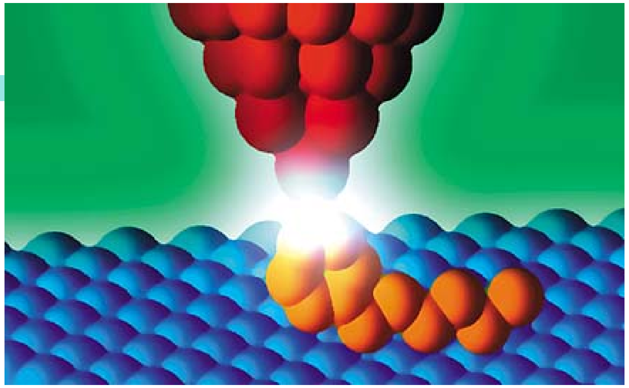
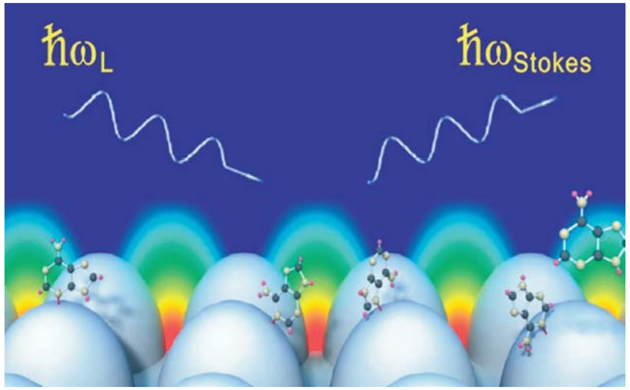
Nanoprobe enhanced optical spectroscopy





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March 20, 2007

Comparison of optical microscopes

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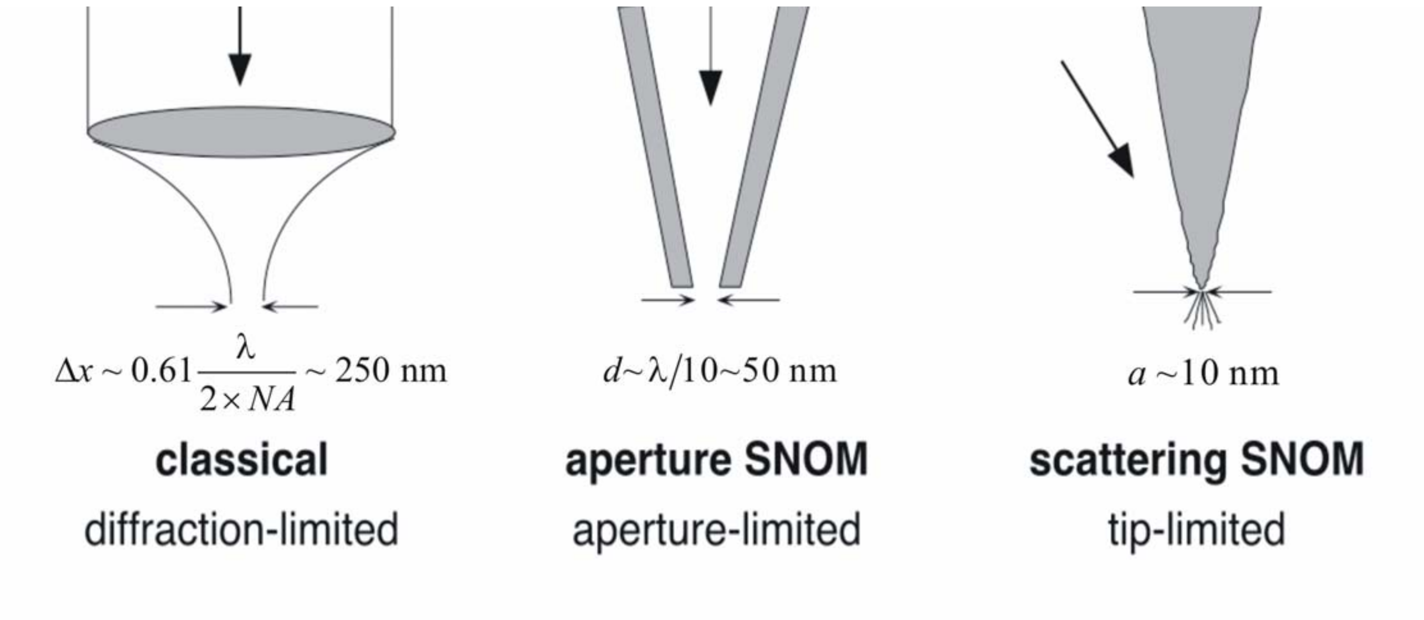
- Performing optical spectroscopy in nanometer scales is one of the critical steps in the development of nanoscience and nanotechnology.
- Taking advantage of localized enhanced field generated by plasmon, optical signal generated in nanometer scale can be observed macroscopically.
- New physics involving light-matter interaction in nanometer scales need to be developed.



Nanoprobe enhanced optical microscopy

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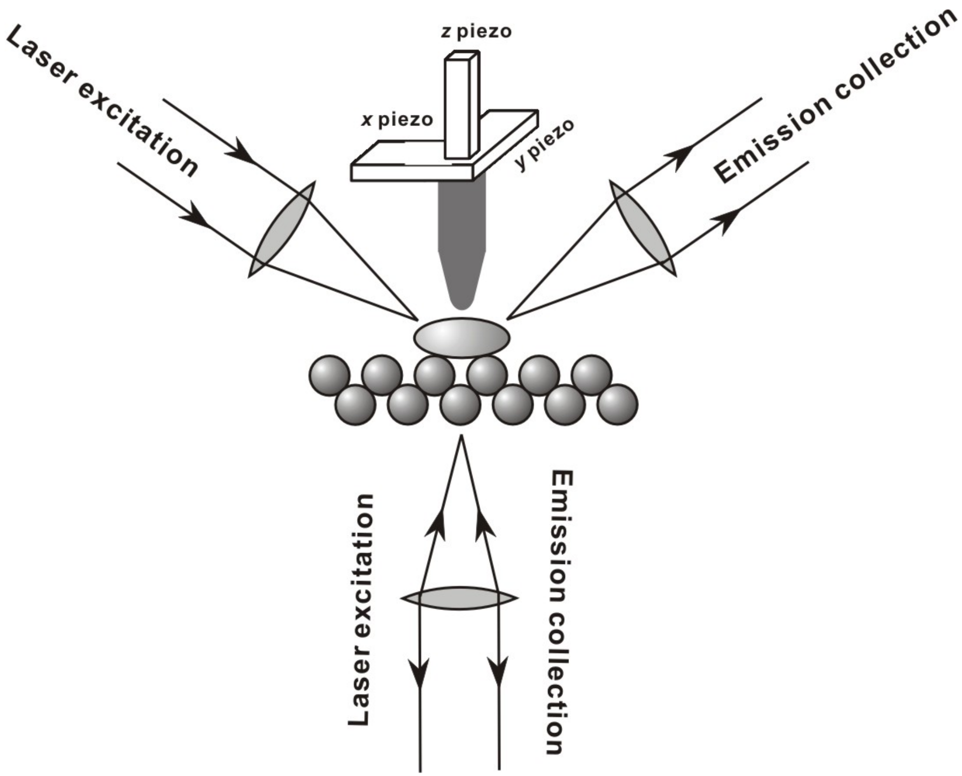
- **Scattering-SNOM**
  - collecting elastic scattering signal
- **Tip-enhanced spectroscopy**
  - collecting inelastic scattering signal (Raman or fluorescence)
- **Nanostructure-enhanced spectroscopy**



Lycurgus Cup in Roman times

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The glass appears green in daylight (reflected light), but red when the light is transmitted from the inside of the vessel.

