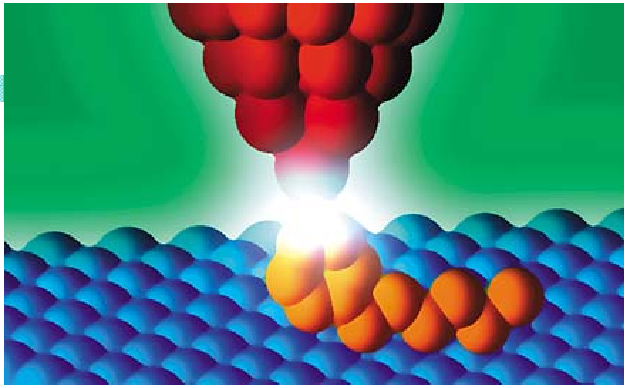
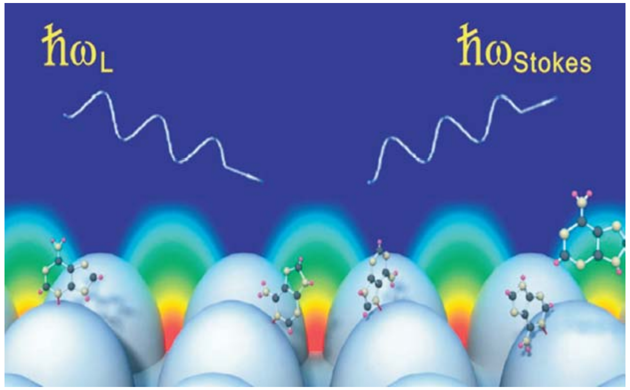
Nanoprobe enhanced optical spectroscopy





Juen-Kai Wang

Center for Condensed Matter Sciences, National Taiwan University
Institute of Atomic and Molecular Sciences, Academia Sinica

April 10, 2008

Collaborators

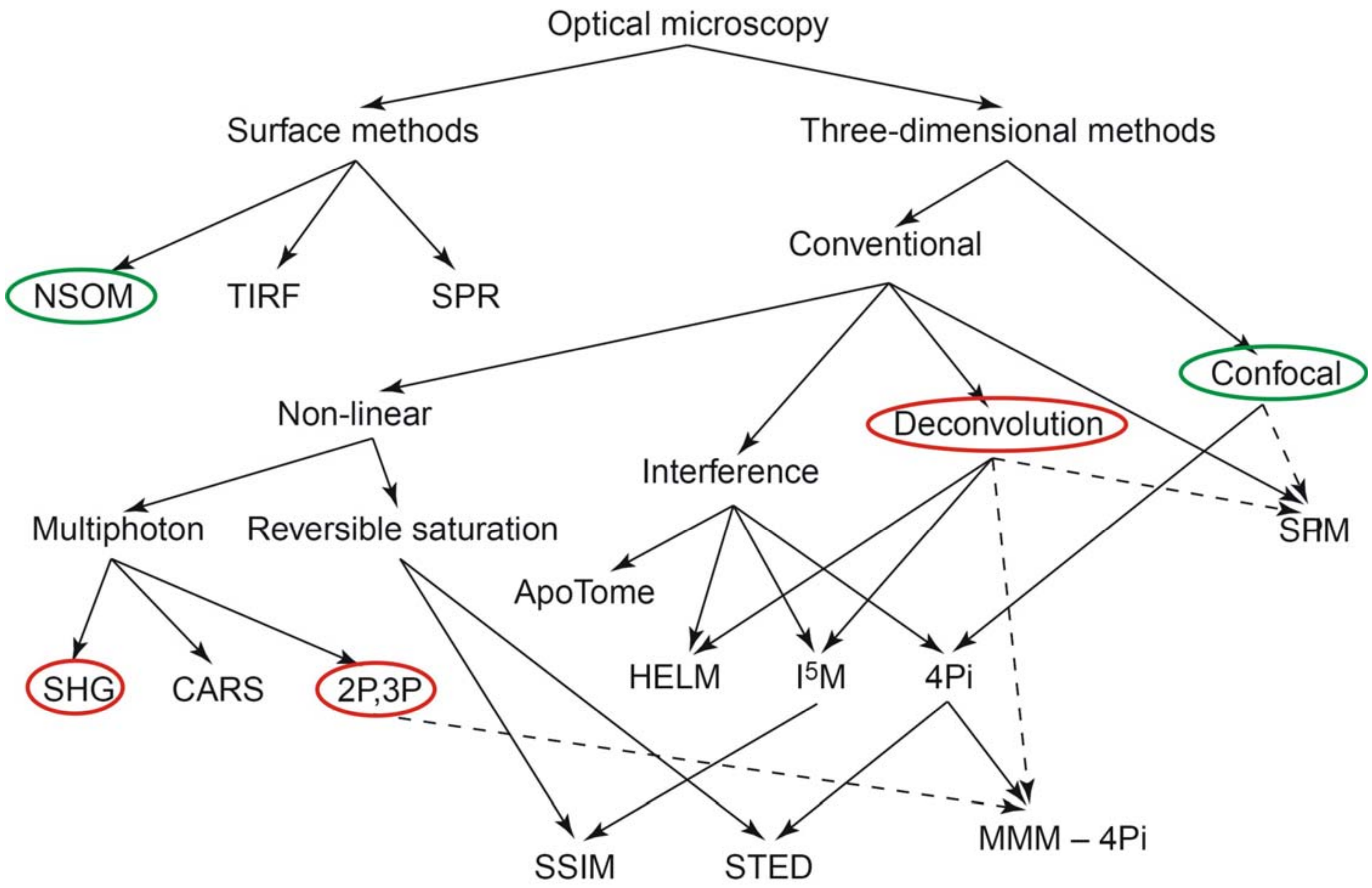
- **Scattering-type SNOM**
  - Dr. Jen-You Chu (朱仁佑博士) (ITRI)
  - Dr. Jyi-Tyan Yeh (葉吉田博士) (ITRI)
  - Mr. Ming-Wei Lin (林明為) (ITRI)
  - Mr. Tien-Jen Wang (汪天仁) (ITRI)
  - Mr. You-Chia Chang (張祐嘉) (ITRI)

- **SERS-active substrates**
  - Dr. Yuh-Lin Wang (王玉麟博士) (IAMS)
  - Dr. Chih-Yi Liu (劉志毅博士) (IAMS)
  - Mr. Huai-Hsien Wang (王懷賢) (IAMS)
  - Dr. M. M. Dvoynenko (IAMS)
  - Prof. Chi-Hung Lin (林奇宏) (NYMU)
  - Dr. Ting-Ting Liu (劉婷婷博士) (NYMU)

Optical microscopy

Dr. Juen-Kai Wang, CCMS, NTU

- Rayleigh criteria:
  - $d_{x,y} = 0.61\lambda/\mathrm{NA}$
  - $d_z = 2\lambda/\mathrm{NA}^2$

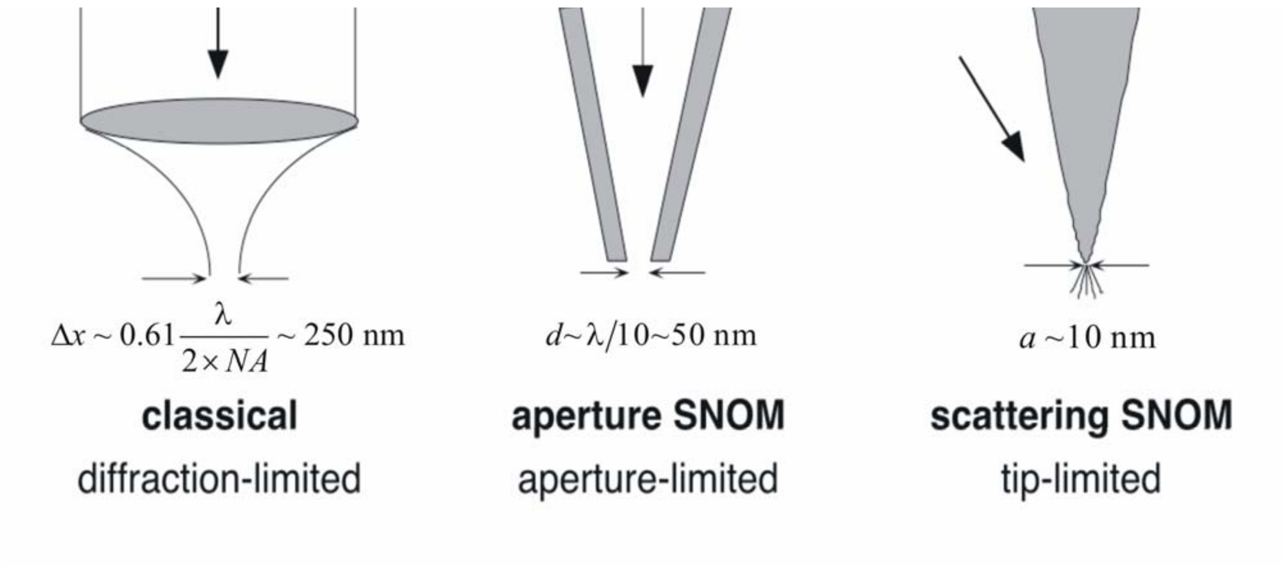


Y. Garini et al., Curr. Opin. Biotech. ***16****, 1 (2005).*

Comparison of optical microscopes

Dr. Juen-Kai Wang, CCMS, NTU

- Performing optical spectroscopy in nanometer scales is one of the critical steps in the development of nanoscience and nanotechnology.
- Two key issues in characterization in nanometer scales:
  - Nanometer-scaled resolution
  - Signal amplification
- New physics involving light-matter interaction in nanometer scales need to be developed.



Lycurgus Cup in Roman times

Dr. Juen-Kai Wang, CCMS, NTU

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

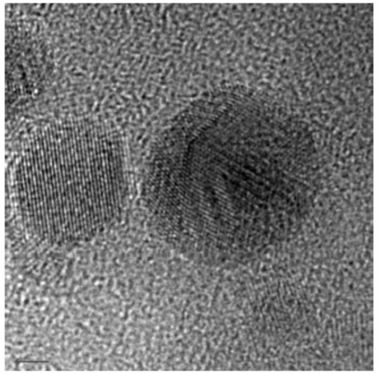
The Lycurgus Cup, Roman (4th century AD), British Museum
*F. E. Wagner et al., Nature **407**, 691 (2000).*

Stained glasses

Dr. Juen-Kai Wang, CCMS, NTU

Reynard the Fox
early 15-th century, *Holy Cross Church*

The Ascent of Elijah
c.1863, *Trinity Methodist Church*

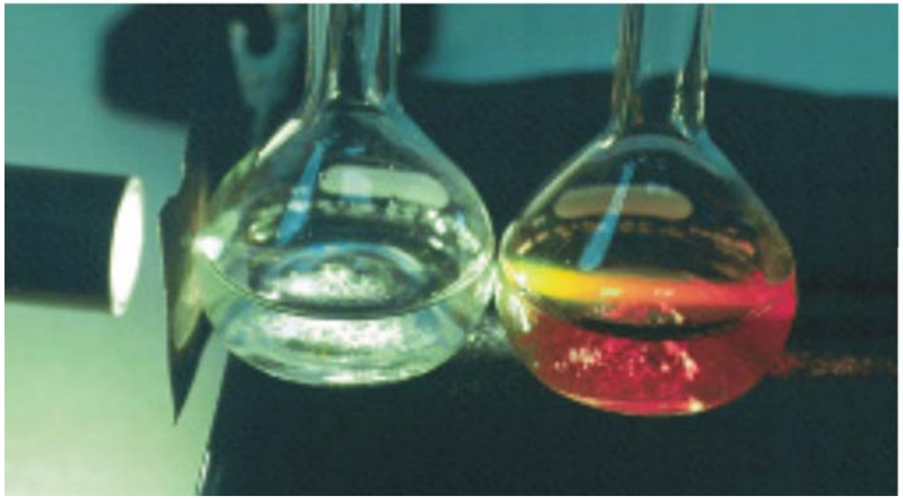


The Stained Glass Museum *(www.stainedglassmuseum.org)*

Faraday's works on Au nanoparticles

Dr. Juen-Kai Wang, CCMS, NTU

Faraday-Tyndall Effect



A solution of gold chloride **Gold colloids**

Faraday's slides
Prepared in 1856, in conjunction with Faraday's research on finely-divided gold
(The Royal Institution of Great Britain)

*M. Faraday, Philos. Trans. R. Soc. London **147**, 145 (1857).*
R. D. Tweney, Department of Psychology, Bowling Green State University, USA (personal.bgsu.edu/_tweney).

Scattering by a metal sphere

Dr. Juen-Kai Wang, CCMS, NTU

Induced dipole by the applied field

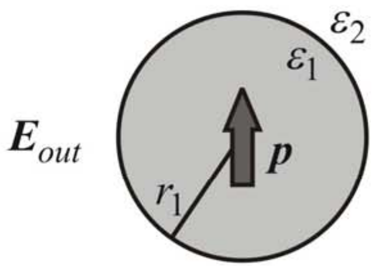
$$\boldsymbol{E}_{out} = E_0\boldsymbol{e}_z + \frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+2\varepsilon_2}\frac{r_1^3}{r^3}E_0\left(2\cos\theta\boldsymbol{e}_r+\sin\theta\boldsymbol{e}_\theta\right)$$

$$\Downarrow$$

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

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)

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

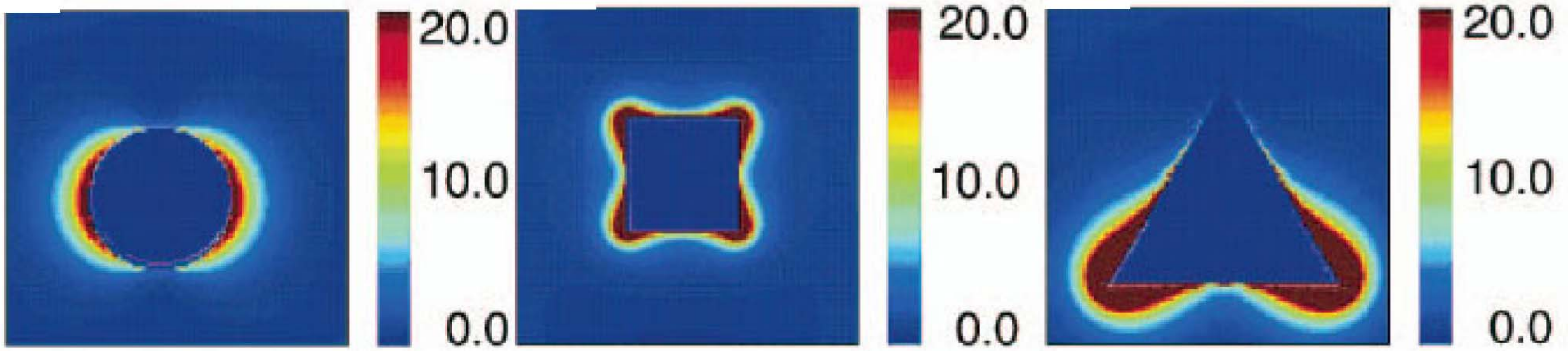
$\boldsymbol{E}$: the near-field electric field by $\boldsymbol{p}(t)$

