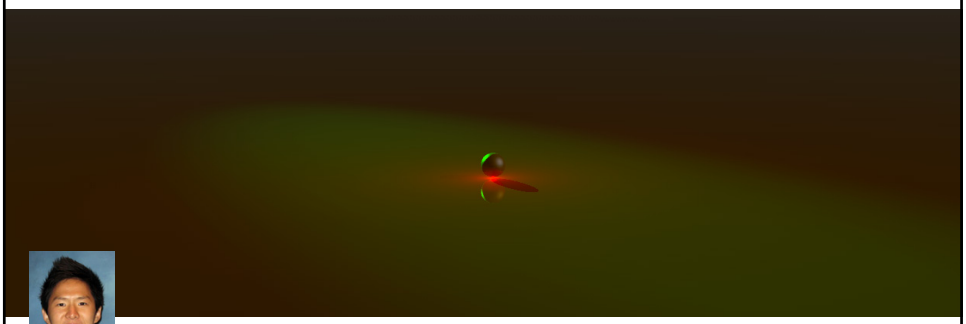
# Single particle spectroscopy of gap plasmon enhanced phenomena

Pieter G. Kik

**CREOL**, The College of Optics and Photonics, UCF, Orlando, FL





Chatdanai Lumdee

Sabbatical host at Stanford: Mark L. Brongersma



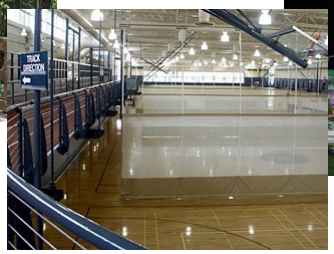
## University of Central Florida (UCF) - campus

Founded 1968, 56000 students

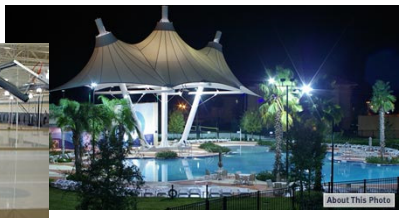
Library



Nature



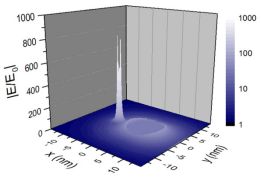
Sports facilities



Lounge pool?

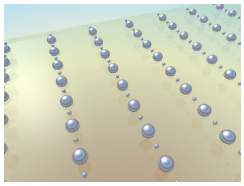

## Where we left off..

APL **100**, 183105 (2012)



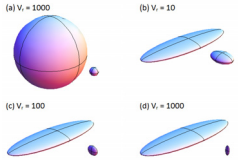
*Cascaded plasmon resonances*

PRB **85**, 45432 (2012)

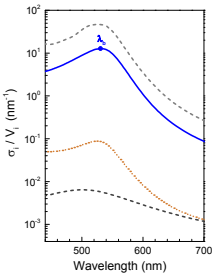


*NLO absorption enhancement in locally cascaded metamaterials*

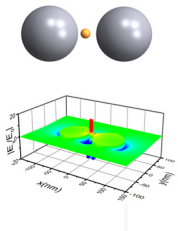
APL **101**, 13116 (2012)



*In-plane cascaded resonances through shape design*

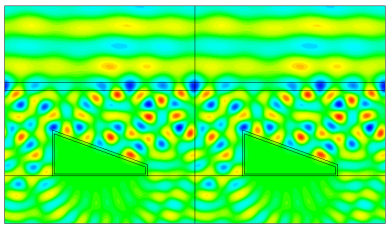


PRB **90**, 205414 (2014)



*100x increase in Au NP photothermal response*

84% transmission at 50% metal coverage (375nm-750nm)



Opt. Lett. **39**, 5114 (2014)

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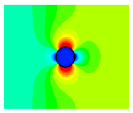
## Introduction

**Last year**: Four new papers on plasmons each office hour - Web of Science

What makes plasmons so special?

