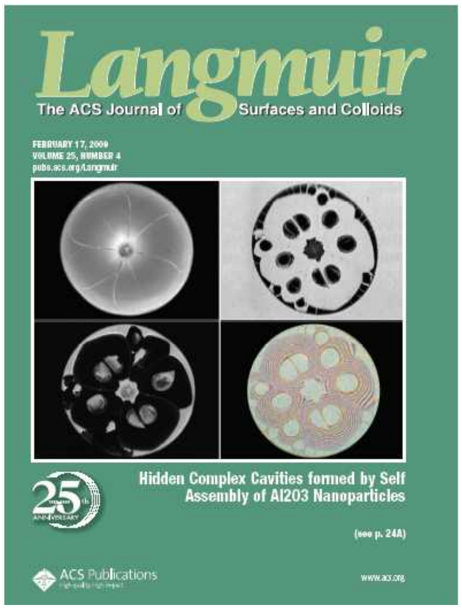
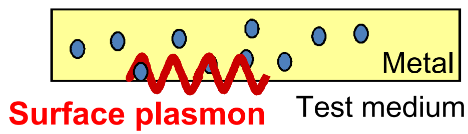
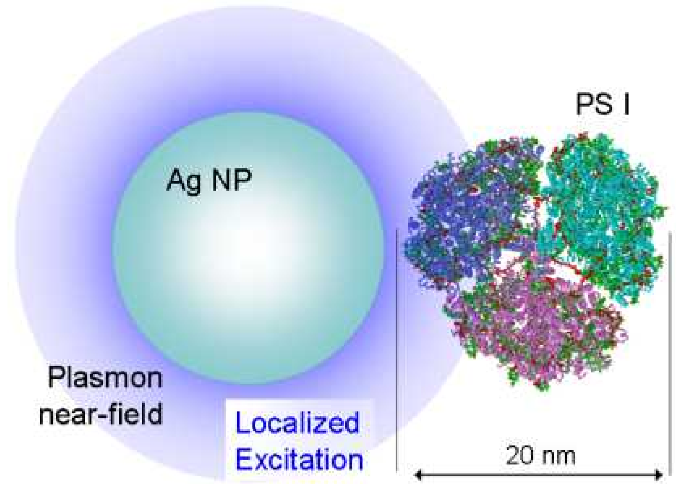
SAND2013-3421P

A label-free mapping of transport properties and energy conversion using surface plasmon resonance (SPR)







[Kim et al. Nano Letters, 2011]

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Sandia National Lab

Apr. 9

Wichita State University

This work was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

U.S. DEPARTMENT OF ENERGY

Sandia National Laboratories

Argonne NATIONAL LABORATORY

Outline

Part 1: Label-free mapping of transport properties using Surface plasmon resonance imaging

Part 2: Energy conversion using nano-biophotonics

- ***Absorption enhancement of photosynthetic molecules thin film device in solar energy harvesting***
- ***Near-field energy transfer enhancement (thermophotovoltaics, enhanced coolers)***

❑ Historical Artifacts

➢ **The Lycurgus Cup (Rome, AD 4th)**

The glass contains tiny amounts of gold and silver particles inducing SPR phenomena

Without light

With light

(Source: British Museum)

Historical Artifacts (Cont.)

- **Labors of the Months (Norwich, England, 1480)**

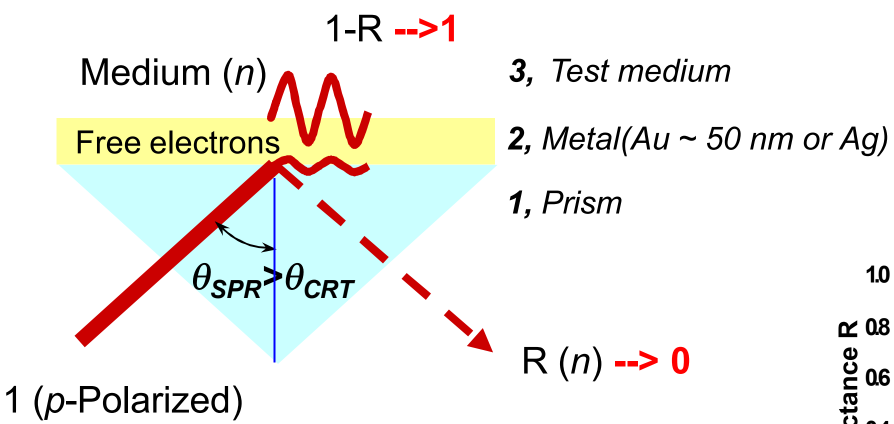
- Stained Glass

"The ruby color is probably due to Embedded gold nanoparticles"

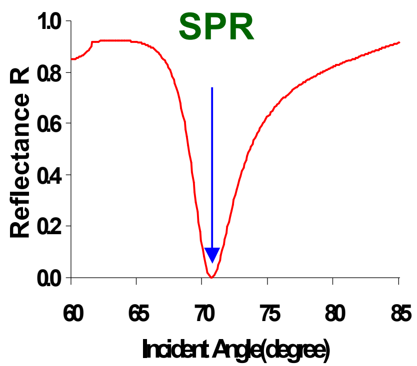
www.vam.ac.uk/vastatic/microsites/1220_gothic/pdf/stained_glass_roundels.pdf

Fundamentals of Surface Plasmon Resonance (SPR)

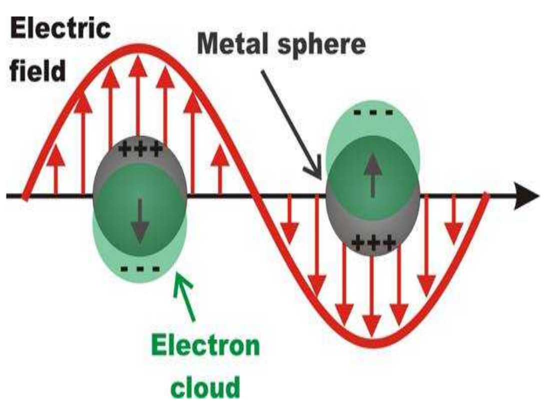
- SP is a **collective oscillation of free electrons** in the interface between metal and test medium
- SPR is phenomena that **SP is excited by the evanescent wave** preliminary generated in total internal reflection configuration
- SPR occurs at the time of **momentum matching between incoming light and SP**
- SPR is known to be highly sensitive to the **RI variation of test medium** with sensitivity **~ *10^-8^* in refractive index unit** in noble metals (Au, Ag, Al, Cu)
- Fresnel equation: $R = |r_p|^2 = f(\varepsilon_{1,2,3}, d, \lambda, \theta)$
- Classification: **Planar (thin film)** and **localized (nanoparticles)**



Planar SPR



*** SPR Reflectance Curve**



Localized SPR

http://willets.cm.utexas.edu/LSPR.html

The Applications of SPR

- **Bio application**
  - Sensor & Imaging (metal nanoparticles and thin film noble metal)
    - .Protein, DNA, molecules, ligand-receptor, antigen-antibody, cell-surface
    - .Imaging contrast improvement
  - Hyperthermia therapy of cancer and tumors, drug delivery
- **Energy conversion**
  - Solar energy harvesting, photovoltaic, thermal-photovoltaic, solar concentrator
- **Nanophotonics**
  - Nano-waveguide, nano laser, nearfield scanning optical microscope, tip enhanced raman scattering, plasmonic circuit, nano-lithography
- **Meta material**
  - Transparent cloak using negative refractive index material, spoof SPR
  - Super resolution optical microscopy
- **In-situ visualization of transport and optical properties**
  - Detect transport properties such as concentration, temperature, salinity, and refractive index in a label-free, real-time, full-field manner

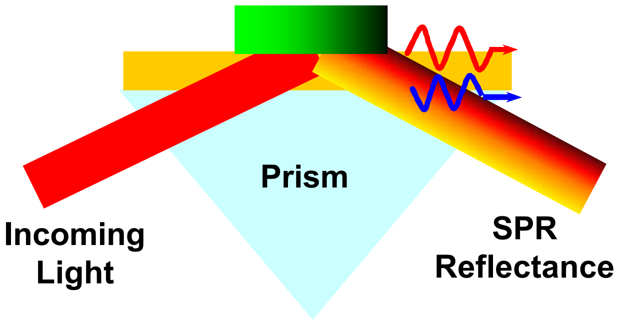
Part 1: Label-free mapping of transport properties using SPR reflectance imaging

I. Research Motivation

II. Development of Full-field SPR Reflectance Imaging System

III. Applications of SPR Reflectance Imaging System

IV. Summary



[Kim and Kihm, 2006, *Exp. Fluids*]

Planar SPR

I. Research Motivation

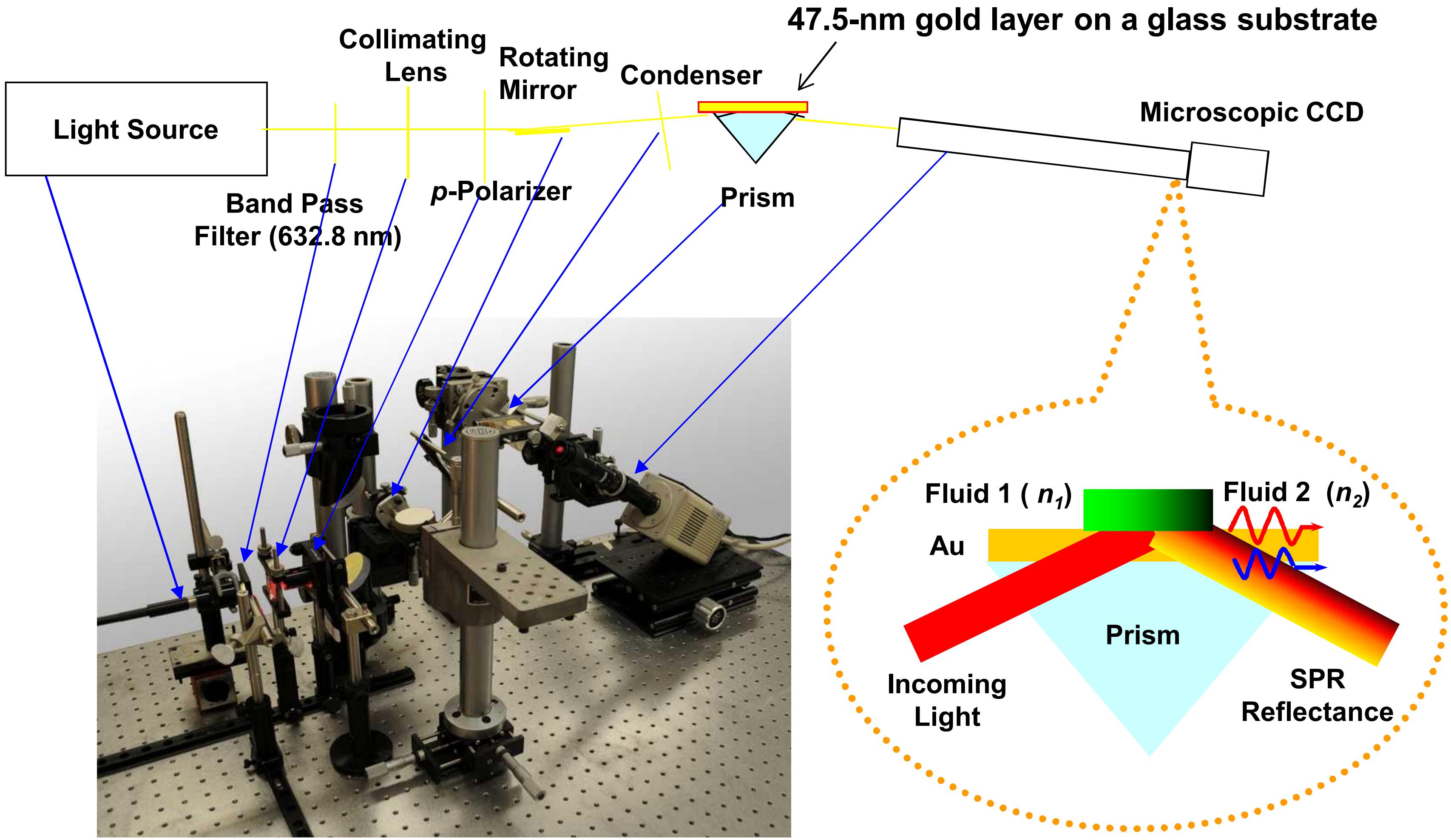
Detect transport & optical properties (concentration, temperature, density, and effective refractive index) in label-free, real-time and full-field without any foreign labels/particles/dyes

