Surface Enhanced Raman Spectroscopy (SERS)

by Dr. Hanna Bandarenka

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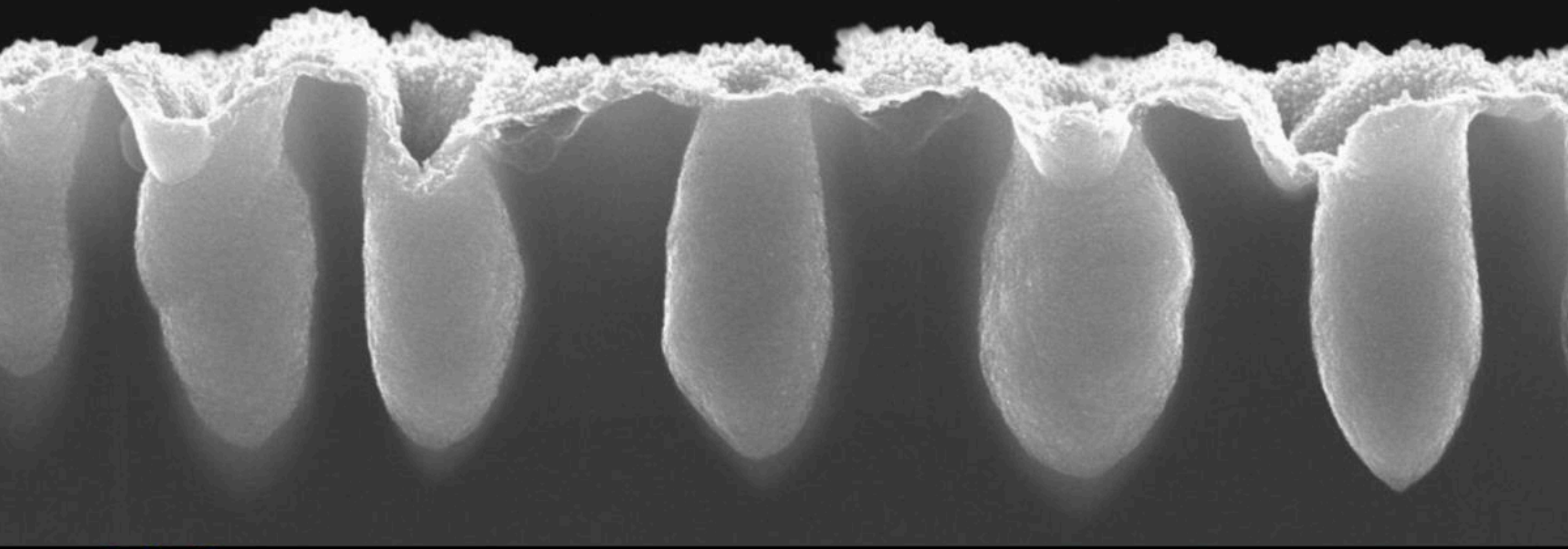
Belarusian State University of Informatics and Radioelectronics



Talk layout

- **History&definition**
- **SERS-active substrates**
  - fabrication
  - properties
- **Application of SERS**

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SERS: history&definition

1928 – Raman scattering discovery

Chandrasekhara Raman

Grigoriy Landsberg

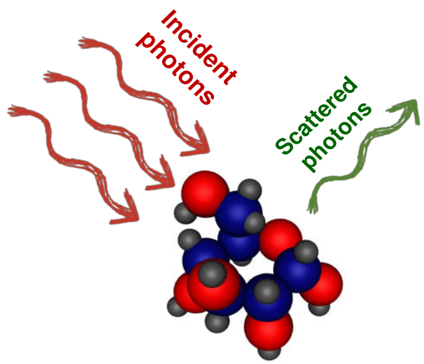
Leonid Mandelstam

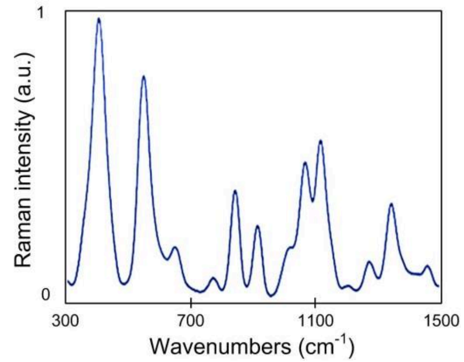
A new radiation
CV Raman
Indian Journal of physics, **1928**

New phenomenon in scattering of light
GS Landsherg, LI Mandelstam
Journal of the Russian Physico-Chemical Society, **1928**

SERS: history&definition

Raman scattering – molecule's fingerprinting





SERS: history&definition

Raman scattering: pros&cons

- non-contact,
- non-destructive,
- high resolution,
- lack interference from water,
- no special sample preparation,
- single wavelength, etc.

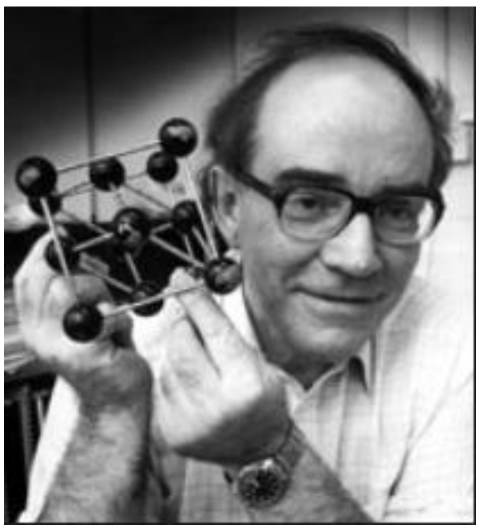
Perfect for chemical and biological sensing

1 out of 10^8 photons is scattered

Non sensitive to low concentrations

SERS: history&definition

1974 – SERS discovery



Martin Fleischmann

Volume 26, number 2 CHEMICAL PHYSICS LETTERS 15 May 1974

RAMAN SPECTRA OF PYRIDINE ADSORBED AT A SILVER ELECTRODE

M. FLEISCHMANN, P.J. HENDRA and A.J. McQUILLAN
Department of Chemistry, The University, Southampton SO9 5NH, UK

Received 27 February 1974

Raman spectroscopy has been employed for the first time to study the role of adsorption at electrodes. It has been possible to distinguish two types of pyridine adsorption at a silver electrode. The variation in intensity and frequency of some of the bands with potential in the region of the point of zero charge has given further evidence as to the structure of the electrical double layer; it is shown that the interaction of adsorbed pyridine and water must be taken into account.

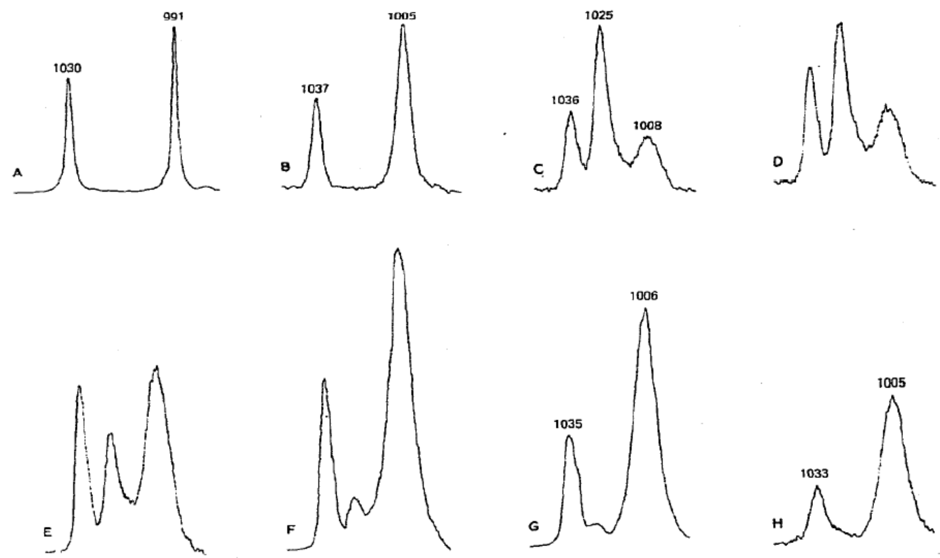
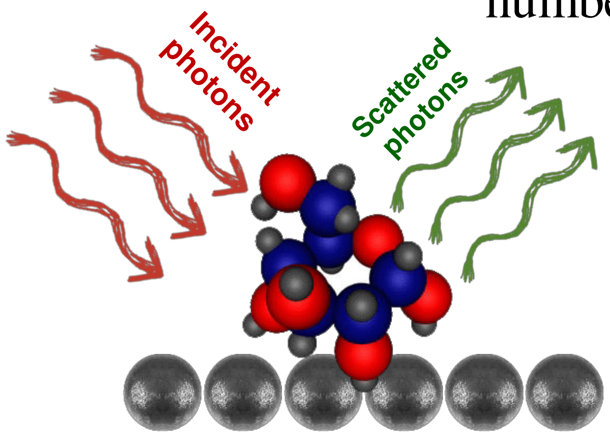


Fig. 2. Raman spectra of pyridine in solution and at the silver electrode. (A) liquid pyridine; (B) 0.05 M aqueous pyridine; (C) silver electrode 0 V (S.C.E.); (D) −0.2 V; (E) −0.4 V; (F) −0.6 V; (G) −0.8 V; (H) −1.0 V.

