

Nanostructured substrates for SERS diagnostics of cell structures

A.A.Semenova

E.A.Goodilin

A.P.Semenov

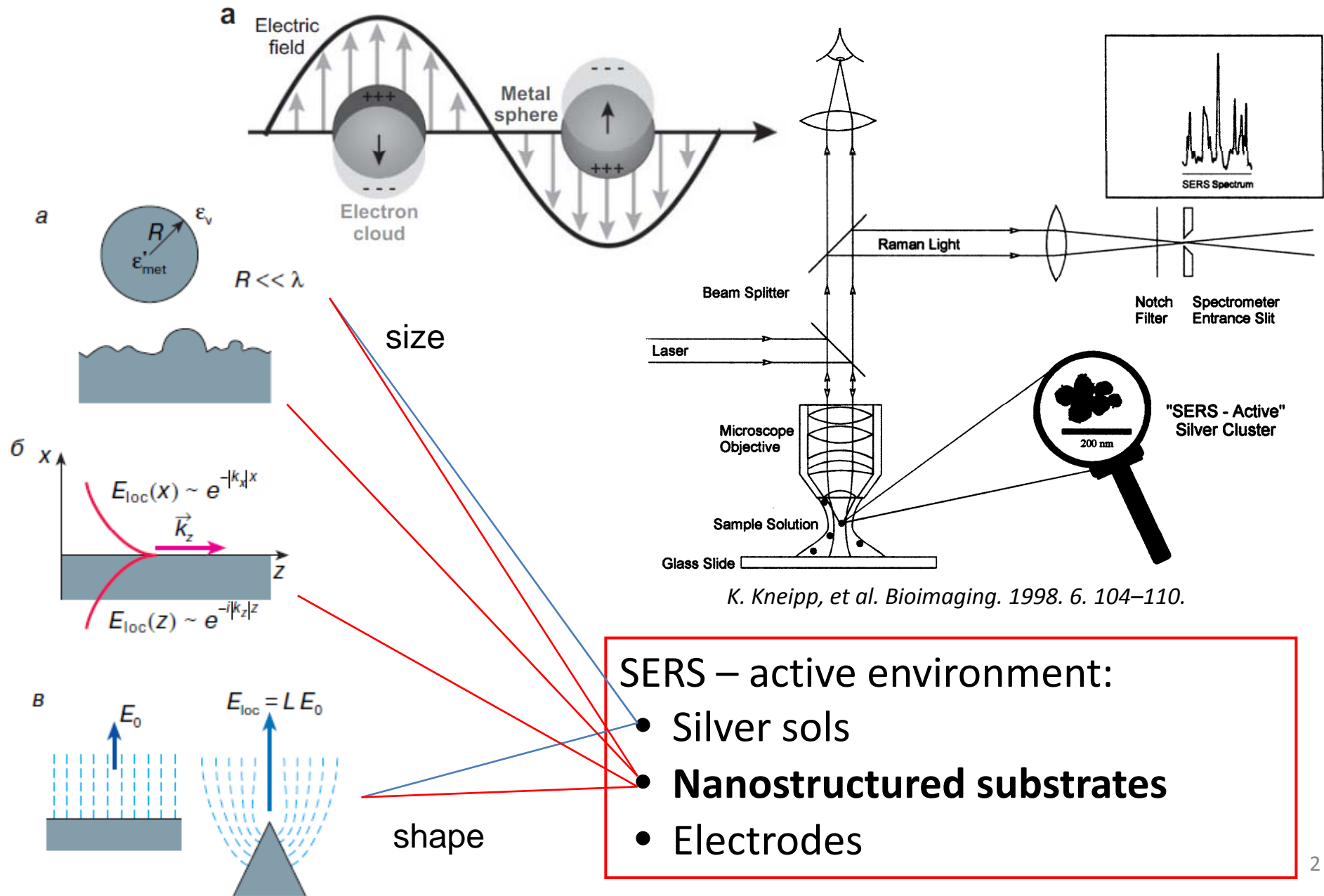
N.A.Brazhe

G.V.Maximov

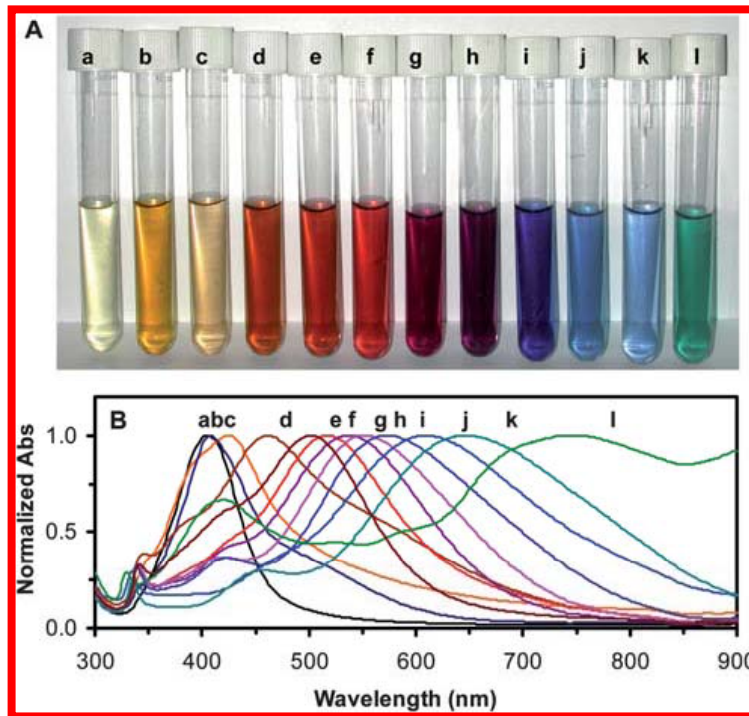
Yu.D.Tretyakov



Surface-Enhanced Raman Scattering Spectroscopy



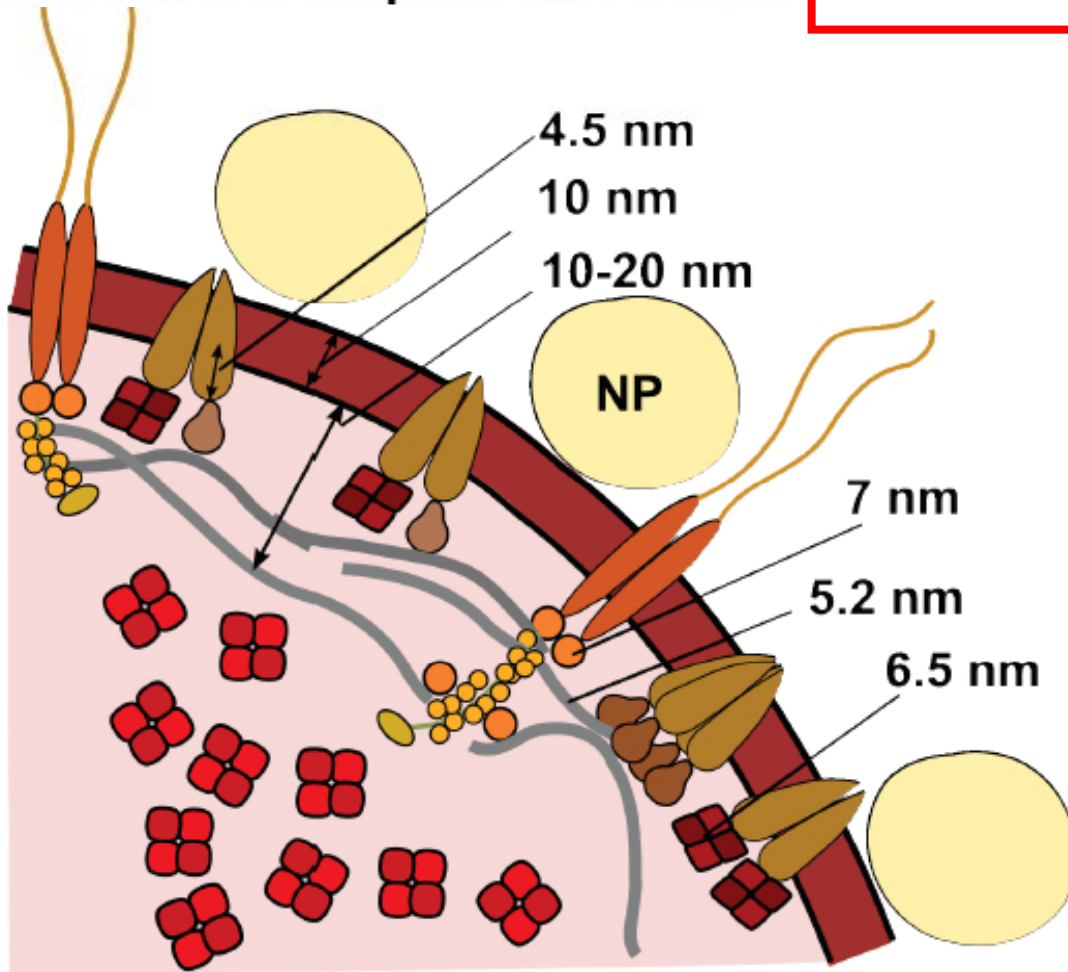
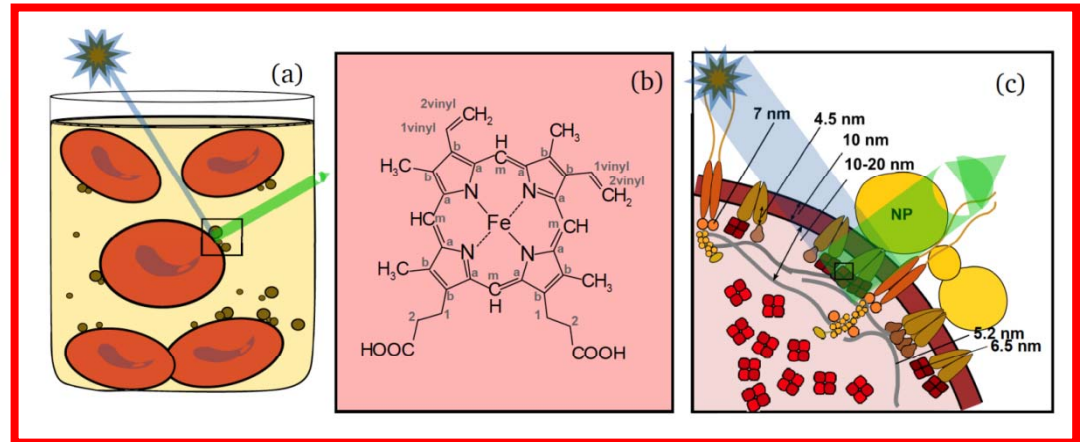
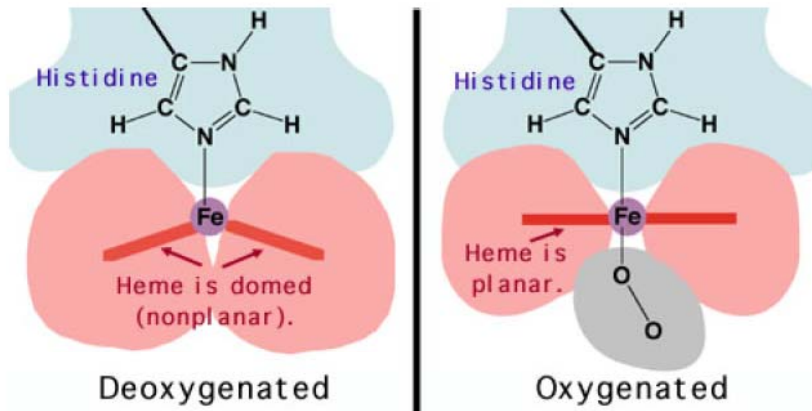
A couple of metals for a big goal






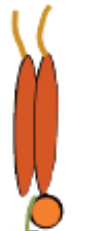





IA																	VIIIA	
H	IIA																	He
Li	Be																	Ne
Na	Mg	IIIB	IVB	VB	VIB	VIB	VIB	VIII	IB	IIIB	Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	