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

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

Enhanced field around nanoparticles

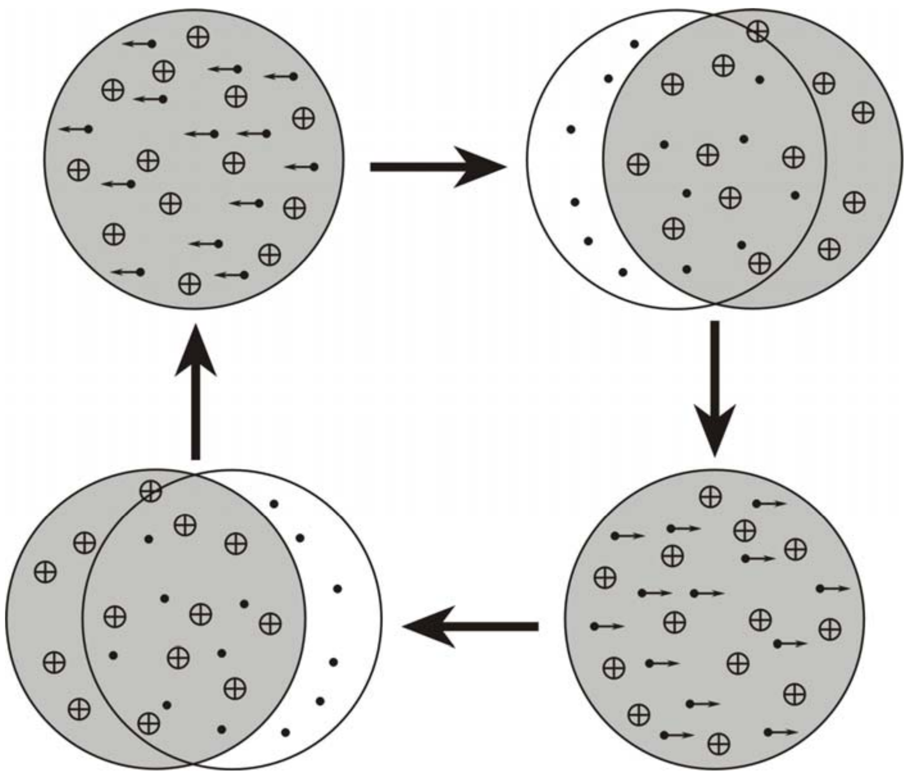
Dr. Juen-Kai Wang, CCMS, NTU



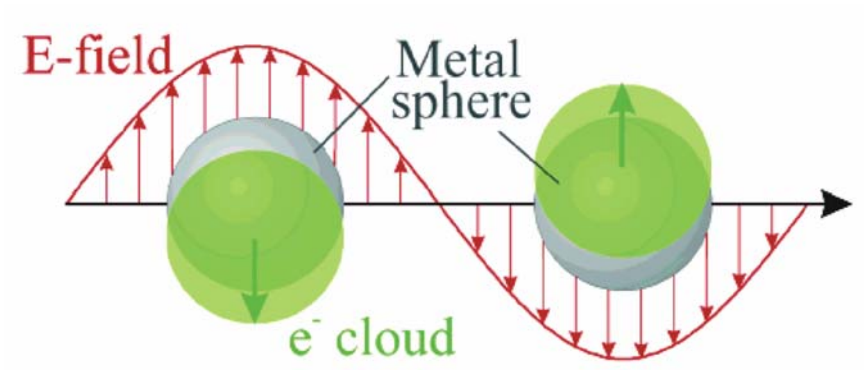
S. A. Kelele et al., J. Nanophoton. ***1****, 012501 (2007).*

Electron collective motion in metal clusters

Dr. Juen-Kai Wang, CCMS, NTU



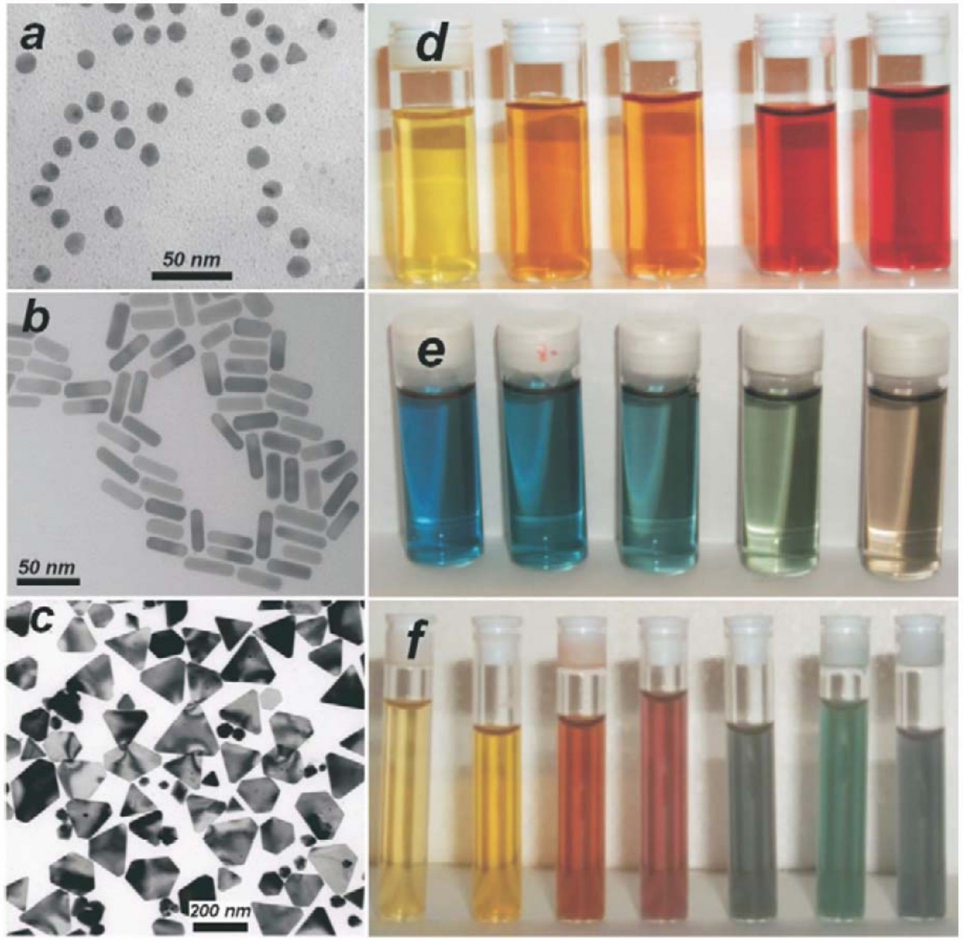
Coherent oscillatory motion



Resonant excitation

Colors in nanometals

Dr. Juen-Kai Wang, CCMS, NTU



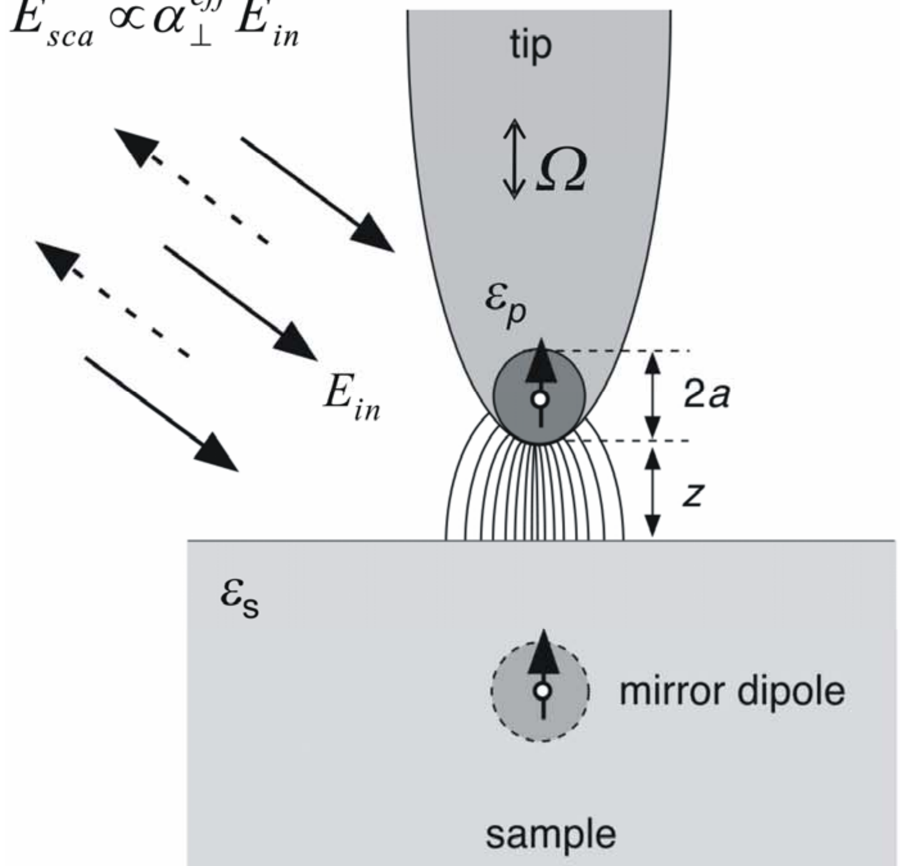
L. M. Liz-Marzan, Materials Today ***26****, February 2004.*

Model of tip-sample near-field interaction

Dr. Juen-Kai Wang, CCMS, NTU

Far-field scattering:

$$E_{sca} \propto \alpha_{\perp}^{eff} E_{in}$$



Polarizability of the tip: $\alpha = 4\pi a^3 \dfrac{(\varepsilon_p - 1)}{(\varepsilon_p + 2)}$

Effective polarizability of tip and sample:

$$\alpha_{\perp}^{eff} = \frac{\alpha(1+\beta)}{1 - \dfrac{\alpha\beta}{16\pi(z+a)^3}}$$

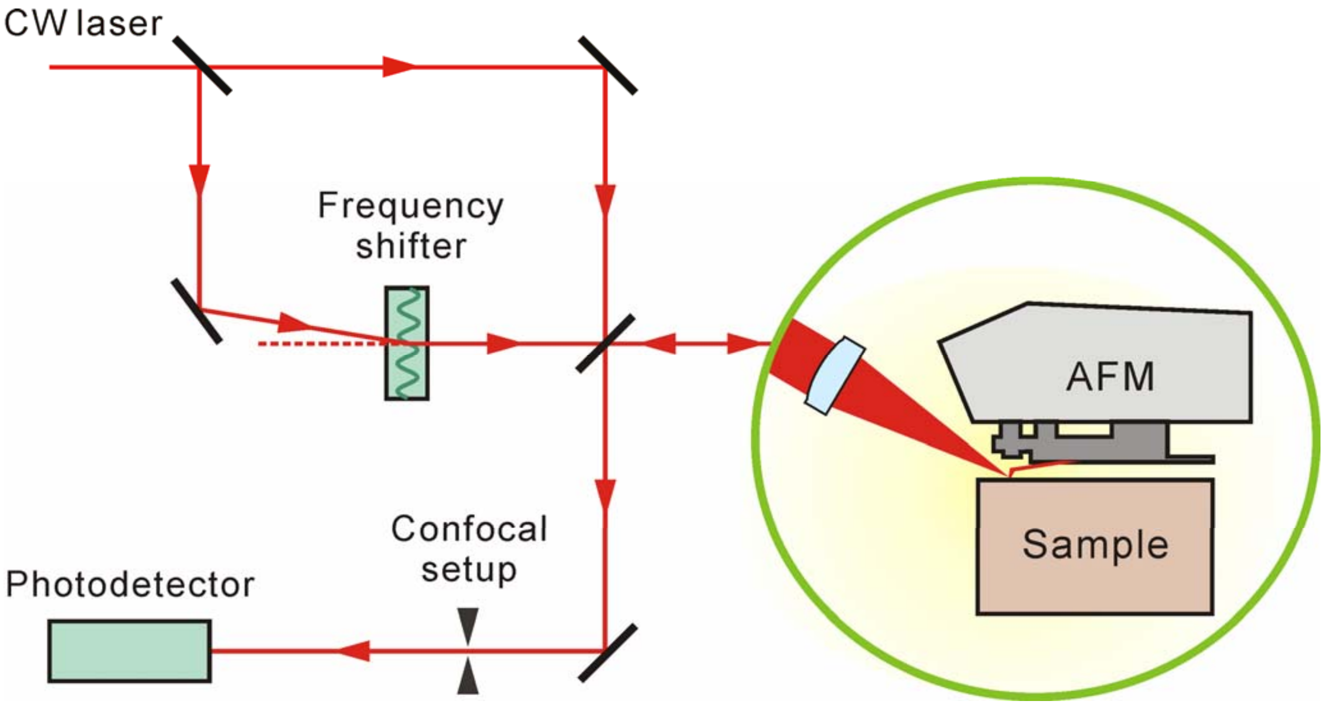
$$\beta = \frac{1-\varepsilon_s}{1+\varepsilon_s}$$

