Sensitive Biosensing Using Surface Plasmons in metallic Nanostructures

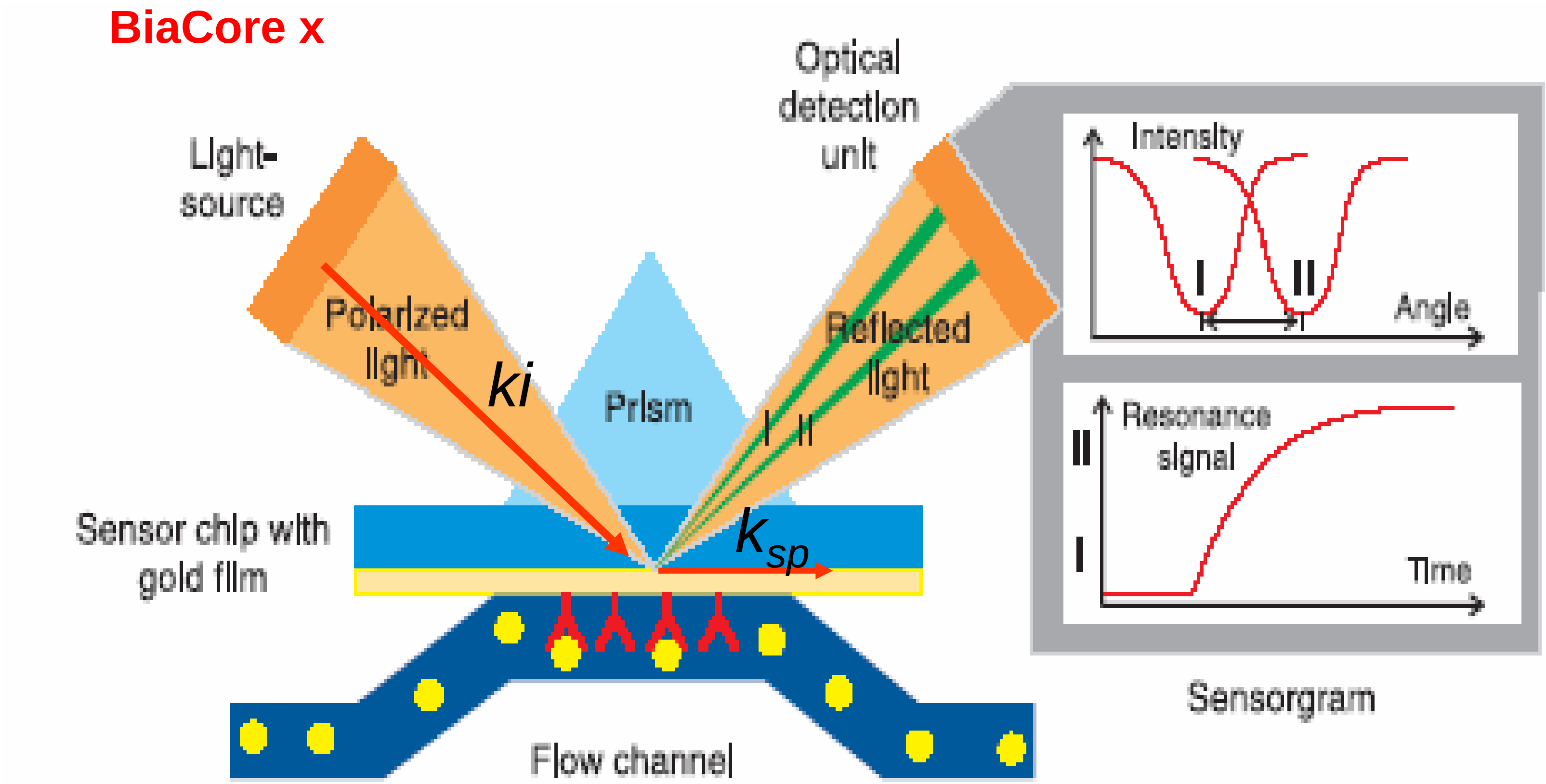
Pei-Kuen Wei

Associate Research Fellow, Research Center for Applied Sciences
Academia Sinica, Taipei, Taiwan

Outline

1. Introduction to Nano-Plasmonics
2. Nano-Plasomonic Sensors

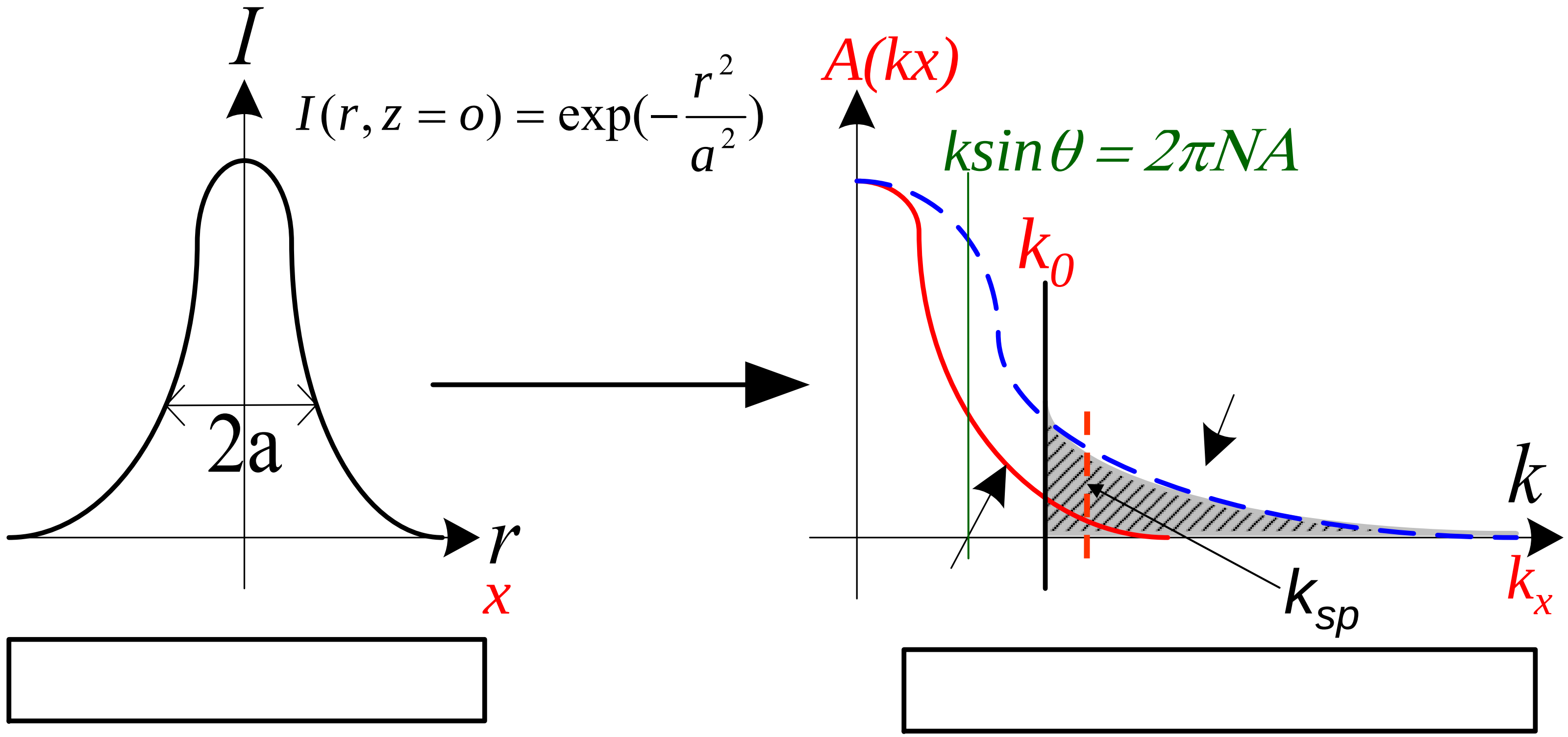
- **Surface Plasmon Resonance for Sensitive Biosensing**



$$k_{ix}=k_0 n_p \sin\theta = k_{sp}$$

$$k_0 n_p \sin\theta = k_x = \varpi / c \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \sim k_0 \sqrt{\varepsilon_2} = k_0 n_2$$

The dielectric constant of metal is negative and much larger than ε_2.



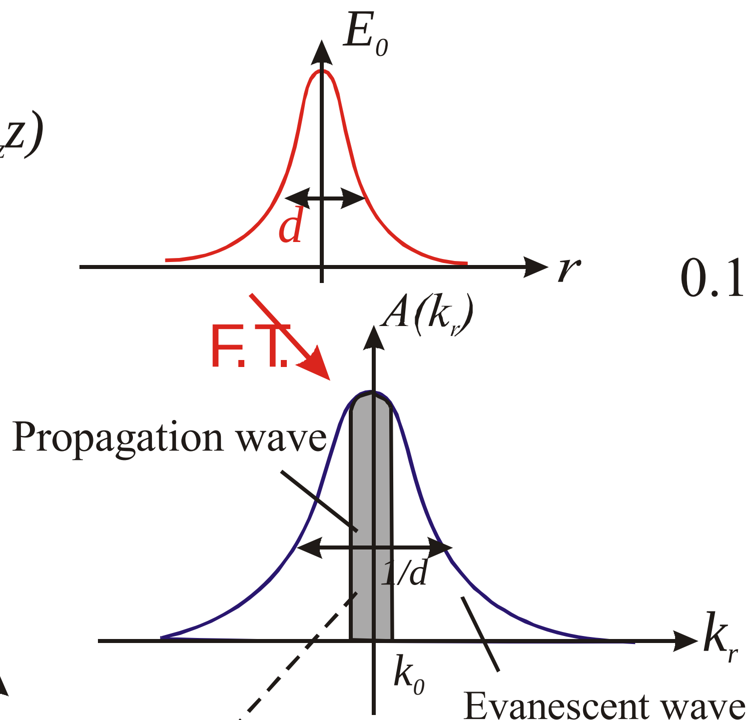
Fourier transform

Optical spot size << wavelength

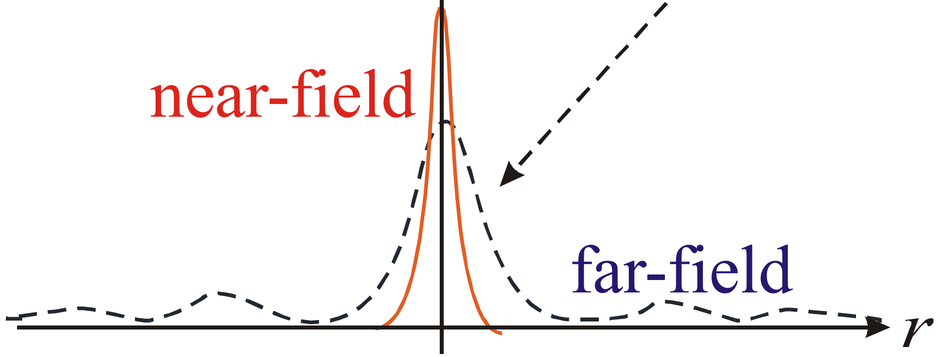
$E(x,z)=E_0(r)\exp(ik_z z)$
$=\Sigma A(k_r)\exp(ik_r r)\exp(ik_z z)$

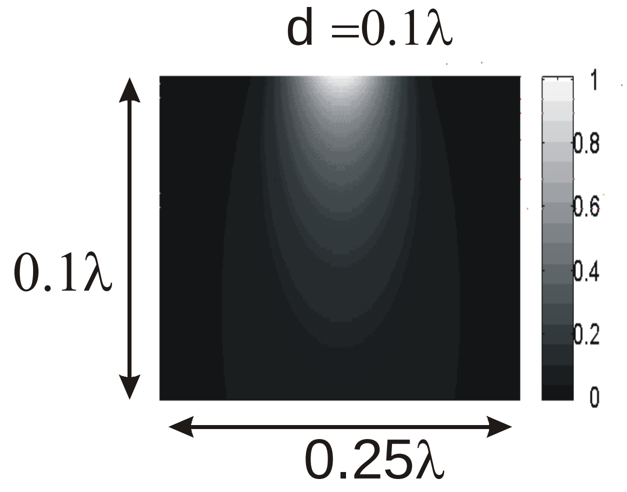
$k_0^2=k_r^2+k_z^2$

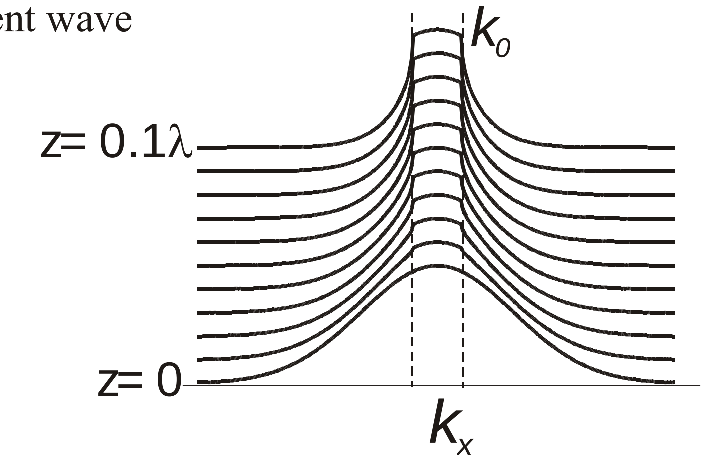
$k_z=\sqrt{k_0^2-k_r^2}$



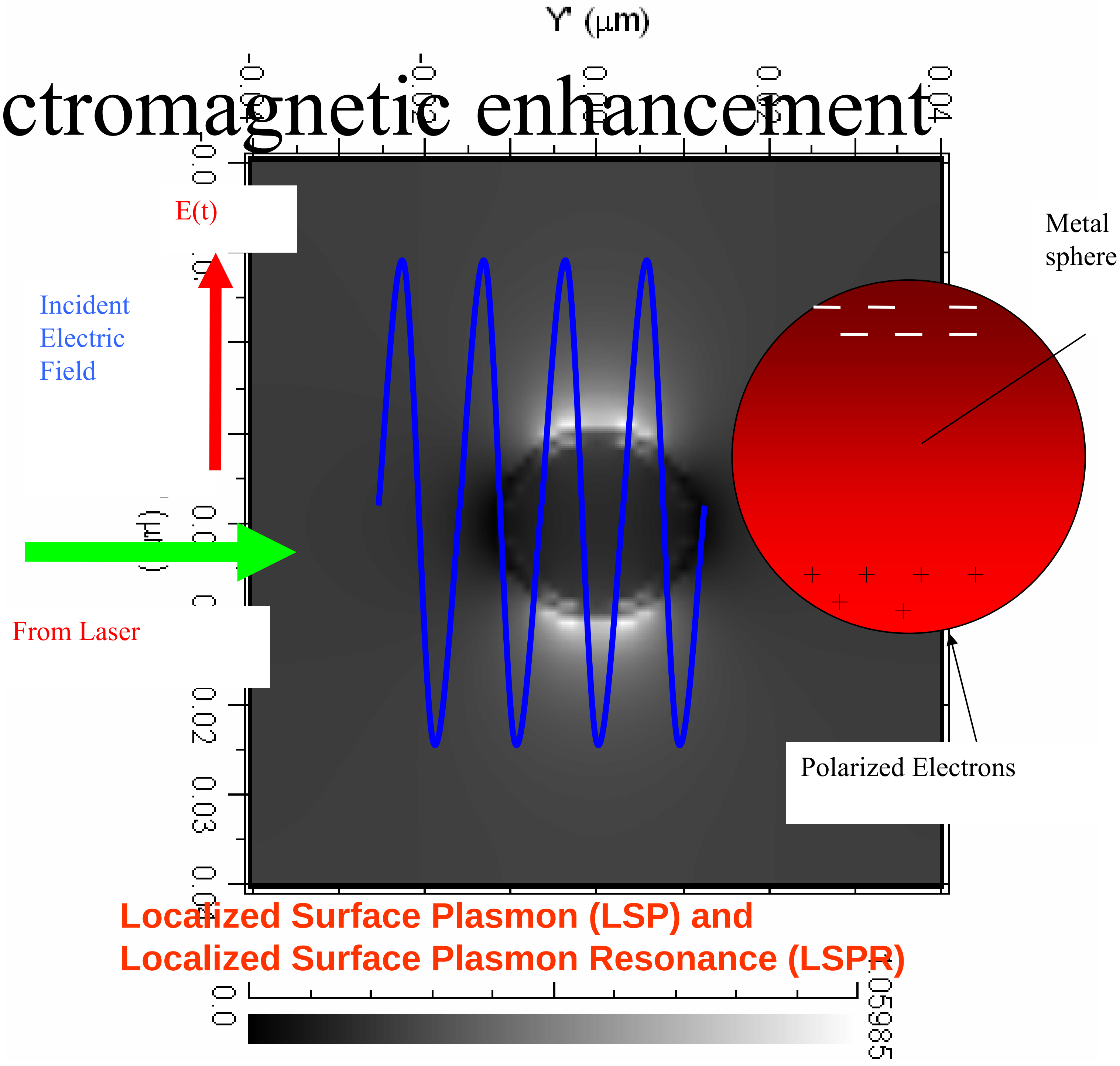
if $k_r<k_0$, k_z is real
=>propagation wave
if $k_r>k_0$, k_z is imaginary
=>evanescent wave





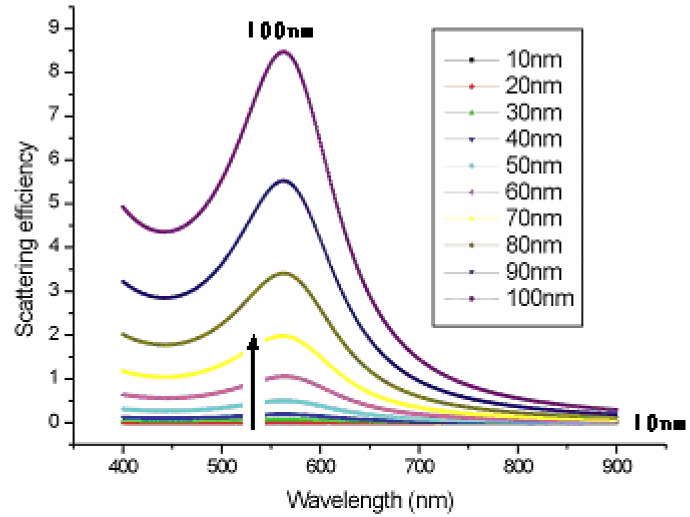


Electromagnetic enhancement

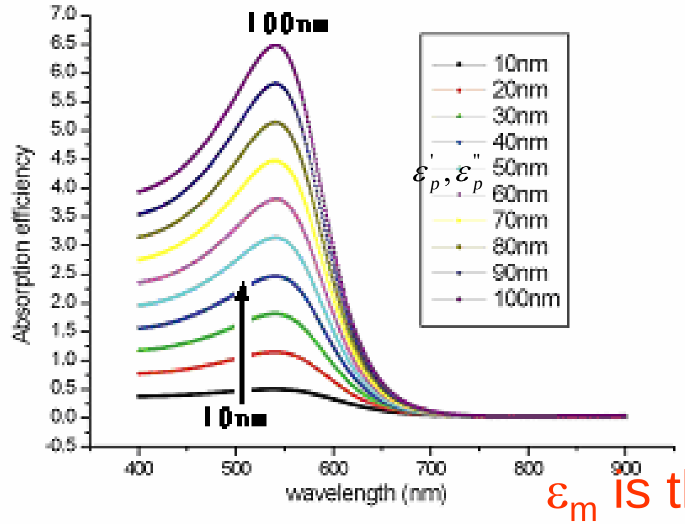


Localized Surface Plasmon (LSP) and
Localized Surface Plasmon Resonance (LSPR)

scattering $C_{sca}(\omega) = 4\pi r^2 \times \frac{32}{3}\pi^4 \left(\frac{r}{\lambda}\right)^4 \varepsilon_m^2 \frac{\left[\varepsilon_p'(\omega)-\varepsilon_m\right]^2+\varepsilon_p''^2(\omega)}{\left[\varepsilon_p'(\omega)+2\varepsilon_m\right]^2+\varepsilon_p''^2(\omega)}$



absorption

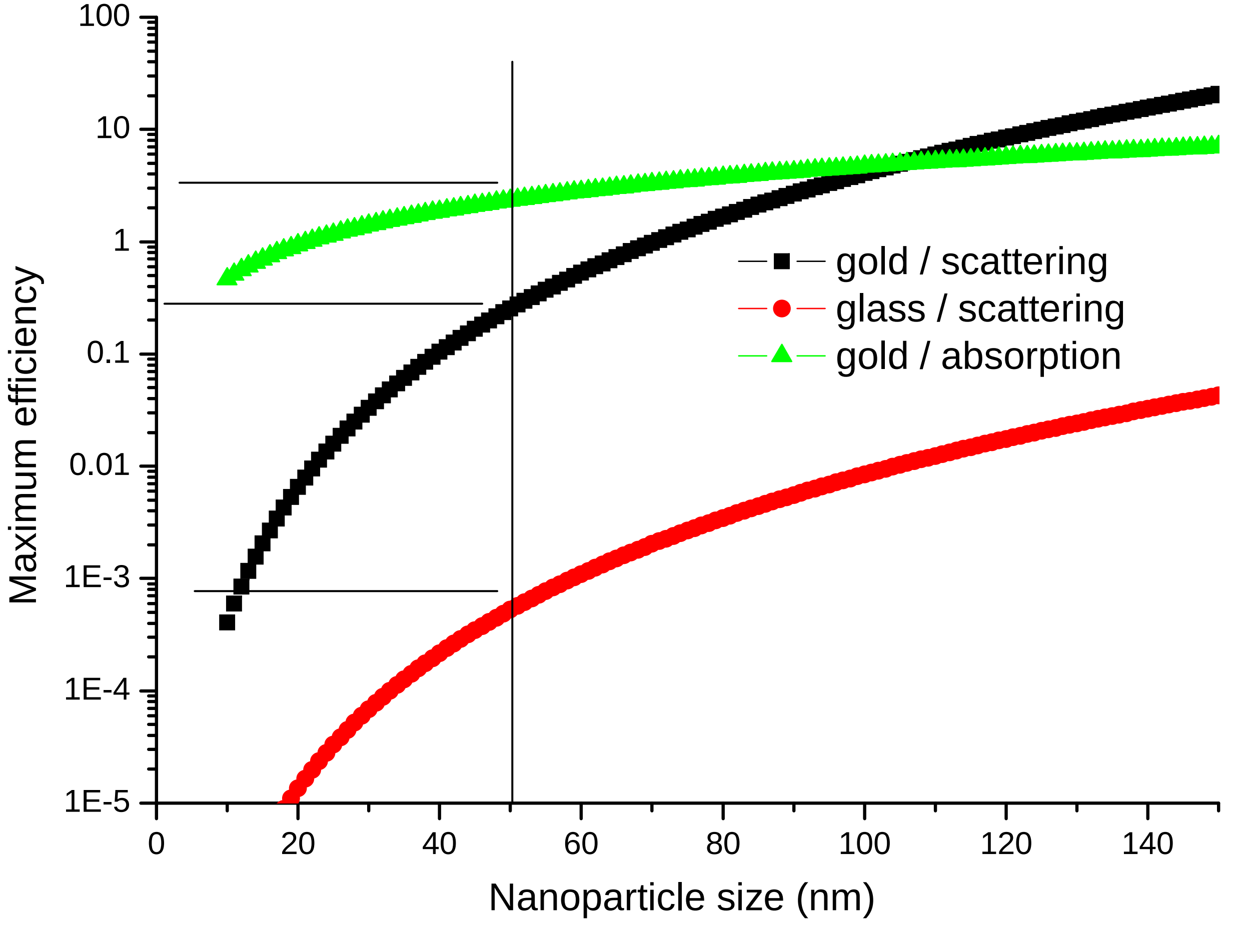


ε_p' and ε_p'' are real part and imaginary part of the metal. Maximum absorption and scattering occur at $\varepsilon'_p = -2\varepsilon_m$。

ε_m is the dielectric of the surrounding medium(1 for air)

$$C_{abs}(\omega) = 4\pi r^2 \times 6\pi \left(\frac{r}{\lambda}\right) \varepsilon_m^{3/2} \frac{\varepsilon_p''(\omega)}{\left[\varepsilon_p'(\omega)+2\varepsilon_m\right]^2+\varepsilon_p''^2(\omega)}$$

Scattering and Absorption of NPs



不同粒徑散射與吸收的最大效率

Rayleigh scattering cross-section

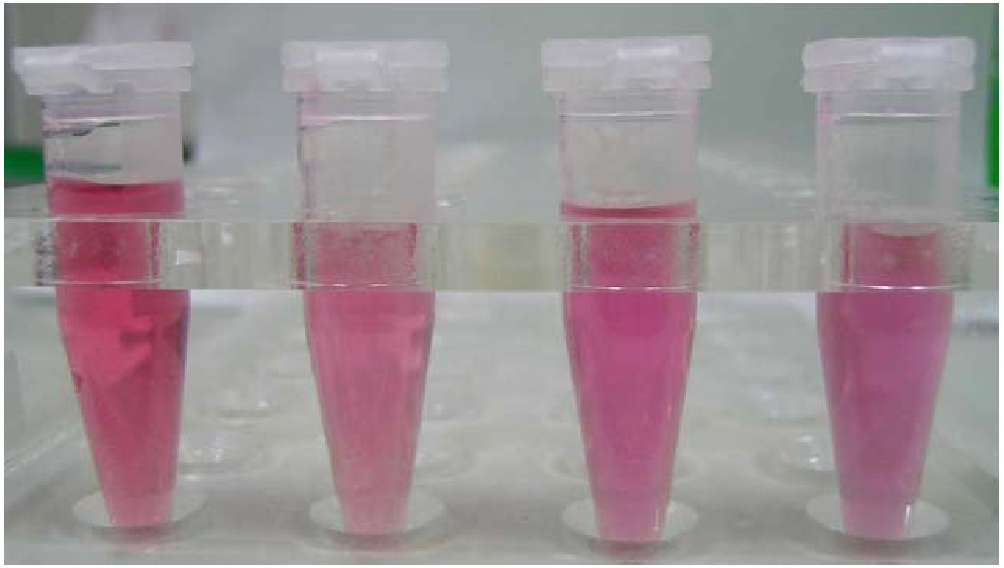
$$\sigma_s = \frac{2\pi^5}{3}\frac{d^6}{\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)^2 .$$

$$C_{sca}(\omega) = 4\pi r^2 \times \frac{32}{3}\pi^4 \left(\frac{r}{\lambda}\right)^4 \varepsilon_m^2 \frac{\left[\varepsilon_p'(\omega)-\varepsilon_m\right]^2 + \varepsilon_p''^2(\omega)}{\left[\varepsilon_p'(\omega)+2\varepsilon_m\right]^2 + \varepsilon_p''^2(\omega)}$$

$$n^2 = \varepsilon_r$$

ε is negative for metals, when it approximates to -2, the absorption and scattering ε is greatly *enhanced !*

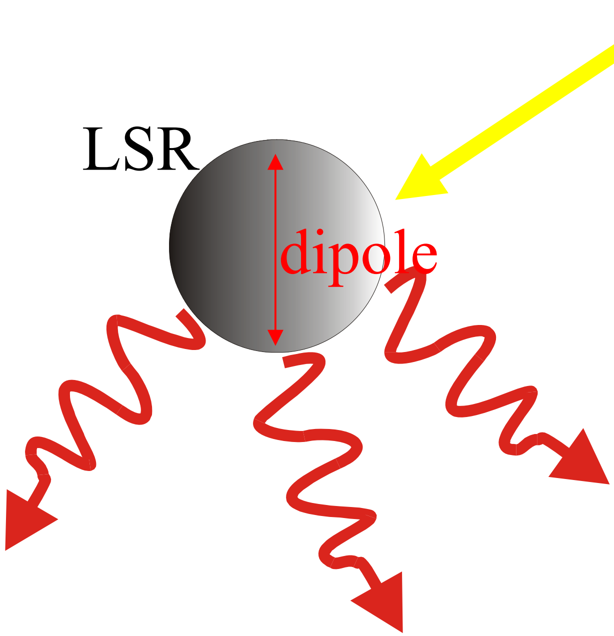
"Labors of the Months" (Norwich, England, ca. 1480).
(The ruby color is probably due to embedded gold nanoparticles.)