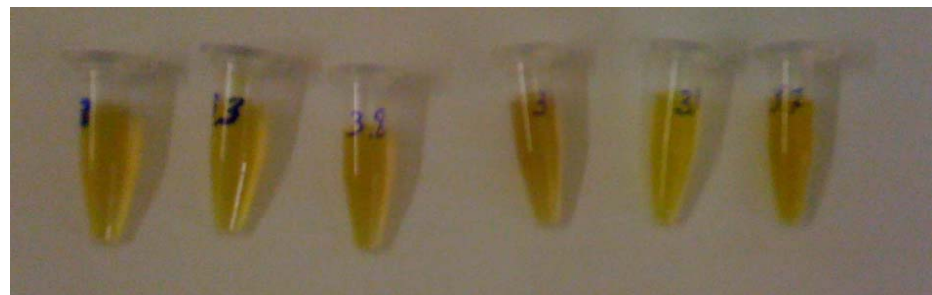
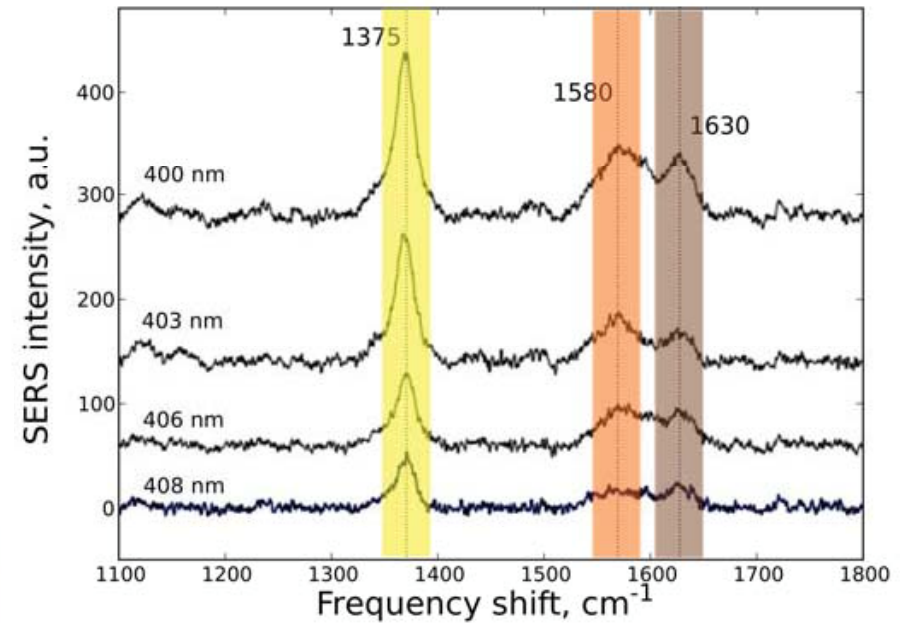
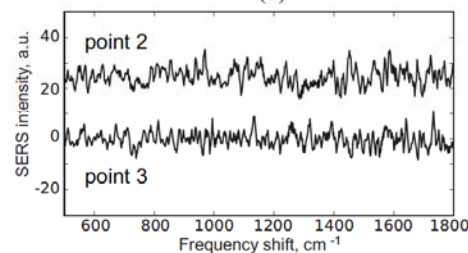
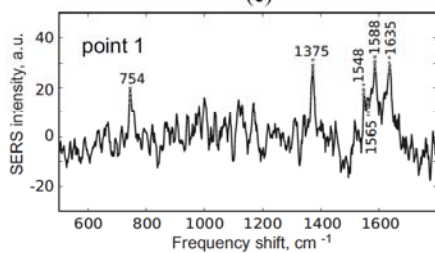
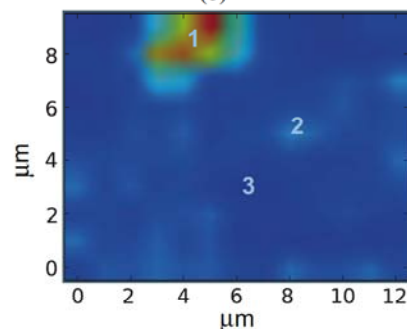
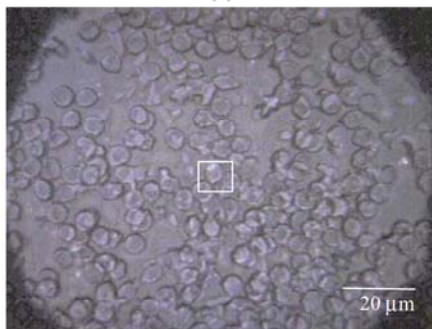
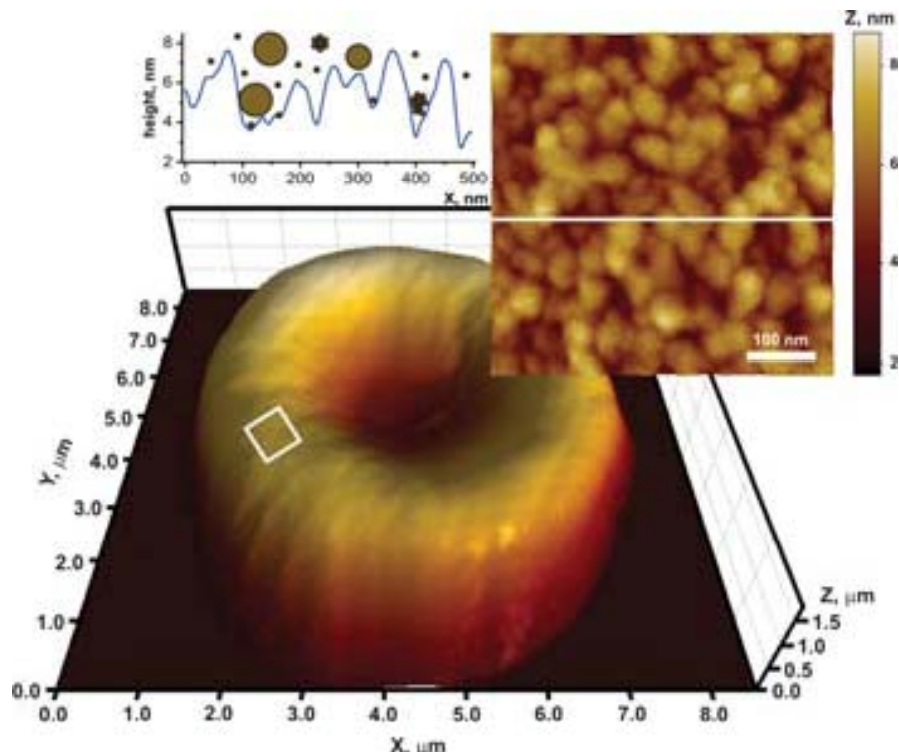
R. Dornhaus. *Festkörperprobleme*. 1982. XXII. 201–228.
 R. Alvarez-Puebla, et al. *Small*. 2010. 6 (5). 604–610.

T. Huang, et al. *J. Mater. Chem.* 2010. 20. 9867–9876.



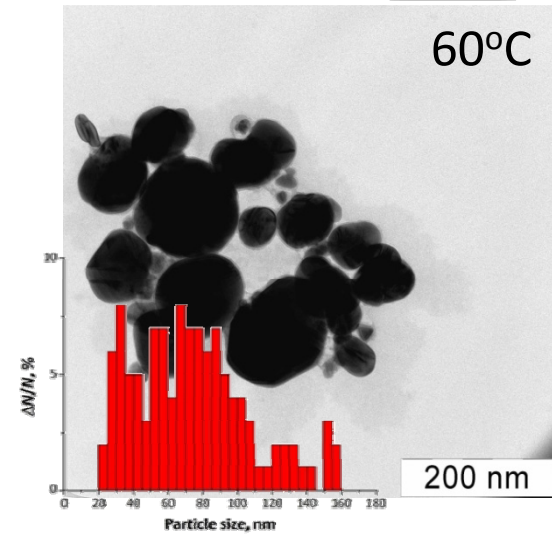
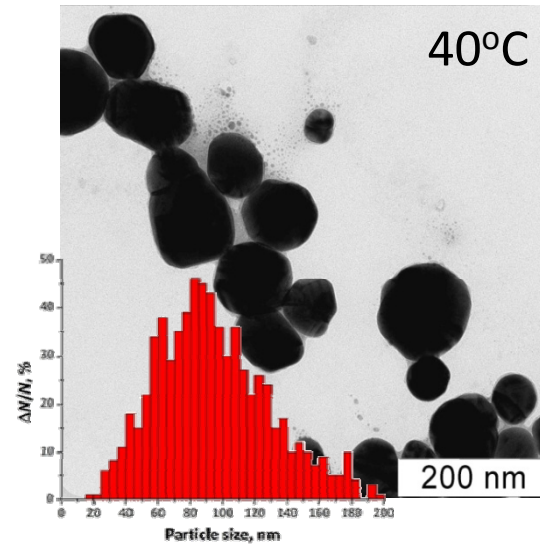
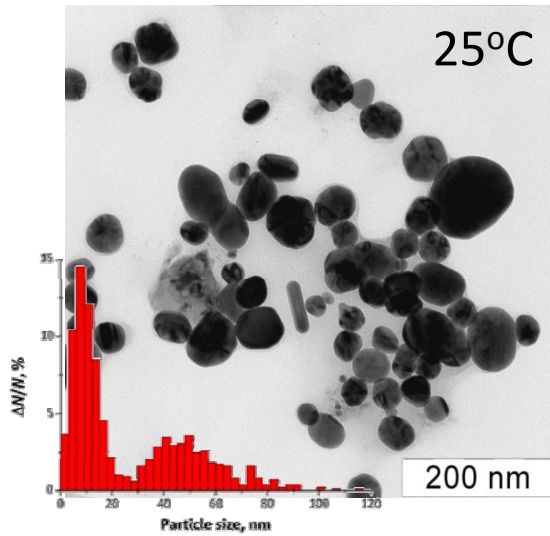
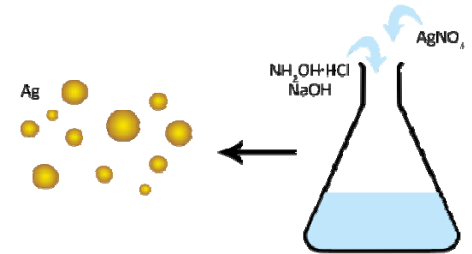
-  NP Nanoparticle
-  Hb_{sm}
-  Hb_c
-  AE1 exchanger (band 3)
-  Ankyrin
-  Glycophorin with oligosaccharide filaments
-  Band 4.1
-  Actin, tropomyosin, tropomodulin
-  Spectrin

A problem of statistics

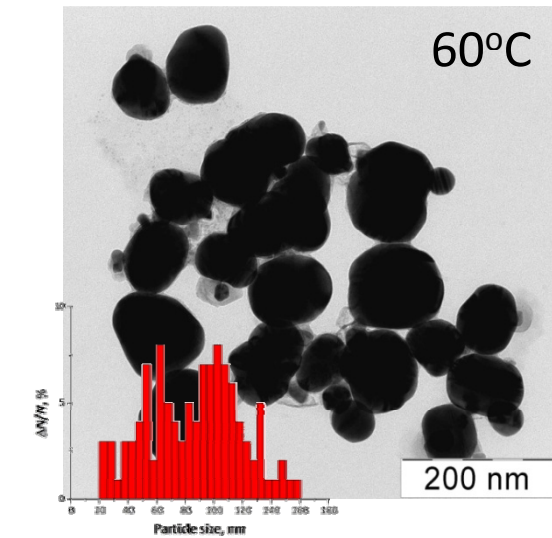
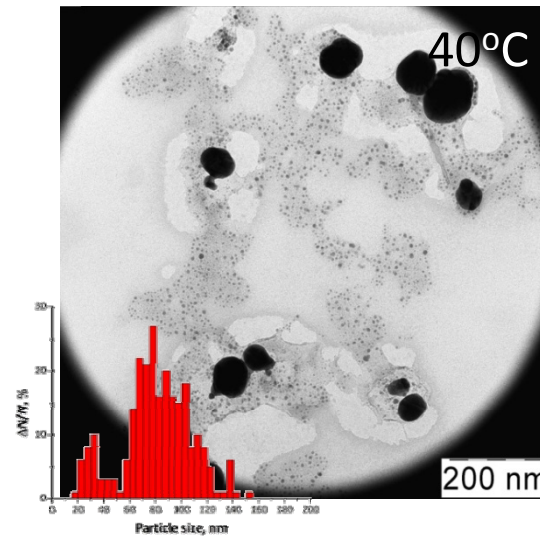
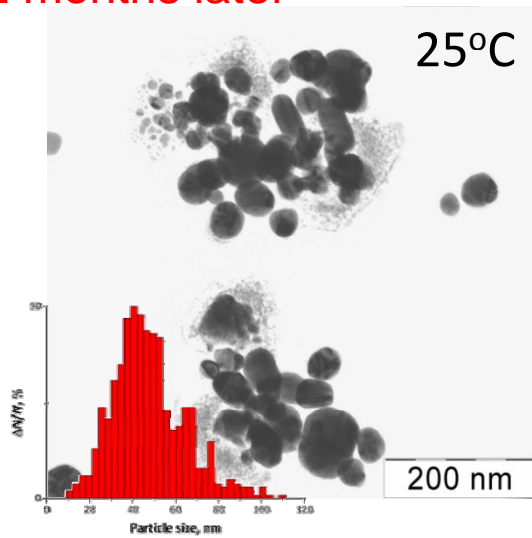


A problem of ageing

as-prepared

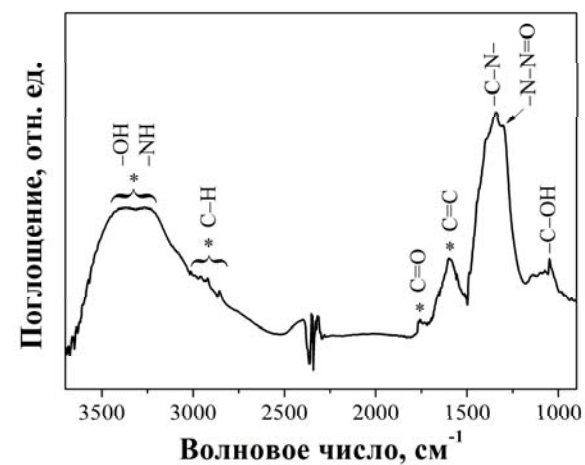
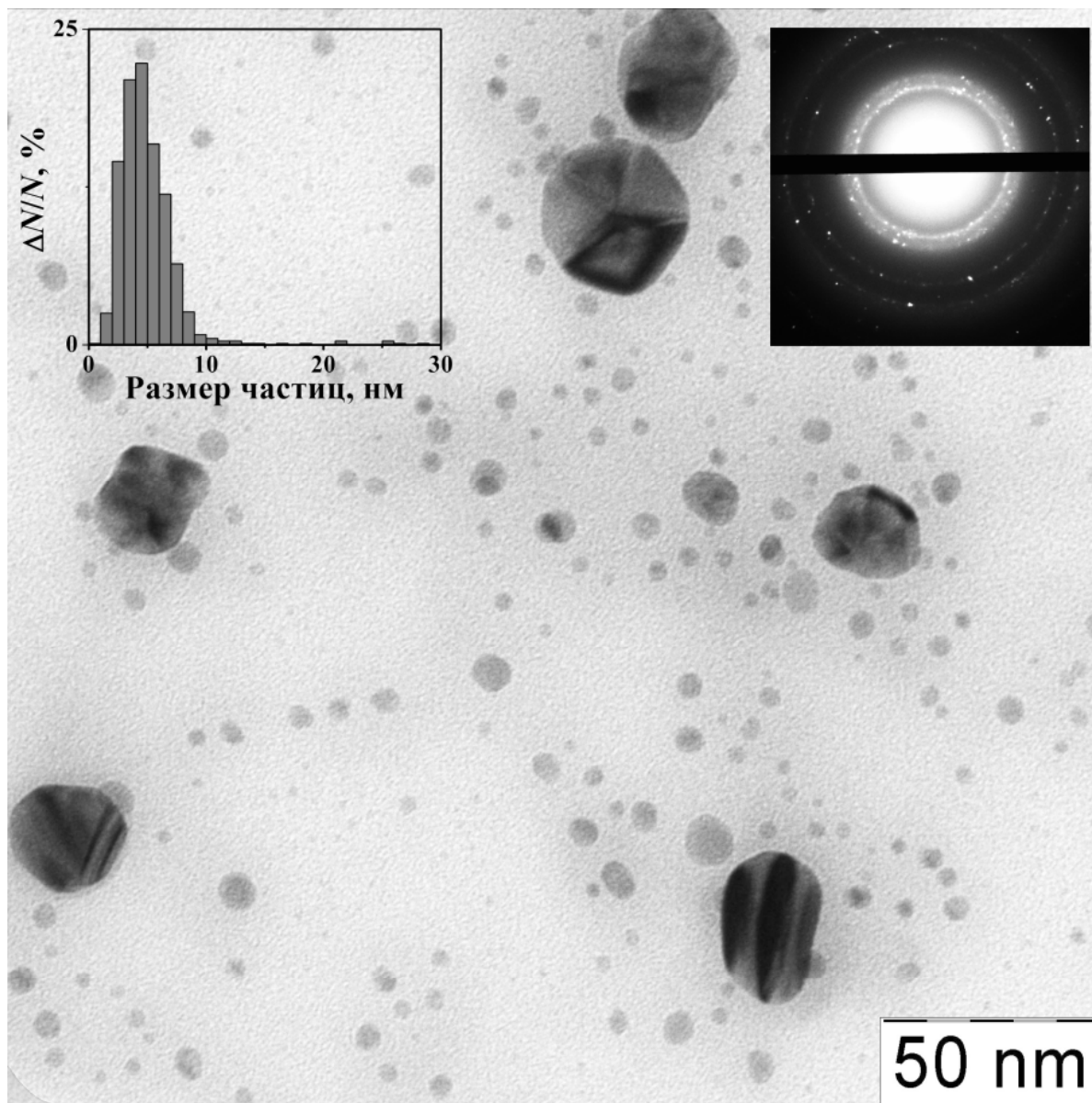