The Lycurgus Cup, Roman (4th century AD), British Museum
*F. E. Wagner et al., Nature **407**, 691 (2000).*

Scattering by a metal sphere

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Induced dipole by the applied field

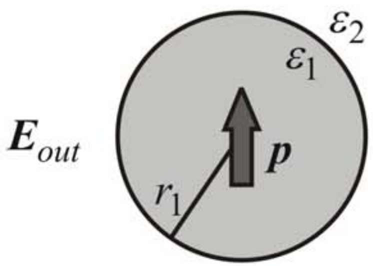
$$\boldsymbol{E}_{out} = E_0 \boldsymbol{e}_z + \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \frac{r_1^3}{r^3} E_0 \left(2\cos\theta \boldsymbol{e}_r + \sin\theta \boldsymbol{e}_\theta\right)$$

$$\Downarrow$$

$$\boldsymbol{p} = \varepsilon_2 \alpha E_0$$

Effective dipole inside the sphere

$$\alpha = 4\pi r_1^3 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}$$



Near-field radiation power from $\boldsymbol{p}(t)$ (near-field scattering cross section)

$$C_{sca}(r) = \int_0^{2\pi} d\theta \int_0^{\pi} d\phi \left|\boldsymbol{E}\right|^2 r^2 \sin\theta = \frac{\alpha^2}{6\pi}\left(\frac{3}{r^4} + \frac{k^2}{r^2} + k^4\right)$$

$\boldsymbol{E}$: the near-field electric field by $\boldsymbol{p}(t)$

$$C_{sca}^{NF} = C_{sca}(r) = \frac{\alpha^2}{6\pi}\left(\frac{3}{r_1^4} + \frac{k^2}{r_1^2} + k^4\right)$$

G. Mie, Ann. Phys. (N.Y.) ***25****, 377 (1908).*

Colors in nanometals

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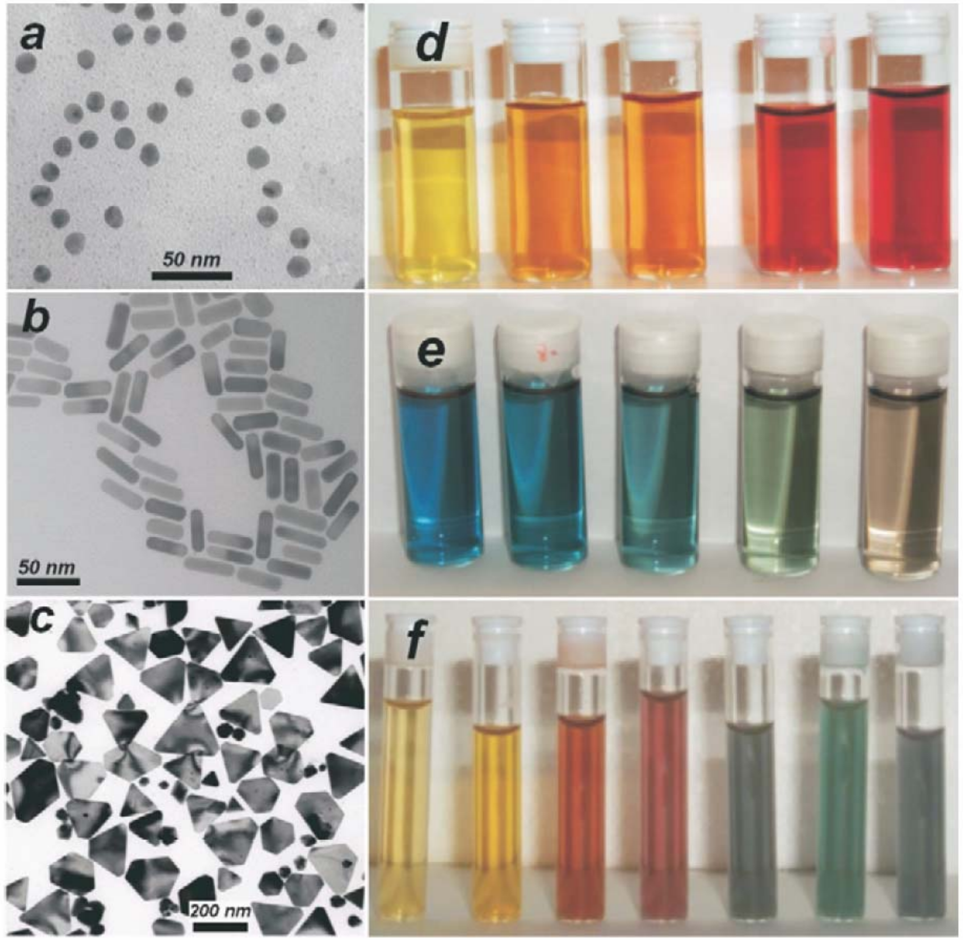

*L. M. Liz-Marzan, Materials Today **26**, February 2004.*

Schematic of *s*-SNOM

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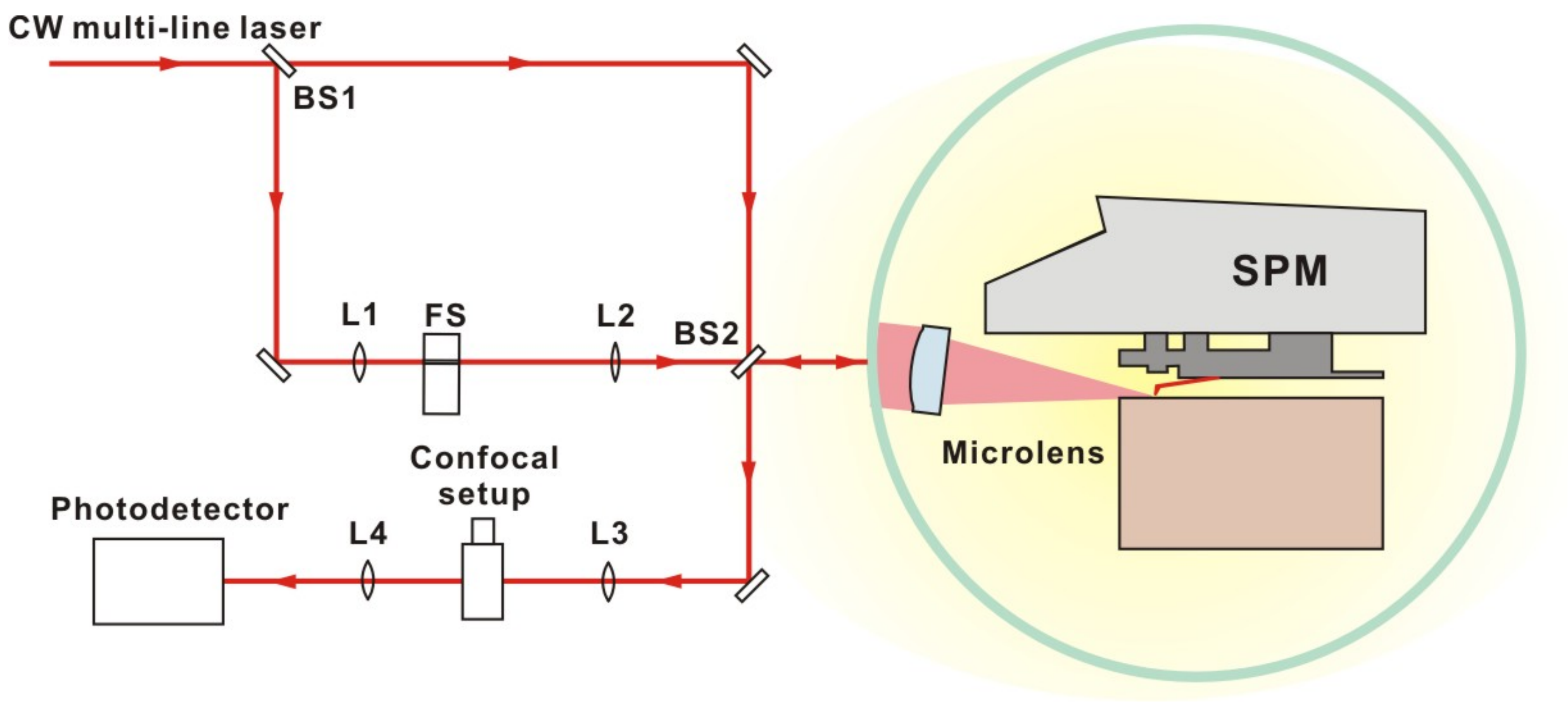

- $$S_{\det} \propto I_{sca} + I_{ref} + 2\sqrt{I_{sca} \times I_{ref}} \cos\left[\left(\Delta + n\Omega\right)t + \varphi\right], \quad I_{sca} \sim 10^{-6} I_{ref}$$
- **Direct probe of optical properties in nanometer scales**
- **Near-field spectroscopy**

