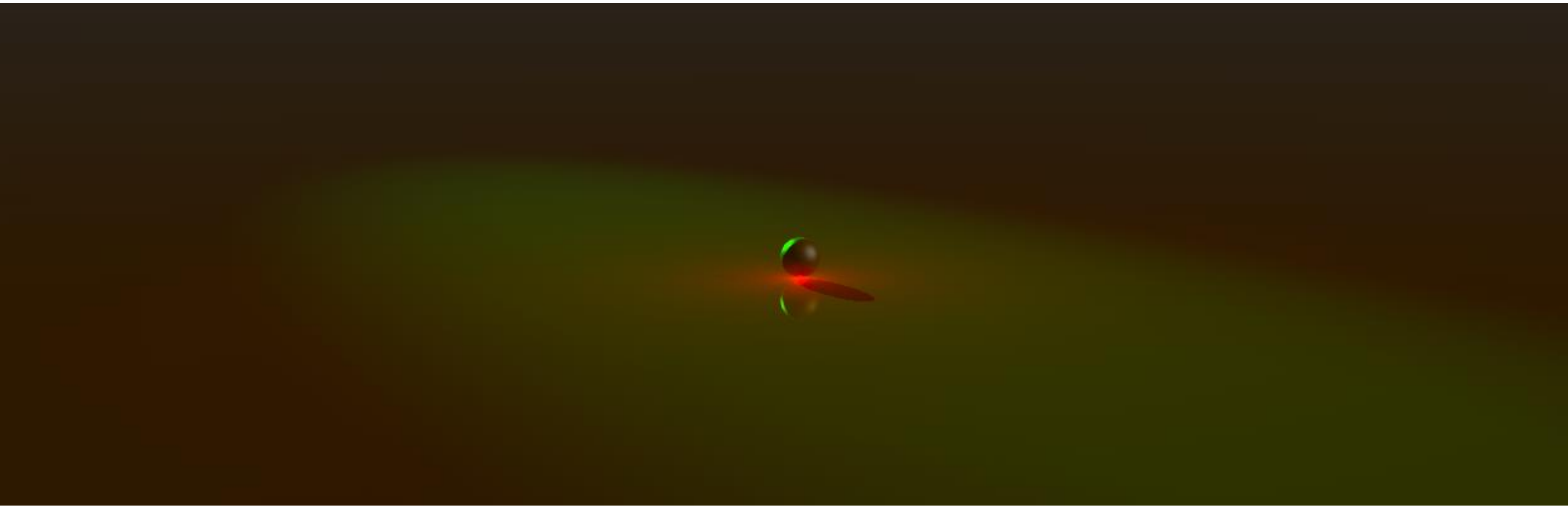
Manipulating Light at the Nanoscale: Gap-Plasmon Enhanced Optical Processes



Chatdanai Lumdee
Advisor: Prof. Pieter G. Kik

Mahidol University
February 23, 2016

Not just yet

Outline

Introduction

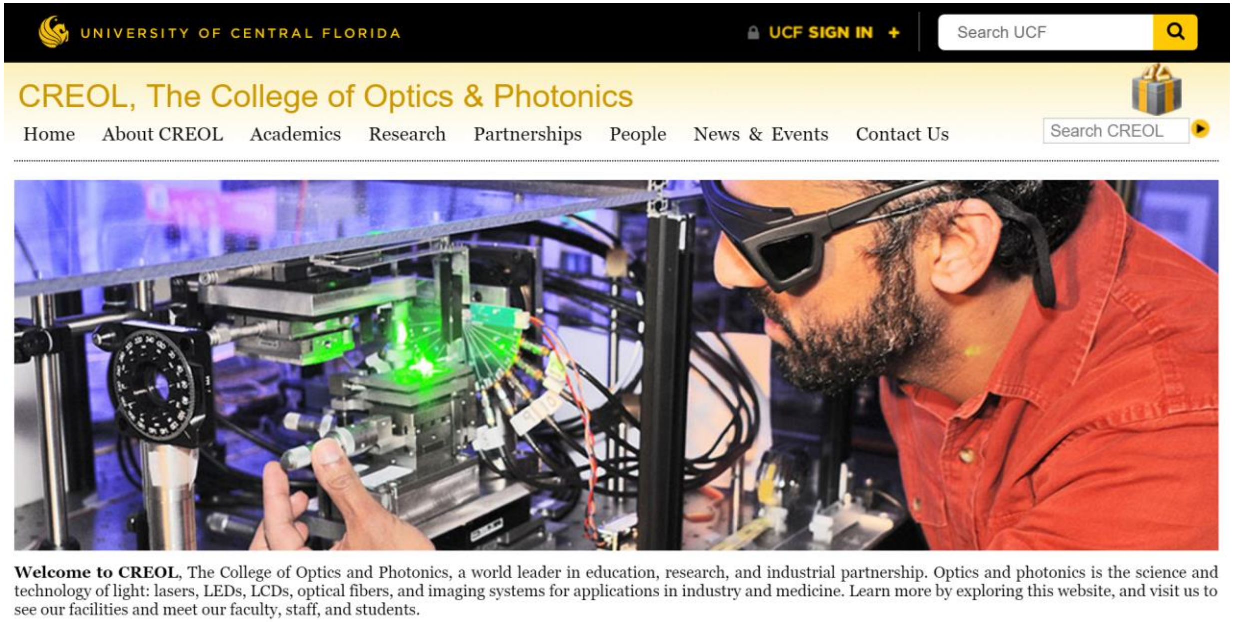
- CREOL
- Nanophotonics?
- Optical near-field
- Gap-plasmon resonance

Gap-plasmons

- **Enhanced scattering and resonance control**
- **Enhanced photoluminescence**
- **Alternative gap-plasmon supporting structure**

Introduction – CREOL

CREOL, the College of Optics and Photonics – www.creol.ucf.edu



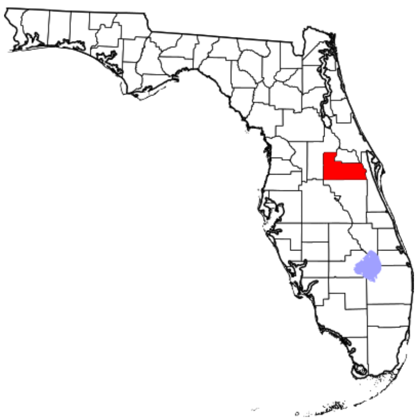
CREOL's trivia

Founded in 1986

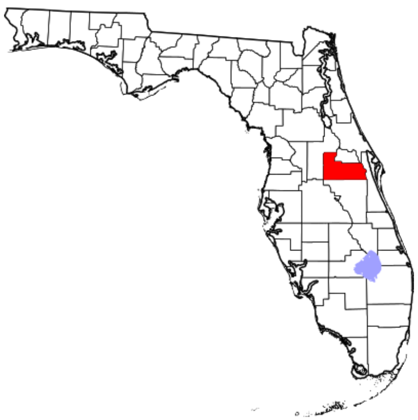
34 faculty members,
17 joint faculty members,
6 emeritus professors,
58 research scientists,
137 graduate students, and
90 undergraduate students

Research areas e.g.
display,
imaging,
integrated photonics,
lasers,
optical fibers,
nonlinear and quantum optics,
sensing, …

Introduction – Orlando, FL



Introduction – Orlando, FL



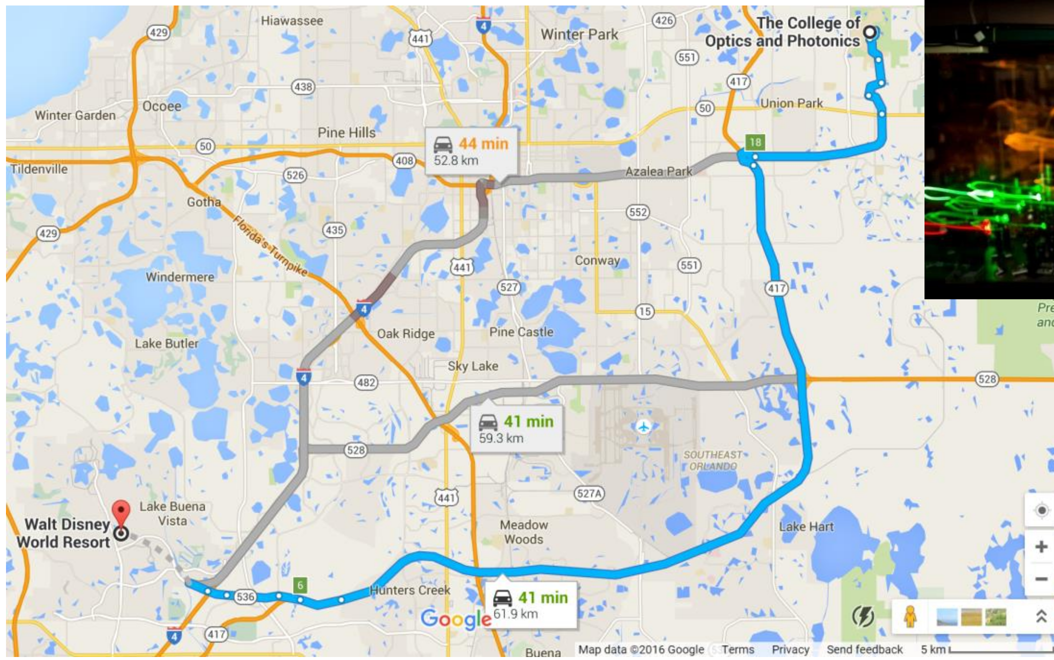
The Walt Disney World Resort

The most visited vacation resort in the world.

The Universal Orlando Resort

The Wizarding World of Harry Potter

Introduction – Orlando, FL



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Gap-plasmons

- **Enhanced scattering and resonance control**
- **Enhanced photoluminescence**
- **Alternative gap-plasmon supporting structure**

Introduction – Nanophotonics

Thanks Wikipedia!

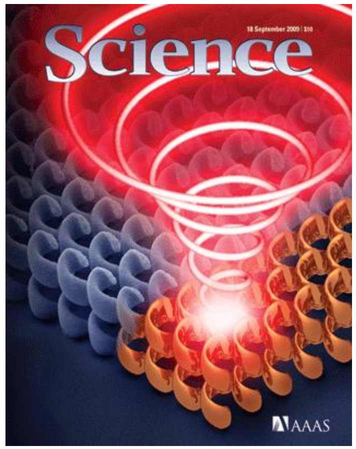
Prof. Pieter G. Kik

NanoPhotonics and Near-field Optics Group - http://kik.creol.ucf.edu/

Nanophotonics? What can it do?

Tons. For example …

Science 325, 1513 (2009)

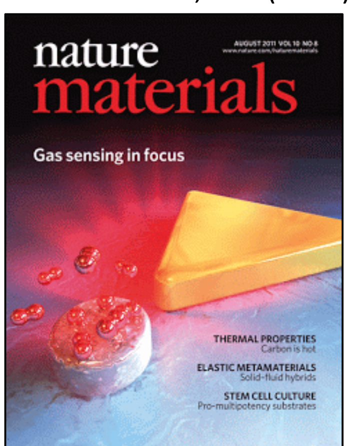


Broadband circular polarizer

Nano Letters 10, 1537 (2010)

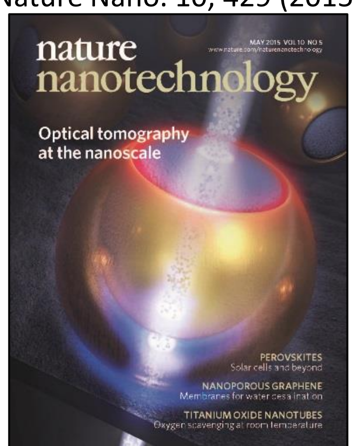
Nanodisk resonators

Nature Mat. 10, 631 (2011)



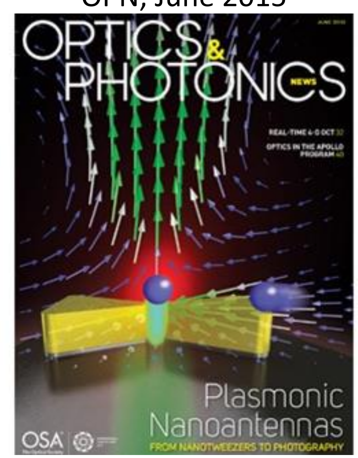
Gas sensor

Nature Nano. 10, 429 (2015)



3D imaging

OPN, June 2015



More …

Introduction – Nanophotonics

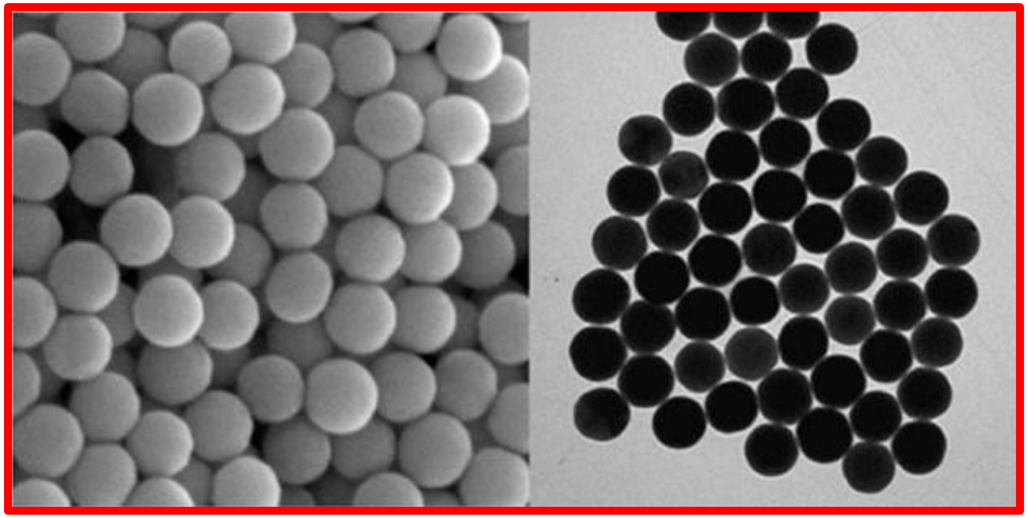
Nanophotonics? What can it do?

Tons. For example …

What's a common element?

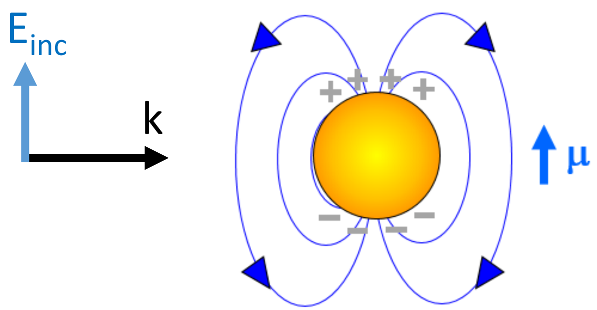
Optical near-field and in some cases **optical resonances** by metallic **nanostructures** (plasmons)

Simplest form → nanosphere



ACS Nano 7, 11064 (2013)

Single NP in free space



Electrostatic approximation

Particle << wavelength

$$\frac{E_{in}}{E_{inc}} = -3\frac{\epsilon_{out}}{\epsilon_{in} + 2\epsilon_{out}}$$ (Homogeneous)

Boundary conditions

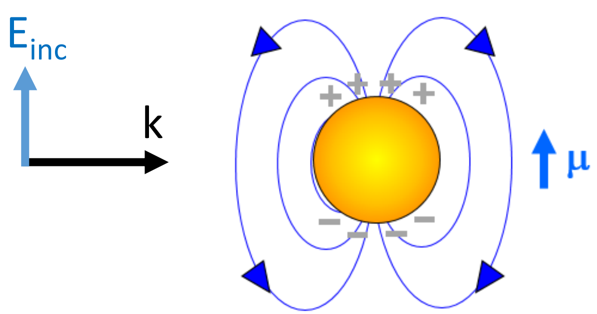
$$\frac{E_{out}}{E_{inc}} = -3\frac{\epsilon_{in}}{\epsilon_{in} + 2\epsilon_{out}}$$ (on NP surface)

Real metal: $\epsilon_{in}(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ $E_{in}\ and\ E_{out} \rightarrow \infty$ $when \quad \epsilon_{in} + 2\epsilon_{out} = 0$

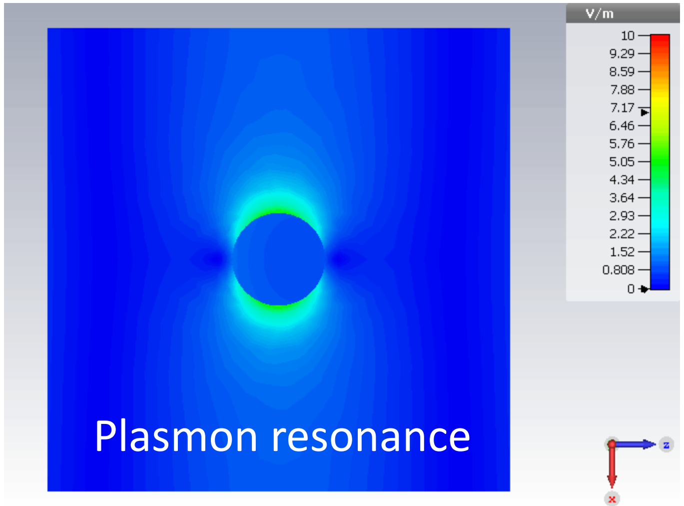
(resonance frequency)

Introduction – Optical Near-field

Single NP in free space



50 nm diameter Au NP in water



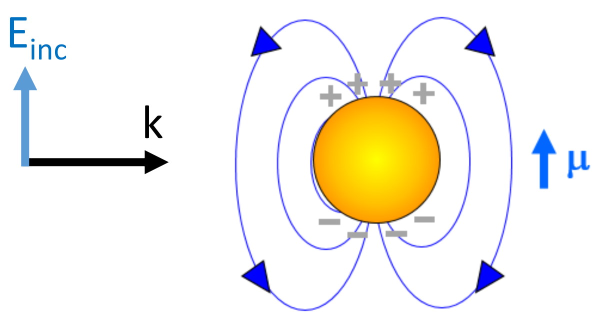
Frequency domain finite-element simulation

Real metal: $\epsilon_{in}(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ $\boxed{E_{in} \; and \; E_{out} \to \infty}$ $when \quad \epsilon_{in} + 2\epsilon_{out} = 0$

(resonance frequency)

Near-field $\propto \frac{1}{r^3}$ Decays quickly → localized in a nm^3 volume (nanophotonics)

Single NP in free space



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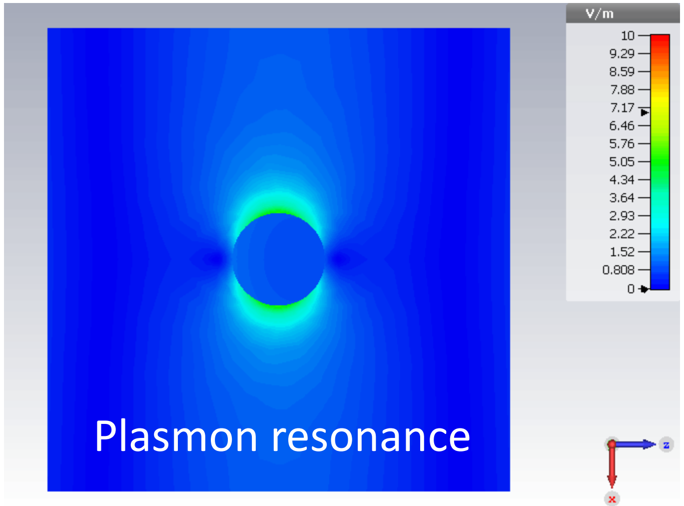


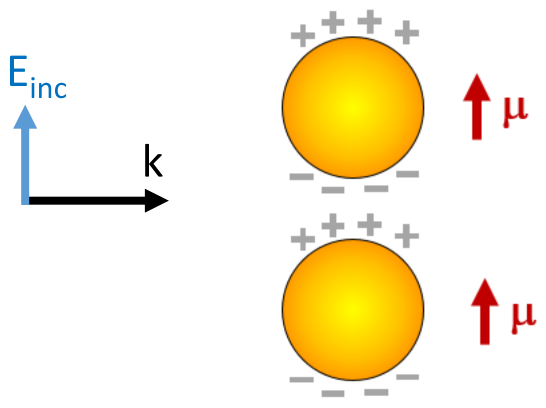
Frequency domain finite-element simulation

Strong field enhancement and scattering at the resonance condition

Question: How do we get stronger and more confined field?