- **Disadvantages of existing technique require foreign materials**
  - Intrusive detection of transport properties with affecting or altering test medium
  - Measurement inaccuracy from the presence of foreign materials
  - Point-wise, mostly limited to bio-applications, and lack of systematic and quantitative approach

SPR reflectance imaging technique to detect transport & optical properties In label-free, real-time, and full-field

II. Development of SPR Reflectance Imaging System

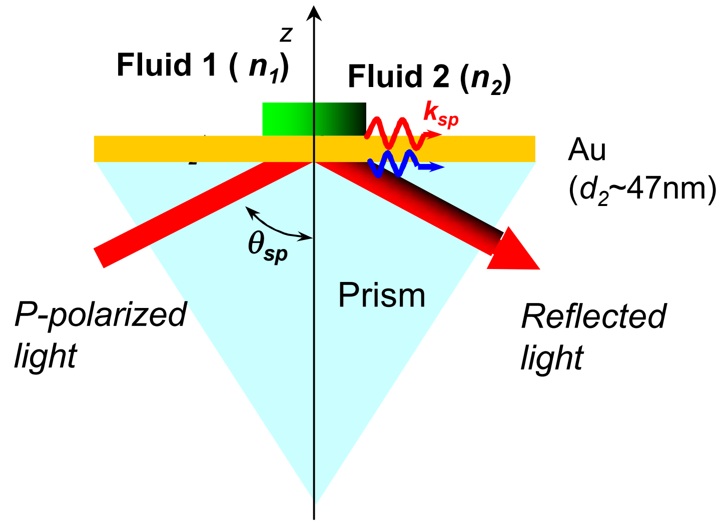
❑ SPR Reflectance Imaging System



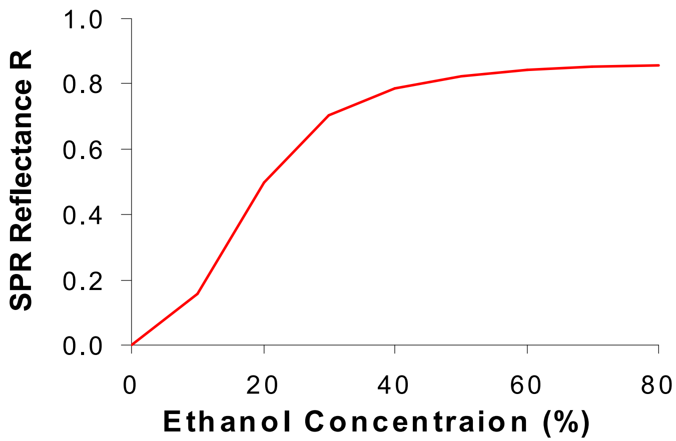
[Kim and Kihm, 2006, *Exp. Fluids*]

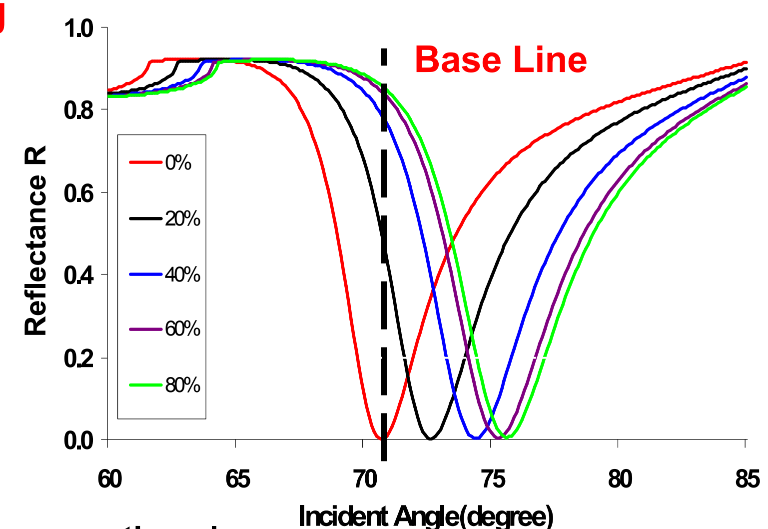
❑ SPR Reflectance Imaging

- ➢ **Fixed SPR angle (θ_{SPR}) & wavelength**
- ➢ **Experimental calibration correlation (Reflectance – Transport properties)**



- SPR reflectance is a **function of refractive index (*n*)* of the test medium** contacting metal film
- **Refractive index of test medium** changes when **transport properties** (concentration, temperature, optical properties) **changes** or **surface binding** occurs





ethanol in water

Fixed SPR angle

[Calculated from Fresnel equation]

- **Linear relationship between R and PGL**

$$R = \frac{SPR\ reflectance\ intensity}{Incident\ light\ intensity} = \frac{PGL - PGL_L}{PGL_H - PGL_L}(R_H - R_L) + R_L$$

III. Applications of SPR Reflectance Imaging Technique

- Micromixing Concentration Field
- Near-wall Salinity Field
- SPR Imaging Thermometry
- Unveiling hidden complex cavities in nanocrystalline self-assembly

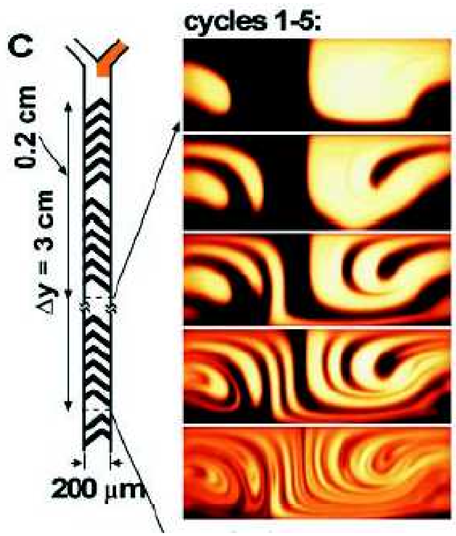
❑ Micromixing Concentration Field

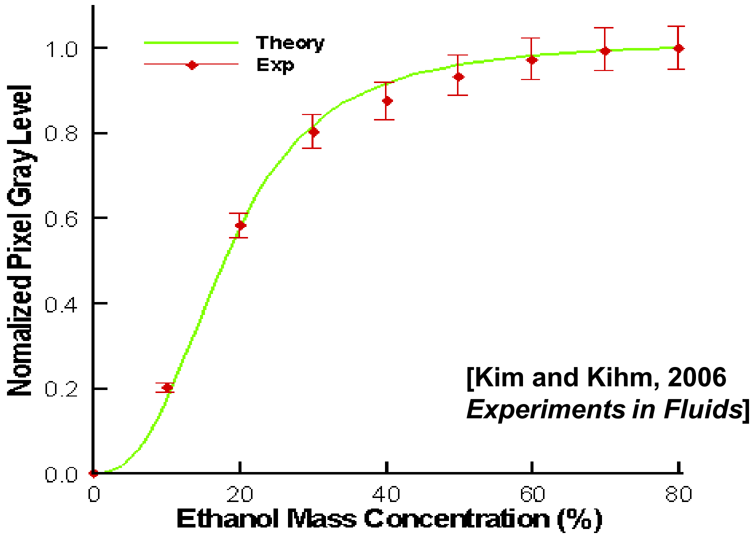
➢ **Ethanol & Water**

- Experimental Calibration Correlation (PGL-C)

- With Foreign Materials (**Fluorescence dye**)

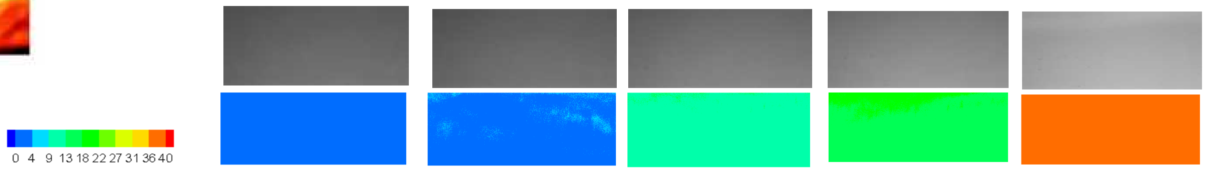
'Chaotic mixer for microchannels'
(Stroock et al. 2002, Science)





- **Based on vertical dash line in SPR-curve**
- **Exp : 95 % confidence interval**
- **Theory from Fresnel equation**

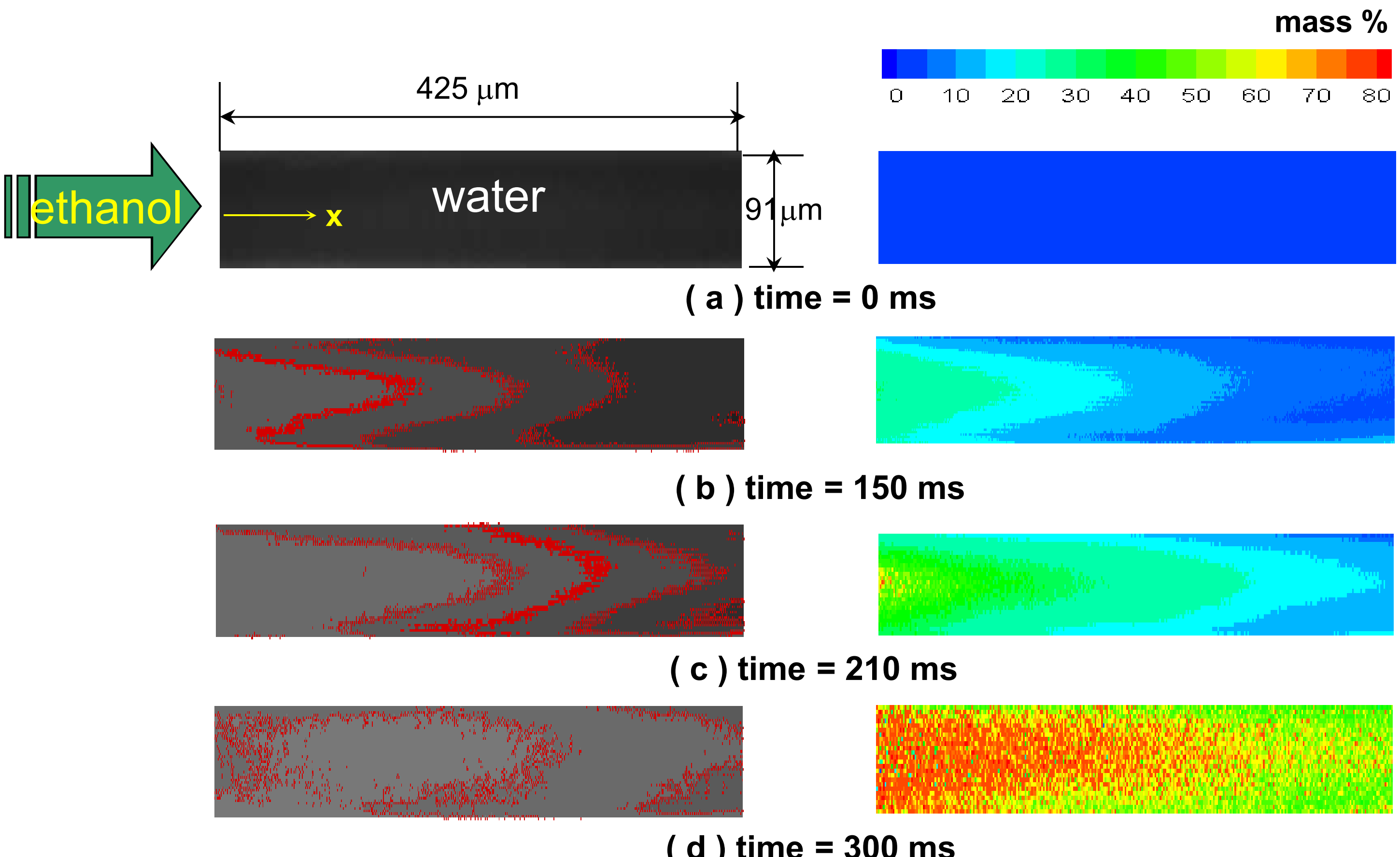
[Kim and Kihm, 2006
Experiments in Fluids]