Nonlinear term

Reproduced from Dr. Keilmann

Schematic layout of *s*-SNOM

Dr. Juen-Kai Wang, CCMS, NTU



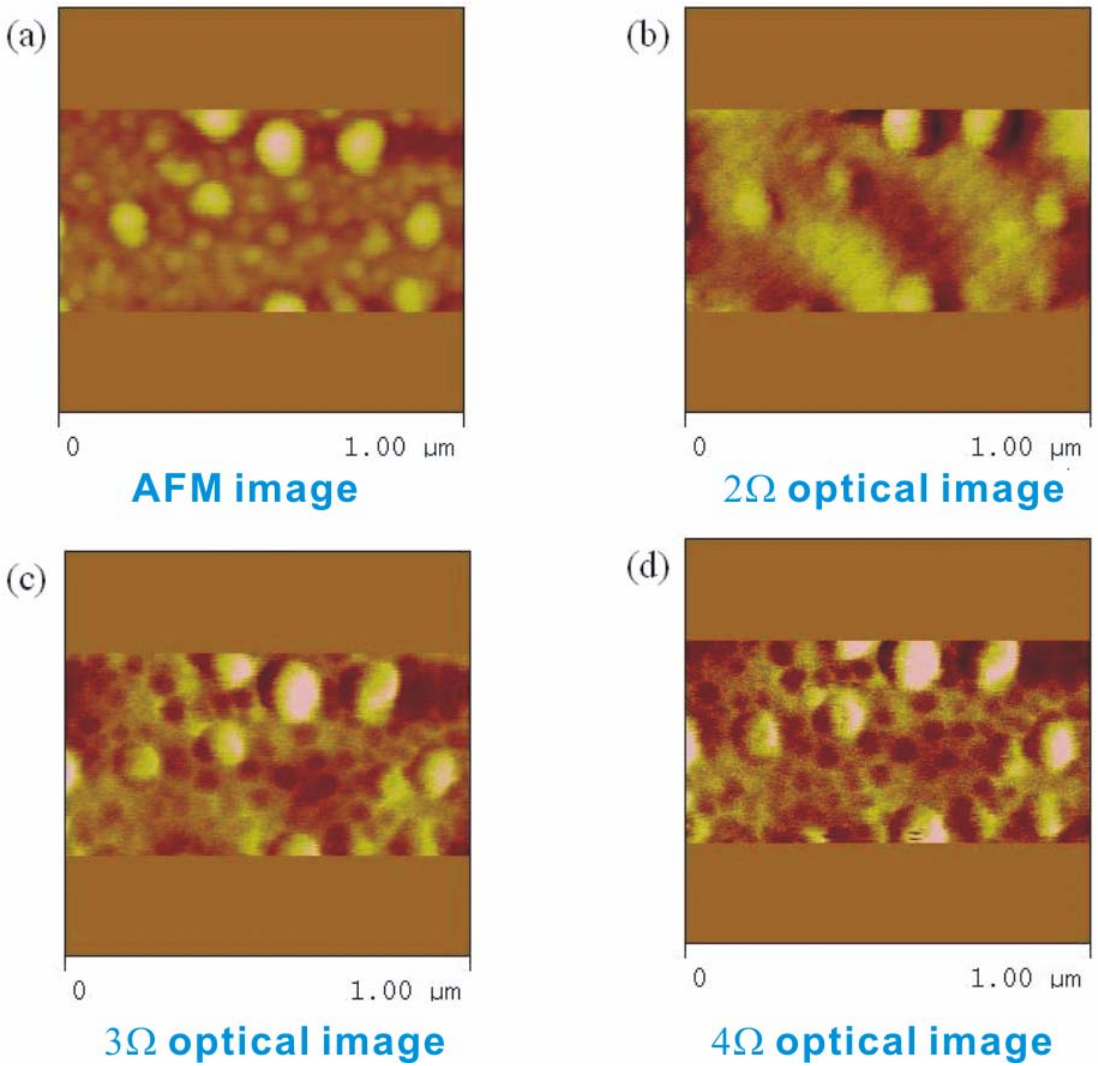
$$S_{\text{det}} \propto I_{sca} + I_{ref} + 2\sqrt{I_{sca} \times I_{ref}}\cos\left[\left(\Delta + n\Omega\right)t + \varphi\right], \quad I_{sca} \sim 10^{-6} I_{ref}$$

- The *s*-SNOM achieves ~5 nm resolution, suitable for the near-field studies of plasmonics.
- Performing *s*-SNOM with different wavelengths is important, because plasmonic properties are wavelength dependent in nature.

R. Hillenbrand and F. Keilmann, Phys. Rev. Lett. ***85****, 3029 (2000).*

Near-field optical images

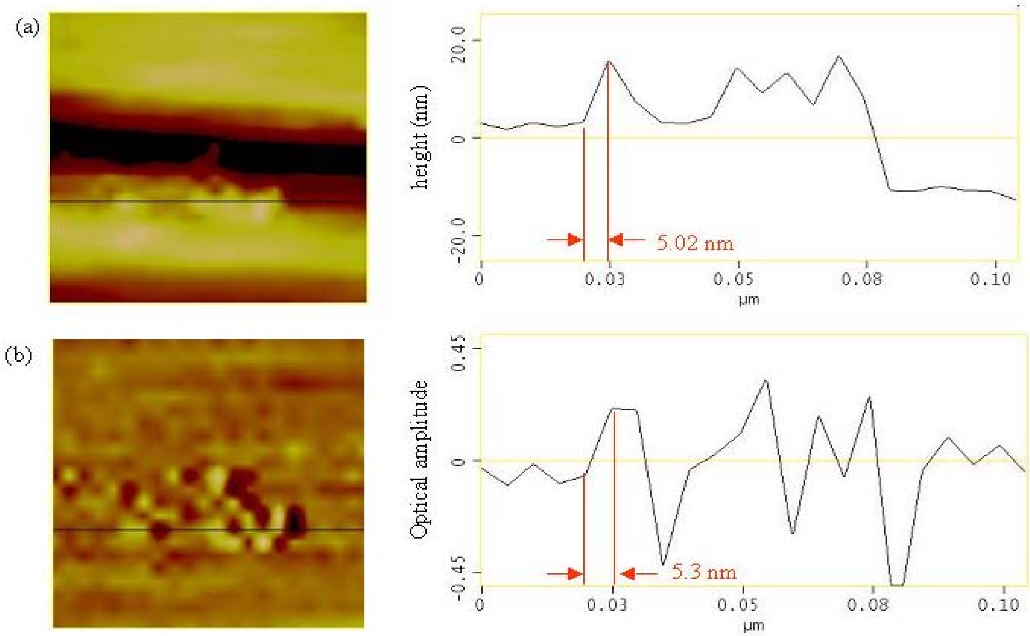
Dr. Juen-Kai Wang, CCMS, NTU



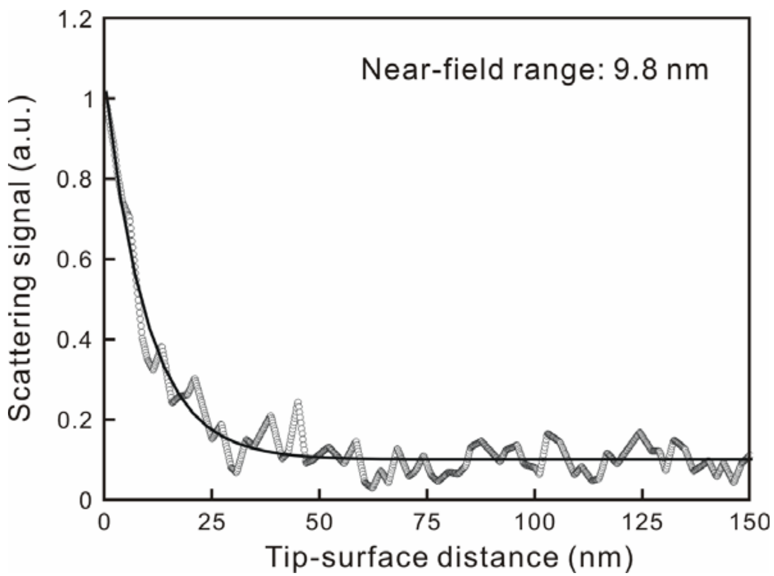
Spatial resolution

Dr. Juen-Kai Wang, CCMS, NTU

AFM image



***s*-SNOM image**



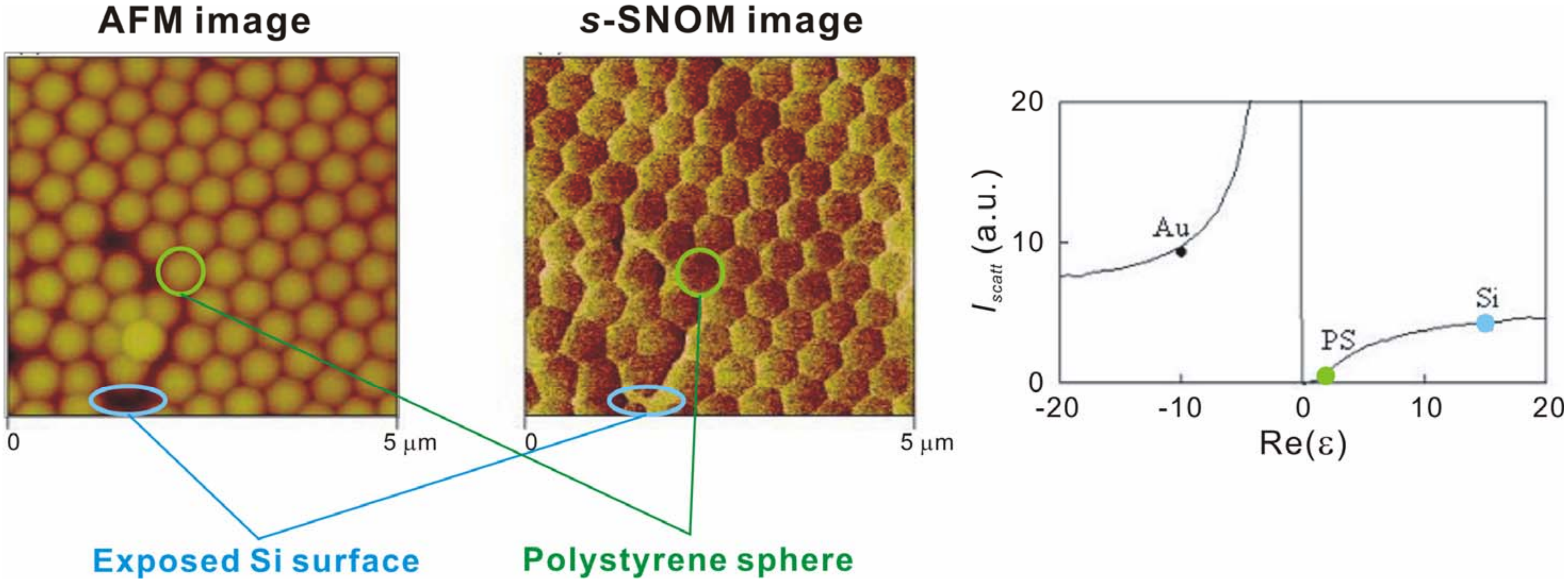
Lateral resolution: 5 nm

Vertical resolution: 10 nm

Material contrast

Dr. Juen-Kai Wang, CCMS, NTU

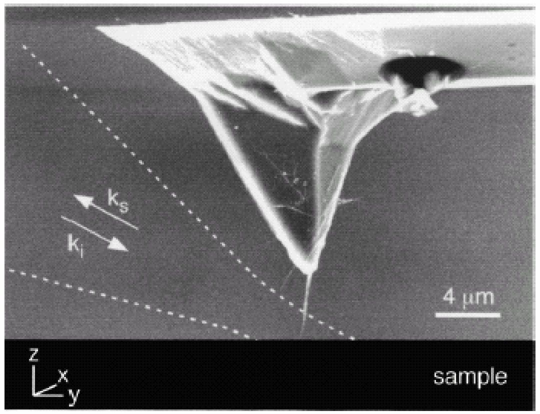
Polystyrene sphere on Si(111)

