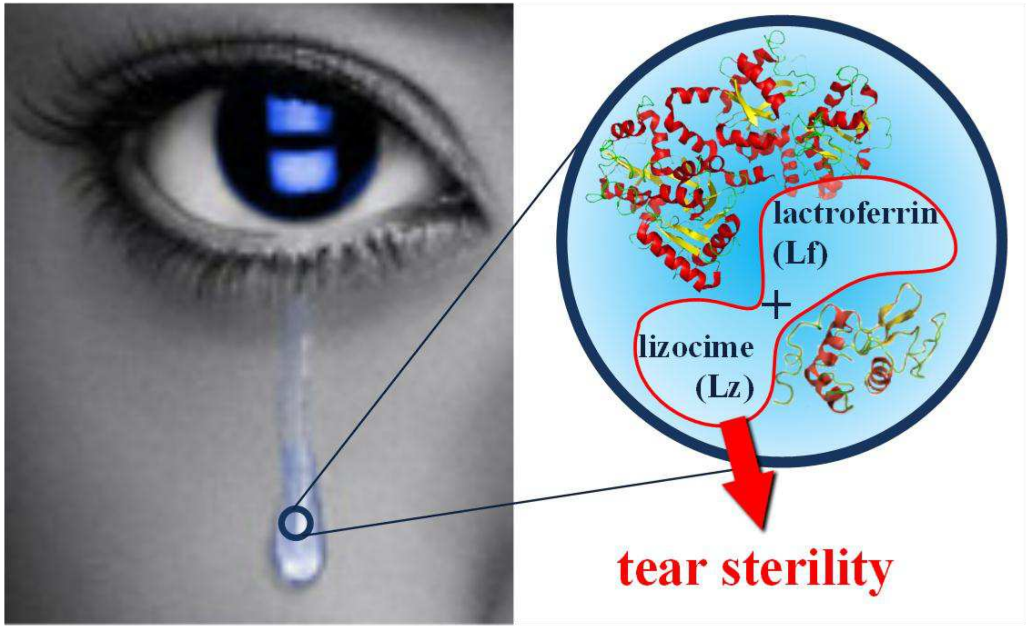


Together with **JINR, laboratory of nanophotonics, center of Raman microscopy** (Russia)