Introduction – Optical Near-field

NP dimer in free space

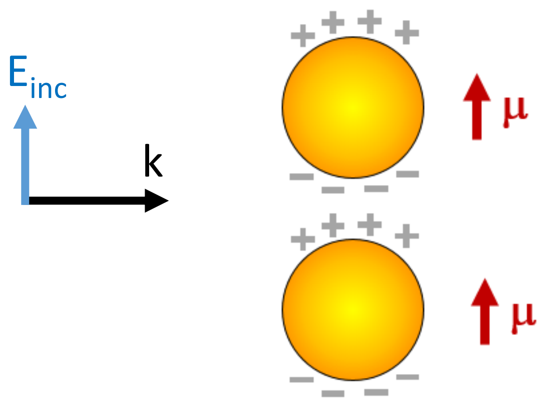


Strong field enhancement and scattering at the resonance condition

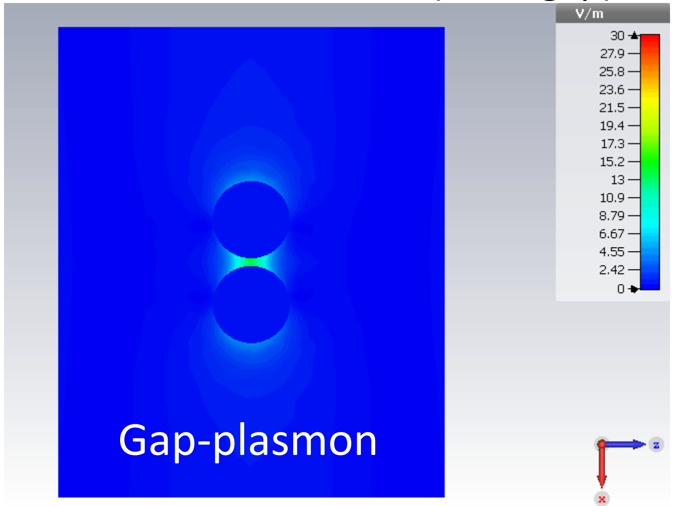
Question: How do we get stronger and more confined field?
Answer: Using more than one particle!

Introduction – Gap-plasmon resonance

NP dimer in free space



50 nm diameter Au NP dimer (5 nm gap) in water



Frequency domain finite-element simulation

Strong field enhancement and scattering at the resonance condition

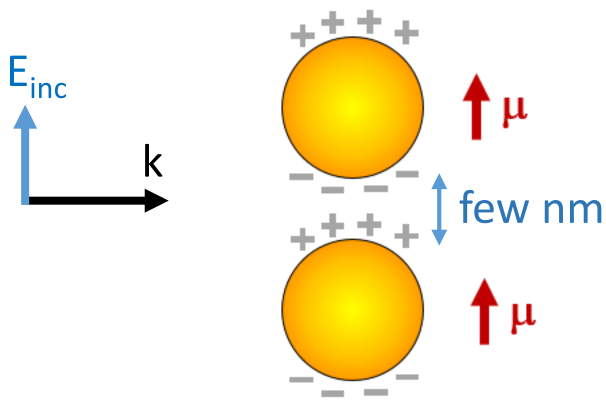
Question: How do we get stronger and more confined field?
Answer: Using more than one particle!

Stronger and more confined field → Gap-plasmon resonance (mode volume □ gap size)

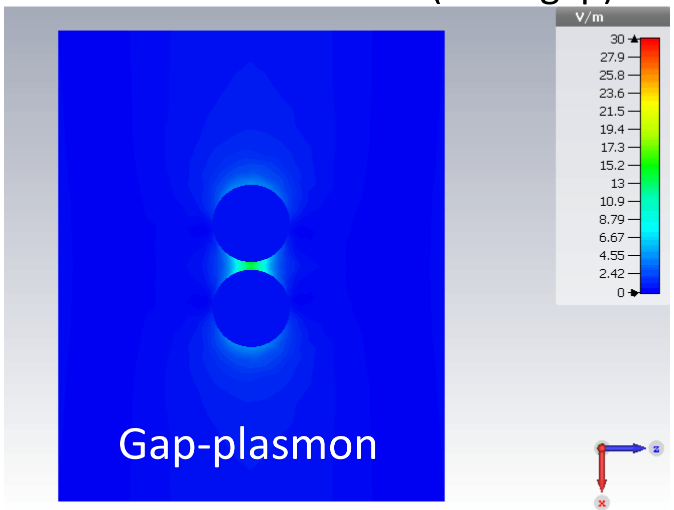
Optical wavelength □ 440 nm in water at this frequency

Introduction – Gap-plasmon resonance

NP dimer in free space



50 nm diameter Au NP dimer (5 nm gap) in water



Frequency domain finite-element simulation

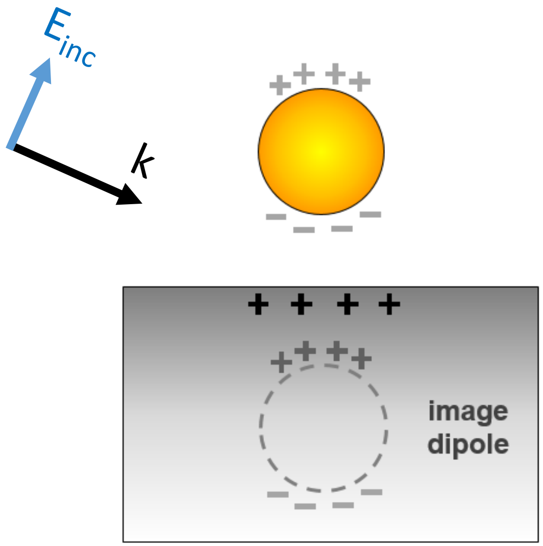
Gap plasmon resonance → stronger field enhancement + confinement

<u>But</u>:
Few nm gap is difficult to make.

Question:
What could be a structure that offers similar field enhancement/confinement but simpler?

Introduction – Gap-plasmon resonance

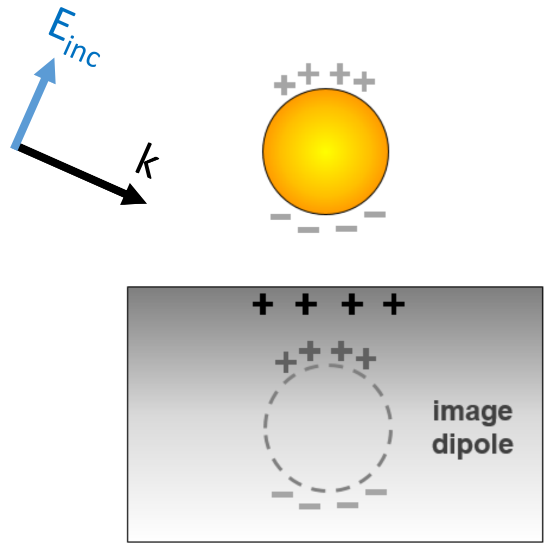
NP on metallic film



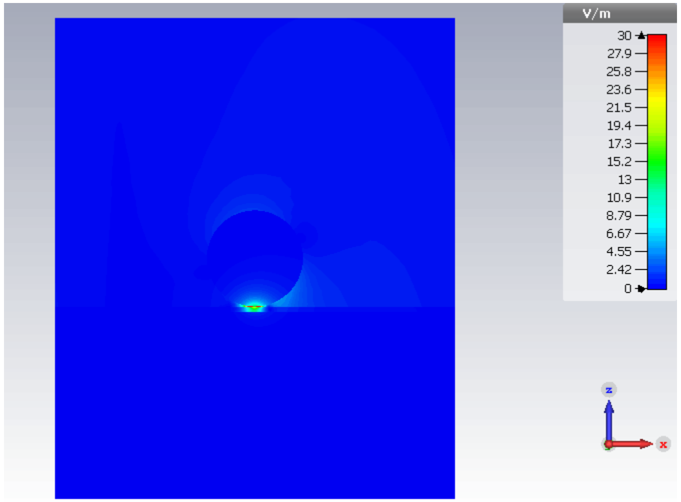
Question: A structure that offers similar field enhancement/confinement but simpler?
Answer: Nanoparticles on supporting metallic film

Introduction – Gap-plasmon resonance

NP on metallic film



60 nm diameter Au NP on oxide coated Al in air (77 AoI)



Frequency domain finite-element simulation

Question: A structure that offers similar field enhancement/confinement but simpler?
Answer: Nanoparticles on supporting metallic film

NP dipole + image dipole dimer → Gap plasmon at the junction!

Much easier and cheaper to fabricate than dimers

This presentation will focus on this structure.

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- Optical near-field
- Gap-plasmon resonance

Gap-plasmons

- **Enhanced scattering and resonance control**
  Different applications require different working frequencies.
  Can we precisely control gap-plasmon resonance frequency?

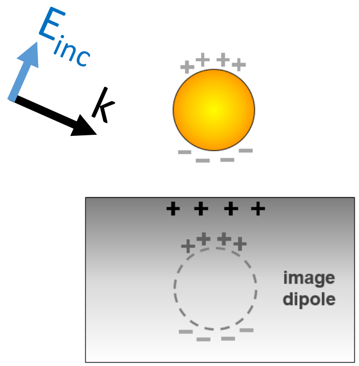
- **Enhanced photoluminescence**

- **Alternative gap-plasmon supporting structure**

Enhanced scattering and resonance control

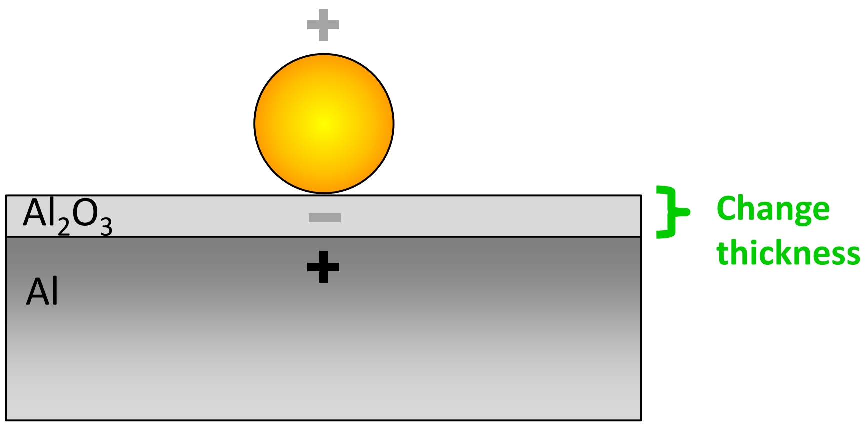
Goal: Precise resonance frequency control of gap-plasmon in NP-on-film structure

Question: How can we achieve that?
Answer: Change the separation distance.



Previous attempts: Organic spacer layer → organic background, not robust

Our structure: Gold nanoparticles on an aluminum film
Aluminum can be oxidized to grow Al_2O_3 spacer



60 nm diameter Au NPs

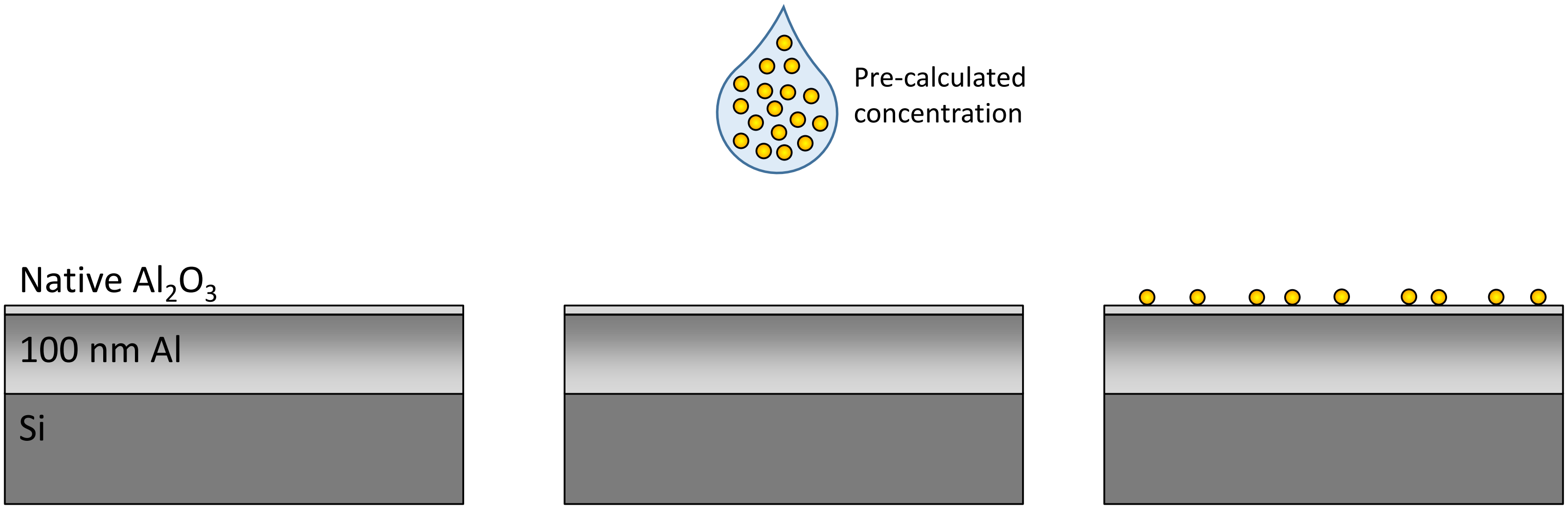
Enhanced scattering and resonance control

Sample preparation (3D = Deposition, Drop, Done)

(i) Al film deposition

(ii) Au NP colloidal drop-coating

(iii) Done!

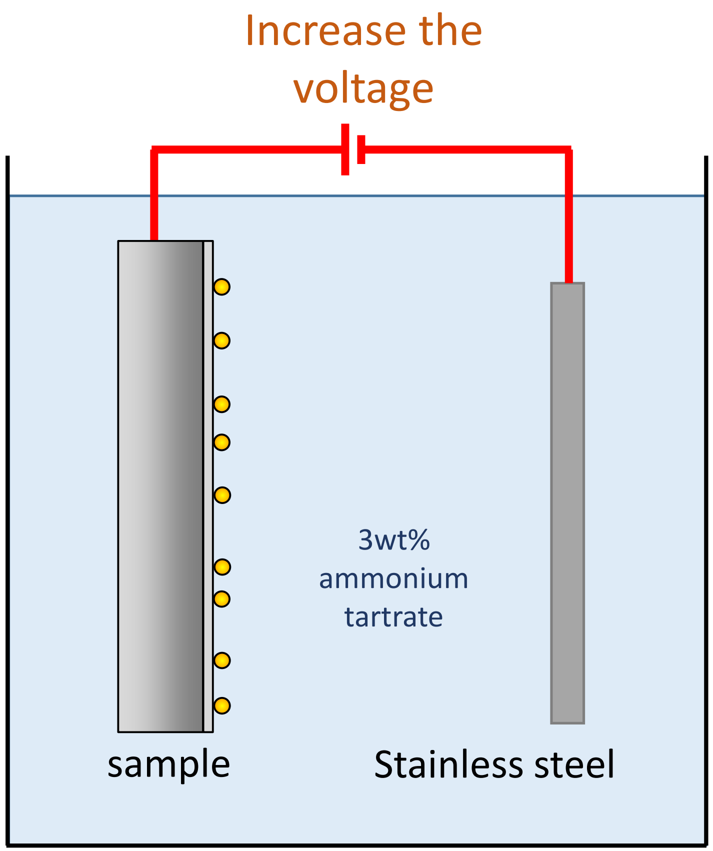


Simple and low-cost → Good!

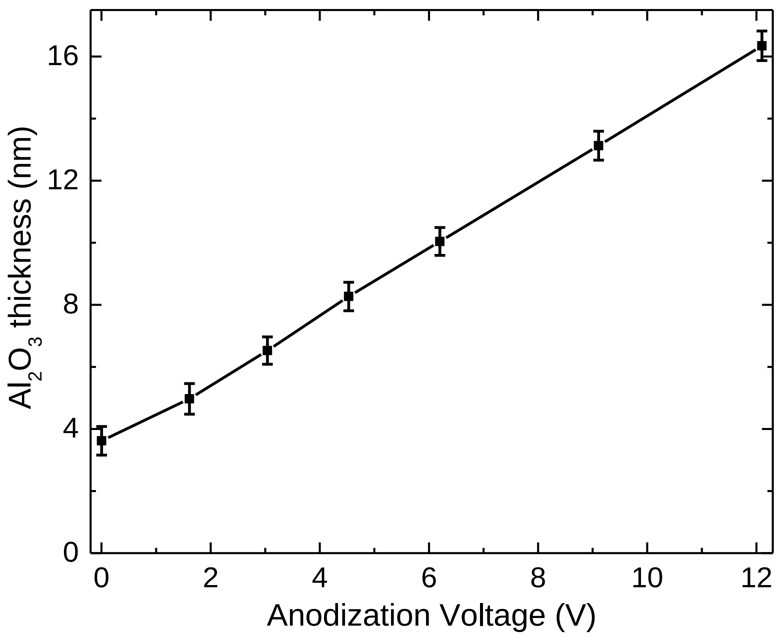
Question: How do we grow Al_2O_3 thickness?