SERS: history&definition

Increase of scattered photons number



nanorough metallic substrate
SERS-active substrate

SERS Enhancement Factor (*EF*)

ratio of the intensities of the scattered radiation for SERS and Raman scattering per molecule

$$EF = (I_{SERS}/N_{SERS})/(I_{RS}/N_{RS})$$

Advantages of **Raman scattering** + ***EF* > 10⁶** ↑ of Raman intensity = sensitivity up to **femtomolar** concentration

SERS: history&definition

SERS mechanisms

Chemical

Electromagnetic

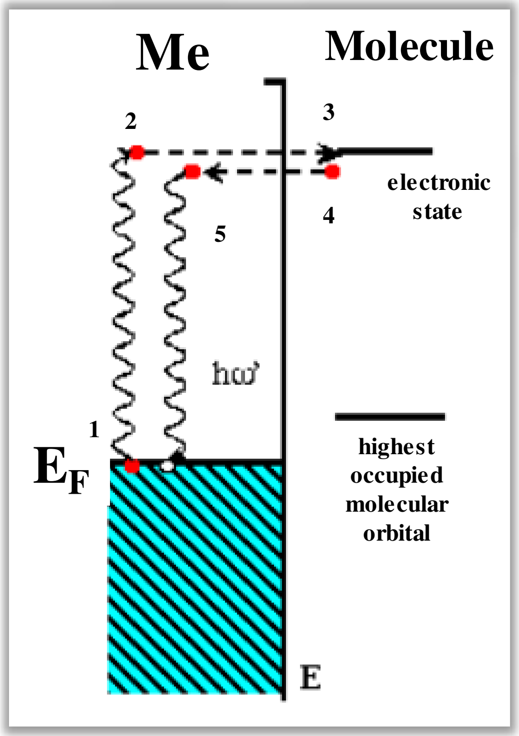
The mechanism of SERS is still an active research topic but today there is an agreement that enhancement has **two** components

SERS: history&definition

SERS mechanisms

Chemical

charge-transfer state between metal and adsorbed molecules

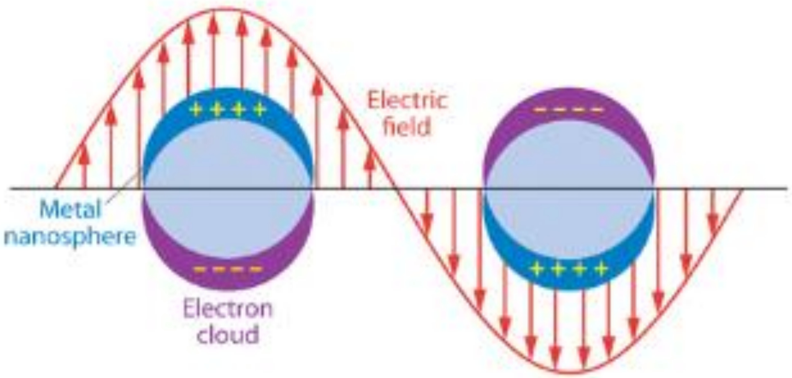


- site-specific
- analyte-dependent
- the molecule must be directly adsorbed to the roughened surface
- contributes an average ***EF*** of 10^3

SERS: history&definition

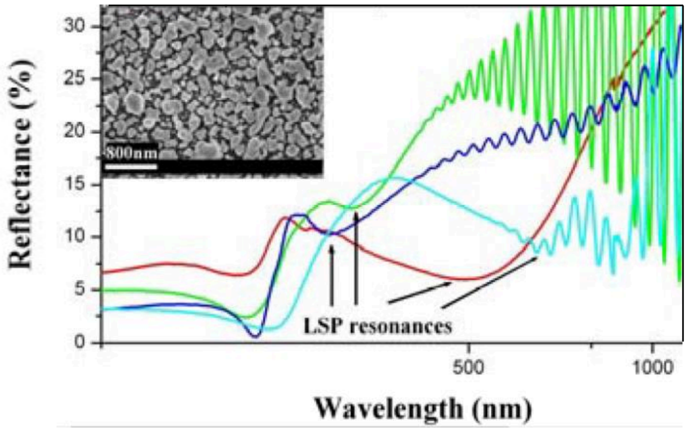
SERS mechanisms

increase of the E-field of the metallic nanostructures due to localized surface plasmon resonance (LSPR)



- can contribute ***EF*** > 10^6

Electromagnetic



Talk layout

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SERS-active substrates

What do we need for SERS-activity?

1. Strong plasmonic metal

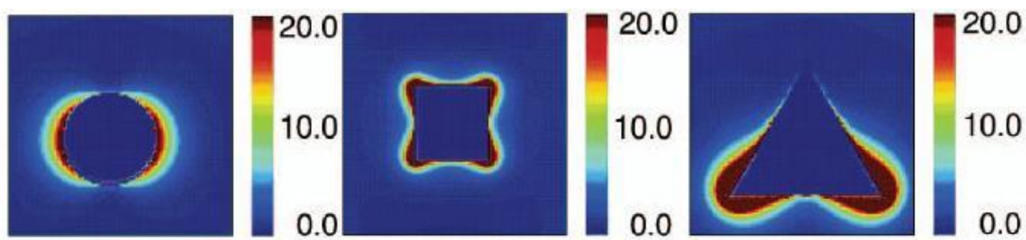
Ag, Au, Cu, ...

SERS-active substrates

What do we need for SERS-activity?

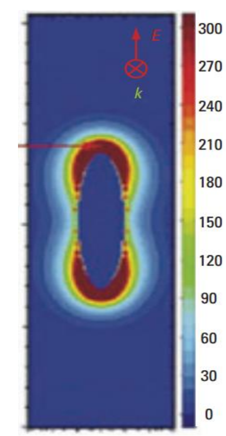
1. Strong plasmonic metal

2. Metal nanostructuring



- spheres,
- cubes,
- triangulars,
- dendrites,
- rods

of nanoscaled dimensions (10 – 150 nm)



SERS-active substrates

What do we need for SERS-activity?

1. Strong plasmonic metal

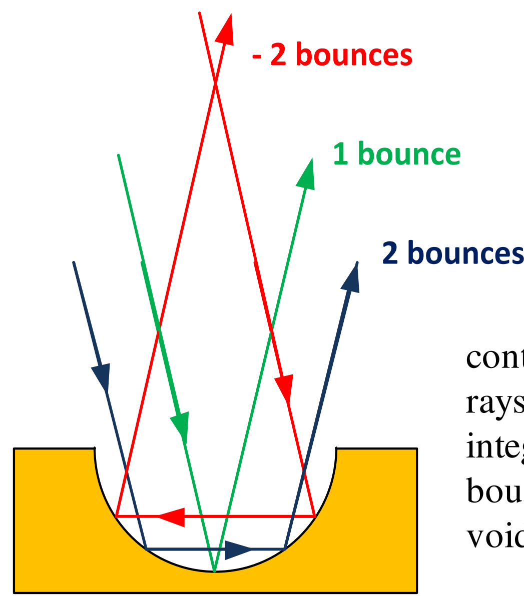
2. Metal nanostructuring

localised plasmon mode of strong rim component

nanovoid diameter: 500 – 2000 nm

[Cole *et al.*, *Opt. Express*, Vol. 17, No 16, 2009]

[Kelf *et al.*, *Phys. Rev*. B, 74, 2006]



contributions from rays of integer numbers of bounces through the void

Plasmonic metal **nanovoid**

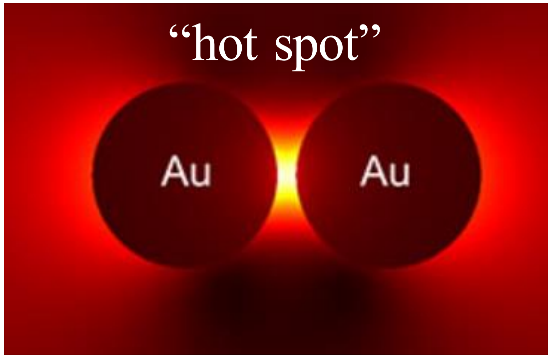
SERS-active substrates

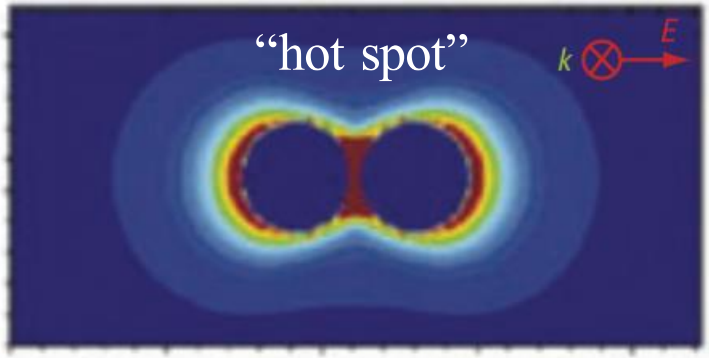
What do we need for SERS-activity?