Vol. % **0 % (DI Water)** **4.2 %** **12.5 %** **21 %** **40 % ethanol**

❑ Micromixing Concentration Field (Cont.)

➢ **Full-field development of ethanol mixture concentrations in microchannel**



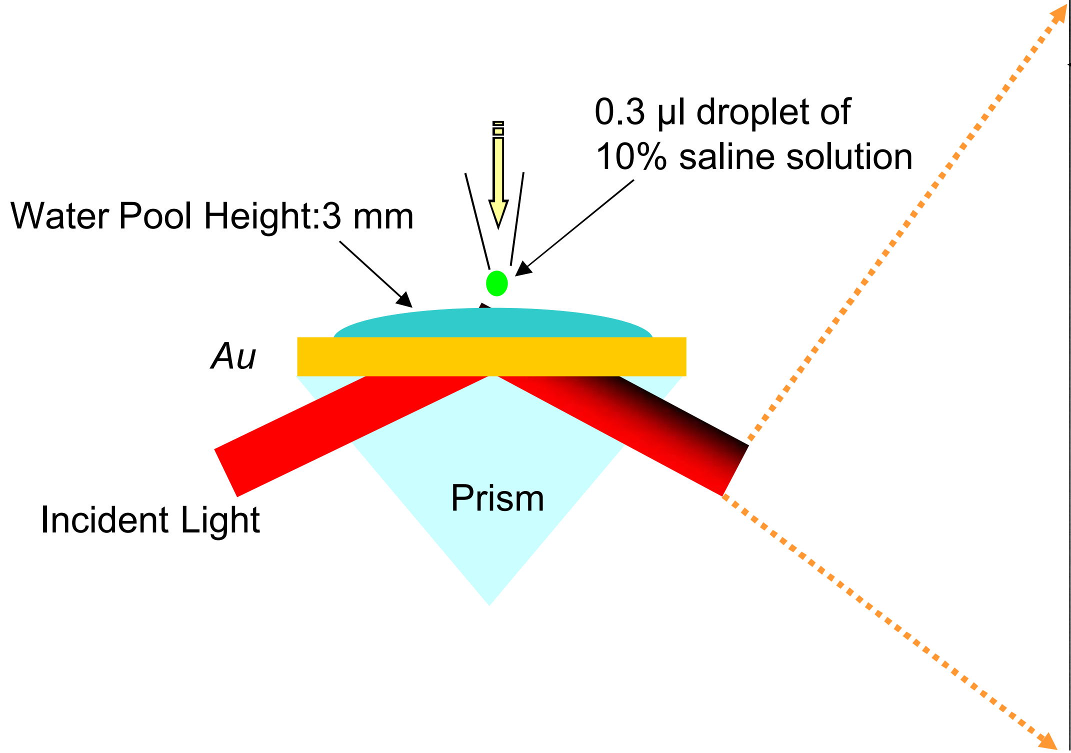
Intensity distribution (Original Images)

Concentration field distribution

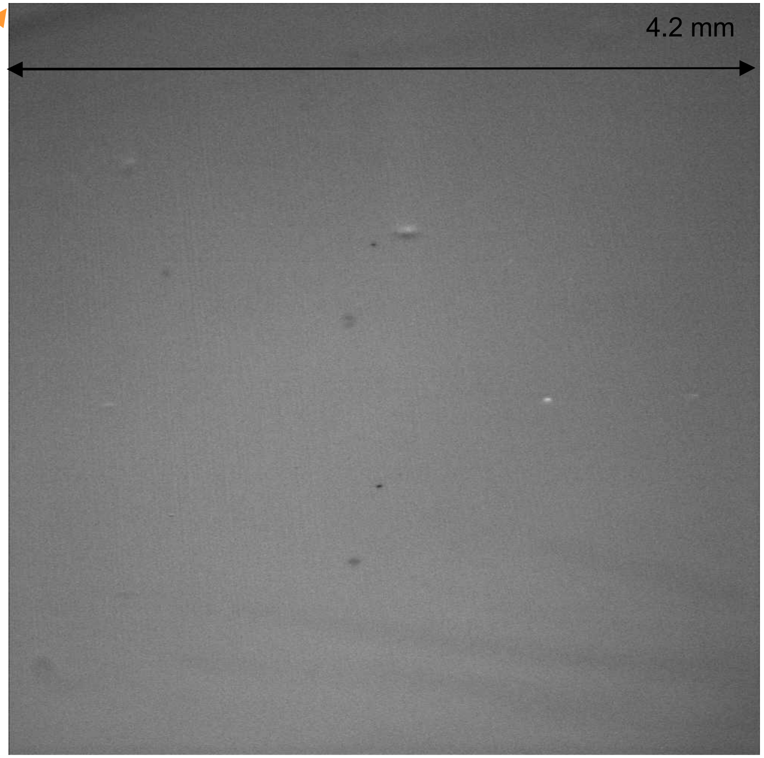
[Kim and Kihm, 2006 *Experiments in Fluids*]
[Kim & Kihm, 2007 J. Heat Trans.]

❑ Salinity Concentration Field

➢ **Full-field and dynamic mapping of near-wall salinity (Movie)**



SPR reflectance image



14

❑ Salinity Concentration Field (Cont.)

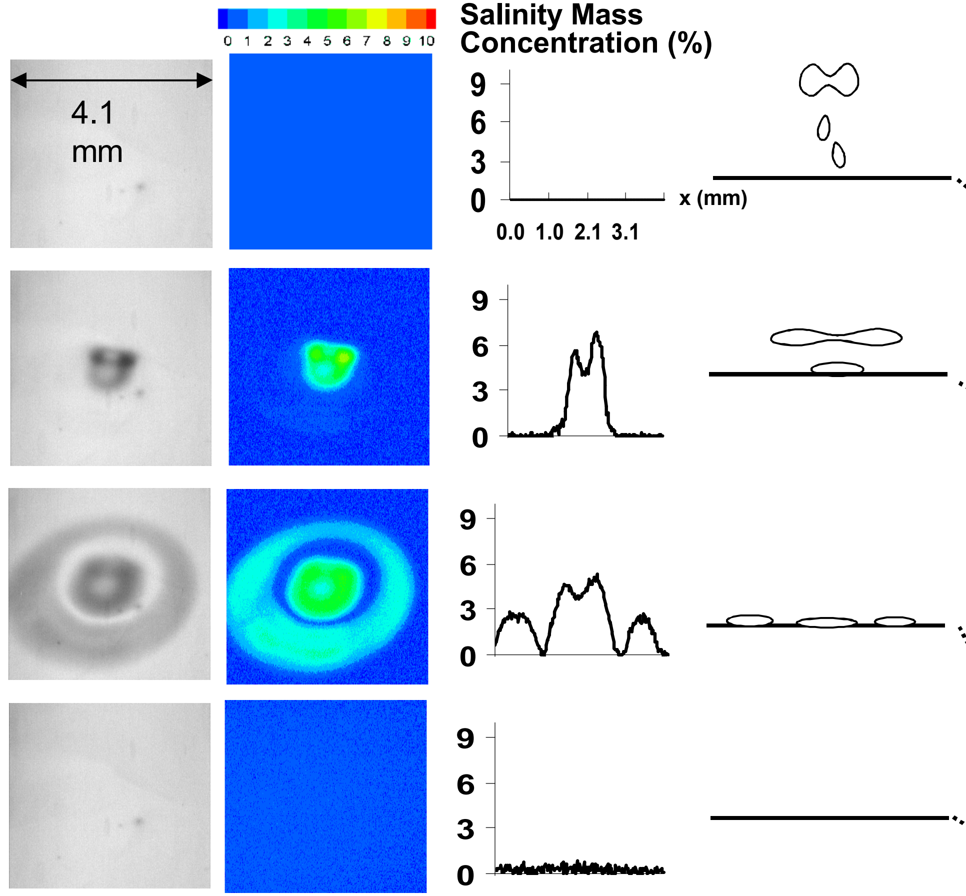
➢ **Full-field and dynamic mapping of near-wall salinity**

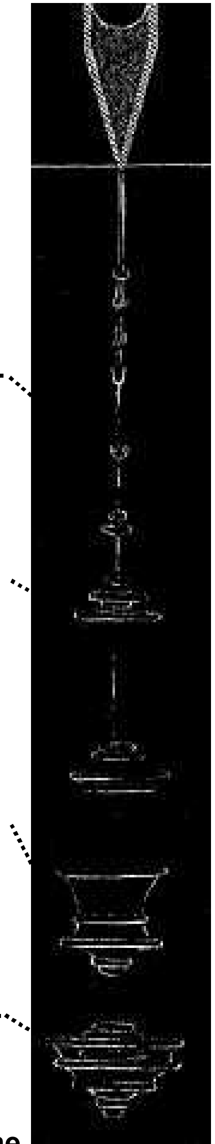
(a) t ~ 0s:
Before contact

(b) t = 0.5s:
Contact of the first & Second Satellite droplet

(c) t = 2.27s:
Near-wall diffusion of salinity

(d) t = 45s:
Complete diffusion of salinity



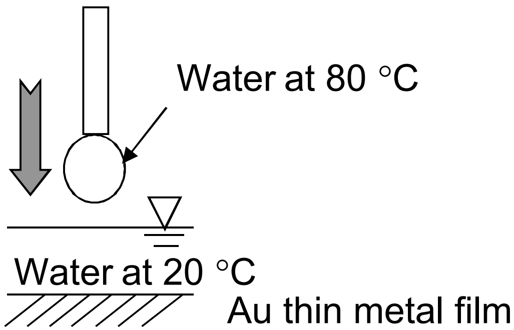


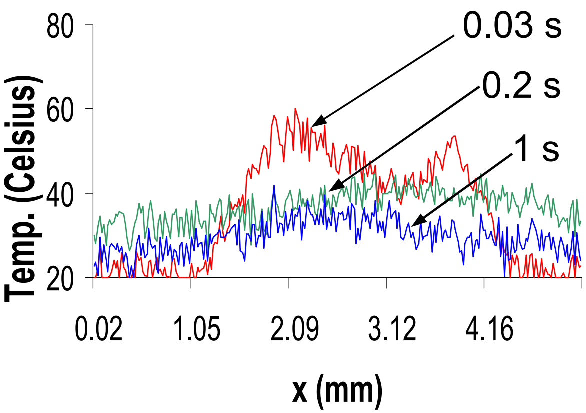
[Kim and Kihm, 2007, Anal. Chem.]