Enhanced scattering and resonance control

Question: How do we grow Al_2O_3 thickness?
Answer: Anodization.
Overall reaction: $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$



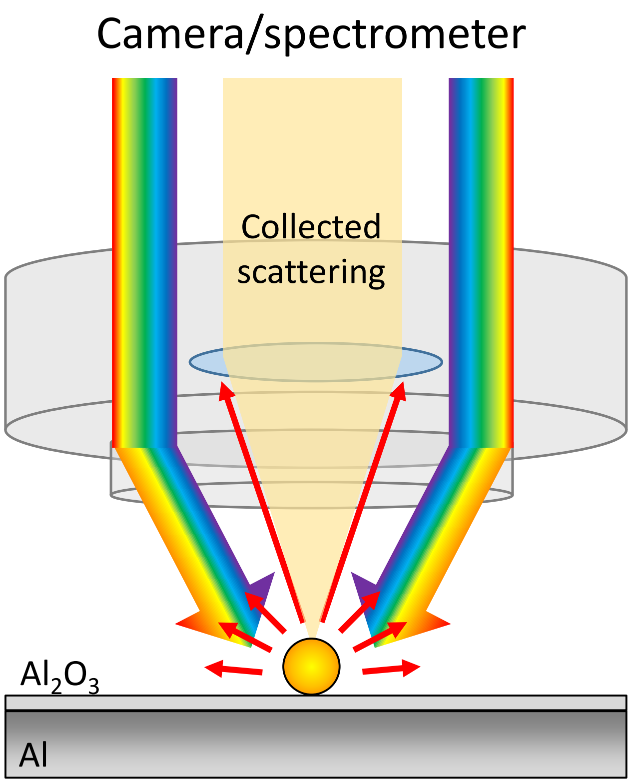
Very well controlled thickness
(measured using an ellipsometer)

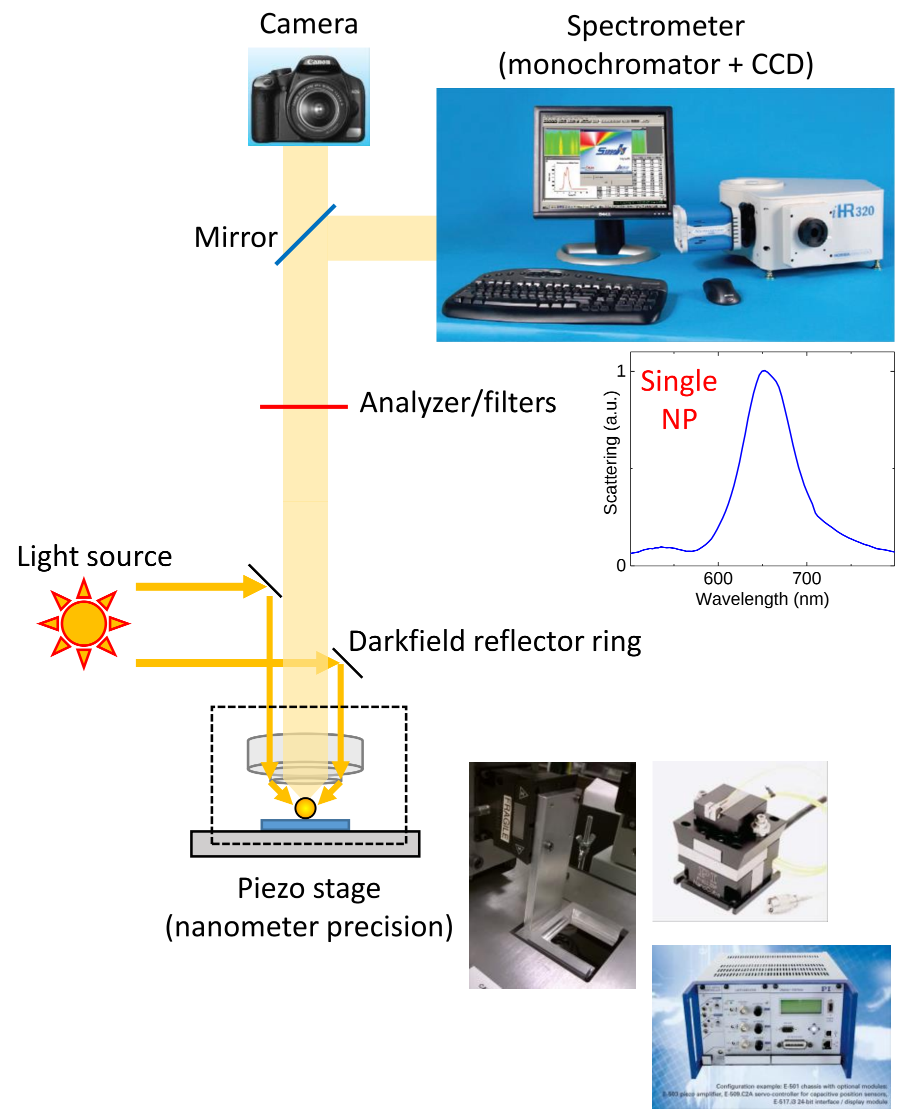


Voltage-limited Al_2O_3 thickness → precise thickness control
Question: How do we investigate these particles?

Enhanced scattering and resonance control

Answer: Darkfield microscopy and <u>single particle</u> spectroscopy

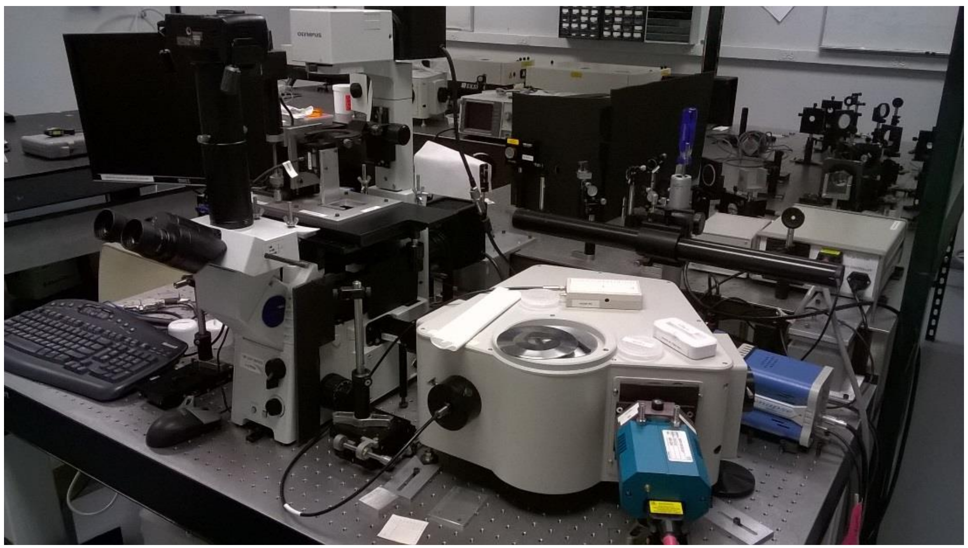




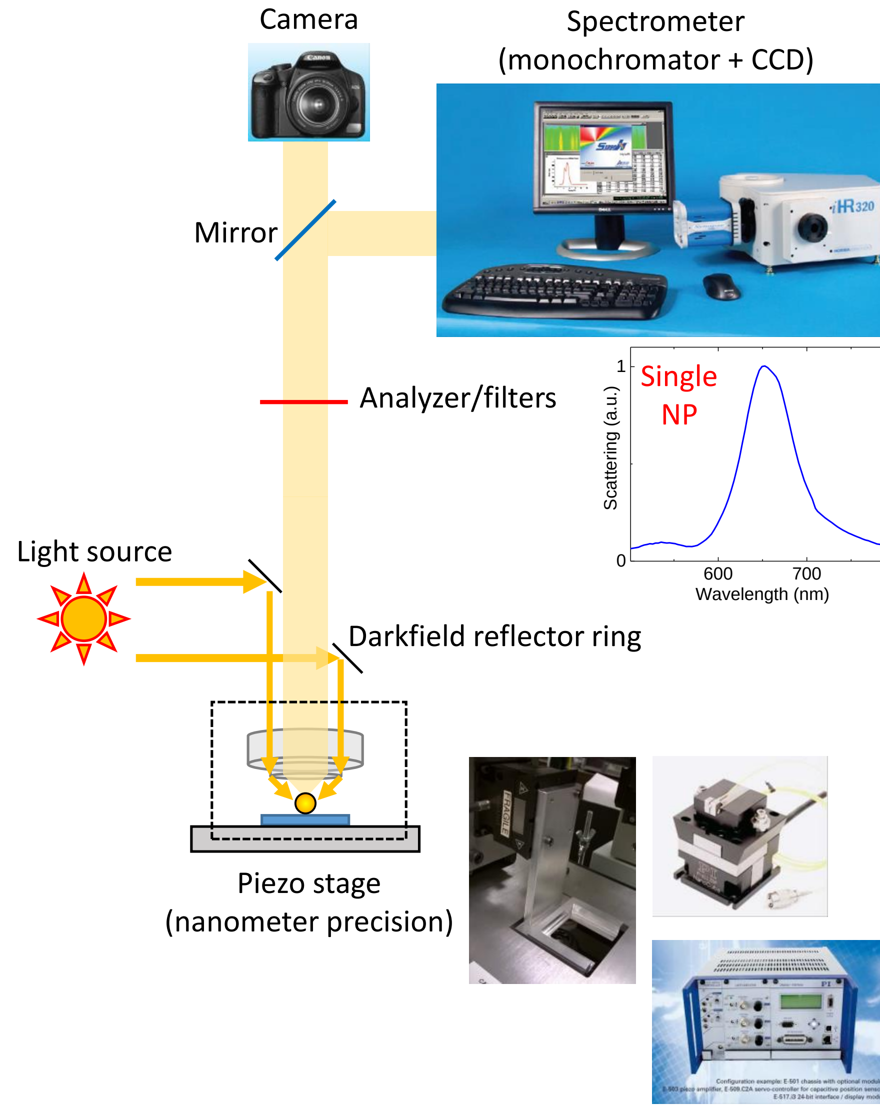
Enhanced scattering and resonance control

Answer: Darkfield microscopy and <u>single particle</u> spectroscopy

It actually looks like this!

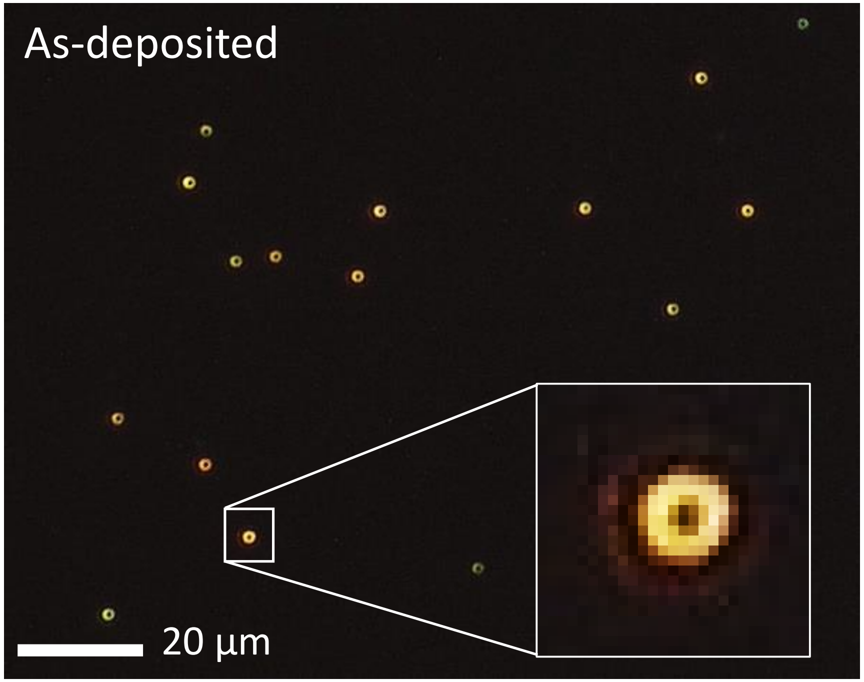


Inverted microscope



Enhanced scattering and resonance control

Darkfield microscopy image of an as-deposited sample

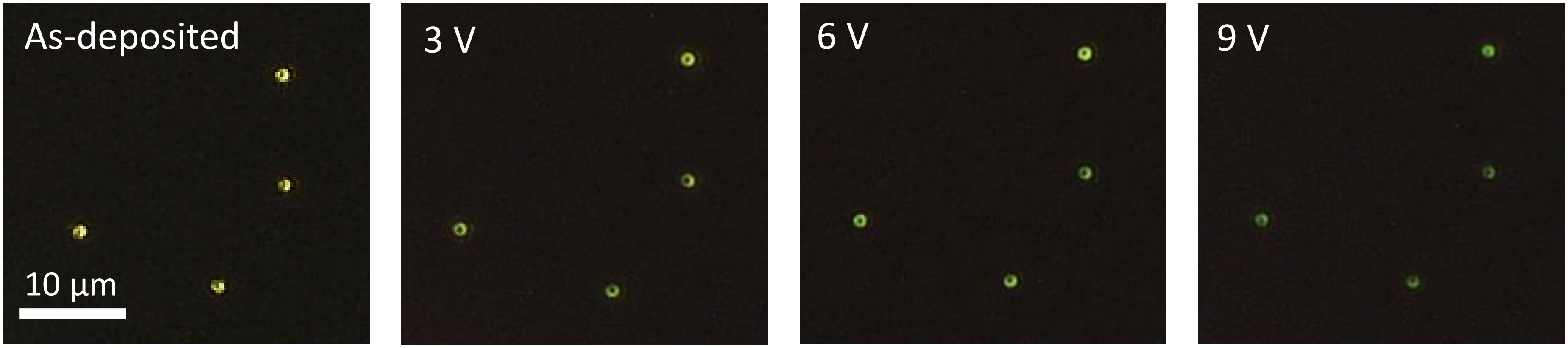


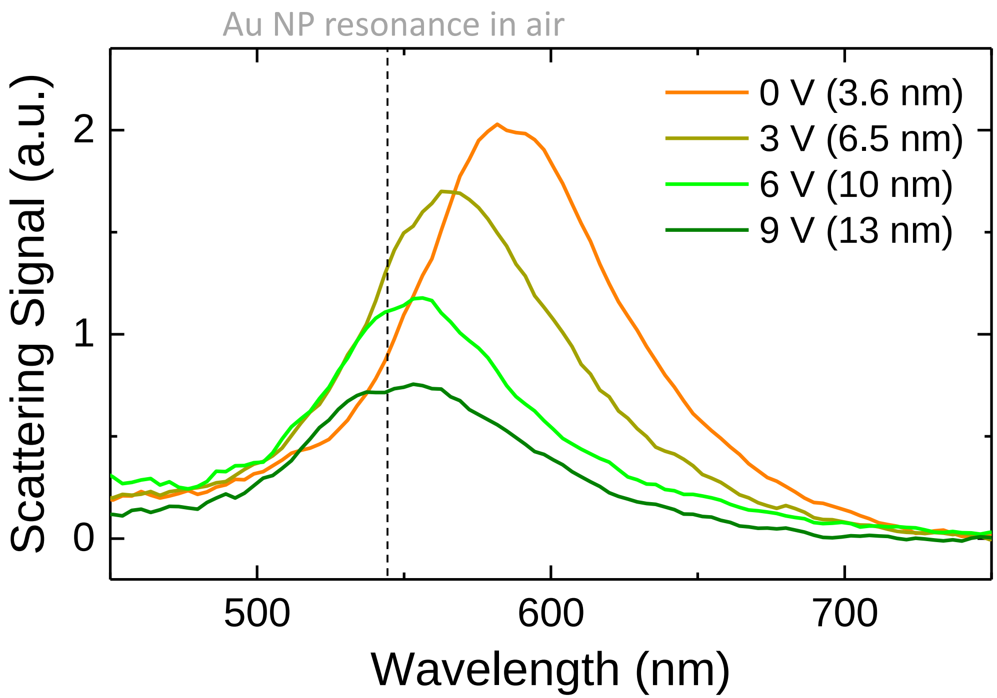
Very well separated scattering spots → can do *single particle* spectroscopy

Ring-shaped scattering spot = indication of a strong vertical electric dipole oscillation
This is expected from a gap-mode of NPs on a metallic film
(please ask if you want to know more)

Enhanced scattering and resonance control

Darkfield microscopy and single particle spectroscopy after each anodization step



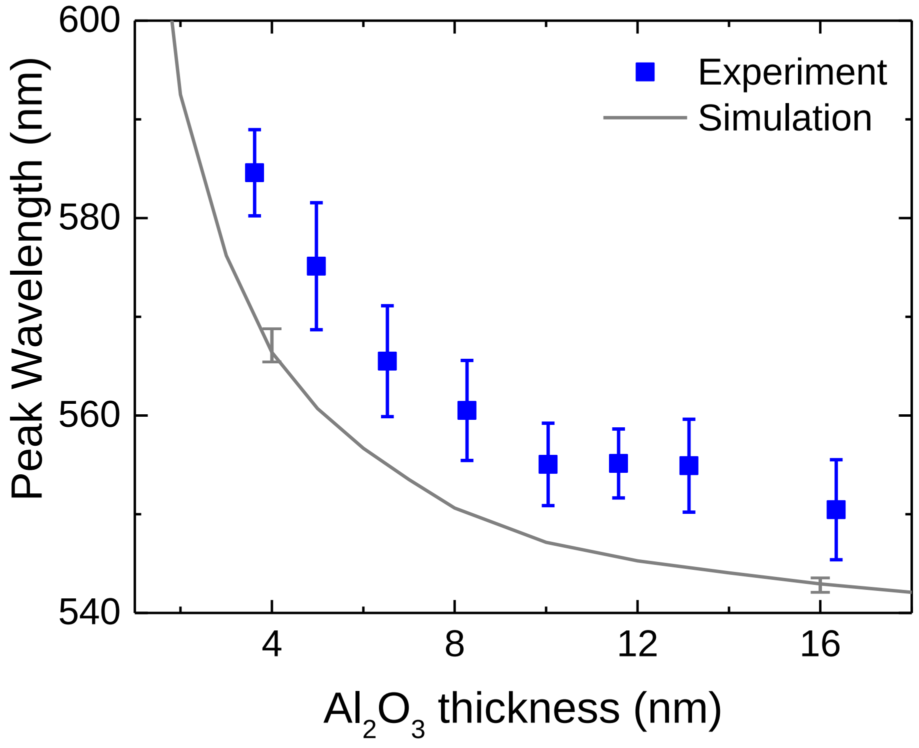


From single NP!

Thinner Al_2O_3 = redder the NPs
Less loss = Stronger scattering

Enhanced scattering and resonance control

Question: Reproducible on many particles?
Answer: Yes! (10 single particles)

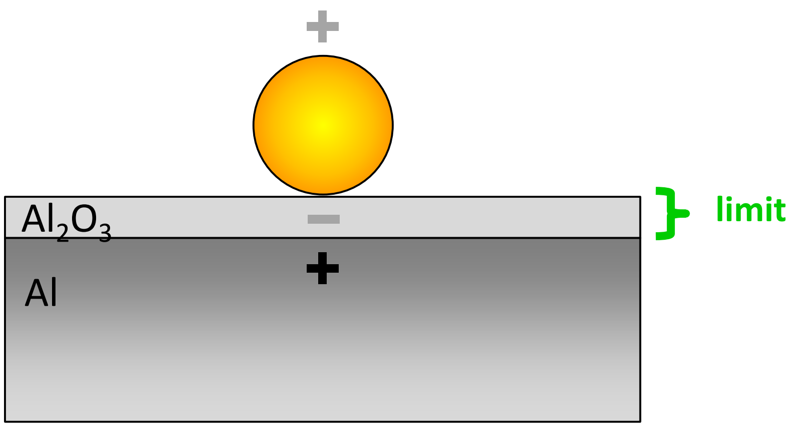


Precise resonance control over 30 nm range (550 – 580 nm)

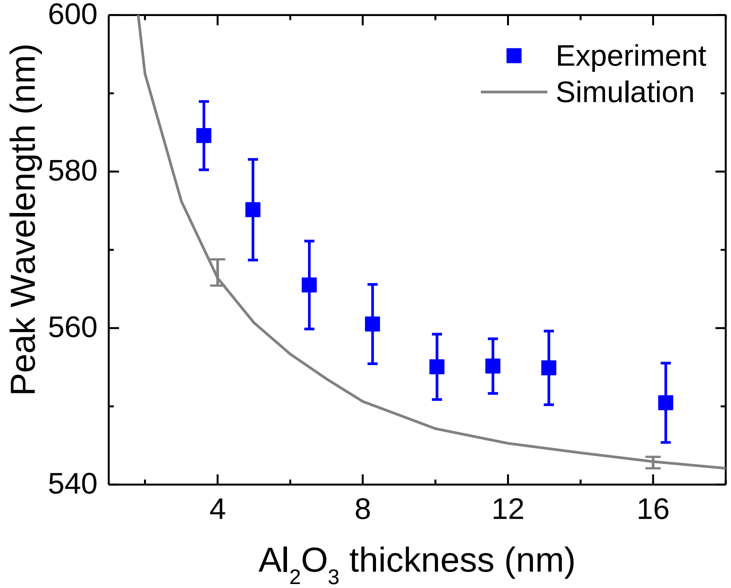
Question: Can we get a larger tuning range?