1. Strong plasmonic metal

2. Metal nanostructuring

3. Extremely small gap between metal nanostructures ~ **2 nm**

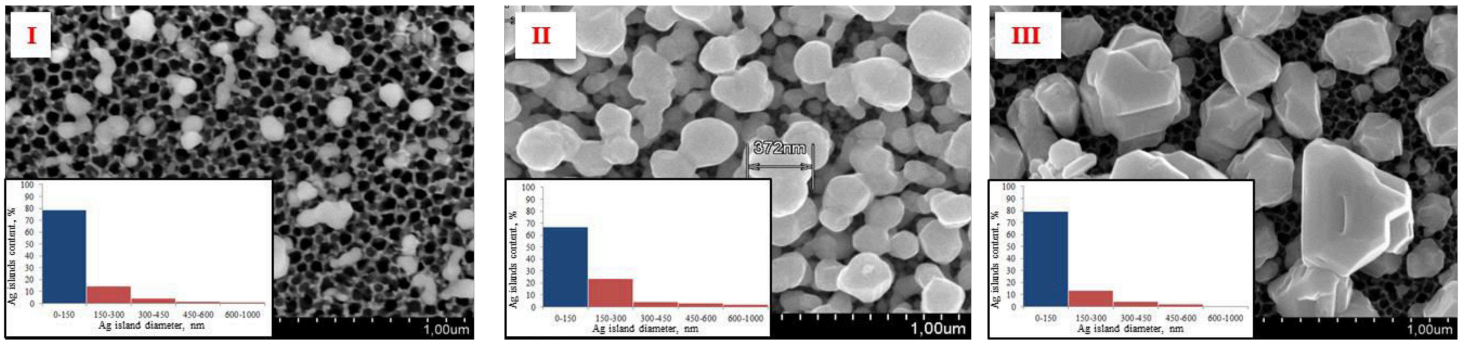


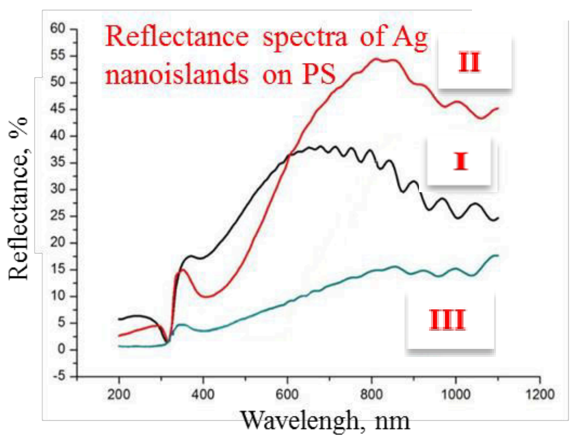


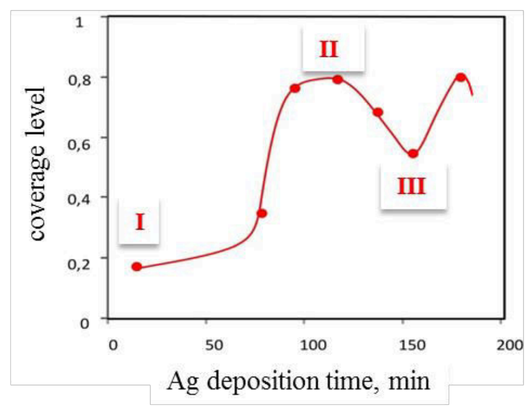
"hot spots" – places of a giant intensity of electric field

SERS-active substrates

SPR dependence on structural parameters

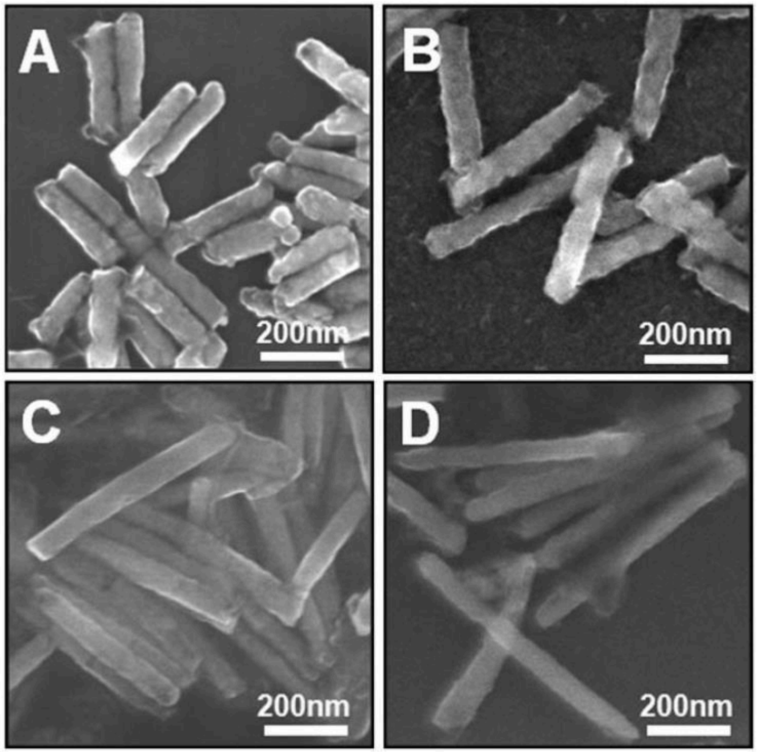






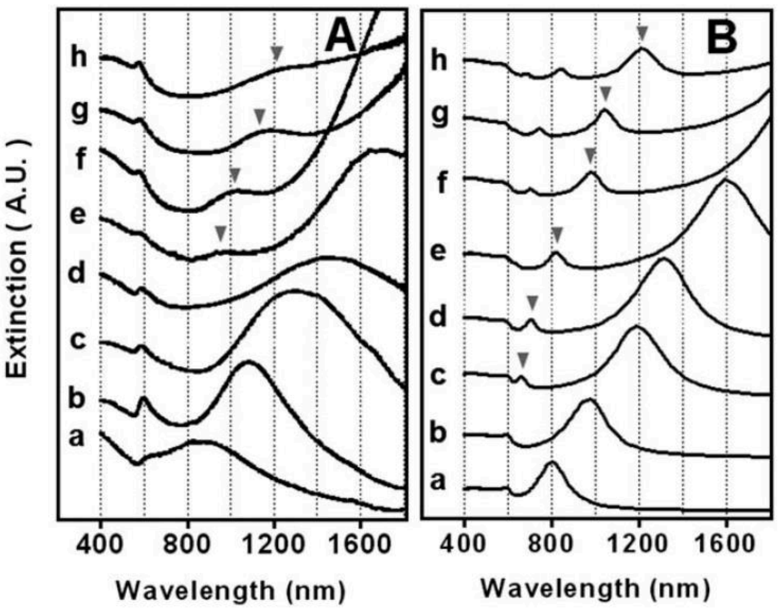
[A.Yu. Panarin et al. Physics, chemistry and application of nanostructures, 2013]

SPR dependence on structural parameters



Cu nanorods D – 64 nm,
(A) L – 234 nm, (B) L – 265 nm,
(B) (C) L – 464 nm, (D) L – 572 nm

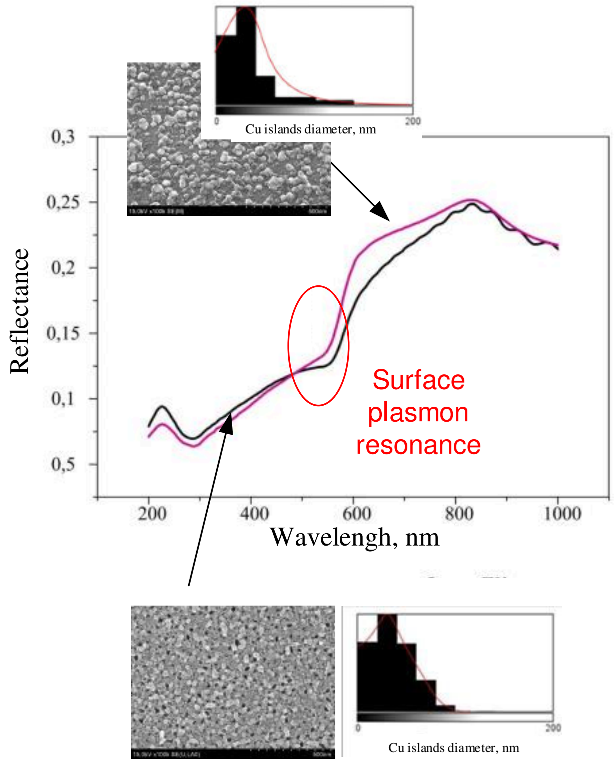
transverse and multiple longitudinal SPR modes at the aspect ratio greater than 4



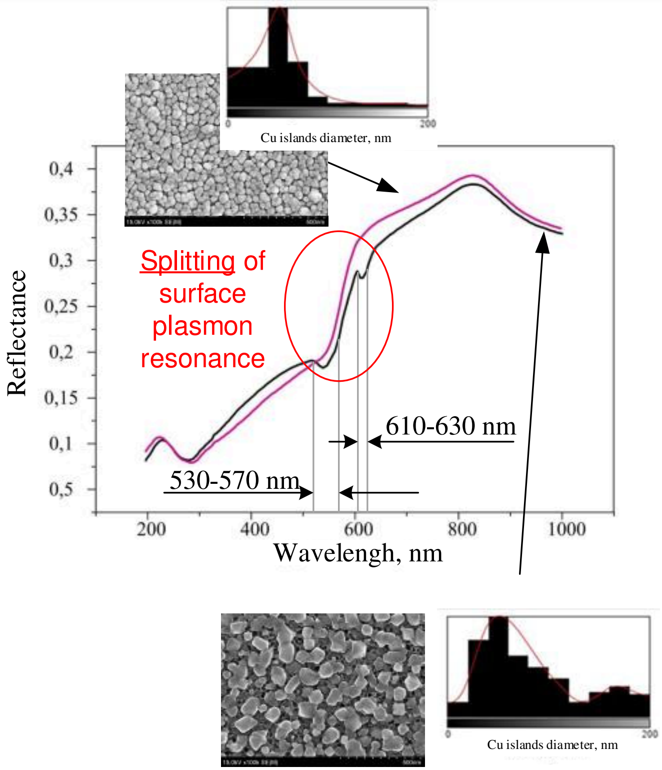
[M. Oh *et al*. J. Mater. Chem., 2011, 21, 19069–19073]