Spatial resolution

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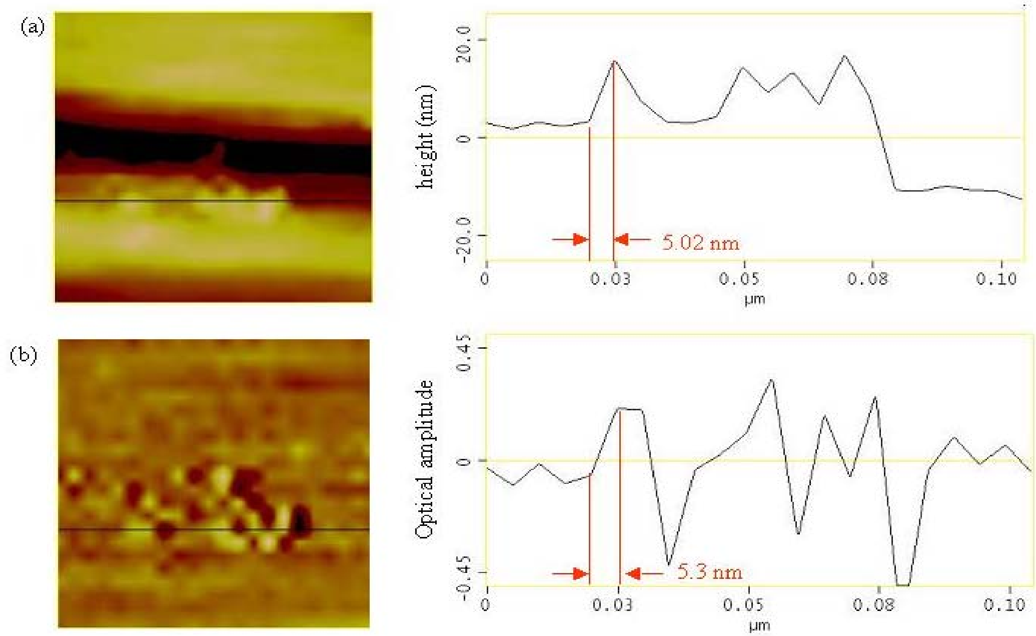
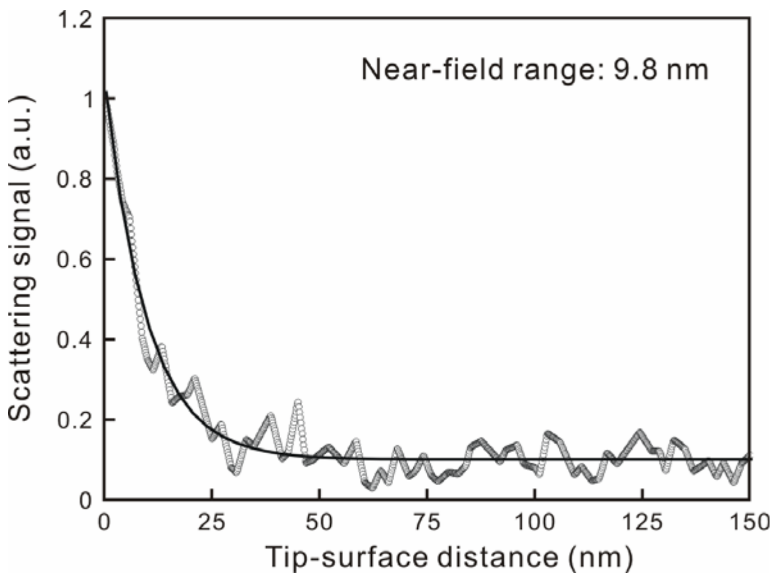
AFM image



s-SNOM image



Lateral resolution: 5 nm

Vertical resolution: 10 nm

Material contrast

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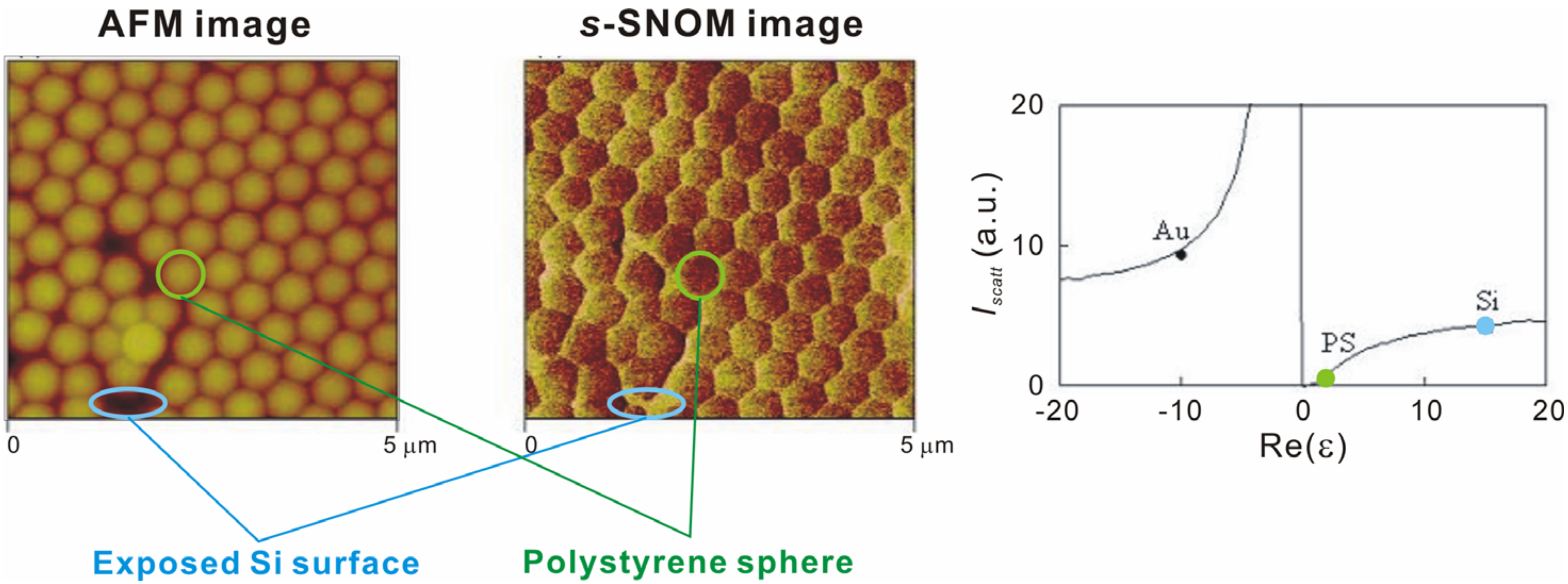
Polystyrene sphere on Si(111)



- **Detection limit of Δ*n*: 0.02**

Scattering-SNOM with single CNT

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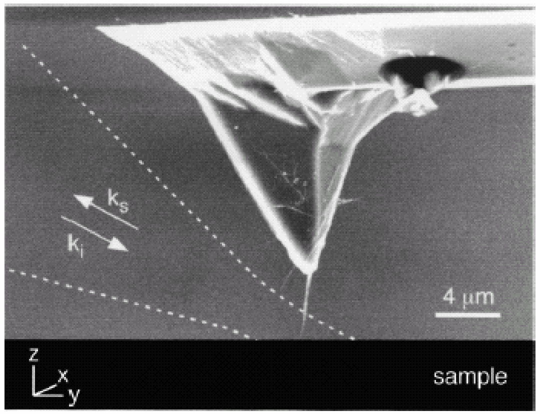
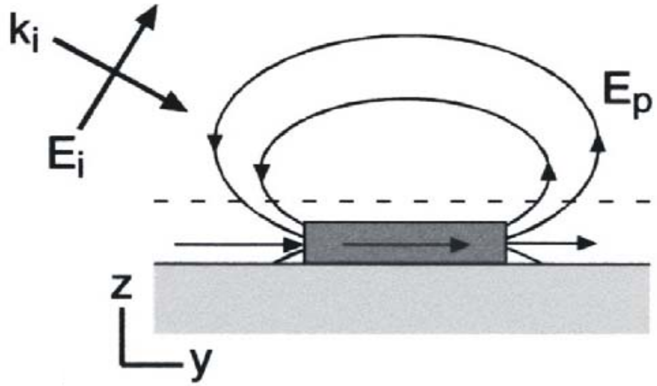
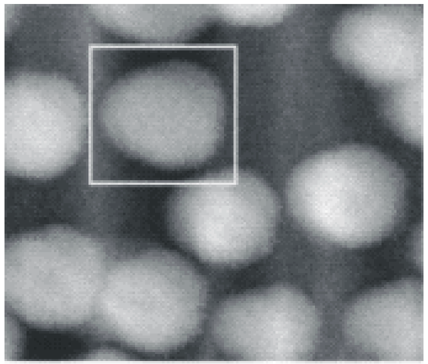
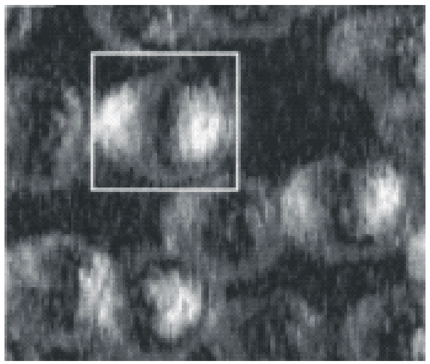