2 months later

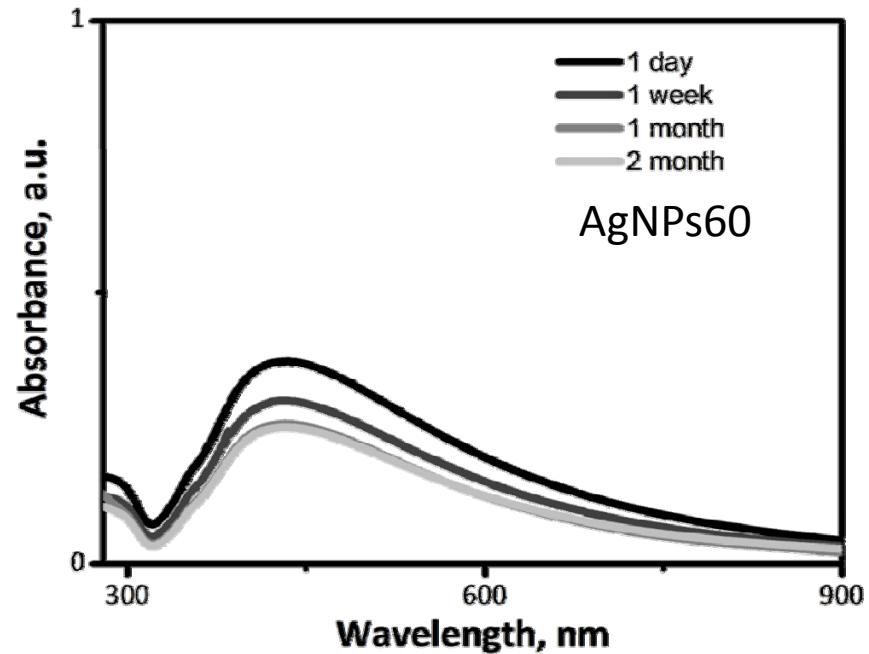
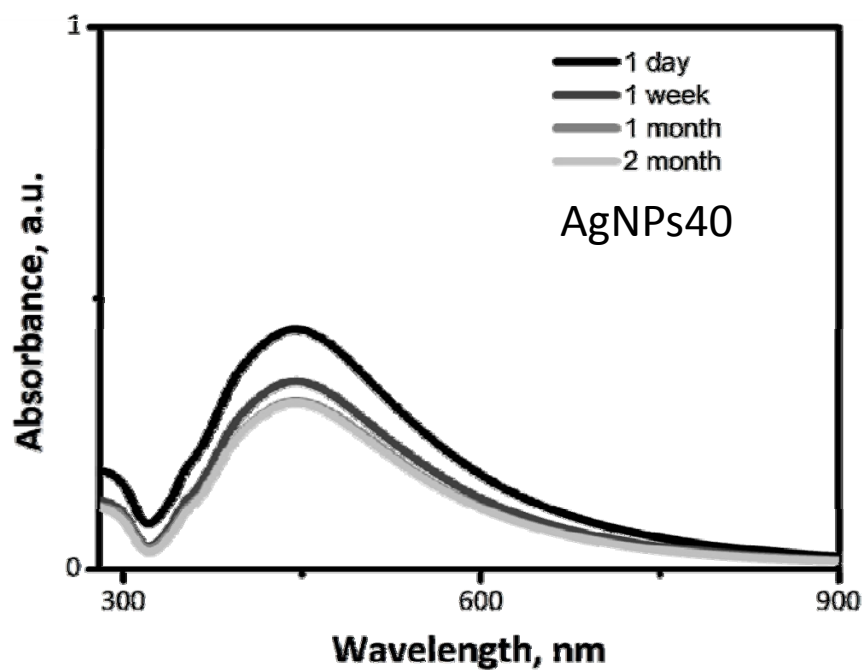
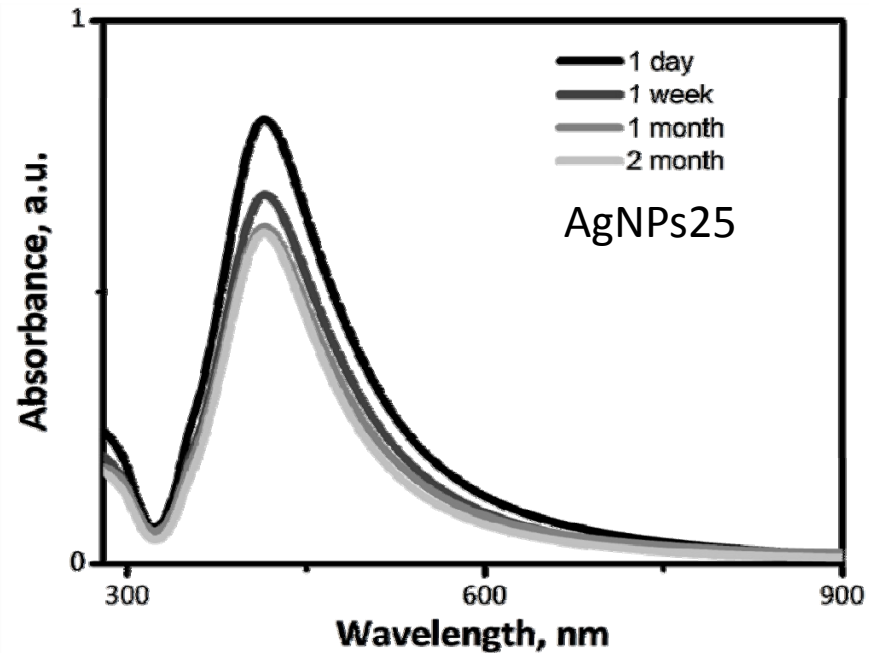
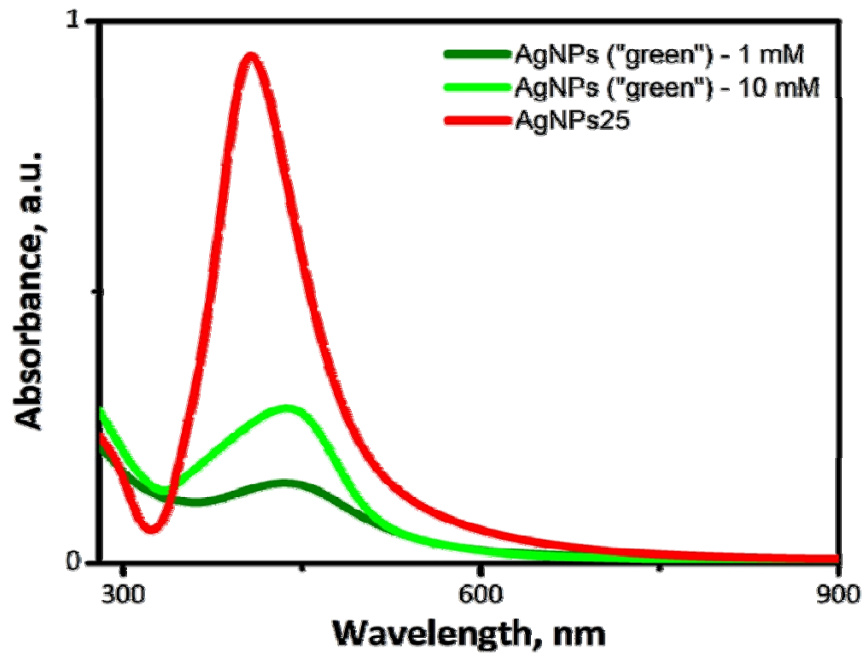


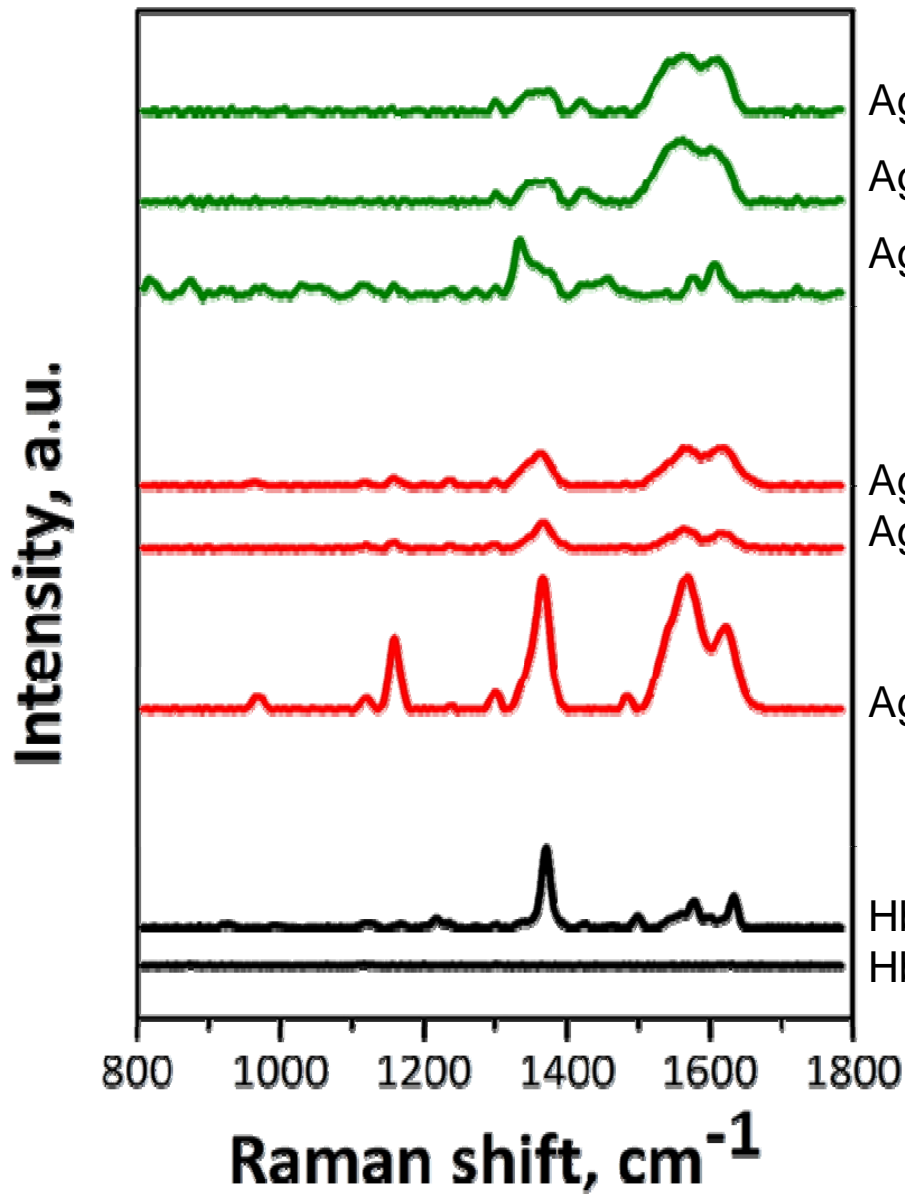
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A “green chemistry” trick



A.A.Semenova, et al. Dokladi Chemistry.





