Material Technologies for Mini- and Nanosensing

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Victor Ovchinnikov, Aalto University, Finland

Material concept

- Traditional or macromaterial – bulk material, including bonded chemical elements, which are physically arranged (crystalline structure, amorphous…)

- Nanomaterial (metamaterial)– nanoengineered classical material, including 1D and 2D materials. Problems with characterization!

Nanomaterials for sensors

- Nanoparticles:
  - Metal based, including oxides
  - Carbon based: fullerenes, buckyballs, CNT
  - Semiconductor based: quantum dots
  - Polymer based: dendrimers (branched polymers)
  - Composite: nanoclays, DNA based biocomposite
  - Core/shell nanoparticles
- Quantum dots
- Carbon nanotubes
- Inorganic nanowires
- Nanoporous materials
- Graphene:
  - Electrochemical (potentiometric) sensor and biosensor (direct electron transfer)
  - Gas sensor – conductance
  - Terahertz plasmonics and sensors
  - 2D membrane.

Panel subtopics

- Electronic techniques for nano-sensing

  Thierry Ferrus

- Bio-Inspired Signal Processing

  Vladimir Privman

- SERS substrate as a nanoengineered surface

  Victor Ovchinnikov

SERS substrate as a nanoengineered surface

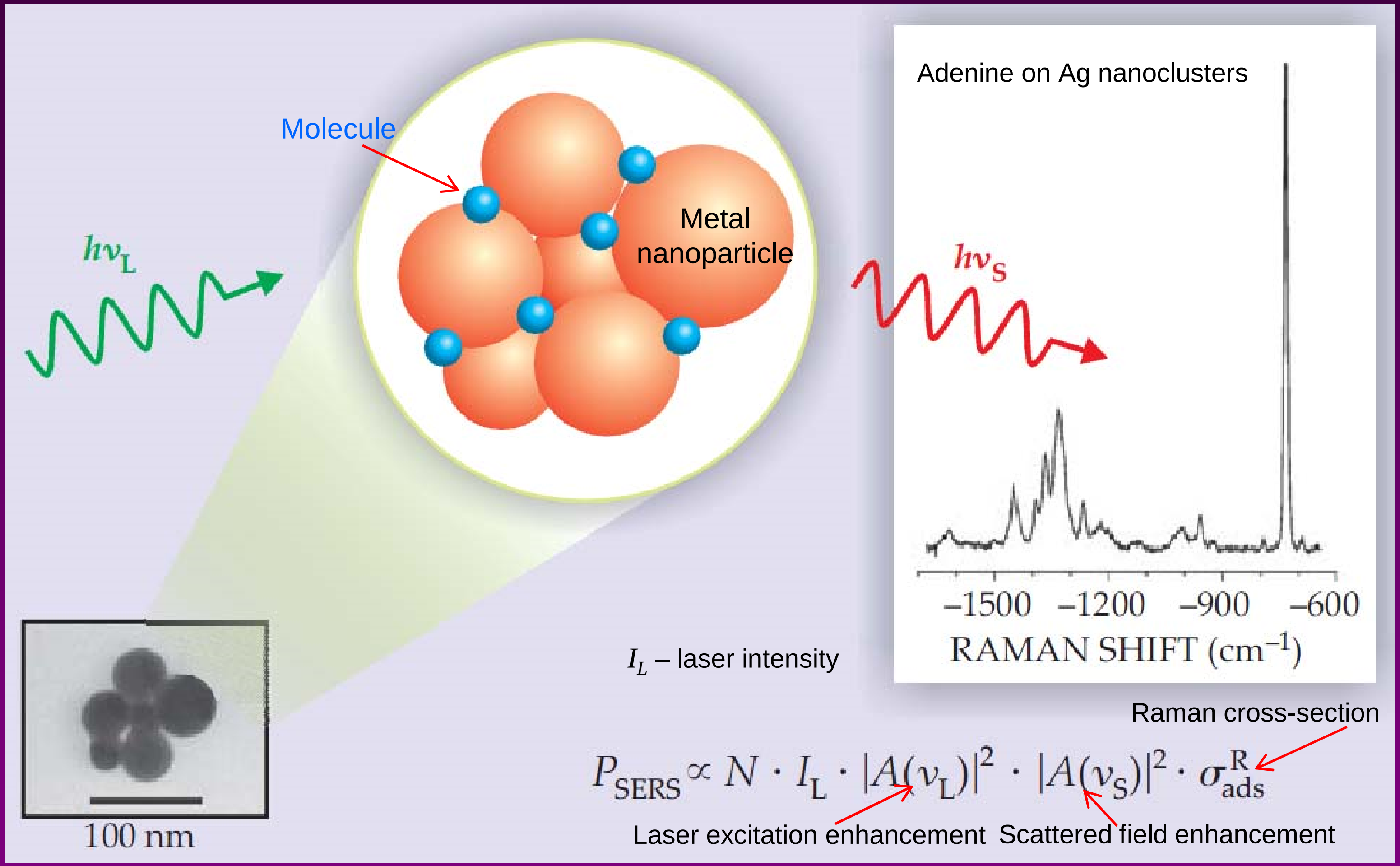
Victor Ovchinnikov
Aalto University, Finland