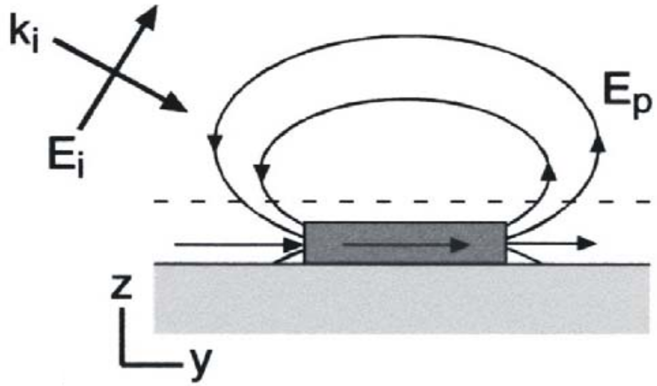


- **Detection limit of Δ*n*: 0.02**

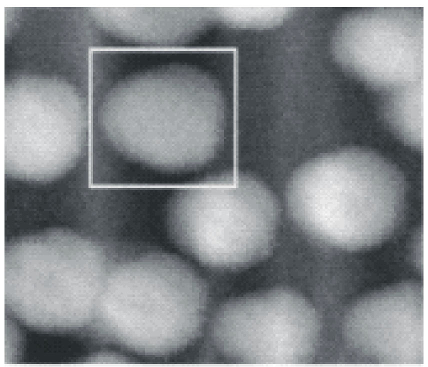
Scattering-SNOM with single CNT

Dr. Juen-Kai Wang, CCMS, NTU

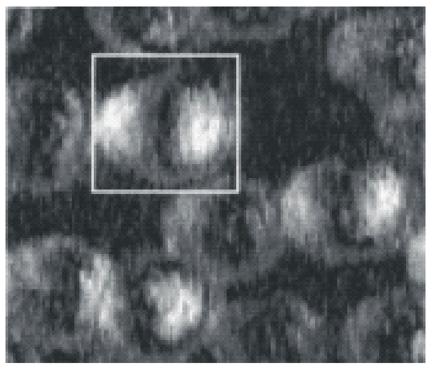




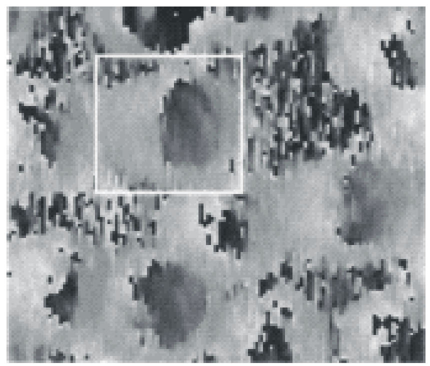
AFM image



Amplitude image



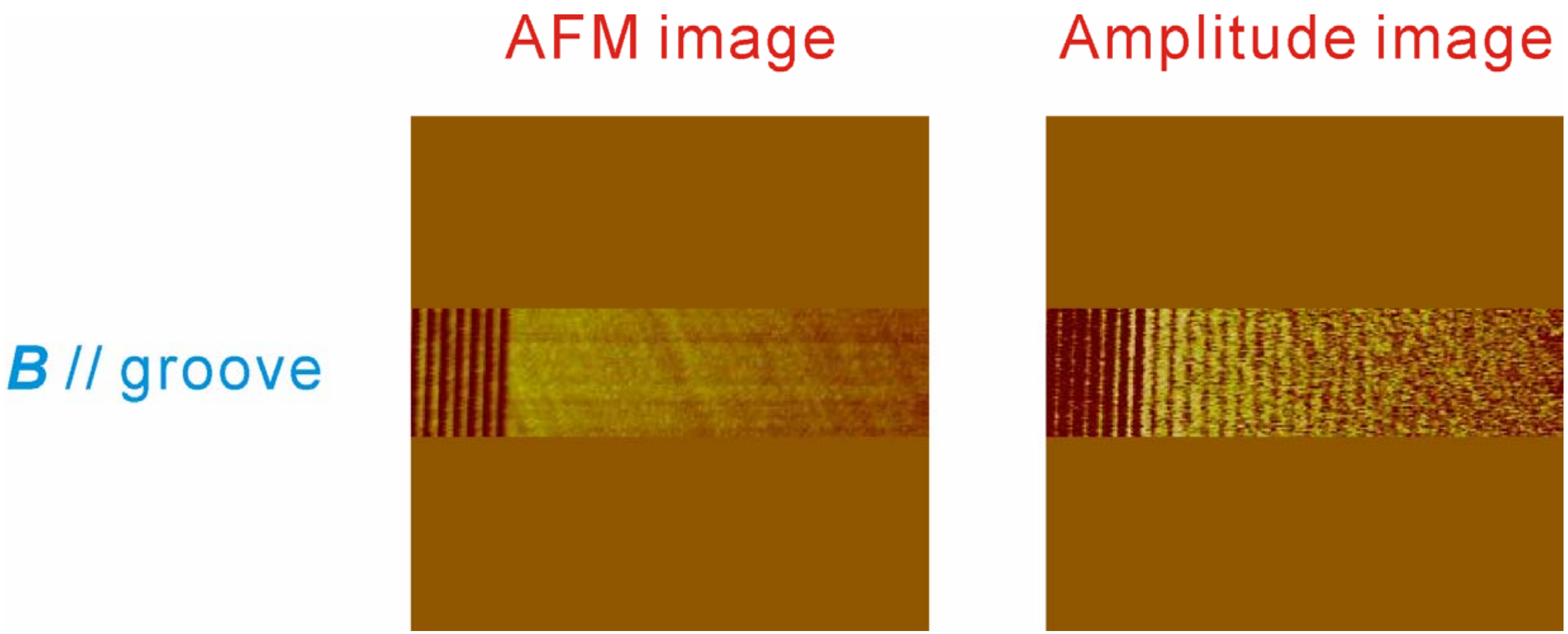
Phase image



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

Near field imaging of a linear grating

Dr. Juen-Kai Wang, CCMS, NTU

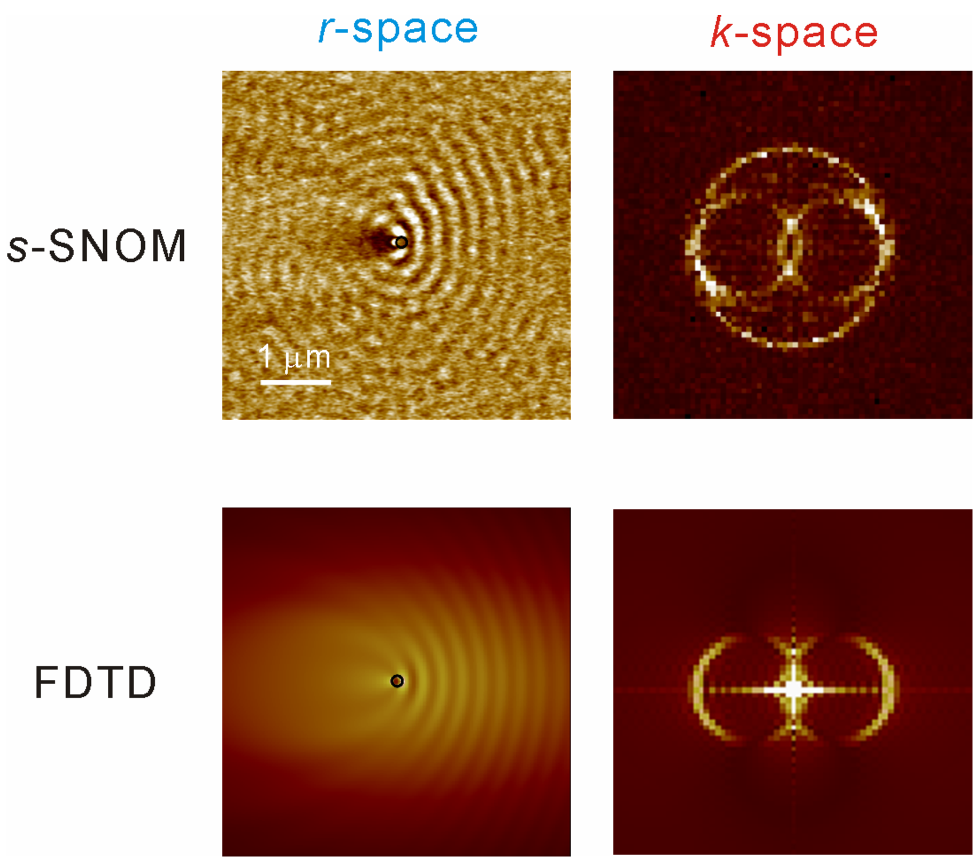


- TM-mode excitation (***B*** // groove) produces interference pattern outside the linear grating, suggesting the generation of surface plasmon wave.
- TE-mode excitation (***B*** ⊥ groove) gives no interference pattern.

k-space analysis of single nanohole image-1

Dr. Juen-Kai Wang, CCMS, NTU

200 nm Ag film
Hole diameter: 150 nm
λ_{ex} = 532 nm

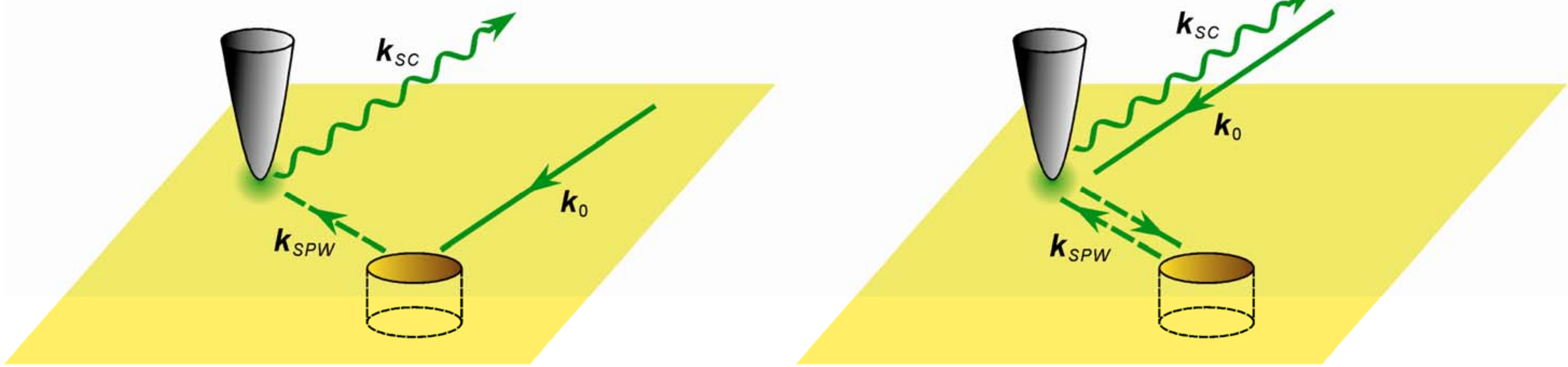


- Through Fourier transform, the obtained *k*-space image exhibits one large circle and two center-shifted small circles and does not agree with the one obtained with FDTD method.

Y.-C. Chang et al., Opt. Exp. 16, 740 (2008).

Scattered field contributions from a single nanohole

Dr. Juen-Kai Wang, CCMS, NTU



Nanohole-induced surface plasmon wave

Tip-induced surface plasmon wave

$$E_{hole-SPW} = A_{hole-SPW}(\boldsymbol{r})\exp\left[i\left(-k_0 \sin\theta \boldsymbol{i}\cdot\boldsymbol{r} + k_{SPW}\cdot r + \phi\right)\right]$$

$$E_{tip-SPW} = A_{tip-SPW}(\boldsymbol{r})\exp\left[i\left(2k_{SPW}\cdot r + \phi'\right)\right]$$

$$k_{SPW} = k_0\sqrt{\varepsilon_{air}\varepsilon_{Ag}\Big/\left(\varepsilon_{air}+\varepsilon_{Ag}\right)}$$

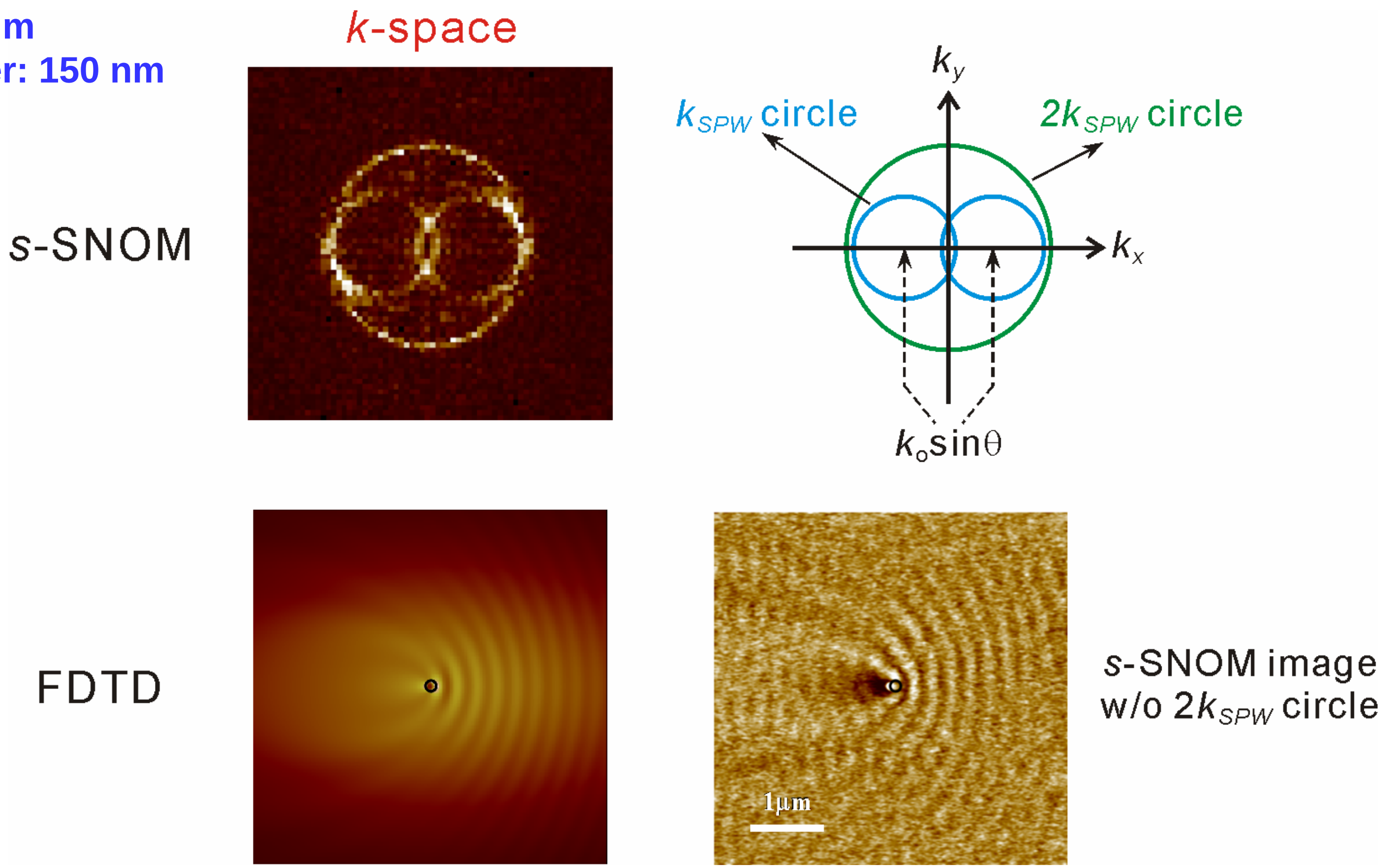
- Nanohole-induced and tip-induced surface plasmon waves
- Both waves contribute to the detected scattering radiation of *s*-SNOM.

Y.-C. Chang et al., Opt. Exp. 16, 740 (2008).

k-space analysis of single nanohole image-2

Dr. Juen-Kai Wang, CCMS, NTU

200 nm Ag film
Hole diameter: 150 nm
λ_{ex} = 532 nm

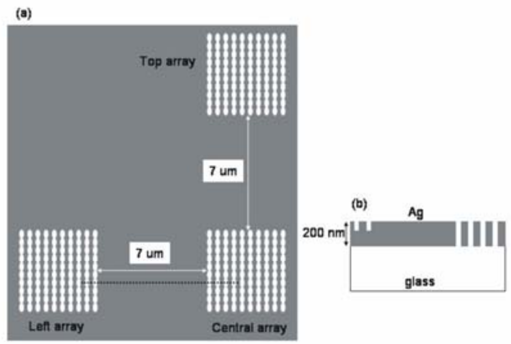


- The s-SNOM image without the $2k_{SPW}$ circle matches with the image calculated without the tip.

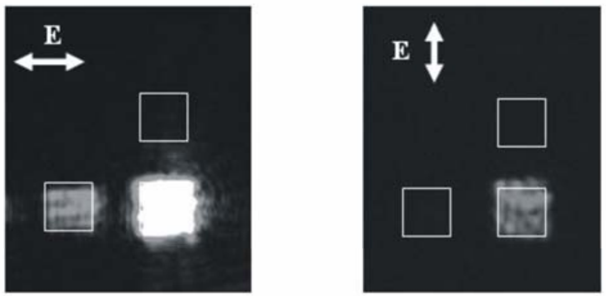
Y.-C. Chang et al., Opt. Exp. 16, 740 (2008).

Near-field observation of ellipical hole arrays

Dr. Juen-Kai Wang, CCMS, NTU

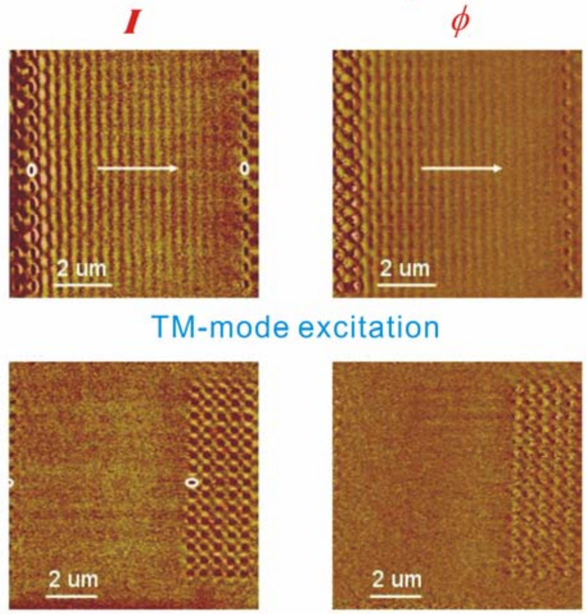


Far-field transmission images



TM-mode excitation   TE-mode excitation

Near-field images



TM-mode excitation

TE-mode excitation

- A TM-mode excitation gives an enhanced transmission image and also produces an emission image at an adjacent pattern.
- Clear surface plasmon only exits in TM-mode excitation and prominent dipole field oscillation emerges at each elliptical hole. This confirms that the surface plasmon is the superposition of local plasmon of holes.

J.-Y. Chu et al., Appl. Phys. A 89, 387 (2007).