Enhanced scattering and resonance control

Question: Can we get a larger tuning range?



60 nm diameter Au NPs



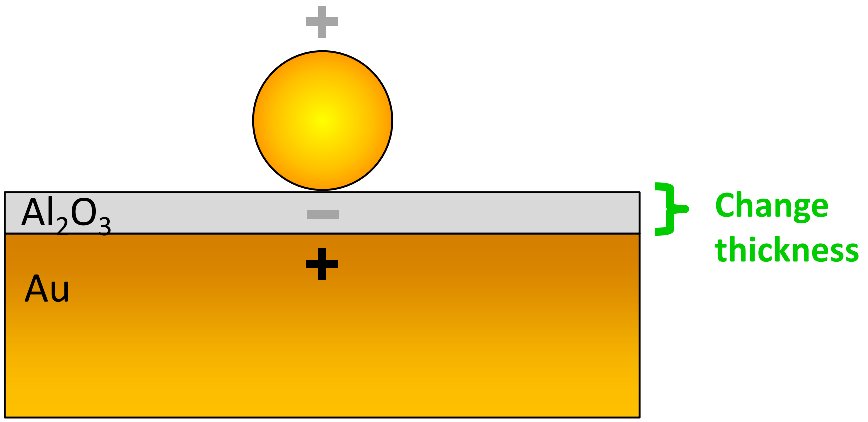
Limiting factor: Native Al_2O_3 on aluminum is almost 4 nm thick

Thinner oxide → more red-shift → larger tuning range

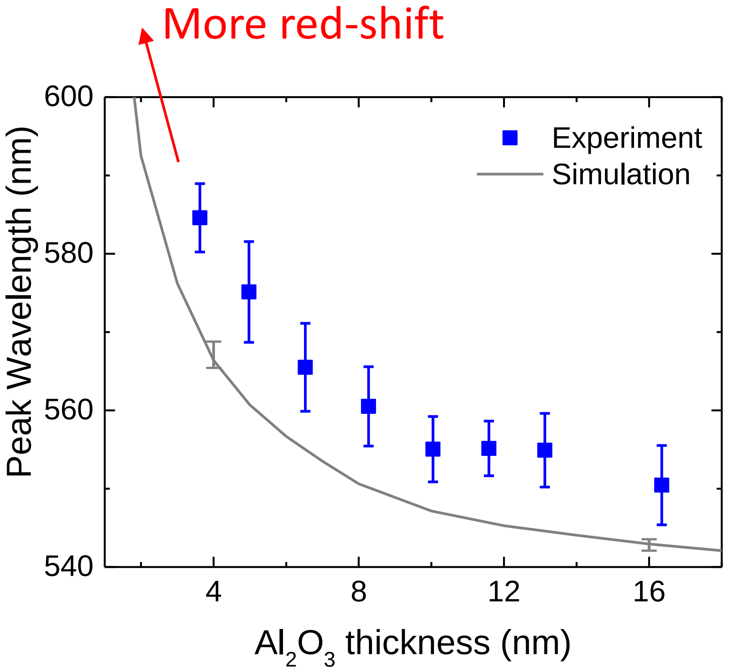
Enhanced scattering and resonance control

Question: Can we get a larger tuning range?

Answer: Yes, but we need to change the substrate material.



60 nm diameter Au NPs



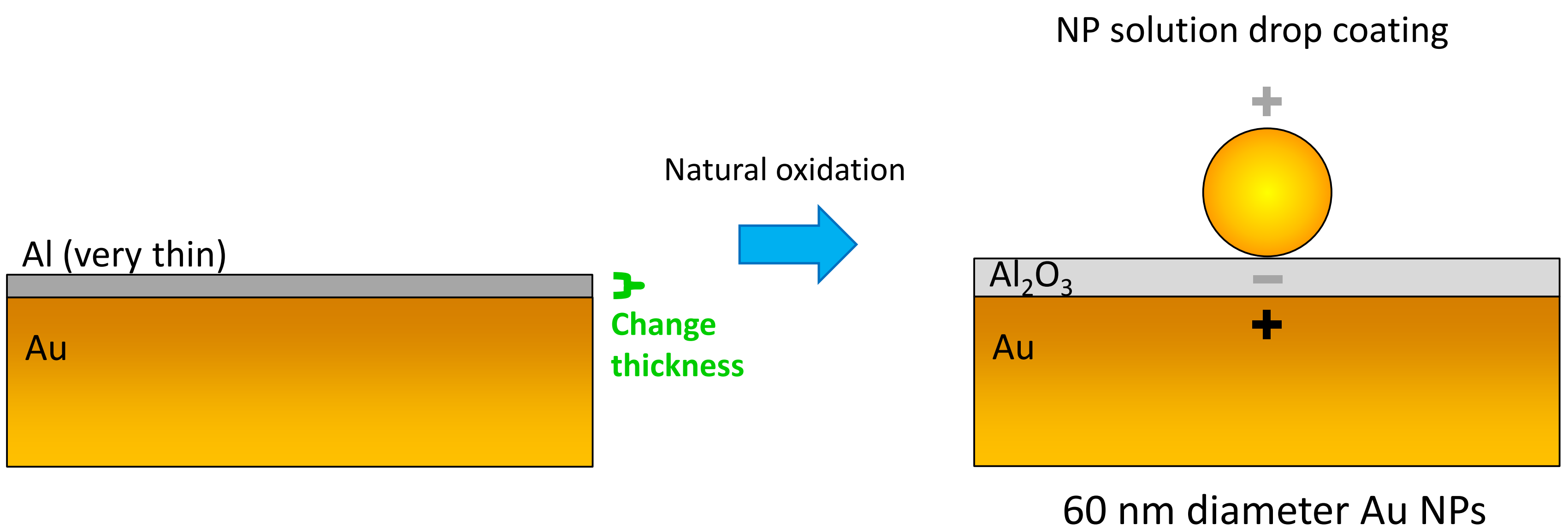
Limiting factor: Native Al_2O_3 on aluminum is almost 4 nm thick

Thinner oxide → more red-shift → larger tuning range

Gold does not oxidize!

Enhanced scattering and resonance control

Question: How do we control Al_2O_3 thickness on gold?
Answer: Regular thin-film deposition

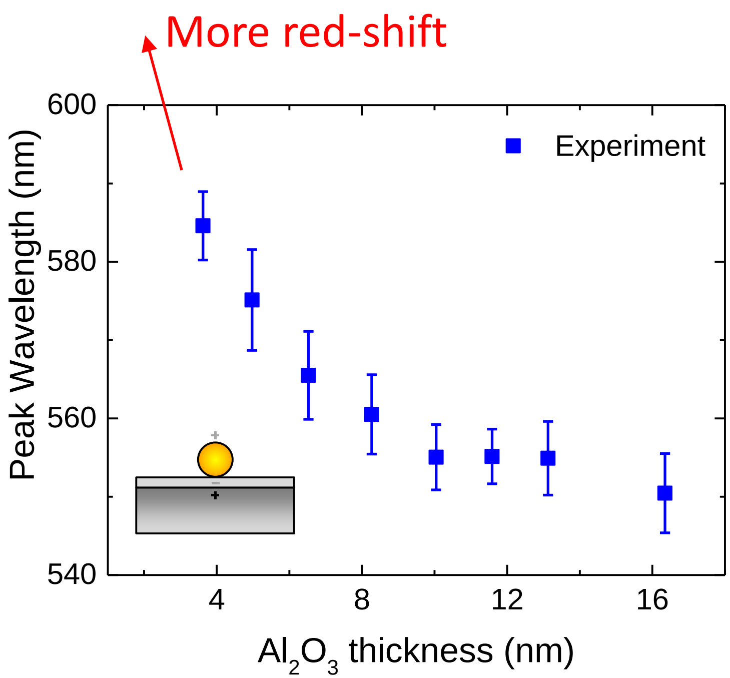


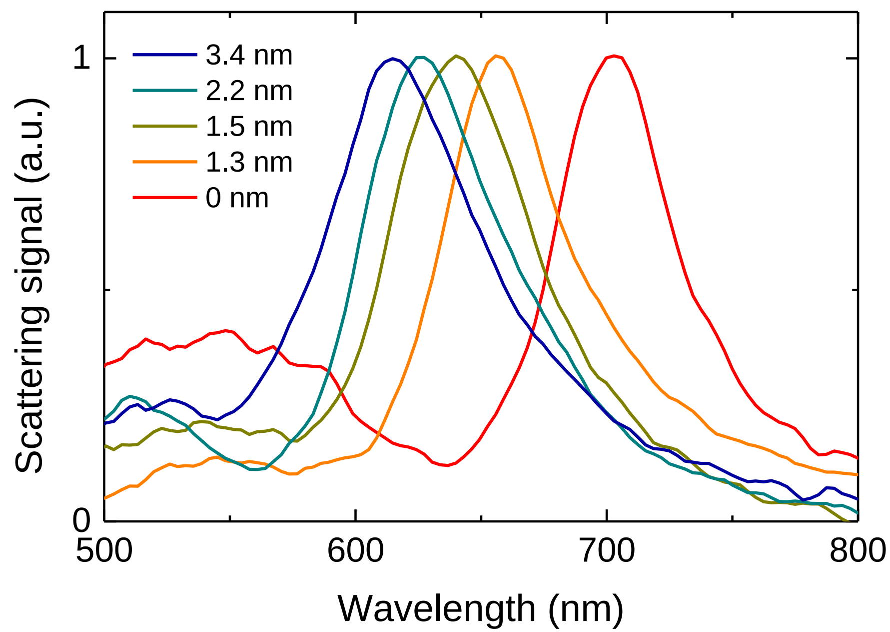
Very thin Al → Entire Al film oxidizes and becomes Al_2O_3

Question: Can we really get more redshift than Au NPs on Al?

Enhanced scattering and resonance control

Answer: Yes, we can. Take a look at darkfield microscopy images and spectra



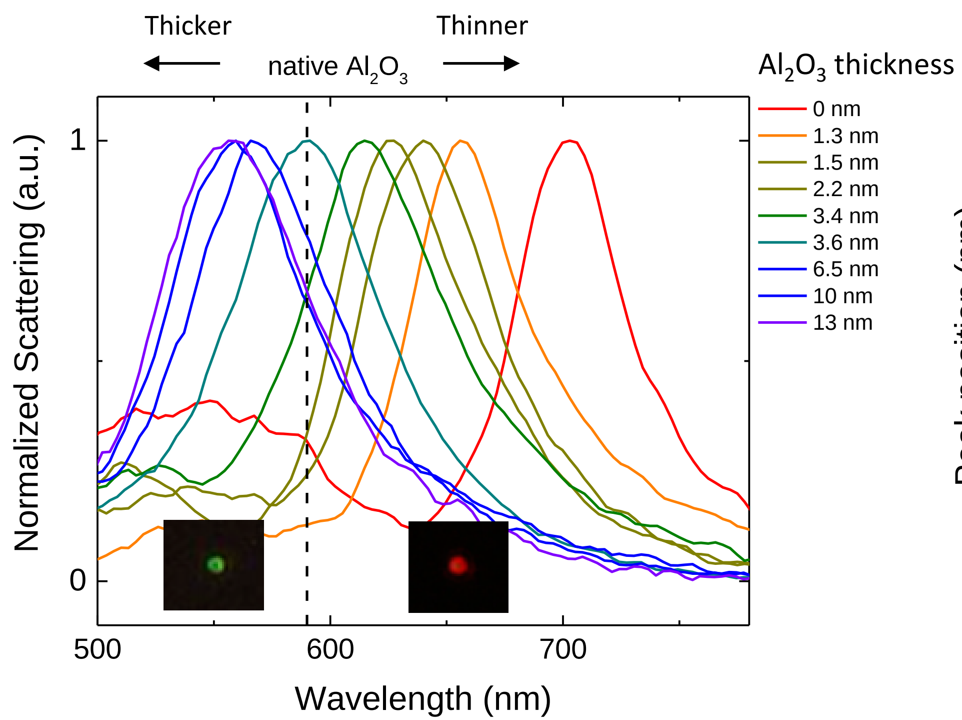


More redshift compared to Au NPs on anodized Al

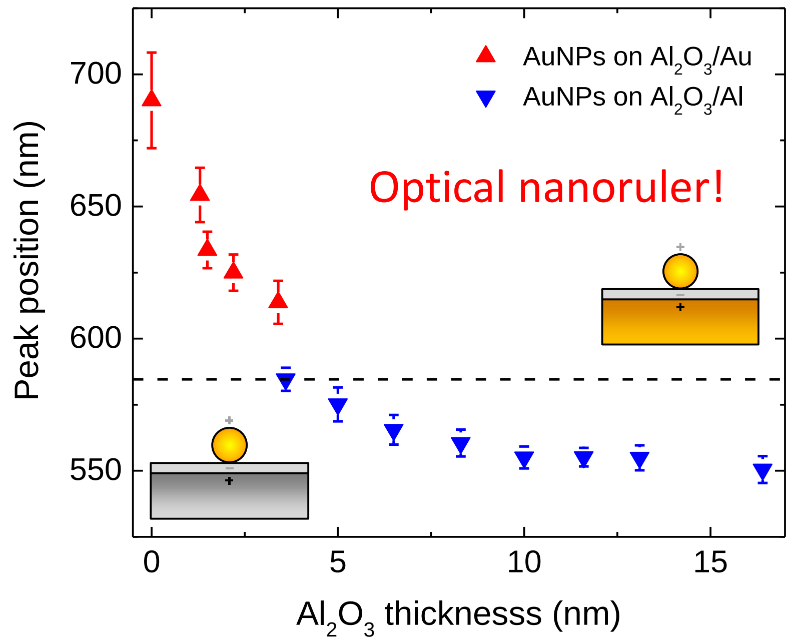
Enhanced scattering and resonance control

Question: What is the total tuning range we achieved?

Answer: > 140 nm, from green to red (good range for Raman measurements)



Statistics from many NPs



Goal: Precise resonance frequency control of gap-plasmon in NP-on-film structure

Mission accomplished!

Outline

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- Optical near-field
- Gap-plasmon resonance

Gap-plasmons

- **Enhanced scattering and resonance control**
  We precisely control gap-plasmon resonance frequency over a broad wavelength range from green to red.

- **Enhanced photoluminescence**

- **Alternative gap-plasmon supporting structure**

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Gap-plasmons

- **Enhanced scattering and resonance control**
  We precisely control gap-plasmon resonance frequency over a broad wavelength range from green to red.

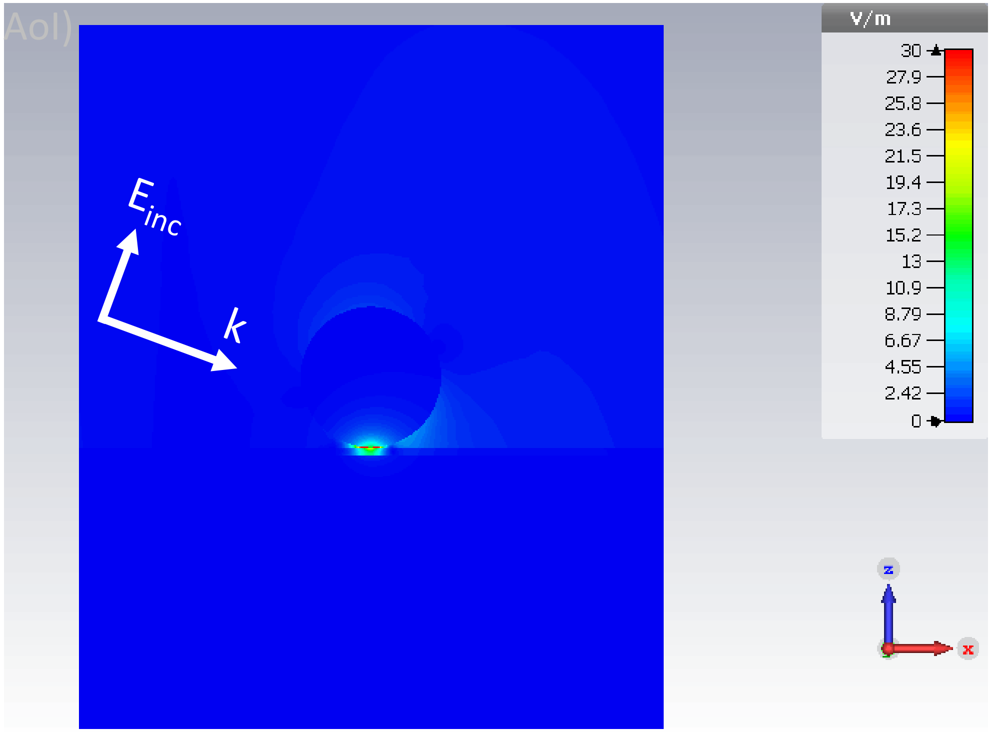
- **Enhanced photoluminescence**
  Gold PL gets enhanced drastically at the gap-plasmon resonance wavelength.
  What role does a gap-plasmon play?

- **Alternative gap-plasmon supporting structure**

Gap-plasmon enhanced photoluminescence

Popular plasmon enhanced sensing scheme → Surface Enhanced Raman Scat. (SERS)

60 nm diameter Au NP on oxide coated Al in air (77



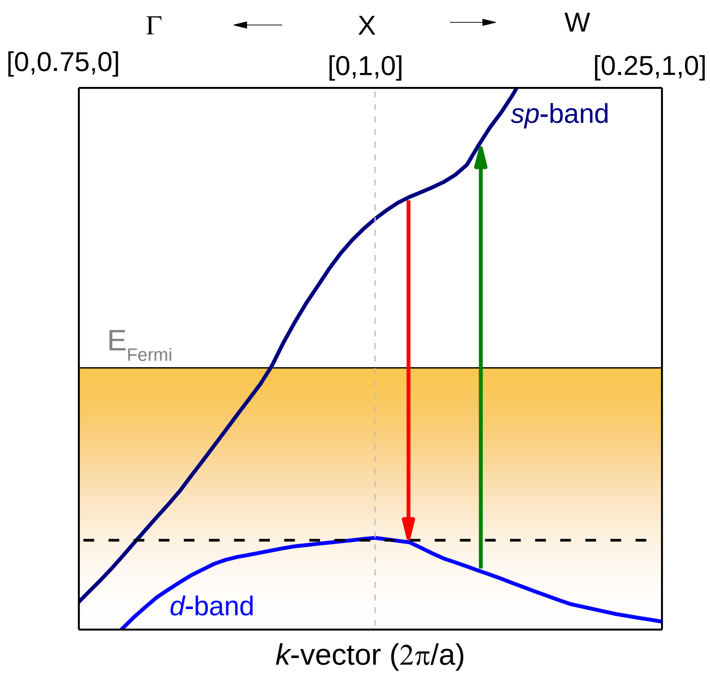
Frequency domain finite-element simulation

We observed plasmon enhanced PL of gold NPs → Let's find out!
(got carried away by curiosity)

Gap-plasmon enhanced photoluminescence

Photoluminescence (PL) → Light emission as a result of photoexcitation of carriers

Band structure of gold
Adapted from: Journal of Chemical Physics 2005, **122**(16), p. 164303.