SERS-active substrates

SPR dependence on structural parameters



Unimodal diameter distribution of Cu islands

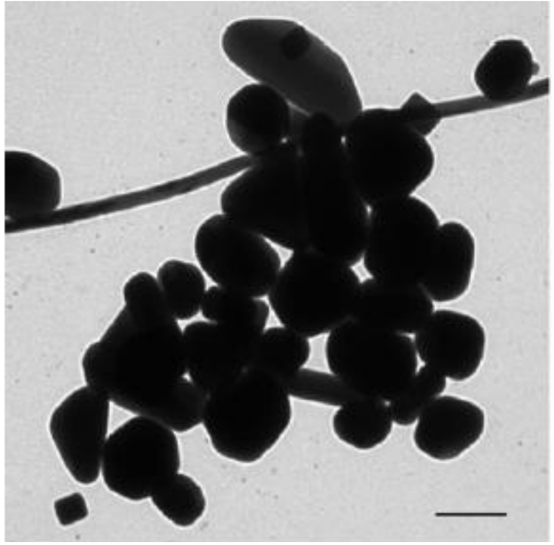


Bimodal diameter distribution of Cu islands

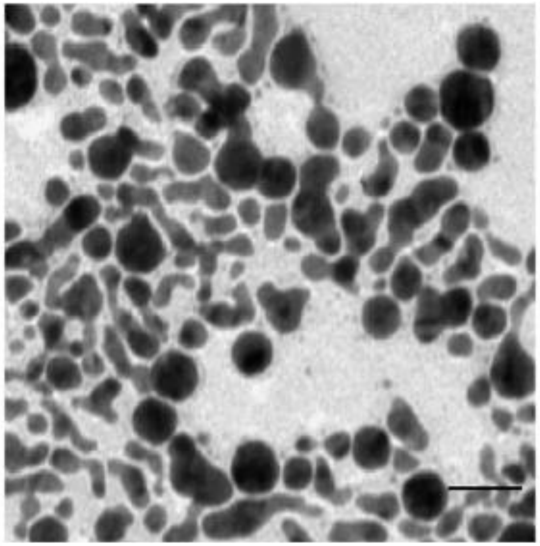
[A. Tikhanova *et al. Proc. 17-th Int. Conf.-Sc. AMT, Palanga, Lithuania*, 2015]

SERS-active substrates: liquid substrates

Ag colloids particles
[Zhao *et al.*, 2006]



chemical reduction



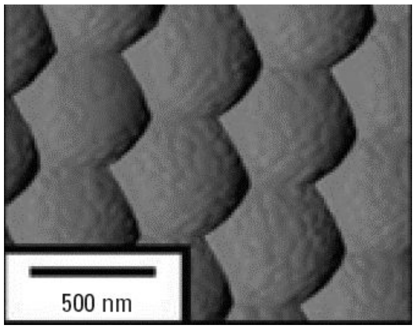
laser ablation

Great enhancement (10^{14})

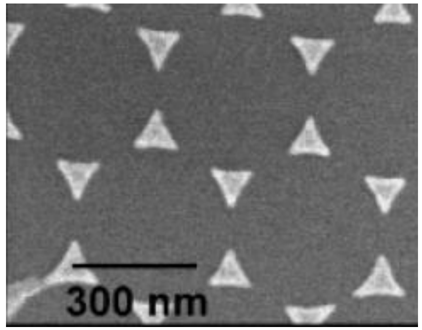
- Weak reproducibility
- Inconvenient to use

→ **difficult to apply practically**

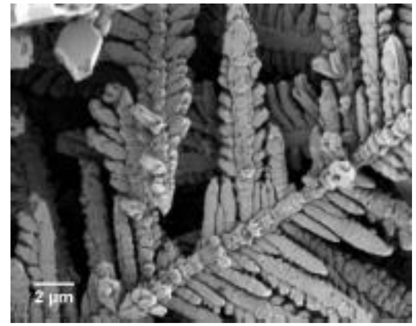
SERS-active substrates: solid substrates



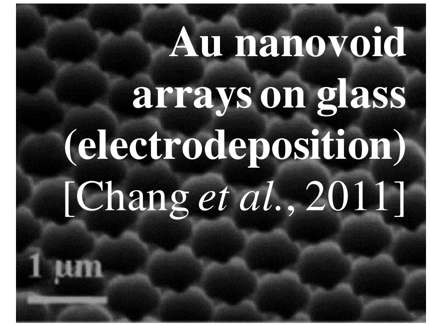
Ag film over nanospheres
[Haynes *et al.*, 2005]



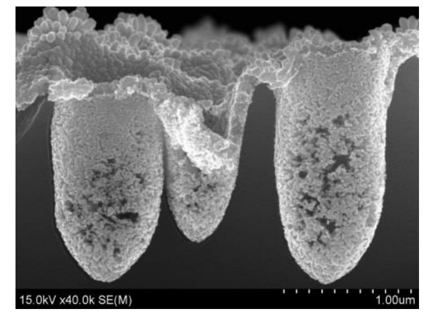
triangular Cu NPs (nanosphere lithography)
[Chan *et al.*, 2007]



Ag dendrites on Al
[Gutes *et al.*, 2010]



Au nanovoid arrays on glass (electrodeposition)
[Chang *et al.*, 2011]



Ag/Ni nanovoids
[Artsemyeva *et al.*, 2013]

- Moderate enhancement (10^6)
- Complicated&Expensive technology

- Good reproducibility
- Convenient to use

very good for practical application

SERS-active substrates: existing commercial products

1. **Thermo Fisher Scientific Inc.** – **Au** colloid
2. **Agiltron**– **Ag** thin film/nanorods on glass
3. **Ocean Optics** – **Au** NPs;
4. **Integrated Optics** – **Ag** nanoislands;
5. **Silmeco** – **Au**, **Ag** nanostructures;
6. **Renishaw Diagnostics (Klarite)** – **Au** thin film on textured Si
7. **EnSpectr** – **Ag** nanostructures

SERS-active substrates: existing commercial products

1. Thermo Fisher Scientific I
2. Agiltron– Ag thin
3. **Ocean Optics – Au NPs.**
4. Integrated Optics – Ag na
5. Silmeco – Au, Ag nanostru
6. Renishaw Diagnostics (Kl
7. EnSpectr – Ag

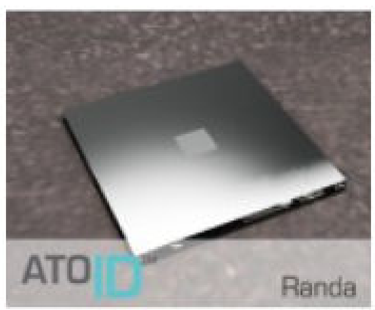
Analyte	Classification	SERS Substrate Active	Lowest Concentration Measured
Explosives			
TNT	explosive	Yes	10^{-4} M
RDX	explosive	No	N/A
Pharmaceuticals & Illicit Drugs			
JWH-018 (1-pentyl-3-(1-naphthoyl)indole)	analgesic (used in synthetic cannabinoids)	No	N/A
Carbamazepine	anticonvulsant	Weakly	Not measured
Nicotinamide	B vitamin	Yes	10^{-4} M
Food & Agriculture			
Melamine	food adulterant	Yes	10^{-3} M
Cyanuric acid	metabolite of melamine	Weakly	10^{-2} M
Crystal violet	fungicide	Yes	10^{-5} M
Taggants & Markers			
1,2-bis(4-pyridyl)ethylene (BPE)	taggant/marker	Yes	10^{-9} M
4-mercaptobenzoic acid	taggant/marker	Yes	10^{-7} M
4-mercaptopyridine	taggant/marker	Yes	10^{-6} M

Substrate shelf life:	~30 days

http://oceanoptics.com

SERS-active substrates: existing commercial products

1. Thermo Fisher Scientific Inc. – Au colloid.
2. Agiltron– Ag thin film/nanorods on glass.
3. Ocean Optics – Au NPs.
4. **Integrated Optics – Ag nanoislands.**
5. Silmeco – Au
6. Renishaw Di
7. EnSpectr – A



SERS substrate 'Randa' (pack of 3)

Unmatched relative enhancement of Raman scattering among commercial SERS substrates. Silver coated - works with wide range of excitation wavelengths - from blue to near infrared (tested). Low cost for truly routine molecular diagnostics.