Gold nanoparticles, 20nm, 40nm ,60nm, 80nm in diameter

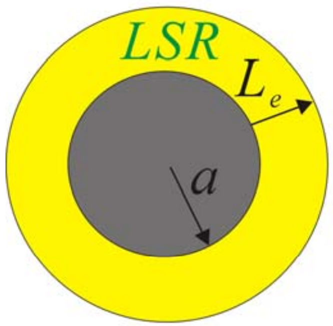
P-K, Wei

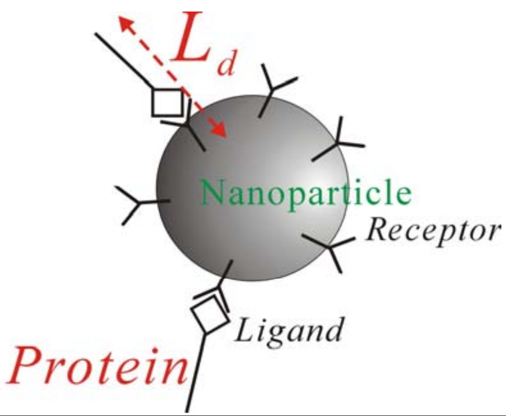
LSR (localized surface plasmon resonance)

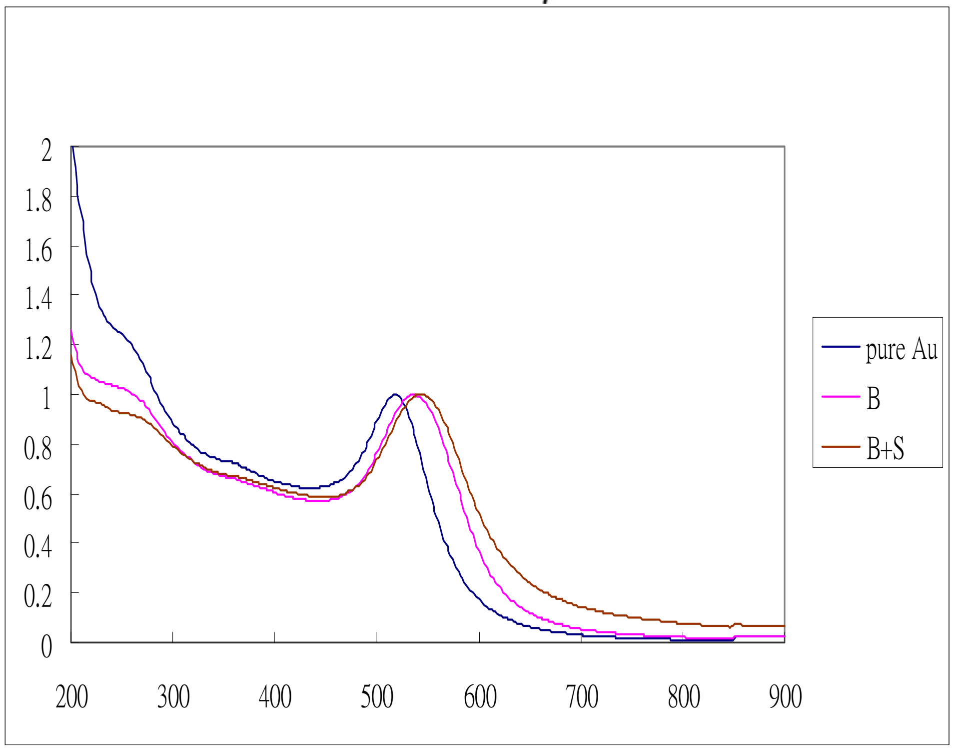


$$C_{sca}(\omega) = 4\pi r^2 \times \frac{32}{3}\pi^4 \left(\frac{r}{\lambda}\right)^4 \varepsilon_m^2 \frac{[\varepsilon_p'(\omega) - \varepsilon_m]^2 + \varepsilon_p''^2(\omega)}{[\varepsilon_p'(\omega) + 2\varepsilon_m]^2 + \varepsilon_p''^2(\omega)}$$

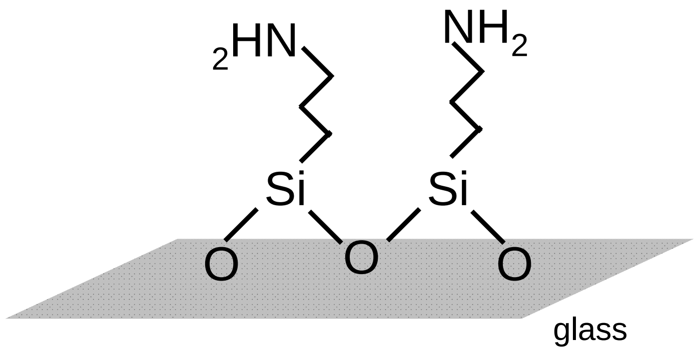
Changing surrounding condition, changing scattering spectrum!

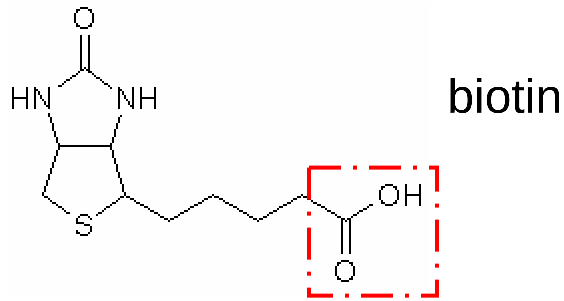


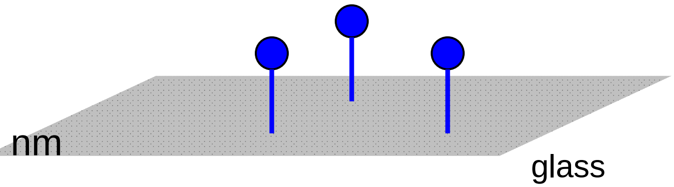


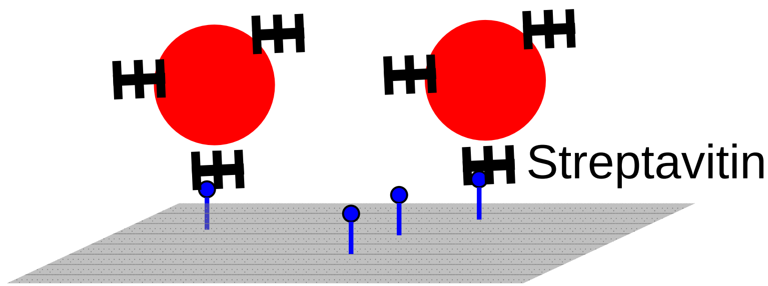


518 nm
536
542

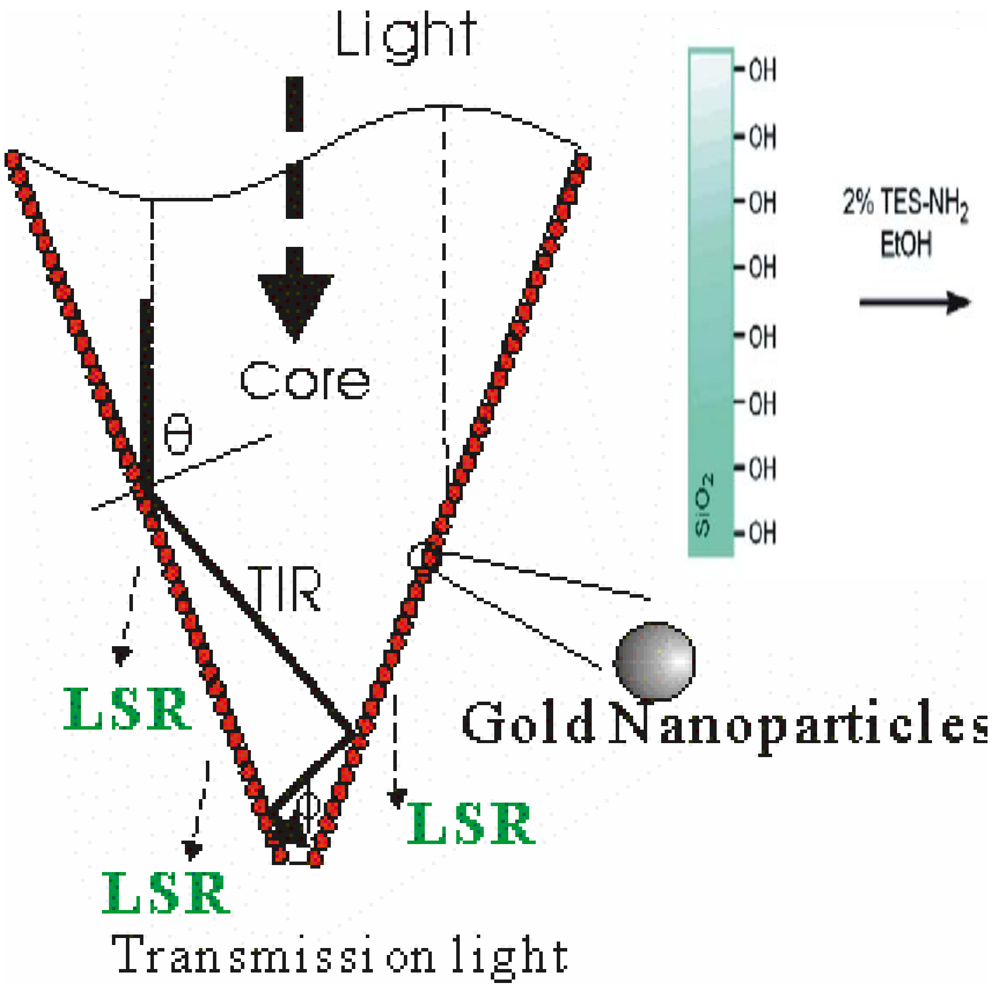


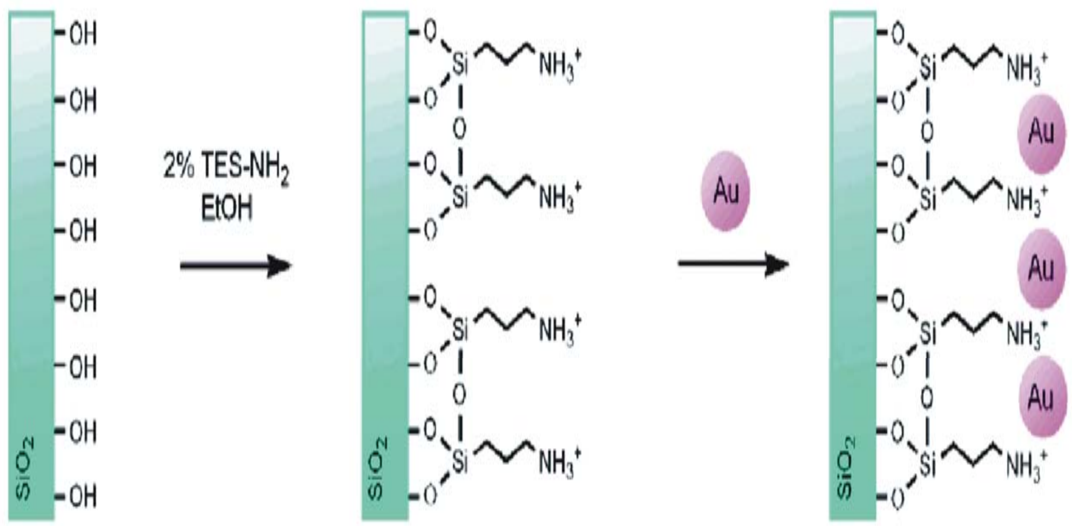


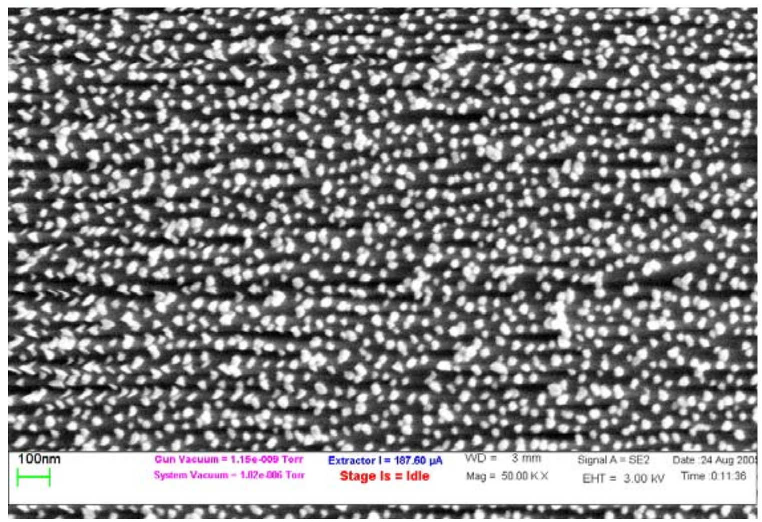




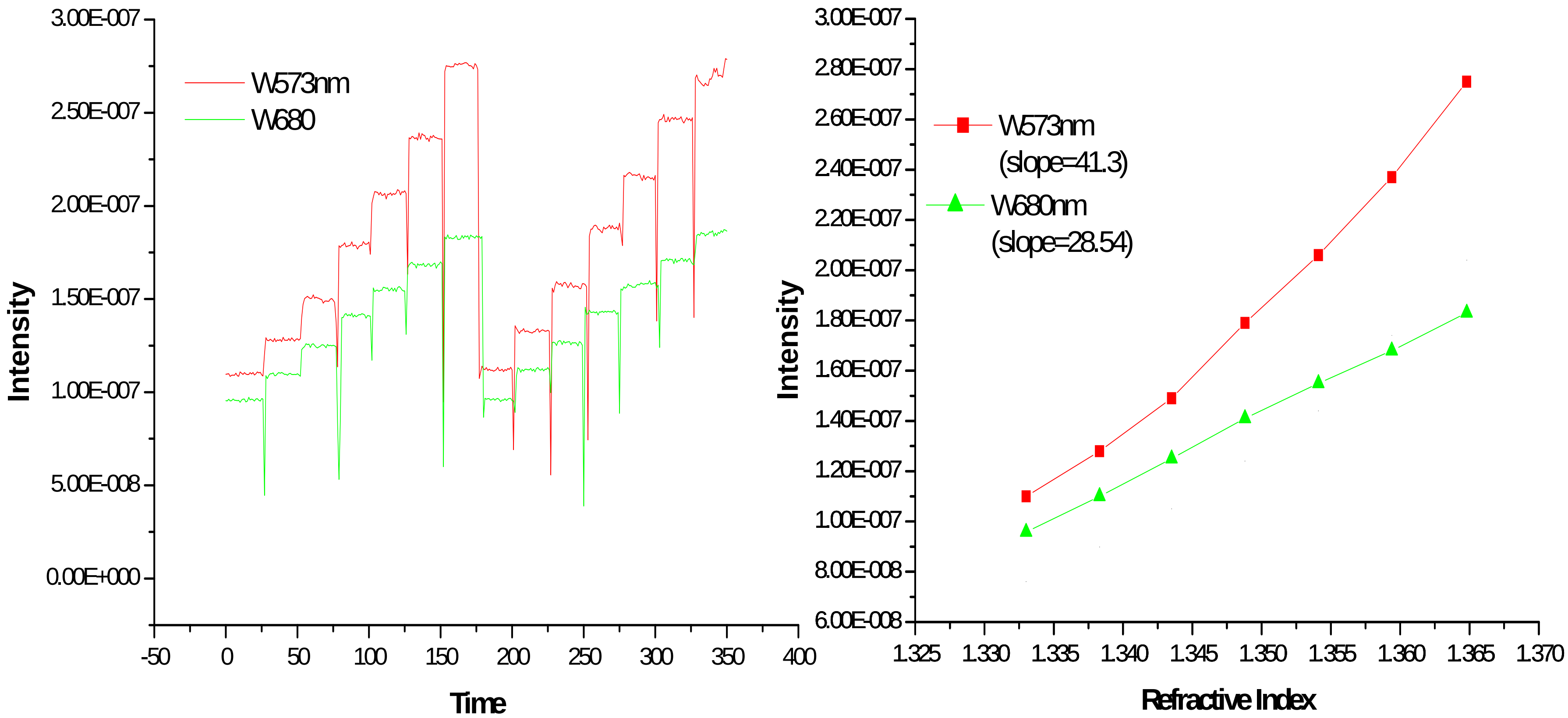
A nanotip with nano particles





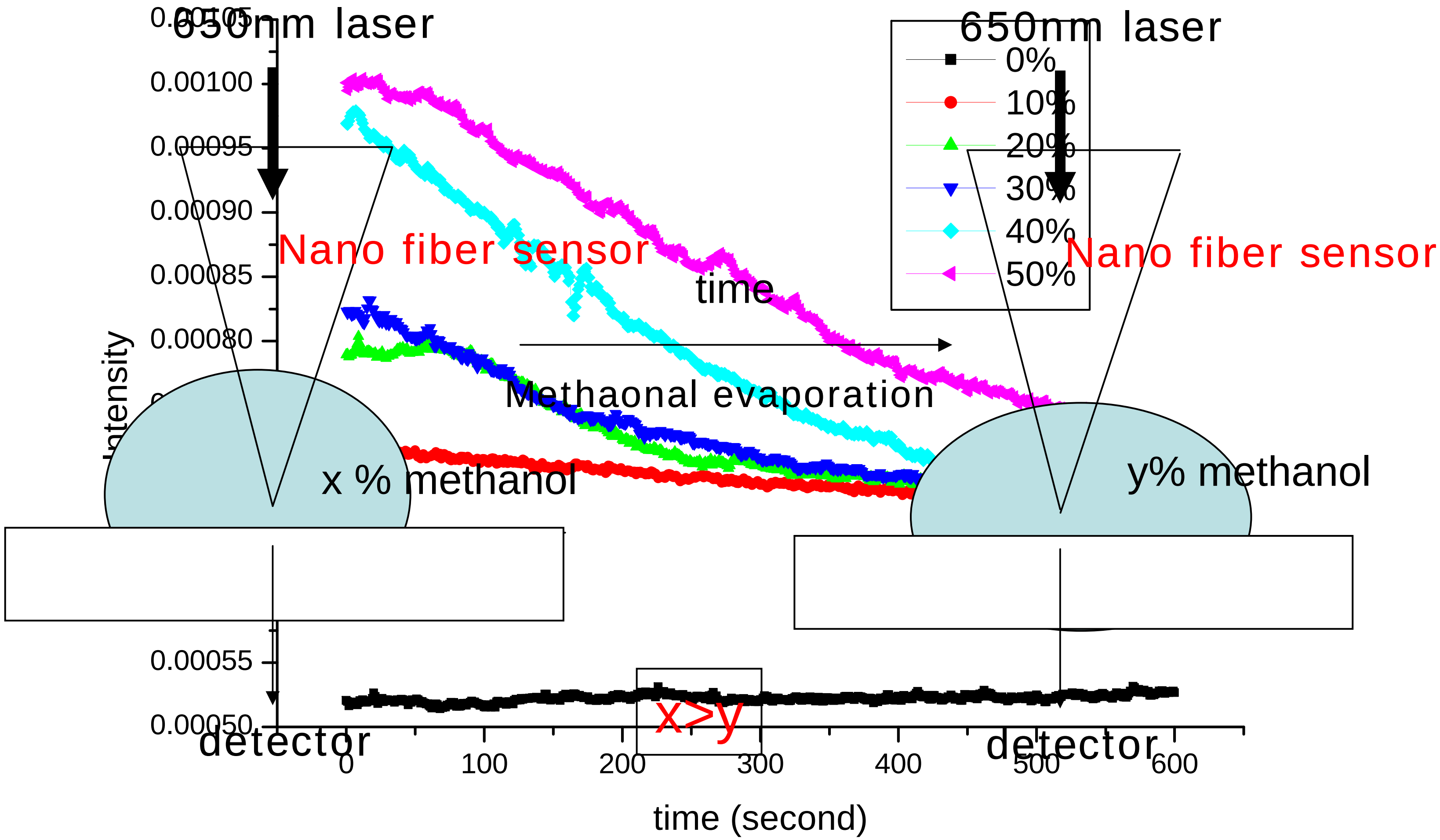


Sensitivity Measurement



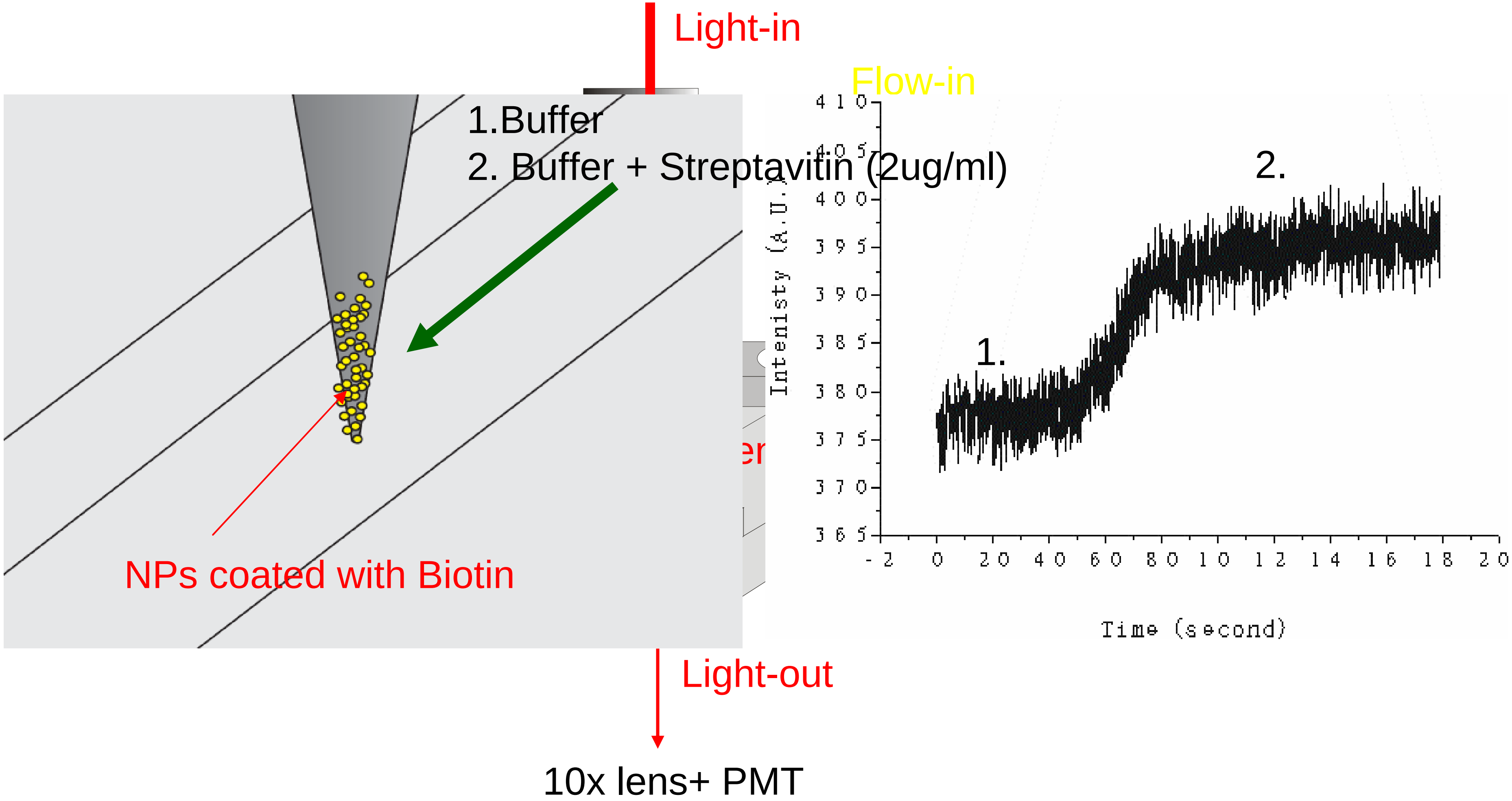
The results indicate ~ 4130 (% RIU^{-1}), it means ~4.84e-5 RIU at 0.2% power stability