AgNPs ("green") – Hb_{cyt} 10⁻⁴

AgNPs ("green") – Hb_{cyt} 10⁻⁴

AgNPs – chlorophyll

AgNPs60 – Hb_{cyt} 10⁻⁴

AgNPs40 – Hb_{cyt} 10⁻⁴

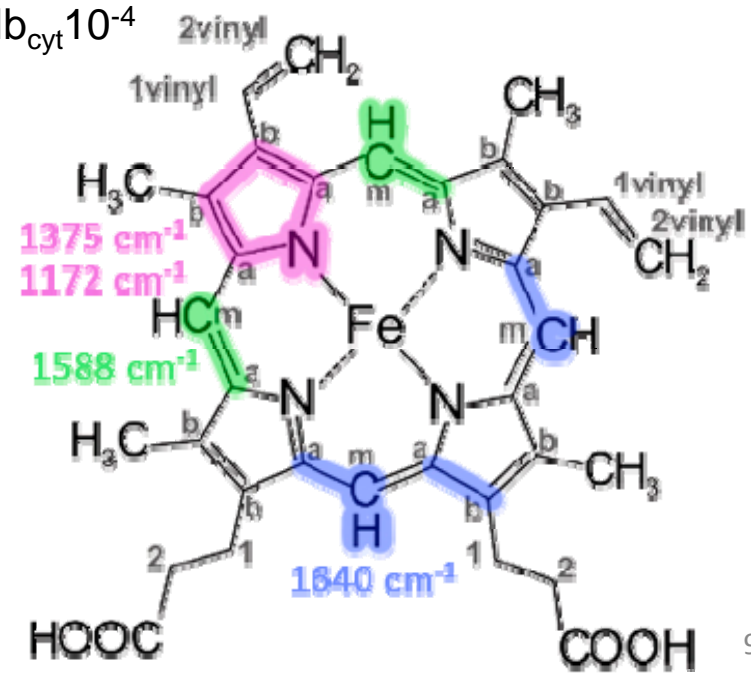
AgNPs25 – Hb_{cyt} 10⁻⁴

Hb_{cyt}

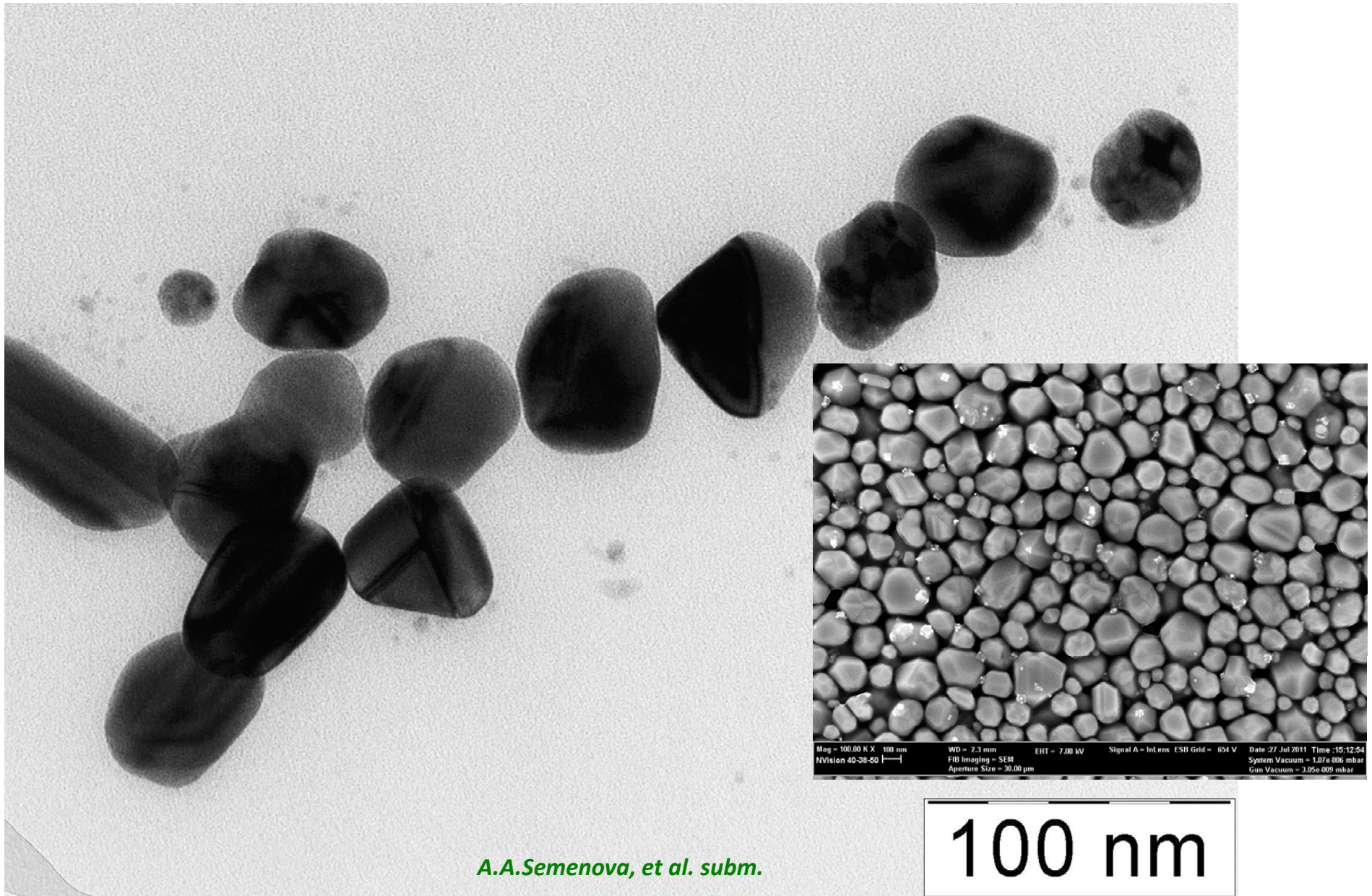
Hb_{cyt} 10⁻⁴

$$EF = \frac{I_{SERS}}{I_{RS}} \cdot \frac{N_{RS}}{N_{SERS}}$$

$$EF \sim 10^4 - 10^7$$

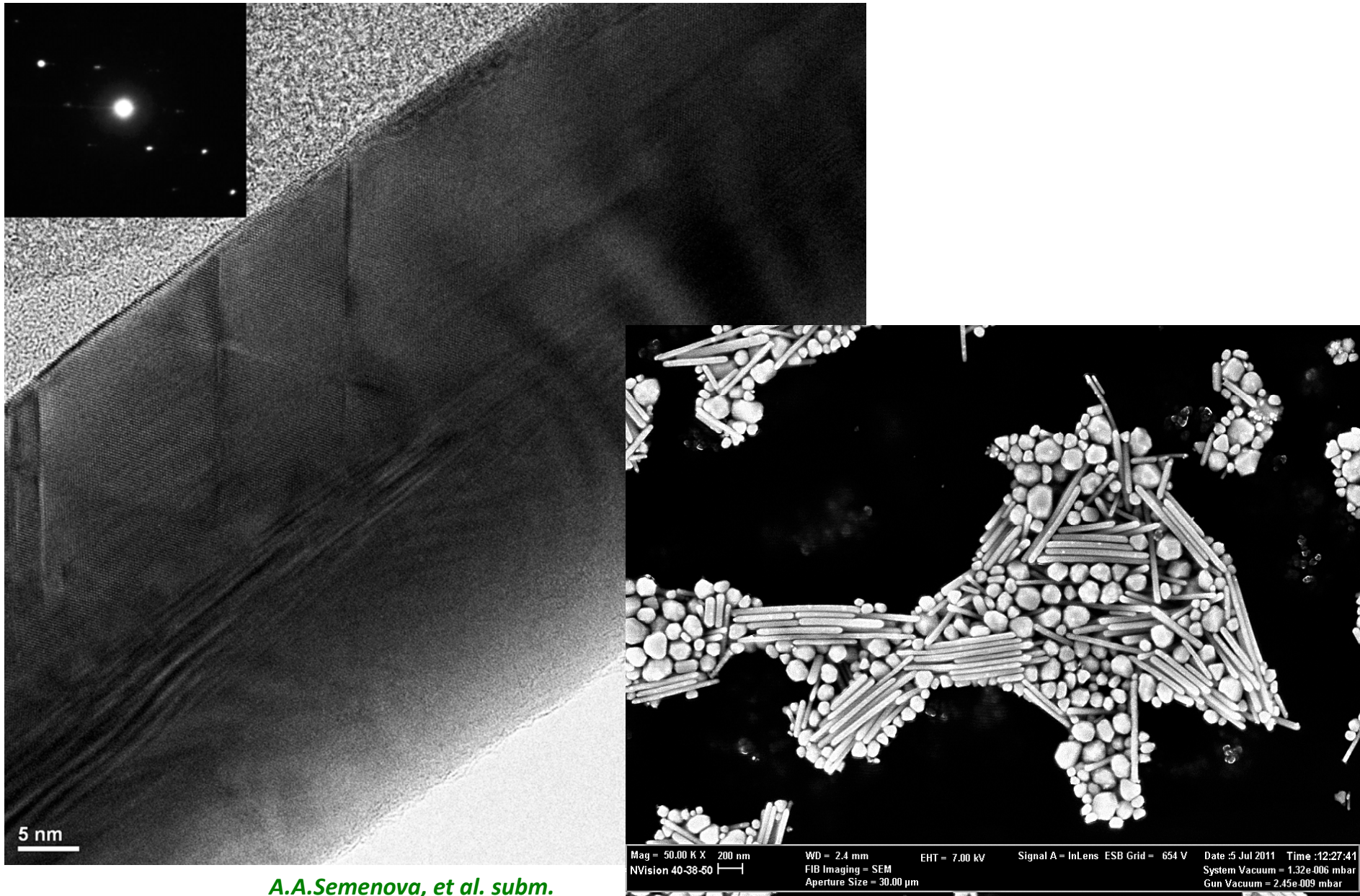


Different Morphologies: *polyhedral*



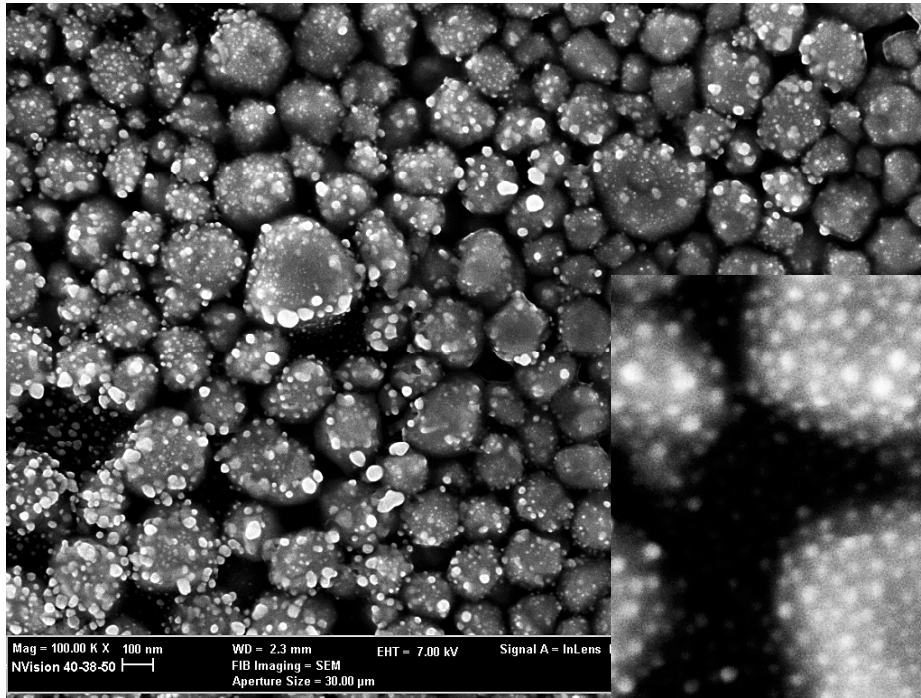
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Different Morphologies: *fibers*

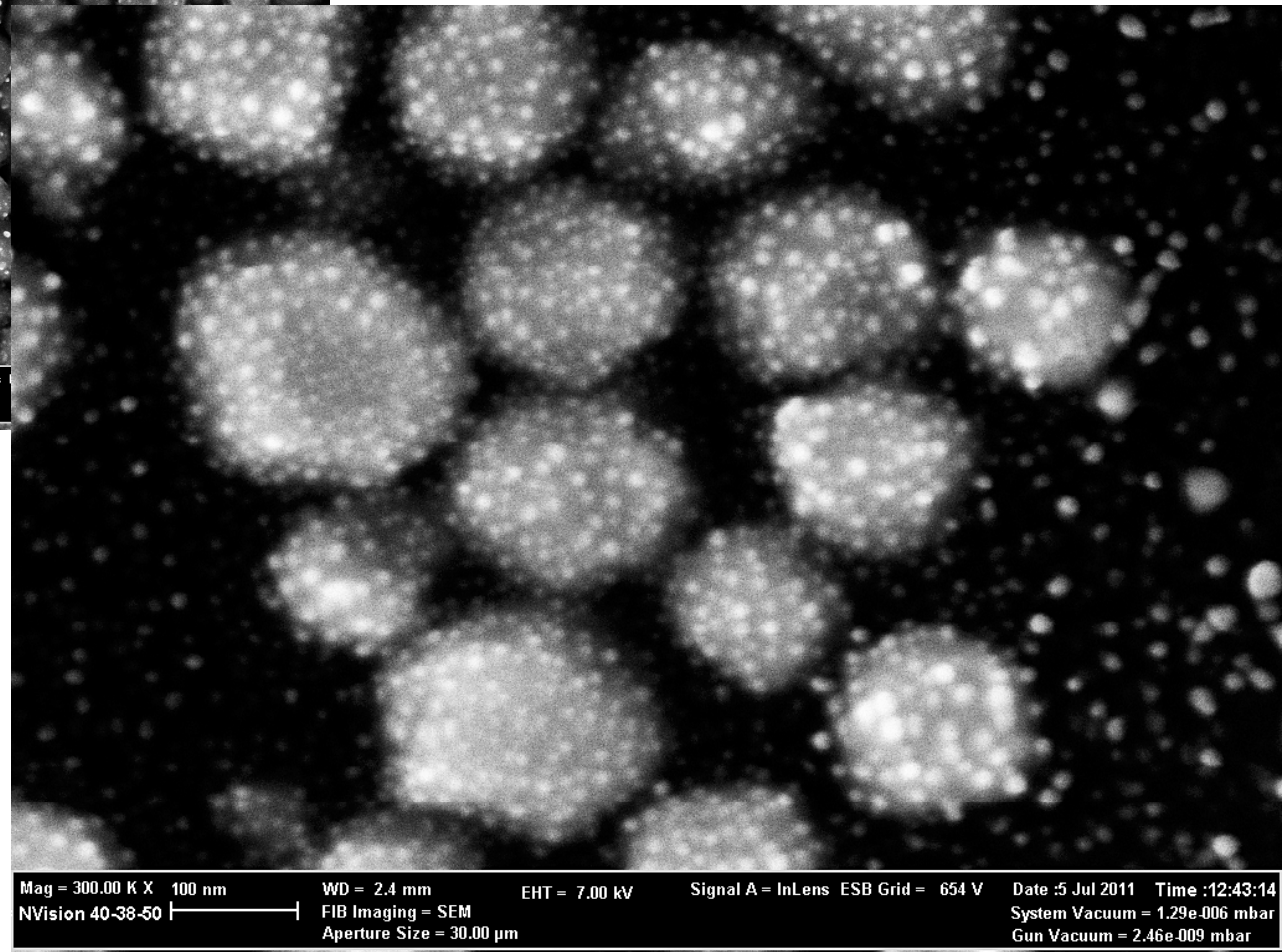


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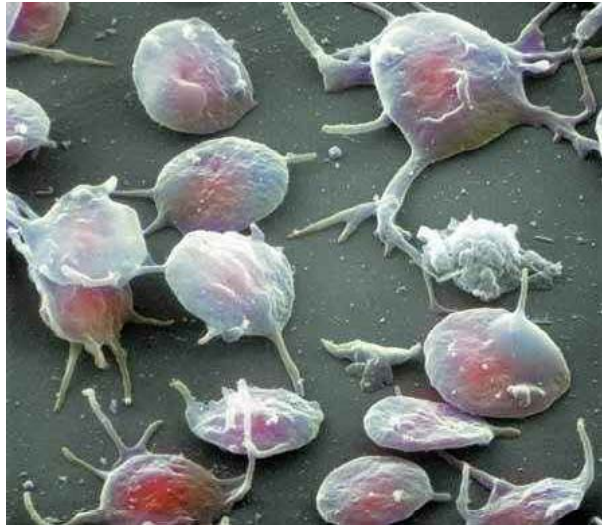
Different Morphologies: *sea-urchins*



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Cell spreading and toxicity problem



... in addition to physical advantages of nanostructured substrates, biological features of intact cells have to be considered:

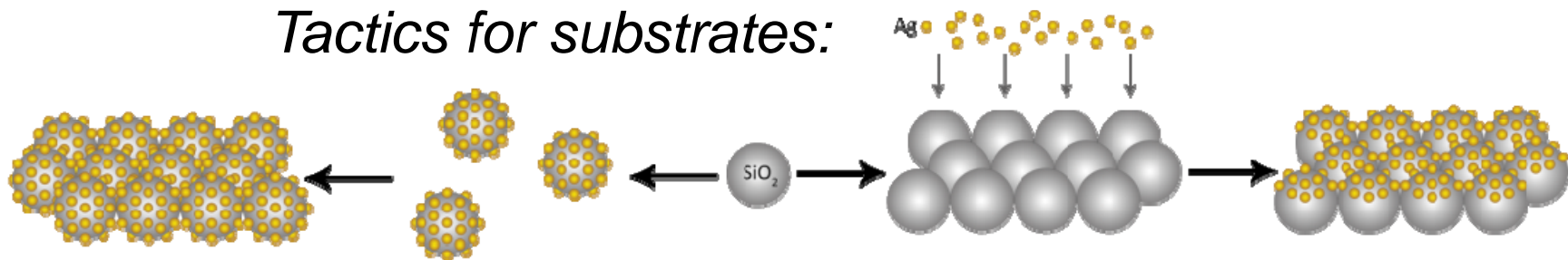
1. spreading on rough surfaces
2. toxicity of surroundings

Tactics for silver nanoparticles:

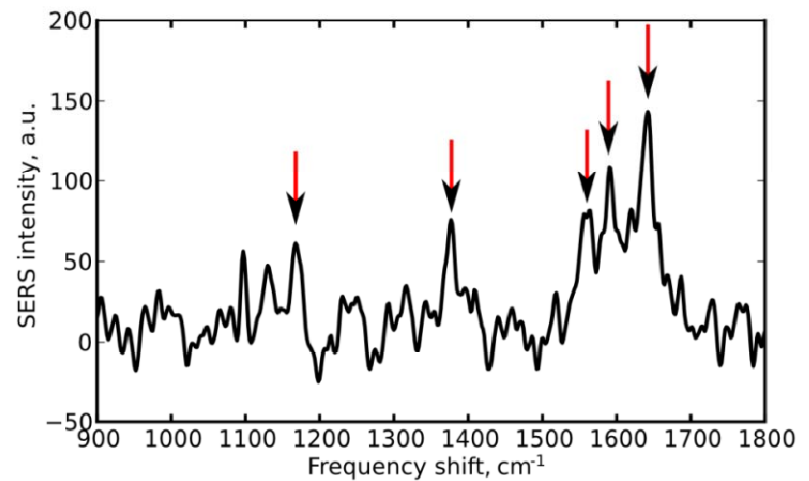
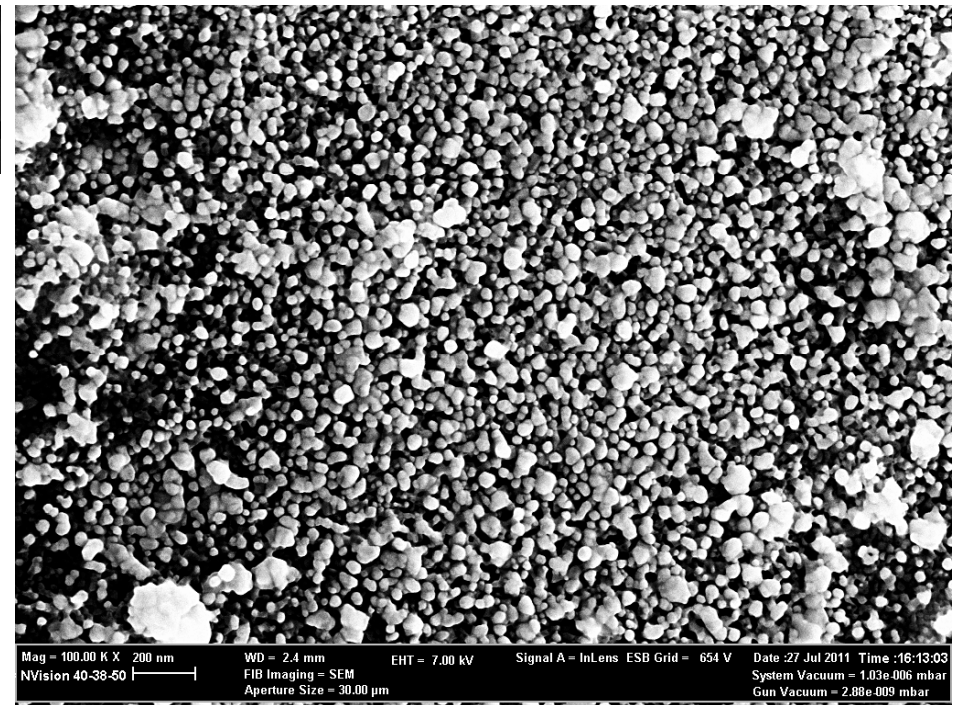
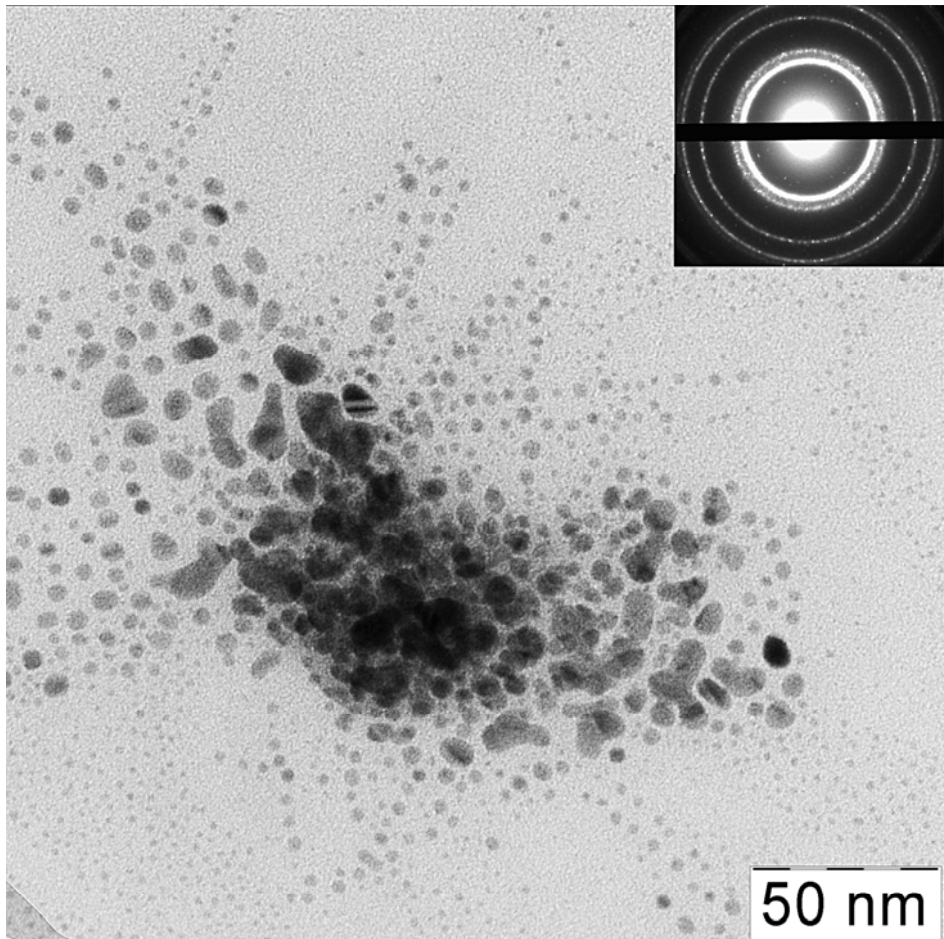
$\text{Ag}^+ + \text{Red} + \text{e}^- = \text{Ag} + \text{Ox}$ (traditional way, Red and Ox can be toxic themselves)

$2[\text{AgL}_2]\text{OH} = 2\text{Ag}_{\text{nano}} + \text{H}_2\text{O} + 4\text{L}_{(\text{gas})} + 1/2 \text{O}_2$ (ideal way, pure silver)

Tactics for substrates:

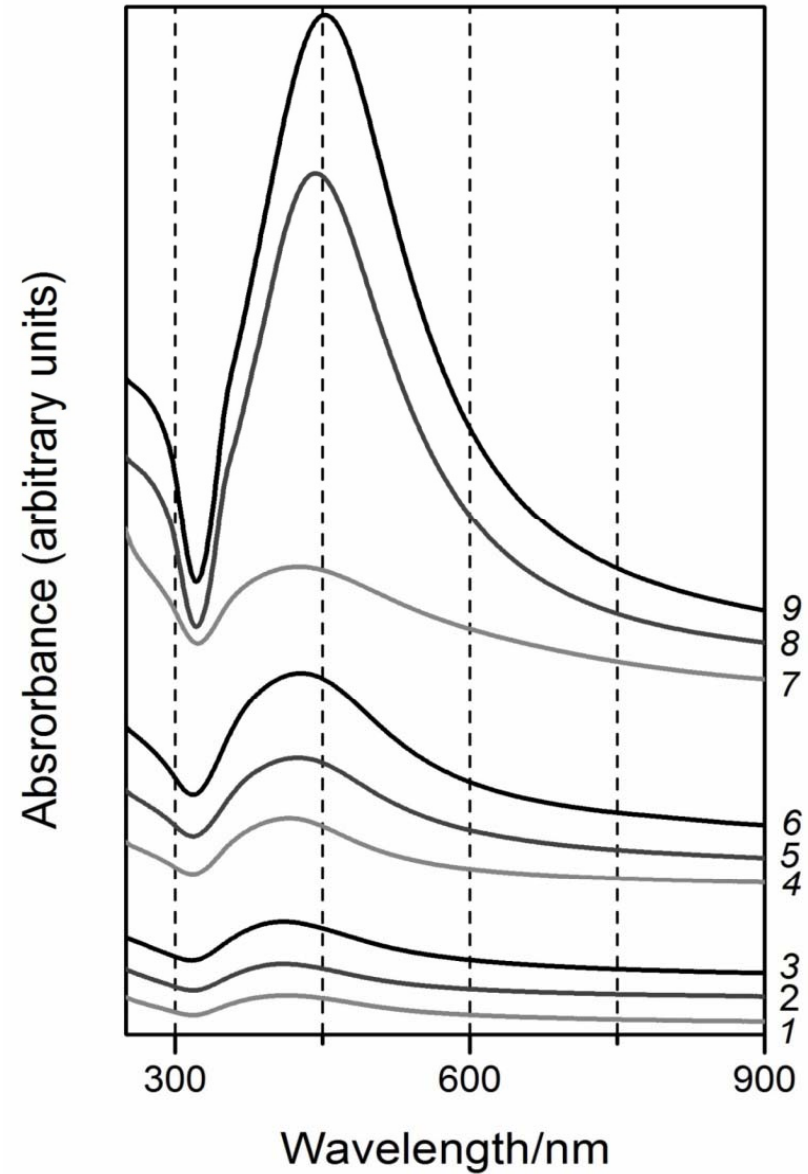
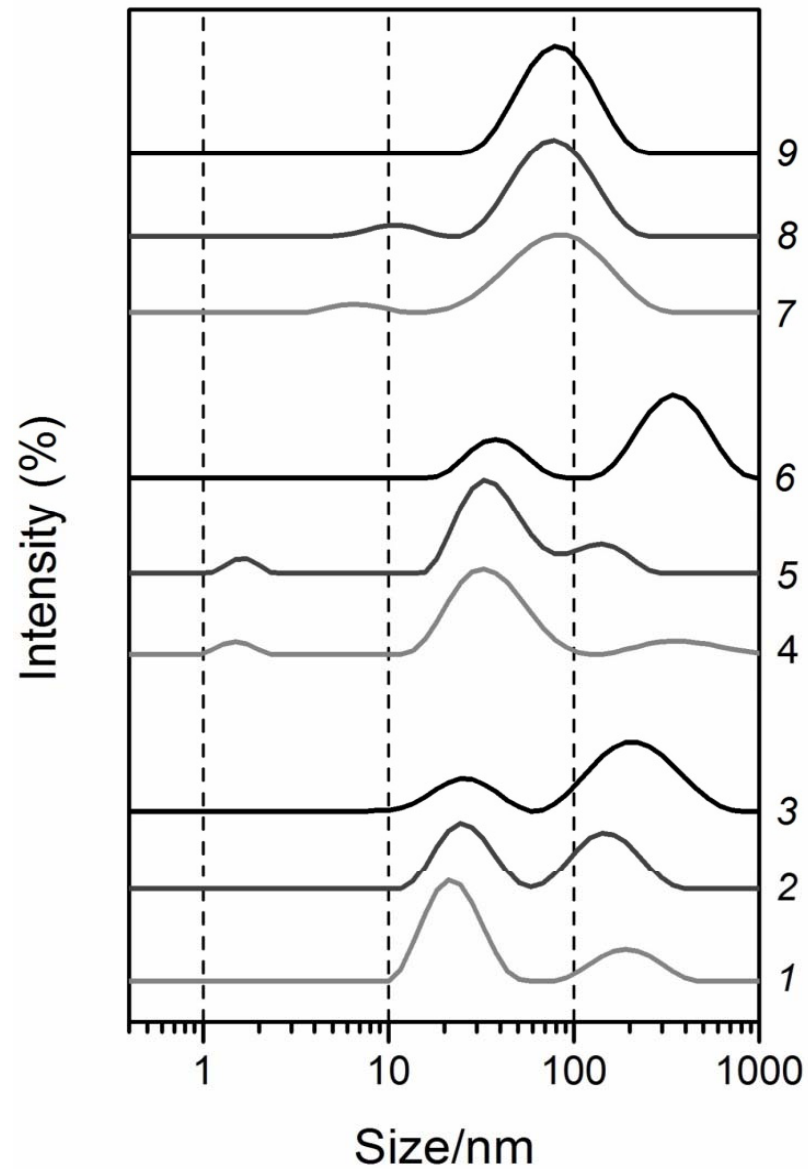