Two-color near-field images of nanohole arrays

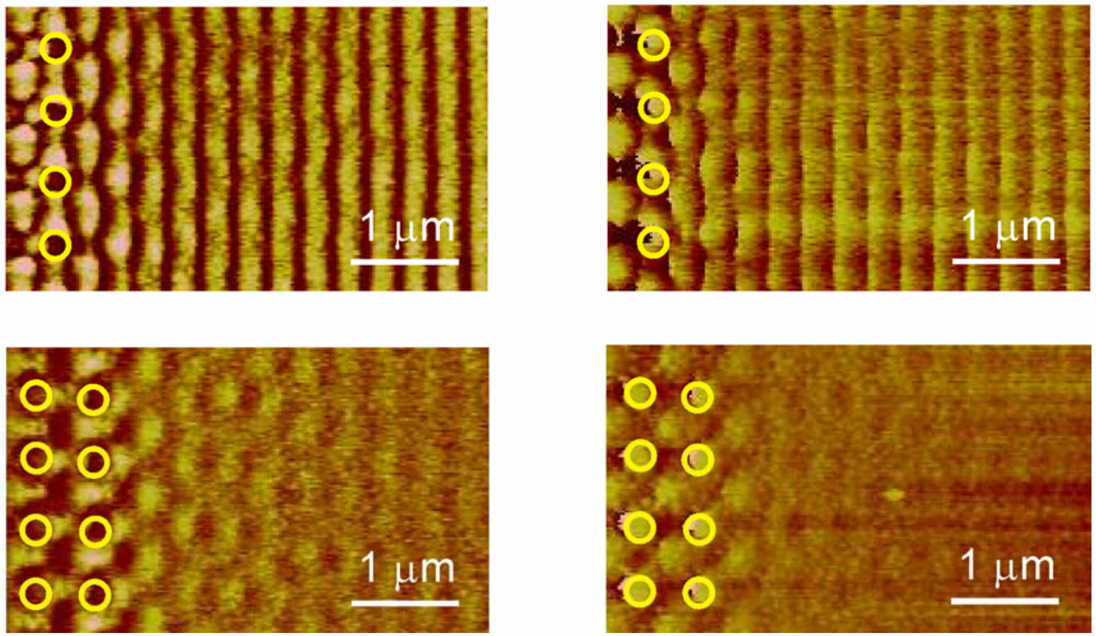
Dr. Juen-Kai Wang, CCMS, NTU

200 nm Ag film
Hole period (*d*): 535 nm
Hole diameter: 150 nm

Amplitude image | Phase image

λ_{ex} = 532 nm

λ_{ex} = 632.8 nm

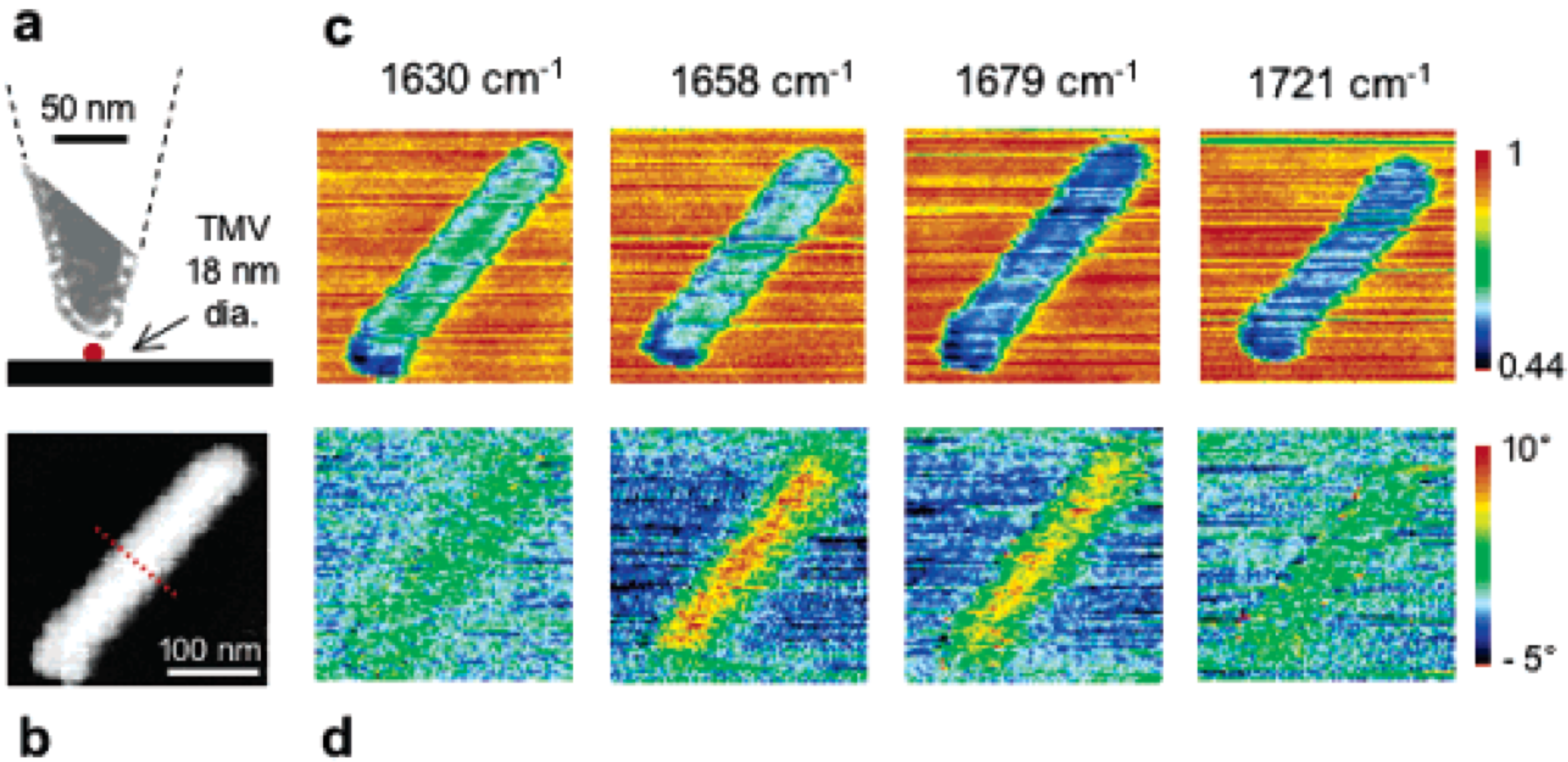


- The period of fringes (278 nm) as λ_{ex} = 532 nm is consistent with the prediction of the in-phase construction requirement of surface plasmon waves (**$k_{SPW} - k_0 \sin\theta = 2\pi n/d$, *n*: integer**).
- The period of hole array is however away from the in-phase construction condition for λ_{ex} = 632.8 nm , yielding no excitation of surface plasmon wave.

J. E. Hall et al., Opt. Exp. 15, 4098 (2007); J. Y. Chu et al., Ultramicroscopy 108, 314 (2008).

Mapping of single virus with *s*-SNOM

Dr. Juen-Kai Wang, CCMS, NTU



M. Brehm et al., Nano Lett. (in press).

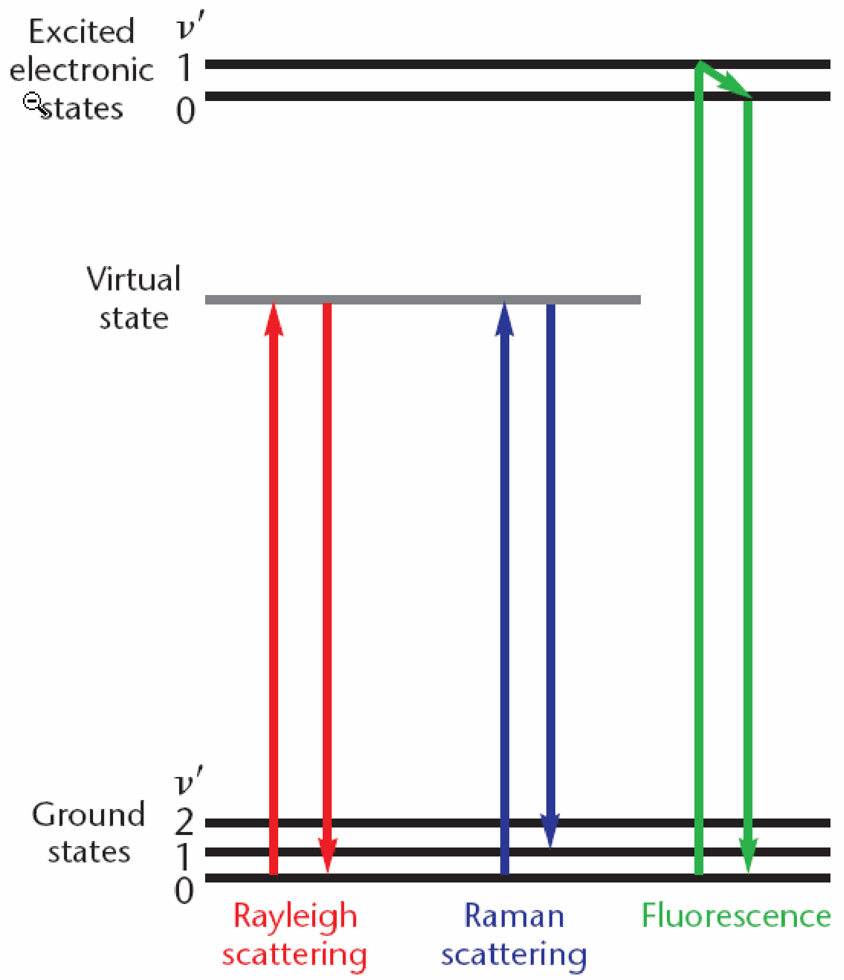
Raman, Rayleigh scattering and Flurescoence

Dr. Juen-Kai Wang, CCMS, NTU

Sir C. V. Raman

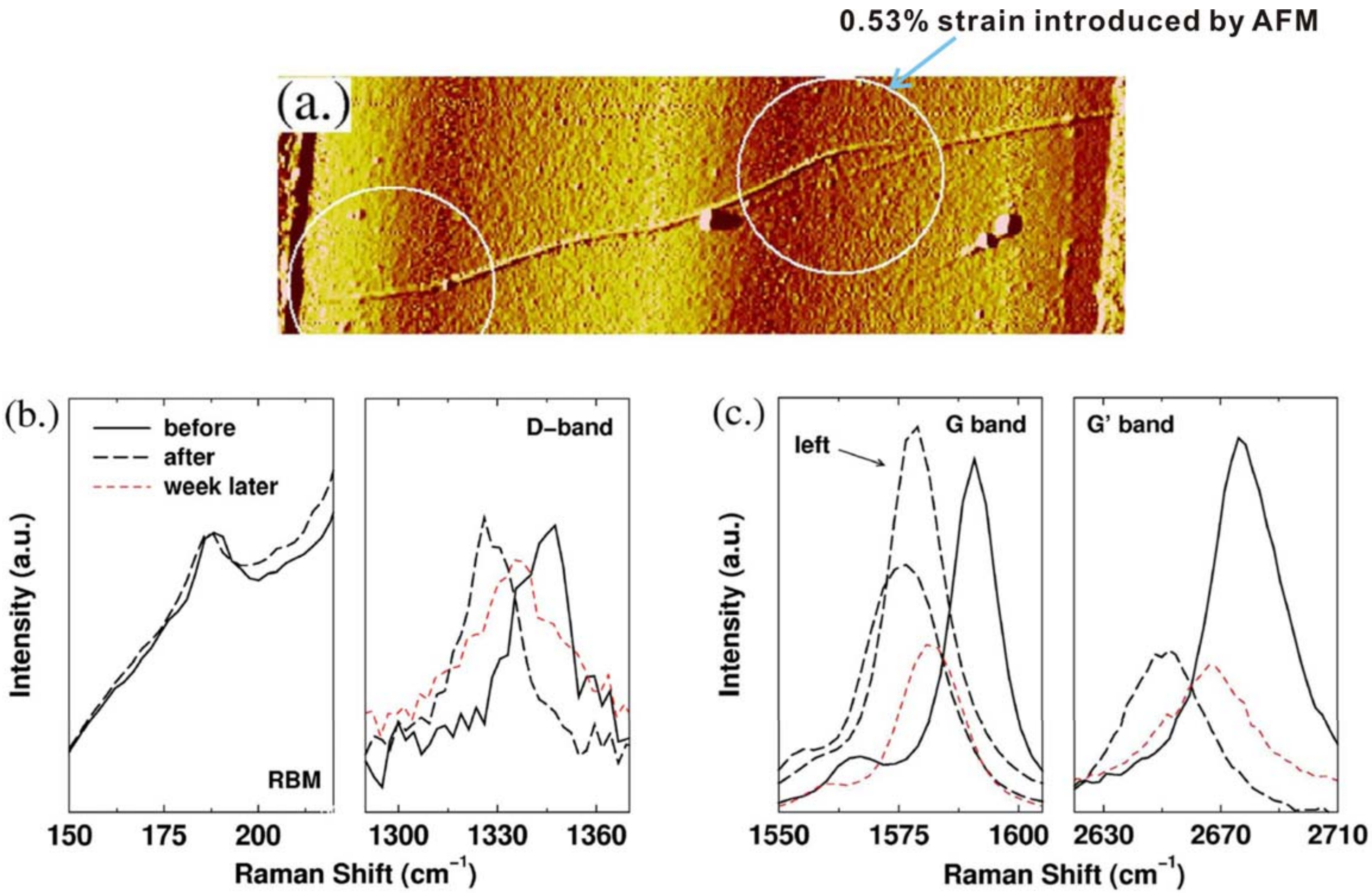
Raman's spectrograph

- Rayleight scattering is an elastic scattering process.
- Laser-induced fluorescence requires resonant absorption.
- Raman scattering is an inelastic scattering processes, providing vibrational information