Methanol evaporation in methanol/water mixture

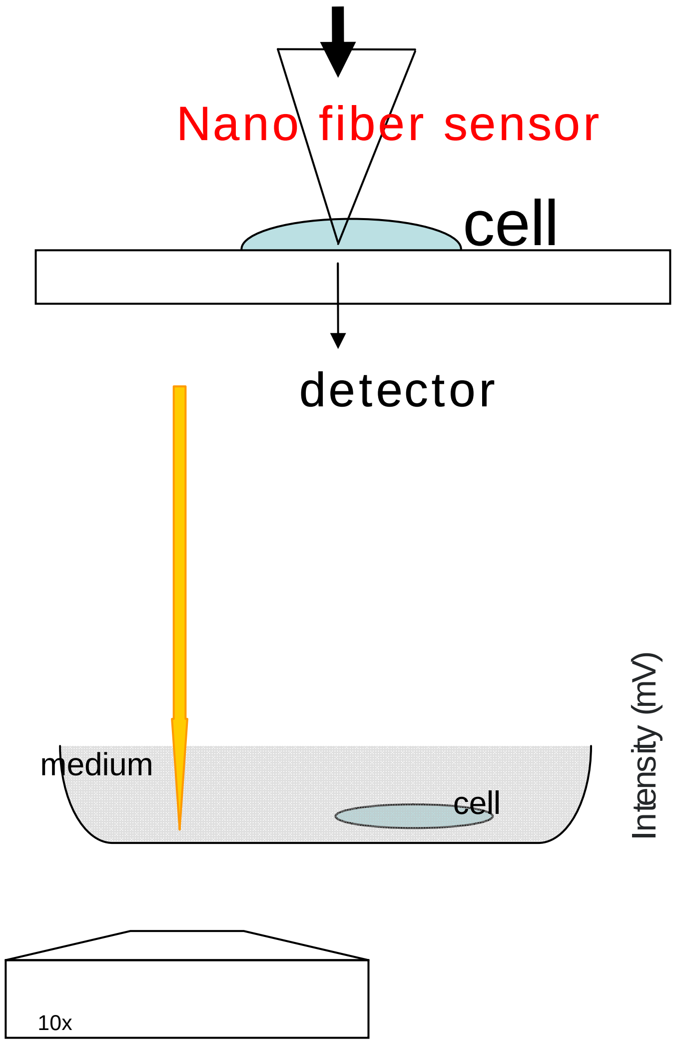


Applications

Dynamic measurement of bio-samples interactions

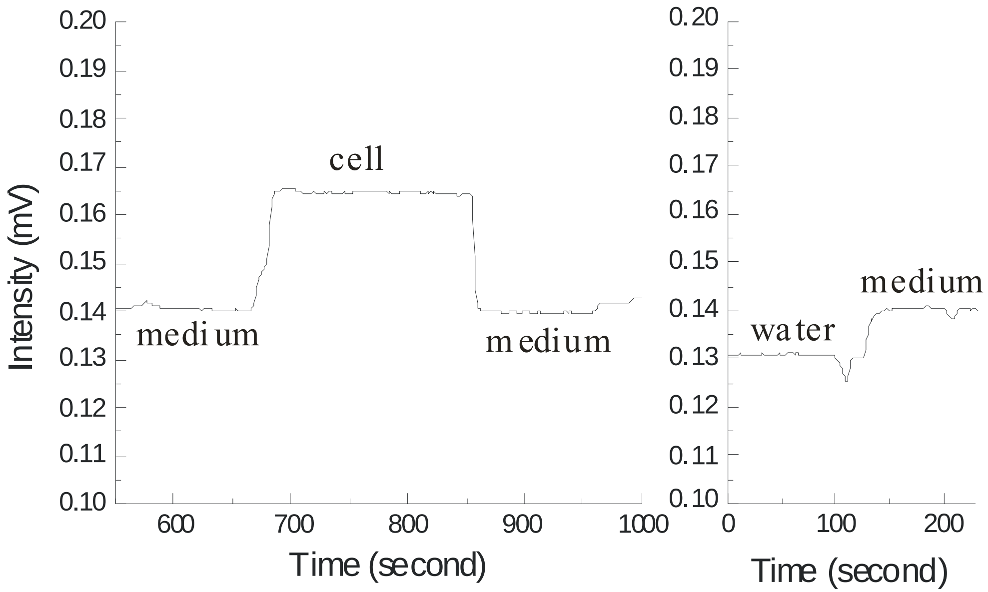


Dynamic measurement of bio-samples interactions



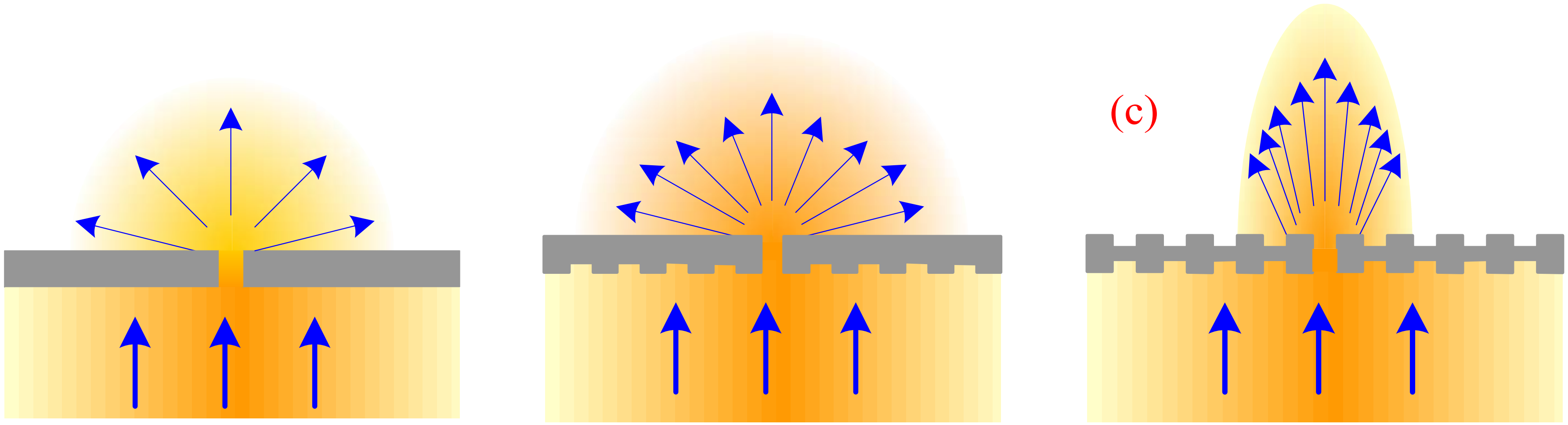
$$\frac{\Delta I}{\Delta n} = \frac{I_{medium} - I_{cell}}{n_{medium} - n_{cell}}$$

$n_{cell} \approx 1.3506$



PK Wei, Appl. Phys. Lett. 2008, Oct.

Extraordinary transmissions in nano metallic structures



Aperture diameter < λ

➔Output light wave is fully diffracted into a half-sphere (a)

By patterning the input side with concentric periodic groove

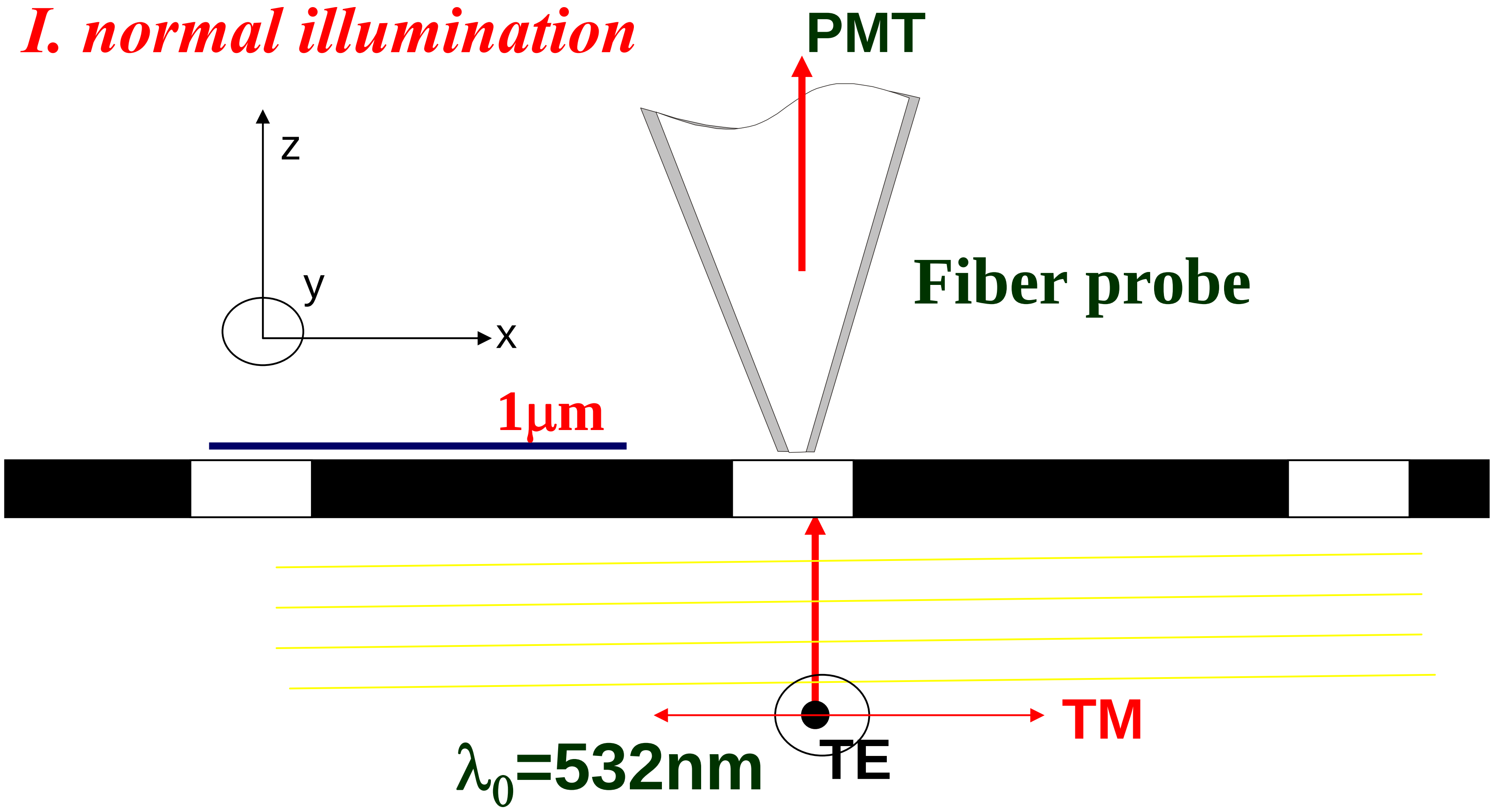
➔ The transmission is boosted at certain wavelengths.

By patterning both sides with concentric periodic groove (b)

➔ The transmission is boosted and focused

E. W. Ebessen, 1998(Nature)   E. W. Ebessen, 2002 (Science)

SNOM (or NSOM) in collection mode

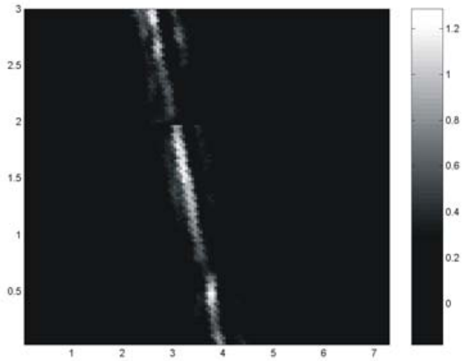


1. Tip/sample regulation by shear-force feedback method
2. Probe made by tapered fiber coated with metal

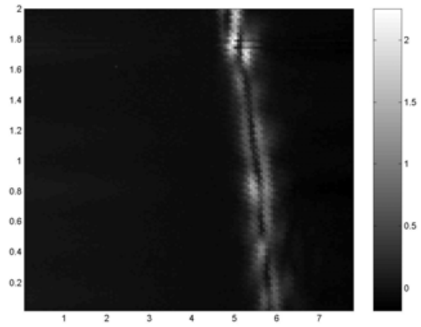
Light in a nano slit

FDTD simulation

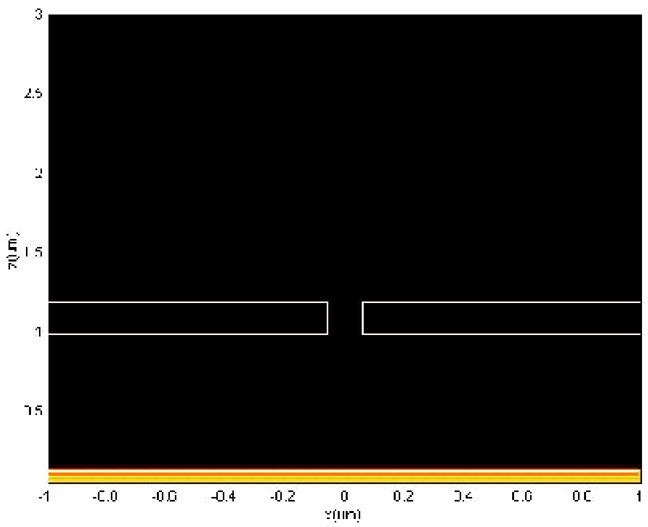
SNOM image (XY)



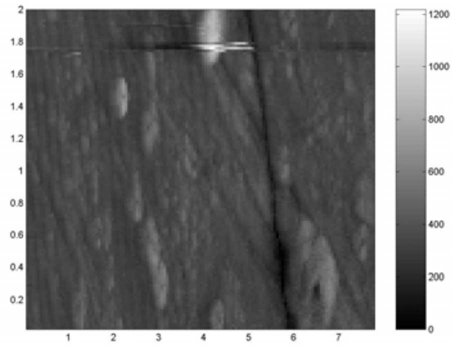
$I_{//}$



$I_{\perp}$

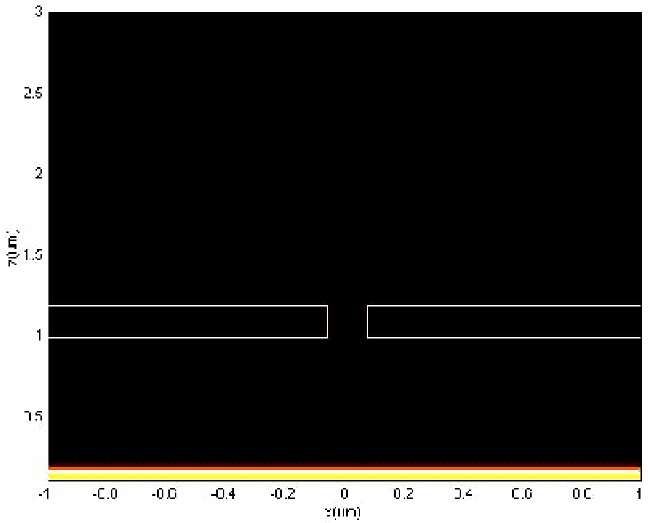


Topography



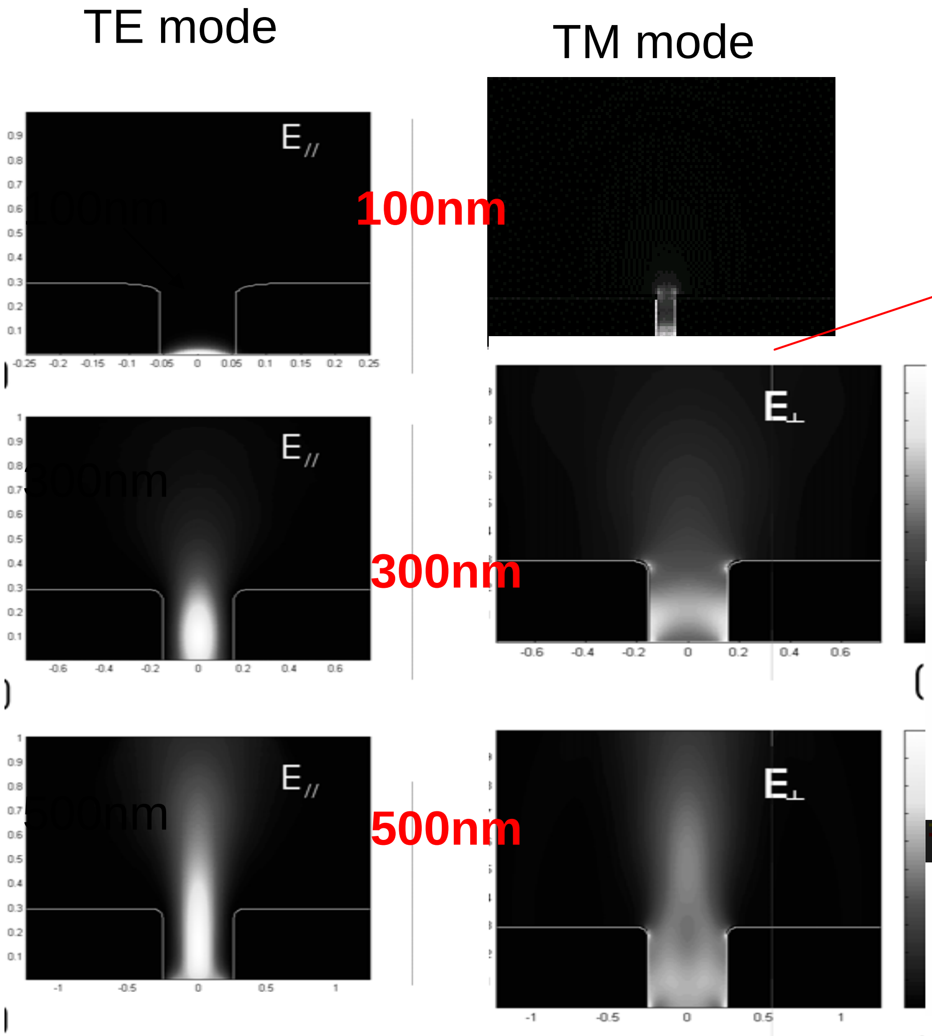
SNOM image (XZ)

$I_{\perp}$



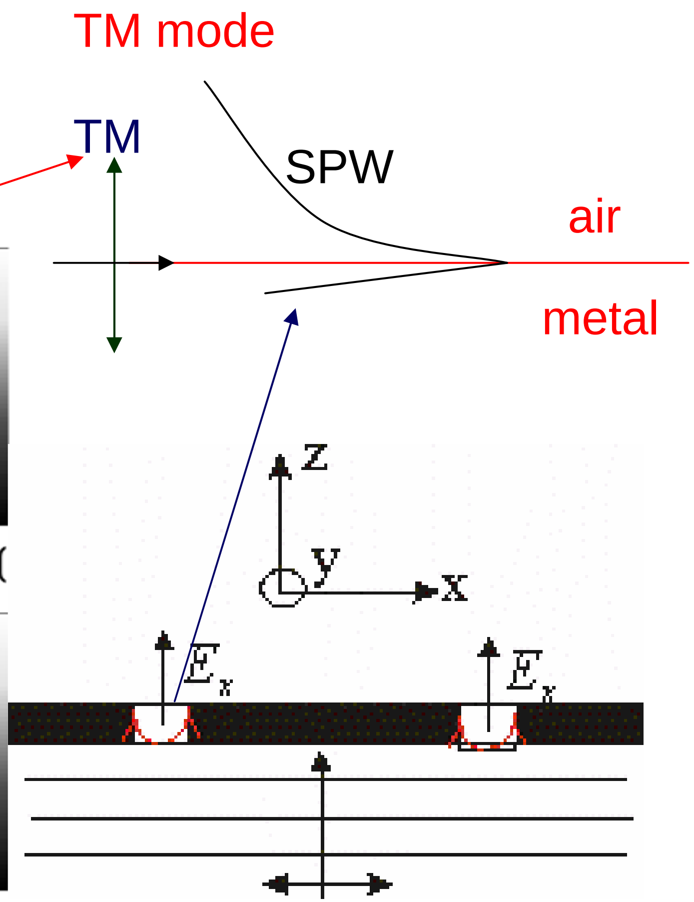
100nm slit

PK Wei, 2002, Opt. Express



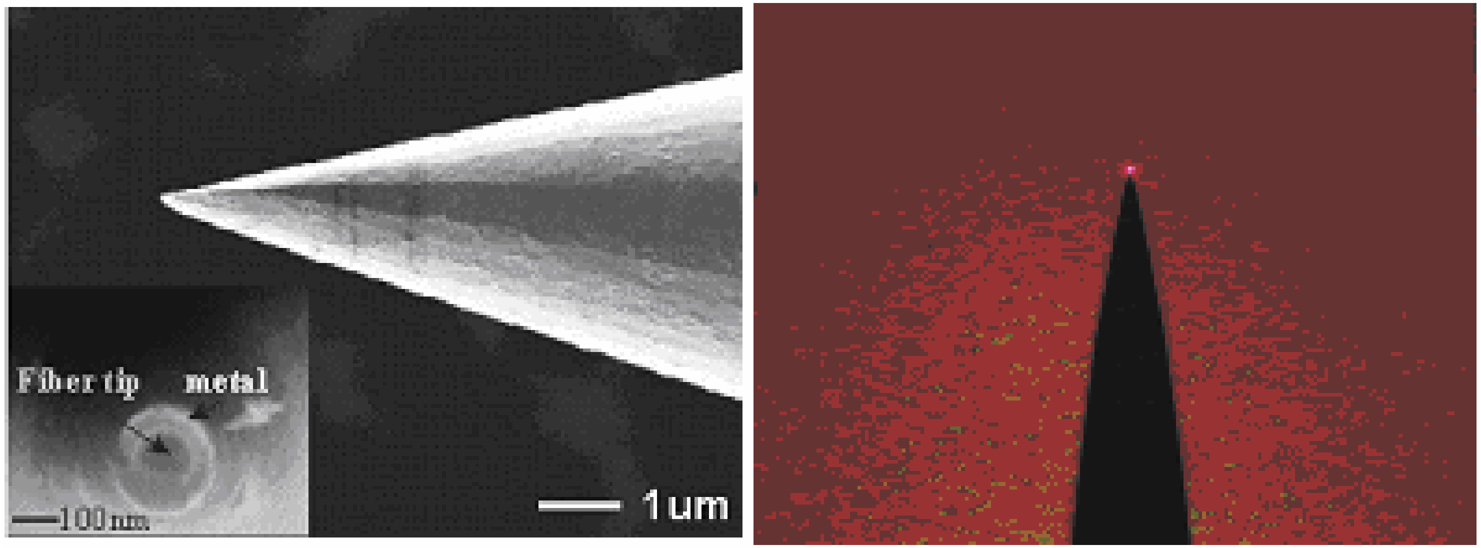
$$n_{eff} = \sqrt{\frac{\varepsilon_m \varepsilon_r}{\varepsilon_m + \varepsilon_r}}$$

$$\lambda_{spw} = \lambda_0 / n_{eff}$$



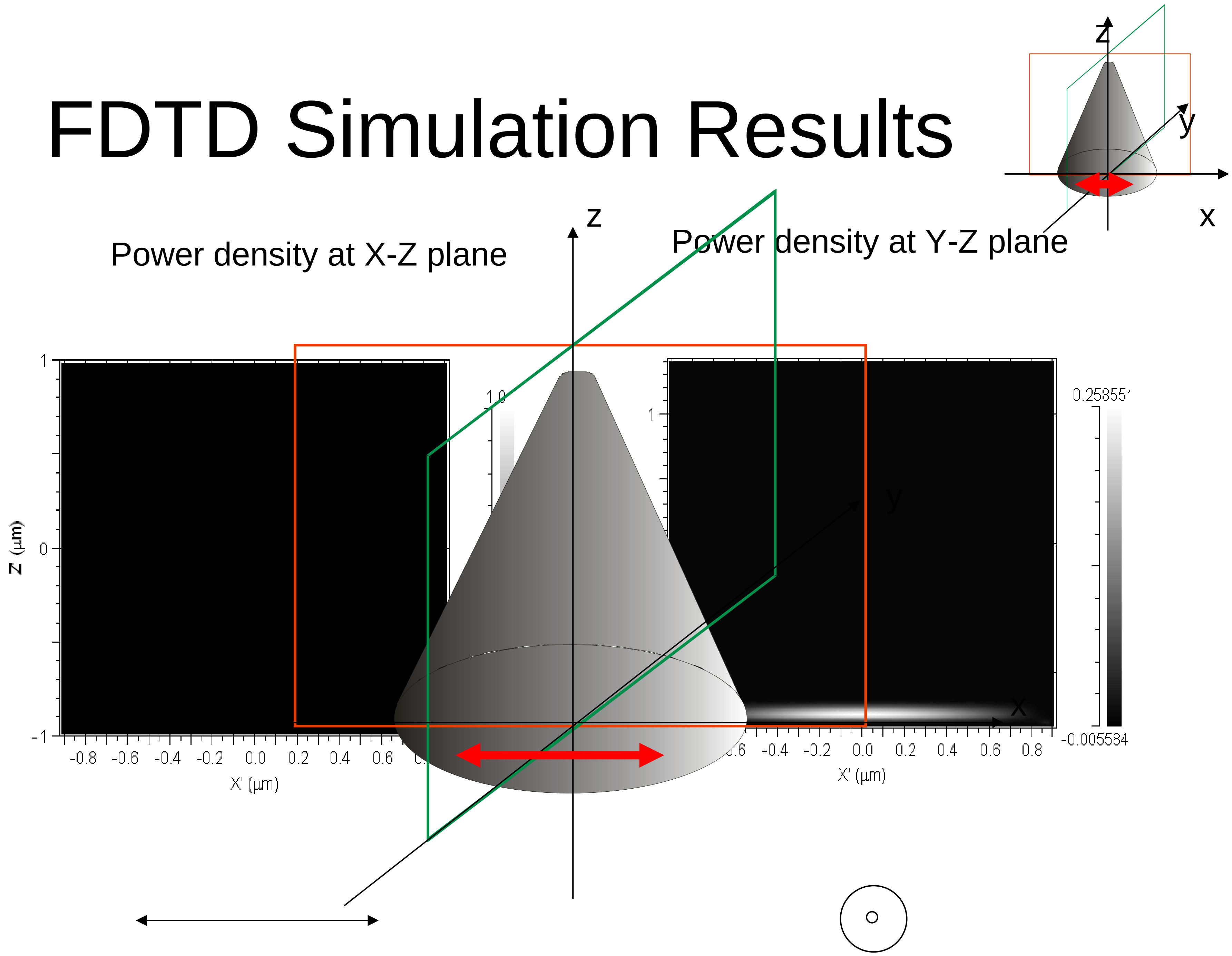
Surface Plasmons can be generated in a metallic nano gap!