Metal PL is extremely weak

PL efficiency of gold is 10^{-10}

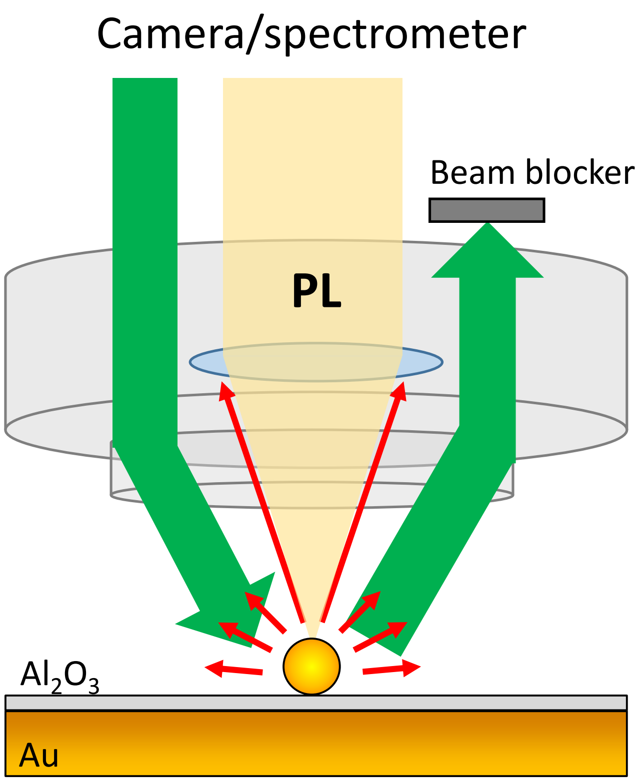
But it was very strong in the measurement (in the next few slides ☺)!
→ gap-plasmon enhanced gold PL!

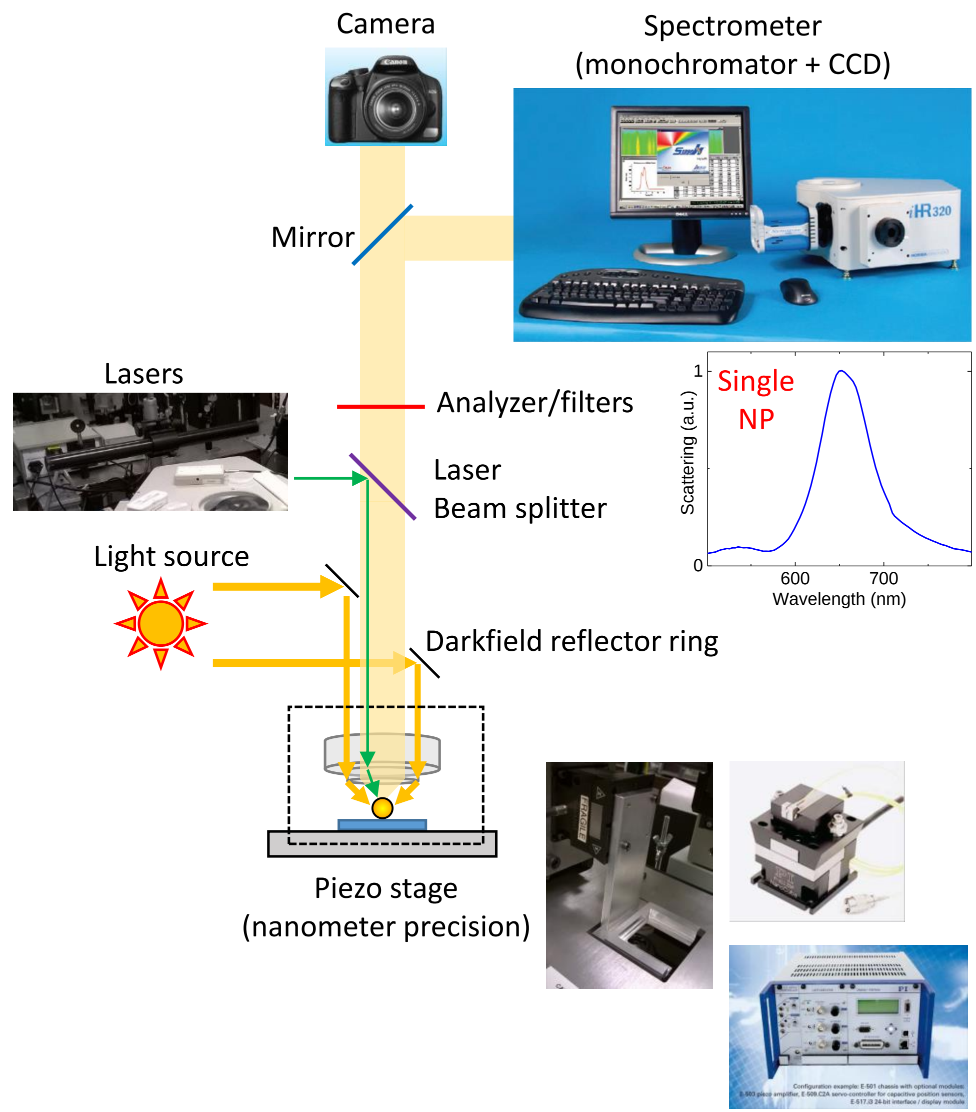
Goal: Explain the process of gap-plasmon enhanced photoluminescence

Gap-plasmon enhanced photoluminescence

Question: How do we do PL experiment?

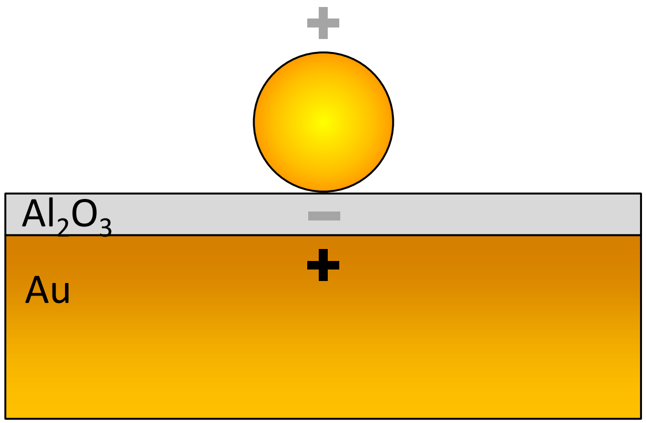
Answer: Similar to darkfield, but with lasers





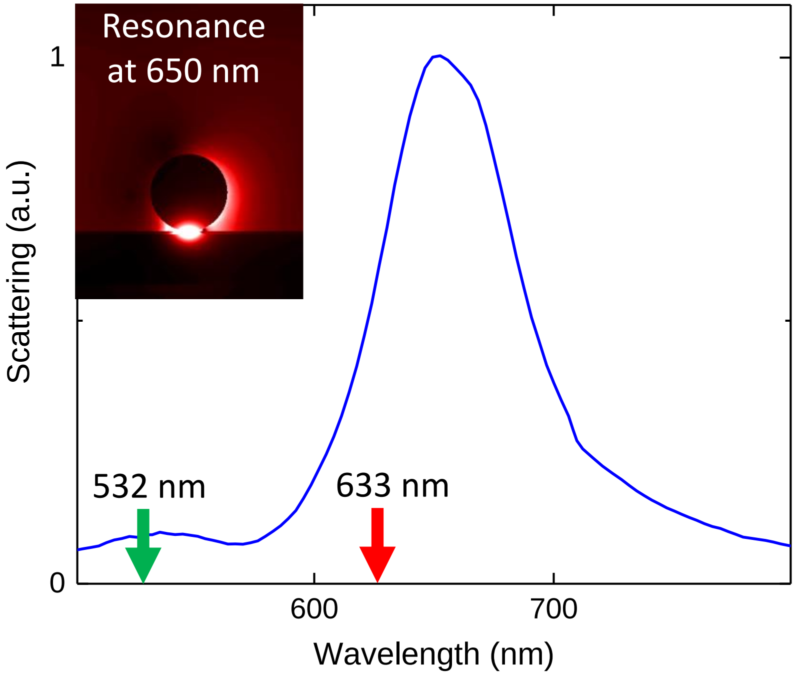
Gap-plasmon enhanced photoluminescence

Scattering spectrum of a AU NP on a gold film



80 nm Au NP on 3.4 nm Al_2O_3 coated Au

Single NP scattering spectrum

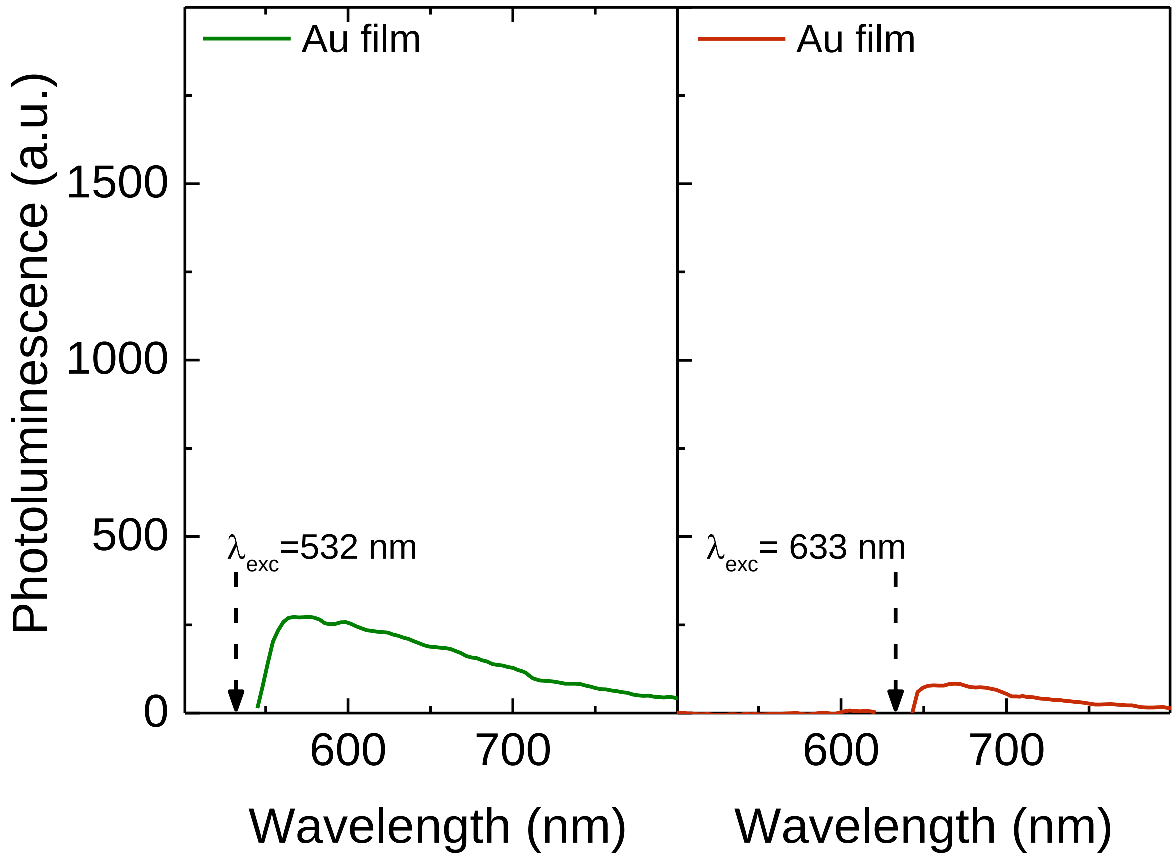


PL at two excitation wavelengths, near and far form the NP resonance wavelength

Gap-plasmon enhanced photoluminescence

Photoluminescence spectra

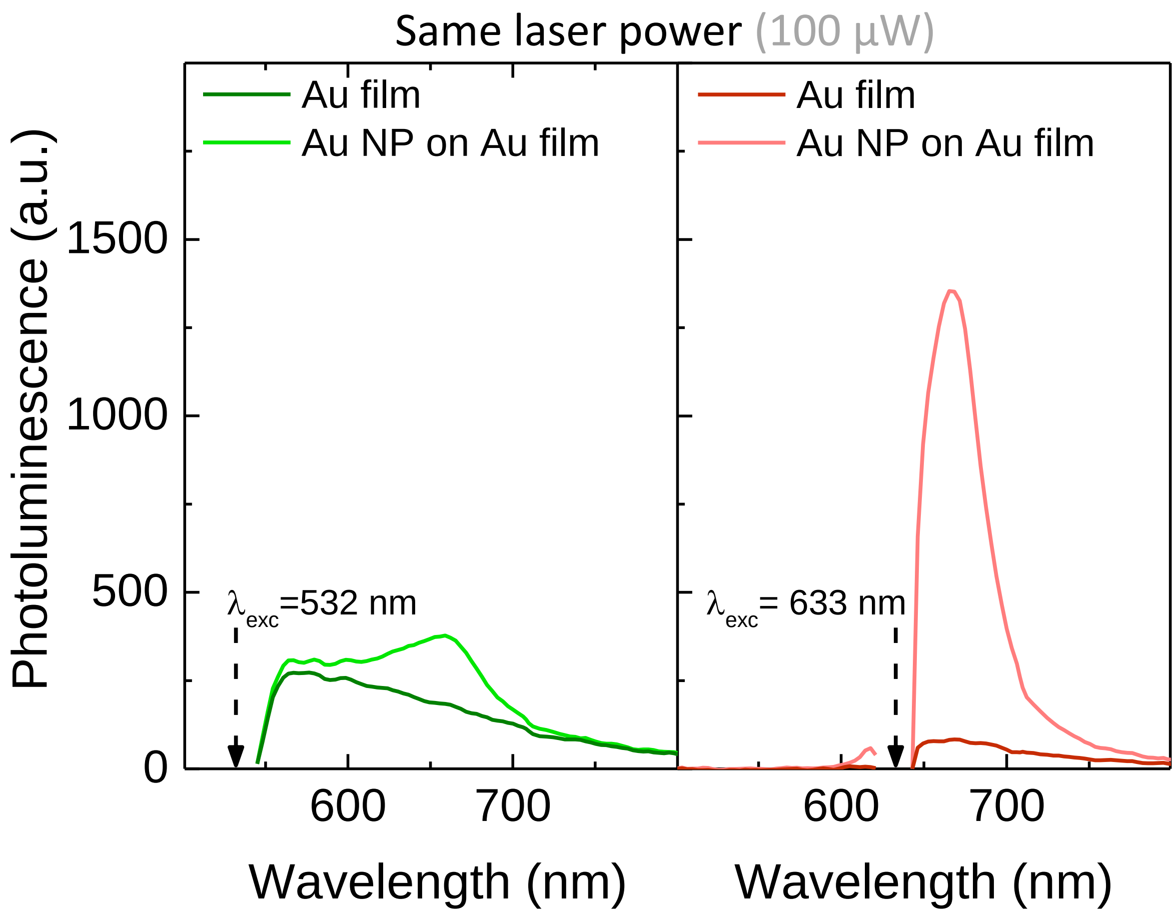
Same laser power (100 μW)



Gold PL is stronger under green laser excitation than under red laser excitation (why?)

Gap-plasmon enhanced photoluminescence

Photoluminescence spectra

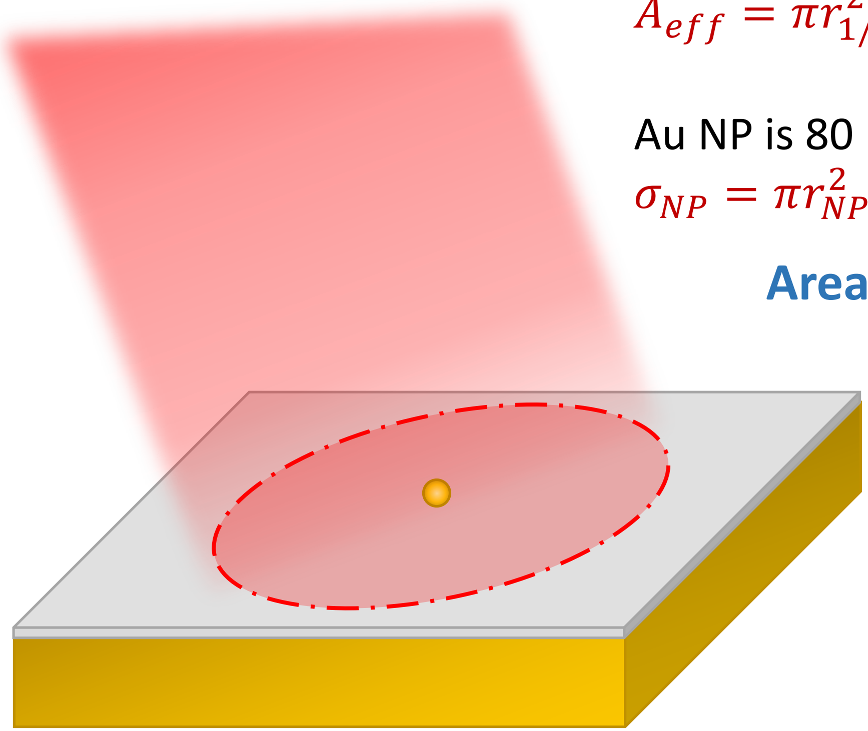


Gold PL is stronger under green laser excitation than under red laser excitation

Adding a NP → 2x and 16x enhancement at the resonance wavelength (not very strong?)

Gap-plasmon enhanced photoluminescence

Photoluminescence enhancement



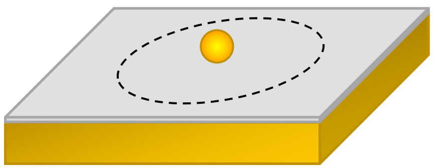
Laser spot FWHM is 2.7 µm

$A_{eff} = \pi r_{1/e}^2$

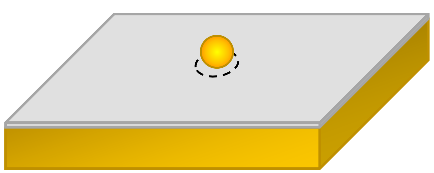
Au NP is 80 nm in diameter

$\sigma_{NP} = \pi r_{NP}^2$

Area ratio > 1000!