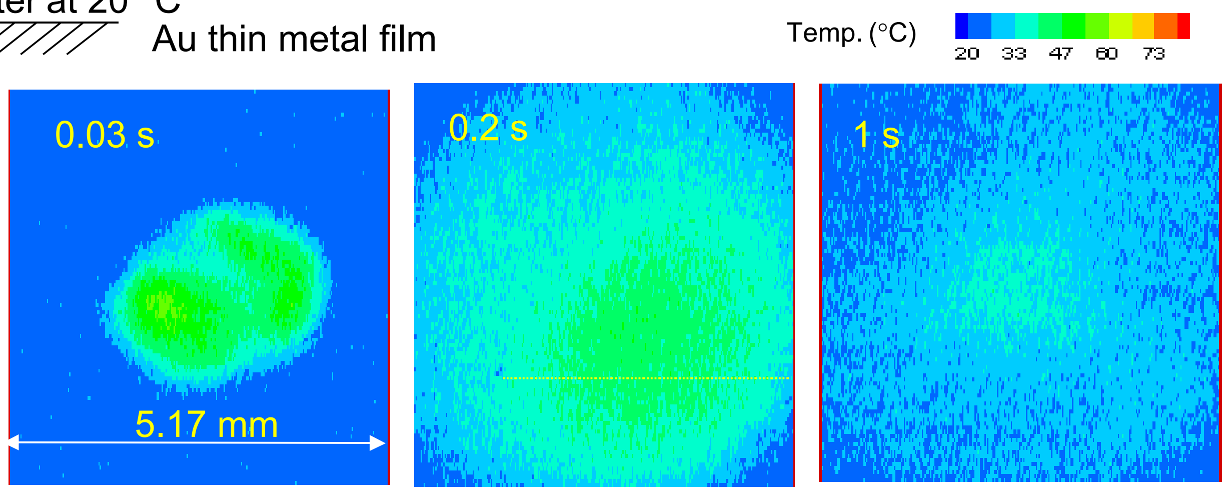
SPR Reflectance Images | **Converted Saline Mass Concentration** | **Centerline Salinity Profiles** | **Schematic of saline drop formation and diffusion** | **Sketch by Thomson & Newall**

❑ Temperature Field

- **Full-field and real-time mapping of transient temperature field**
  - Water environment



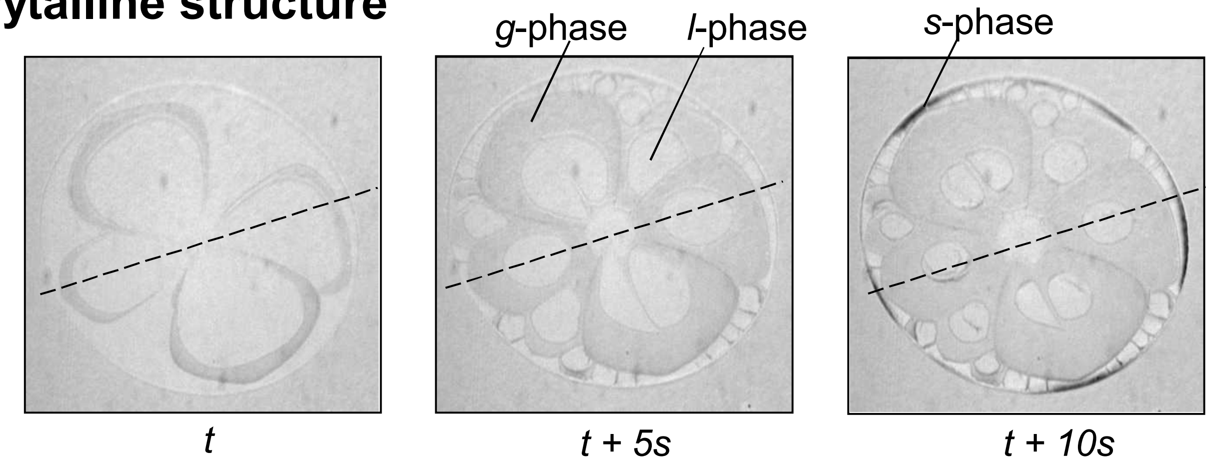




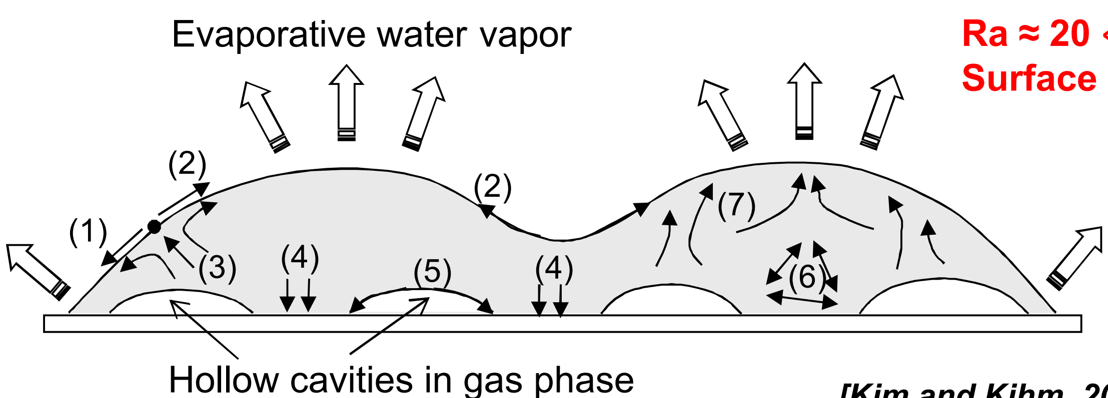
[Kim and Kihm, 2007, Opt. Lett.]

❑ Unveiling hidden complex cavities formed during nanocrystalline structure

➢ **Sequential SPR images for the phase change detection of nanocrytalline structure**



➢ **Schematic for the hollow cavities formation**

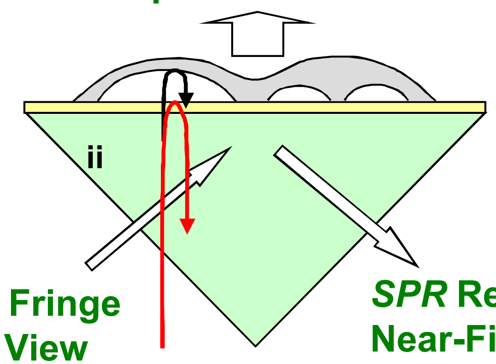


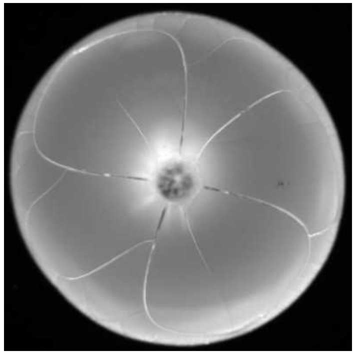
Ra ≈ 20 ≪ 1708
Surface Tension/Convection ~ 60

[Kim and Kihm, 2009, Langmuir as Cover page]

❑ Unveiling hidden complex cavities formed during nanocrystalline structure (Cont.)

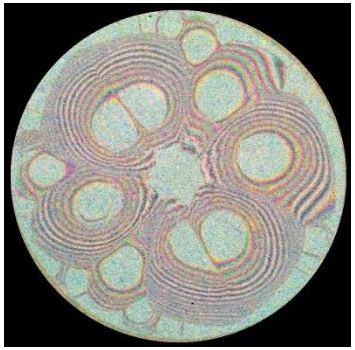
➢ **Full dry-out pattern of nanofluids : 47 nm Al_2O_3, 10% concentration**



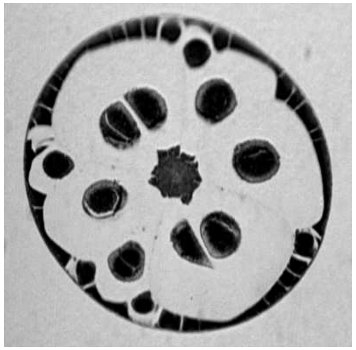


Before shell remove

After shell remove



RGB Combination of natural fringe

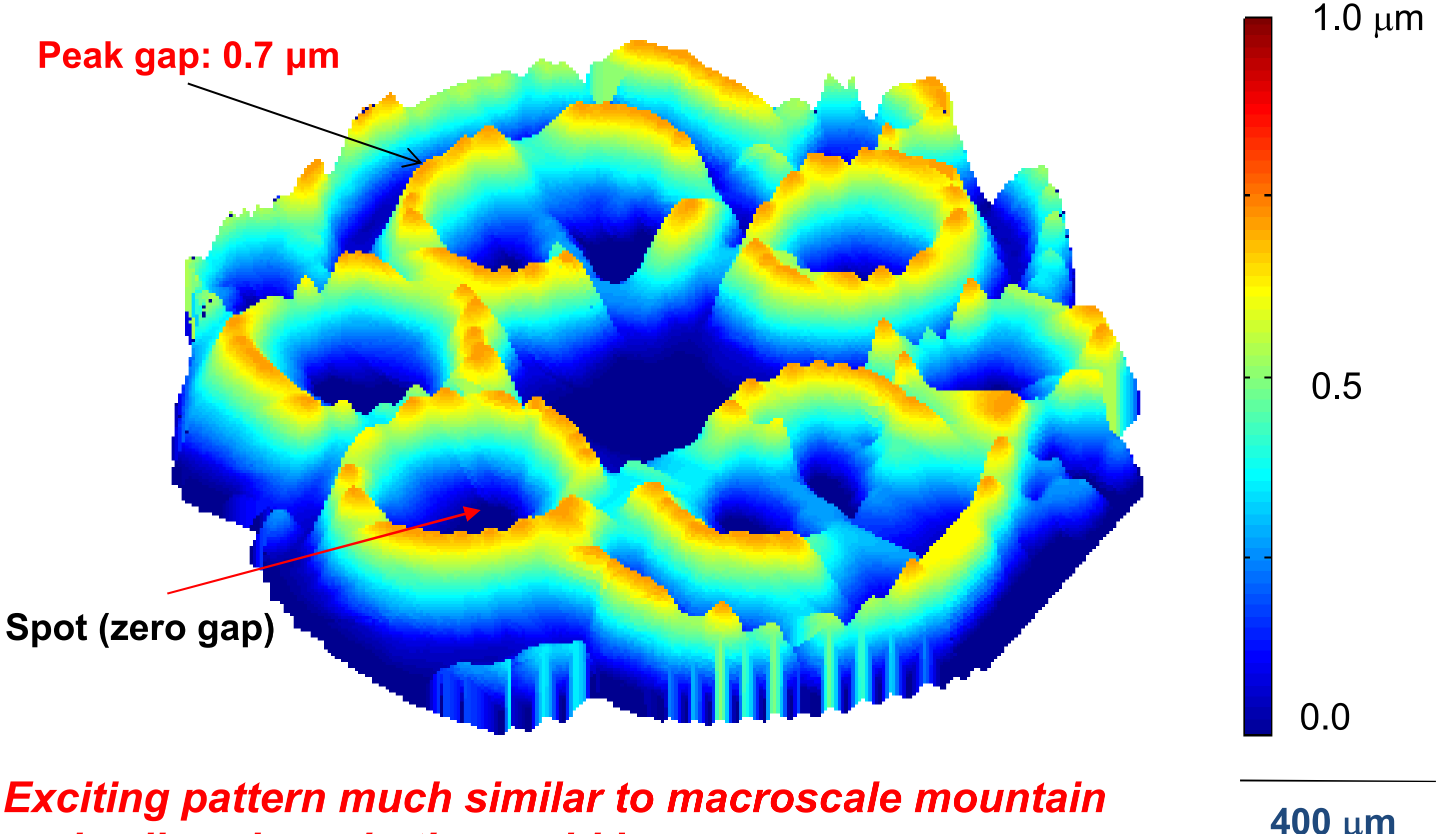


SPR

[Kim and Kihm, 2009, Langmuir as Cover page]

❑ Unveiling hidden complex cavities formed during nanocrystalline structure (Cont.)