Side View

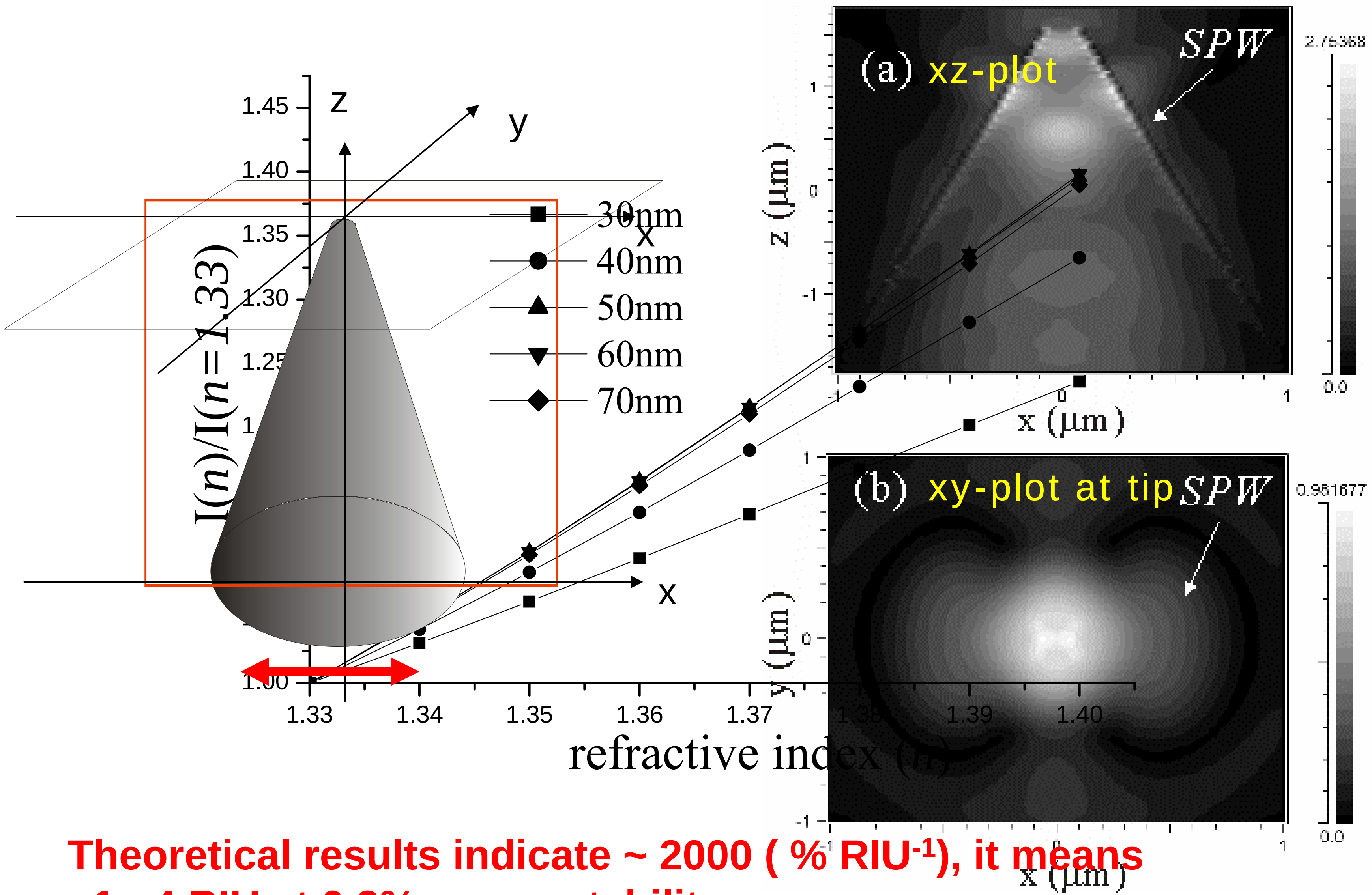


(a) (b)

FDTD Simulation Results

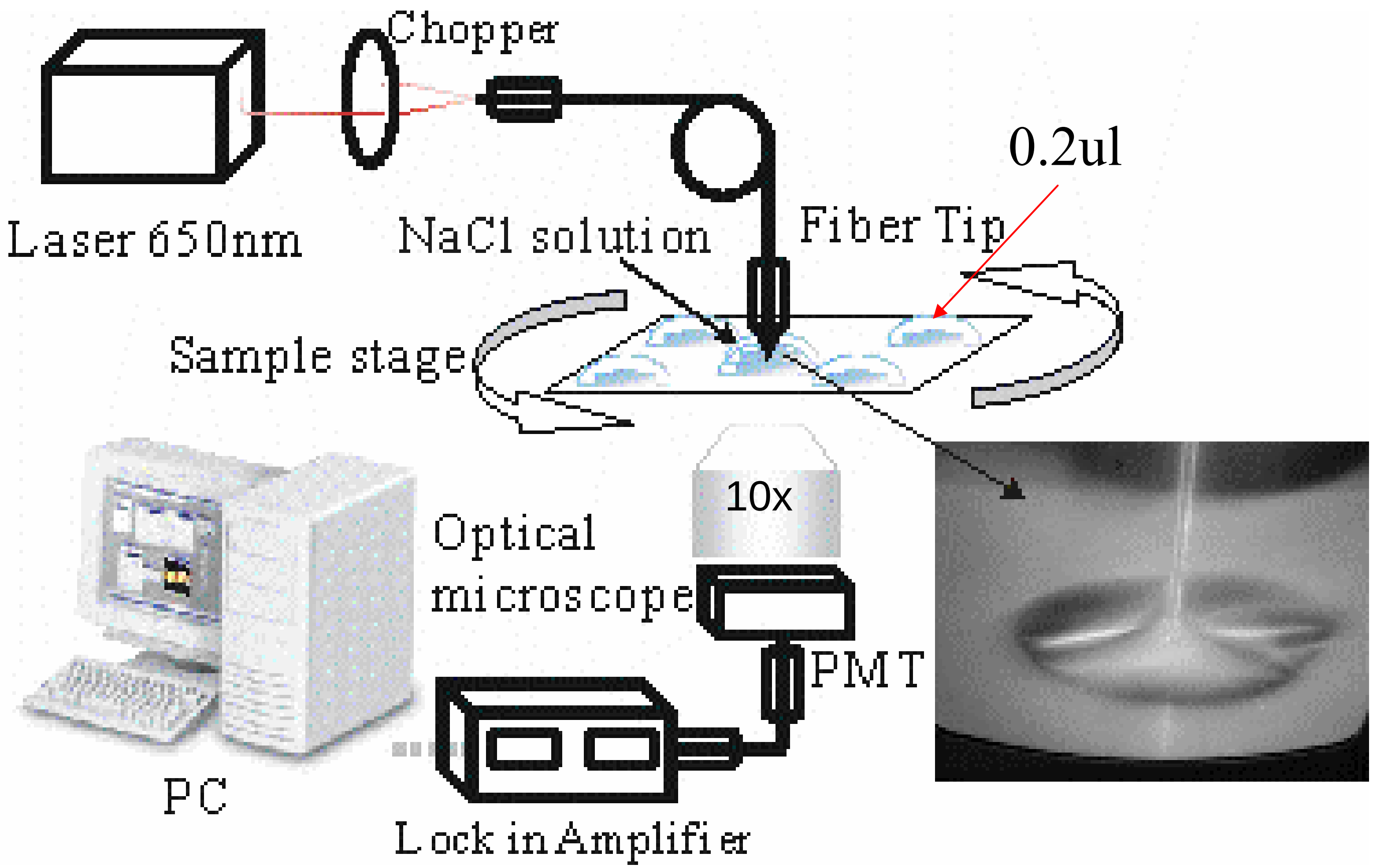


3D-FDTD simulation results

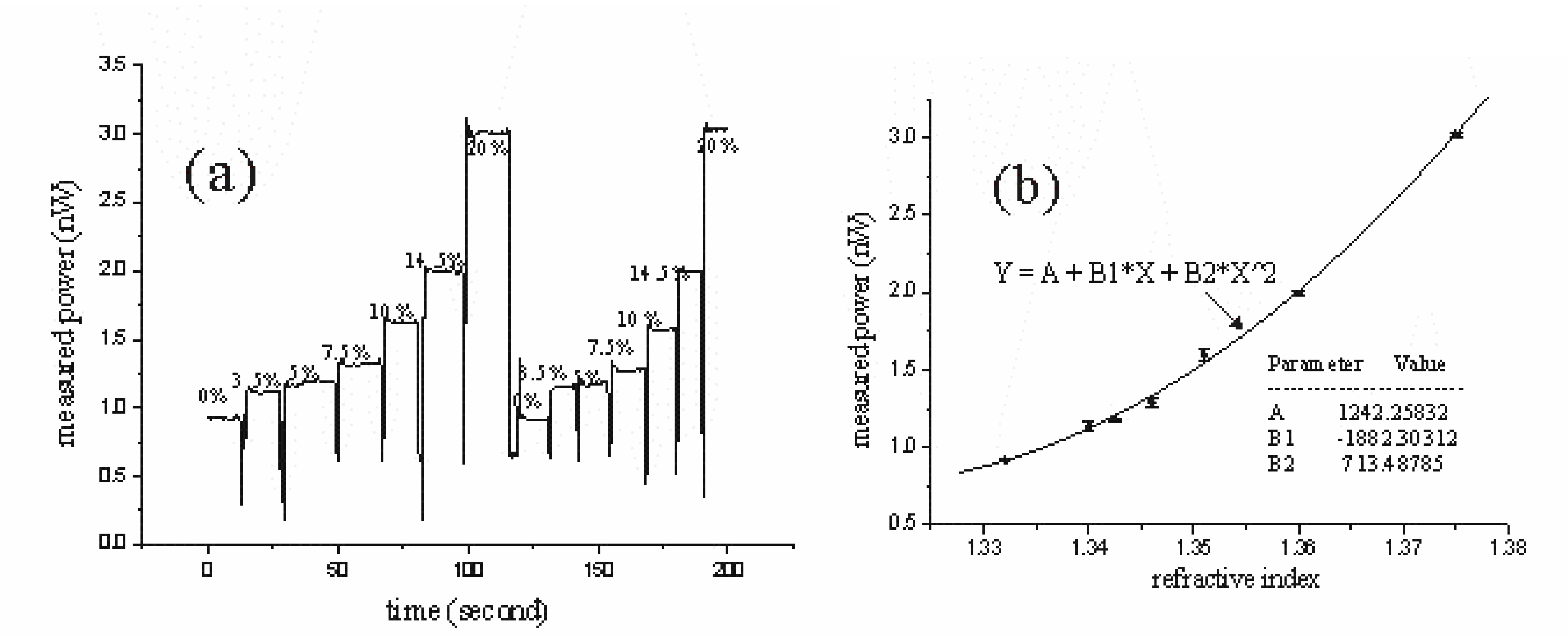


Theoretical results indicate ~ 2000 (% RIU^{-1}), it means ~1e-4 RIU at 0.2% power stability

Experimental Setup



Sensitivity Measurement



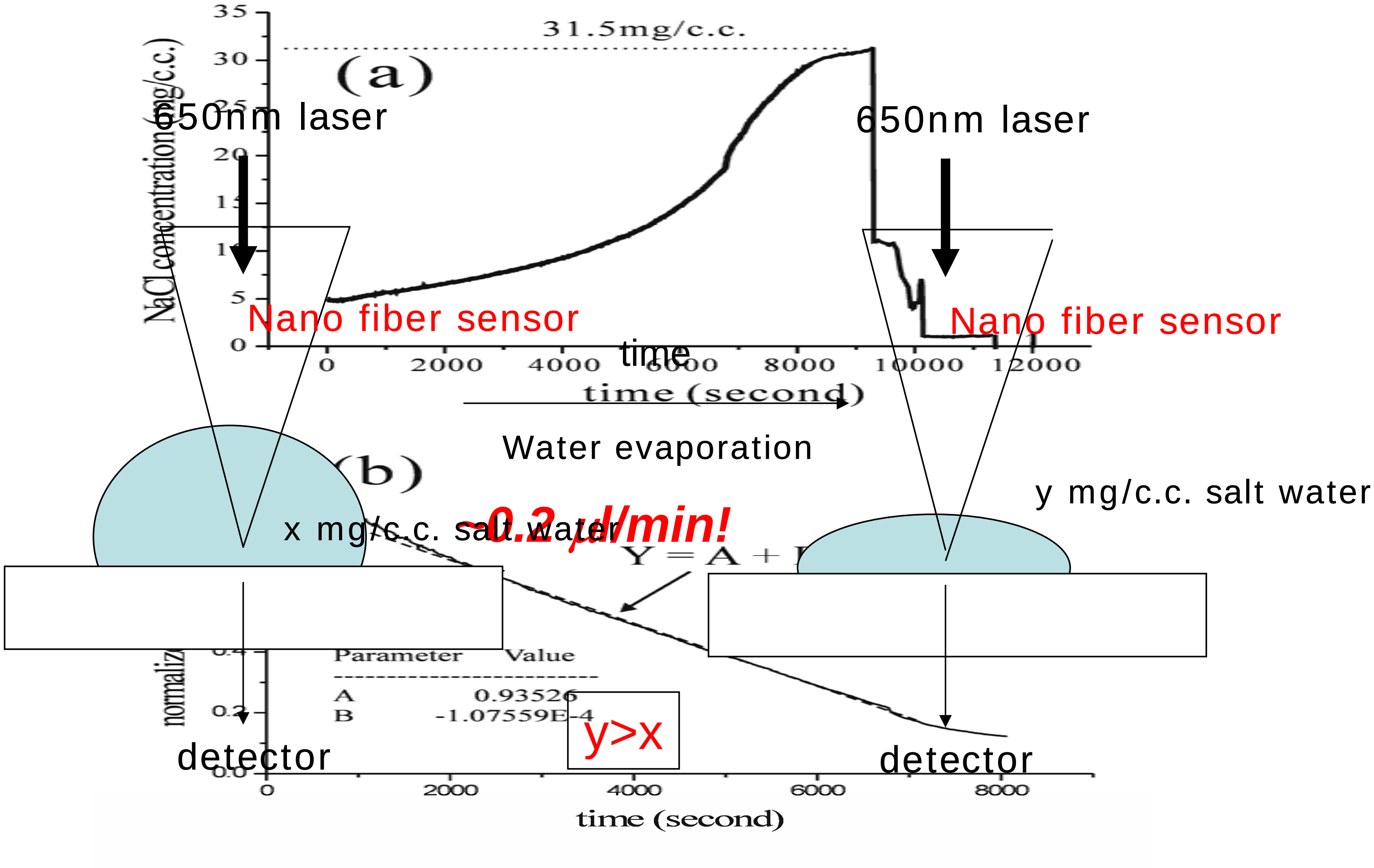
Intensity Increase with salt water concentration. Good repetition of the measurement

The results indicate ~ 3704 (% RIU^{-1}), it means ~ 5.4e-5 RIU at 0.2% power stability

Yu-Jen Chang, Yi-Chun Chen, Hui-Ling Kuo and Pei-Kuen Wei, “Nano Fiber-Optic Sensor based on the Excitation of Surface Plasmon Wave Near Fiber Tip”, *J. Biomedical Optics*, 2006, Vol. 11, 014032

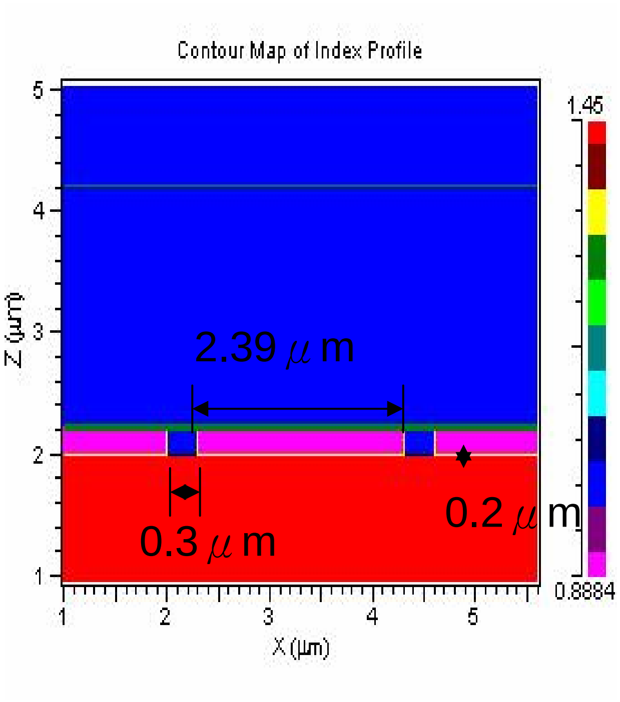
Evaporation rate measurement

Water evaporation in salt water

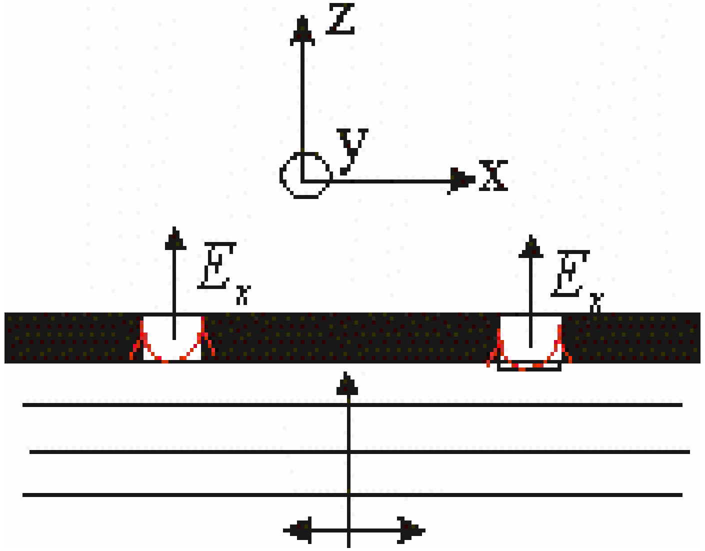


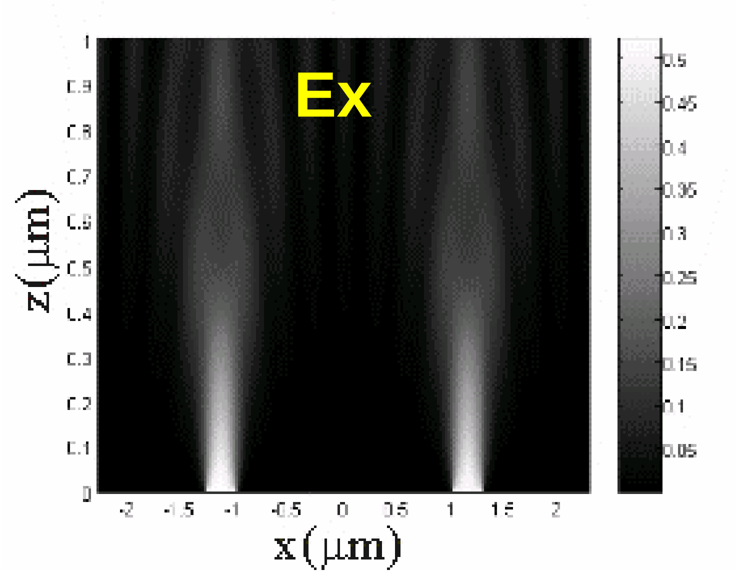
P.K. Wei, J. Biomedical optics (2006)

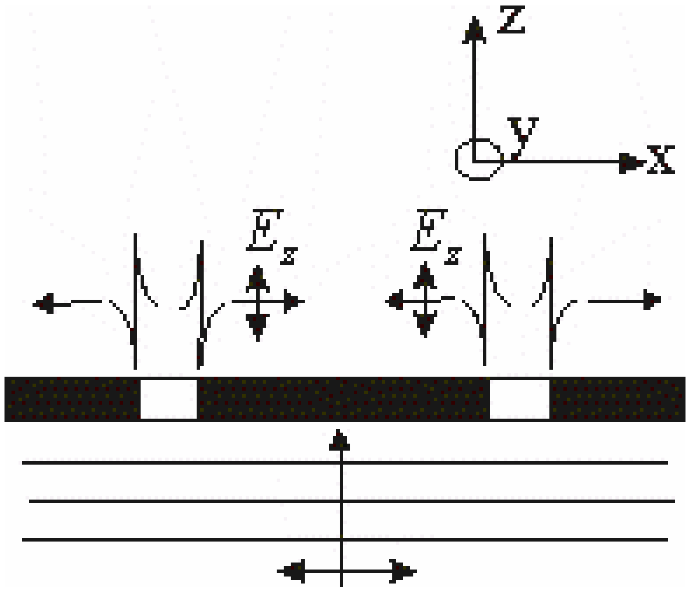
III. Light in Periodic Nano Slits

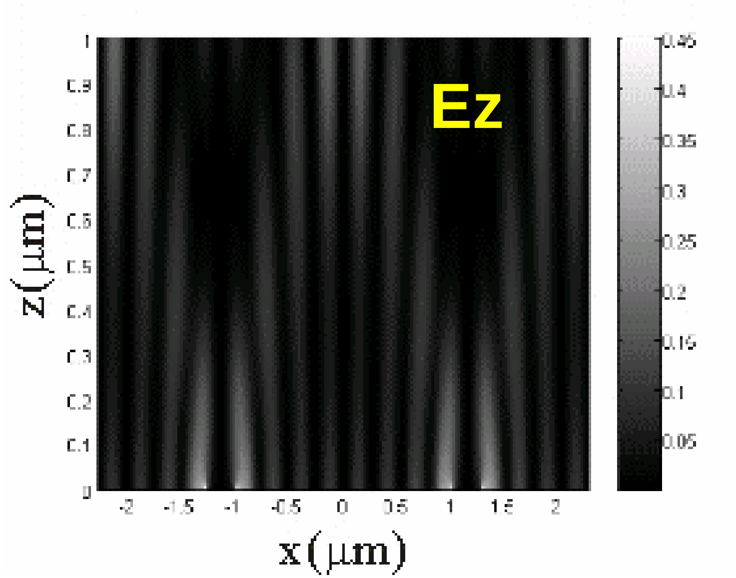


For TM polarized wave, we have Ex, Ez and Hy fields

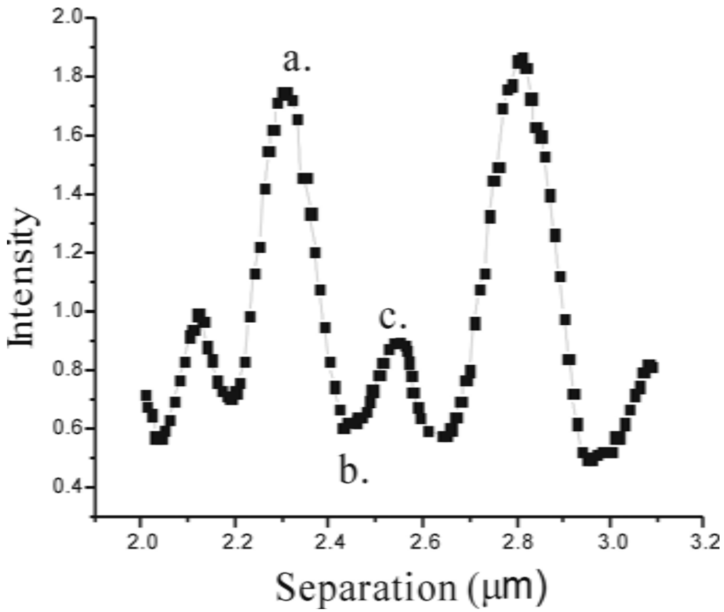








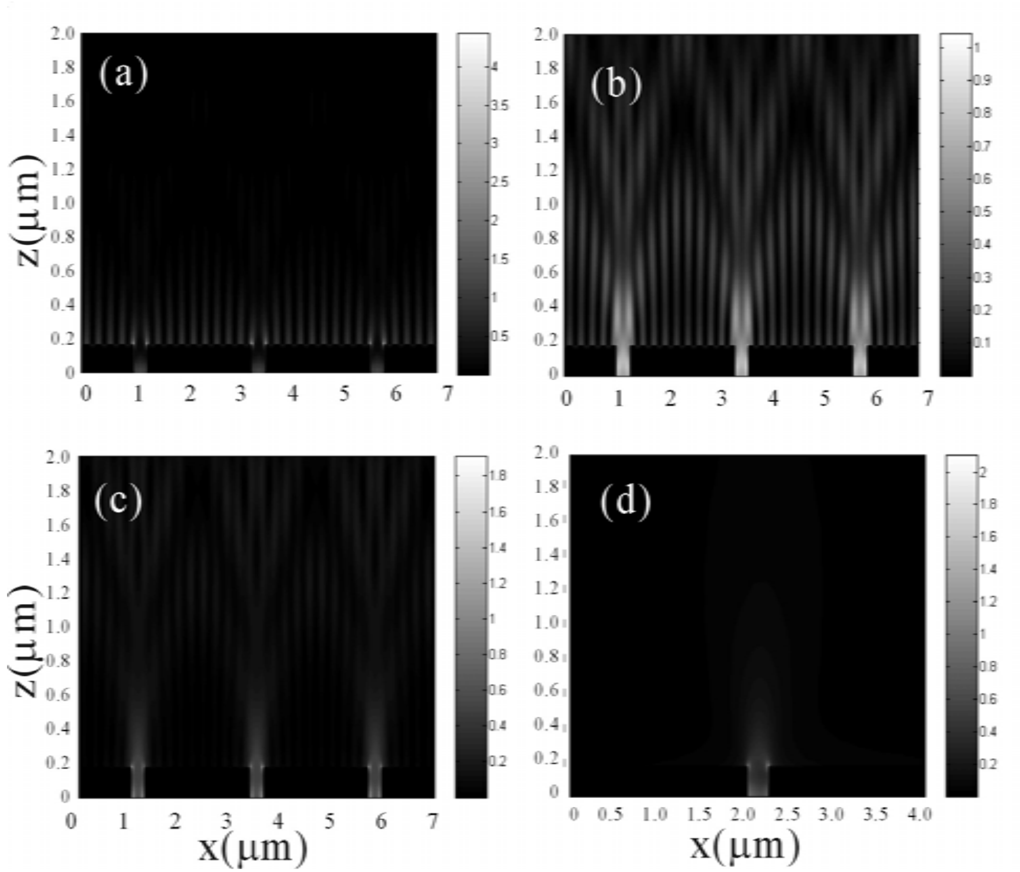
The near field distribution in multiple slits with varied separations