Resonant local field enhancement



- Faster optical excitation rates, stronger NLO response, enhanced Raman, enhanced PL

Ultrasmall mode-volume

- Highly sensitive to local index, ultrafast plasmon laser modulation, strong coupling in cavity electrodynamics

Strong optical scattering per $nm^3$

- light redirection using little material in thin film PV, optical markers, …

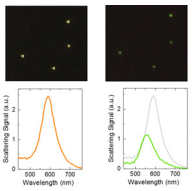
Strong optical absorption per $nm^3$

- Strongly localized and fast thermal effects, thermal treatment, …

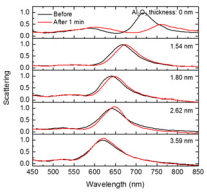


## Outline

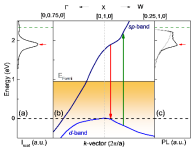
1. Gold nanoparticle scattering on anodized Al film
   - single particle spectroscopy
   - voltage control of NP resonance
   - polarization selectivity, reproducibility




2. Gold nanoparticle scattering on $Al_2O_3$ coated Au film
   - thinner oxides, larger tuning range
   - all-inorganic structure
   - stable against radiation



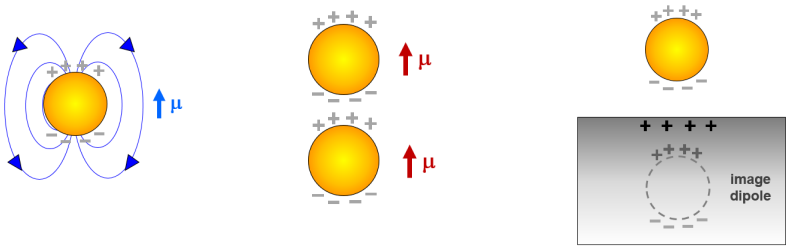

3. Gold photoluminescence enhancement using gap plasmons
   - excitation frequency dependence
   - numerical model, enhancement of excitation and emission
   - photoluminescence as indirect probe of field enhancement



## Part 1 - Gold nanoparticle scattering on anodized Al film

**Challenge**: metal nanospheres have just 'one resonance frequency'

**Solution**: plasmon resonances are affected by induced polarization charge




Free: $\omega_{LSP} = \sqrt{\frac{\omega_p}{3}}$ Dimer : $\omega_{res,L} < \sqrt{\frac{\omega_p}{3}}$ Supported NP: $\omega_{res,L} < \sqrt{\frac{\omega_p}{3}}$

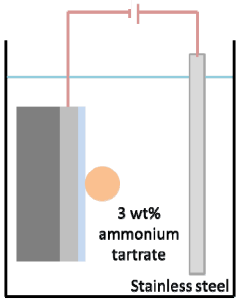
**Goal**: control plasmon resonance using interaction with substrate

**Challenge**: how do we 'suspend' a particle above a metal surface?



## Resonance control by anodization

**Goal**: method for production of thermally and structurally stable substrate-tuned NP

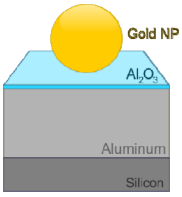



**Approach**: anodization of Al film

Overall reaction: $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

Result:

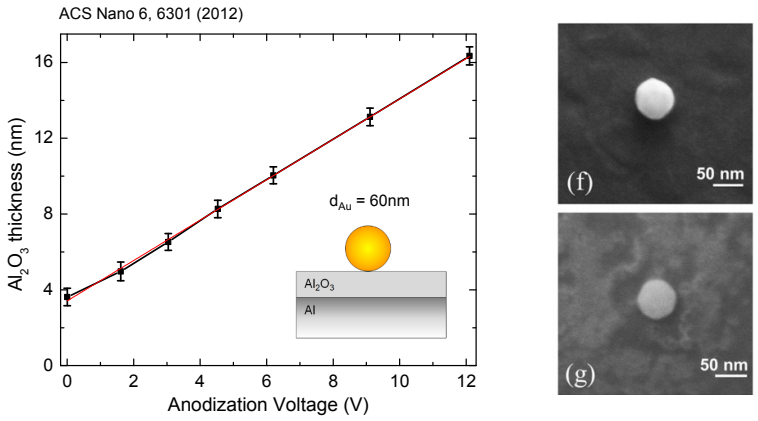
- dense $Al_2O_3$ film
- Thickness controlled by voltage
- Conformal to metal film