Steps of Raman development

- Laser application
  - Dramatically improved power of excitation and Raman signal
- SERS effect (1974)
  - Enhanced method sensitivity up to 10^{14}
- Raman microscope
  - Decreased probe volume (light spot diameter below 1 μm)
- Portable SERS
  - Mobility of analyses

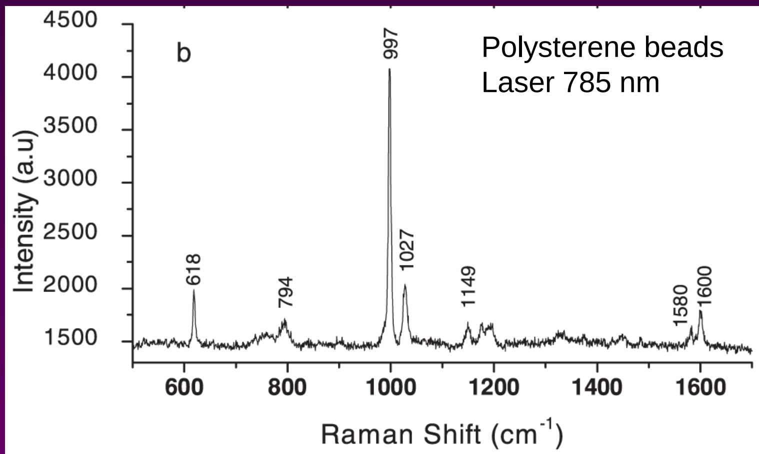
C. Douketis et al., J. Chem. Phys. 2000, **113**, 11315-23

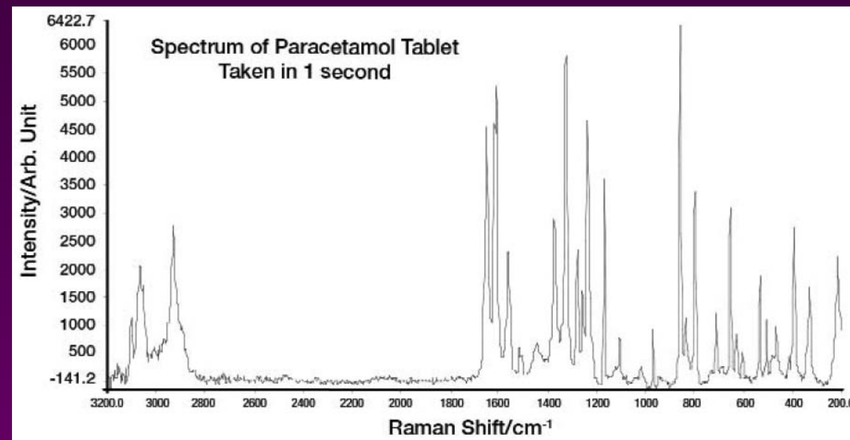
A! Electromagnetic enhancement in near-field

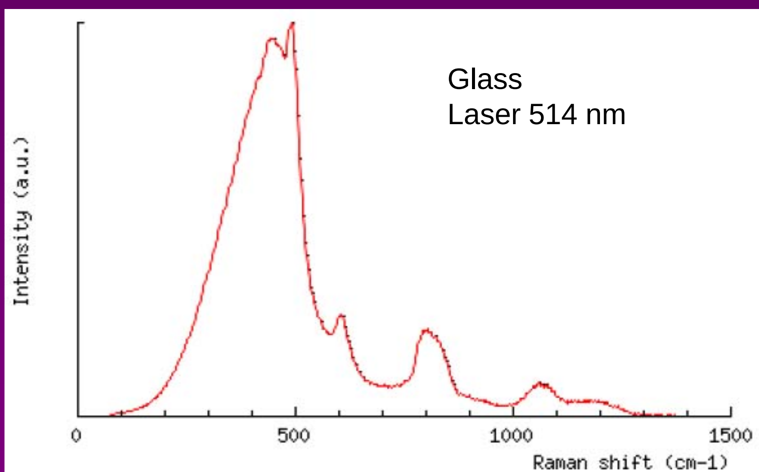


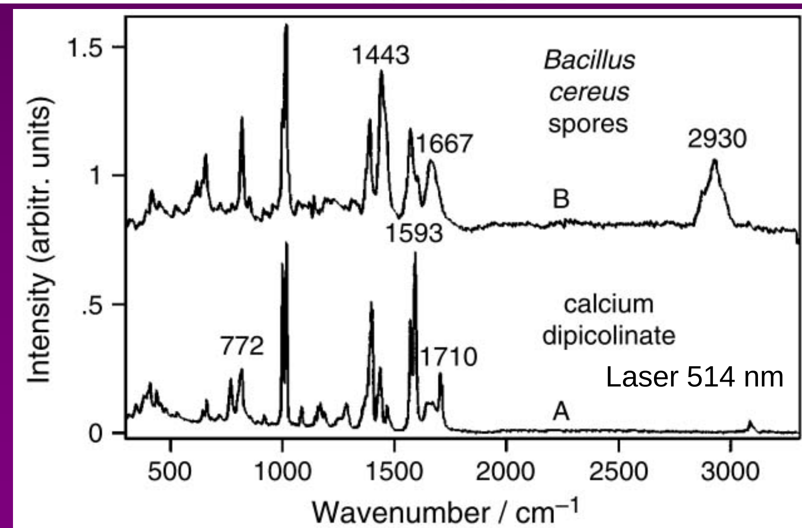
K. Kneipp, Physic Tody, **60**(11), 2007, p. 40-46