Micro Raman of CNT under local strain

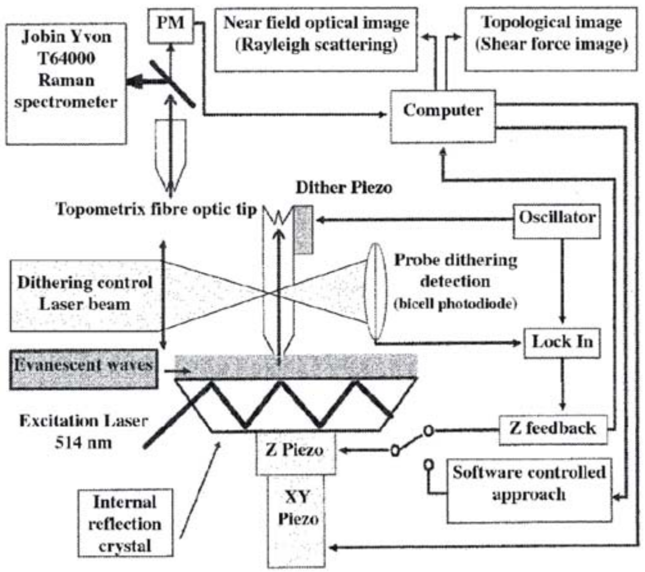
Dr. Juen-Kai Wang, CCMS, NTU

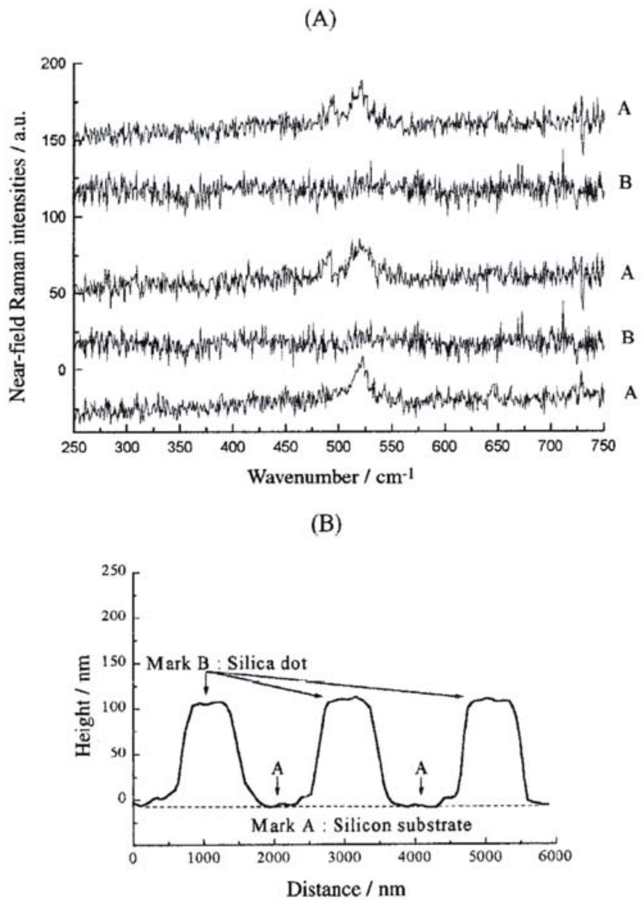


S. B. Cronion et al., Phys. Rev. Lett. 93, 167401 (2004)

Near-field Raman spectroscopy

Dr. Juen-Kai Wang, CCMS, NTU

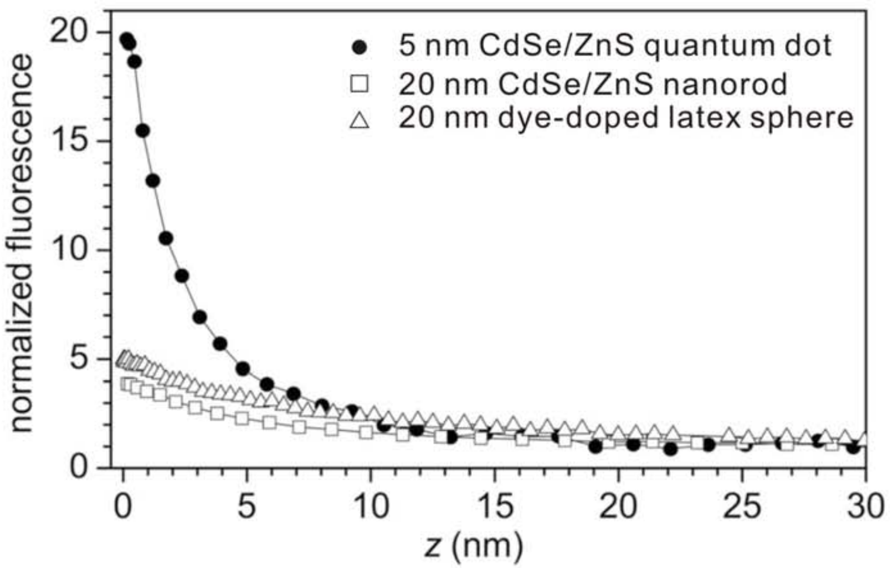




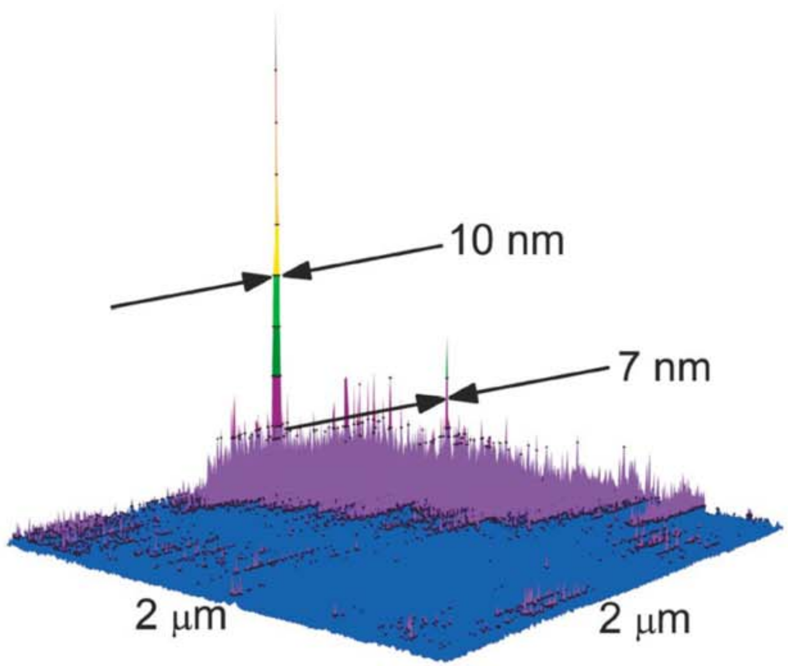
J. Grausen et al., J. Raman Spectrosc. 30, 833 (1999).

Near-field fluorescence spectroscopy

Dr. Juen-Kai Wang, CCMS, NTU



Fluorescence enhancement near a silicon tip

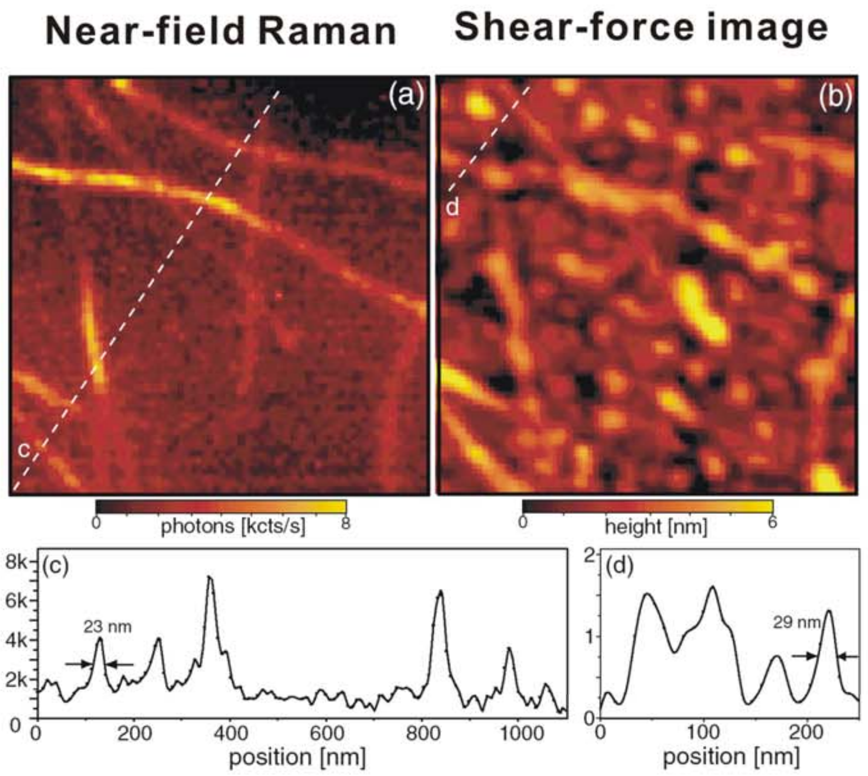


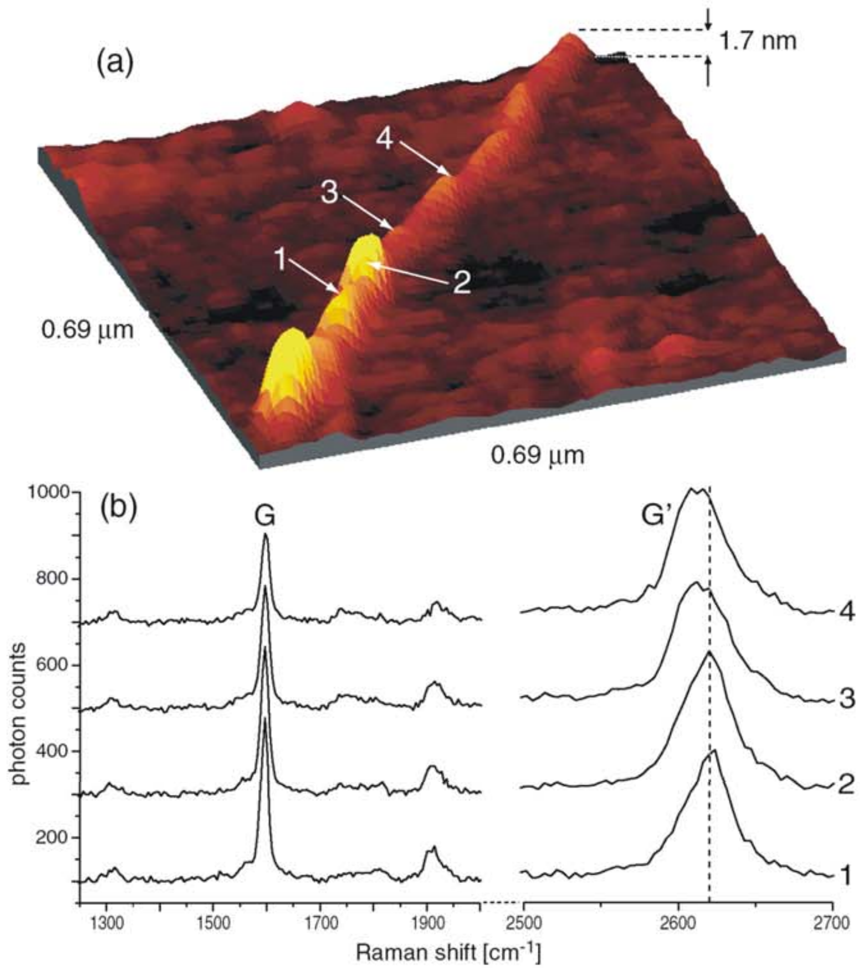
Tip-enhanced fluorescence image of quantum dots