PUre Silver Hydrosol (PUSH) method



Enhancement factor $\sim 10^4$

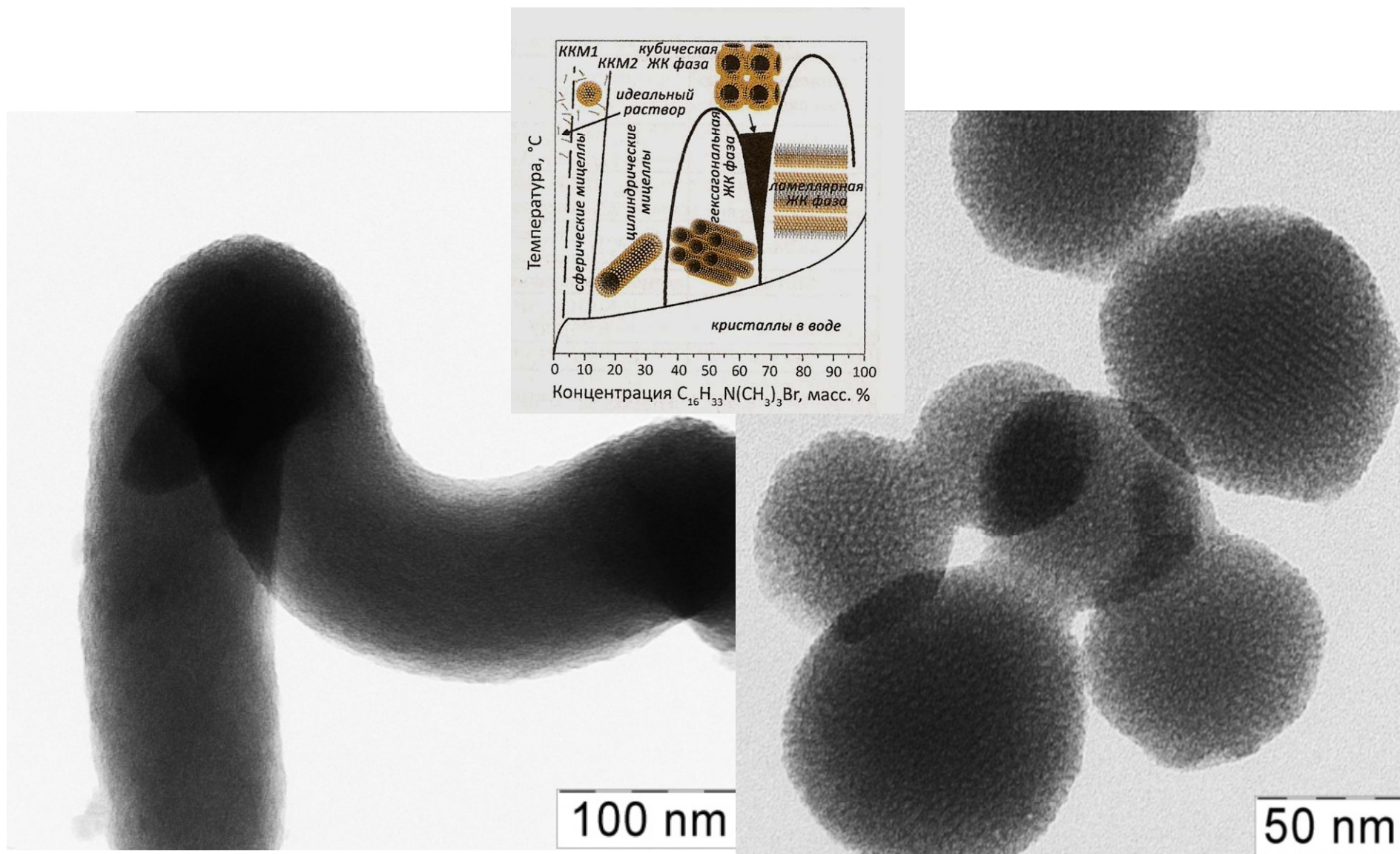
Size factor and optical properties



PUSH - data

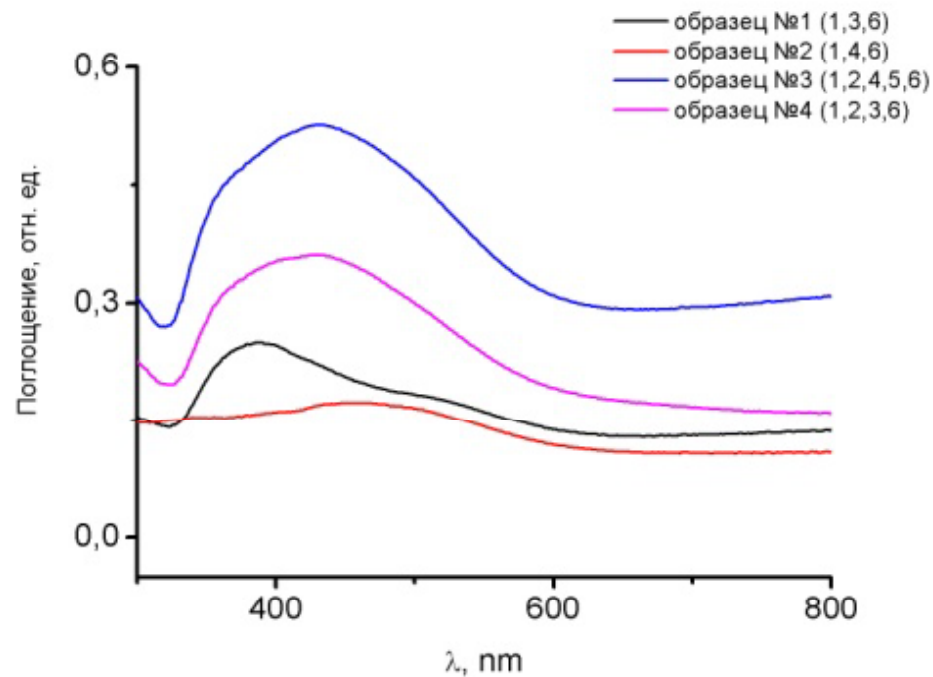
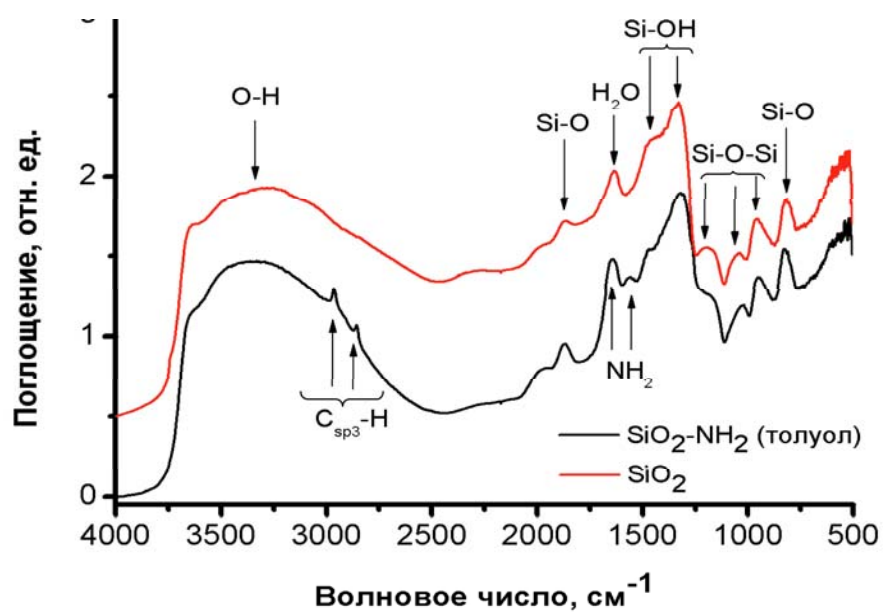
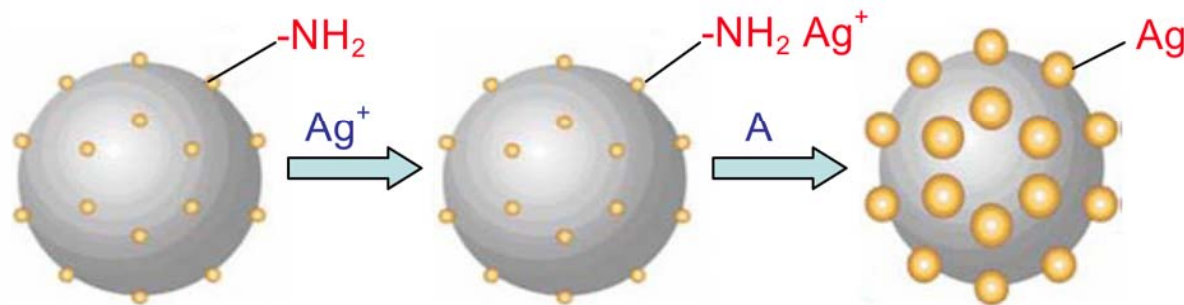
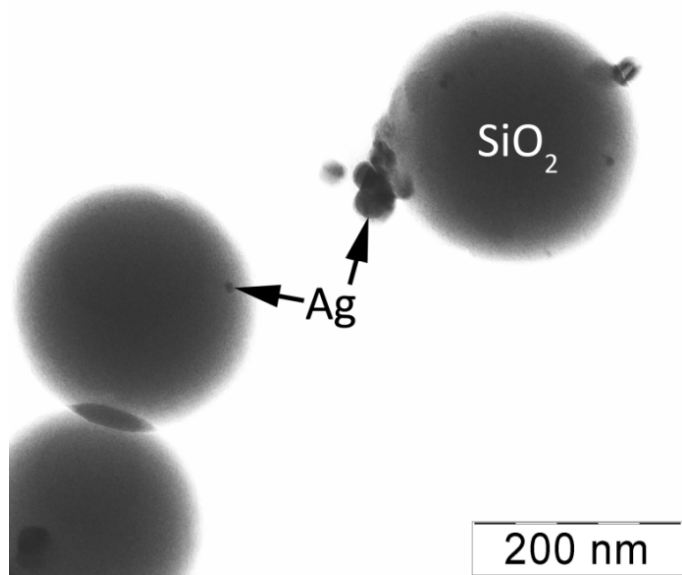
Sample preparation conditions		Mean size of nanoparticles according to DLS, nm	Zeta - potential, mV	Plasmon peak position according to UV – vis spectroscopy, nm	pH of the solution
Solution volume of added silver oxide complex, ml	Reaction time, min				
0.1	20	23; 202	-35	412	7.5
0.5	20	2; 38; 409	-42	417	8.5
2.5	20	7; 92	-51	430	10.0
0.1	30	27; 158	-30	410	7.5
0.5	30	2; 40; 144	-42	425	8.5
2.5	30	11; 84	-49	443	10.0
0.1	60	26; 234	-41	412	7.0
0.5	60	40; 365	-44	427	7.0
2.5	60	87	-48	452	9.0

Nanoparticle mesoporous carrier

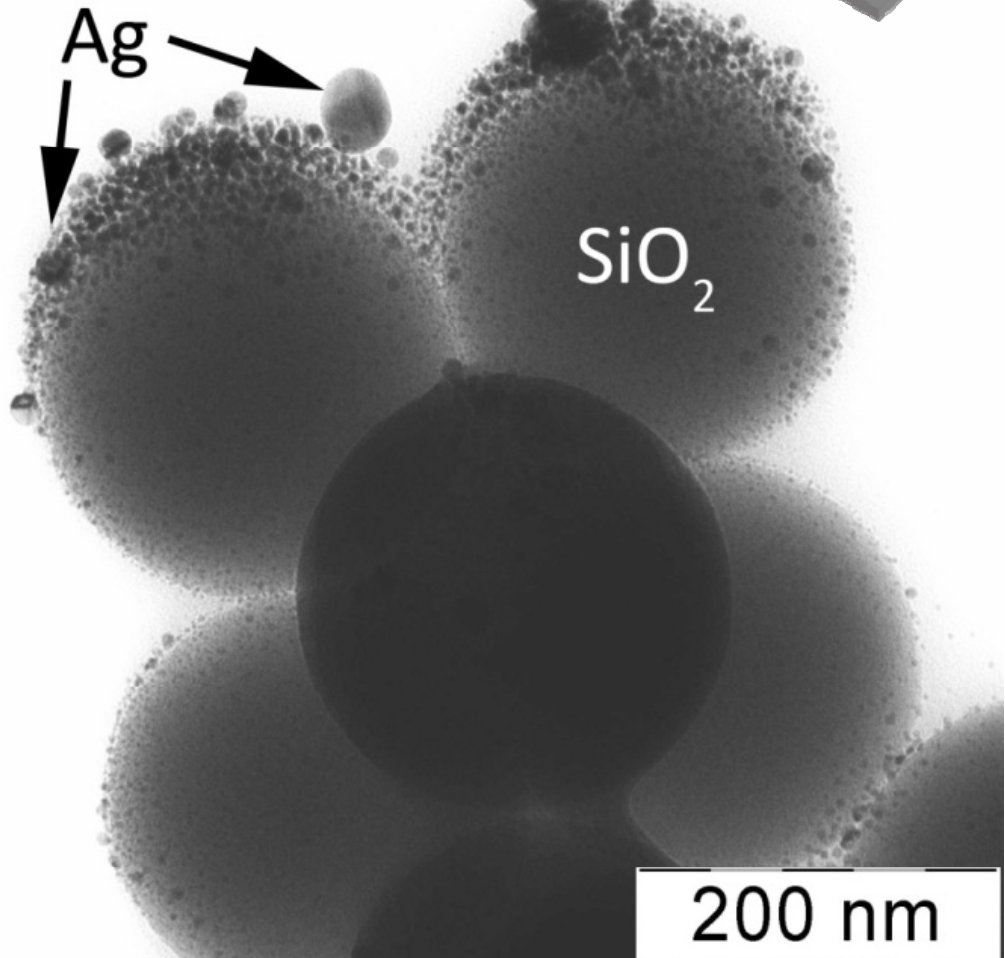
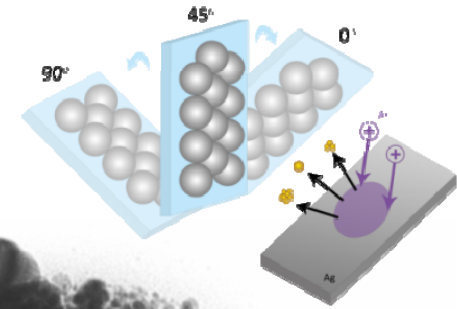
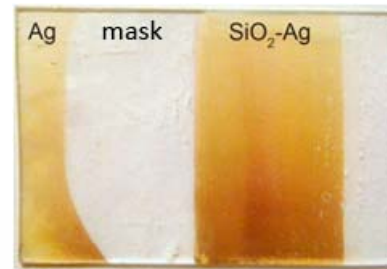
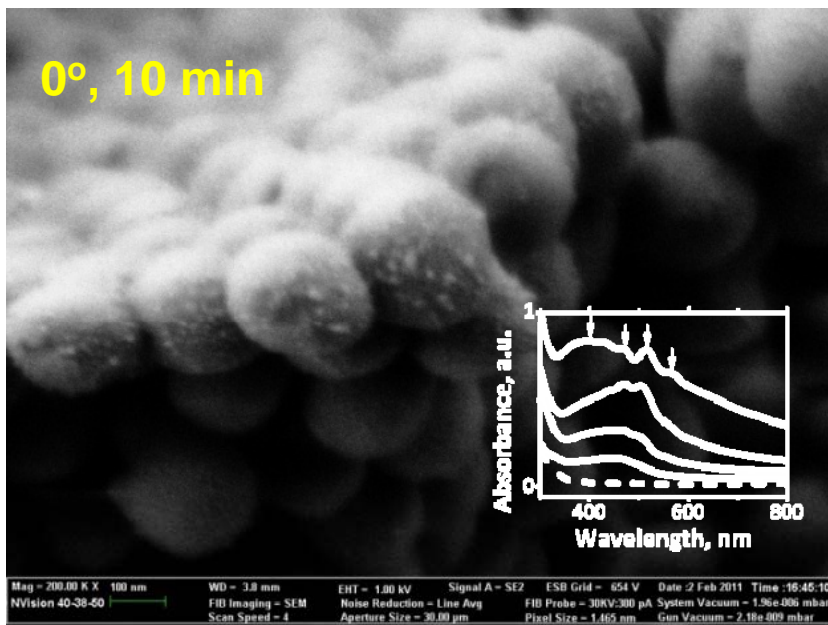
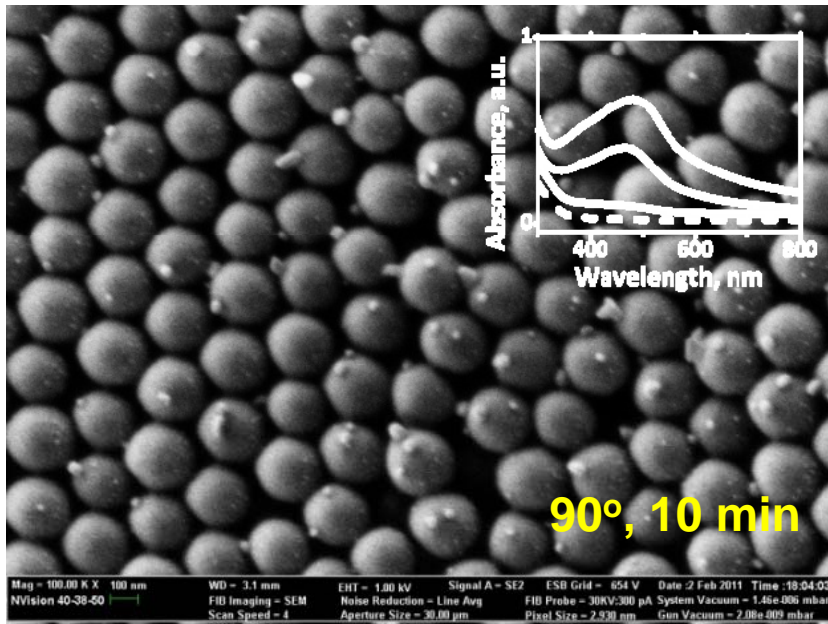