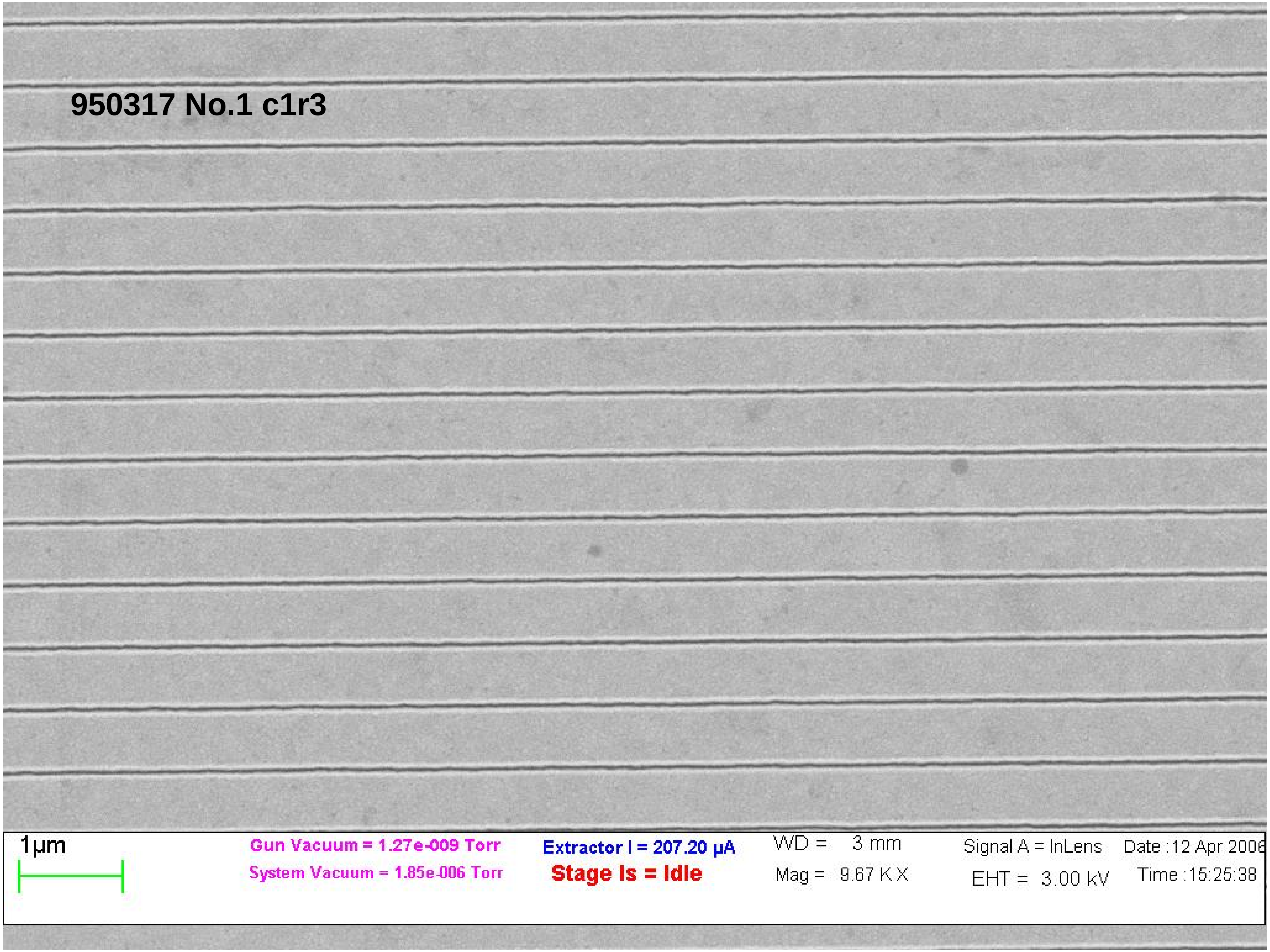


$$n_{eff} = \sqrt{\frac{\varepsilon_m \varepsilon_r}{\varepsilon_m + \varepsilon_r}}$$

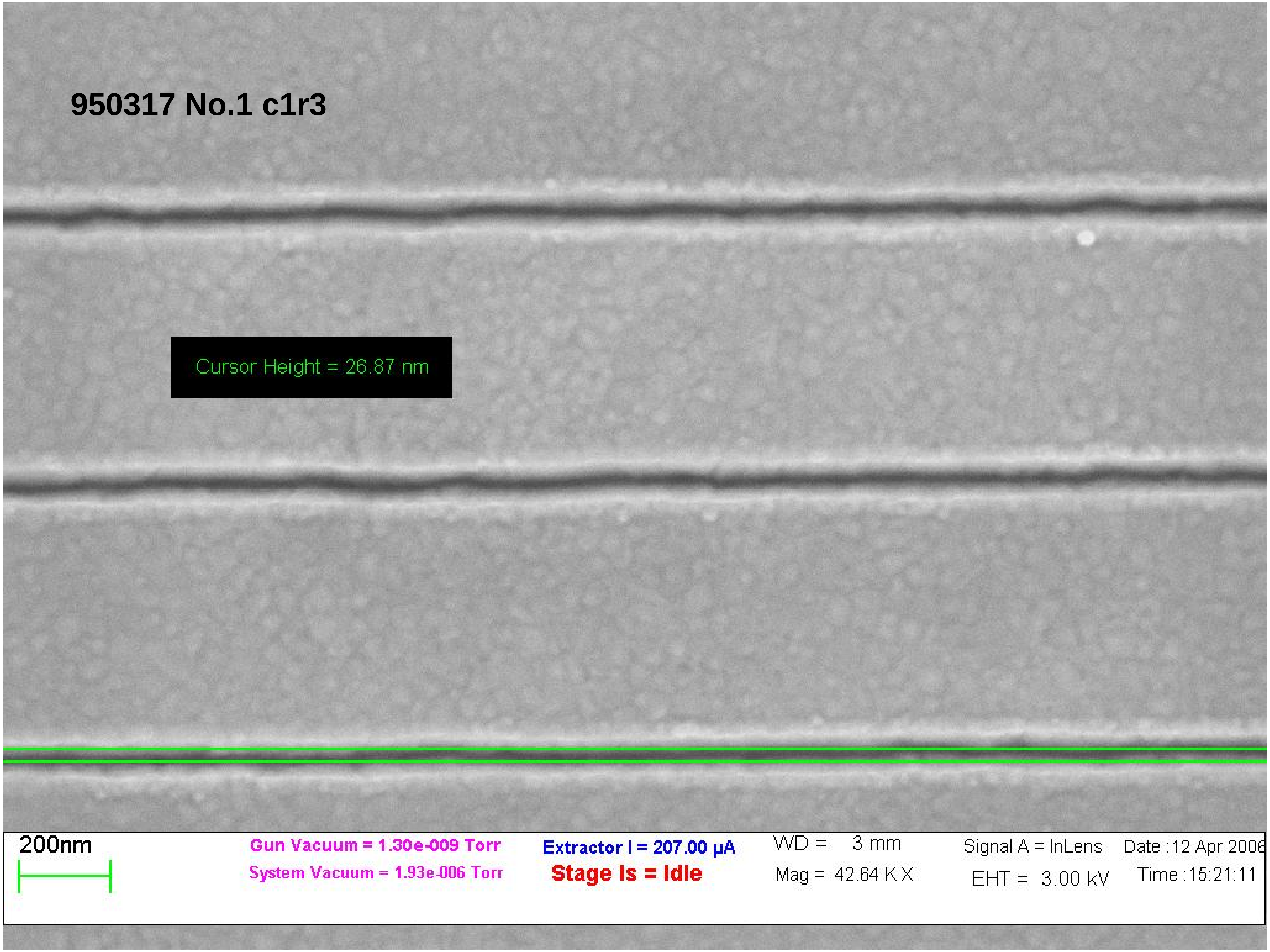
$$\lambda_{spw} = \lambda_0 / n_{eff} = m \times Period$$

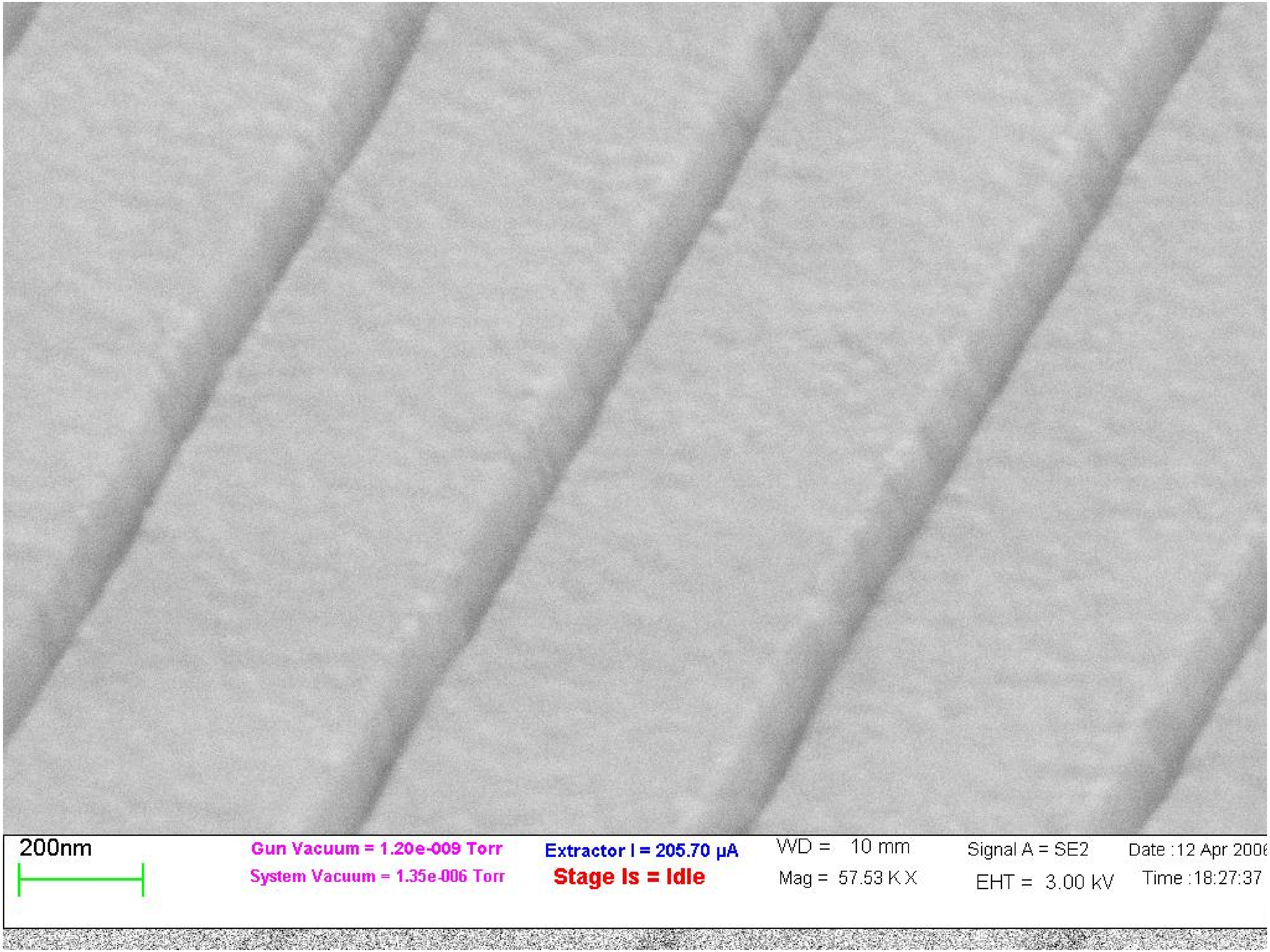
In resonance:



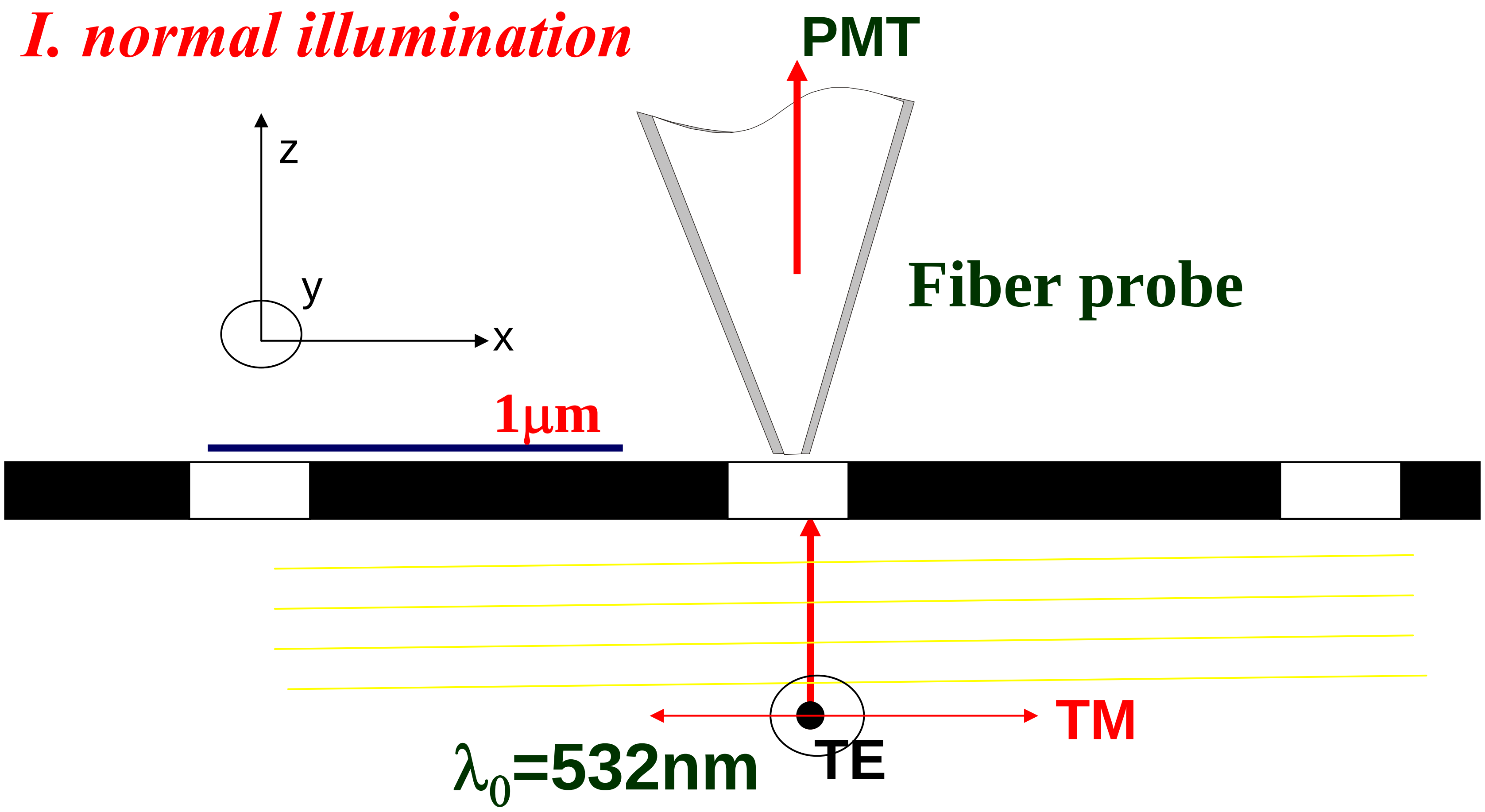

950317 No.1 c1r3
1µm
Gun Vacuum = 1.27e-009 Torr
System Vacuum = 1.85e-006 Torr
Extractor I = 207.20 µA
Stage Is = Idle
WD = 3 mm
Mag = 9.67 K X
Signal A = InLens
EHT = 3.00 kV
Date :12 Apr 2006
Time :15:25:38

950317 No.1 c1r3

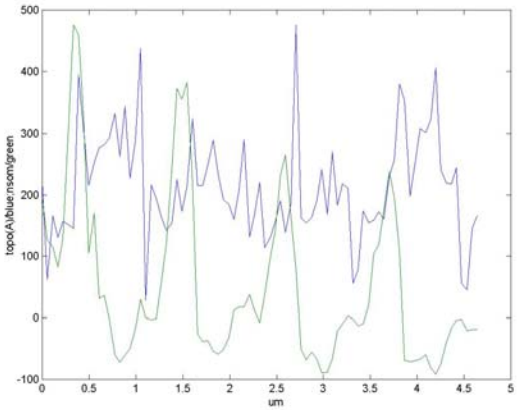



200nm
Gun Vacuum = 1.20e-009 Torr
System Vacuum = 1.35e-006 Torr
Extractor I = 205.70 µA
Stage Is = Idle
WD = 10 mm
Mag = 57.53 K X
Signal A = SE2
EHT = 3.00 kV
Date :12 Apr 2006
Time :18:27:37

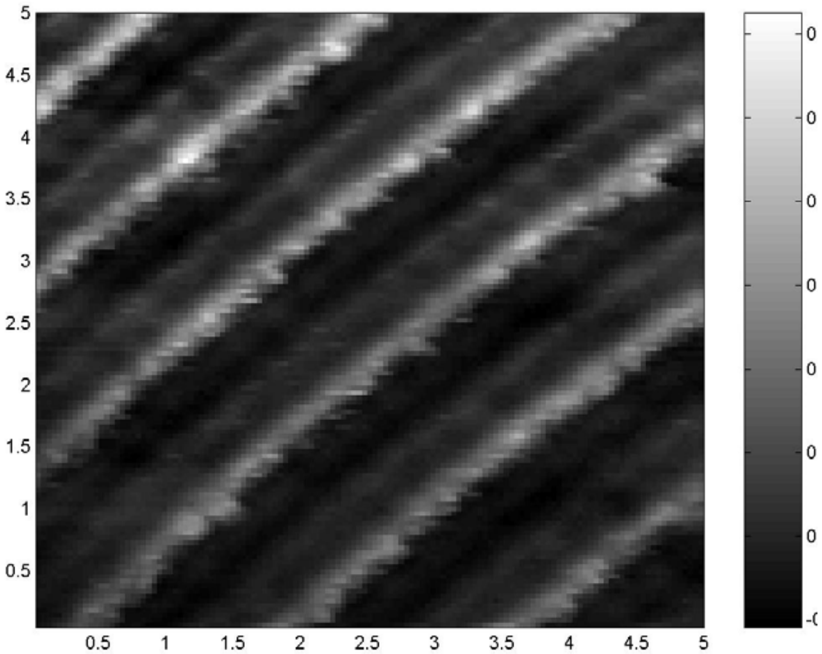
SNOM (or NSOM) in collection mode



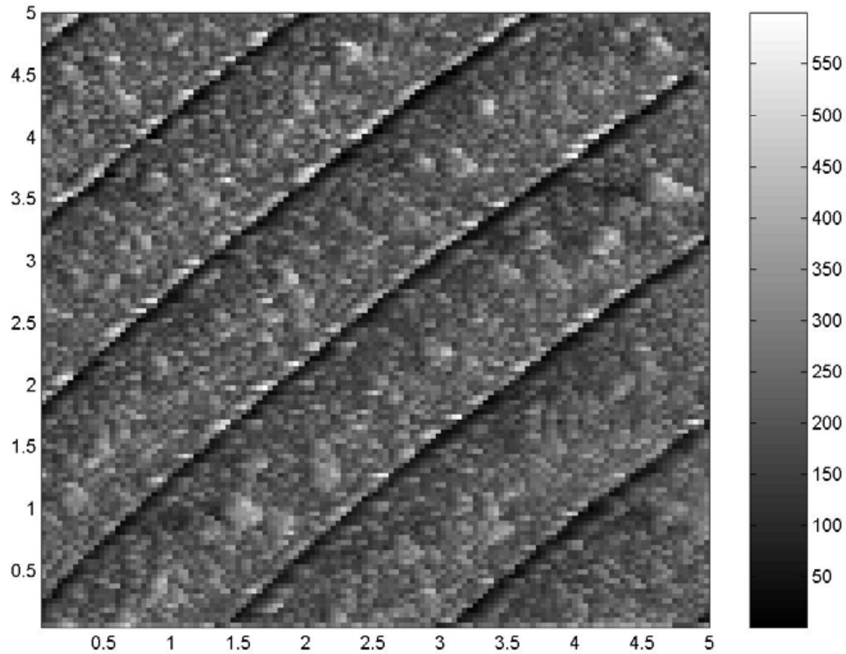
1. Tip/sample regulation by shear-force feedback method
2. Probe made by tapered fiber coated with metal



500
400
300
200
100
0
-100
0 0.5 1 1.5 2 2.5 3 3.5 4 4.5 5
um

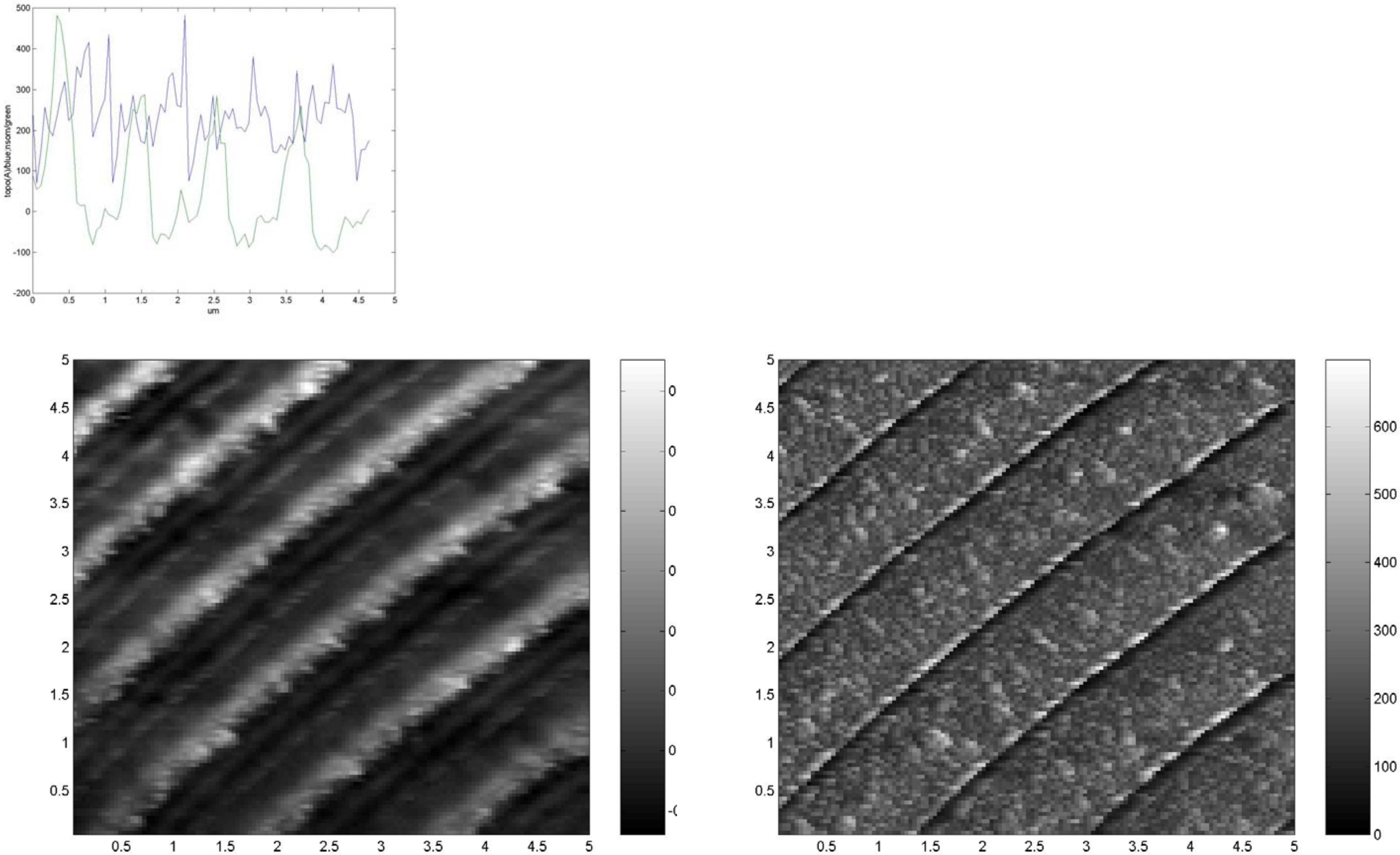


5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0.5 1 1.5 2 2.5 3 3.5 4 4.5 5