75,00 €

View

Select to compare

http://integratedoptics.eu

SERS-active substrates: existing commercial products

Klarite SERS*	Slide Mounted	Unmounted Chips
Size (mm)	75 x 25 x 2	6 x 10 x 0.5
Active area	4 mm x 4 mm	
Active surface	Gold coated textured silicon	
Sampling methods	Evaporated from solution Materials that bind to gold can be measured in solution	
Raman excitation parameters	633 nm, 785 nm >5 microns spot size (>100 microns recommended) 2mW per 10 square microns	
Enhancement factor, relative to a non-enhancing surface	>10,000 for most materials >1,000,000 for binding molecules	
Product code	**302**	**303**

Item	Product Code	Product Name	Quantity	List Price £	Unit Discount (%)	Total £
1	303	Unmounted Klarite Substrate	5	75.00	0.00	**375.00**

1. Thermo Fisher Sc
2. Agiltron– Ag thin
3. Ocean Optics – A
4. Integrated Optics
5. Silmeco – Au, Ag
6. **Renishaw Diagnostics (Klarite)** – **Au** thin film on textured Si.
7. EnSpectr – Ag nanostructures.

SERS-active substrates: existing commercial products

1. Ther
2. Agil
3. Ocea
4. Integ
5. Silm
6. Reni

EnSpectr substrate	Unmounted Chips
Size (mm)	6x6x0.5
Active area (mm)	ø 5
Sampling methods	Liquid drop deposition-evaporation Liquid drop spin coating Immersion Vapour phase deposition
Laser excitation parameters	λ 450 – 550 nm Spot size – arbitrary Power density < 5000 W/cm^2
Enhancement factor, relative to a non-enhancing surface	$>10^5$ - for neutral substances $>10^7$ - for resonant Raman analytes and substances exhibiting affinity to silver
Relative standard deviation in signal	<10%
Twofold reduction of the enhancement factor at open air	70 hours after opening the package

7. **EnSpectr** – **Ag** nanostructures.

SERS-active substrates: existing commercial products

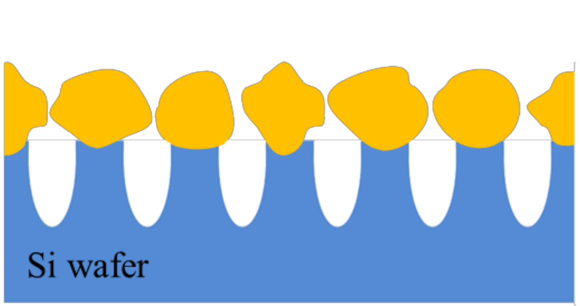
- Detection limit $10^{-2} – 10^{-9}$ M depending on the analyte
- EF – 10^{6} - 10^{7}
- Extremely expensive
- Interval of exitation is limited by the material of the substrate (Ag, Au)
- Weak storage stability

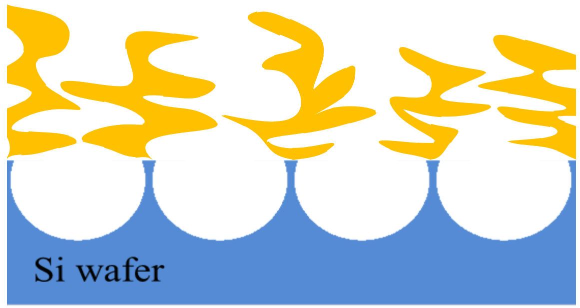
↓

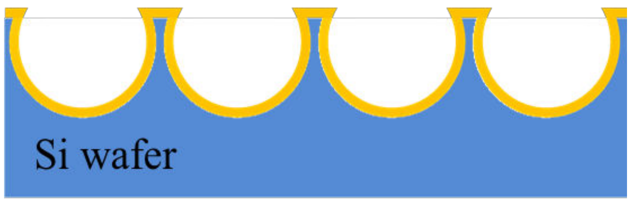
development of SERS-active substrates with improved parameters is still an urgent goal

SERS-active substrates: our approach

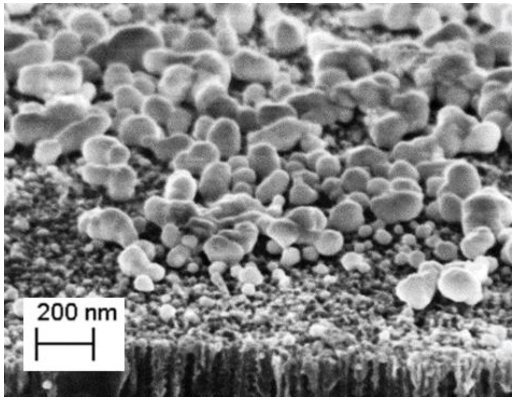
Using porous silicon template to define sizes, shape and spacial location of the depositing metal structures