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

Near-field Raman spectroscopy of CNT

Dr. Juen-Kai Wang, CCMS, NTU



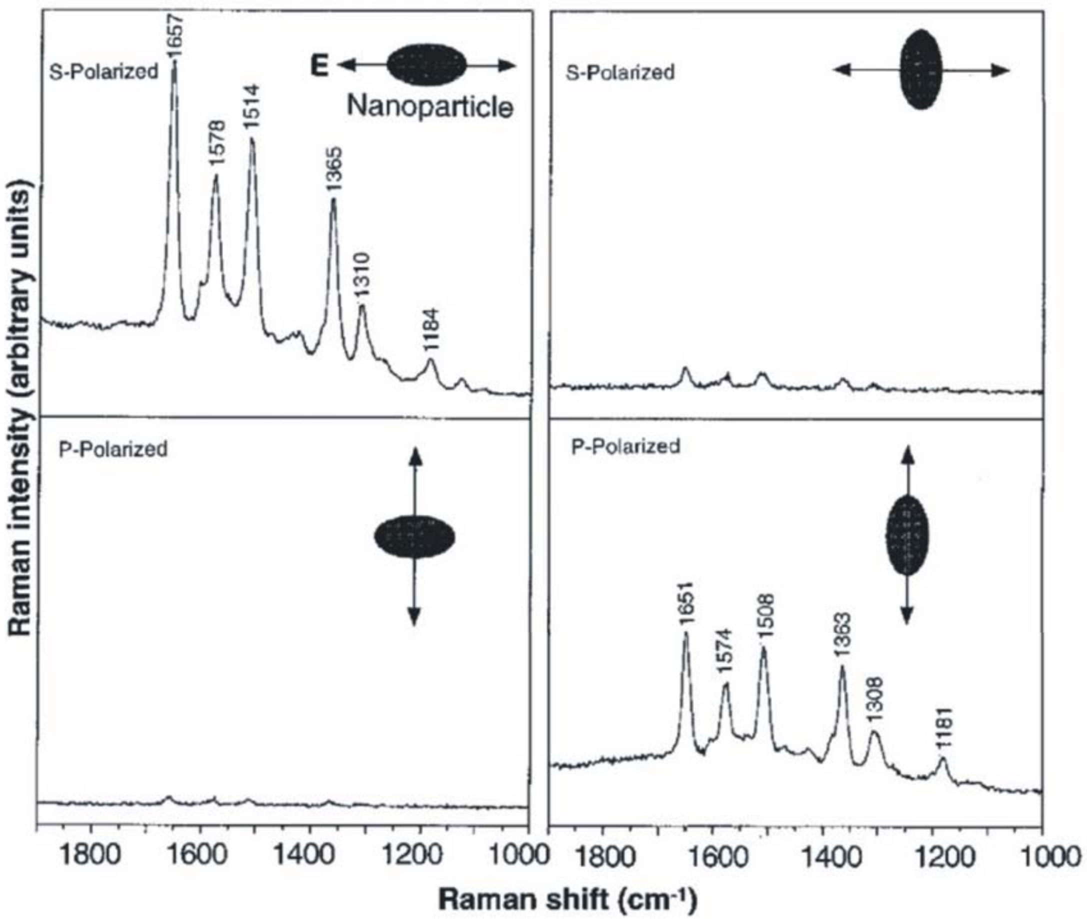


A. Hartschuh, E. J. Sánchez, X. S. Xie, and L. Novotny, Phys. Rev. Lett. 90, 095503 (2003).

Single-molecule Raman spectroscopy

Dr. Juen-Kai Wang, CCMS, NTU

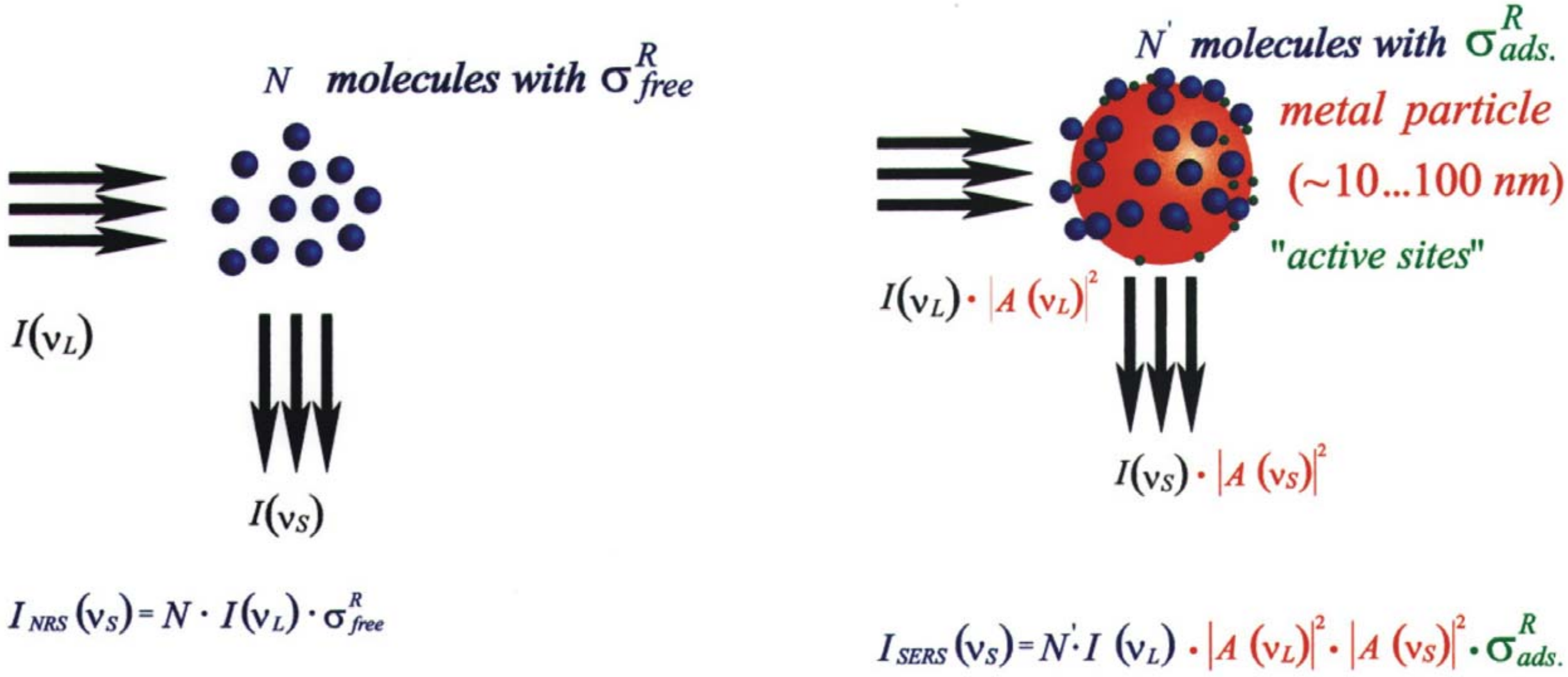
Polarized single molecule Raman spectra of dye-to-colloidal particles



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

Comparison between Raman and SERS

Dr. Juen-Kai Wang, CCMS, NTU



Unenhanced Raman scattering

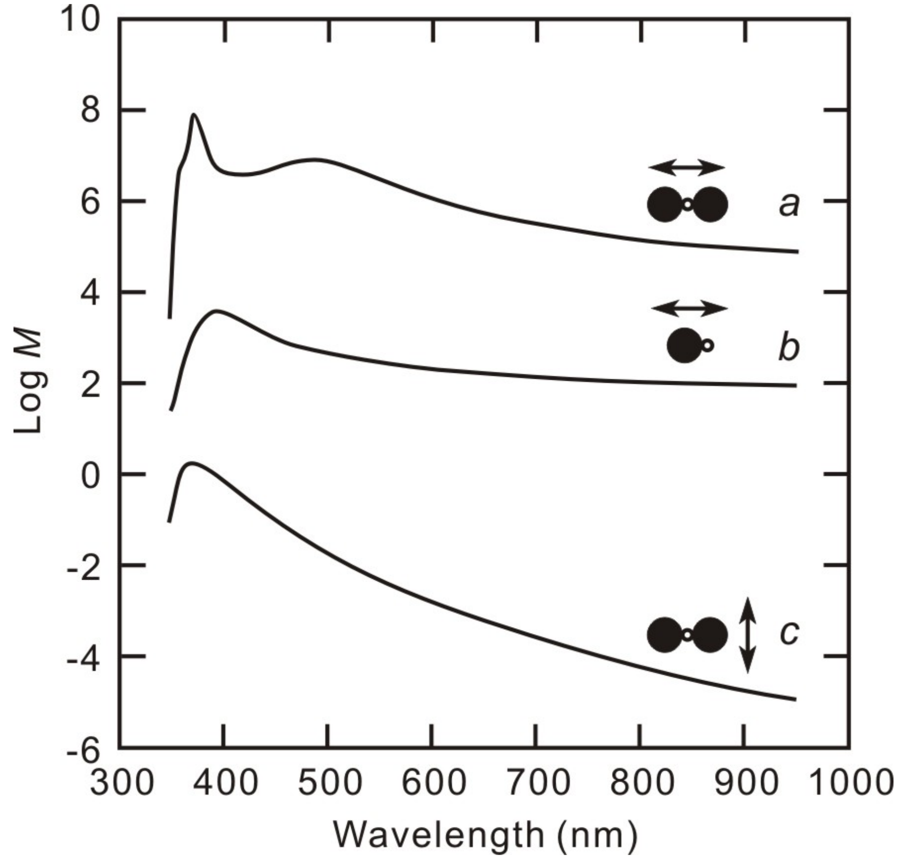
SERS

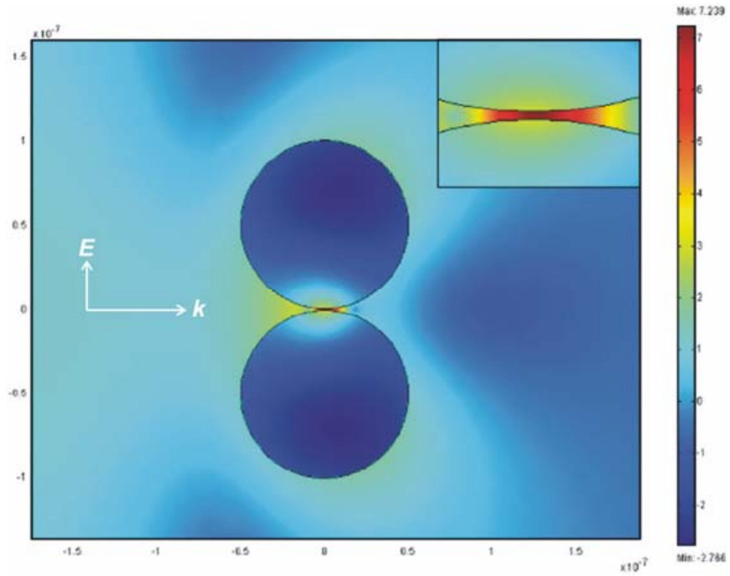
K. Kneipp et al., Bioimaging 6, 104 (1998).

Interparticle field enhancement in SERS

Dr. Juen-Kai Wang, CCMS, NTU

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

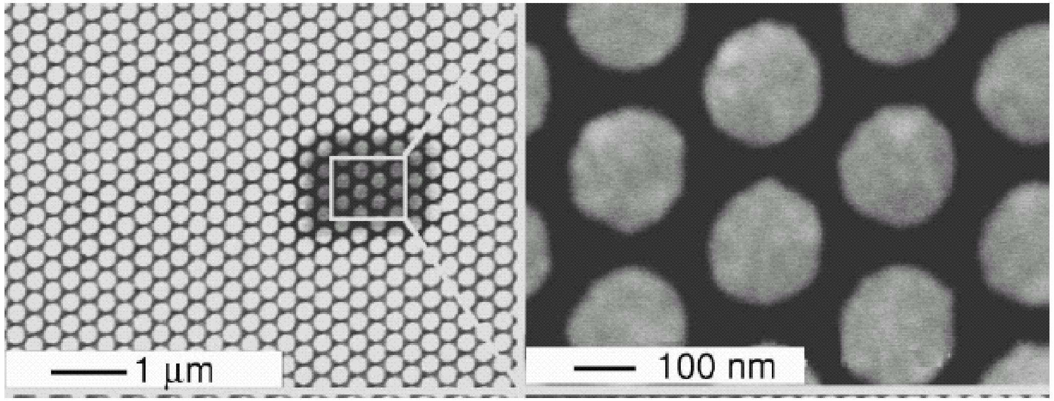


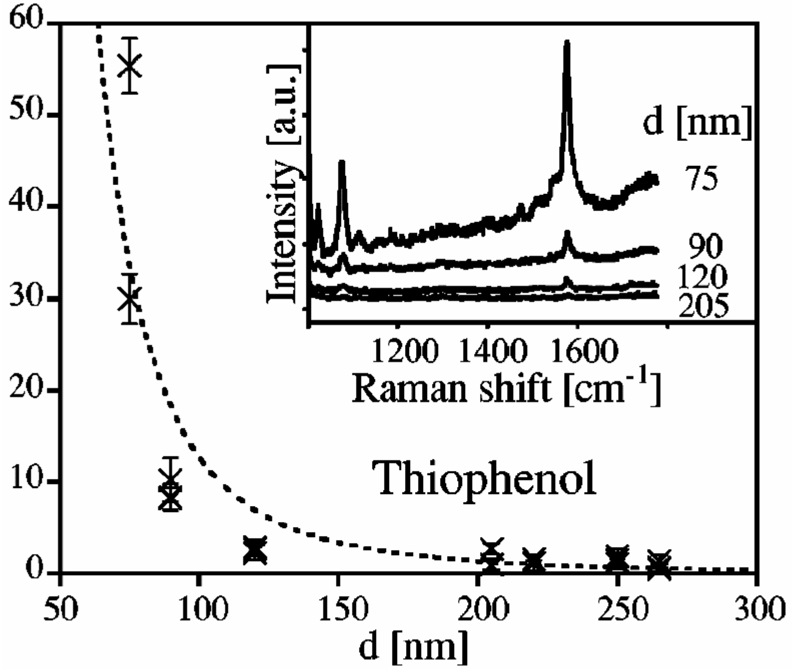


H. Xu, J. Aizpurua, M. Käll and P. Apell, Phys. Rev. B 62, 4318 (2000).

Substrates made by E-beam lithography

Dr. Juen-Kai Wang, CCMS, NTU





- Interparticle plasmon coupling was investigated, while theoretical analysis was preliminary.
- 'Hot junctions' with sub-10 nm gaps were not achieved.
- Expensive fabrication method: E-beam lithography

L. Gunnarsson, E. J. Bjerneld, H. Xu, S. Petronis, B. Kasemo, and M. Kall, Appl. Phys. Lett. 78, 802 (2001).

Sculpted SERS substrates

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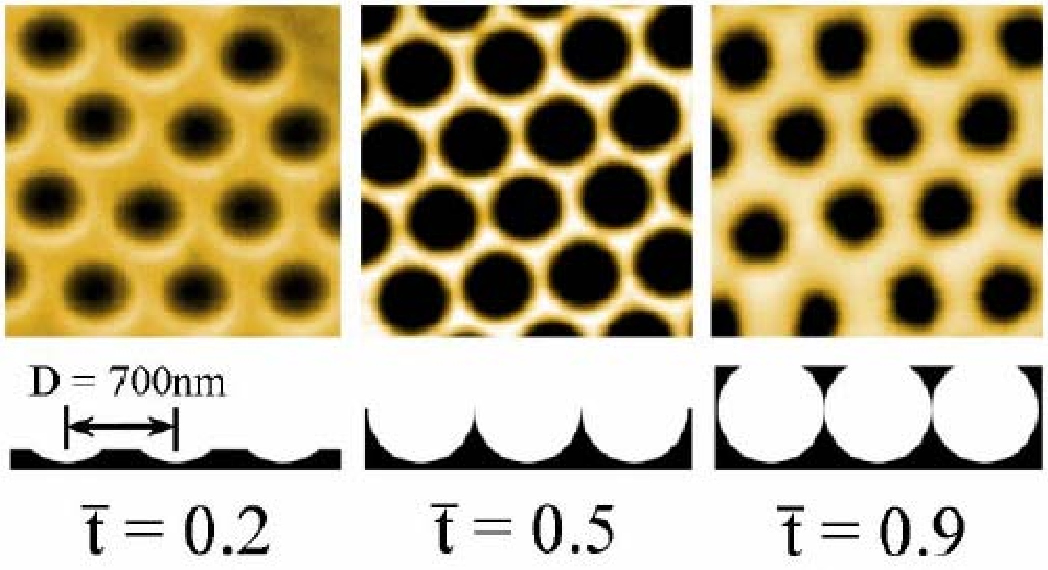
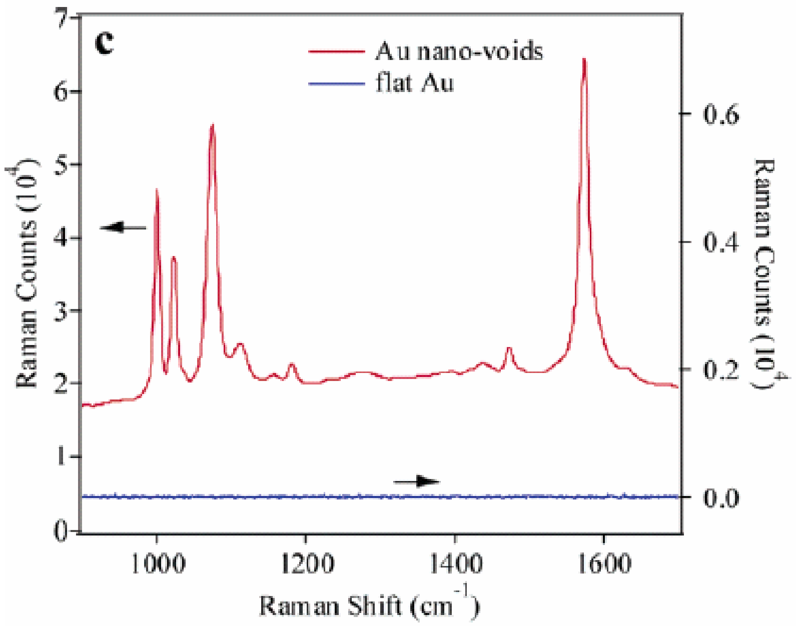


Benzenethiol



- Electrodeposition of metal on self-assembled latex nanosphere monolayer followed by dissolving nanospheres
- Uniform Raman enhancement