- **Cavity profile (Fringe patterns digital analysis)**



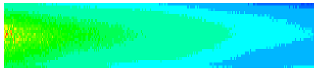
- ***Exciting pattern much similar to macroscale mountain and valley shape in the world !***

[Kim and Kihm, 2009, Langmuir as Cover page]

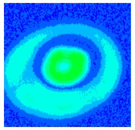
IV. Summary

- **Successful development and implementation of SPR reflectance imaging technique to detect transport & optical properties in a label-free, real-time, and full-field manner**

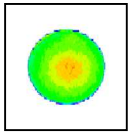
- **Innovative use of SPR reflectance imaging technique**
  - **Micromixing concentration of binary mixture**



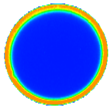
    - Capillary phoretic suction of ethanol into pure water in microchannel



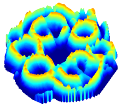
  - **Near-wall salinity profile**
    - Convective diffusion of salinity into pure water bath



  - **SPR imaging thermometry**
    - Thermal diffusion of hot water droplet into air or cold water bath



  - **Optical characterization of nanofluids**
    - Near-field nanoparticle concentration of evaporating nanofluids



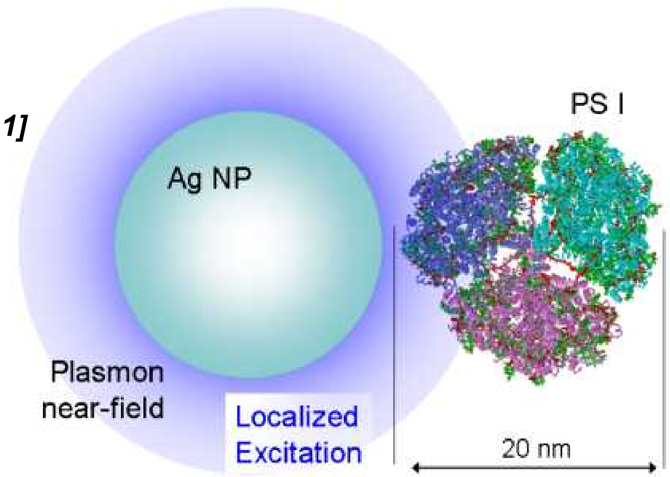
  - **Unveiling of hidden complex cavities**
    - Formation of hidden cavities during evaporation-induced nanocrystalline structure self-assembly

- **Solid framework for opto-bio-chemical sensor and visualization tool**

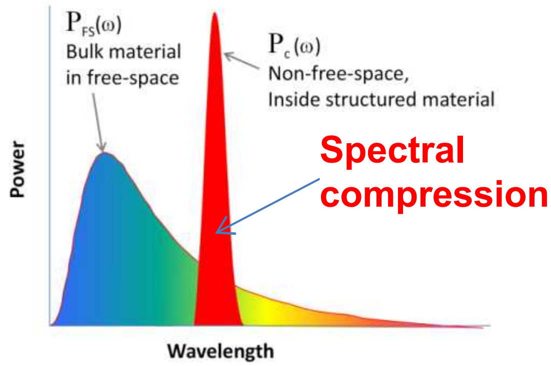
Part 2: Energy conversion using nano-biophotonics

-Absorption enhancement of photosynthetic molecules thin film device in solar energy harvesting
-Near-field energy transfer enhancement (thermophotovoltaics, enhanced coolers)

[Kim et al. Nano Letters, 2011]

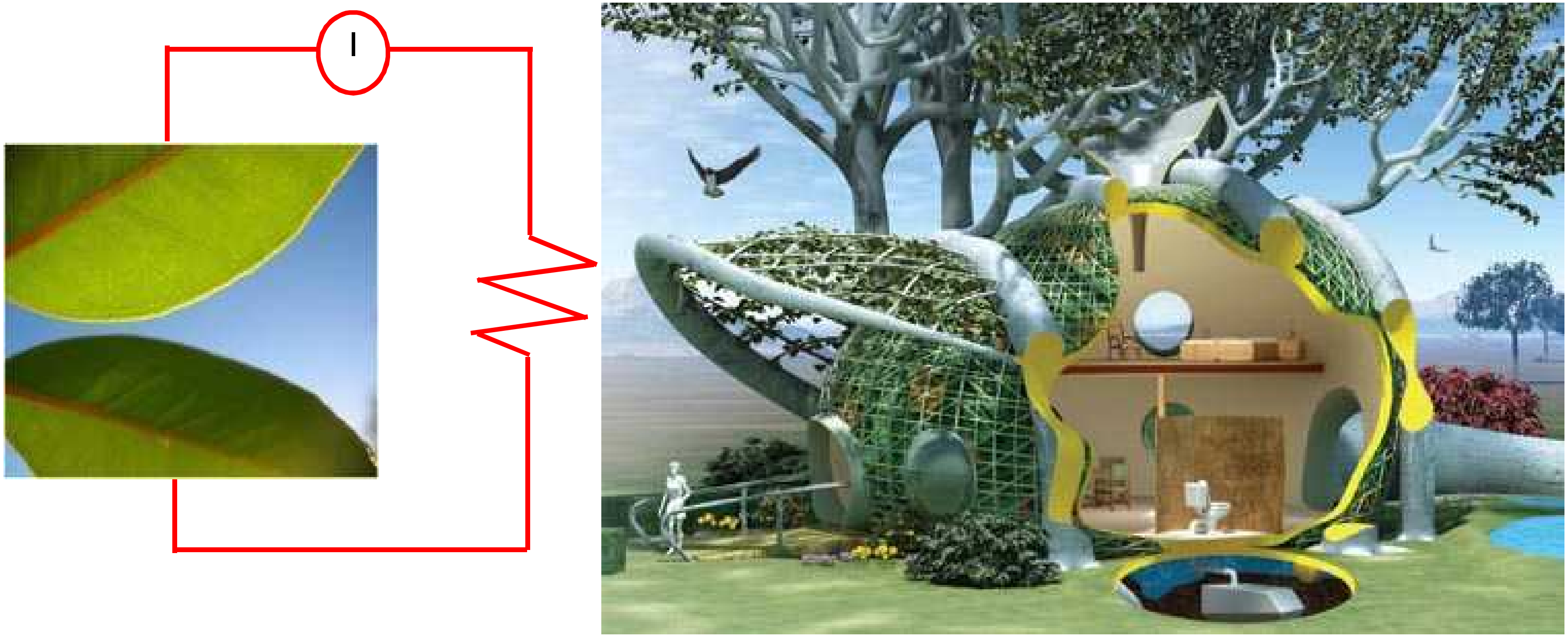


Solar Energy Harvesting



Near-field energy transfer enhancement

❑ Green tree house with solar power from leaves



[http://dornob.com/]

Solar Energy Harvesting

I. Research Motivation

- Develop an efficient solar energy harvesting thin film with photosynthetic molecules (Photosystem I; PSI) and metal nanoparticles using surface plasmon resonance phenomena

- Enhance absorption efficiency of PSI by metal nanoparticles

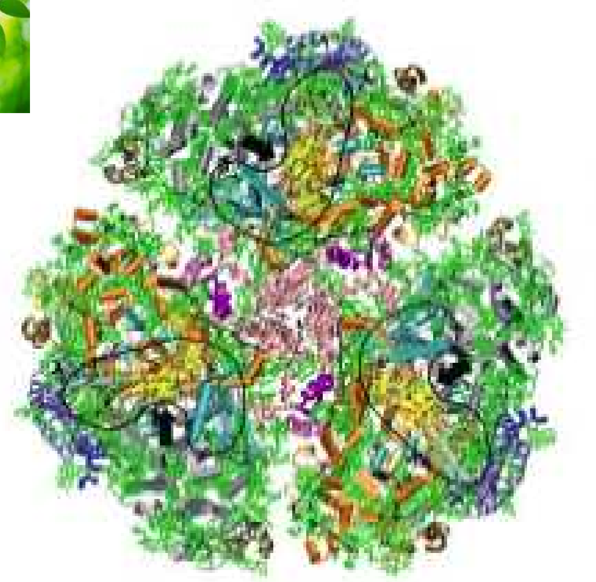
- Image energy transfer in photosynthetic molecules coupled with metal nanoparticles in ultrafast and nanoscale manner

PSI has received increasing attention as a prototype for a next-generation material with applications in photoelectronics, phoelectrochemical cells, and hydrogen production because of it large voltage generation and nanoscale dimension

Solar Energy Harvesting

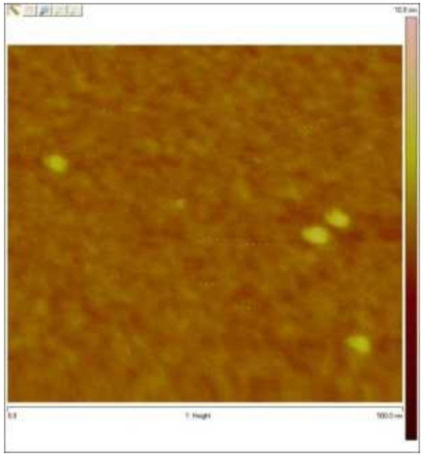
II. Experiment

- **Photosystem I (PSI): One of fundamental photosynthetic molecules**
  - PSI is one of the most robust and efficient light harvesting complexes in nature which has developed over 3 billion years with earth history
    - **=> Potential material for *molecular electronic device* in the future**
    - **=> Need to increase its absorption efficiency**
  - Composed of antenna complexes and reaction centers
  - Dimension: Trimetric structure (20 nm in diameter and 10 nm in height)



Schematic picture of PSI

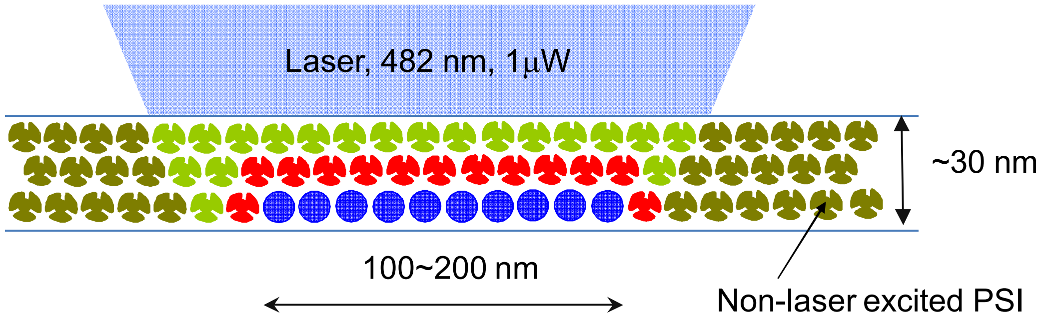
[Grotjohann et al. 2005, Photosynthesis Research]