Application

Tear proteins detection



C(Lf or Lz) ≈ 10^{-6} M

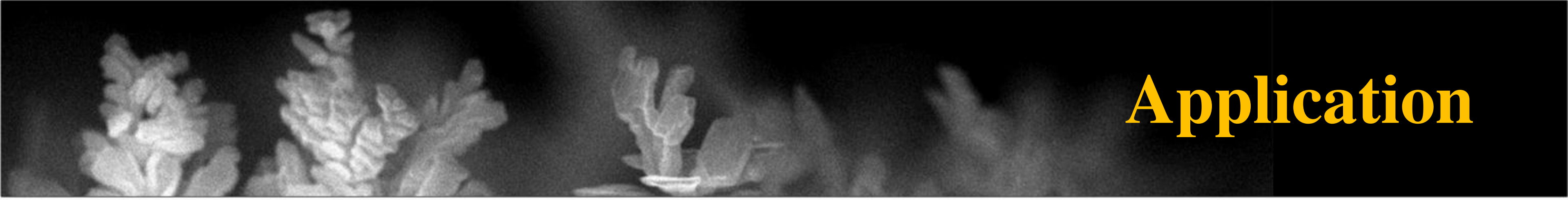
healthy eye

C(Lf or Lz) < 10^{-6} M

eye disease

Proper therapy of eye diseases

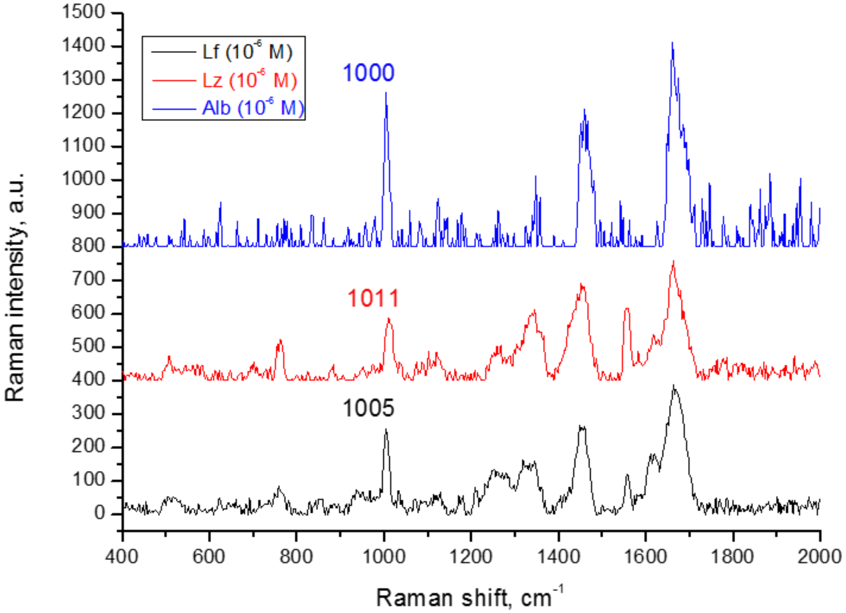
fast analysis of tear liquid micro-/nanomolar **sensitivity**

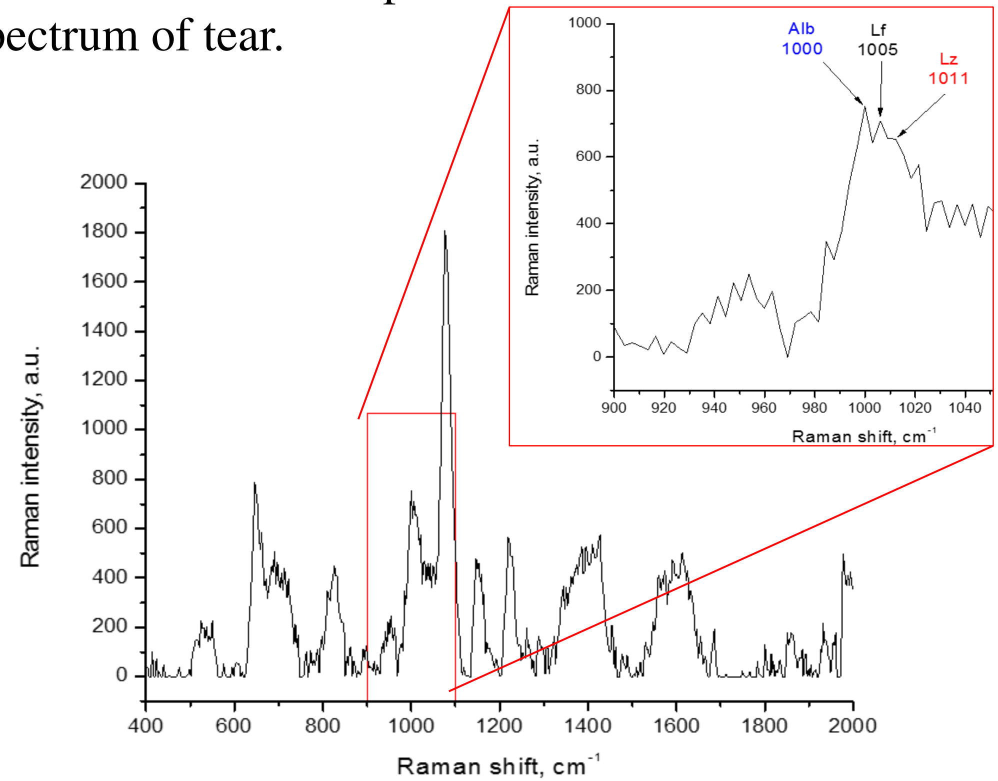


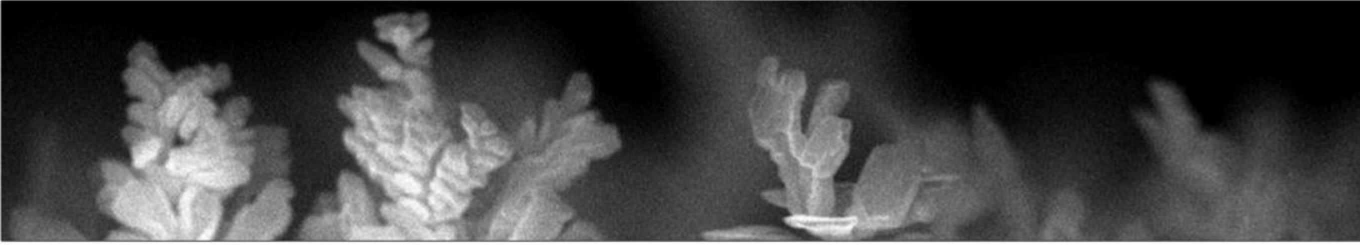
Application

Tear proteins detection

- SERS-spectra of Lf, Lz and Alb have typical bands for these proteins.
- Proteins can be distinguished in SERS-spectrum of tear.