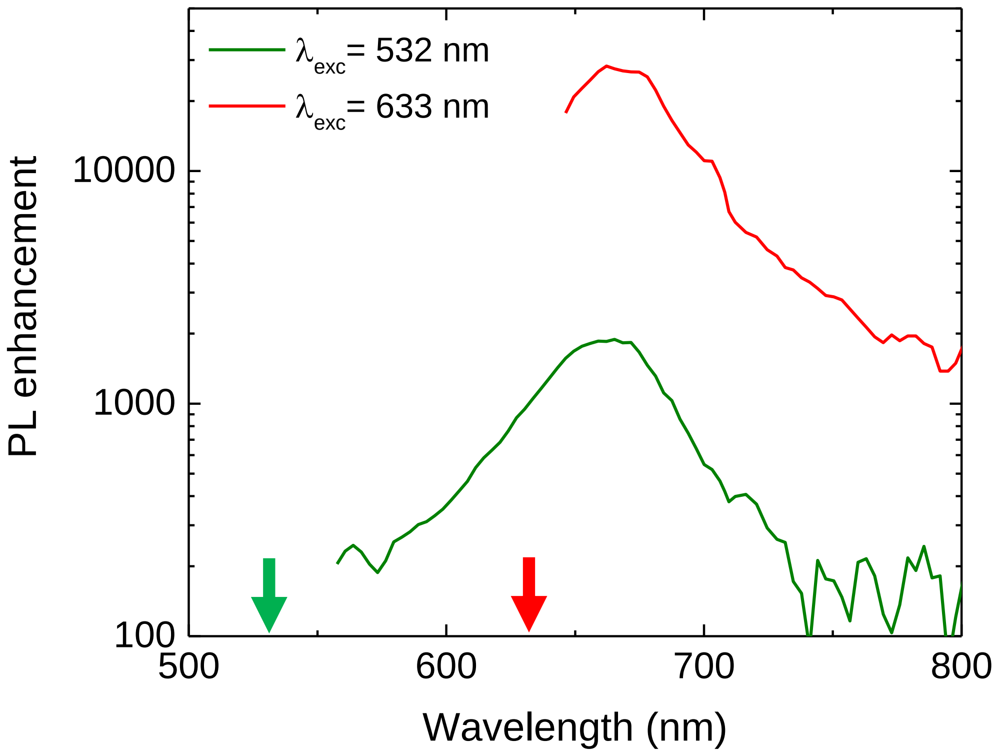
$$g_{PL}(\lambda_{exc}, \lambda_{em}) = \frac{I_{NP} - I_{film}}{I_{film}} \frac{A_{eff}}{\sigma_{NP}}$$



PL enhancement relative to PL from an area of Au film = NP cross-section

Gap-plasmon enhanced photoluminescence

Photoluminescence enhancement spectra

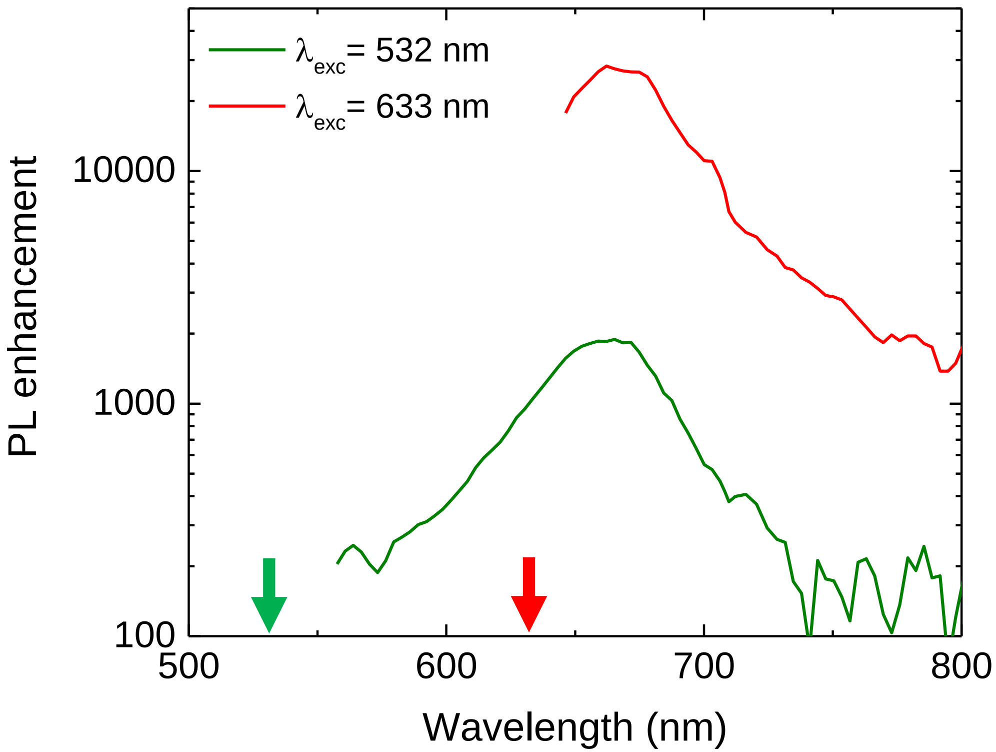


PL = Light <u>emission</u> as a result of photo<u>excitation</u> of carriers

Red excitation show stronger PL enhancement than green excitation
Suggests → Gap-plasmon enhanced excitation

Both green and red excitations show max. PL enhancement resonance wavelength (650 nm)
Suggests → Gap-plasmon enhanced emission

Photoluminescence enhancement calculation



Question: Microscopic model of PL?

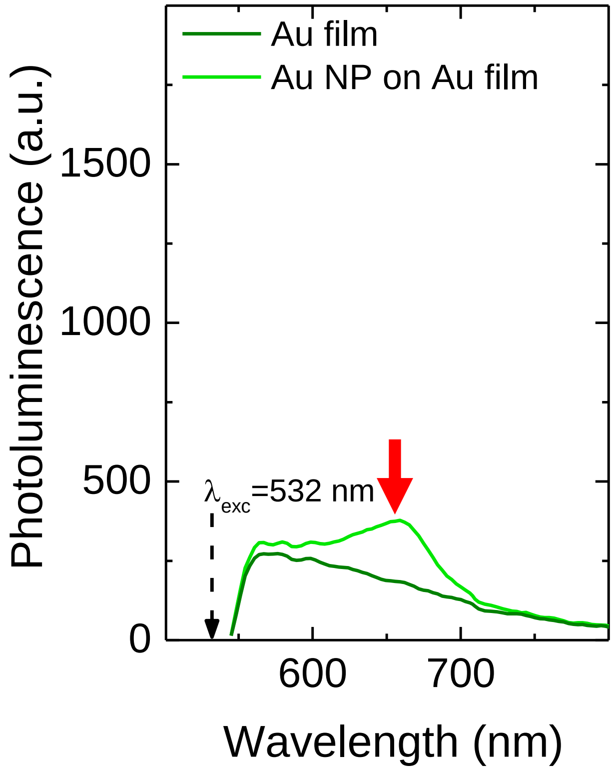
Enhanced emission (assume reciprocity)

$$R_{PL}(\omega_{exc},\omega_{em},\vec{r}\,) \propto \epsilon''_{IB}(\omega_{exc})\left|\vec{E}(\omega_{exc})\right|^2 \times \gamma_{bulk}(\omega_{exc},\omega_{em}) \times \left|\frac{\vec{E}(\omega_{em})}{\vec{E}_0(\omega_{em})}\right|^2$$

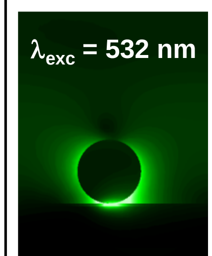
Excitation

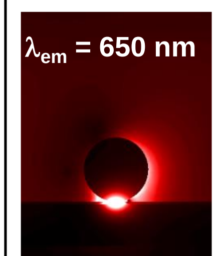
Gap-plasmon enhanced photoluminescence

Photoluminescence enhancement calculation



$$PL(\omega_{exc},\omega_{em}) \propto \iiint_{Au\ NP+film} \left| \text{[field map at } \lambda_{exc} = 532\text{ nm]} \right|^2 \times \left| \text{[field map at } \lambda_{em} = 650\text{ nm]} \right|^2 dV$$





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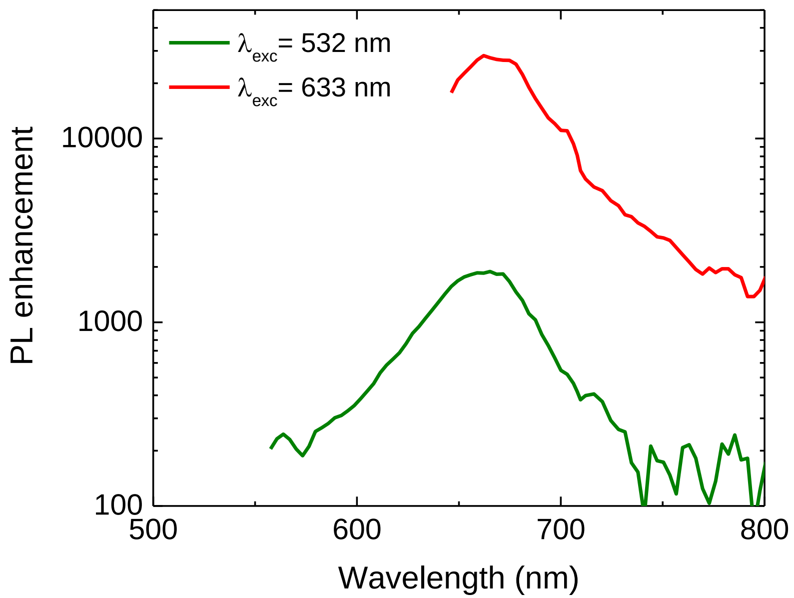
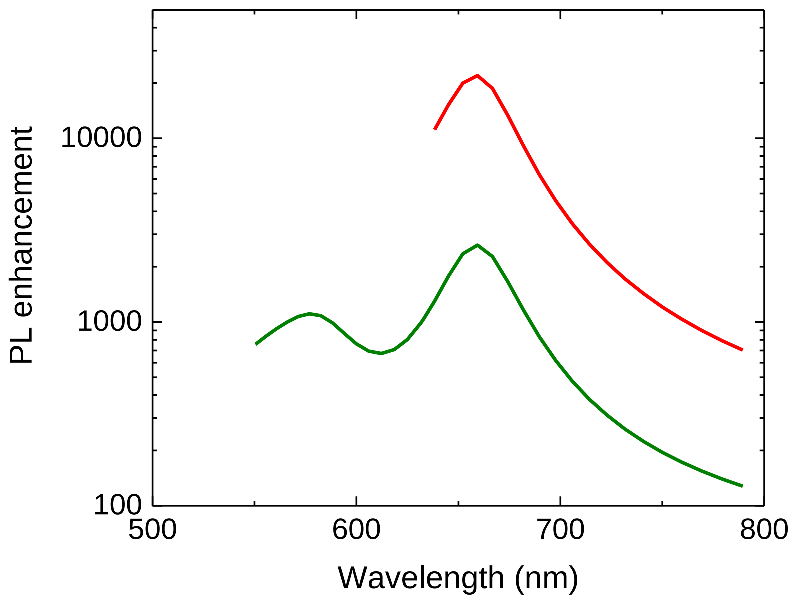
Excitation

Gap-plasmon enhanced photoluminescence

Photoluminescence enhancement calculation

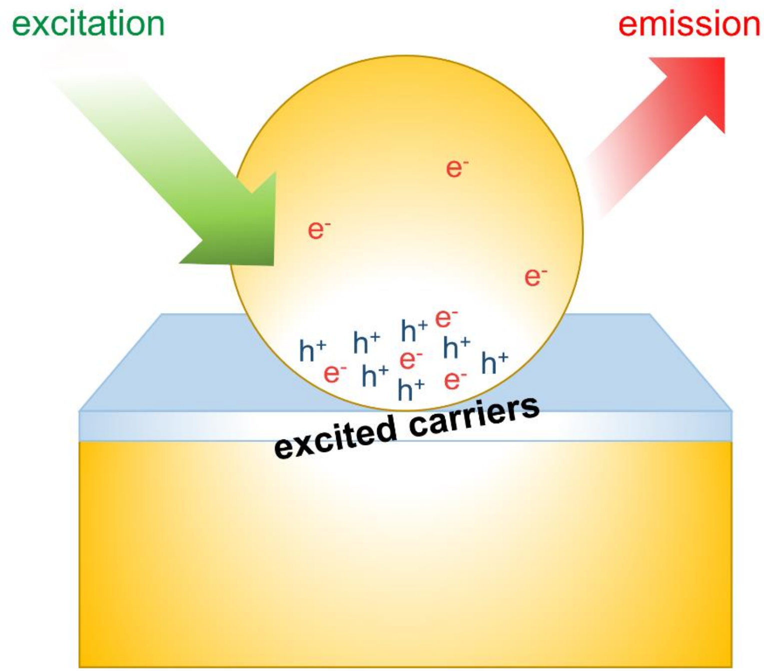
No free parameters!

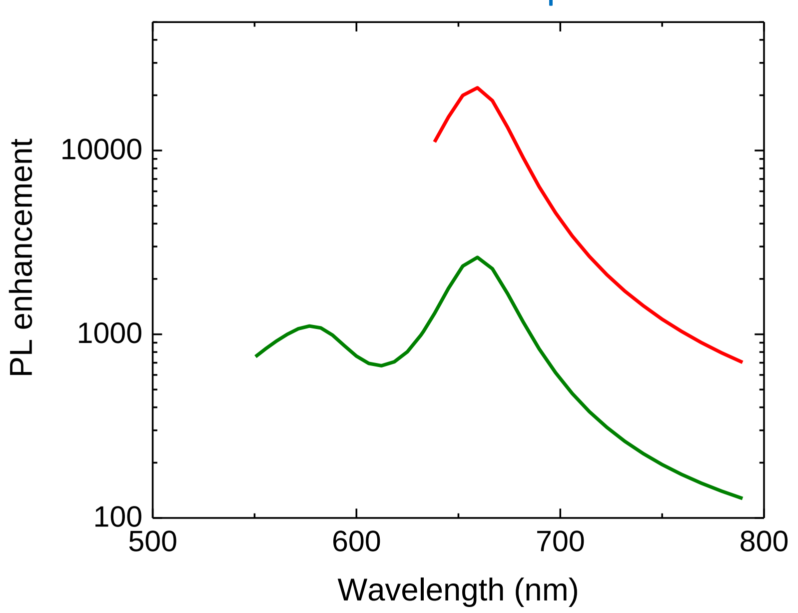




Gap-plasmon enhanced photoluminescence

Photoluminescence enhancement calculation





Now we understand and can quantitatively predict gap-plasmon enhanced PL

<u>Goal</u>: Explain the process of gap-plasmon enhanced photoluminescence

Mission accomplished!

Outlines

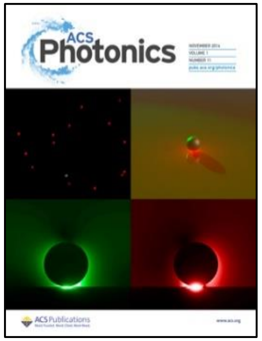
Introduction

- CREOL
- Nanophotonics?
- Optical near-field
- Gap-plasmon resonance

Gap-plasmons

- **Enhanced scattering and resonance control**
  We precisely control gap-plasmon resonance frequency over a broad wavelength range from green to red.

- **Enhanced photoluminescence**
  Gold PL gets enhanced drastically at the gap-plasmon resonance wavelength.
  A numerical model is developed to explain the phenomenon



- **Alternative gap-plasmon supporting structure**

Outlines

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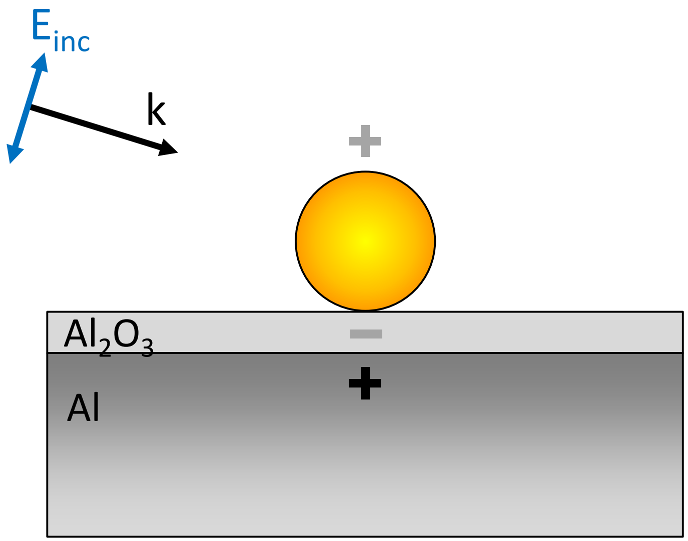
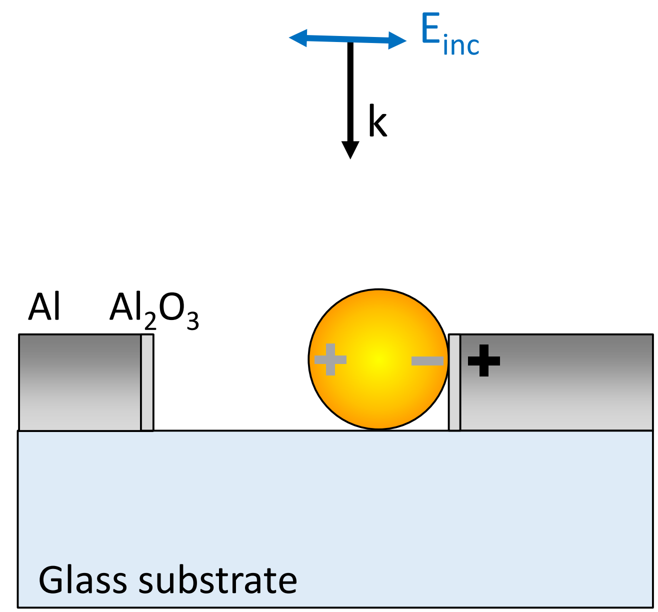
- **Alternative gap-plasmon supporting structure**
  Gap-plasmons of NP-on-metallic film = a high angle of incidence + difficult to reach
  An alternative gap-plasmon supporting structure that is easier to access?

Alternative gap-plasmon supporting structure

<u>Goal</u>: Gap plasmon supporting structure that is easier to access (optically and physically)



VS.

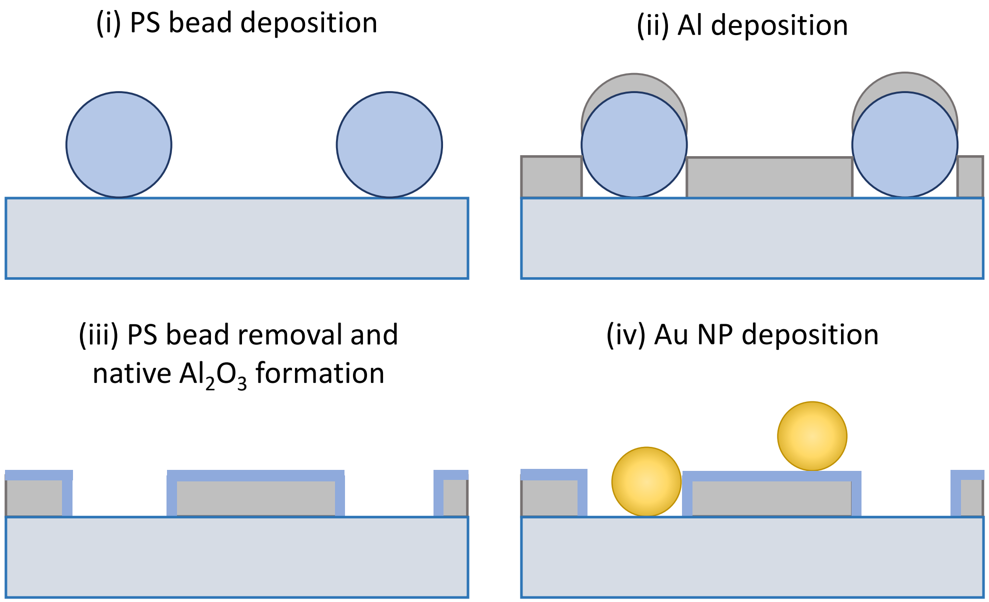


Normal incidence excitation
Unhindered hot-spot

Question: How do we make it?