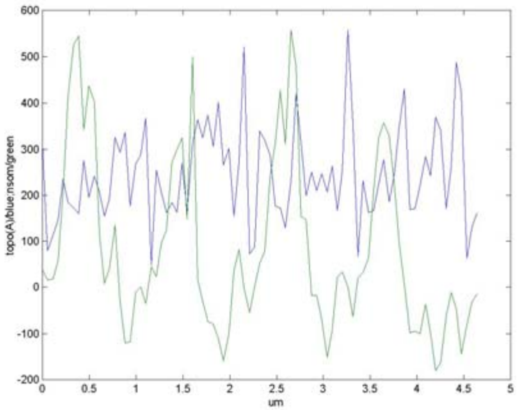


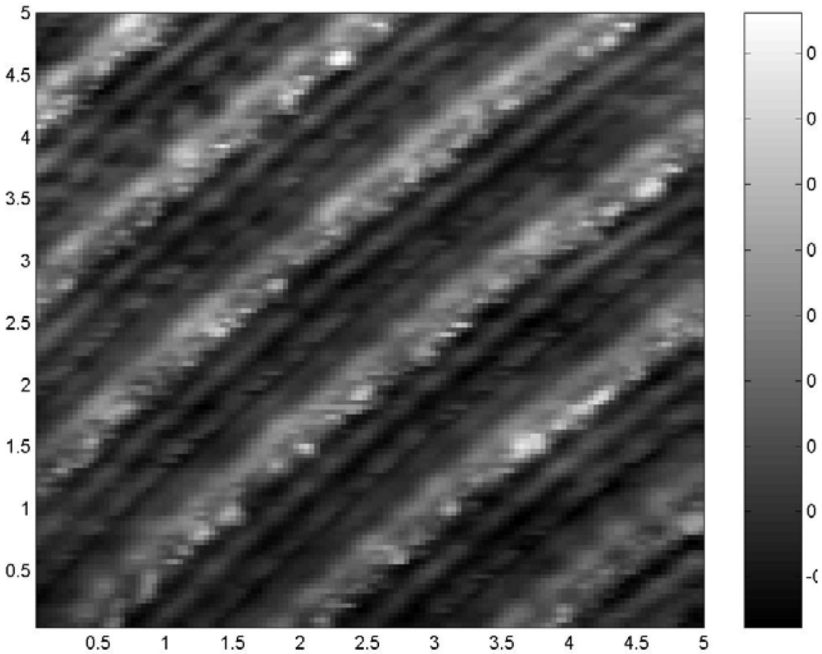
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0.5 1 1.5 2 2.5 3 3.5 4 4.5 5
550
500
450
400
350
300
250
200
150
100
50

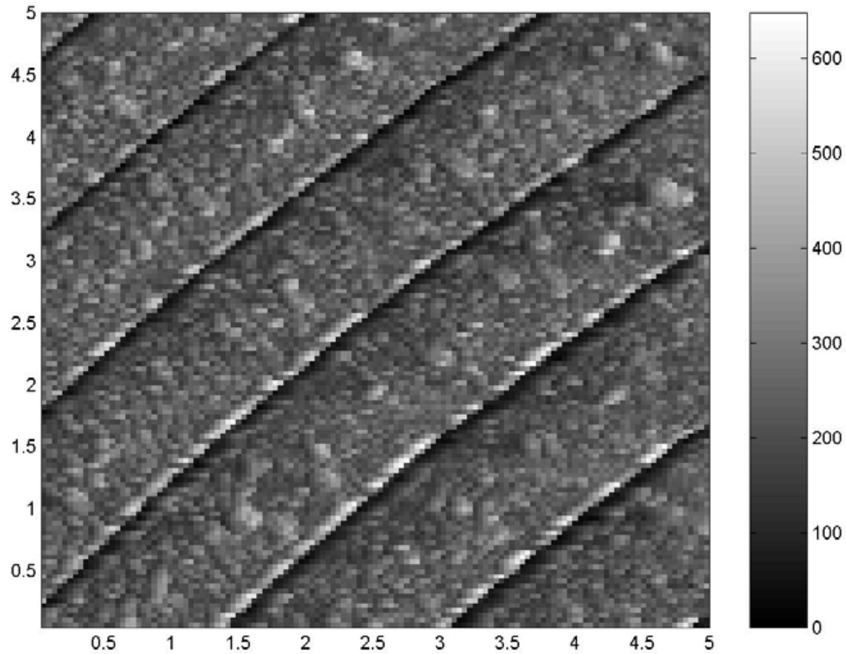
TE (pol=0)



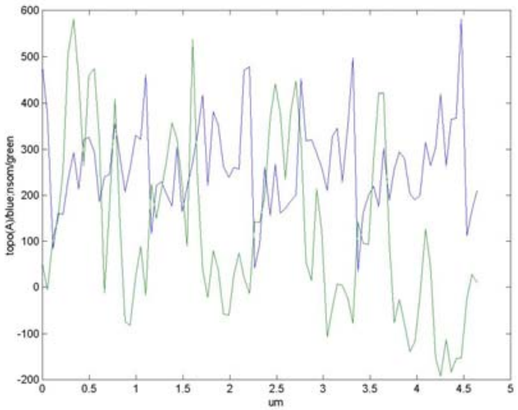
Pol=20

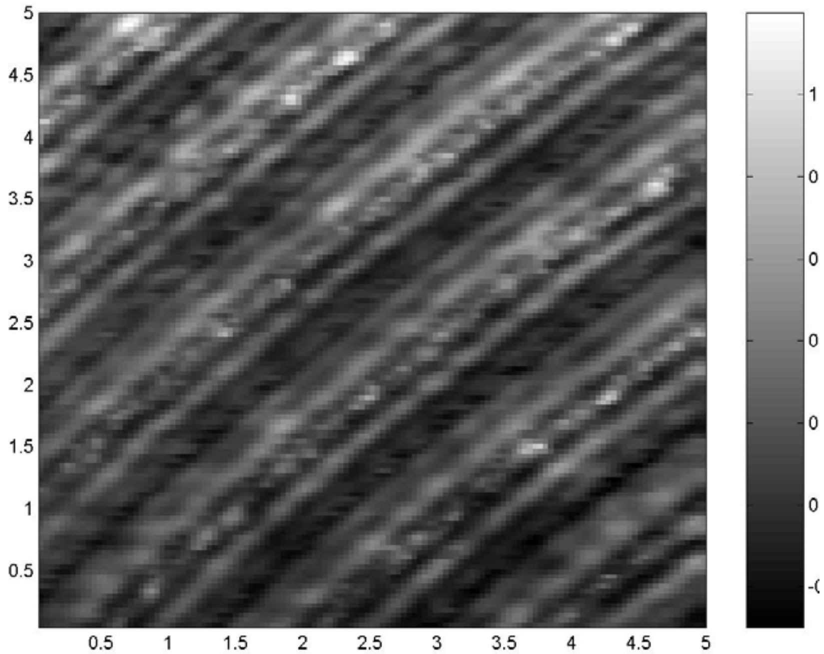


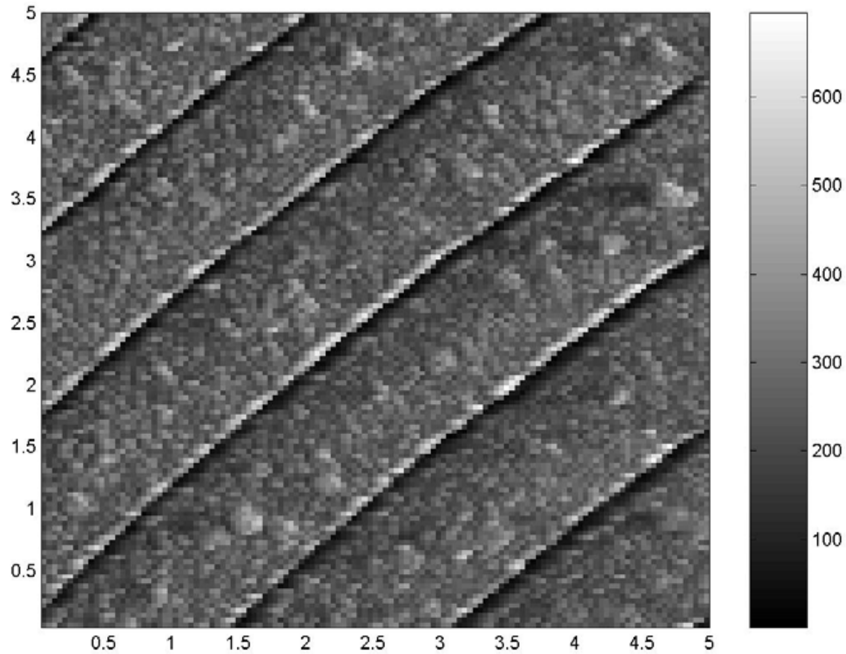




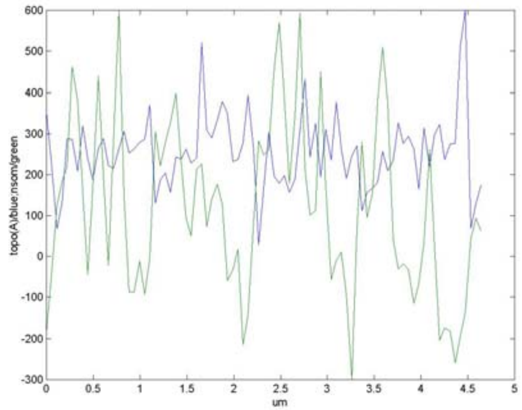
Pol=40

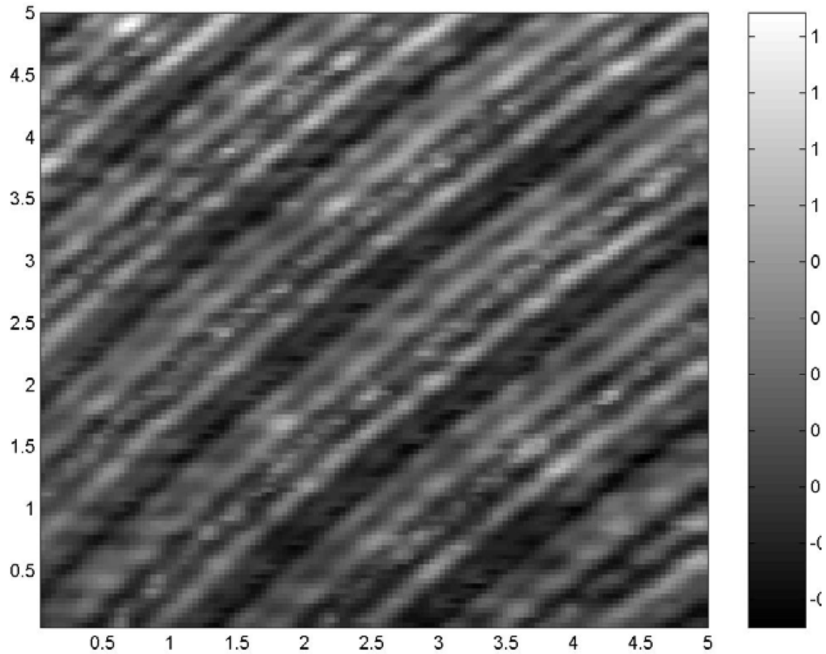


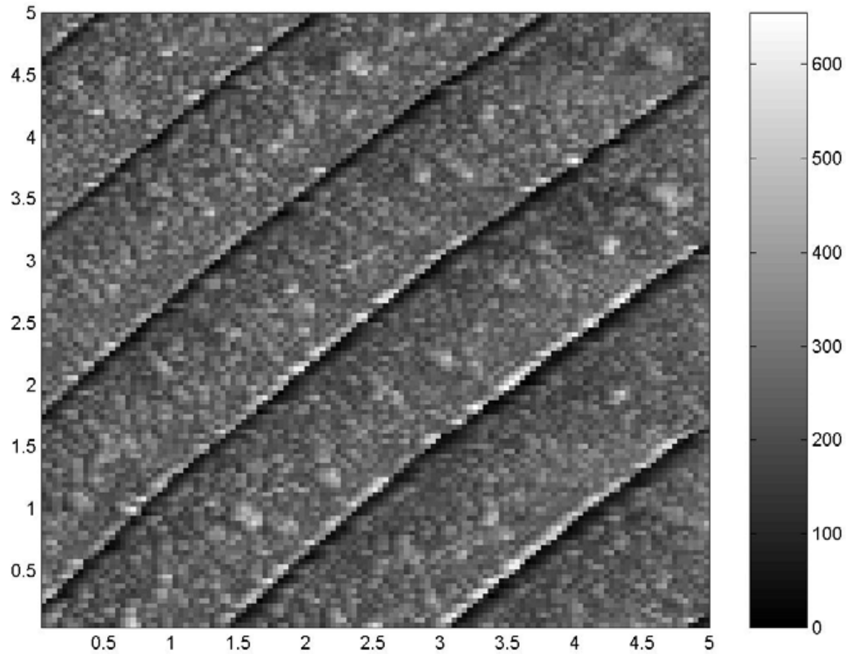




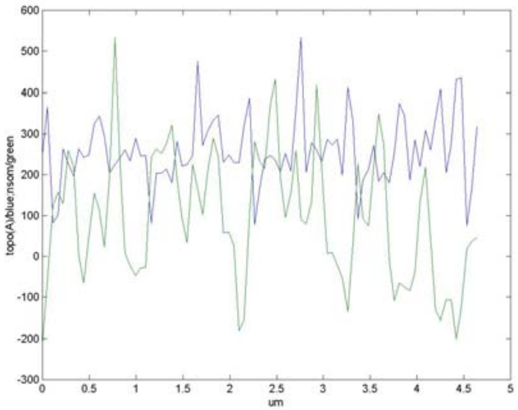
Pol=60

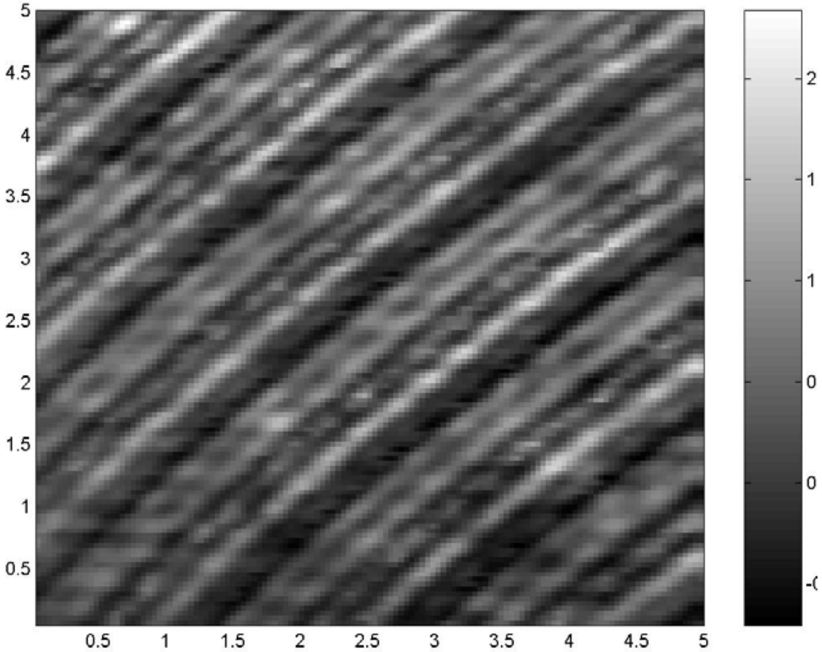

topo(A),blue;nsom/green
um
600
500
400
300
200
100
0
-100
-200
-300
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5

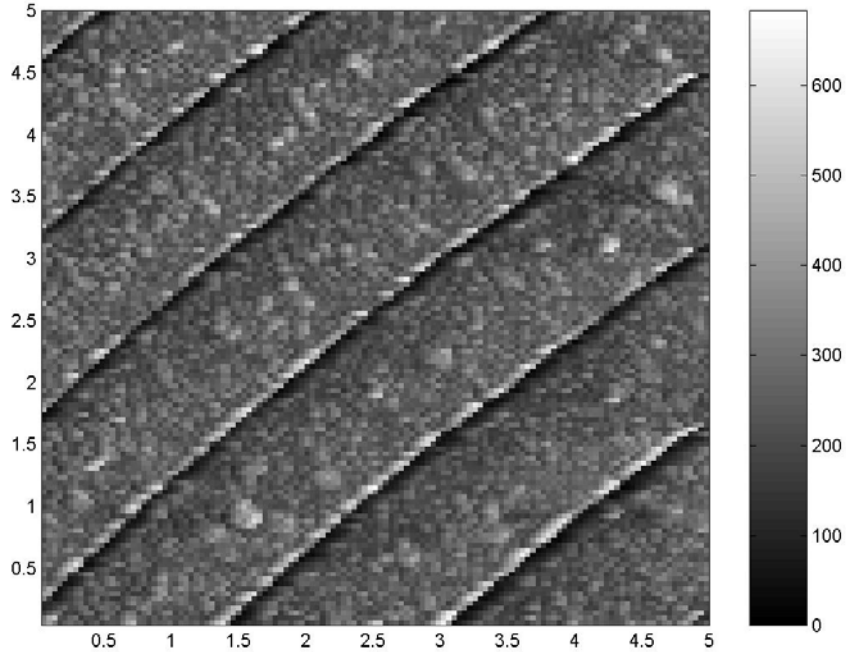

5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5


5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
600
500
400
300
200
100
0

Pol=80

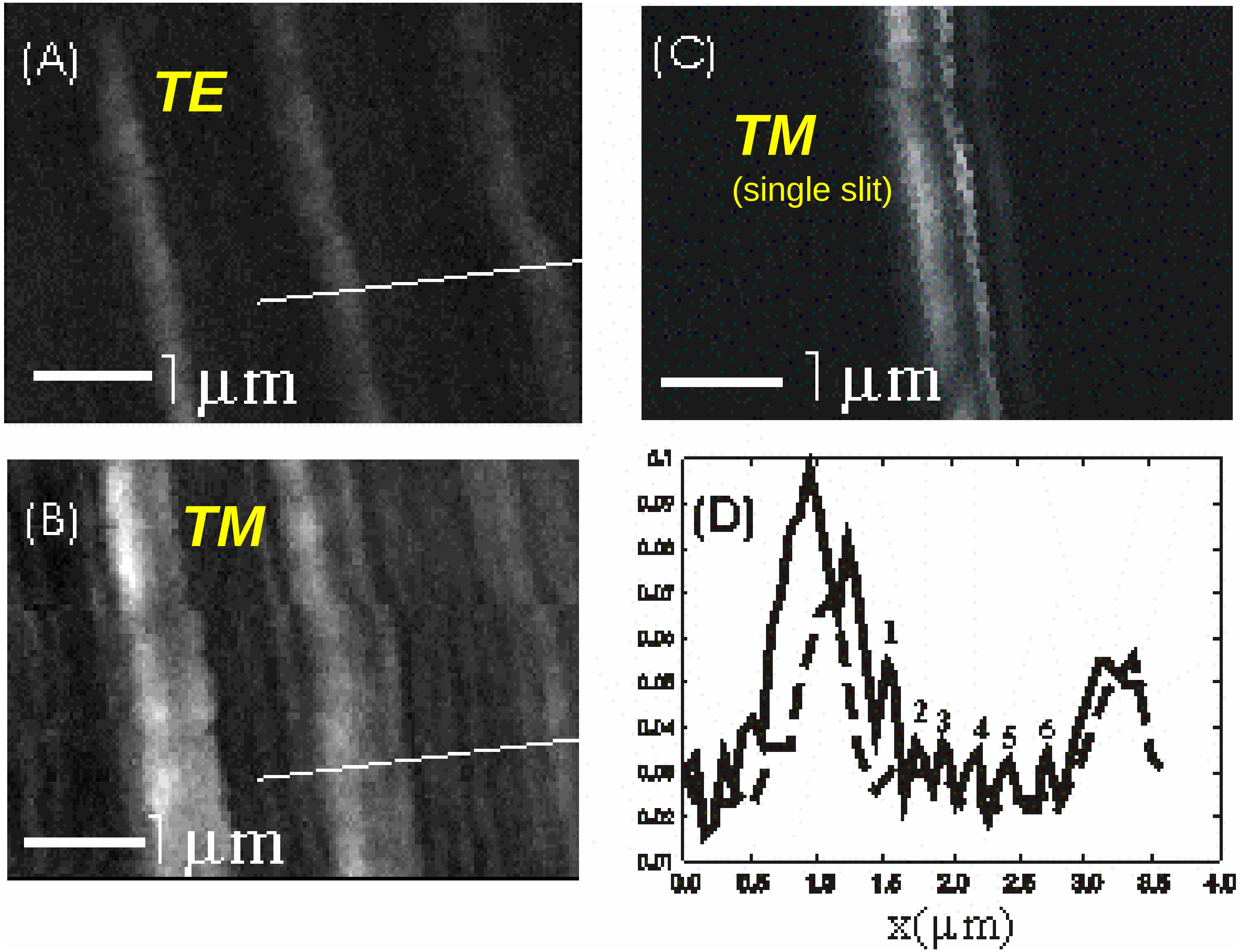






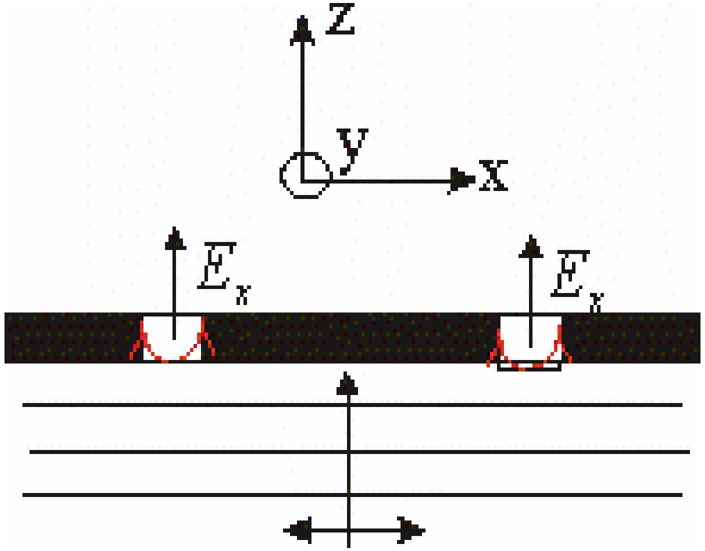
Pol=100 (~TM mode)

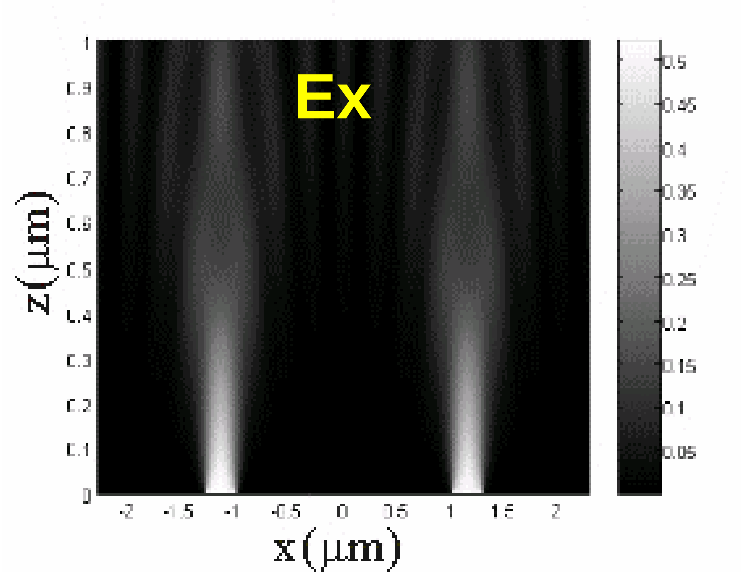
Light in multiple nano slits
NSOM Results

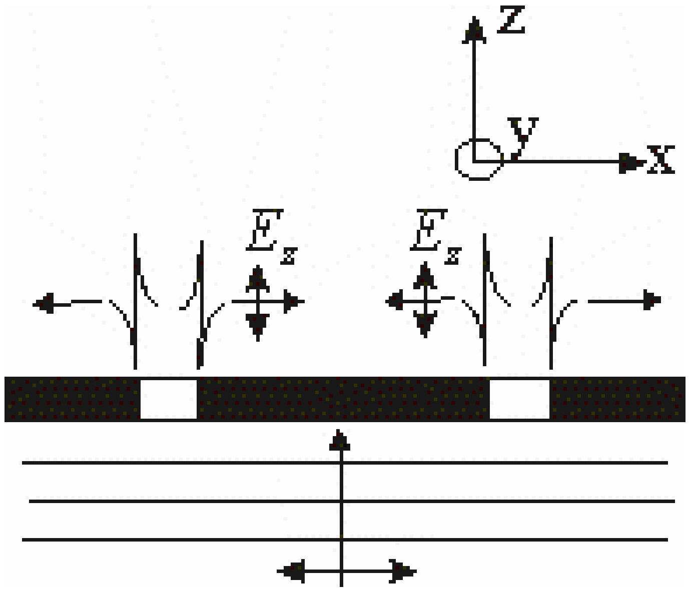


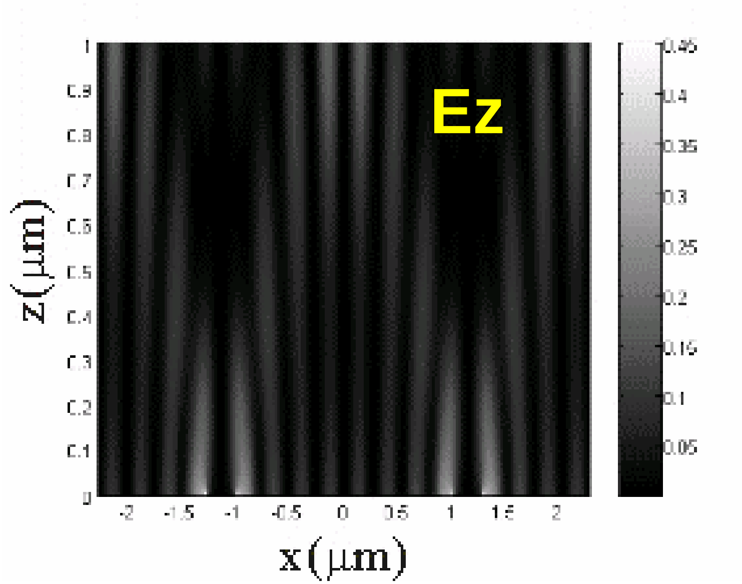
P.K. Wei, Opt. Com. 2005

For TM polarized wave, we have Ex, Ez and Hy fields

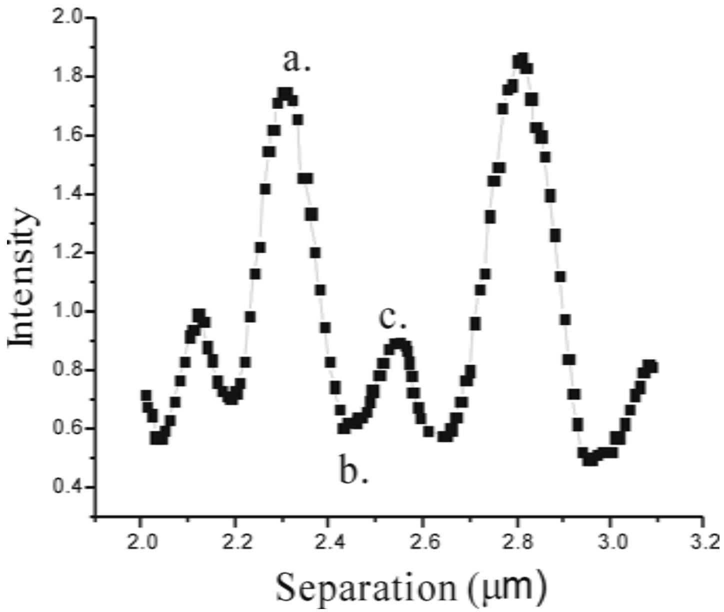








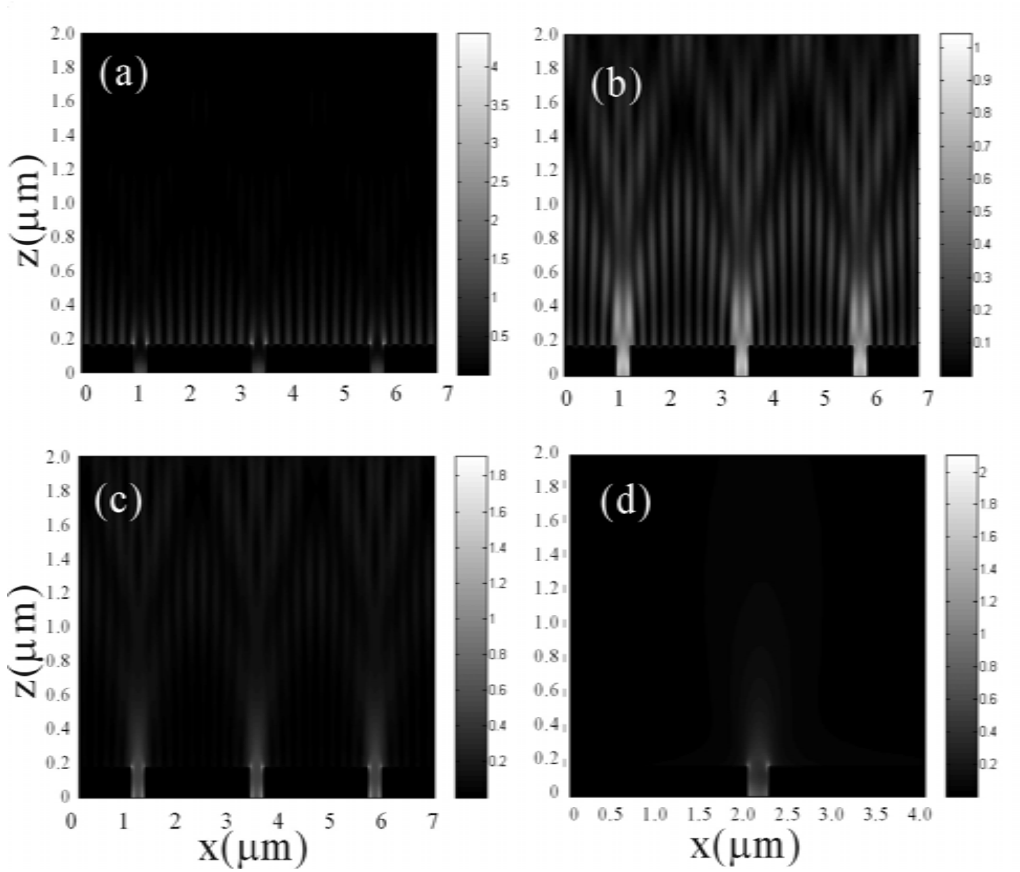
The near field distribution in multiple slits with varied separations