J. J. Baumberg et al., Nano Lett. 5, 2262 (2005).

Fabrication procedure of Ag-particle arrays

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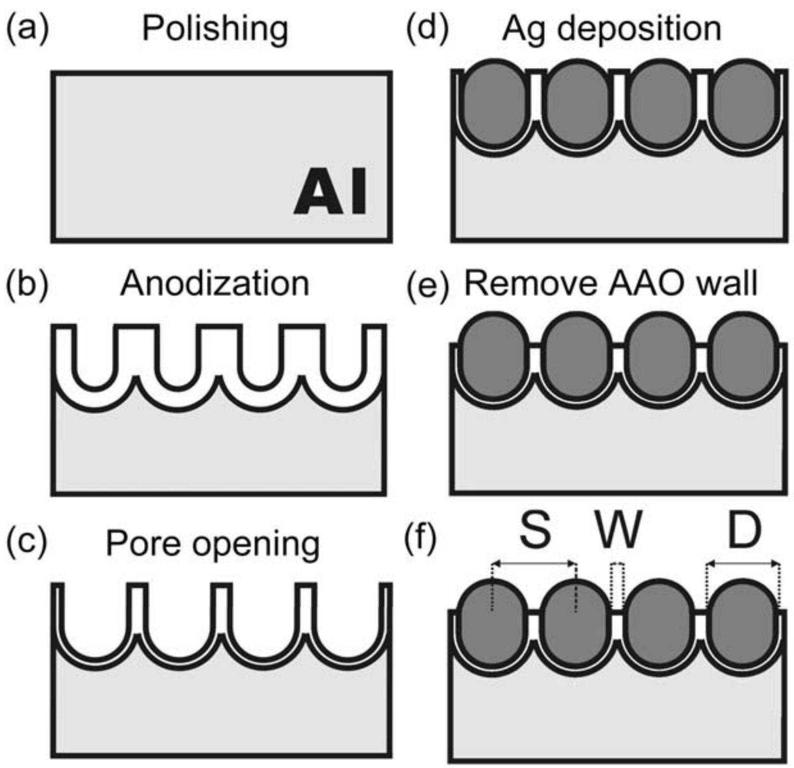
- High-purity aluminum foil is electropolished to 1-nm surface roughness.
- The foil is then anodized using different voltages to obtain arrays of self-organized nanochannels with specific interchannel spacings.
- Identical channel diameter is created by controlled etching for the substrates with different 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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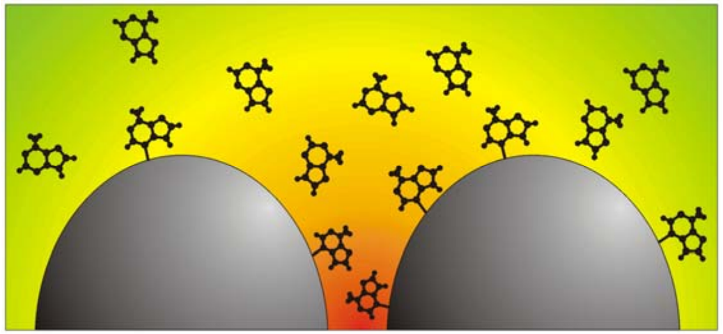
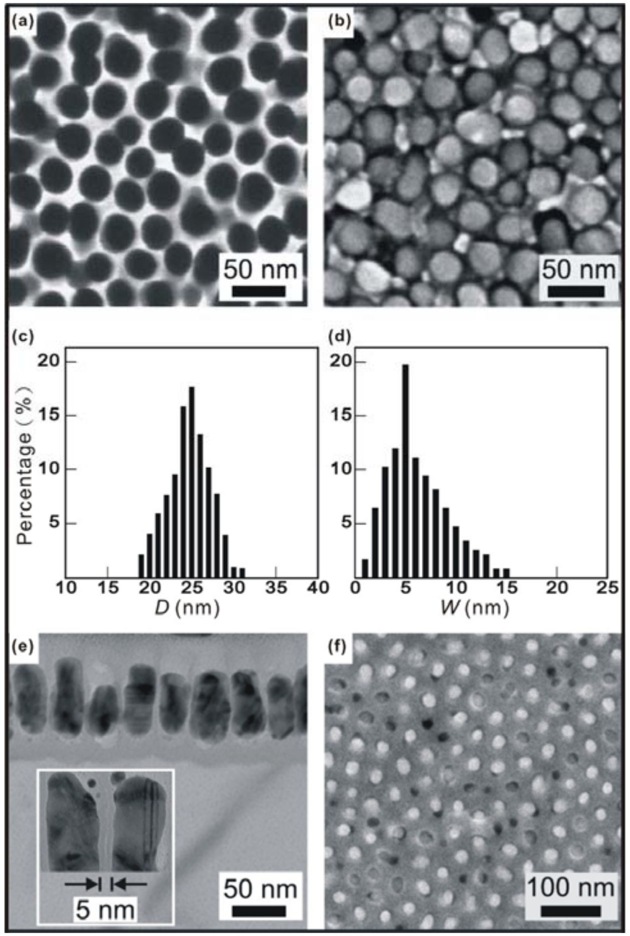
- The spread of the distribution of *D* and *W* is ~5 nm.
- The hot junctions were further examined by cross-sectional transmission electron microscopy.
- In this study, the gap is tuned from 5 to 25 nm, while maintaining the particle diameter to be 25 nm.





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).

Enhancement & dynamical range

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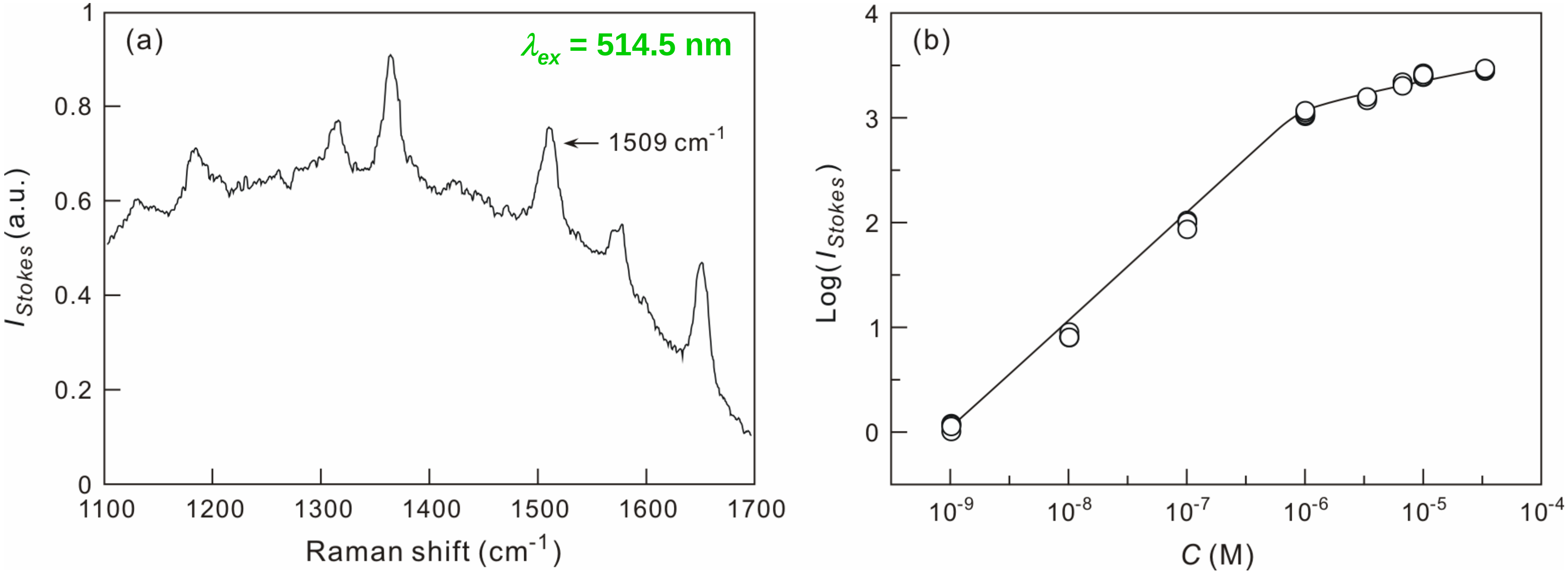
Rhodamine 6G in water



- 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)

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).

Gap dependence of SERS signal-I

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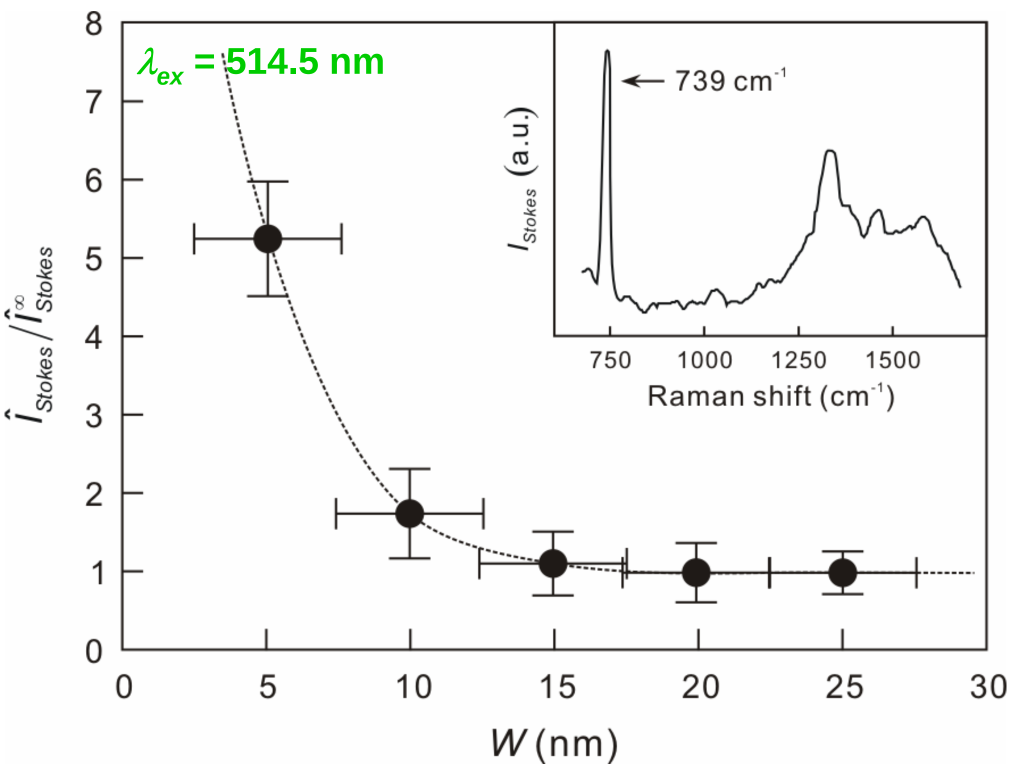
- Adenine: no fluorescence background from 514.5-nm excitation
- 739 cm^{-1}: purine ring breathing mode
- $\hat{I}_{Stokes}$: average Raman signal per particle
- $\hat{I}^{\infty}_{Stokes}$: for substrates with infinitely large *W*
- The average Raman signal per particle at 739 cm^{-1} starts increasing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

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



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).

SERS characterization of bacteria

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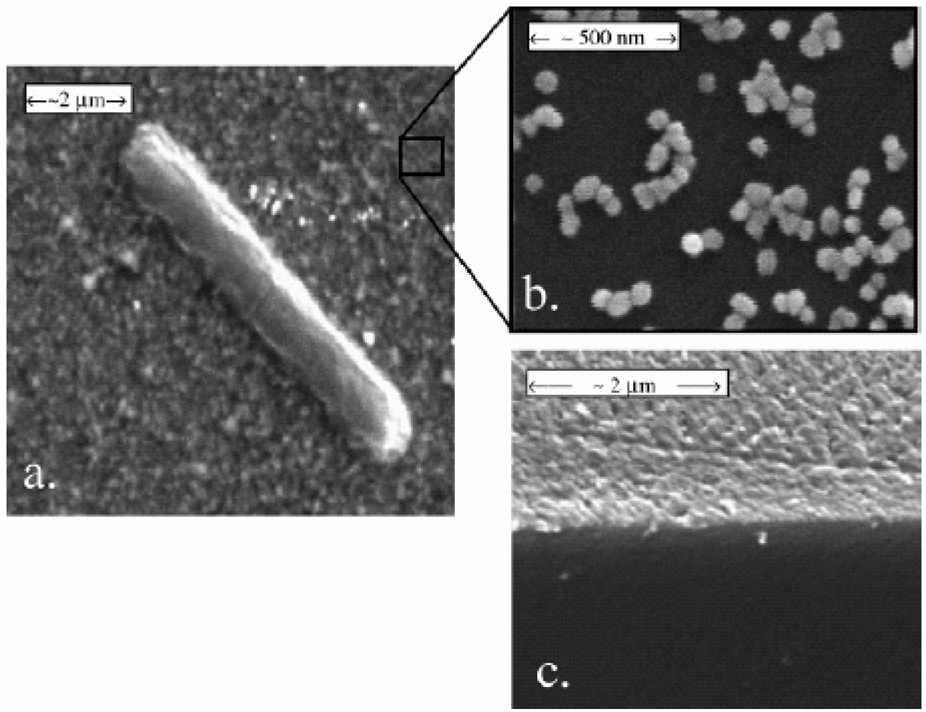
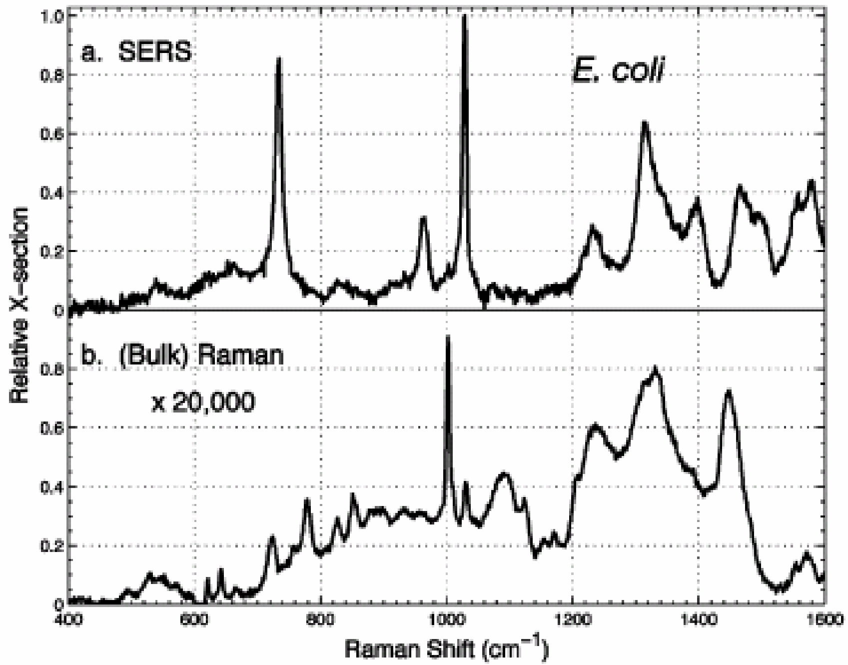
Bacteria on thermally evaporated Au nanoparticles





- 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

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- 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.