Alternative gap-plasmon supporting structure

Answer: Nanosphere lithography + NP self-assembly

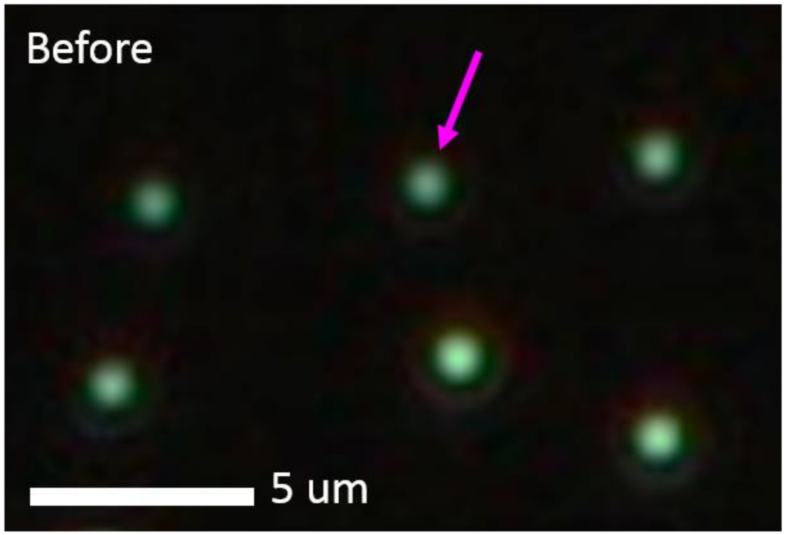


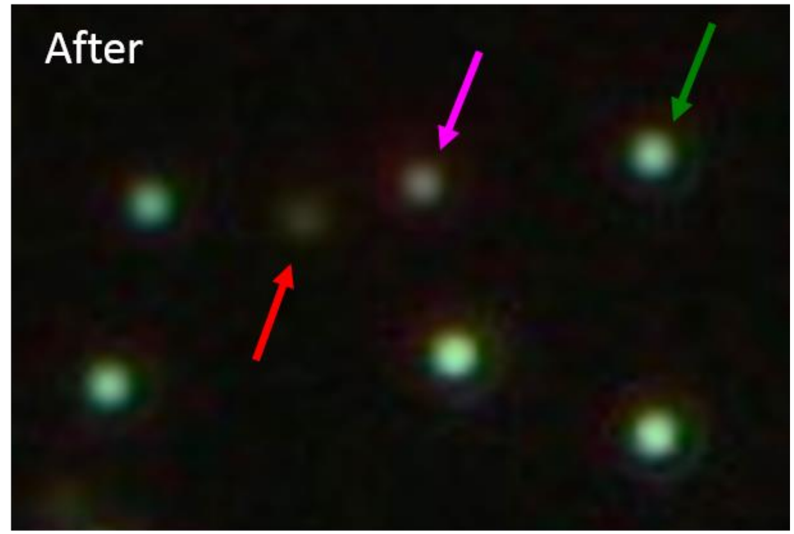
Important question: How do we know which nanoholes have a particle in it?

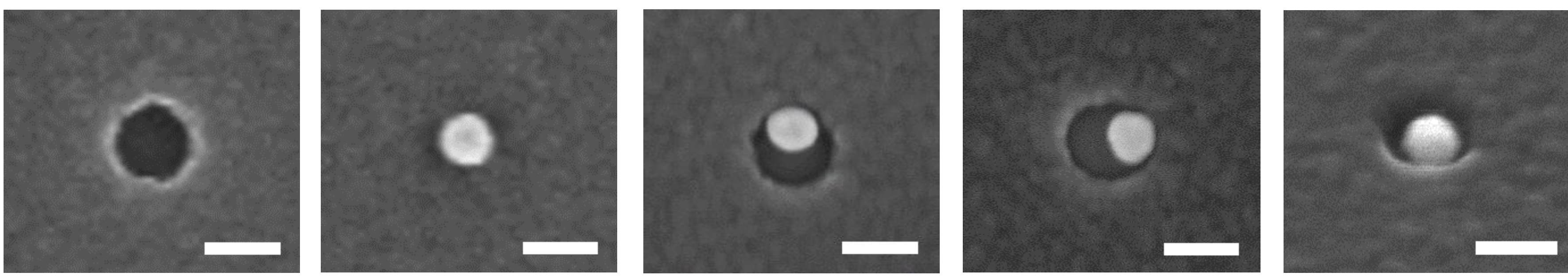
Alternative gap-plasmon supporting structure

Question: How do we know which nanoholes have a particle in it?

Answer: Compare pictures before and after NP drop coating (not trivial)







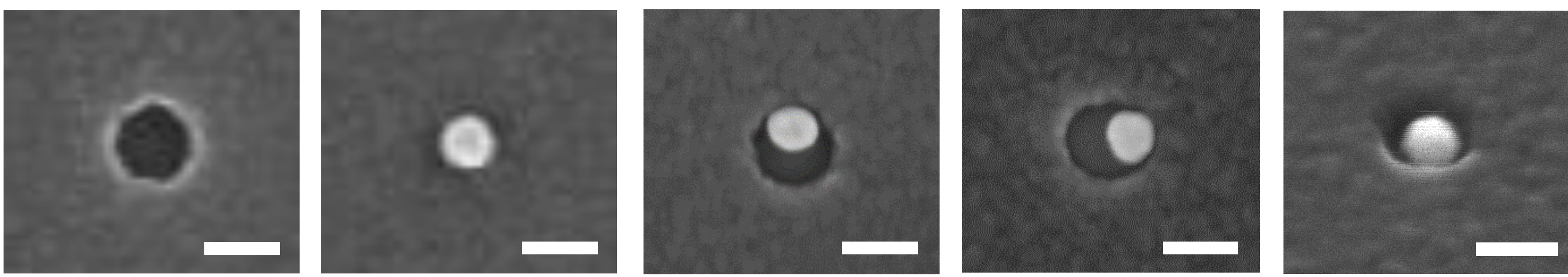
Scale bar: 100 nm

Hole-in-One

Found a few of them, make markers, and do SEM (scanning electron microscopy)

Alternative gap-plasmon supporting structure

Question: How do we know which nanoholes have a particle in it?
Answer: Compare pictures before and after NP drop coating (not trivial)



Scale bar: 100 nm

Hole-in-One

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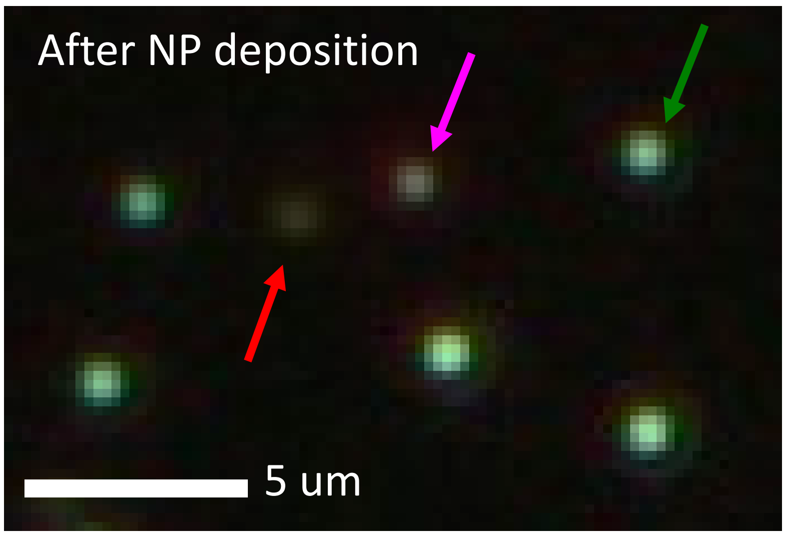
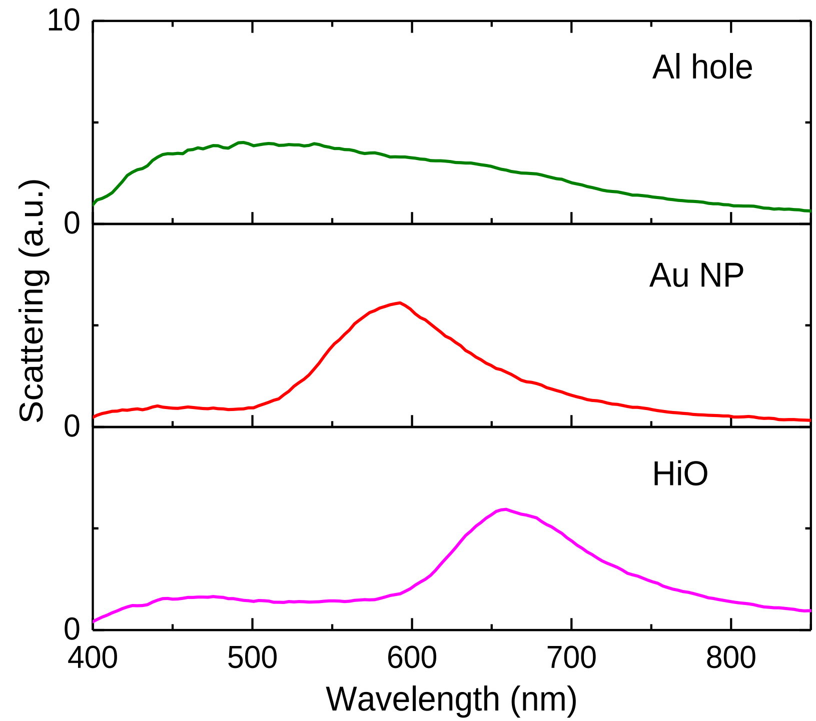
Alternative gap-plasmon supporting structure

Scattering spectra (nanohole vs. NP-on-Al vs. HiO)

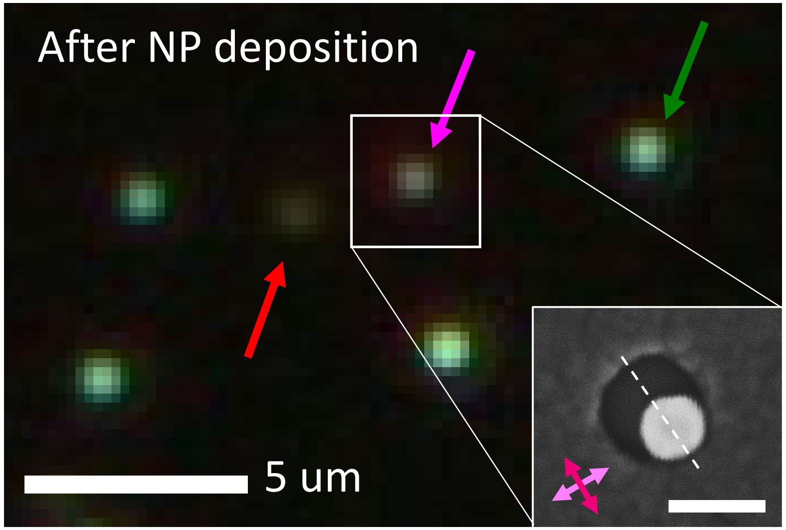




HiO has a gap-plasmon mode 650 nm

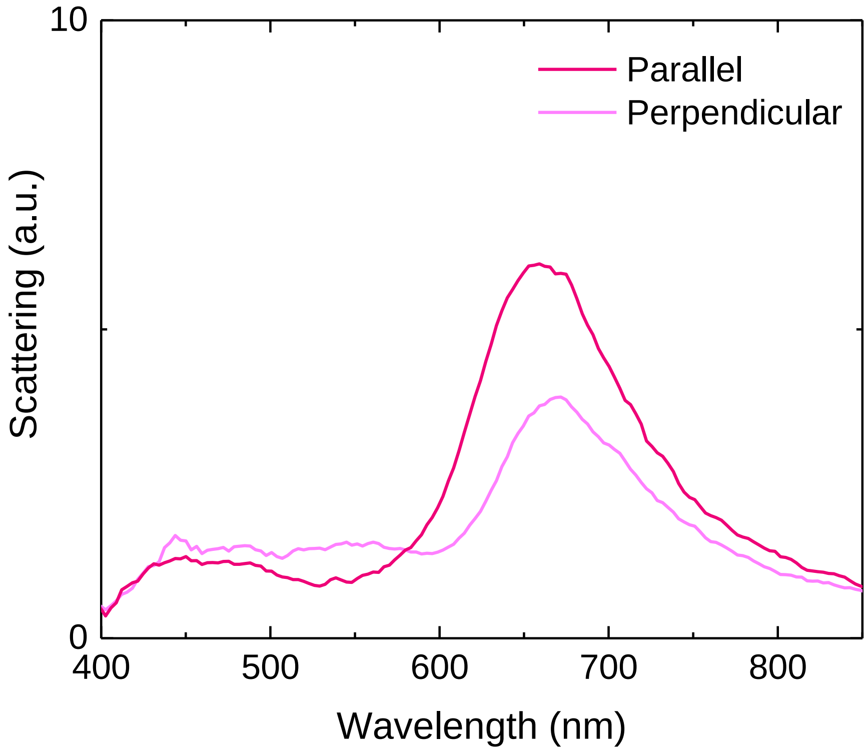
Alternative gap-plasmon supporting structure

Scattering spectra (nanohole vs. NP-on-Al vs. HiO)



Scale bar: 100 nm

The scattering is reddest and strongest when the analyzer angle // HiO symmetry axis



HiO has a gap-plasmon mode 650 nm

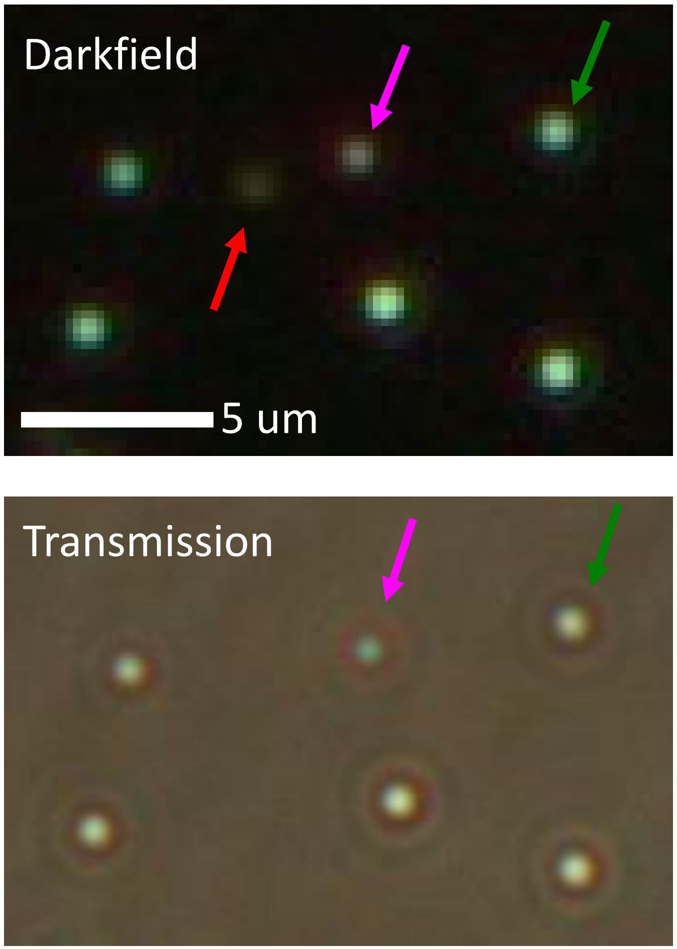
SEM shows that the NP is off-center → Polarization dependent scattering spectrum

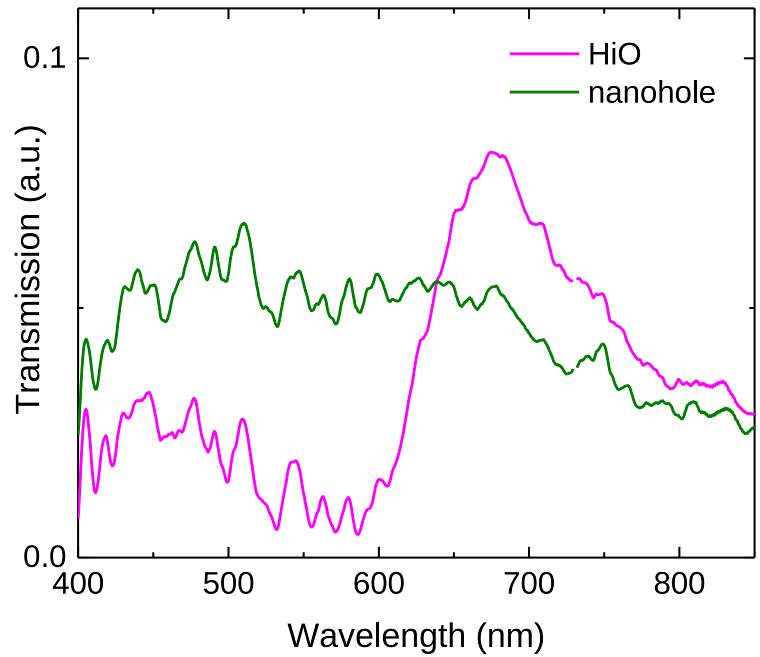
Question: Didn't we want normal incidence excitation?

Alternative gap-plasmon supporting structure

Question: Didn’t we want normal incidence excitation?
Answer: We do. We observe gap-plasmon resonance in transmission (normal incidence)

After NP deposition





~ the same resonance wavelength and linewidth as in the scattering spectrum

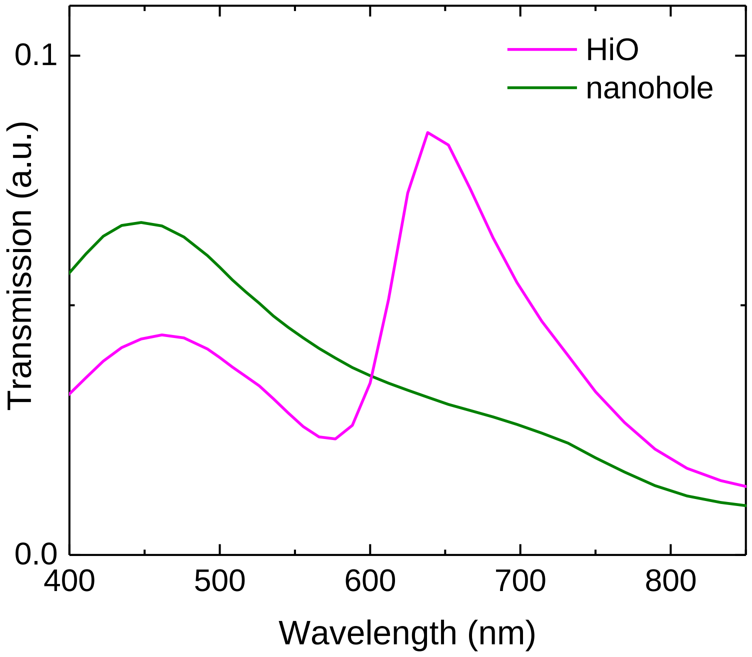
SUCCESS!