Spectrum examples





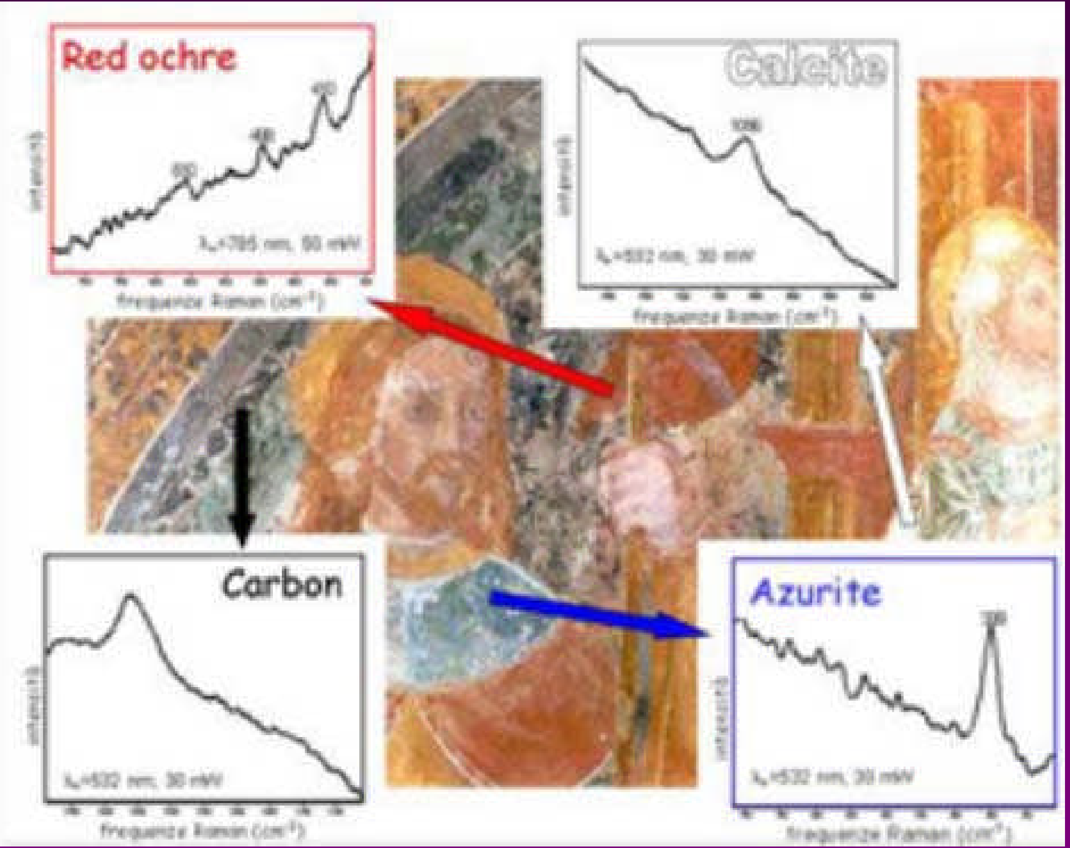




Bankapur A et all, (2010) .PLoS ONE 5(4): e10427.
doi:10.1371/journal.pone.0010427.
Laboratoire de Sciences de la Terre ENS-Lyon

www.perkinelmer.com , Introduction to Raman Spectroscopy
J. Raman Spectrosc. 2004; 35: 82–86