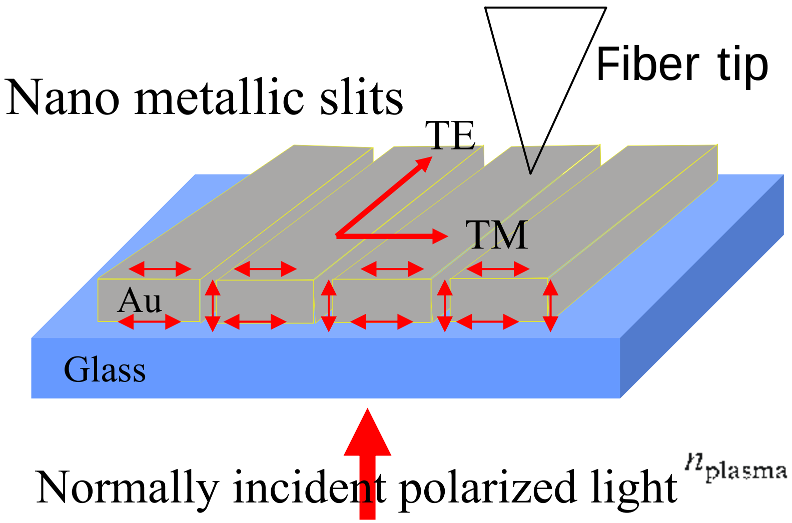
$$n_{eff} = \sqrt{\frac{\varepsilon_m \varepsilon_r}{\varepsilon_m + \varepsilon_r}}$$

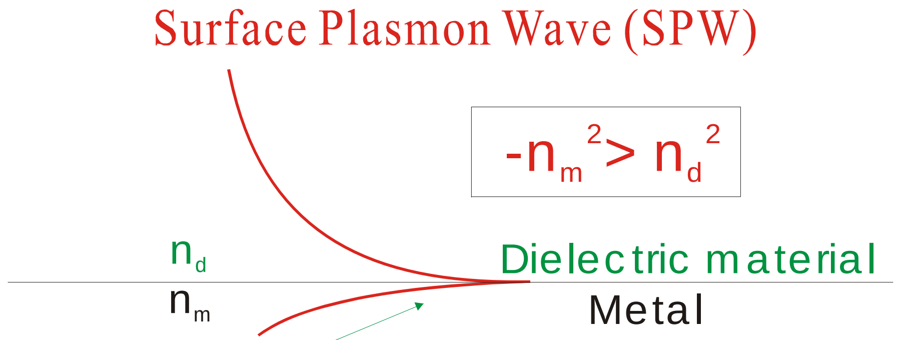
$$\lambda_{spw} = \lambda_0 / n_{eff} = m \times Period$$

In resonance:



Optical Near-Field of Surface Plasmon Wave on Au Surface

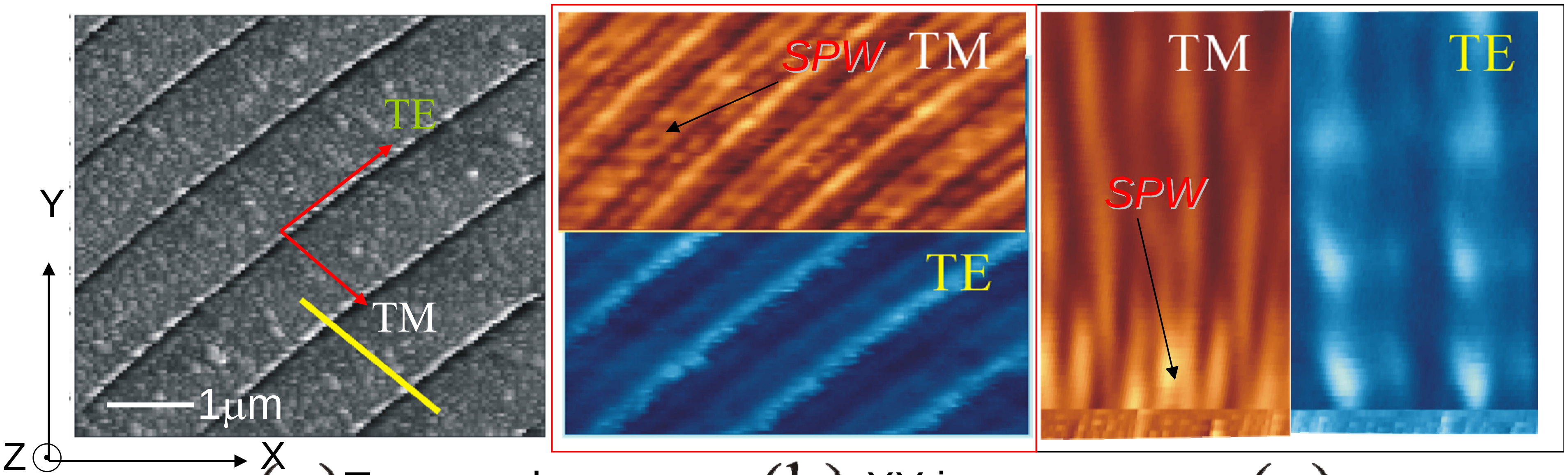




$$n_{\text{plasma}} = \frac{\beta}{k_0} = \sqrt{\frac{n_d^2 n_m^2}{n_d^2 + n_m^2}}$$

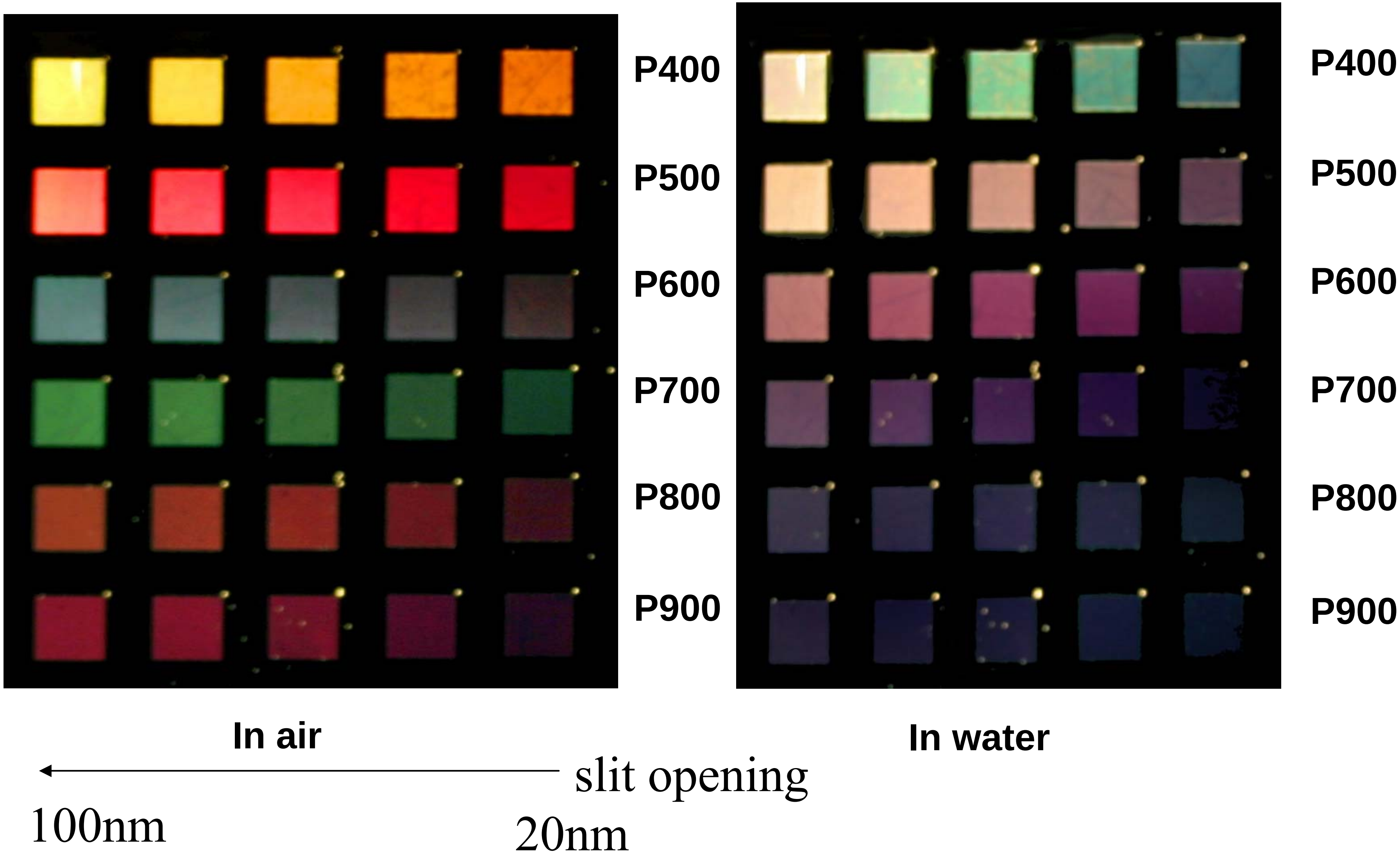
$$E_{\text{metal}} \propto \exp(-\sqrt{n_{\text{plasma}}^2 - n_m^2} \cdot k_0 x)$$

$$E_{\text{dielectric}} \propto \exp(-\sqrt{n_{\text{plasma}}^2 - n_m^2} \cdot k_0 x)$$



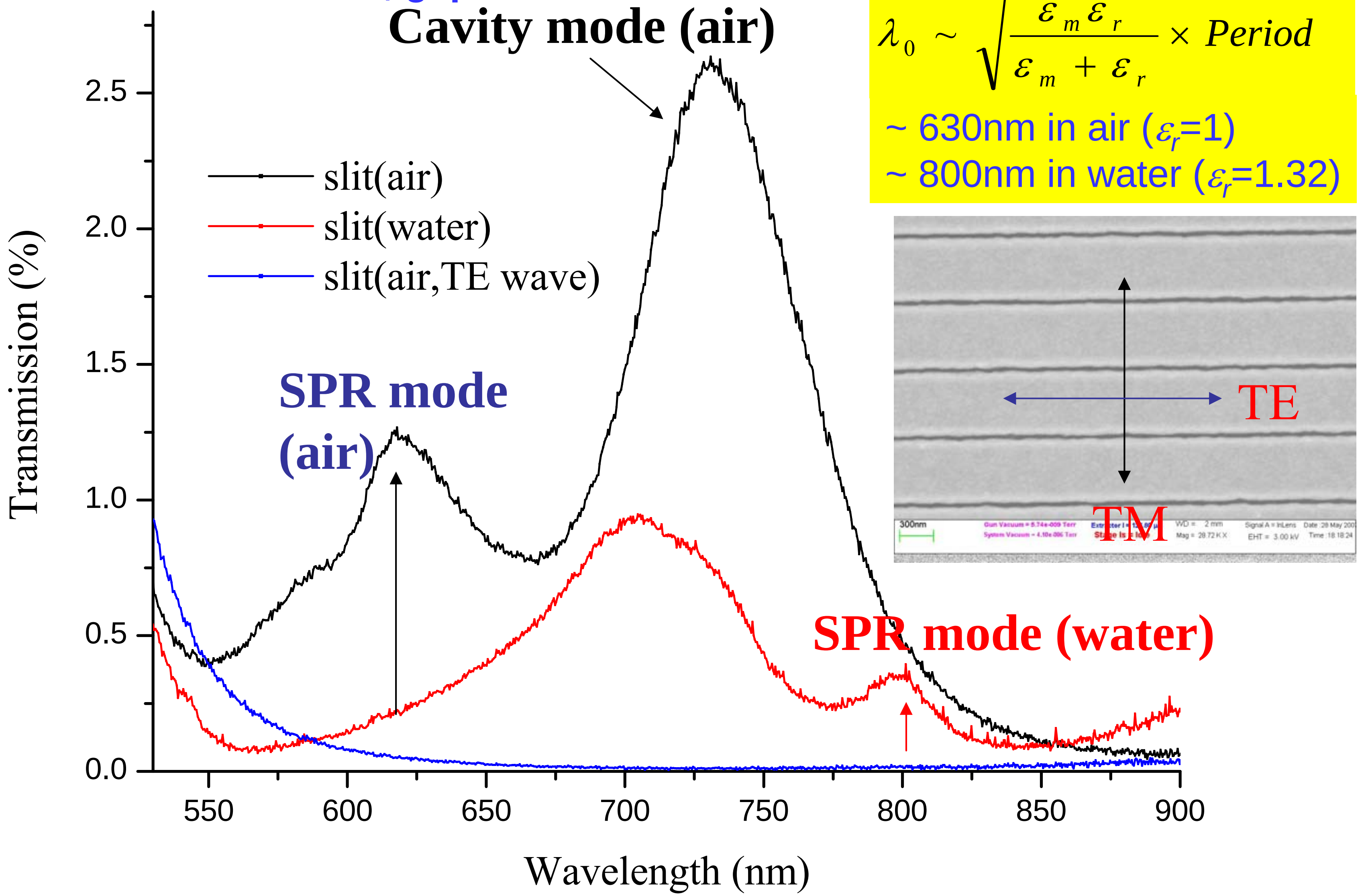
(a) Topography (b) XY image (c) XZ image

Colors of nanoslit arrays with different periods and slit openings



Transmission Spectra of a nanoslit array

Period =600nm, gap =60nm

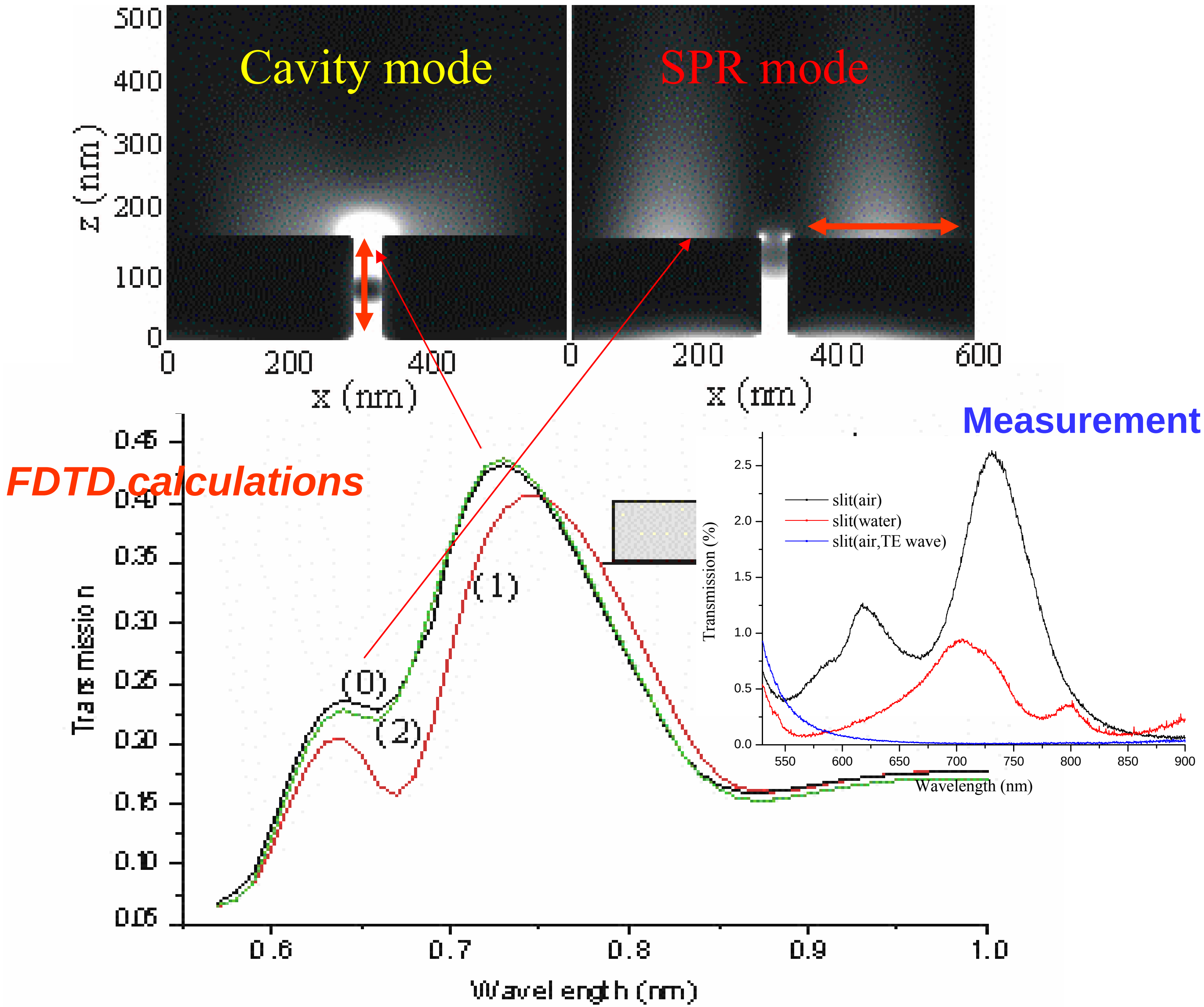


For fundamental SPR mode

$$\lambda_0 \sim \sqrt{\frac{\varepsilon_m \varepsilon_r}{\varepsilon_m + \varepsilon_r}} \times Period$$

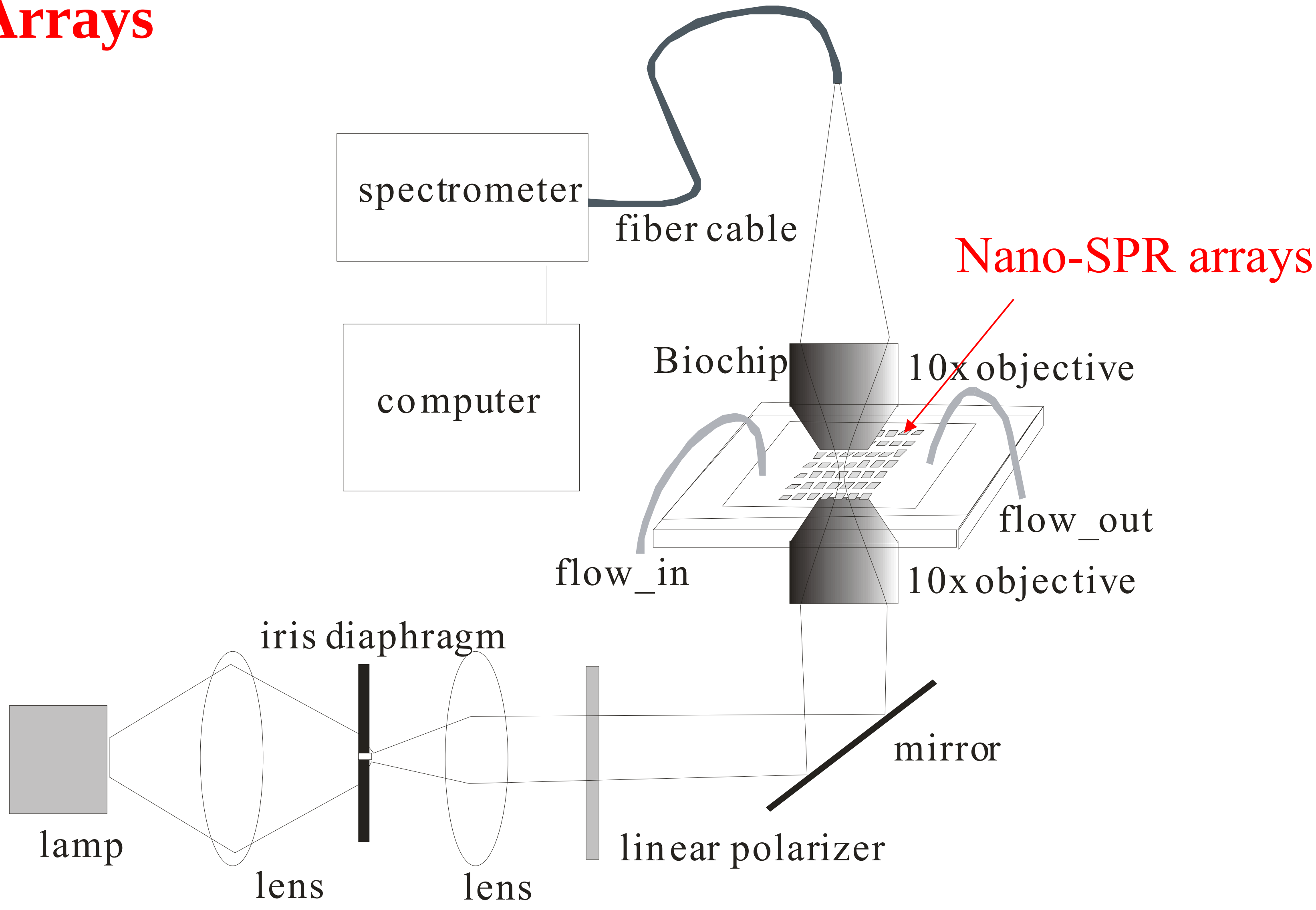
~ 630nm in air (ε_r=1)

~ 800nm in water (ε_r=1.32)