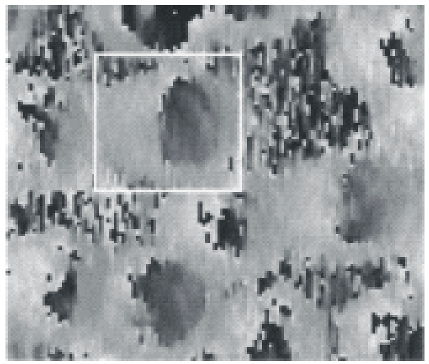
AFM image



Amplitude image



Phase image



R. Hillenbrand et al., Appl. Phys. Lett. ***83****, 368 (2003).*

Near-field fluorescence spectroscopy

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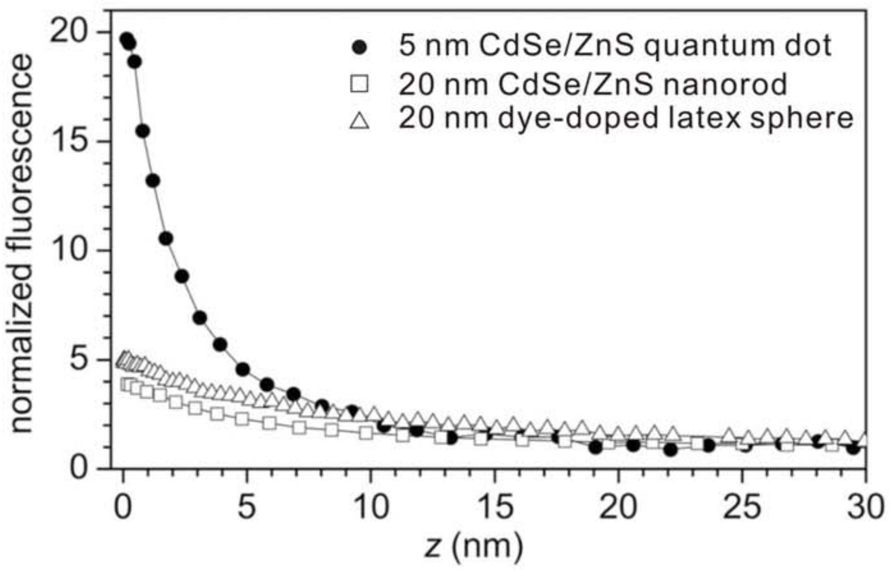

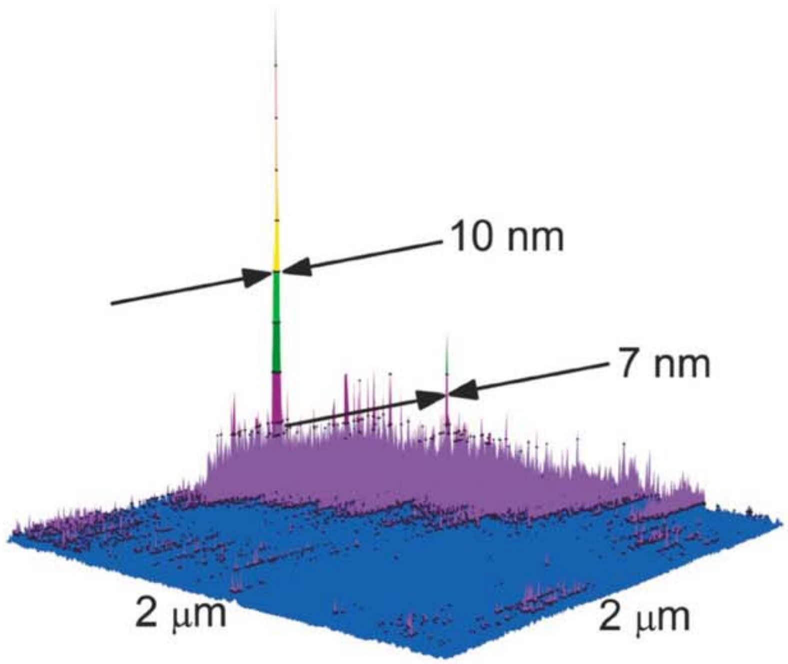

Fluorescence enhancement near a silicon tip

Tip-enhanced fluorescence image of quantum dots

J.M. Gerton et al., Phys. Rev. Lett. ***93****, 180801 (2004).*

Near-field Raman spectroscopy of CNT

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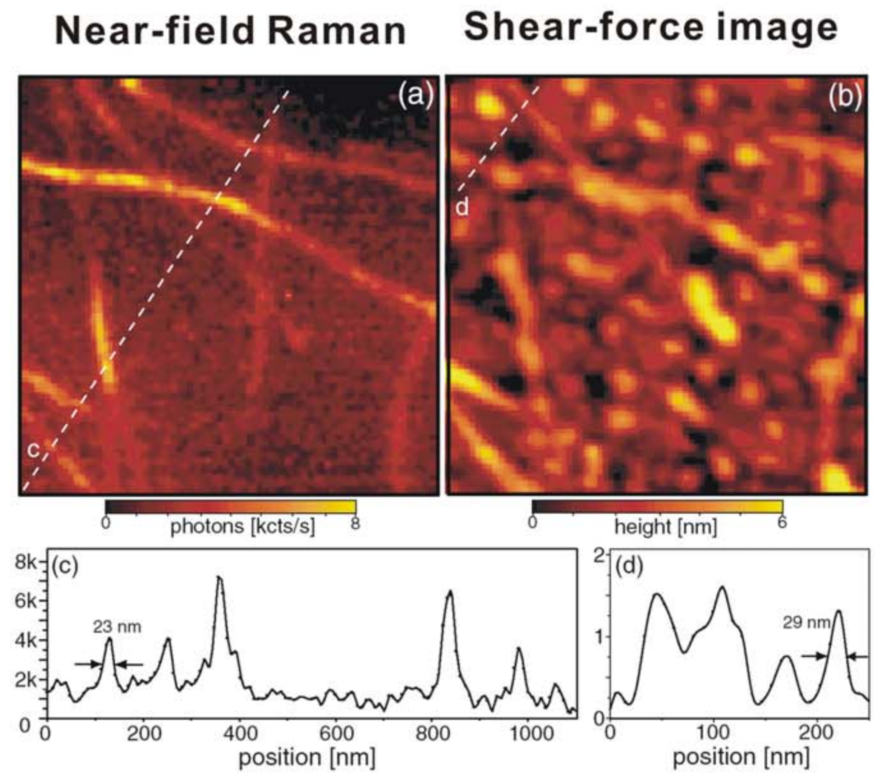