Portable Raman

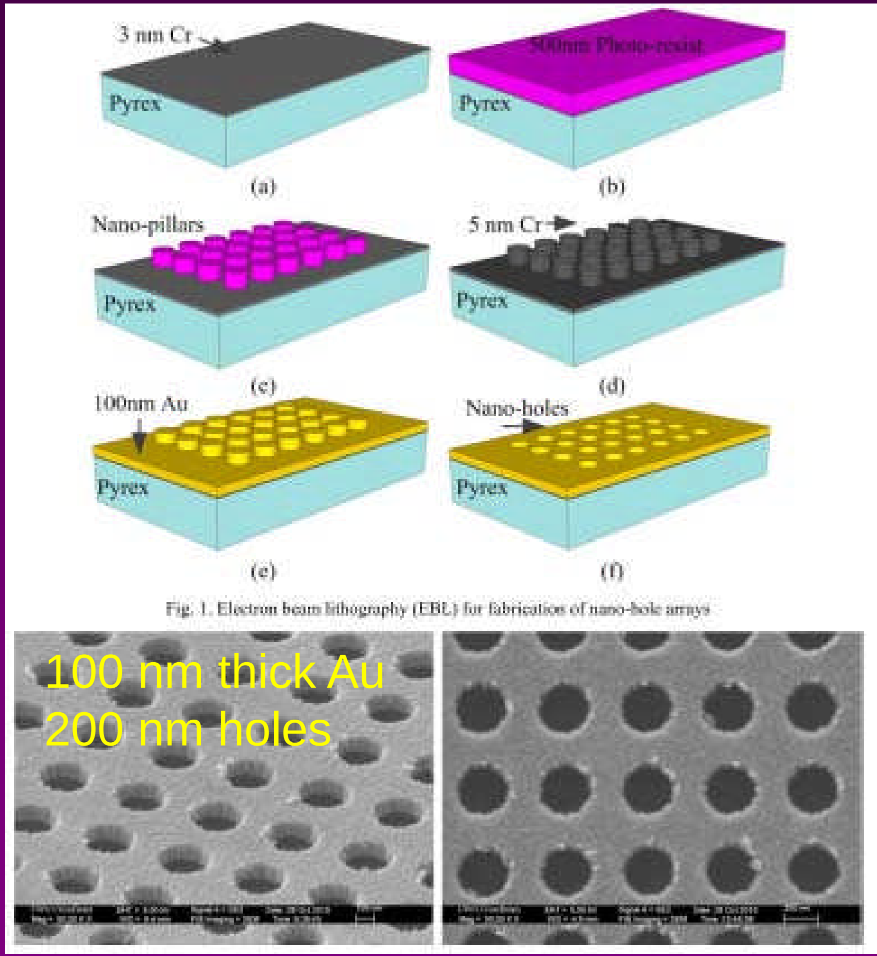


www.jascoinc.com, RMP-300 Portable Raman Spectrometer

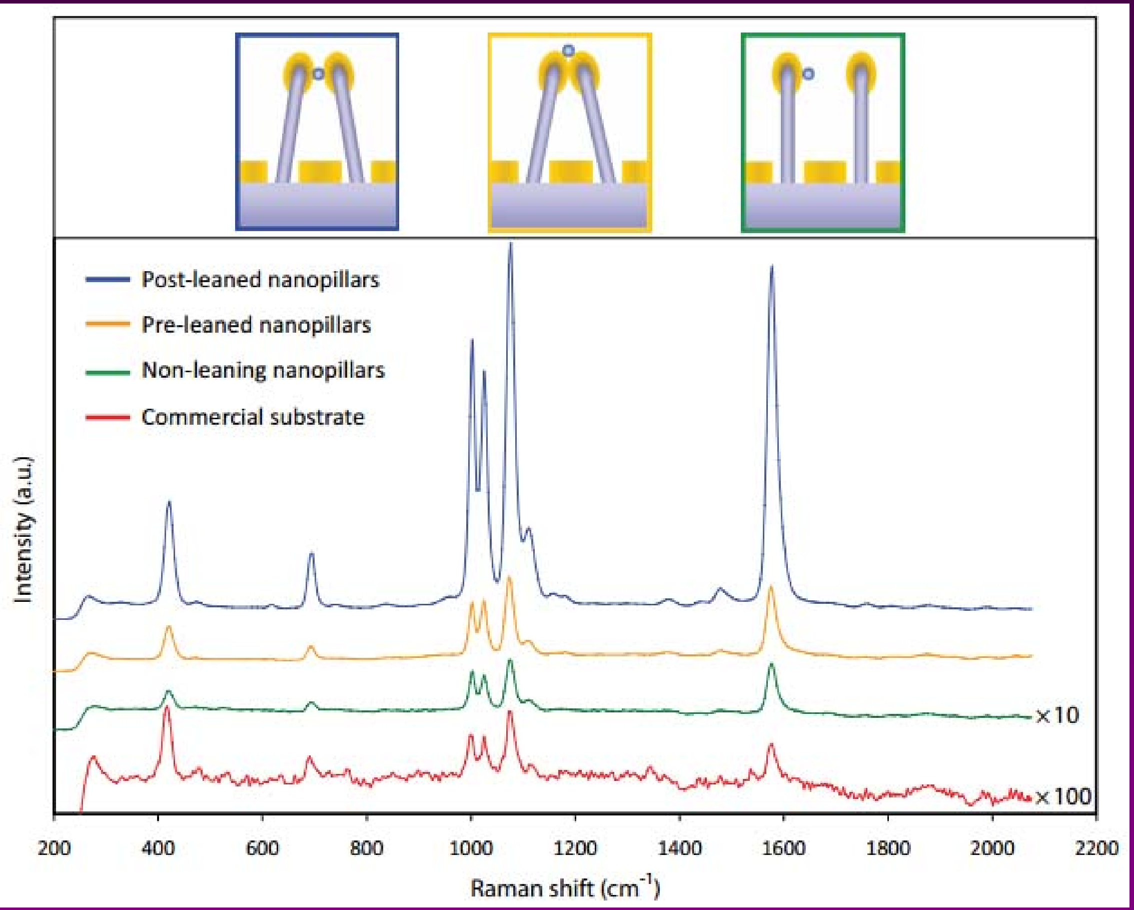
SERS substrate is nanoengineered surface!