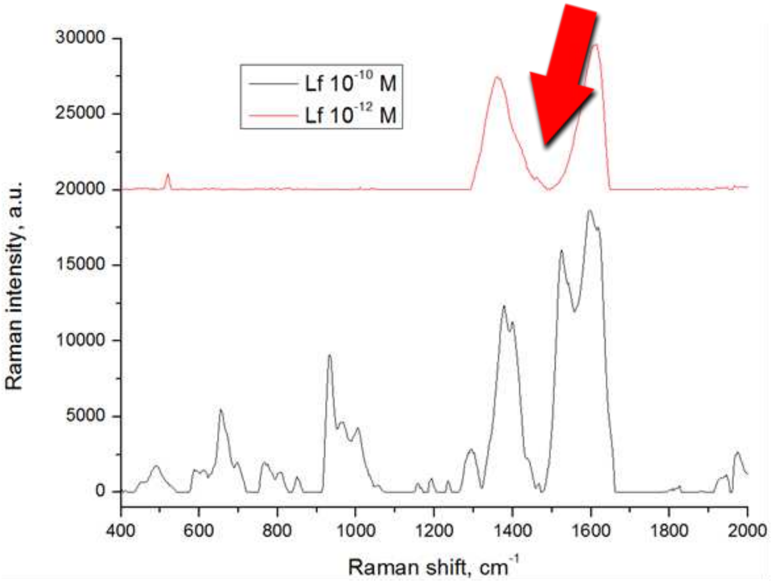


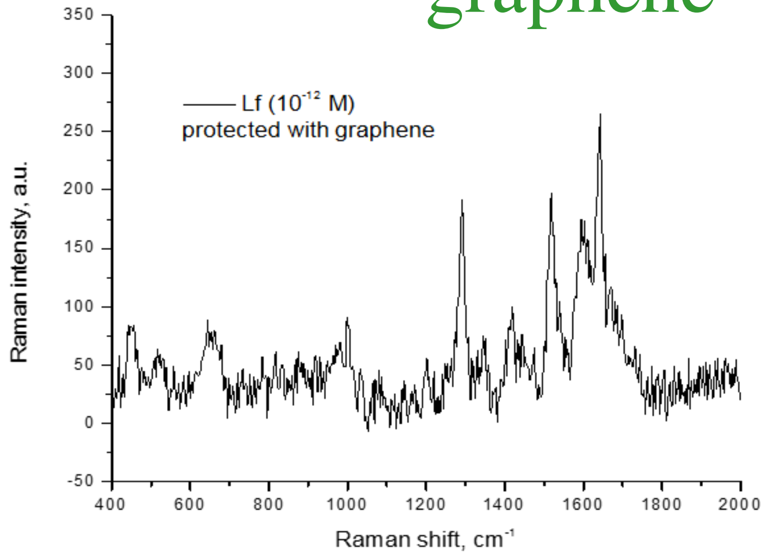


Application

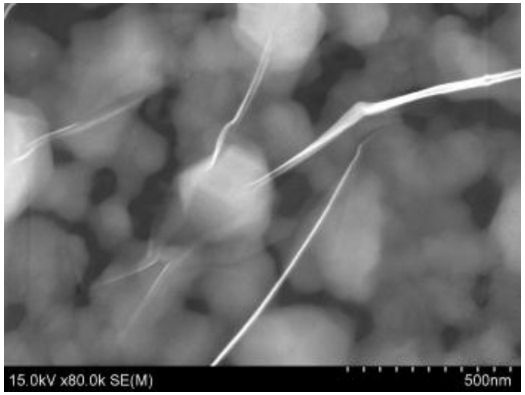
Lf, Lz at picomolar concentration
are destructed under laser exitation