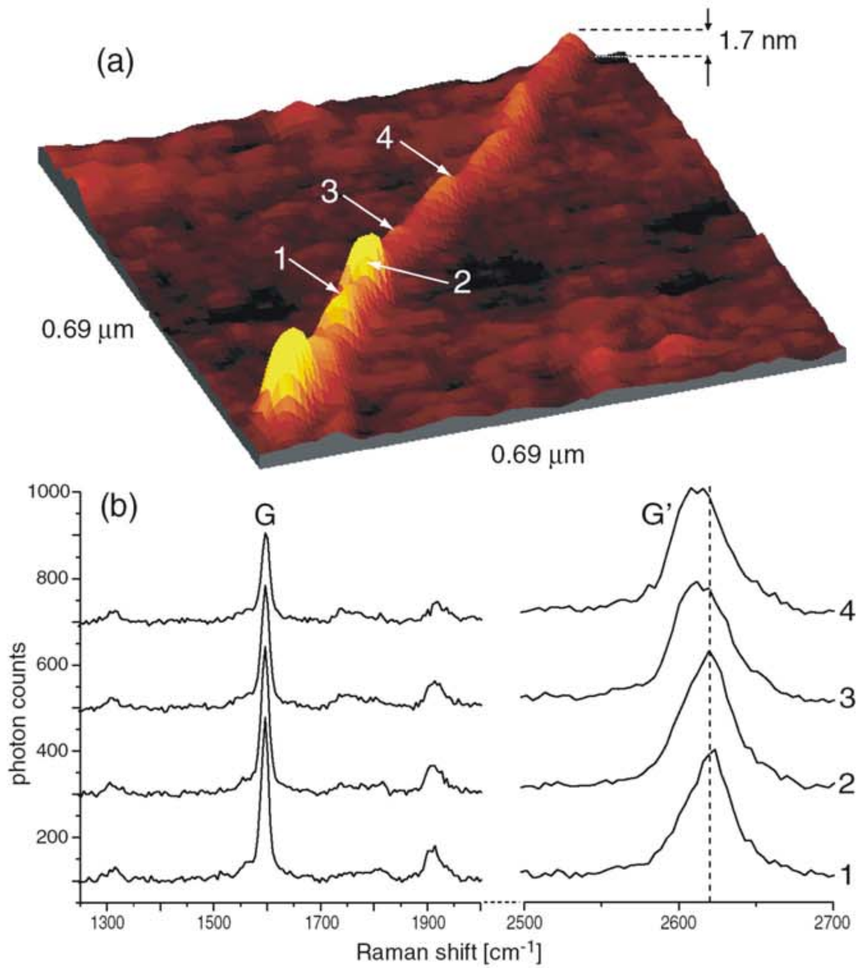

A. Hartschuh, E. J. Sánchez, X. S. Xie, and L. Novotny, Phys. Rev. Lett. ***90****, 095503 (2003).*

Single-molecule Raman spectroscopy

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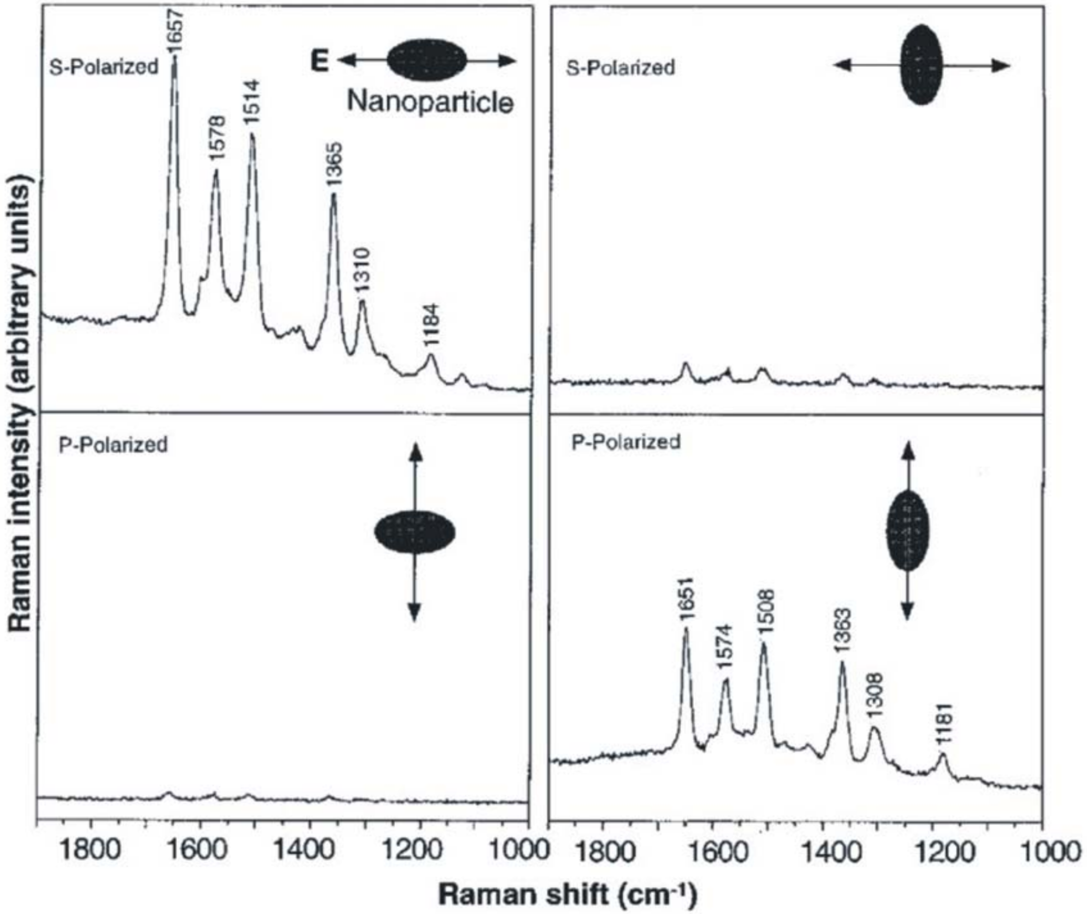
Polarized single molecule Raman spectra of dye-to-colloidal particles



*S. Nie and S. R. Emory, Science **275**, 1102 (1997).*

Comparison between Raman and SERS

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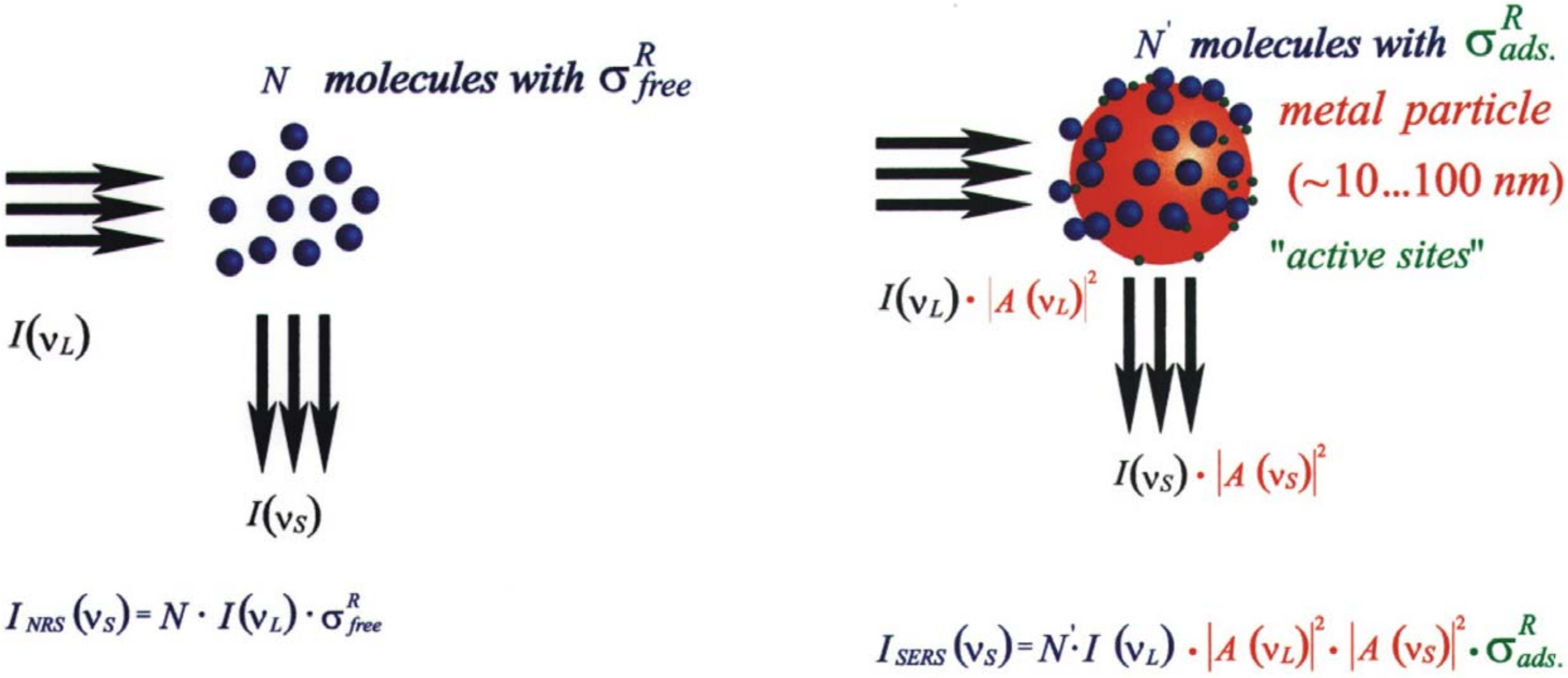