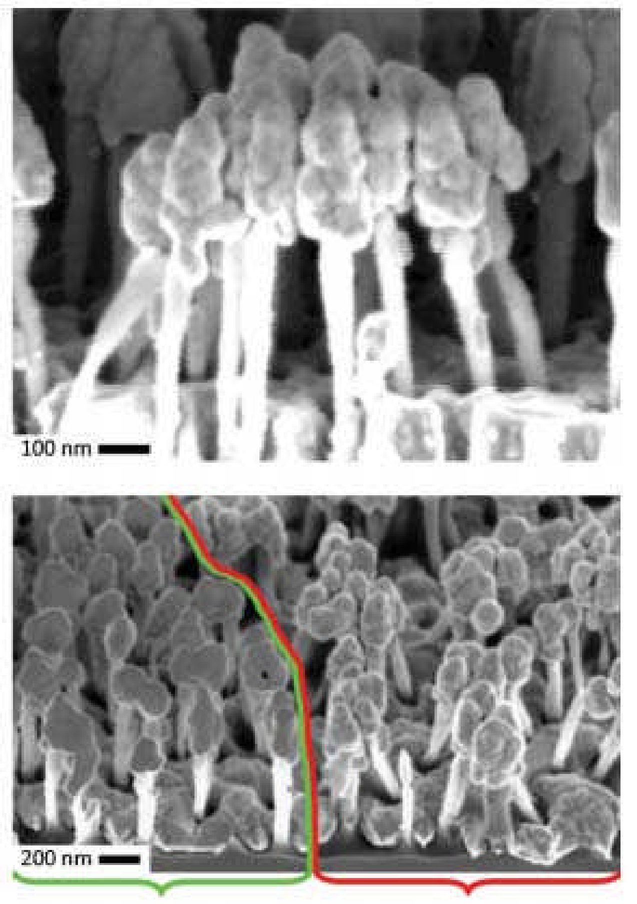
Simplest SERS substrate is Ag nanoparticle colloid, but its efficiency is low.

Mass production of cheap SERS substrates is a problem!
- Patterning
- Metal dry etching
- Adhesion sublayer



Leaning Si pillars





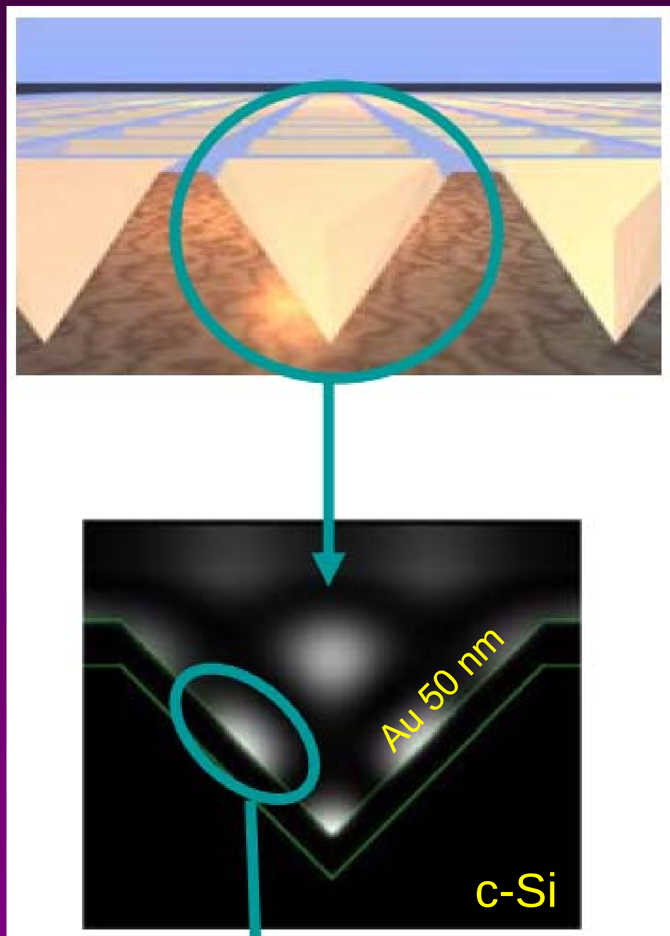
M.S. Schmidt et al., Adv. Mater. 2012, 24, OP11–OP18