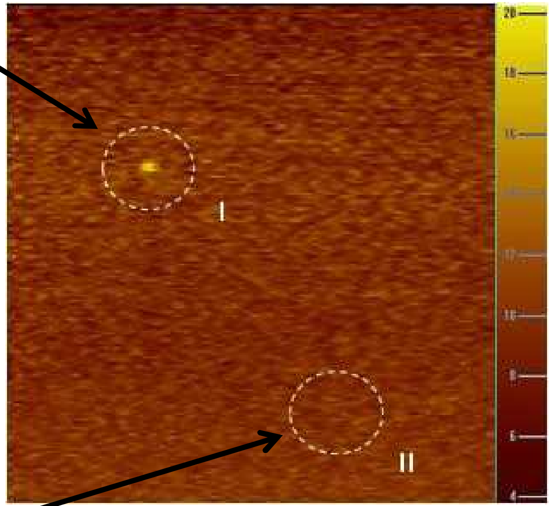
AFM scan of PSI

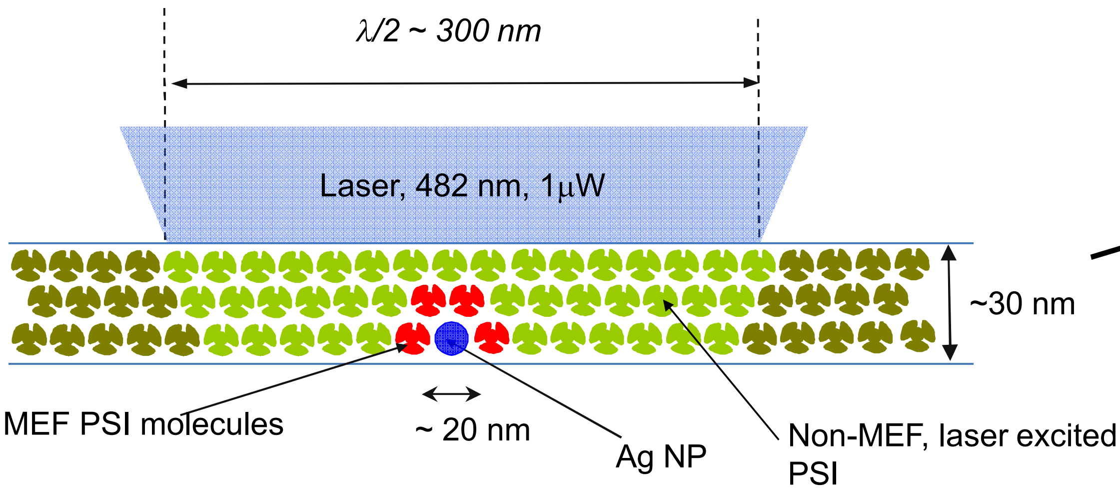
Solar Energy Harvesting

❑ PSI & Ag nanoparticles thin film



Aggregated Ag nanoparticles





Single Ag nanoparticle

Large enhanced fluorescence is due to strong scattering signal from aggregated NPs

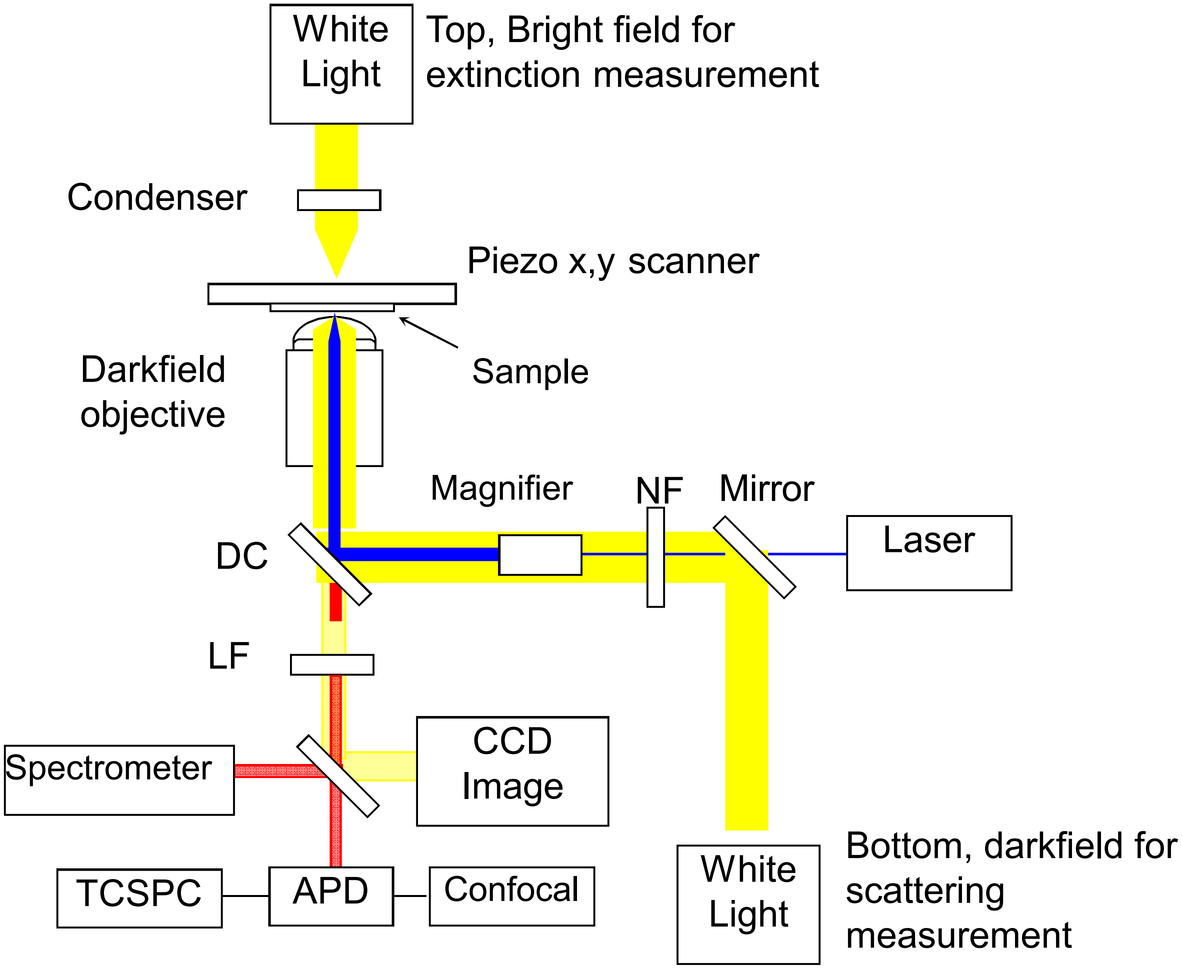
[Kim et al. Nano letters, 2011]

Solar Energy Harvesting

❑ Correlated optical system

- Confocal fluorescence, darkfield imaging, lifetime & spectroscopy

- To detect same area in a sample sequentially in nanoscale without moving sample

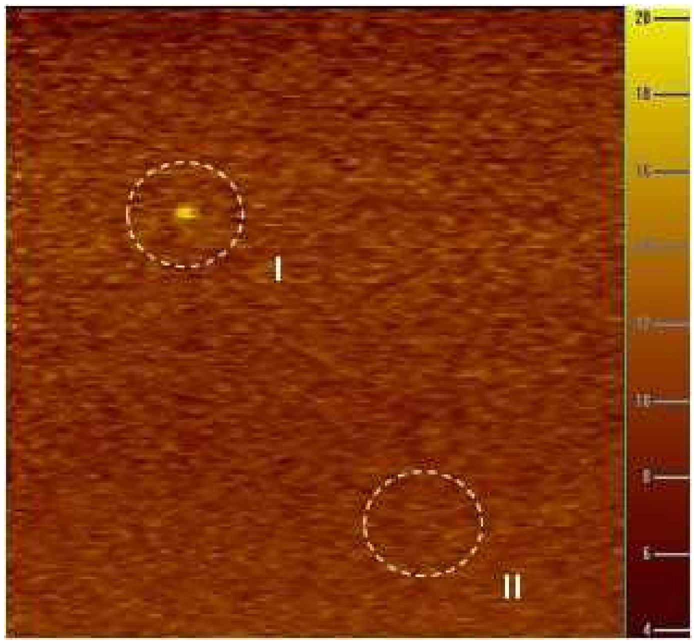


[Kim et al. Nano letters, 2011]