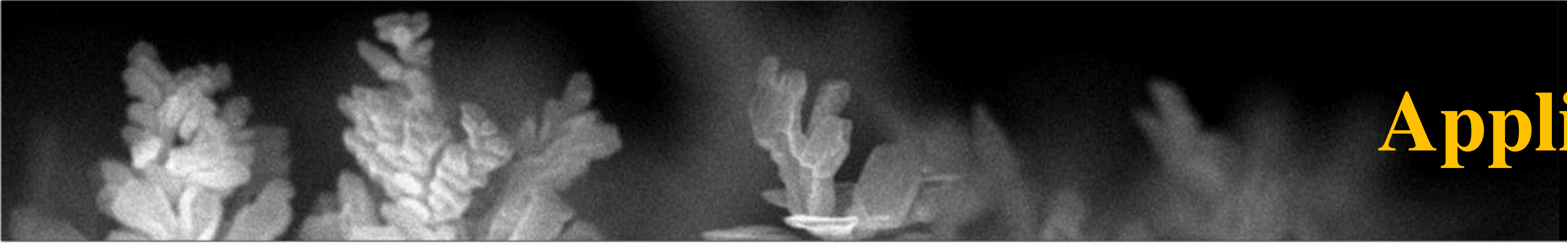
protection with graphene



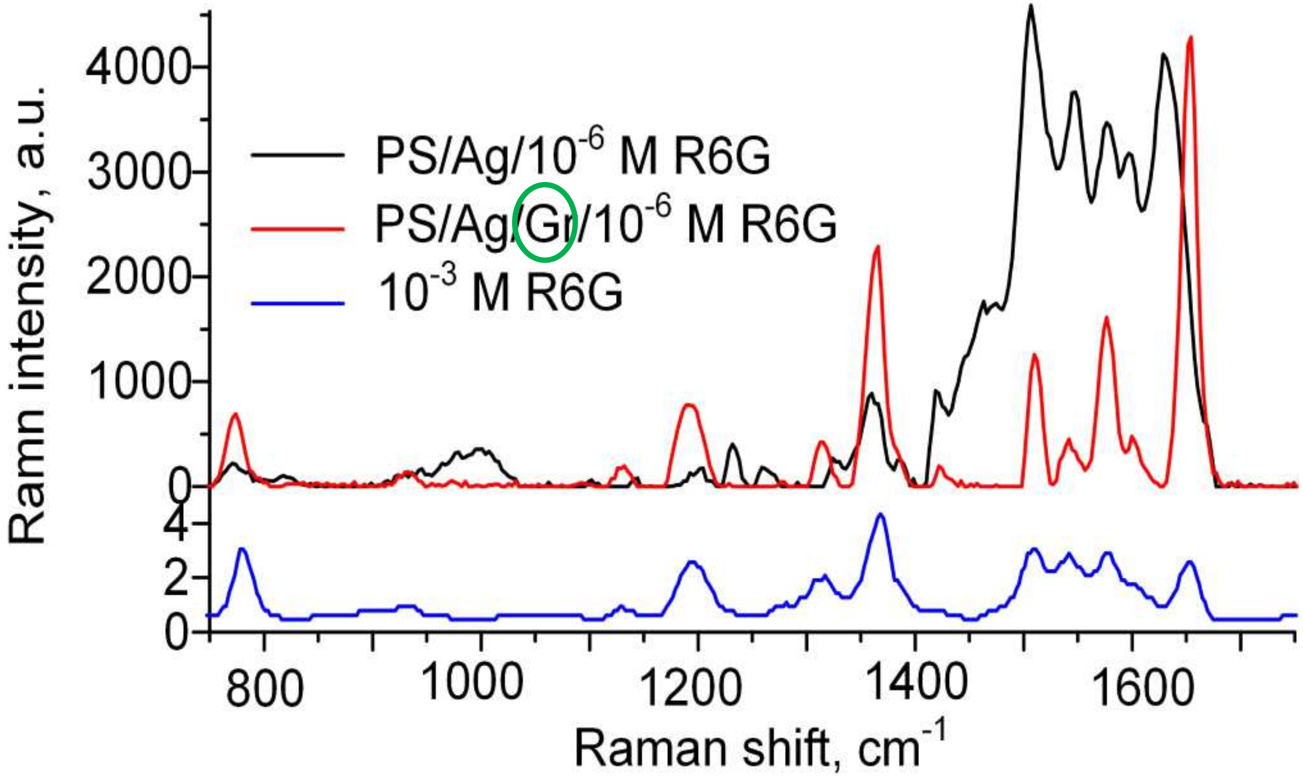


- Detection limit of proteins on Gr-free substrates reaches 10^{-10} M.
- Proteins at 10^{-12} M are not detected due to their destruction under laser excitation.