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Building unit modifying

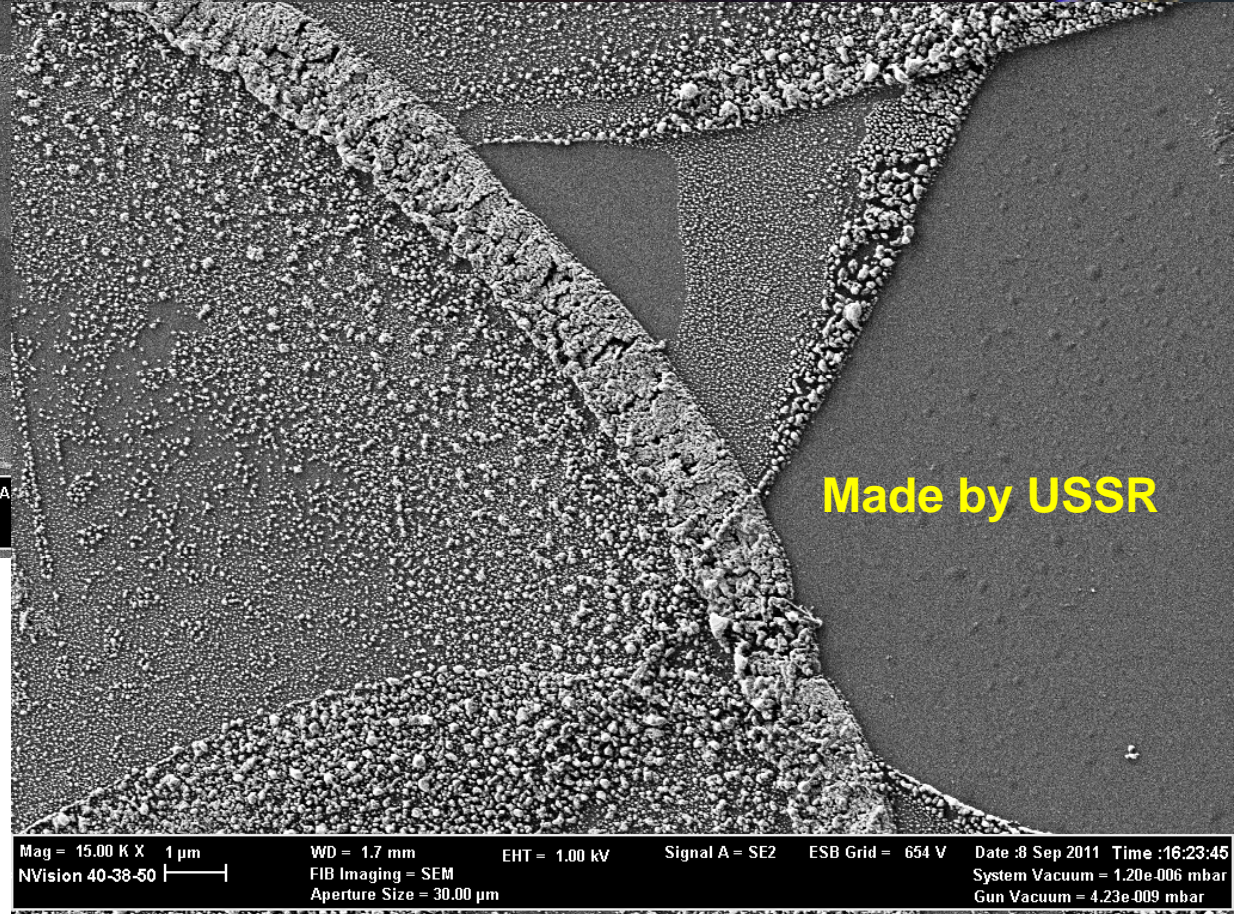
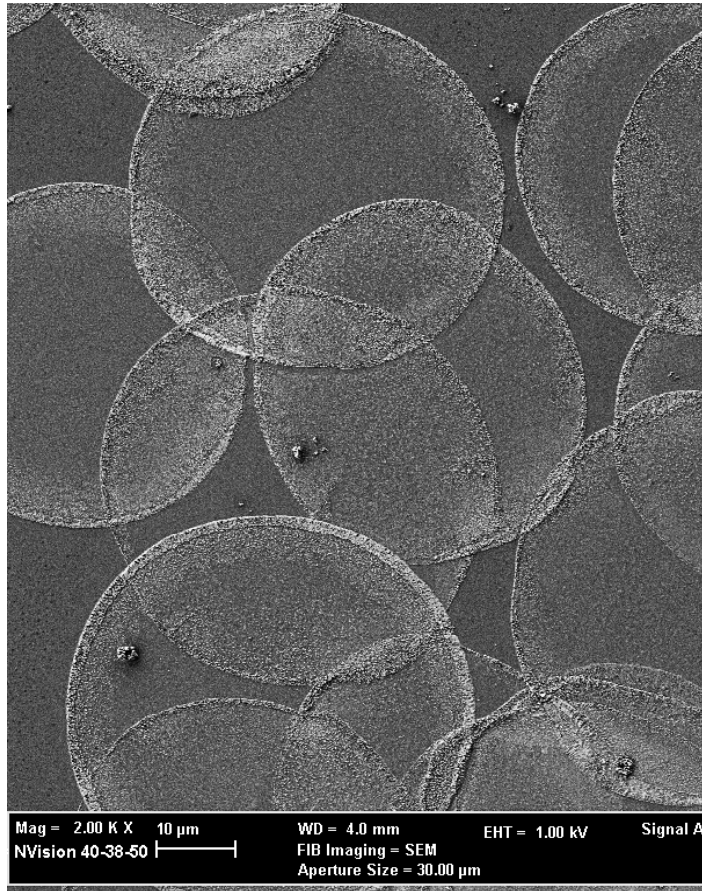
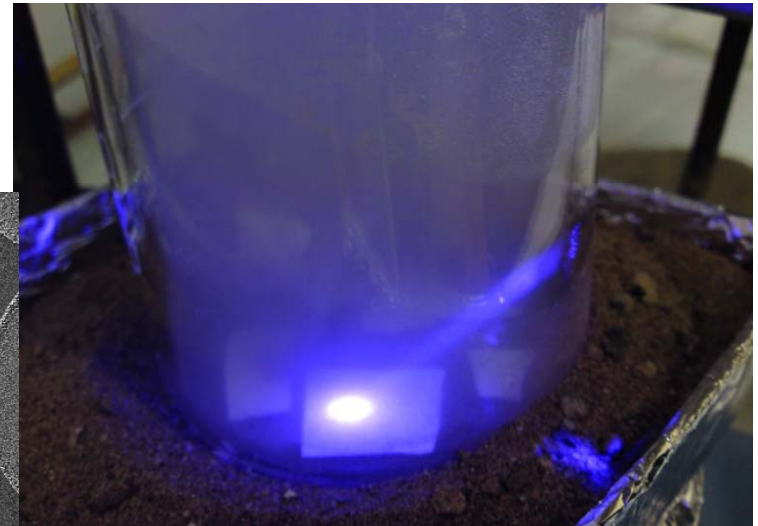


Ion sputtering using a patterned substrate



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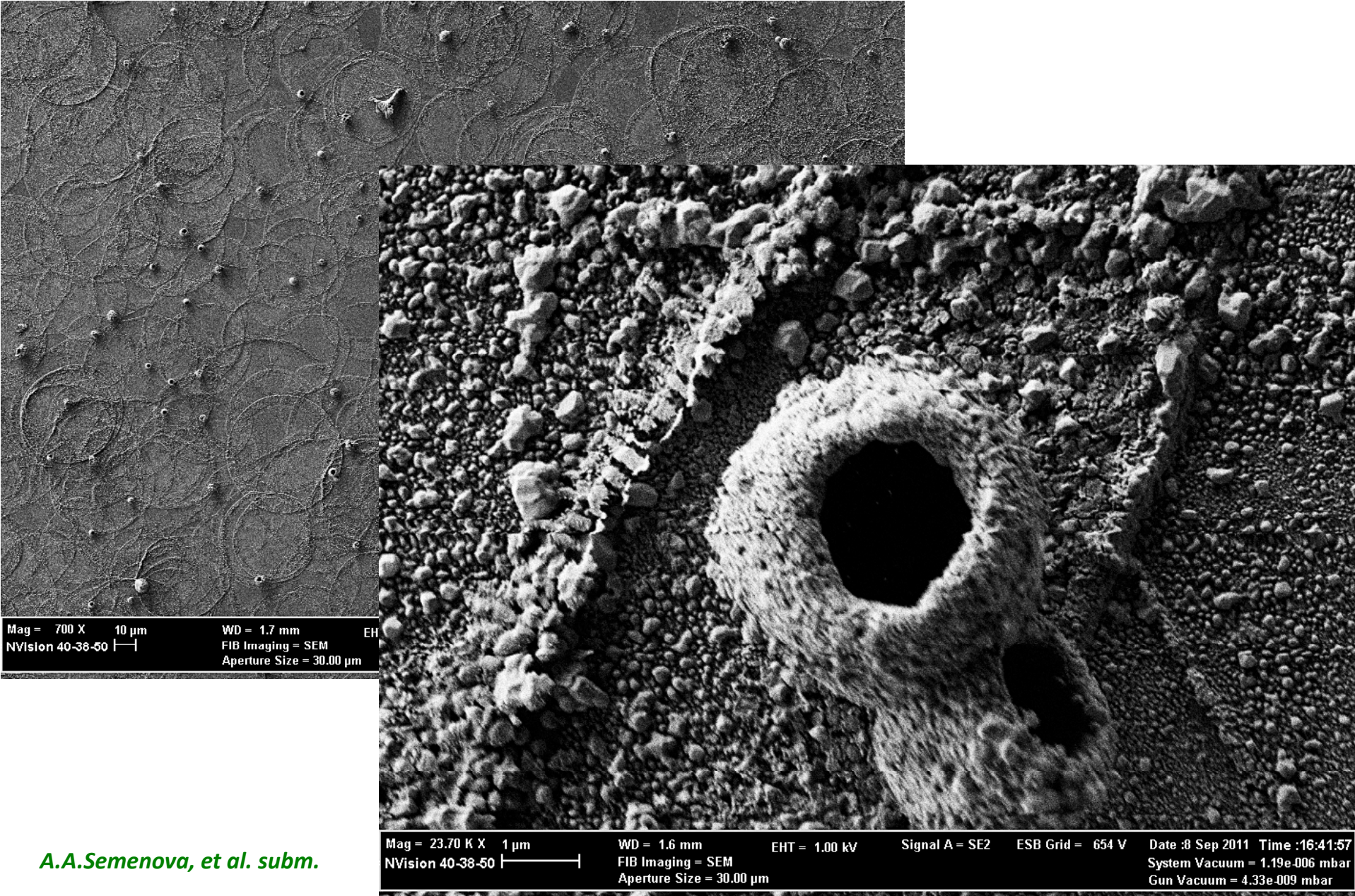
UltraSonic Silver Rain