Unenhanced Raman scattering **SERS**

K. Kneipp et al., Bioimaging ***6****, 104 (1998).*

Interparticle field enhancement in SERS

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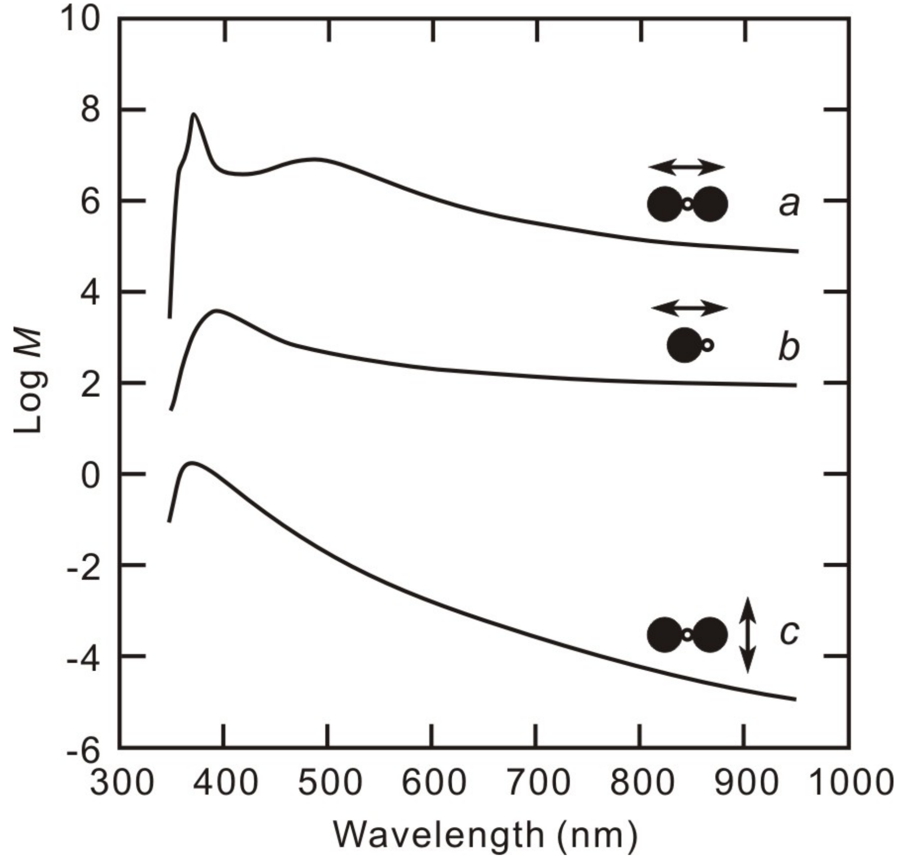
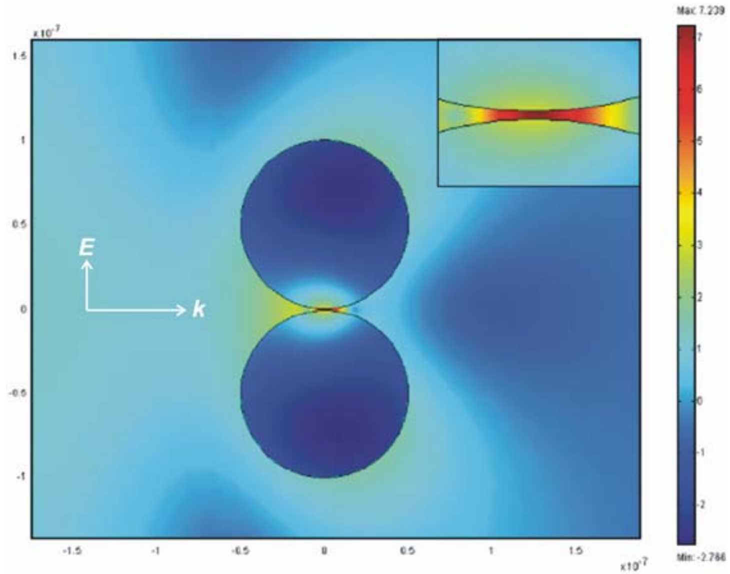
$$M = \left[E_L(\omega_l) / E_I(\omega_l) \right]^2 \cdot \left[E_L(\omega_S) / E_I(\omega_S) \right]^2$$





H. Xu, J. Aizpurua, M. Käll and P. Apell, Phys. Rev. B **62**, 4318 (2000).

Fabrication procedure of Ag-particle arrays

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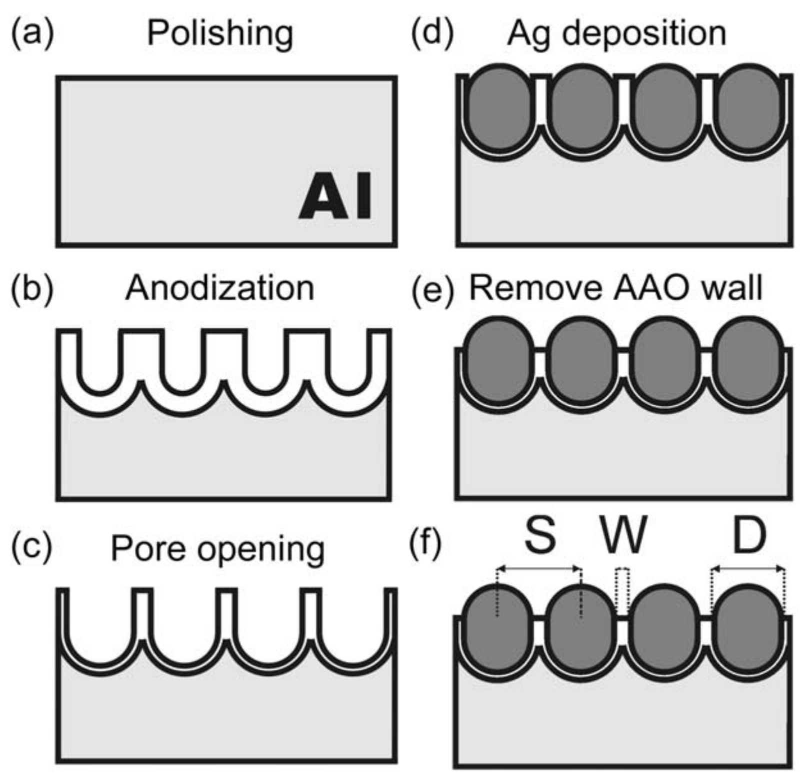
- High-purity aluminum foil is electropolished to 1-nm surface roughness.
- The foil is then anodized using different voltages to obtain arrays of self-organized nanochannels with specific interchannel spacings.
- Identical channel diameter is created by controlled etching for the substrates with different pore spacings.
- By AC electrochemical plating procedure, Ag nanoparticles are grown in the AAO nanochannels.
- The 'hot junctions' are then created by subsequent etching of alumina walls.



H.-H. Wang, C.-Y. Liu, S.-B. Wu, N.-W. Liu, C.-Y. Peng, T.-H. Chan, C.-F. Hsu, J.-K. Wang, and Y.-L. Wang, Adv. Mater. ***18****, 491 (2006).*

SEM and TEM examination

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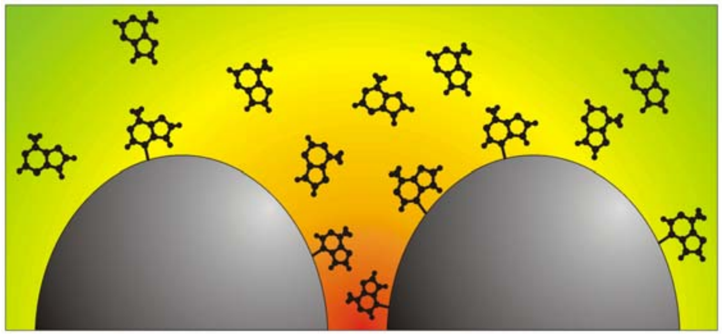
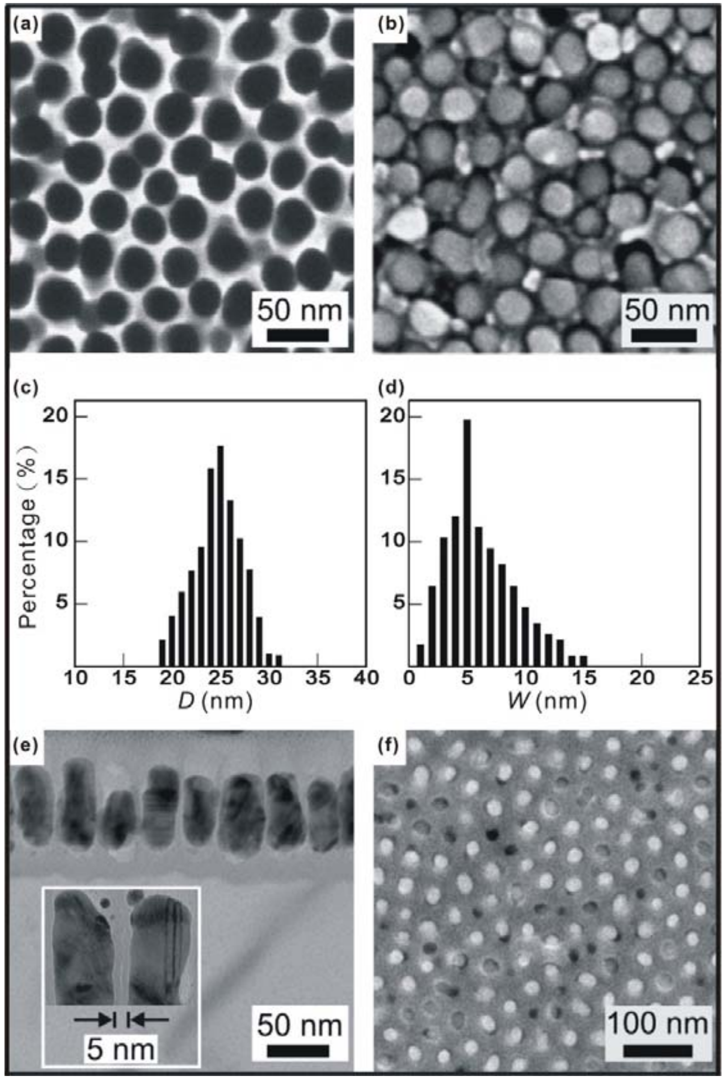
- The spread of the distribution of *D* and *W* is ~5 nm.
- The hot junctions were further examined by cross-sectional transmission electron microscopy.
- In this study, the gap is tuned from 5 to 25 nm, while maintaining the particle diameter to be 25 nm.





