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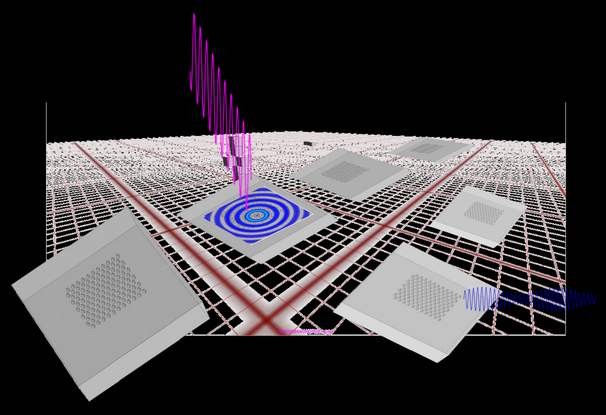

Nanostructure Array Pixels for Surface-Plasmon Material Imager

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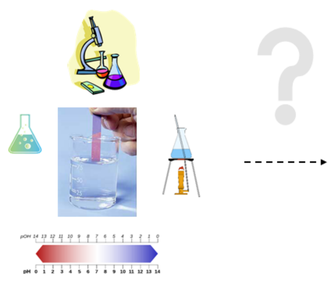
Oasis 8

On-Chip Silicon Photonics Devices A.L.E.O. Advanced Laboratory of Electro-Optics

JCT LEV ACADEMIC CENTER

1. Goal

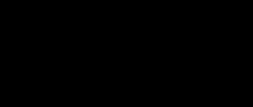
- The past century has seen tremendous progress in imaging technology:



- Can one **image** (the pH of) a **chemical reaction**?
  - In real time?
  - Using Raman Spectroscopy?

2. pH and Raman Spectra

(Spontaneous) Raman Scattering –
- vibrational/phonon modes mix with an optical excitation
- emitted spectrum gives material signature

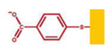


S. Rochmann

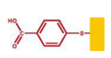
ParaMercaptoBenzoic Acid - pMBA - ($HSC_6H_4CO_2H$): a thiol which adheres to Silver/ Gold

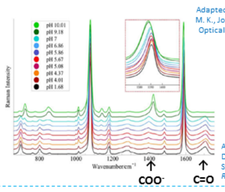
❖ Carboxyl group COO^- , C=O double bond → vibrationary normal modes → Raman Peaks

- **High pH** – basic solution – H^+ dissociate:
  - COO^- peak dominates



- **Low pH** – acidic solution – H^+ remain:
  - C=O peak dominates





Adapted from Bishnoi, S.W., Rozell, C.J., Levin, C.S., Gheith, M.K., Johnson, B.R., Johnson, D.H., & Halas, N.J. (2006). All-Optical Nanoscale pH Meter. *NanoLetters*, 6(8), 1687-1692.

Adapted from A. William, K.J. Flynn, Z. Xia, & P.R. Dunstan, (2016). Multivariate spectral analysis of pH SERS probes for improved sensing capabilities. *J. Raman Spectrosc.*, DOI: 10.1002/jrs.4910

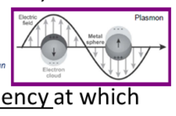
COO^- C=O

The ratio between the COO^- and the C=O peaks can be used to measure the pH

3. SERS/TERS

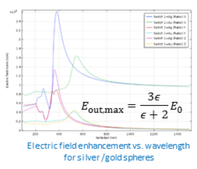
Raman Scattering is very weak. In Surface-Enhanced Raman Scattering several mechanisms **enhance** both the incoming excitation and emitted radiation:

1. **Localized Surface Plasmons** (LSP) - An ambient field induces a dipole moment in a metal particle, which produces an additional field outside:



Ovchinnikov, V. (2012), *Surface Enhanced Raman Scattering (SERS), Tutorial.*

- In an oscillating field there is a resonant frequency at which the induced field is maximal $\mathrm{re}(\epsilon(\omega)) = -2$



Electric field enhancement vs. wavelength for silver/gold spheres

2. **Lightning Rod Effect** -

Electric fields intensify near metal points

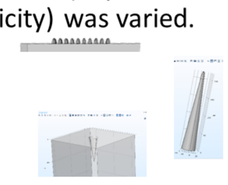
$$\frac{\partial E}{\partial n} = -E\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Hommelhoff et al. (2015)

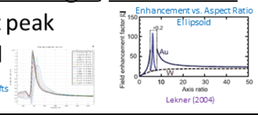
→ **Tip**-Enhanced Raman Scattering (TERS)