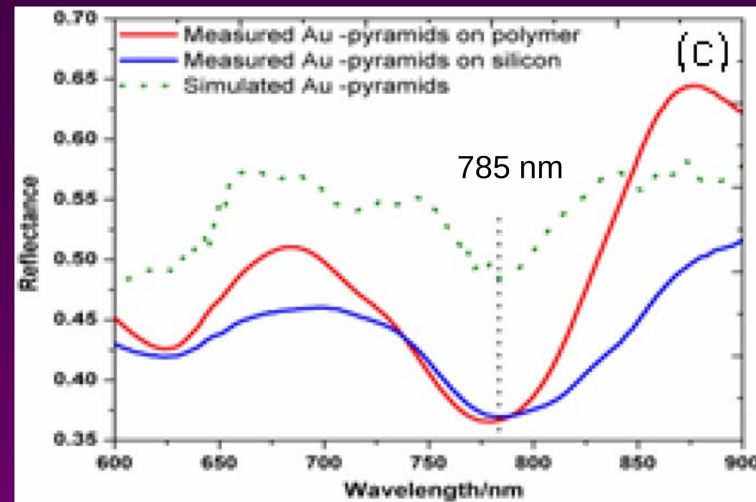
no leaning

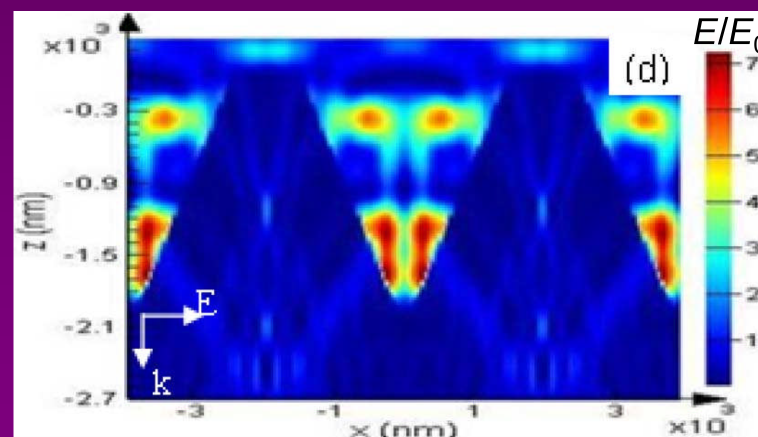
leaning

Commersial SERS substrate (Klarite)

Very high enhancements are ‘sacrificed’ in favor of homogeneity and reproducibility







www.d3technologies.co.uk - www.renishawdiagnostics.com/en/klarite-sers-substrates

ZHIDA XU, Master Thesis, University of Illinois at Urbana-Champaign, 2011

Applications

- Chemical identification (bonds)
- Physical identification (crystallinity, phases, graphene)
- Stress and diameter measurements (carbon nanotubes)
- Trace analysis (explosives and drug detection)
- Process monitoring (in-situ measurements)
- Uncovering painting
- Biology (DNA) and medicine (glucose *in-vivo*)
- Pharmacology

IDEA 1: Can Bio-Inspired Signal Processing Steps Be Realized as Synthetic Biochemical Processes?

(additional slides were shown for this topic, not reproduced here)

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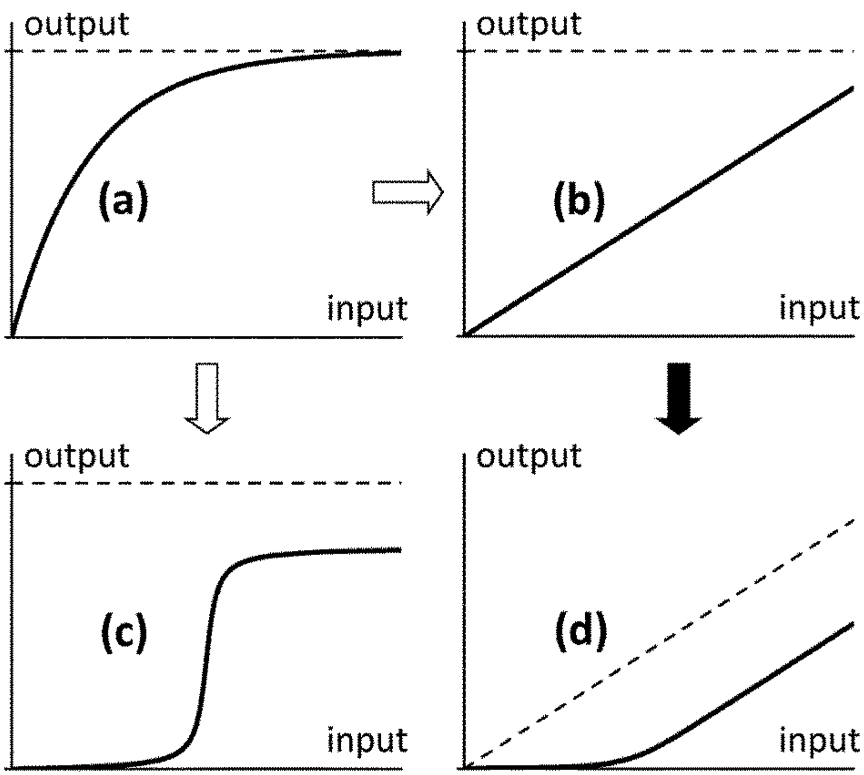
Now: Modifications and networking of biochemical response for biosensor applications:



Idea: Different paradigm of the input, X, vs. output, Y, signals(t) for incorporation of bioinspired concepts:

$Y(t)$ as a function of $X(t)$;

$$\frac{dX(t)}{dt} = R_{ext}(t) + \text{reaction terms}.$$

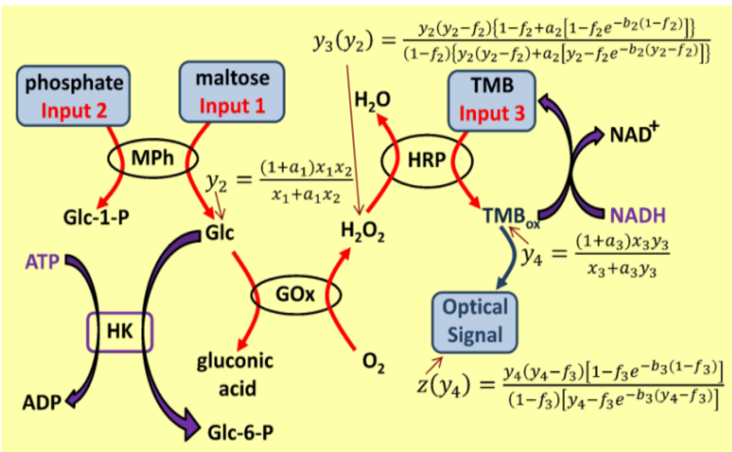
See: V. Privman and E. Katz, Physica Status Solidi **A 212**, 219-228 (2015)

Here we had $Y(t_g)$ vs. $X(0)$.

IDEA 2: "Mesoscale" substrates and scaffolds for increasing complexity and for utilizing nanosize objects for (bio)sensing

Vladimir Privman privman@clarkson.edu

Now: Increasing the complexity of processing steps in biosensor applications (involving biomolecular and other chemical reactions), and other sensor applications (involving nanoparticles):



Networked enzymatic gates with added "filtering" reactions, and their modeling.

Idea: Ultimately, for increased complexity and also to reduce environmental impact (for nanoparticles/nanoobjects), both biomolecules (e.g., enzymes) and nanoparticles will have to be immobilized and "fuctionalized" on various substrates or "scaffolds".

See comments on the next slide.

Realized as a "chemical soup".

Comments for IDEA 2: substrates and scaffolds for increasing complexity and for utilizing nanosize objects for (bio)sensing

Clarkson University

Vladimir Privman privman@clarkson.edu

(Bio)molecule (and, in fact, also nanoparticle/nanoobject) immobilization can involve complicated electrode surface structures and forms of (bio)chemical anchoring to accomplish charge transfer and (bio)chemical/catalytic activity, as well as long-duration stability.

"Scaffolds" for nanoparticles and other nanoobjects (and, in fact, also for biomolecules) can be "mesoscopic" and made from DNA, micro-fibers, various polymeric structures, combined structures (such as DNA origami wound around a conducting carbon nanotube), etc.

Electronic techniques for nano-sensing

Thierry Ferrus

Hitachi Cambridge Laboratory

Outline

Single Electron Transistors and Quantum Point Contacts

Reflectometry measurements and dispersive measurements

Measuring spin states

Feedbacks action and weak measurements

SETS and QPC

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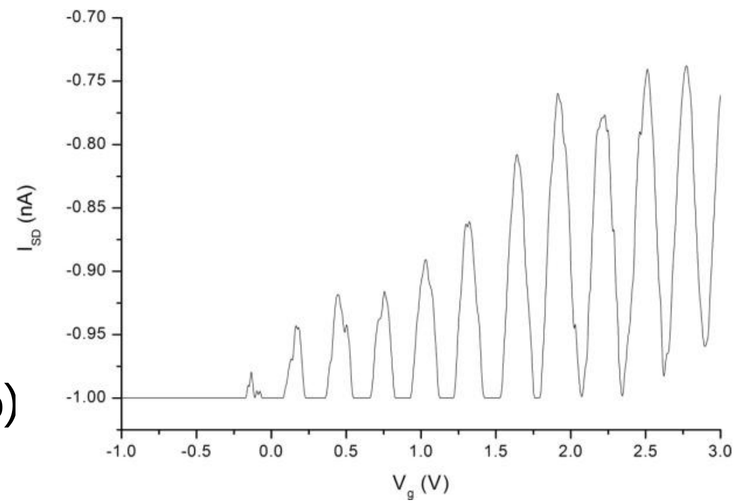
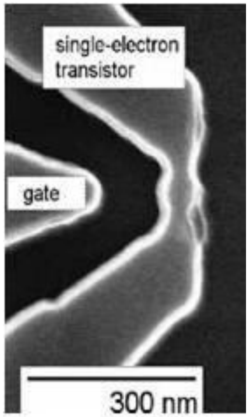
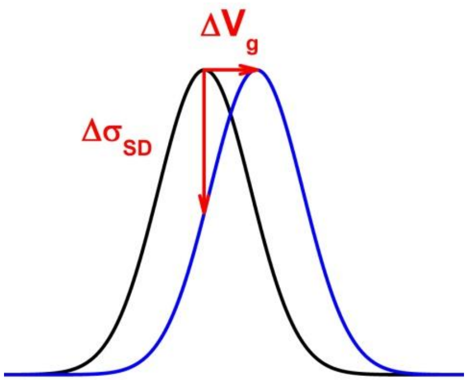
- Single electron transistor (2 barriers), QPC (1)
- Coulomb blockade, oscillations
- Capacitive detection, shifts
- Limited detection efficiency (2%)
- Improvement by :

  switching between current paths

  increasing confinement (E_c)