Enhancement & dynamical range

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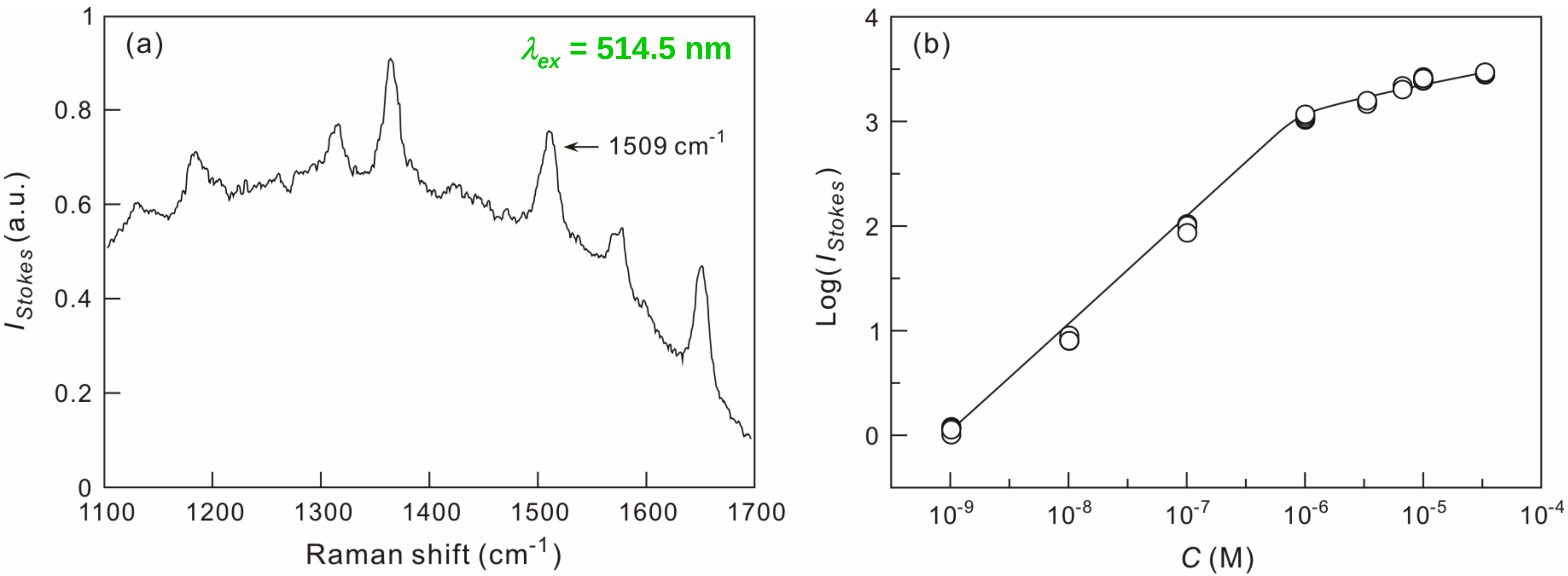
Rhodamine 6G in water



- Uniform Raman enhancement (<5% for different locations of a substrate)
- 10^5 more Raman enhancement than the substrate of ~30 nm Ag nanoparticles thermally deposited on a silicon surface
- Large dynamical range (>1000)

Gap dependence of SERS signal

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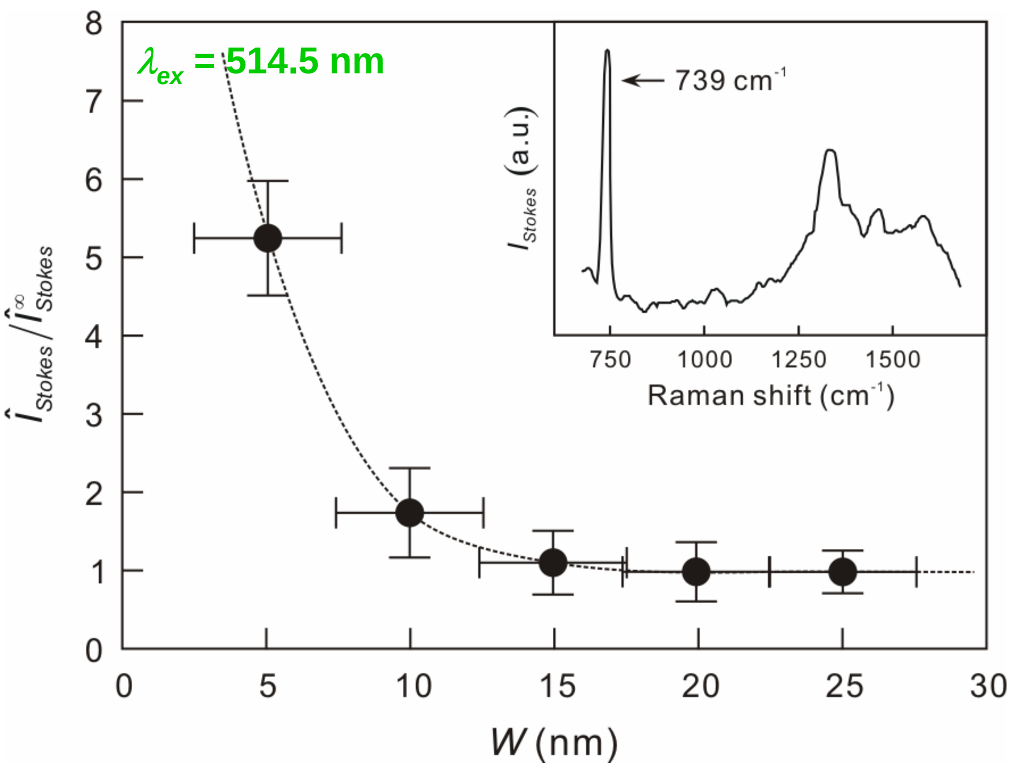
- Adenine: no fluorescence background from 514.5-nm excitation
- 739 cm^{-1}: purine ring breathing mode
- $\hat{I}_{Stokes}$: average Raman signal per particle
- $\hat{I}^{\infty}_{Stokes}$: for substrates with infinitely large *W*
- The average Raman signal per particle at 739 cm^{-1} starts increasing drastically as *W* decreases below 10 nm.

Adenine in water (10^{-4} M)



SERS as a biomedical diagnostic tool

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- Raman spectroscopy, providing molecular vibrational information, can become a powerful and useful method to identify molecular species if its scattering cross section can be enhanced many orders of magnitude.
- Surface-enhanced Raman scattering (SERS) may serve as the solution.
- Most of Raman enhancers have suffered two major drawbacks: low reproducibility and small dynamical range. Therefore, a lot of efforts have been made to control its enhancement mechanisms such that uniform high sensitivity can be achieved.
- One key point is whether it is possible to control precisely the electromagnetic enhancement factor induced by plasmonic resonance.
- Theoretical and experimental studies indicate that the precise control of gaps between nanostructures in the sub-10 nm regime, ‘hot junctions’, is likely to be critical for the fabrication of SERS-active substrates with uniformly high Raman enhancement factor.