Made by USSR

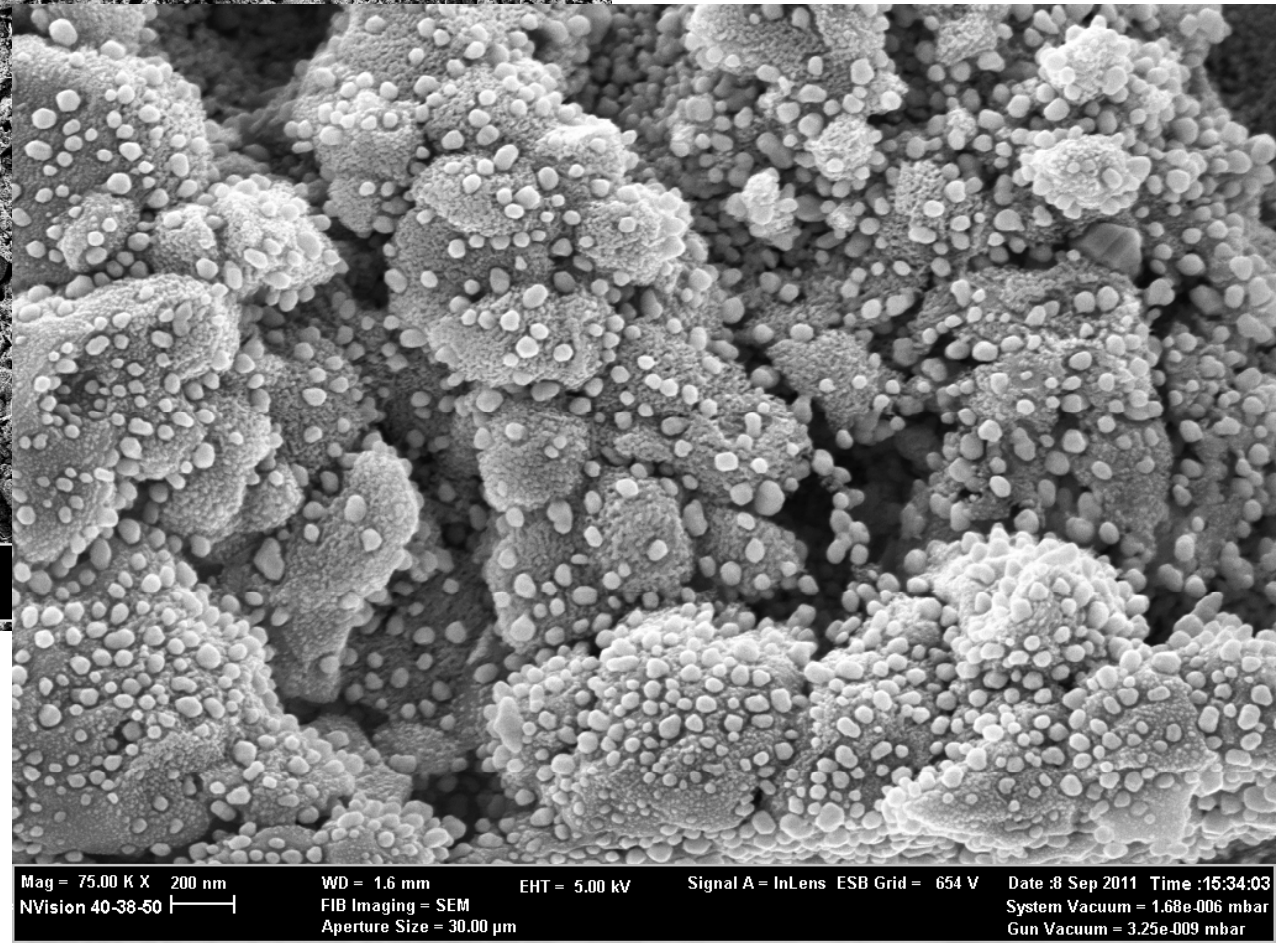
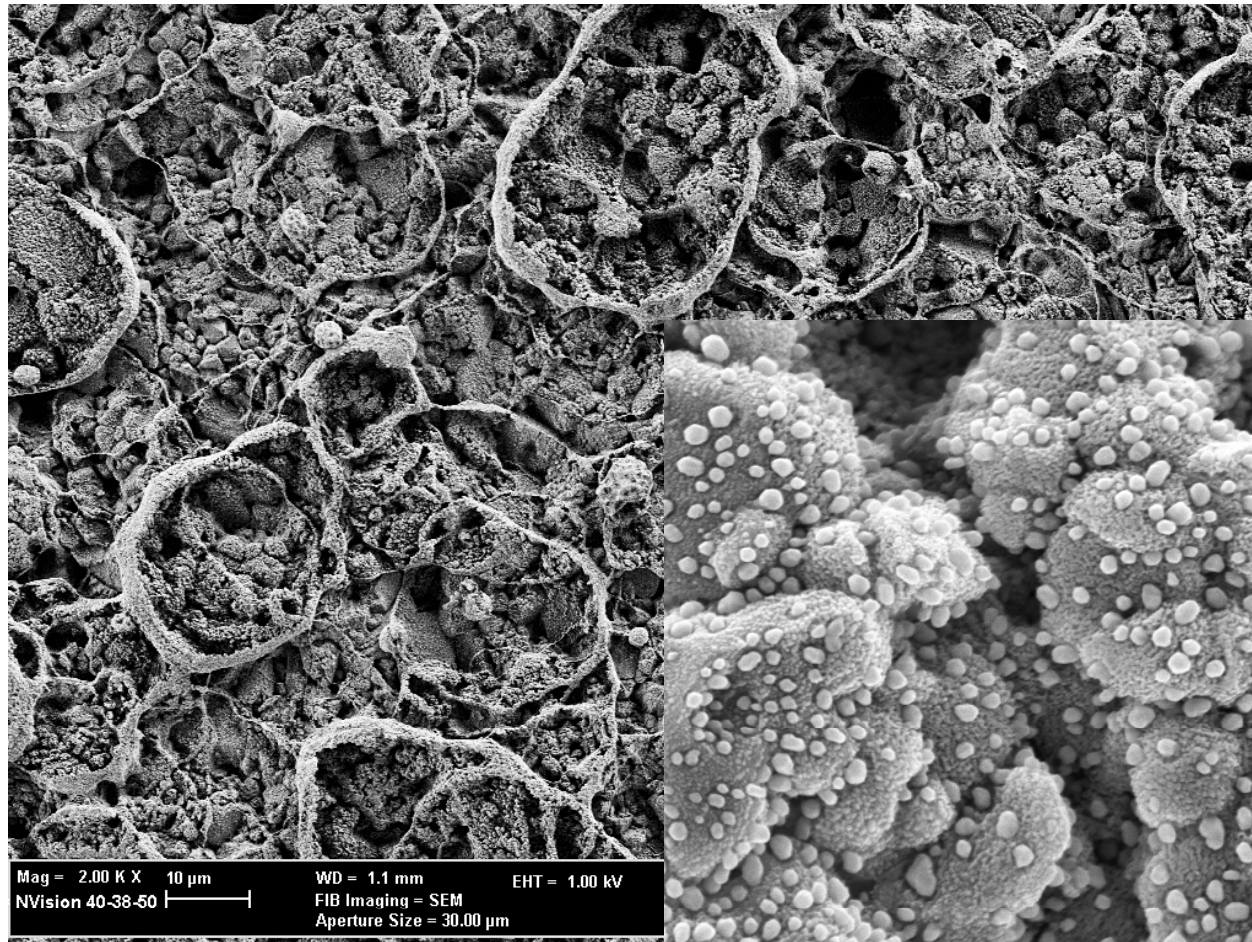
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Porous microstructured substrates



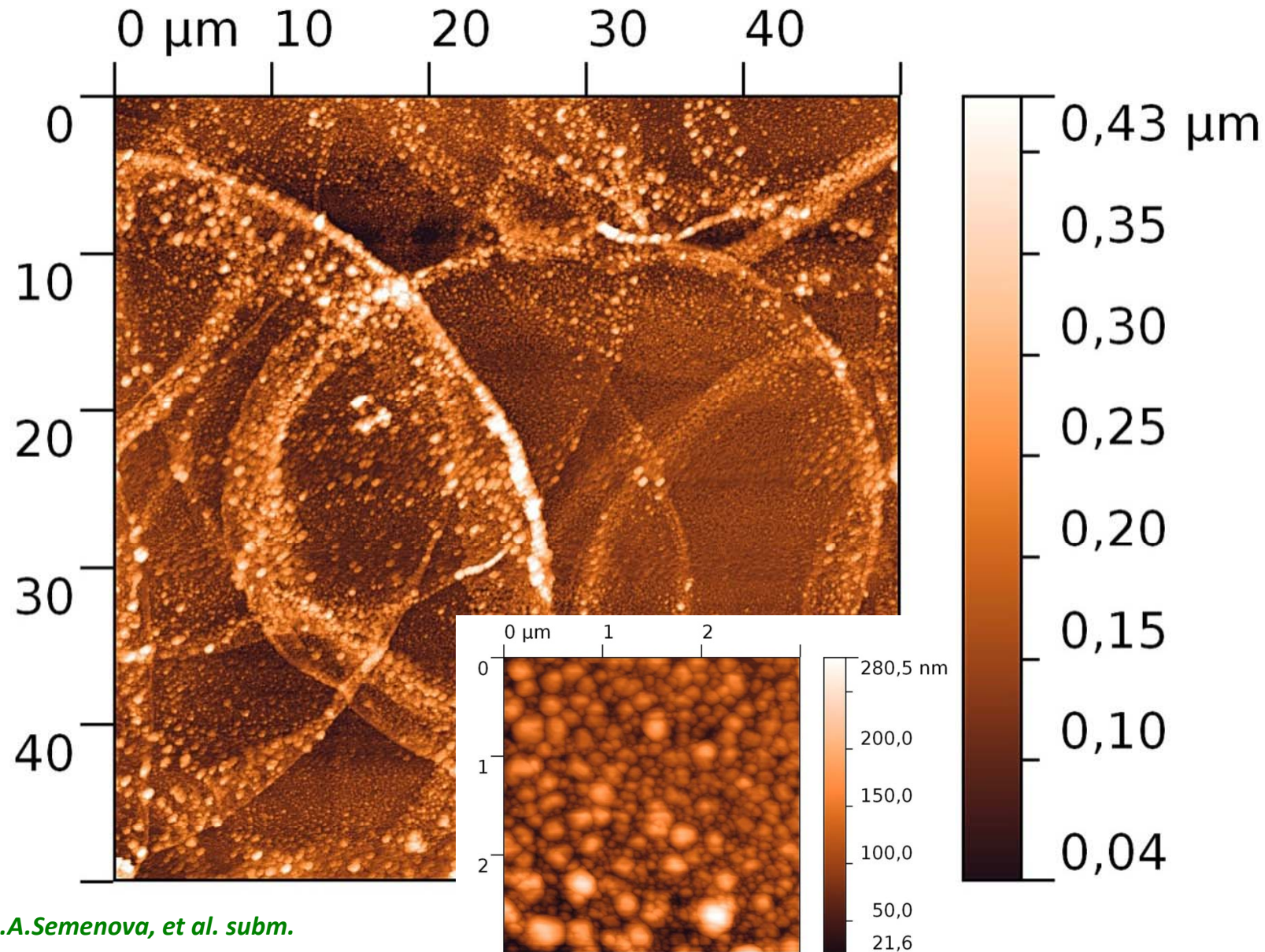
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Hierarchic structuring



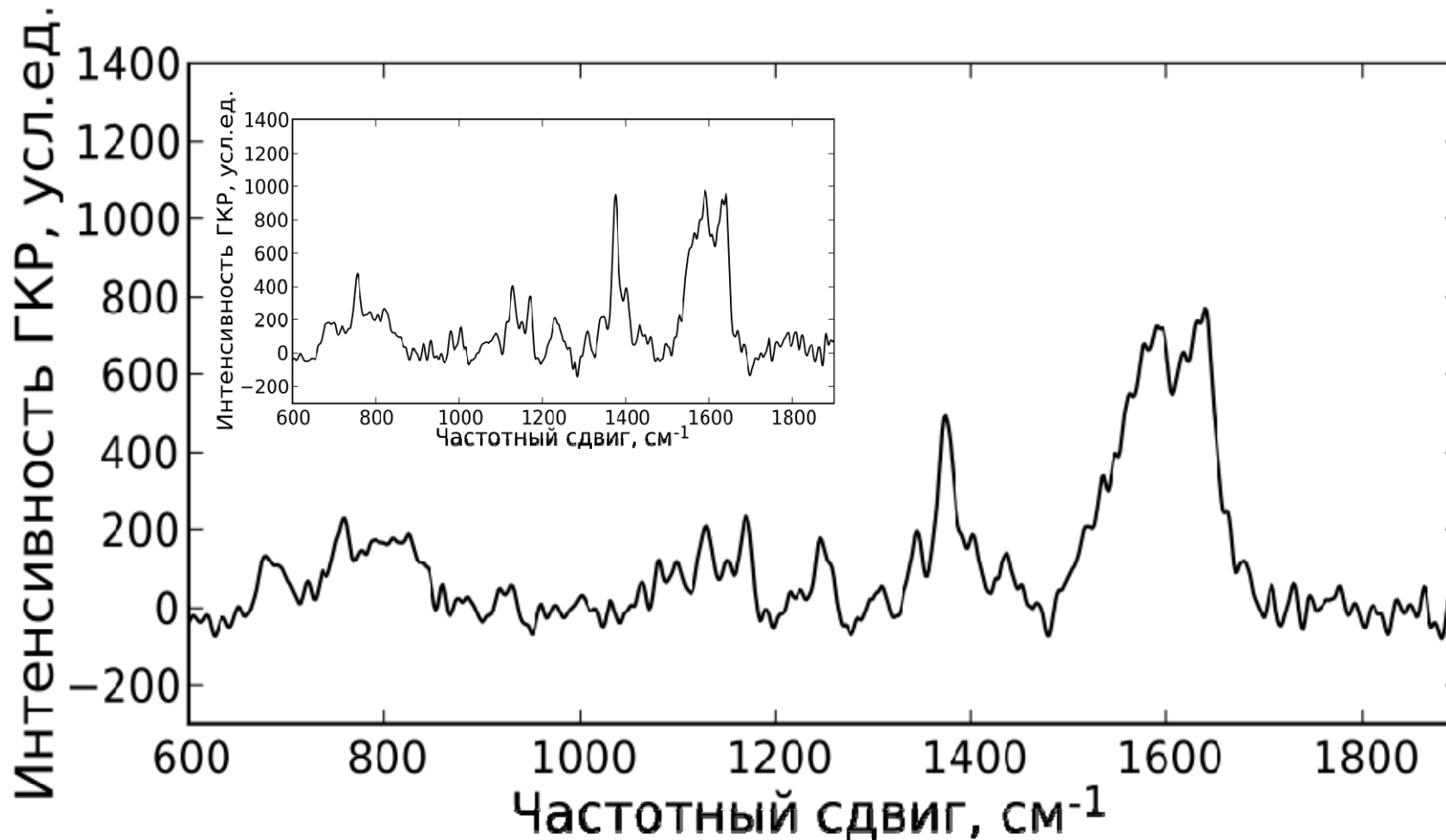
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Rough Ag-coated surfaces



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UltraSonic Silver Rain: SERS



InVia Renishaw, laser 532 nm, 2.5 mW, 60 s spectra averaging, Ag/Al₂O₃ substrate.

Enhancement factor ~ 5000 (at least)

Blood cell survival on the substrate ~ 30 – 60 min (at least)

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Conclusions

- SERS demonstrates unique sensitivity, simplicity of sample preparation and the ability to take *advantages* of **intact** cell analysis.
- New preparation routes of silver nanoparticles allow to produce in the easiest way either SERS – active sols or nanostructured silver substrates taking *advantages* of **mild** conditions and the **absence** of toxic impurities.
- ... silver still has a lot of secrets!