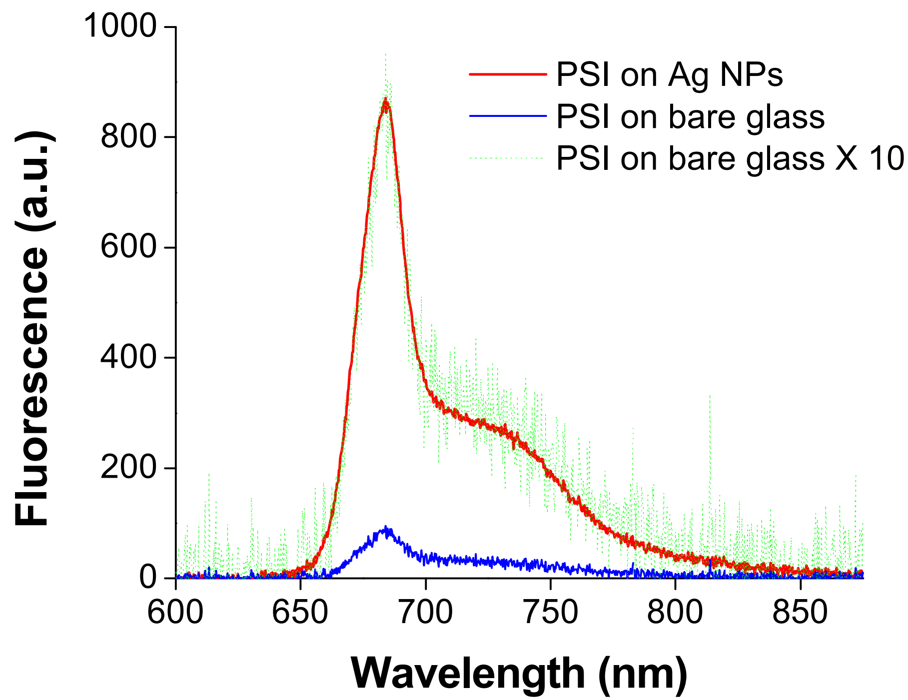
III. Results

❑ Confocal and enhanced fluorescence

- **Confocal fluorescence**



- **Enhanced fluorescence**

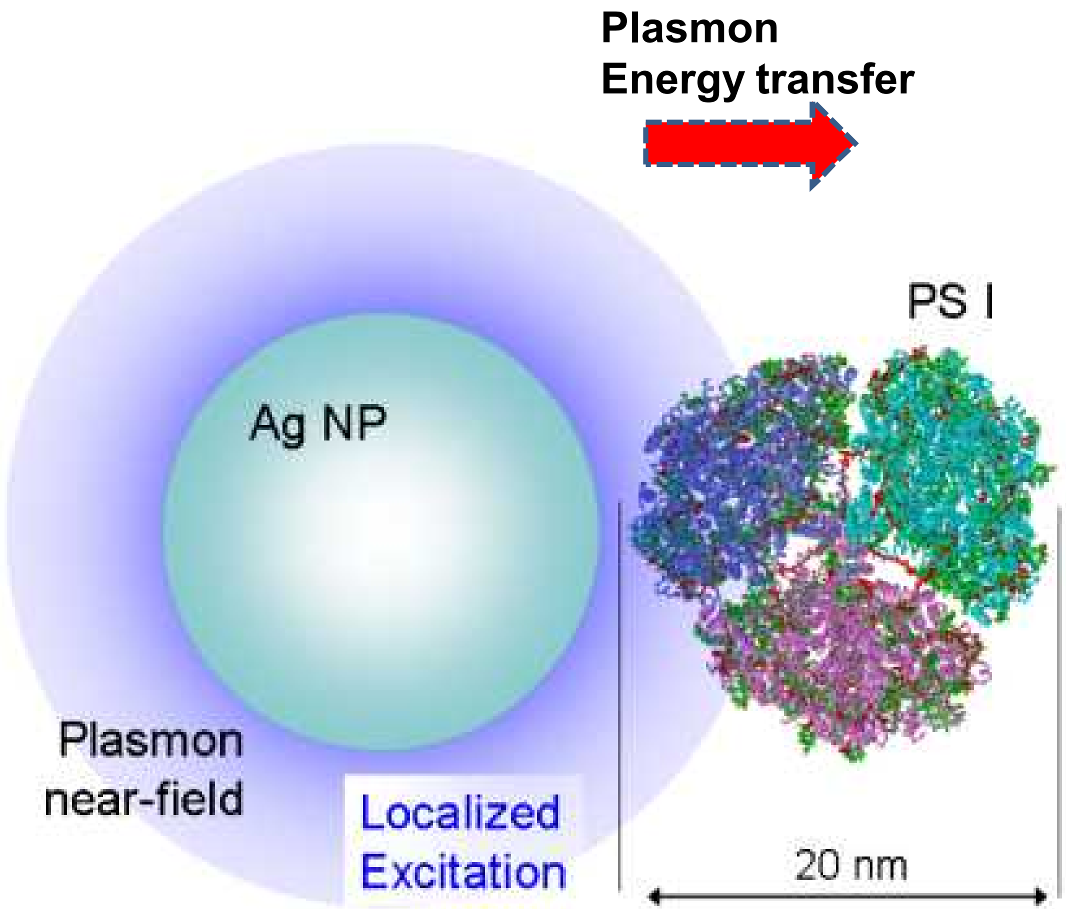


- **Little lifetime change, Distinct darkfield spectroscopic feature**

- **Calculation shows absorption is dominant in enhanced fluorescence**

[Kim et al. Nano letters, 2011]

Solar Energy Harvesting



[Kim et al. Nano letters, 2011]

Solar Energy Harvesting

IV. Summary

- It is shown that metal nanoparticles can enhance absorption efficiency of photosynthetic molecules more than 20 fold for solar energy harvesting using localized Surface Plasmon Resonance

- Plasmon resonance energy transfer (PRET) is observed between metal nanoparticles and photosynthetic molecules to provide very substantial basic data for the optimized energy transfer applications in near-field

- Energy transfer between nanoparticles and photosynthetic molecules are being investigated through near-field interaction for energy conversion (solar, photochemical)

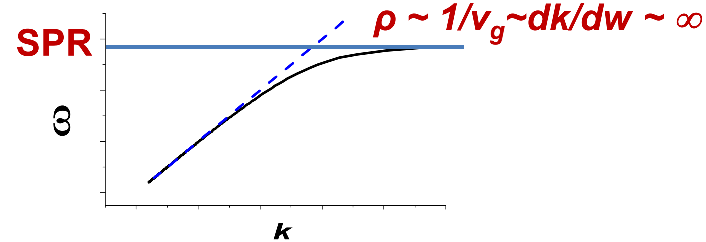
- *Financial support from the DOE BES CSGB funding for the postdoctoral fellowship*
- *Argonne CNM nanocenter's user program to use cutting edge equipment to the fullest mea sure*

Near-field energy transfer enhancement

I. Research Motivation

Surface plasmon resonance (SPR) dispersion control for energy conversion such as near-field thermophotovoltaics and enhanced coolers

- **Why surface plasmon resonance dispersion (frequency) control?**
  - Photonic density of states (PDOS, *ρ*) can be maximum at SPR frequency

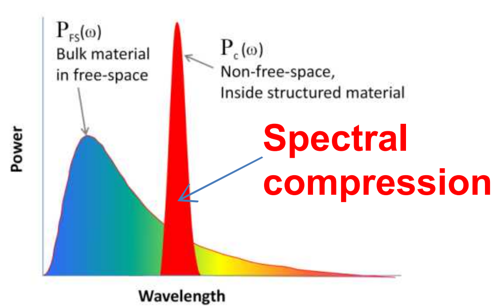


SP dispersion curve

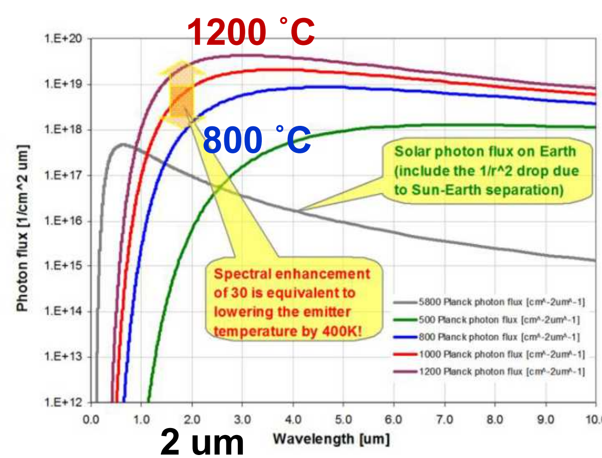
- **PDOS, *ρ* is a key element determining spectral energy distribution**

$$u(\omega) = \hbar\omega\rho(\omega)/(e^{\hbar\omega/kT} - 1)$$

- SP structure is desirable for high PDOS



Energy distribution



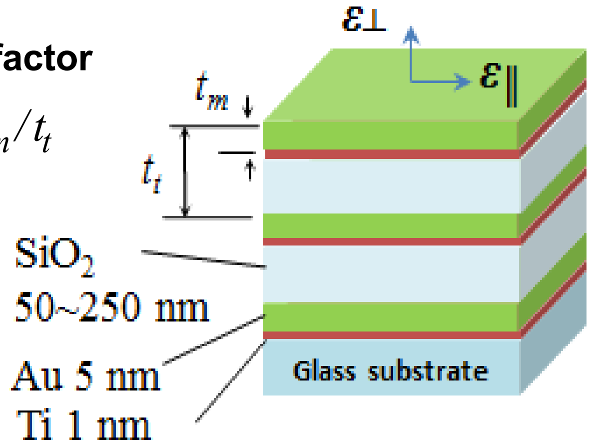
Higher energy transfer due to spectral compression

Near-field energy transfer enhancement

- How do we get **Surface Plasmon Resonance Dispersion Control?**
  - => **Hyperbolic metamaterials (HMM)**
    - **- Dispersion control by filling factor & using surface mode**

Filling factor

$f = t_m / t_t$



HMM schematic

$$\frac{k_\perp^2}{\varepsilon_\parallel} + \frac{k_\parallel^2}{\varepsilon_\perp} = k_0^2$$

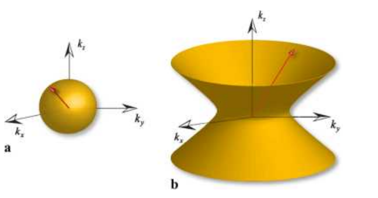
Dispersion relation

$$\varepsilon_\parallel = f\varepsilon_m + (1-f)\varepsilon_d$$

$$1/\varepsilon_\perp = f/\varepsilon_m + (1-f)/\varepsilon_d$$

Permittivity

$\varepsilon_\parallel \varepsilon_\perp > 0$ $\varepsilon_\parallel \varepsilon_\perp < 0$



Elliptic **Hyperbolic**

[Jacob et al, APB, 2010]

Hyperbolic Metamaterials

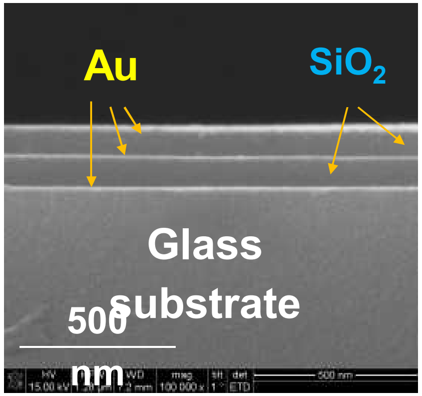
- One of metamaterials which is artificial materials with properties that may not exist in nature
- It shows combined properties of metal and dielectric with different signs => $\varepsilon_\parallel \varepsilon_\perp < 0$
- Applications: subwavelength imaging, enhanced spontaneous emission, and near-field thermophotovoltaics

* Existing techniques (semiconductor ,conductive oxides) show the limitations of decreasing mobility with high doping level and short range of dispersion (frequency) control