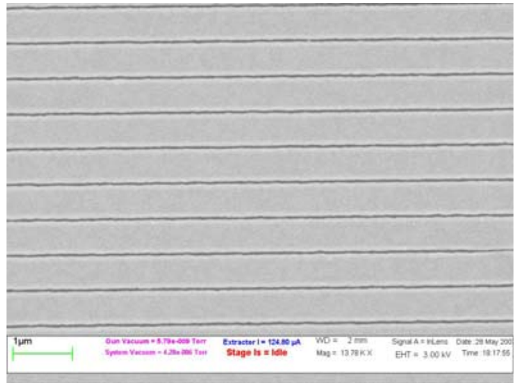


P. K. Wei, Appl. Phys. Lett. 2007

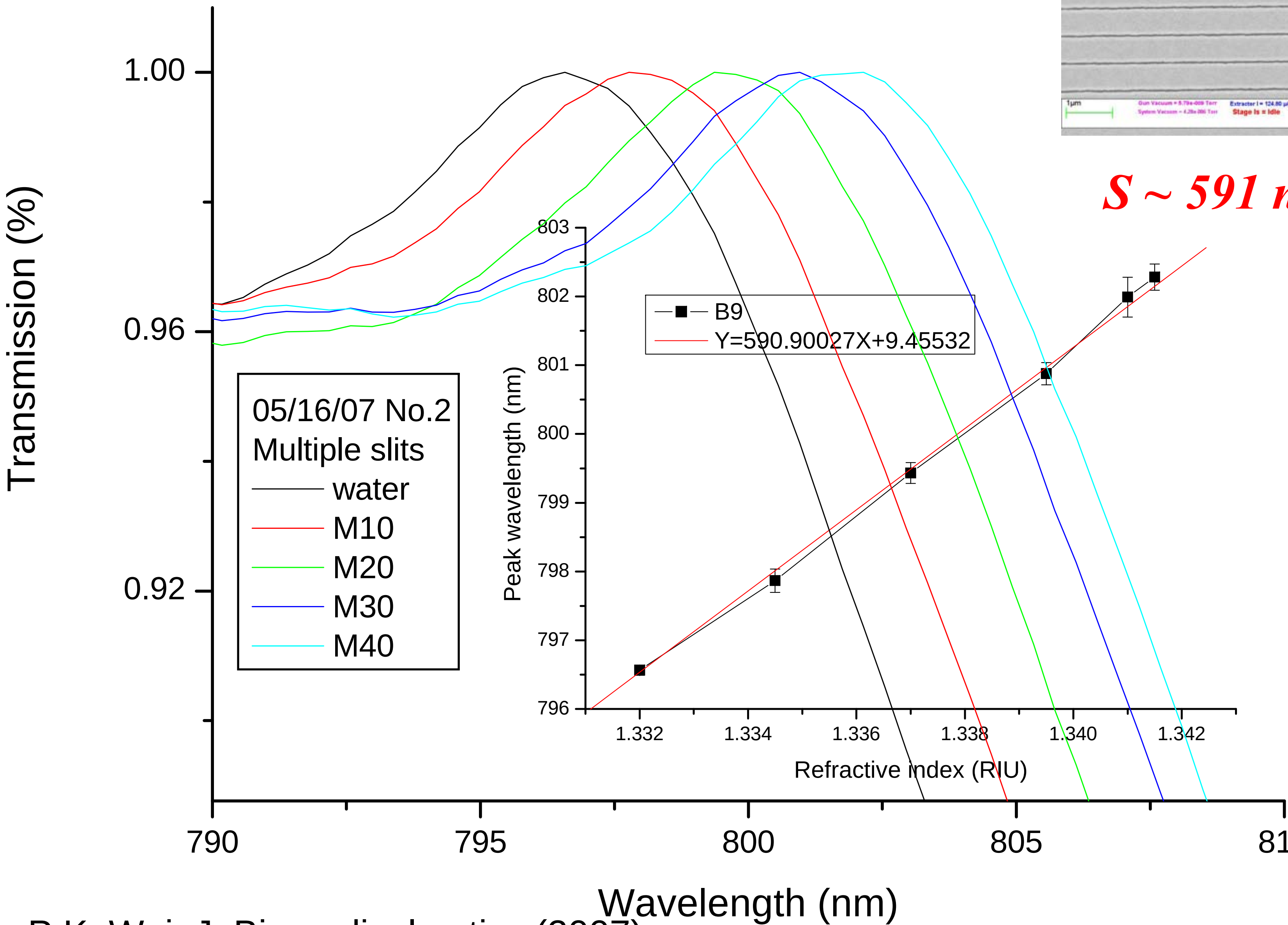
Optical Setup for the Measurement of Nano-SPR Arrays



Sensitivity of a nanoslit array



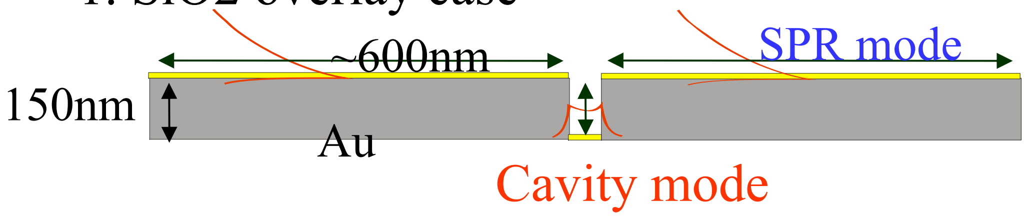
S ~ 591 nm/RIU

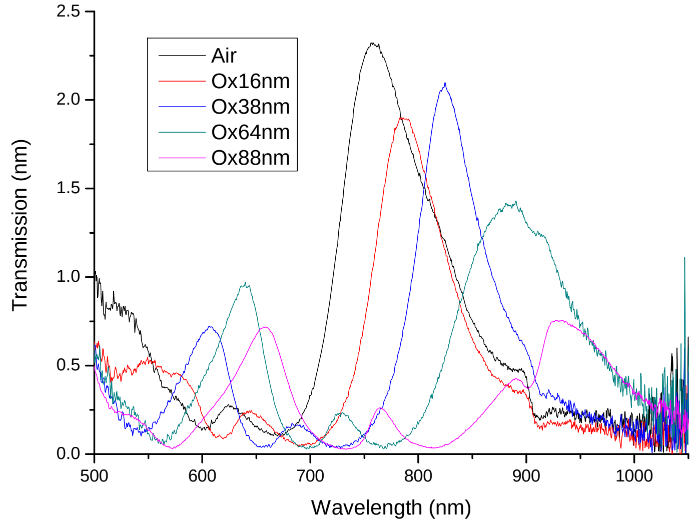


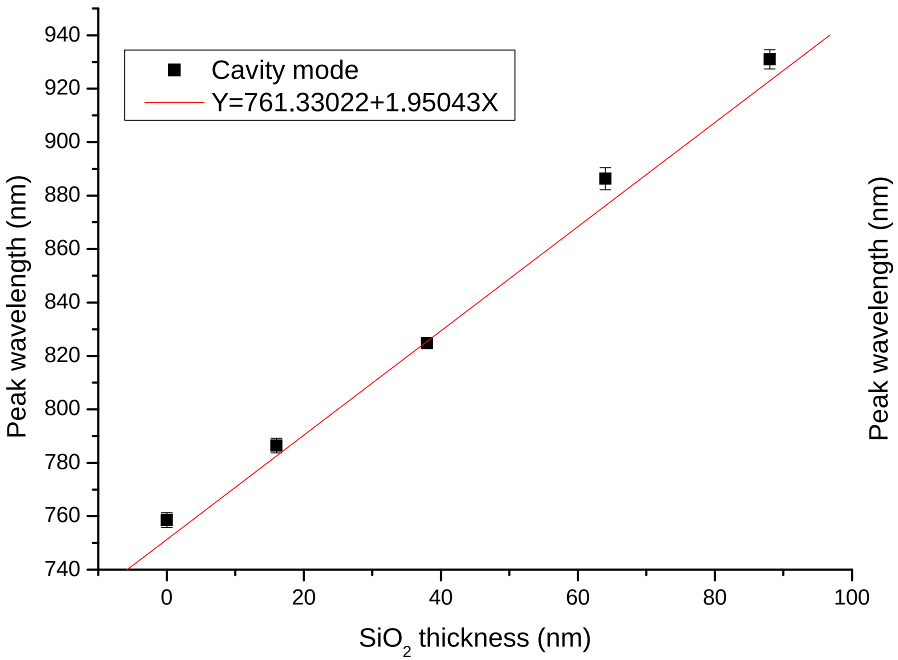
P.K. Wei, J. Biomedical optics (2007)

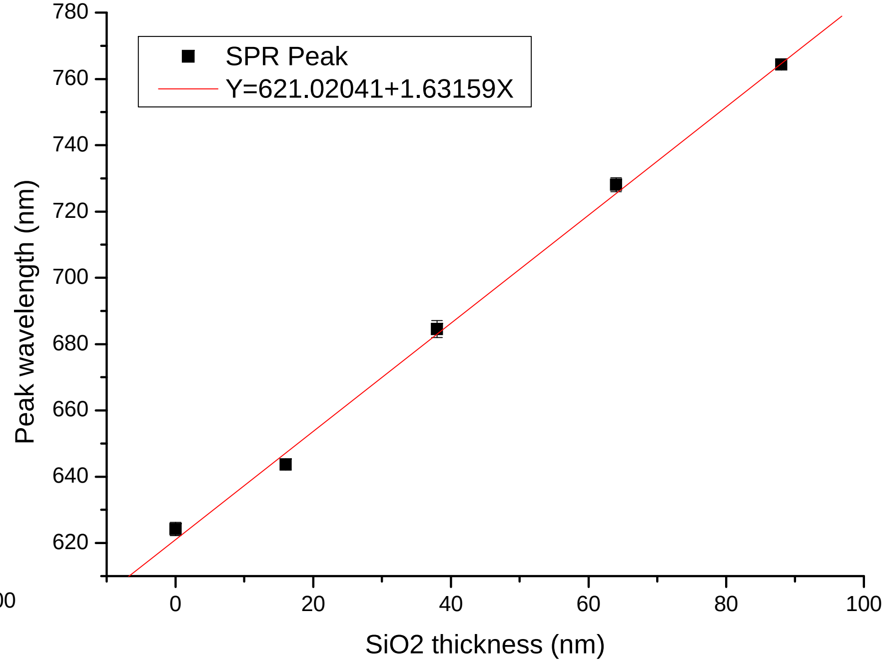
SPR mode vs. Cavity mode

1. SiO2 overlay case

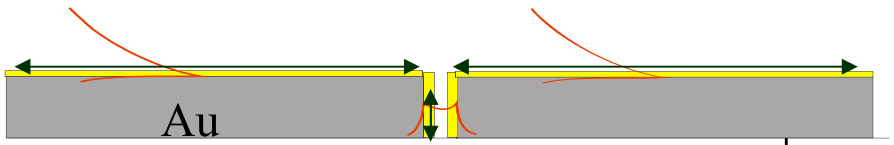






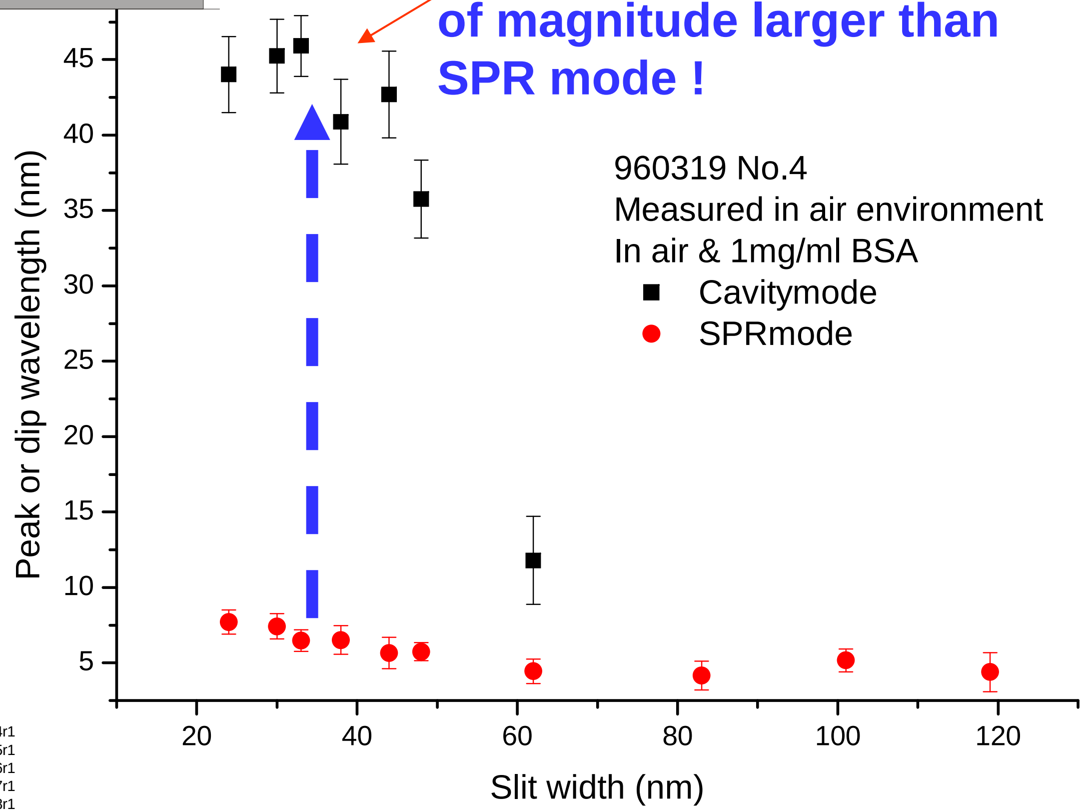


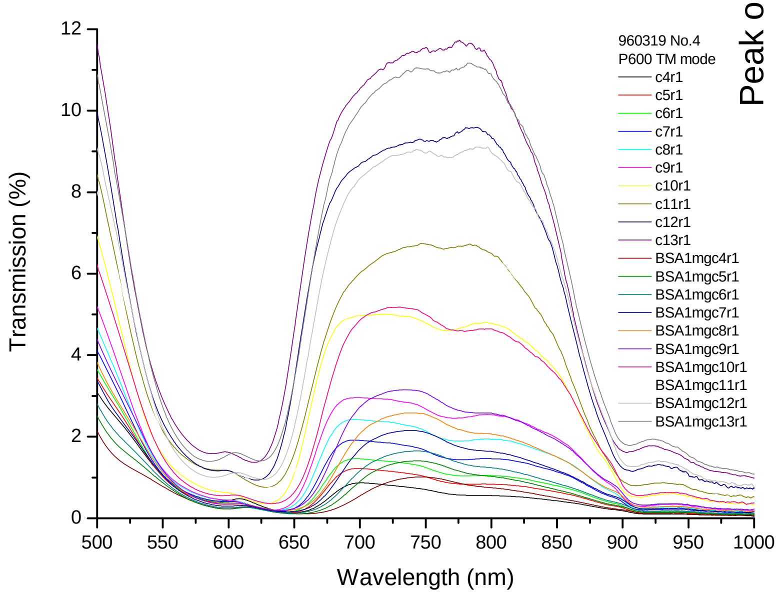
2. monolayer case



Nanoslit array (Film thickness: 110 nm)
Measured in air environment
In 10 mM PBS and 1 mg/ml BSA

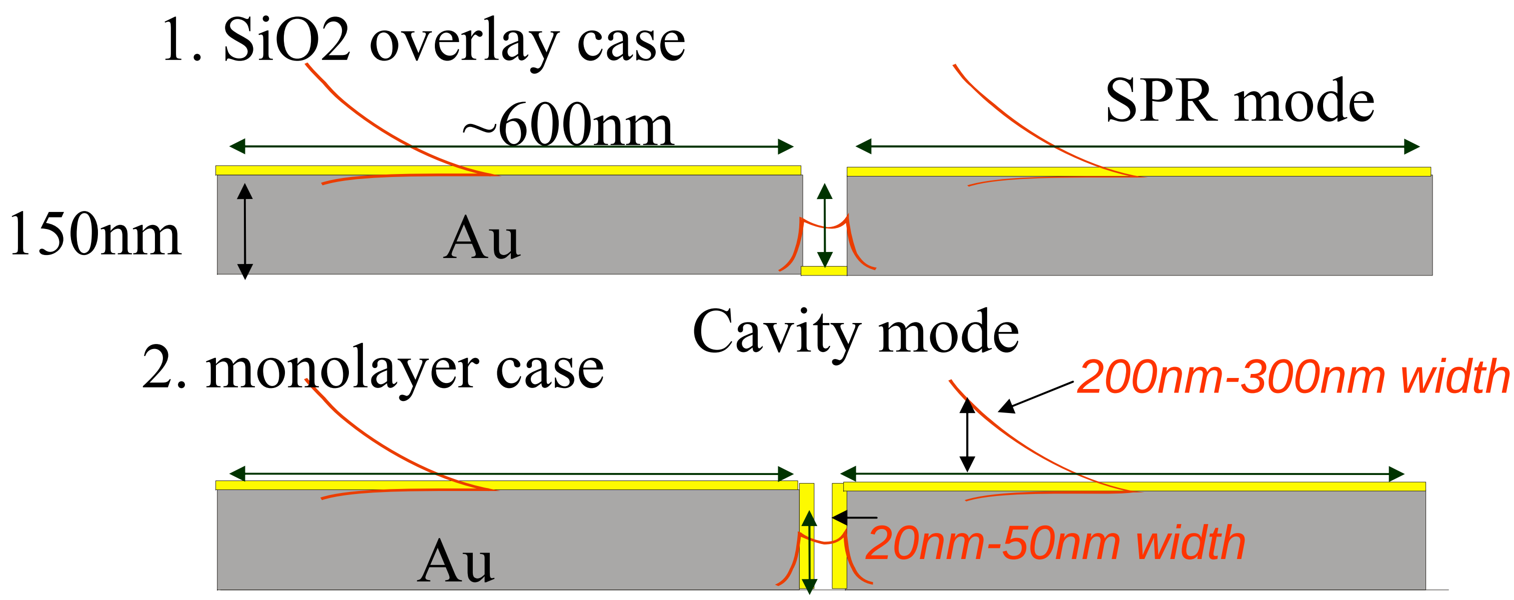
Cavity mode is one order of magnitude larger than SPR mode !





Kuang-Li Lee, Way-Seen Wang and Pei-Kuen Wei,*,"Sensitive Label-Free Biosensors by Using Gap Plasmons in Gold Nanoslits", *Biosensors and Bioelectronics* (2008)

Discussion



For unfilled outside medium, the sensitivity is modified as

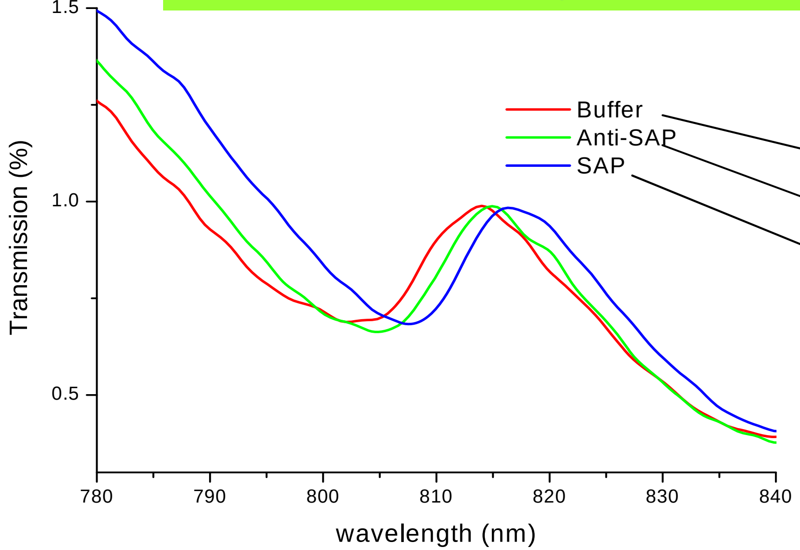
$$S = \frac{\Delta\lambda_{max}}{\Delta n} \sim \Gamma W\,(nm/RIU)$$

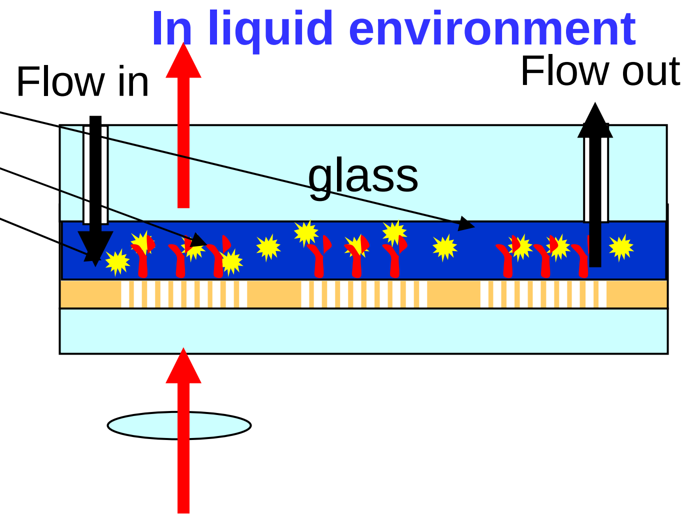
W= size of plasmonic wave

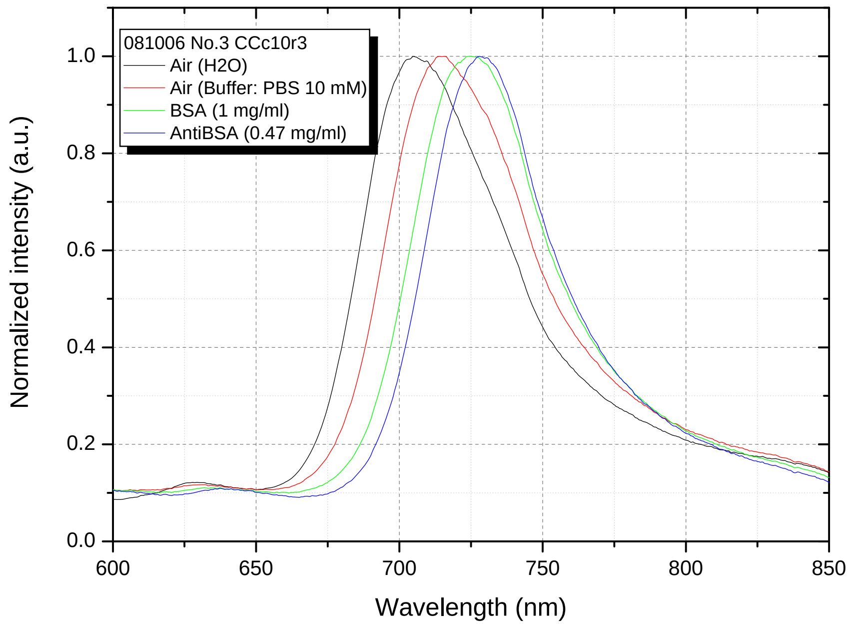
Γ is the overlap integral between the mode profile and the medium distribution. Obviously, the cavity mode has larger Γ, and its value increased with the decrease of gap width.

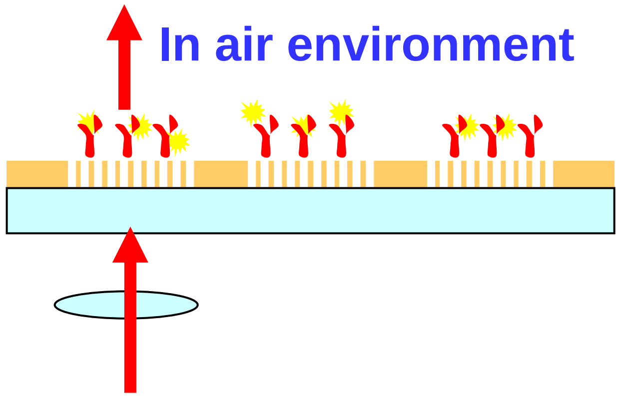
Some Applications

1: Antibody-antigen interaction in water or air environment





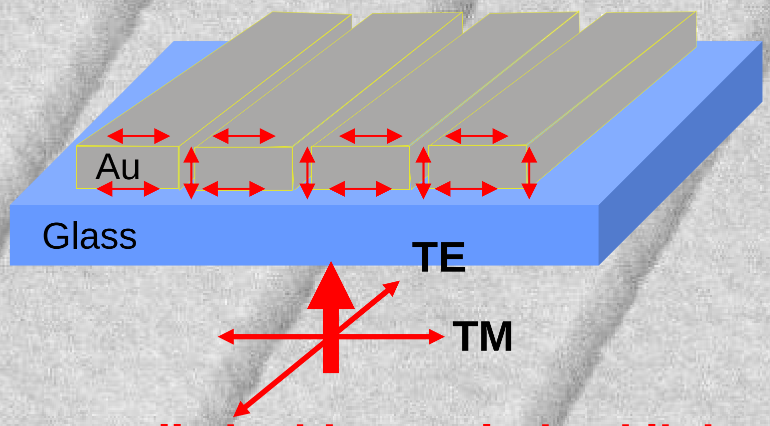


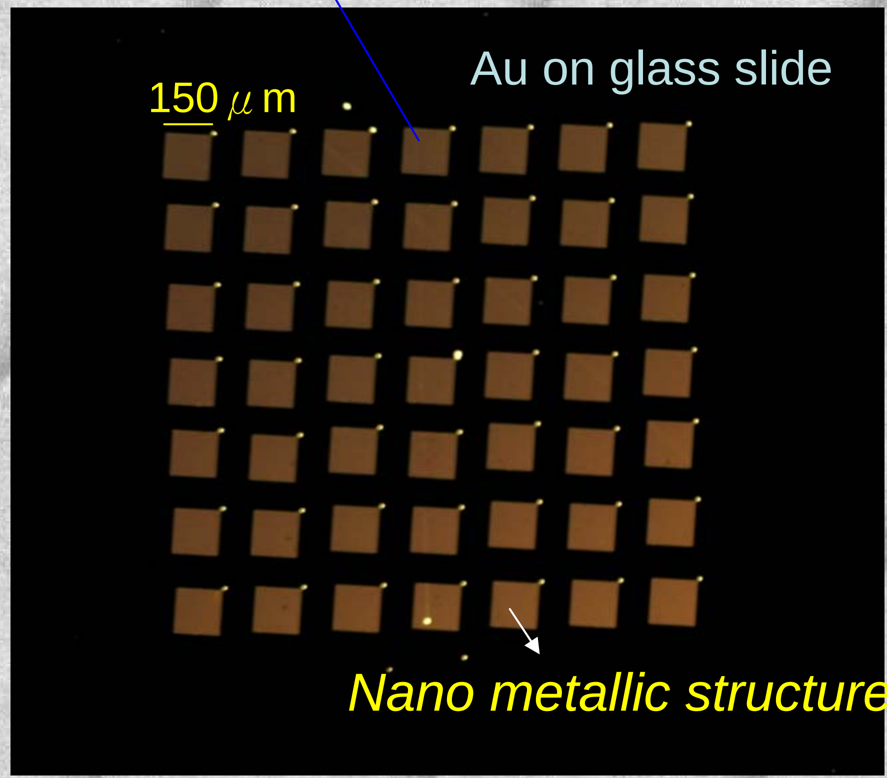


microarray SPRchip

- Label-Free
- High surface sensitivity
- High throughput
- Simple in optical detection
- Water environment

Nano metallic slits





Normally incident polarized light

200nm | Gun Vacuum = 1.20e-009 Torr | System Vacuum = 1.34e-006 Torr | Extractor I = 205.70 µA | Stage Is = Idle | WD = 10 mm | Mag = 30.19 K X | Signal A = SE2 | EHT = 3.00 kV | Date :12 | Time :1

Conclusions

- **Surface plasmons are generated in nanometer metallic gaps.**
- **Using plamonsic effect (SPR or LSR) in a metallic nano-gap. It has the advantages of**

(1) High sensitivity

(2) Small sample volume

(3) High throughput