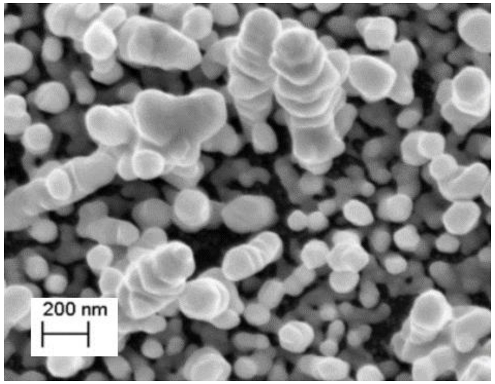


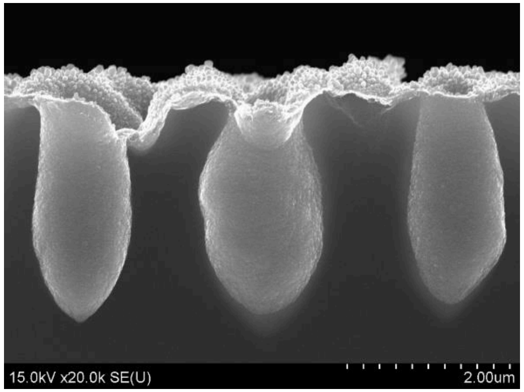




Ag NPs **Ag dendrites** **Ag/Ni nanovoids**

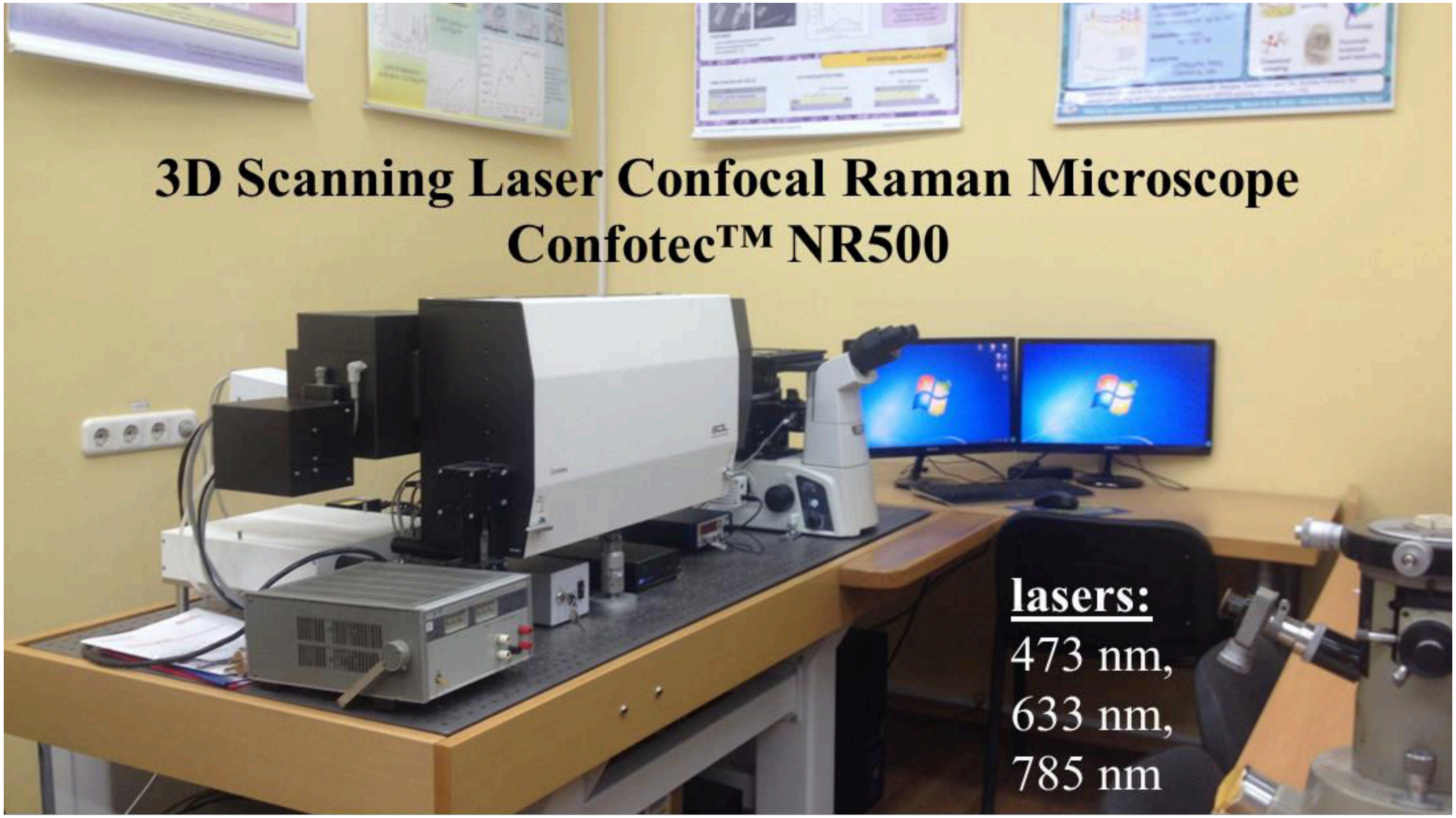




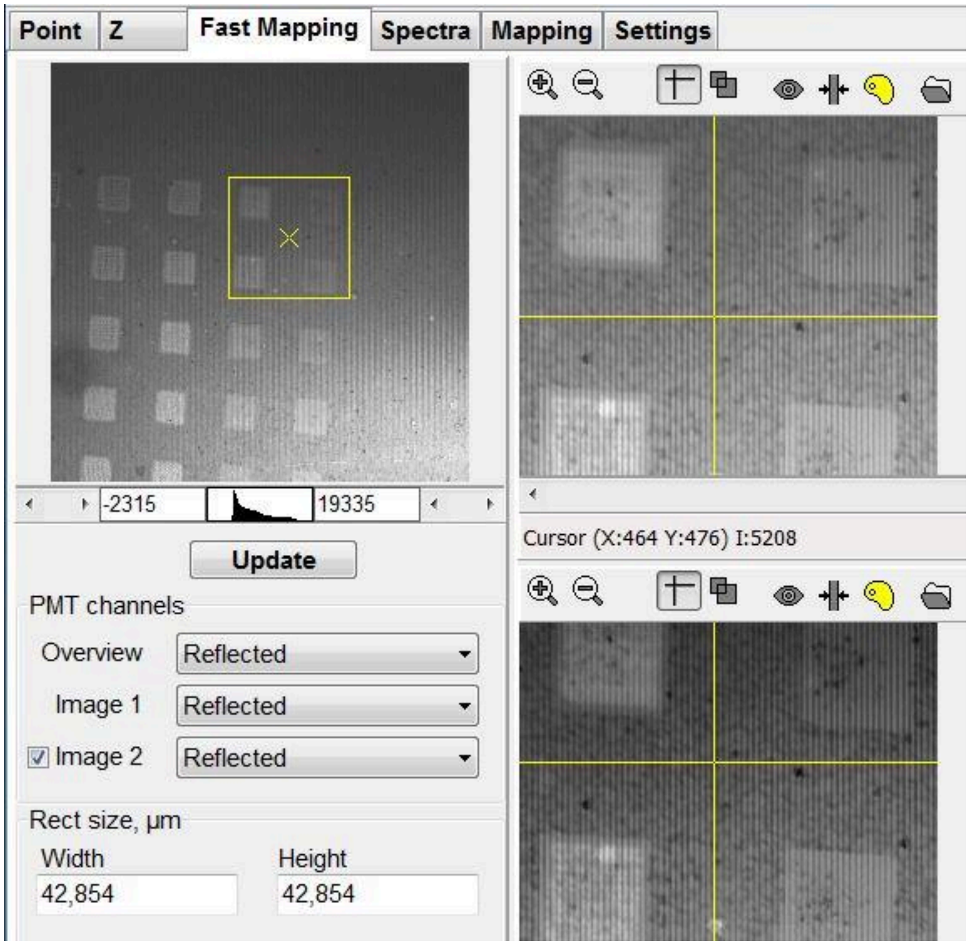


SERS-active substrates: our approach

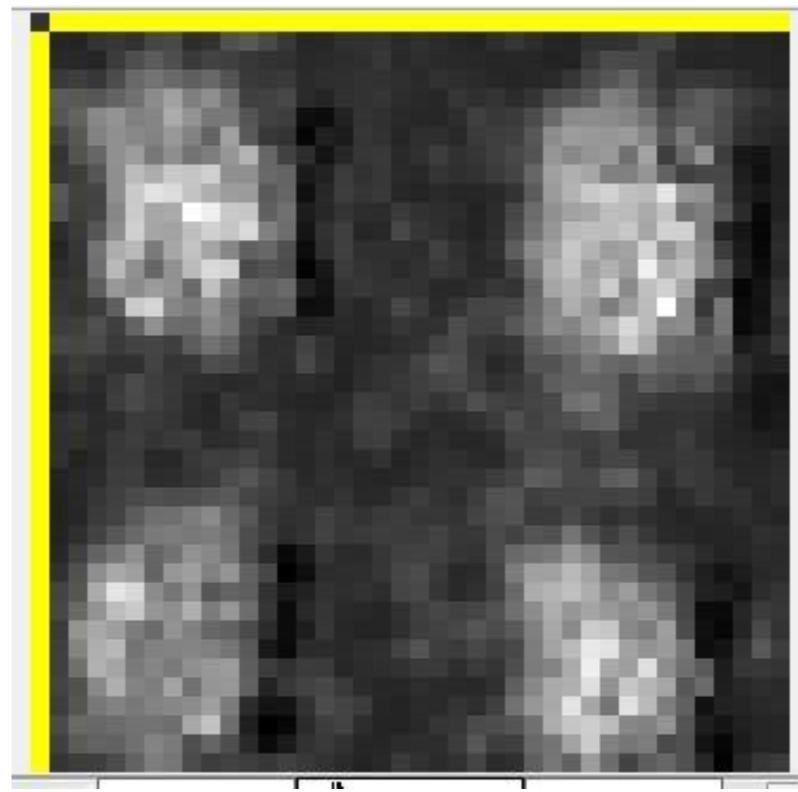
Our equipment



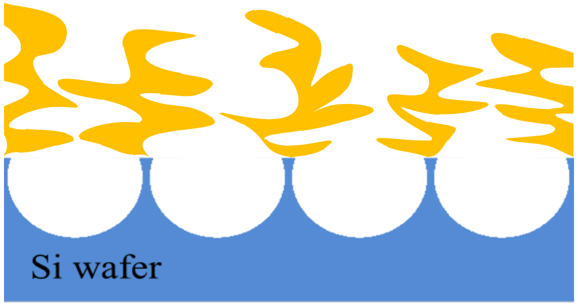
SERS-active substrates: our approach



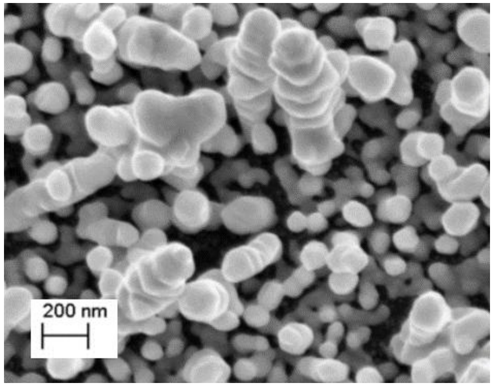
Mapping



SERS-active substrates: our approach



Ag dendrites

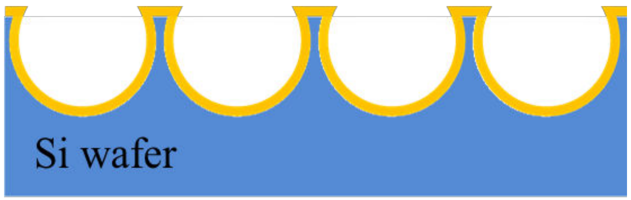


Analyte: organic dye R6G

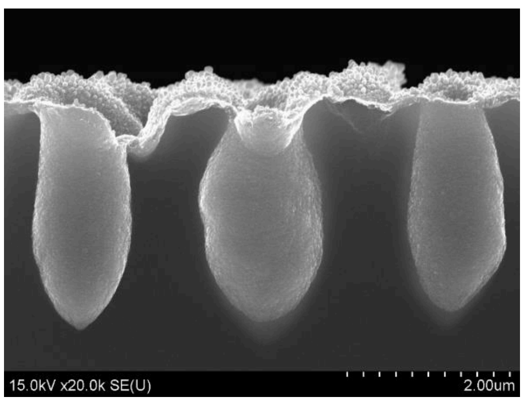
Detection limit at 473 nm: 10^{-13} M

Detection limit at 785 nm: 10^{-6} M

SERS-active substrates: our approach



Ag/Ni nanovoids

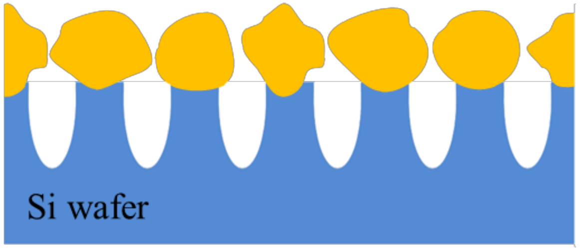


Analyte:
cationic Cu(II)-tetrakis(4-N-methylpyridyl) porphyrin

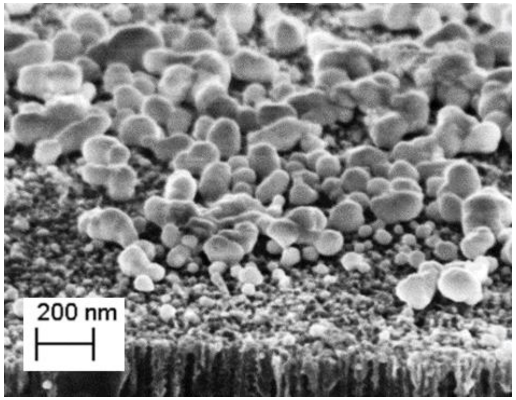
Detection limit at 473 nm: 10^{-11} M

[K. Artsemyeva et al. *ECS Trans.*, 2013, 53(11), 85-95]

SERS-active substrates: our approach



Ag NPs



Analytes:

- organic dyes R6G, methylene blye, etc.
- cationic Cu(II)-tetrakis(4-N-methylpyridyl) porphyrin
- Zn-meso-tetra [4-N-(2'-oxyethyl) pyridyl] porphyrin
- proteins (albumin, lysozyme, lactoferrin)
- oleic, palmitic, and stearic acids

Detection limit at 473, 532 nm: $10^{-10} – 10^{-12}$ M

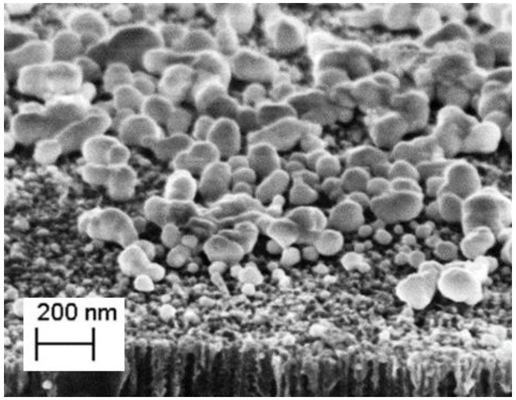
EF = $2 \cdot 10^8$

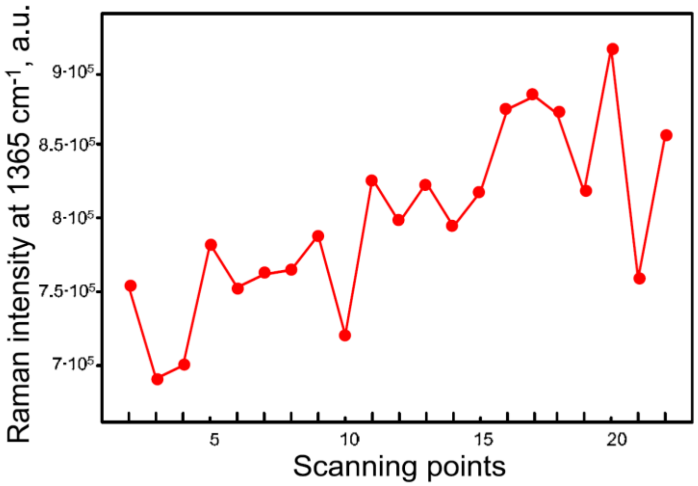
[A. Yu. Panarin et al. *J. Appl. Spectroscopy*, 2009, 76(2), 281-287]

SERS-active substrates: our approach

Stability of SERS-signal intensity

Ag NPs



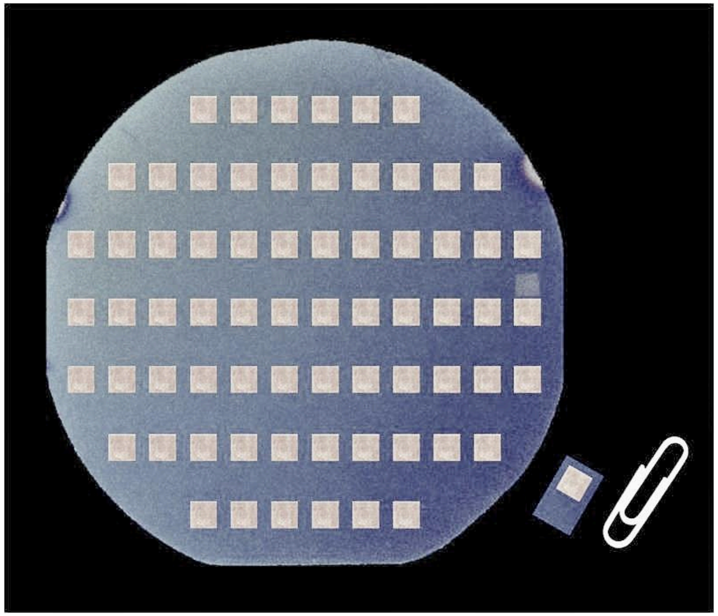


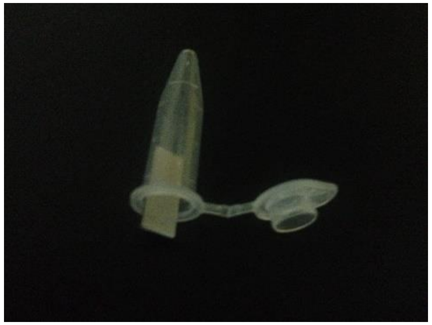
- Spot-to-spot I_{SERS} variation < 15 %
- Sample-to-sample I_{SERS} variation < 15 %
- Storage stability of I_{SERS} > 6 months

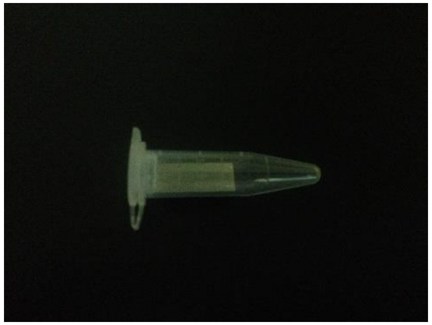
[Artsemyeva *et al.*, PSS (c), 2013]

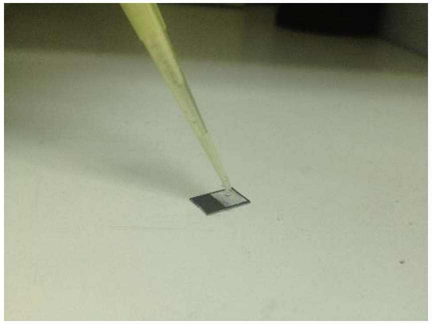
SERS-active substrates: our approach

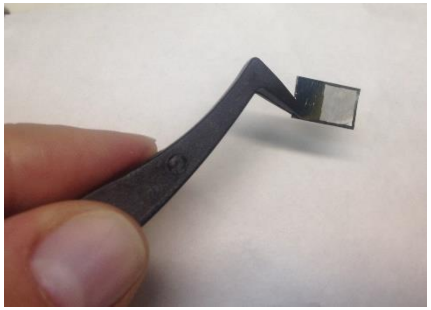
Prototype of SERS-active substate









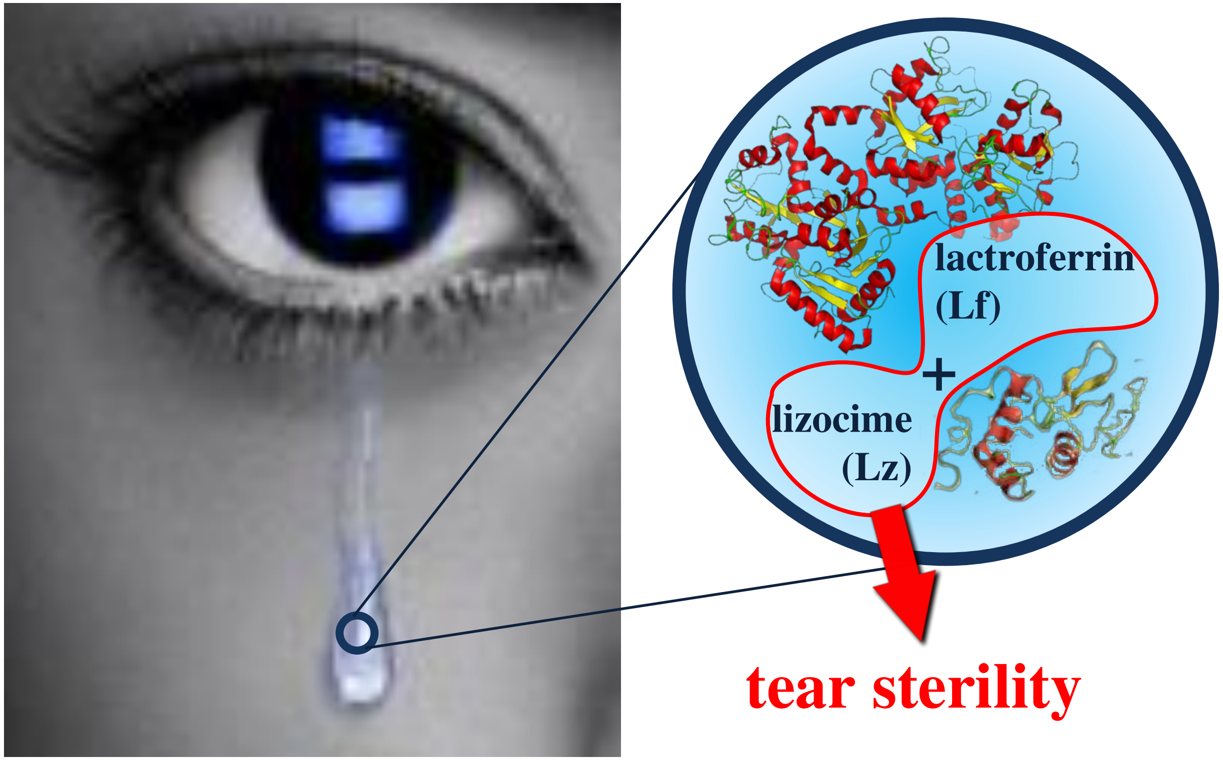


Talk layout

- **History&definition**
- **SERS-active substrates**
  - fabrication
  - properties
- **SERS application**