Substrates made by nanosphere lithography

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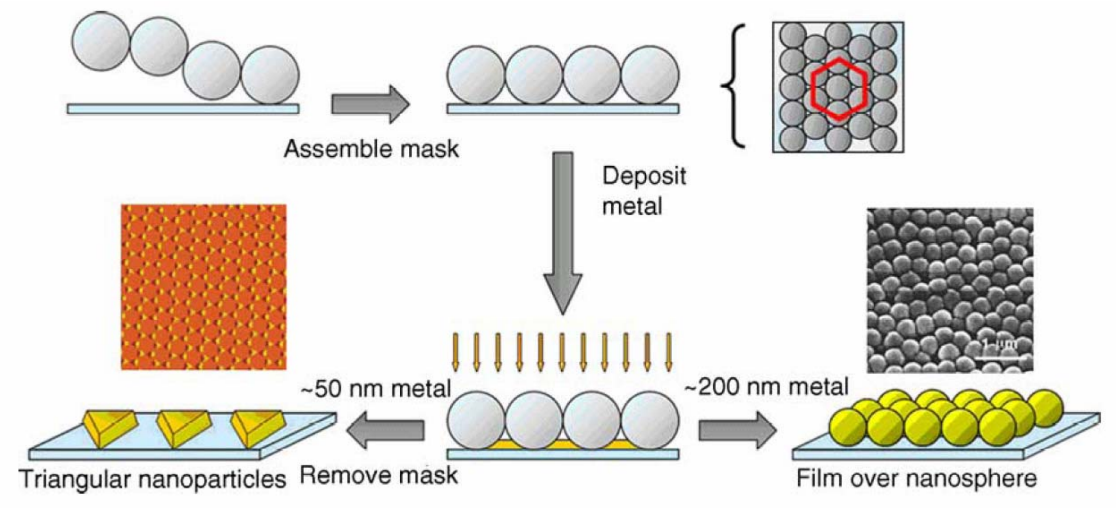

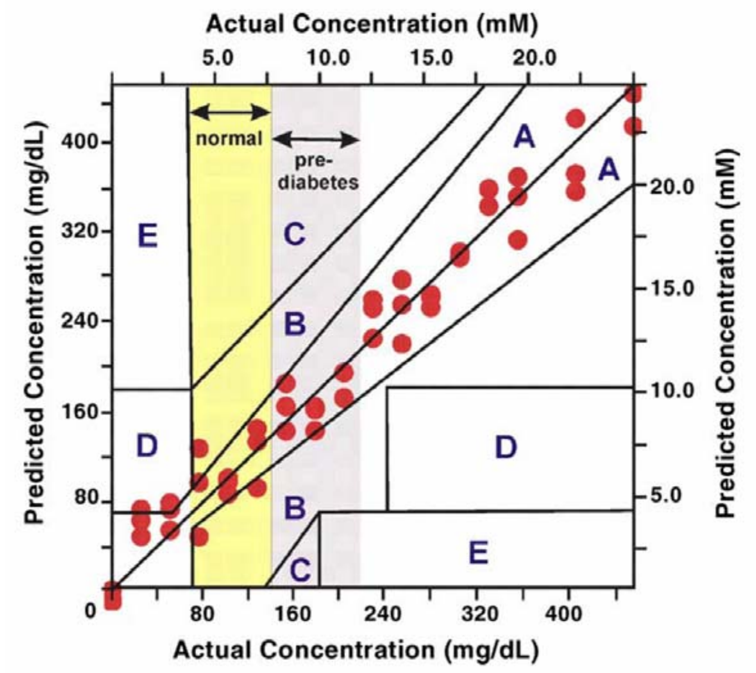

- Nanosphere lithography: triangular nanoparticle array or metal film over nanosphere
- Uniform Raman enhancement
- Glucose detection

*C. R. Yonzon et al., Talanta **67**, 438 (2005).*

SERS characterization of bacteria

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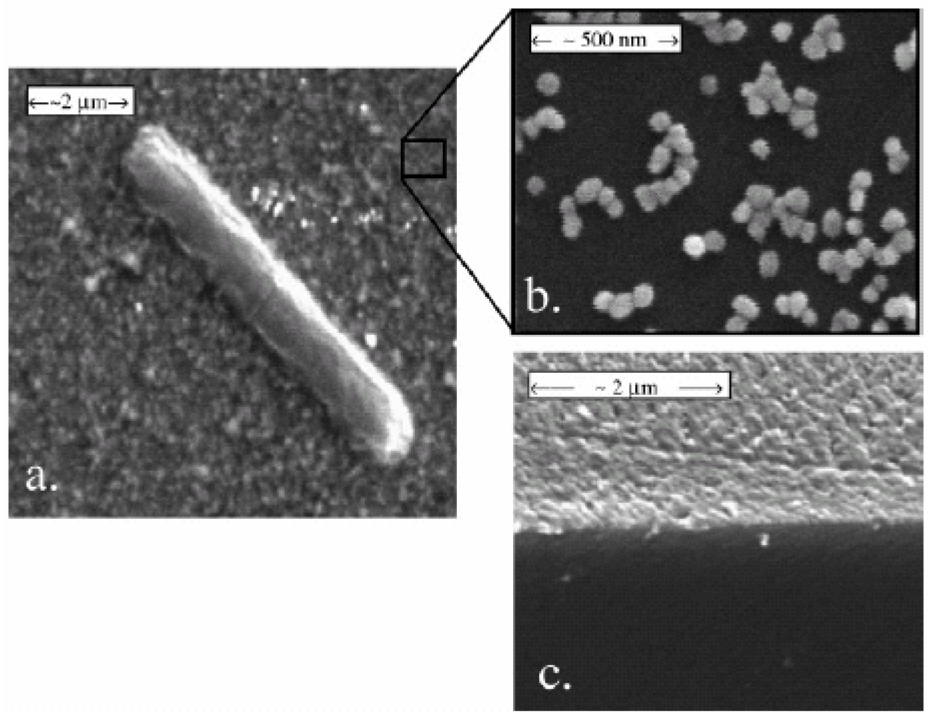
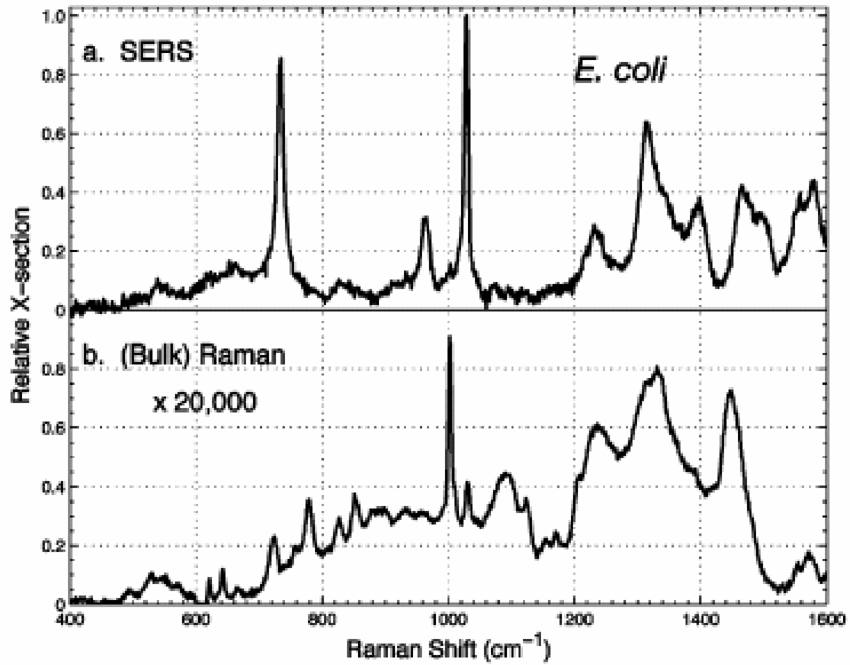
Bacteria on thermally evaporated Au nanoparticles





- Poor reproducibility within one substrate (~15%) and even poorer from substrate to substrate
- Different vibrational signatures between SERS and bulk Raman

*W. R. Premasirili et al., J. Phys. Chem. B **109**, 312 (2005).*

Conclusions

Dr. Juen-Kai Wang, CCMS, NTU

- Scattering-type SNOM has been demonstrated to serve as a nanoprobe to investigate local optical properties and to probe local field distribution.
- Tip-enhanced optical spectromicroscope makes direct link between structure and property in nanometer scale.
- The uniform and highly reproducible SERS-active properties and the wide dynamical range facilitate the use of SERS for chemical and biological sensing applications with high sensitivity.