Reflectometry and dispersive measurements

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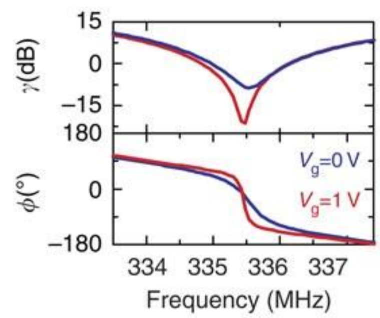
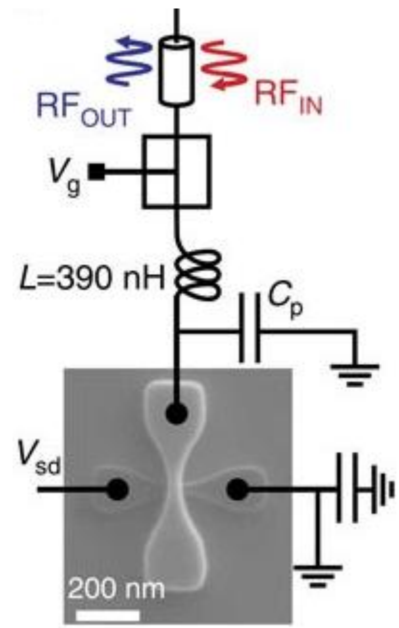
- Formation of a RLC circuit
- Resonance ν_0 in the 100 MHz





- Measure of reflected signal at $\nu \neq \nu_0$ (amplitude and phase)

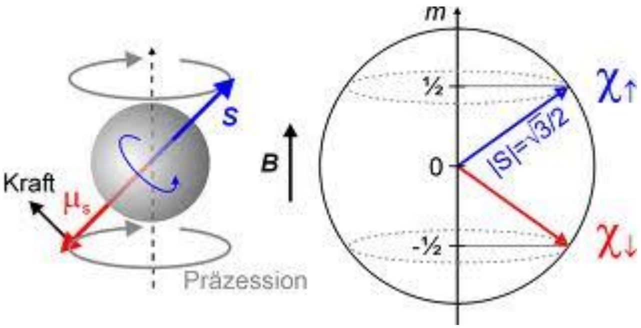
  V_g varies *R* and *C*

- Bandwidth ~ 8 MHz, higher than SET (*C* due to wires, except HEMT near devices)
- Problems : RF / μwave may disturb devices if sensitive to ν

  Possible strong attenuation in presence of dopants, traps

Spin measurements

- Difficulty in measuring spin directly

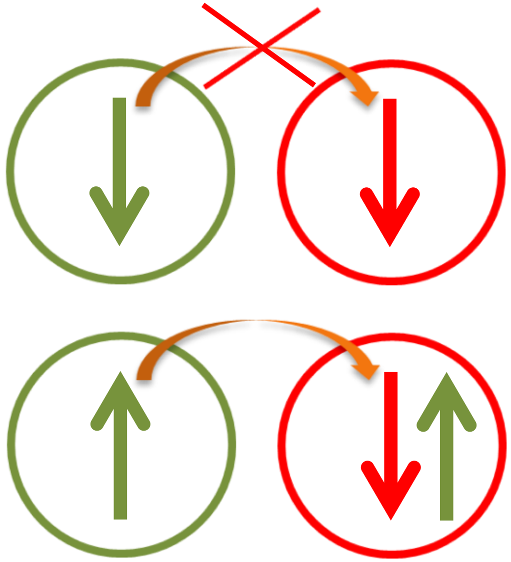


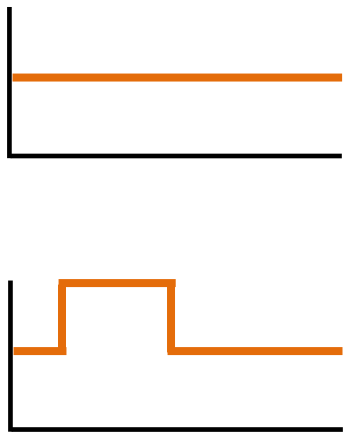
- Spin-to-charge conversion : Pauli blockade

- Singlet-triplet :

  Energy selection,

  tuned by E, Vg





Feedback action and weak measurements

- Feedback action from detector to the device (state change)

- Depends on tunneling time (*R*), measurement time (*C*)

- Strong measurement on the detector but weak coupling

- Efficient measurement or repetitive measurements (bandwidth)

END

Electronic techniques for nano-sensing

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