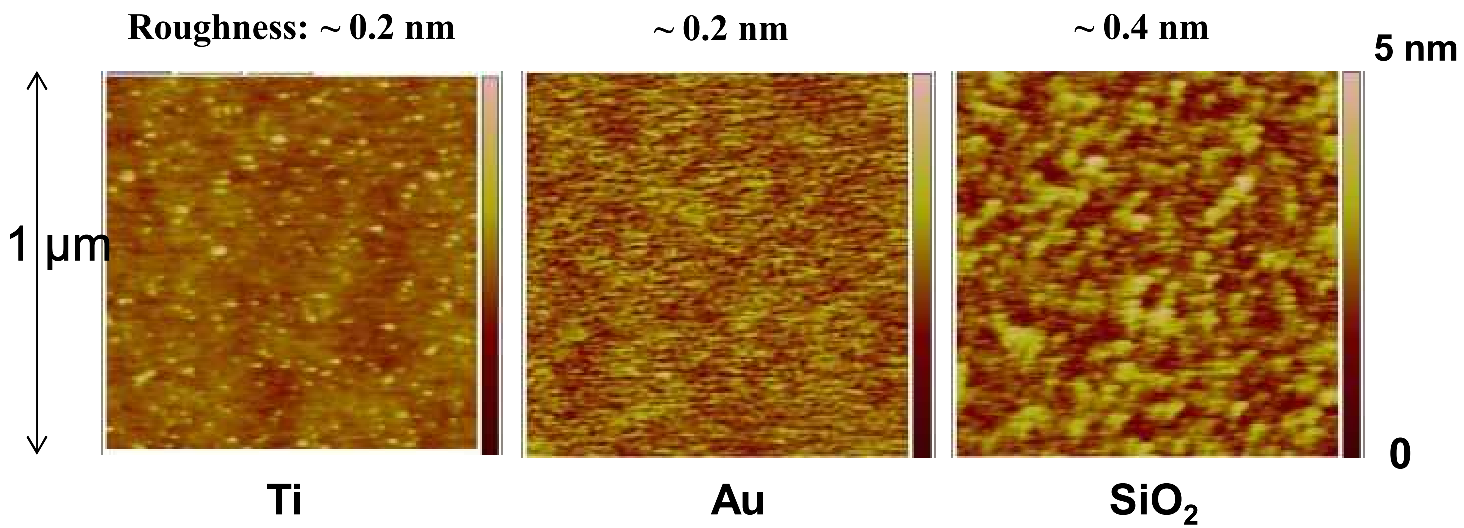
Near-field energy transfer enhancement

II. Experimental Set-up & Characterization

- Sample preparation: E-beam deposition
  - Characterization



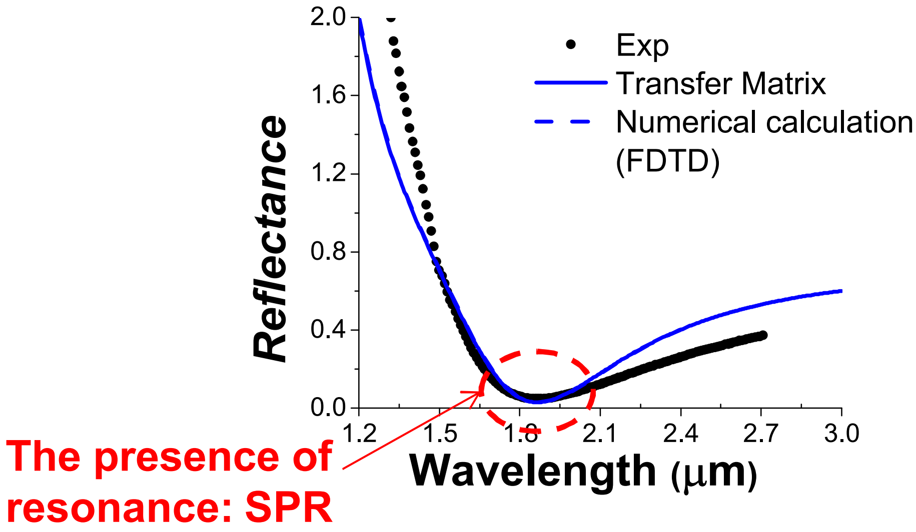
SEM cross-section image



AFM

Near-field energy transfer enhancement

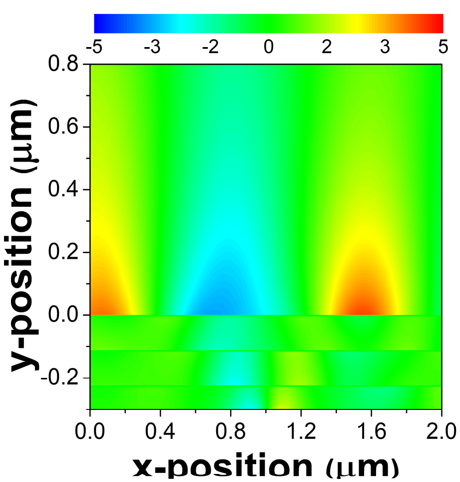
❑ Signatures of Surface Plasmon Resonance (SPR)



- Hyperbolic metamaterials can excite SPR in near-IR range which can be a good candidate for high photonic density of states.
- For the time experimentally demonstrated

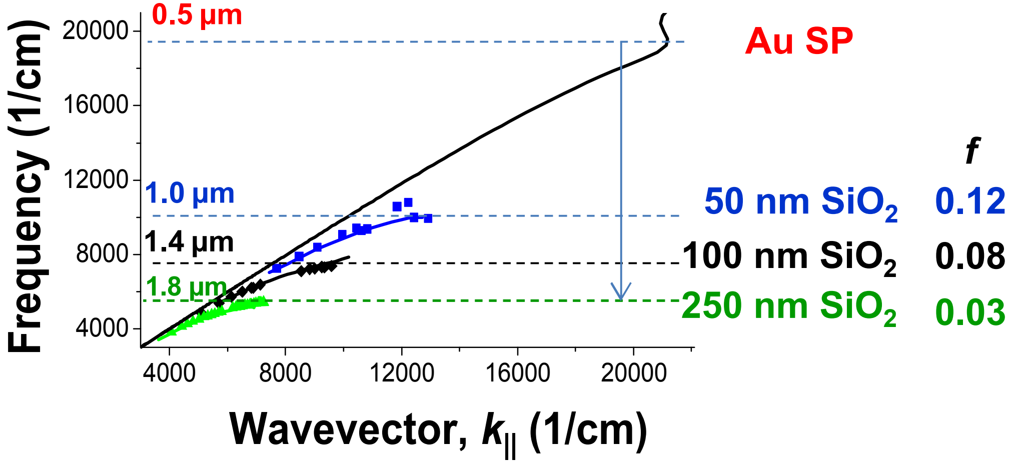
➢ Electric field pattern of SPR on the surface

- The presence of SPR excitation oscillating along the surface



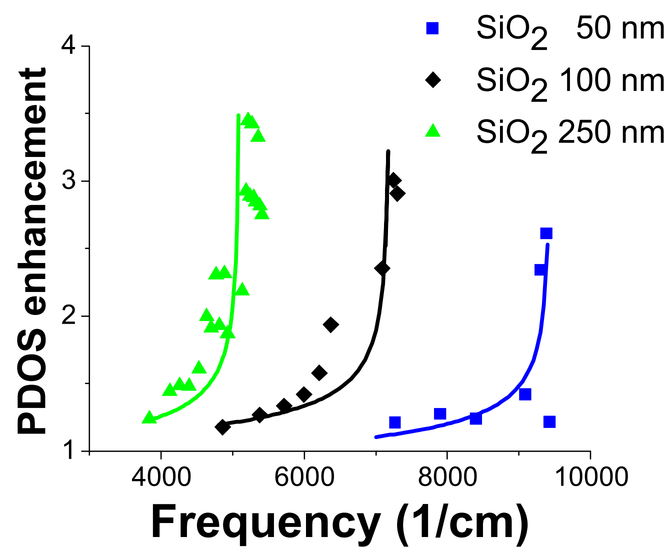
Near-field energy transfer enhancement

❑ SPR Dispersion Control



- More than 3x increase Surface Plasmon Resonance Dispersion Control

❑ Photonic density of states (PDOS)



- PDOS, ρ(ω) : 3~4 with filling factors

$$u(\omega) = \hbar\omega\rho(\omega)/(e^{\hbar\omega/kT} - 1)$$

Near-field energy transfer increase

Thermophotovoltaic, enhanced coolers

Near-field energy transfer enhancement

IV. Summary

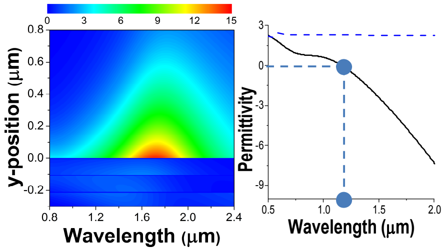
- ❑ For the first time experimentally the existence of Surface Plasmon Resonance (SPR) in near-ir range using hyperbolic metamaterials

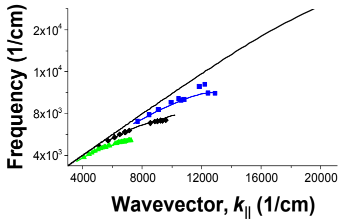
- ❑ High Surface Plasmon Resonance Dispersion Control from 1 to 1.8 µm; more than 3 x increase than bulk Au

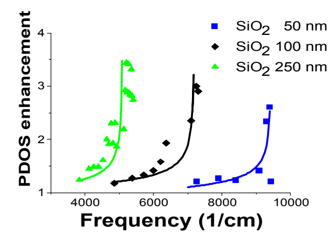
- ❑ Photonic Density of States (PDOS) of 3~4 with filling factors

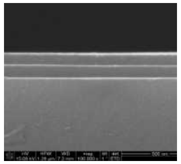
- ❑ High quality thin films are fabricated with the filling factor as low as 0.03

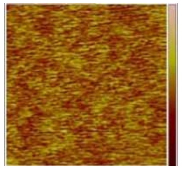
⇒ Higher photonic density of states (PDOS) material in near-field experiment for high energy transfer device in energy conversion





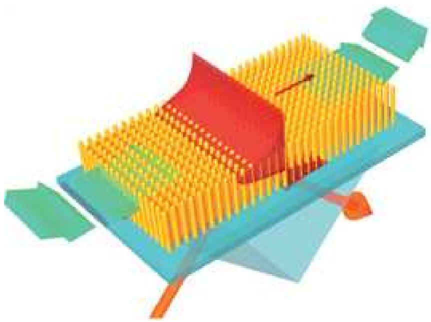






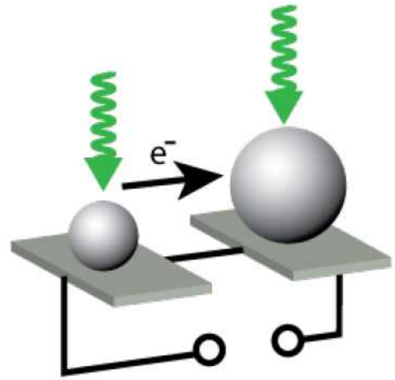
Energy conversion using Nano-biophotonics

Ultra-sensitive portable chemical-bio sensing based on perfect absorption



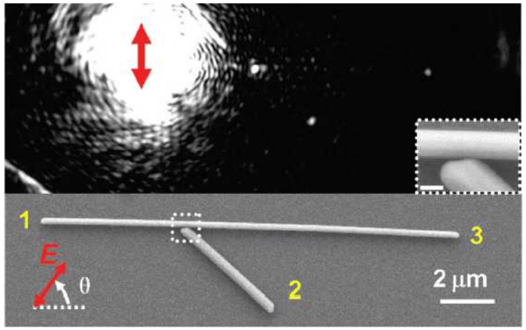
Kabashin et al Nature Mat. 2009

Plasmonic generator



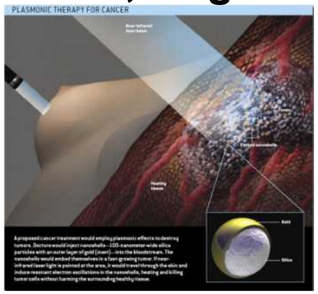
Sheldon & Atwater, Arxiv

Silver Nanowires as Controllable Plasmon Routers



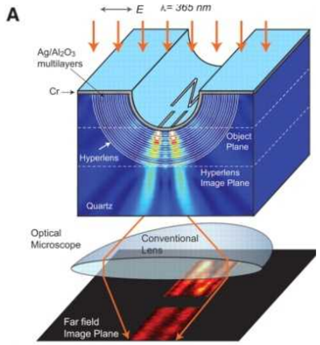
Fang et al Nano Letters , 2010

Hyperthermia Therapy (Photon, Magnetic)



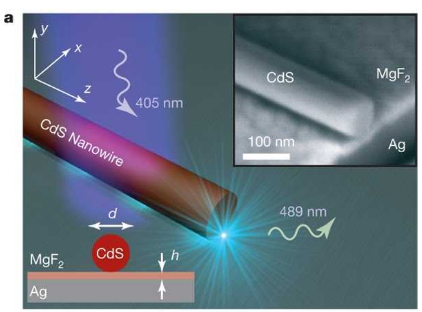
Atwater, Sci. Amer. 2007

Super Resolution



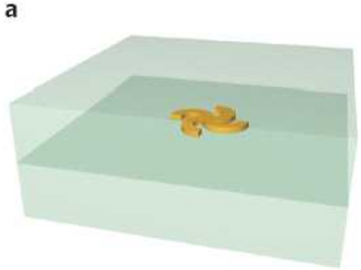
Liu et al Science, 2007

Nano Laser



Oulton et al Nature , 2009

Nanoscale Plasmon Motor



Liu et al Nature Nanotech. 2010