POROUS SILICON TEMPLATING OF METAL NANOSTRUCTURES: an approach to stable and ultrasensitive SERS substrates

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

Fabrication → electrochemical anodization of Si

- time of anodization → thickness
- current density → porosity

\[
\text{Pore diameter, } \ D \\
\text{Distance between pore centers, } \ L
\]

HF-based solution

\[
\text{Si} + 2\text{HF} + \text{nH}^+ \rightarrow \text{SiF}_2 + \text{H}^+ + (2 - \text{n})\text{e}^-
\]

(Porosity %) \( p = \frac{V_{\text{pores}}}{V_{\text{Si}}} \times 100 \)

cross sectional dimension of Si elements, \( h \)

definition of sizes, shape and spacial location of the depositing metal structures

\( D, L, H, h \)

Si type + anodizing regimes
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

- Porosity, $p = 75\%$
- PS thickness, $h = 1 - 20\, \mu m$
  (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

Me salt+H$_2$O: Si oxidation + Me reduction

Me$^{n+}$ + n$^{e-}$ → Me$^0$
Si$^{n-}$ + 2H$_2$O → SiO$_2$ + 4H$^+$

Me salt+H$_2$O+HF: ...+ Si dissolution

SiO$_2$ + 6HF → 2H$^+$ + SiF$_6^{2-}$ + 2H$_2$O

Negative redox potential

Positive redox potential
Partial connection of NPs, PS surface covering with Ag SILVER nanoparticles on mesoporous silicon

Structure and reflectance

NPs of sizes favorable for SPR

Reflectance spectra of Ag NPs on PS

[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

Detection limit

473 nm

473 nm
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

![Graph showing Raman shift vs. intensity]
SERS-active substrates based on microporous silicon

Structure and reflectance

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

785 nm accumulation 1 s

Test analyte: palmitic acid

solid palmitic acid
473 nm
30 s

10^{-5} M palmitic acid
785 nm
5 s
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
BIMETAL nanovoids on macroporous silicon

SPR in red region

SPR in UV region

Wavelength, nm

Reflectance, %

Controllable SPR + great enhancement in nanovoid

the strongest plasmonic metal

Ag nanoparticles

Ag

Ni

Cu

SERS-active substrates based on macroporous silicon
Fabrication and structure of bimetallic nanostructures:

1) Ni (Cu) electrodeposition
2) Ag immersion deposition
SERS-active substrates based on macroporous silicon

Fabrication of substrates demonstrating SERS-activity in the required region of excitation wavelength
SERS-active substrates based on macroporous silicon

SERS-activity

10^{-6} \text{ M CuTMpyP4}

441.6 \text{ nm}

- Ag/mesoPS
- Ag/Ni/macroPS

\times 0.2

\text{Intensity (a.u.)}

\text{Wavenumber (cm}^{-1}\text{)}
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.

**Price:**

5 – 7 Euro/substrate

**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 months

**How to use?**

- **Step 1:** Drop analyte solution on SERS chip
- **Step 2:** Measure with confocal Raman spectrometer
- **Step 3:** Identify the analyte

**Applications:**

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

**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

* depending on analyte
** depending on substrates type
*** rinse with HCl before use
Test analytes: **metallic porphyrines**

**porphyrin derivatives – photosensibilizators**

in photodynamic therapy of cancer

![Graph showing Raman intensity vs. concentration of CuTMpyP4](image.png)

**Detection limit**

$10^{-11}$ M

dependence of SERS intensity in the $1365$ cm$^{-1}$ line on concentration of CuTMpyP4
Test analytes: phospholipids

part of early diagnostics of pulmonary, hepatic, sclerotic diseases

Together with JINR, laboratory of nanophotonics, center of Raman microscopy (Russia)
Proper therapy of eye diseases

fast analysis of tear liquid micro-/nanomolar sensitivity
**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.
Lf, Lz at picomolar concentration are destructed under laser excitation 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.
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 – **meet requirements for commercial product**
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lasers:
473 nm,
633 nm,
785 nm
...and thank YOU for your attention😊