**Experiment**:

- Thermal evaporation of Al film on Si
- Deposition of 60nm diameter Au NP onto the as-deposited Al film
- Dark-field microscopy, spectroscopy, ellipsometry → anodize → repeat

## Fine control of nanoparticle-metal separation




**Steps:** deposit Al film / drop-coat particles / measure ↔ anodize

**Ellipsometry** : near-perfect linear relation between voltage and thickness

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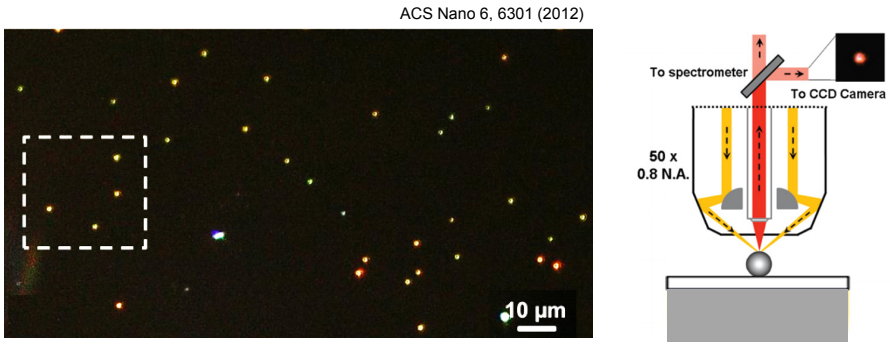
## Darkfield microscopy of Au on $Al_2O_3$ on Al




Darkfield microscopy: selective detection of scatterers

**Observed**: isolated Au nanoparticles, visible by eye

⇒ can optically investigate isolated identifiable nanoparticles

**Next**: stepwise anodization: thicker oxide spacer → less red-shift (= blue shift)

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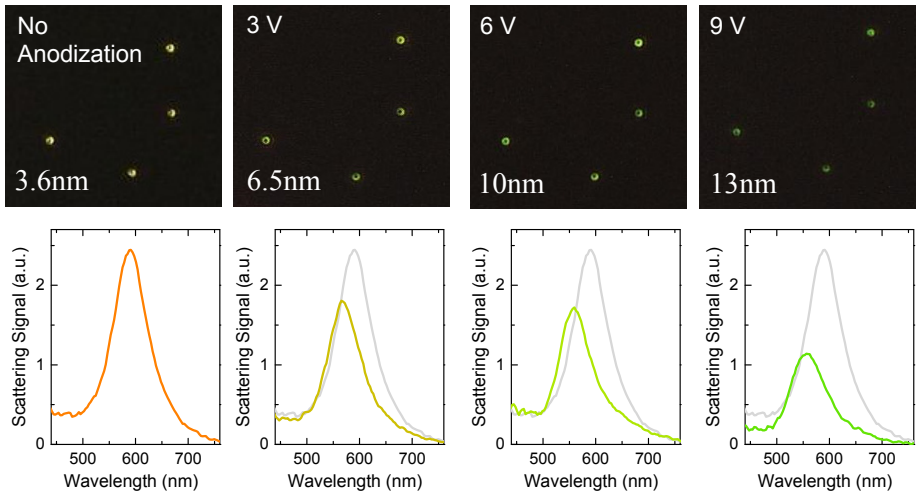
## Voltage dependent dark-field scattering




ACS Nano 6, 6301 (2012)