Examples of application

Tear proteins detection



Examples of 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**

Determination of tear proteins by surface enhanced Raman scattering

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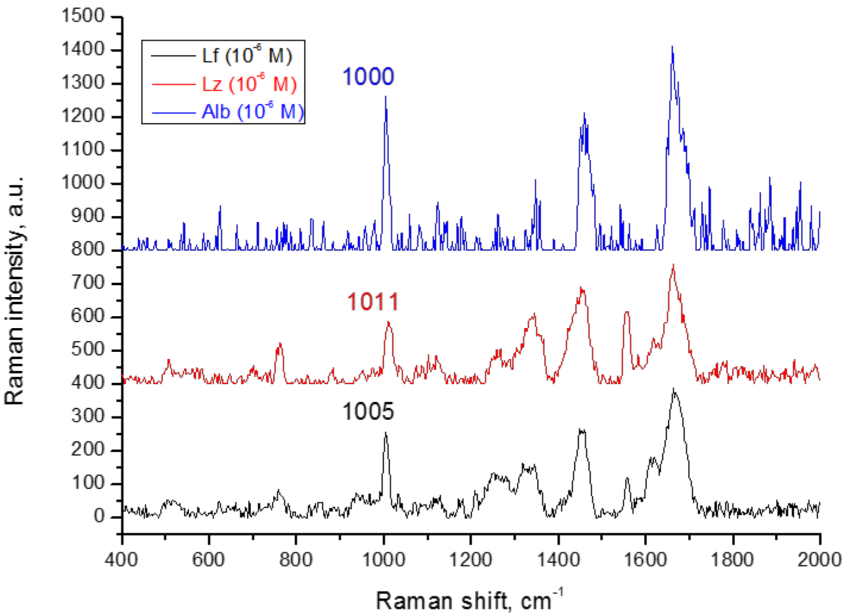
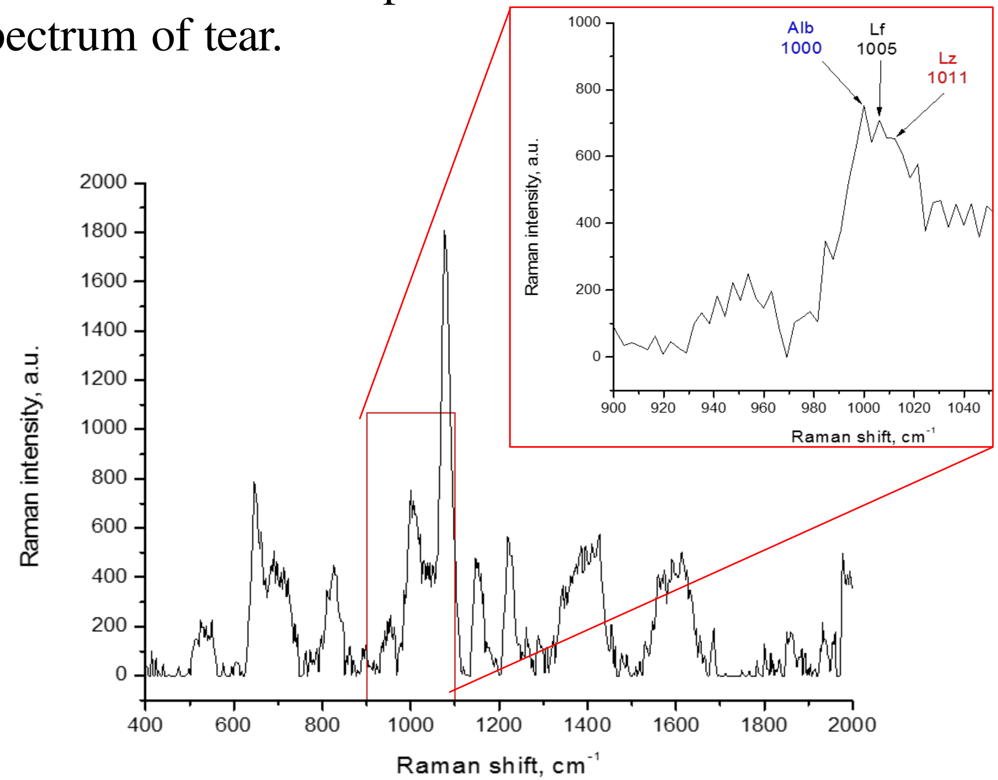
Examples of application

Tear proteins detection

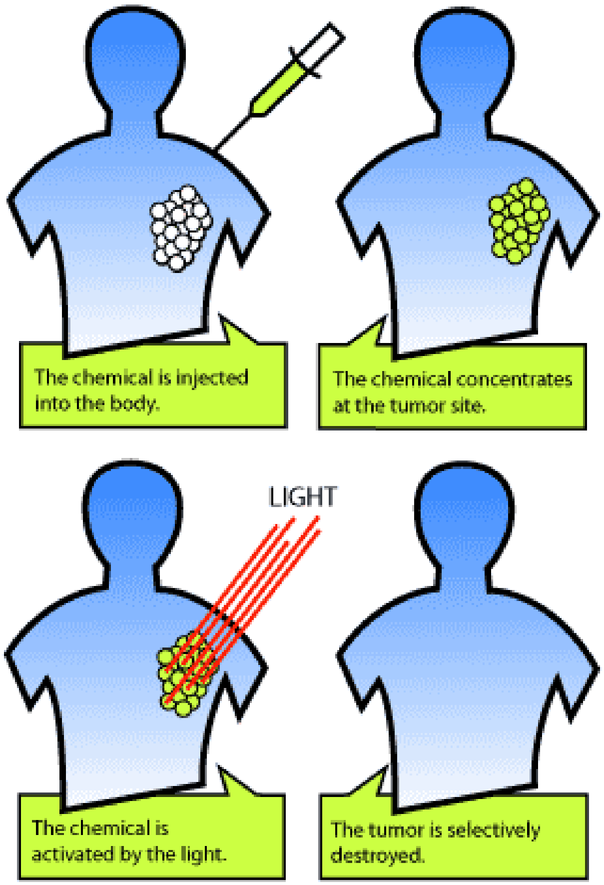
- SERS-spectra of Lf, Lz and Alb have typical bands for these proteins.
- Proteins can be distinguished in SERS-spectrum of tear.





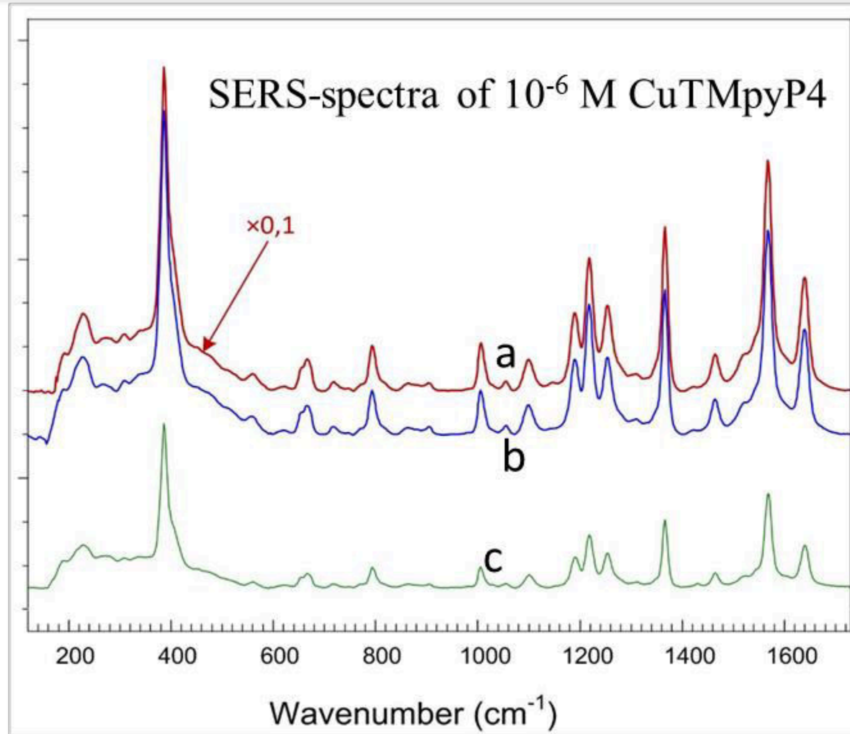
Examples of application

Photodynamic therapy of cancer



http://www.photochembgsu.com/applications/therapy.html

Detection of photosensitizers in physiological fluids




RAMAN SPECTROSCOPY

A comparative study of surface-enhanced Raman scattering from silver-coated anodic aluminum oxide and porous silicon

S. N. Terekhov,[a*] P. Mojzes,[b] S. M. Kachan,[c] N. I. Mukhurov,[a] S. P. Zhvavyi,[a] A. Yu. Panarin,[a] I. A. Khodasevich,[a] V. A. Orlovich,[a] A. Thorel,[d] F. Grillon[d] and P.-Y. Turpin[e]

Applications survey

- **Chemical sensing**
- **Biomedical sensing**

Detection of pharmaceuticals medicines in physiological fluids
Living cells, cancer gene and bacteria, pathogen detection
Glucose detection
Detection platforms for biological toxins

- **Forensic science and security**

Drugs and poisons detection
Explosives detection

- **Ecology**

Detection of pesticides and pollutants

Determination of quality and adulteration of tequila through the use of surface plasmon resonance

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In this work, the surface plasmon resonance (SPR) technique is used to determine the quality or adulteration of tequila beverages. Graphic analyses of the position and width of the SPR curve are related to the complex refractive index of the sample, showing differentiated regions where one can easily and unambiguously identify white, aged, or extra-aged tequilas, and even adulterated or low qual-

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