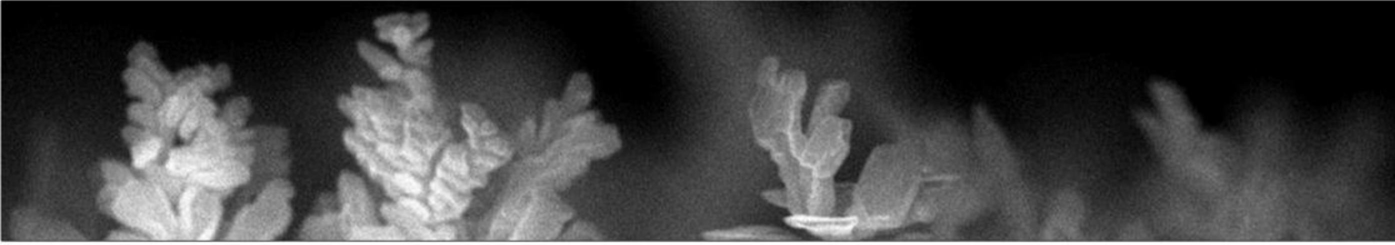




Application



- Gr-free substrates result in hiding R6G spectra in carbon bands due to reactions between analyte molecules and Ag
- Gr was found to prevent corrosion of Ag in analyte solution.
- Thus, Gr-protected substrates resulted in clear analyte spectrum.



Concluding comments

- PS template allows fabrication of rich morphological family of SERS substrates: **metallic nanoparticles, rods, dendrites, nanovoids**
- SERS structures based on metalized PS can provide milli- … **femptomolar** detection limit
- Fabrication process of SERS substrates based on PS is very simple and **cost-effective** (Ag, Cu, Ni; two-step liquid technology)
- PS-based SERS substrates are suitable for different excitation wavelengths (**441.6, 473, 514, 532, 633 and 785 nm**)
- PS provides improved spot-to-spot, sample-to-sample and storage stability (**7 – 10 %, 6 months**) of SERS substrates – <u>**meet requirements for commercial product**</u>

Acknowledgements

This research has been carried out under support of

- the Belarusian Foundation for Fundamental Research (Grants № X14MB-008, T13M-161, T11OB-057, T10M-089);
- the task 2.3.06 of Ministry of Education of Belarus in the range of the State program of scientific research “Electronics and Photonics”
- Joint Institute for Nuclear Research (Russian Federation, Dubna) in the range of the contract № 400-601

The special thanks to my colleagues and our partners...

Prof. Vitaly Bondarenko

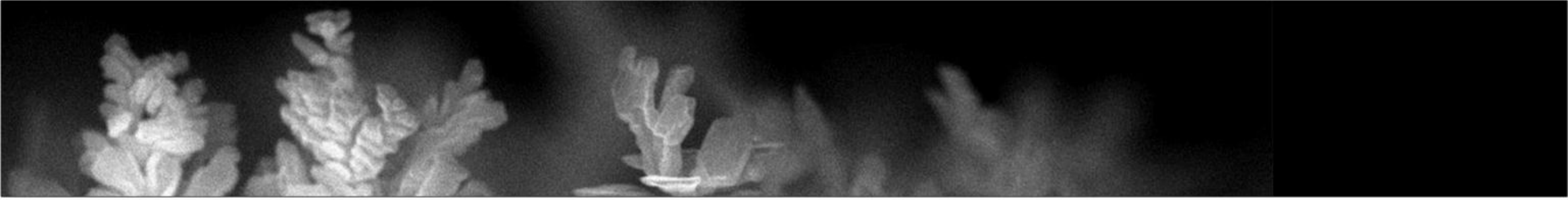
Dr. Sergey Terekhov

Dr. Andrei Panarin

Ph.D. Student Kseniya Girel

- Dr. Vladimir Lukashevich
- Dr. Valentina Sedakova
- Dr. Grigoriy Arzymanyan
- Dr. Valeriy Tsybulskiy
- Dr. Kazimir Yanushkevich
- Dr. Sergey Shashkov
- Master student Stanislau Niauzorau
- Student Roman Buchko
- Student Ekaterina Yantsevich
- Student Andrei Syman

3D scanning laser Raman microscope Confotec®
see more at the 7th booth
learn more at http://solinstruments.com/



...and thank YOU for your attention☺