4. Nanostructure Geometry

- **Raman Enhancement** is estimated using $\int_{surface} \|\bar{E}\|^4 dA$
- The Electric fields were computed in Comsol Multiphysics using the Finite Element Method (FEM)
- **Hemiellipsoidal** (prolate hemispheroid) tips were simulated. Aspect Ratio (eccentricity) was varied.
- Other geometries investigated:
  - Hybrid **cone+ellipsoid**
  - **Inverted** tips (open cavities)
  - **Nanoshell**



- **Optimization** w.r.t. aspect ratio/cone angle/shell width
  - Plasmon excitation → enhancement peak
  - Resonance wavelength can be **tuned**

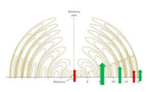


Lekner (2004)

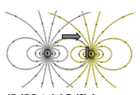
Nanoshell resonance wavelength shifts with varying metal layer thickness

5. Multiple Nanostructures – Interactions

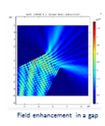
- Single nanoparticles possess a small cross section – **multiple structures** are necessary
- Adjacent metal nanostructures -
  - **Mutually enhance** in the radiation field



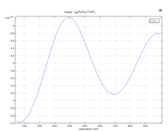
  - **Mutually suppress** in the near field



  - **Develop Gap Plasmons** for separations $\lesssim$ 5 nm; very high enhancement (10^{11}) is attainable at hot spots



Field enhancement in a gap



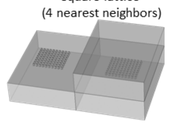
SERS from a pair of ellipsoid nanostructures as a function of separation

6. Pixel Design

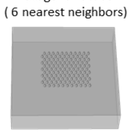
- Pixel Design - finite lattice of silver nanostructures
- **Optimization** is necessary:

  for a fixed area , high density of structures ⇒
  - Large # of structures ↔ increased scattering
  - Smaller separation ↔ increased suppression

Square lattice (4 nearest neighbors)



Hexagonal lattice (6 nearest neighbors)



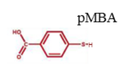
Nanostructure Geometry	Prolate Spheroid
Material	Ag
Eccentricity	0.943
Aspect Ratio	3.00
Base radius	20 nm
Separation	75 nm
Array size	750 nm x 750 nm
Array Area	0.5625 μm²
Array size (# of structures)	11 X 11
Total Structures	121

- Sensor **Fabrication** - Focused Ion Beam (FIB)

Bar Ilan's Institute for Nanotechnology and Advanced Materials (**BINA**)

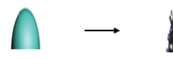
Nano Development Lab, Portland State University

7. Surface Functionalization



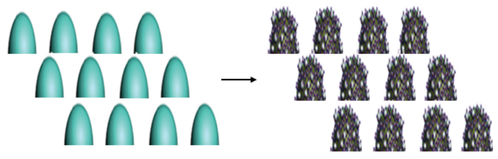
pMBA

Overnight soak:



Adapted from Alvarez-Puebla, R. A., & Liz-Marza, L. M. (2012). Traps and cages for universal SERS detection. *Chem. Soc. Rev.*, *41*, 43–51.

Thiol (pMBA) molecules are adsorbed onto nanostructure surface.

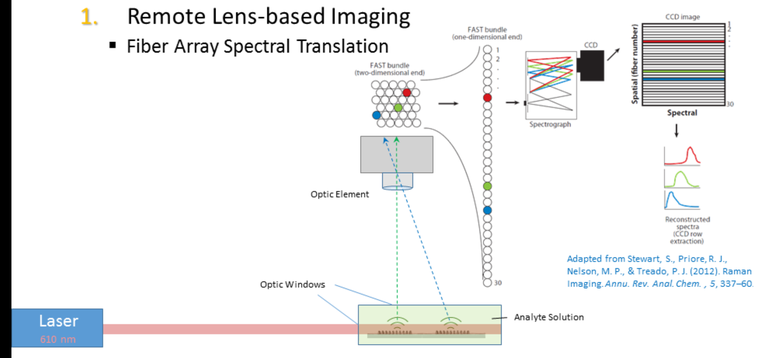


- Bond strength nearly covalent

Self-assembly in 2 stages:
1. Adsorption
2. Alignment

8. Detection – Hyperspectral Image

1. Remote Lens-based Imaging
   - Fiber Array Spectral Translation



Adapted from Stewart, S., Priore, R. J., Nelson, M. P., & Treado, P. J. (2012). Raman Imaging. *Annu. Rev. Anal. Chem.* , *5*, 337–60.

2. Second Generation Device – on-site detection
   - Pixel to Fiber – Challenge: crosstalk elimination
   - Near Field Collection → Plasmonic Waveguide: 'Plantenna'