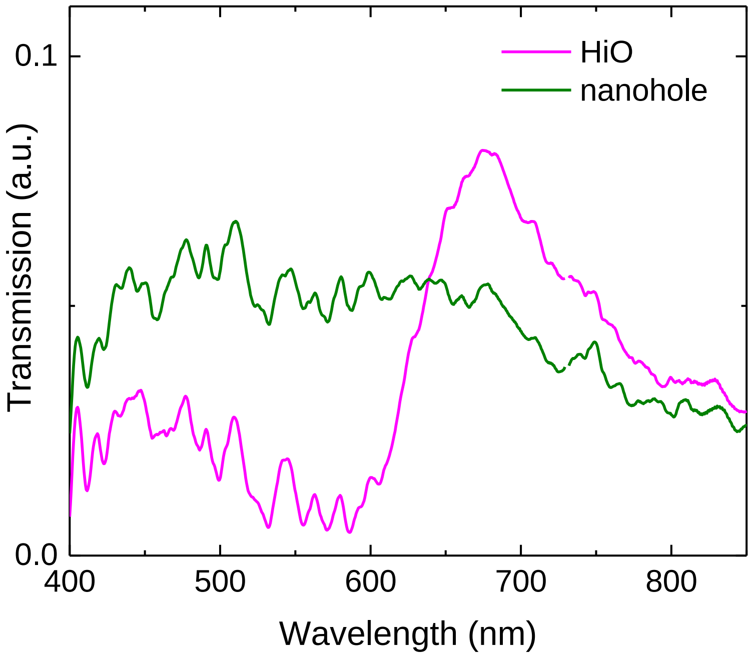
Alternative gap-plasmon supporting structure

Question: Didn't we want normal incidence excitation?

Answer: Yes, we did. And we had it!

Simulation





~ the same resonance wavelength and linewidth as in the scattering spectrum

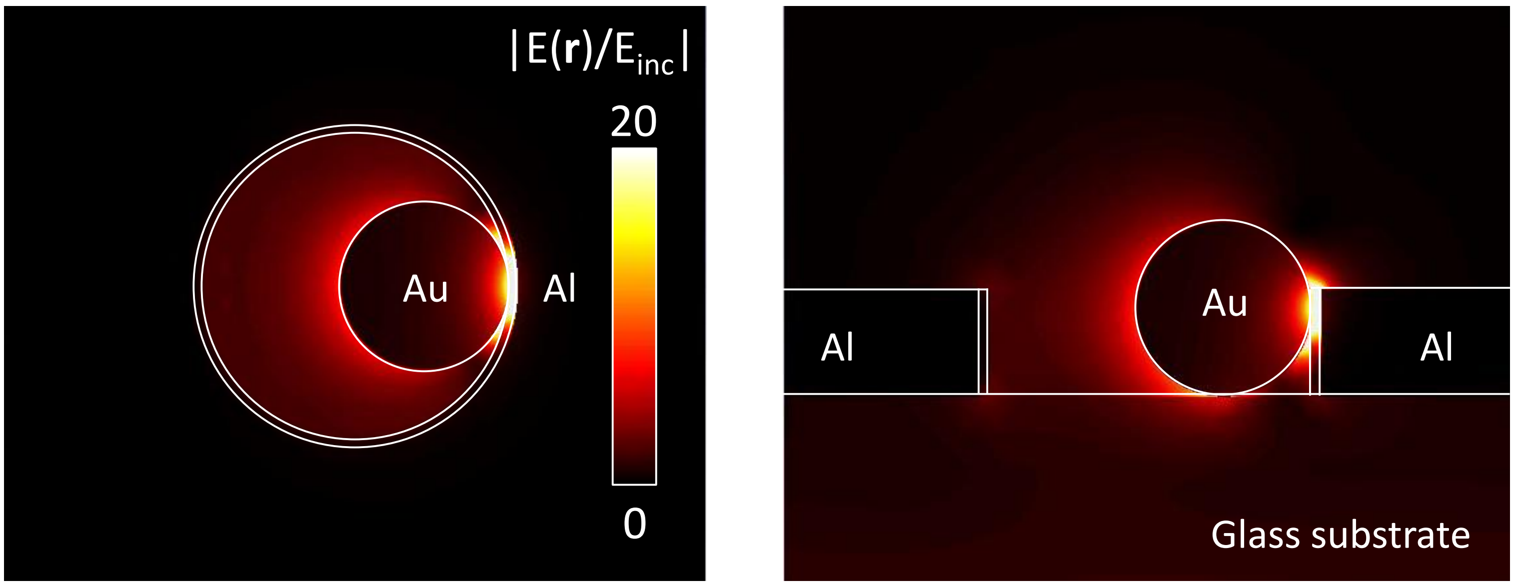
SUCCESS!

Question: Where is the hot-spot? Is it easily accessible?

Alternative gap-plasmon supporting structure

Question: Where is the hot-spot? Is it easily accessible?
Answer: Yes! We purposely chose Al thickness.

Simulated electric field at the resonance wavelength
Normal incidence

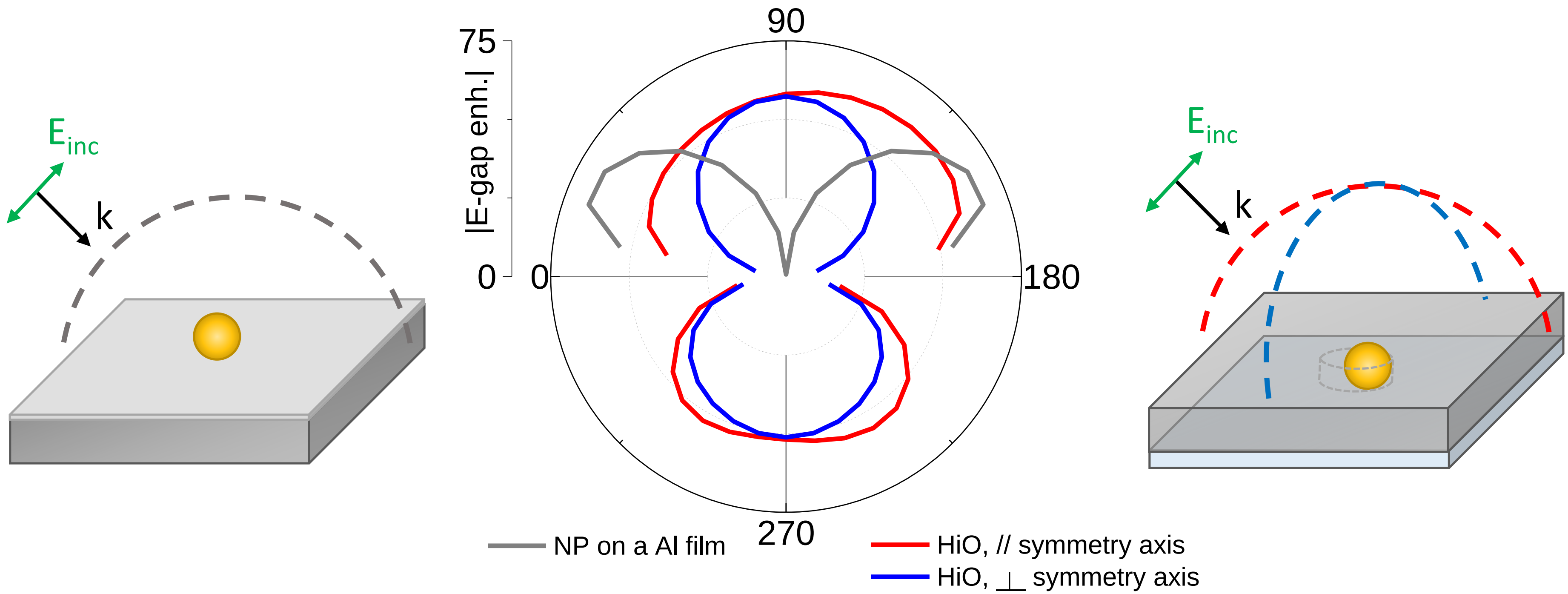


Sidewall gap-plasmon!

Question: Is the electric enhancement still strong at different excitation angles?

Alternative gap-plasmon supporting structure

Question: Is the electric enhancement still strong at different excitation angles?
Answer: Yes. Better than NP-on-film.



Omnidirectional gap-plasmon excitation, top illumination and bottom illumination

Goal: Gap plasmon supporting structure that is easy to access (optically and physically)

Mission accomplished!

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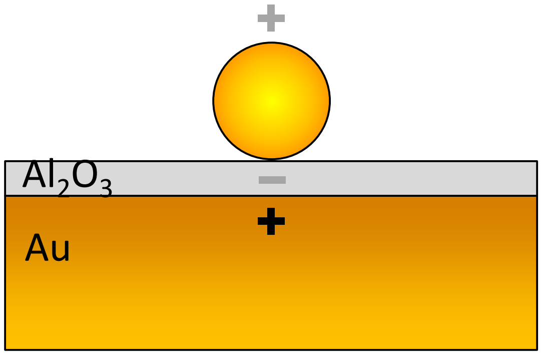
- **Enhanced photoluminescence**
  Gold PL gets enhanced drastically at the gap-plasmon resonance wavelength.
  A numerical model is developed to explain the phenomenon

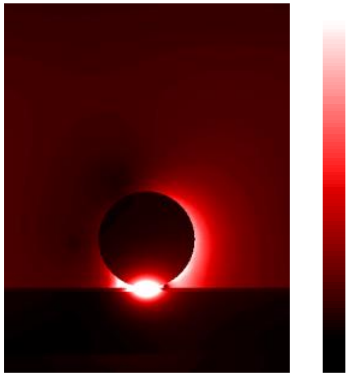
- **Alternative gap-plasmon supporting structure**
  Gap-plasmons of NP-on-metallic film = a high angle of incidence + difficult to reach
  Hole-in-one structure offers sidewall gap-plasmons that is easily accessible

Summary

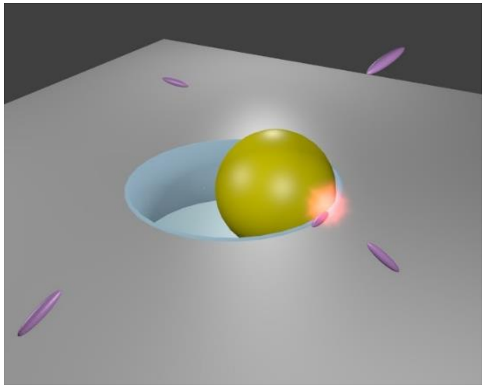
Enhanced scattering and resonance control
- NPs on oxide coated metallic films
- Precise resonance control > 140 nm tuning range
- Simple, background free, and robust



Gap-plasmon enhanced gold photoluminescence
- Two excitation wavelengths
- Gap-plasmon enhanced excitation and emission
- Nicely explained by the numerical model

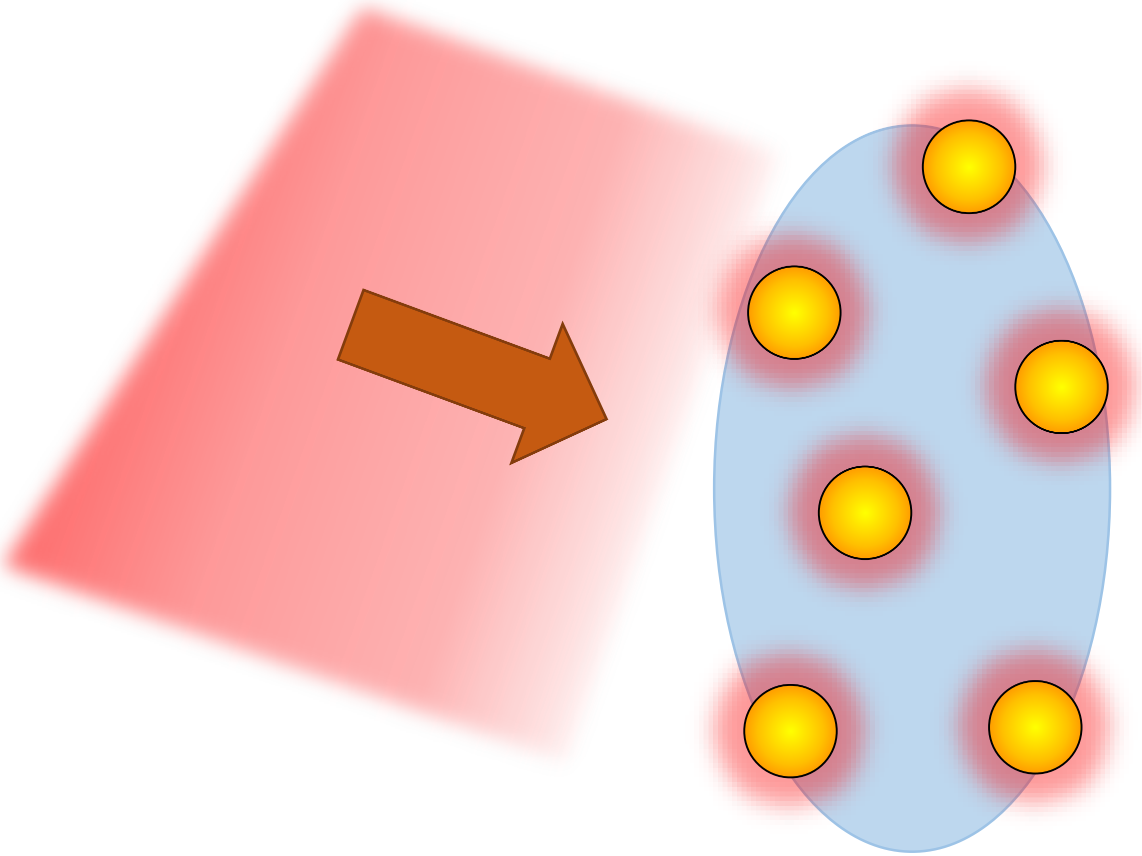


Hole-in-One structure
- Sidewall gap-plasmon in hybrid Au-Al nanopore
- Broad range of excitation angles
- Easily accessible hot-spot



Applications?

- Phototherapy
- Plasmon enhanced photocatalysis (manuscript in preparation)
- Plasmon enhanced solar absorption
- Nonlinear photon conversion
- Sensing



Related Publications

CREOL UCF

JOURNAL PUBLICATIONS

C. Lumdee and P. G. Kik, "**Omnidirectional Excitation of Sidewall Gap-Plasmons in a hybrid Gold-Aluminum Nanopore Structure**," *submitted*.

C. Lumdee, B. Yun, and P. G. Kik, "**Effect of Surface Roughness on Substrate-tuned Gold Nanoparticle Gap Plasmon Resonances**," *Nanoscale* 2015, **7**, 4250-4255.

C. Lumdee, B. Yun, and P. G. Kik, "**Gap-Plasmon Enhanced Gold Nanoparticle Photoluminescence**," *ACS Photonics* 2014, **1**, 1224-1230. ***(Cover article)***

C. Lumdee, B. Yun, and P. G. Kik, "**Wide-band Spectral Control of Au Nanoparticle Plasmon Resonances on a Thermally and Chemically Robust Sensing Platform**," *J. Phys. Chem. C* 2013, **117**, 19127-19133.

C. Lumdee, S. Toroghi, and P. G. Kik, "**Post-Fabrication Voltage Controlled Resonance Tuning of Nanoscale Plasmonic Antennas**," *ACS Nano* 2012, **6**, 6301-6307.

CONFERENCE PRESENTATIONS (with a conference proceeding)

(Invited talk) C. Lumdee and P. G. Kik, "**Numerical Prediction of the Effect of Nanoscale Surface Roughness on Film-coupled Nanoparticle Plasmon Resonances**," Proc. 9163-91631I (2014) - SPIE Optics + Photonics, San Diego, CA.

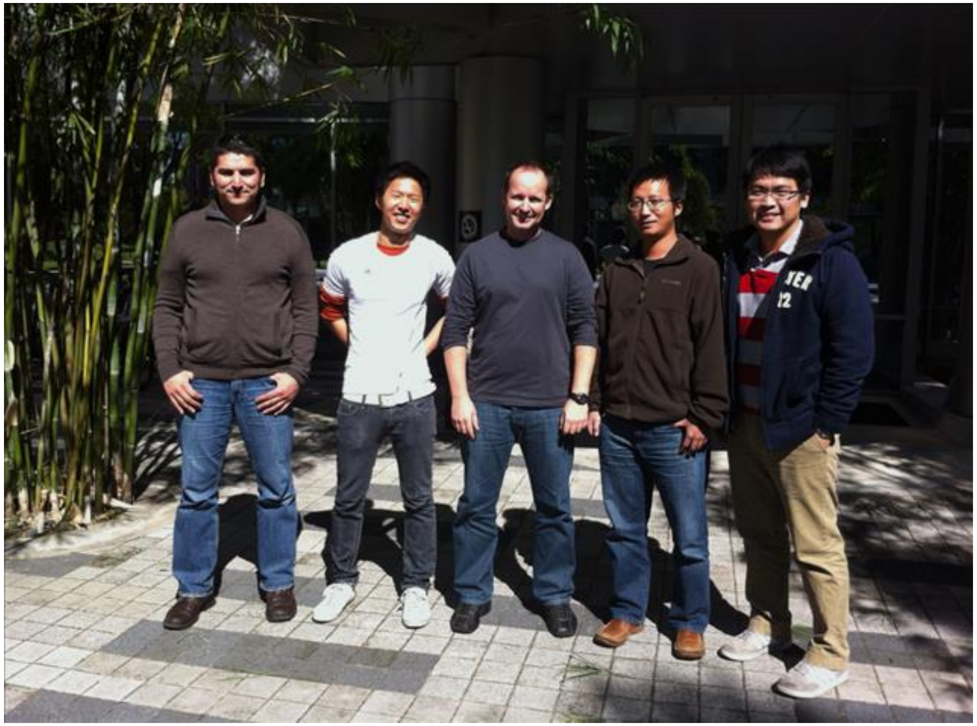
C. Lumdee, B. Yun, and P. G. Kik, "**Controlled Surface Plasmon Resonance on Stable Substrates as an Optimized Sensing Platform**," FTh3C. 8 (2013) - OSA Frontiers in Optics, Orlando, FL.

C. Lumdee, B. Yun, and P. G. Kik, "**Optical Characteristic and Numerical Study of Gold Nanoparticles on Al2O3 coated Gold Film for Tunable Plasmonic Sensing Platforms**," Proc. 8809-88091S (2013) - SPIE Optics + Photonics, San Diego, CA.

C. Lumdee and P. G. Kik, "**Voltage Controlled Nanoparticle Plasmon Resonance Tuning through Anodization**," Proc. 8457-84570T (2012) - SPIE Optics + Photonics, San Diego, CA.

Acknowledgments

Kik group (Oct 2012)



Prof. Pieter G. Kik
Dr. Seyfollah Toroghi
Dr. Binfeng Yun
Yu-Wei Lin

+ CREOL's faculty and staff

Special thanks:
Dr. Pongsakorn Kanjanaboos
Faculty of Science, Mahidol University

And you all!