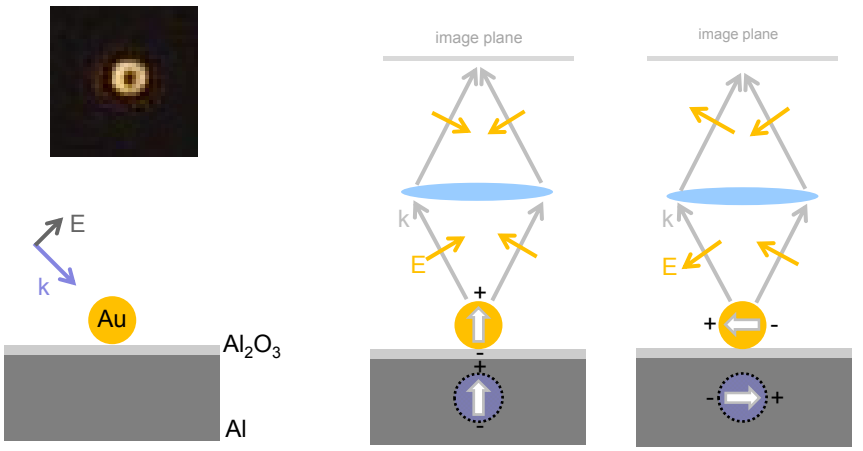
**Fortuitous:** anodization does not remove NP from substrate

**Success:** precise control of individual NP plasmon resonance wavelength



## Polarization selective excitation and radiation

Interesting observation: ring shape scattering image ⇒ z-polarized dipole

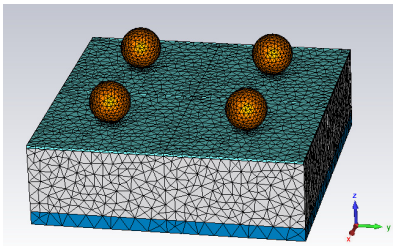


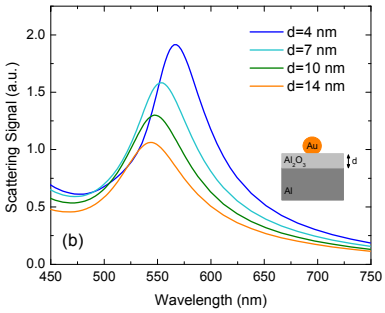

⇒ Can simulate resonance spectra by monitoring z-dipole in NP

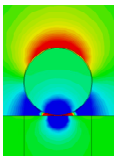
## Numerical simulation

Simulate excitation at angle corresponding to NA of dark-field objective

Determine z-dipole moment. Radiation assumed to scale with $P_{rad} \propto |\mu|^2 \omega^4$





gap plasmon

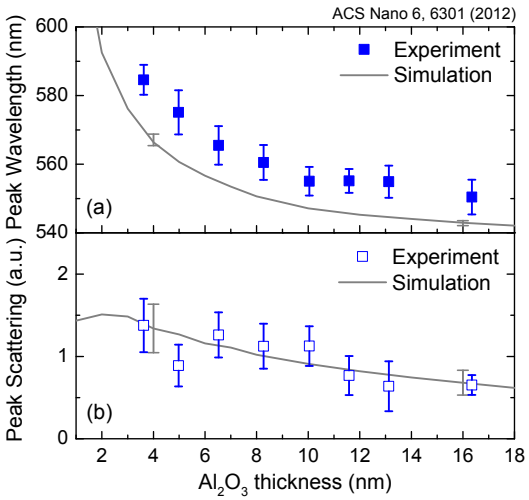
Simulation results match experimental observations

Similar resonance shift, similar reduction in peak scattering signal

**Note**: field concentrated between NP and metal substrate = "gap plasmon"



## Comparison simulation and experimental results




Tuning range >30nm, **stable oxide** as spacer layer, NP material chemically stable

**Non-ideal**: native $Al_2O_3$ thickness sets lower limit on $t_{spacer}$ and $\lambda_{res}$

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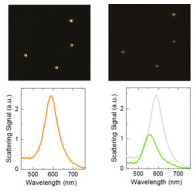

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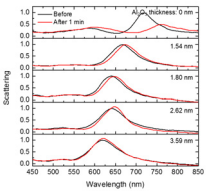

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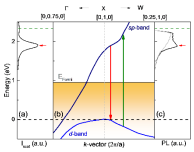
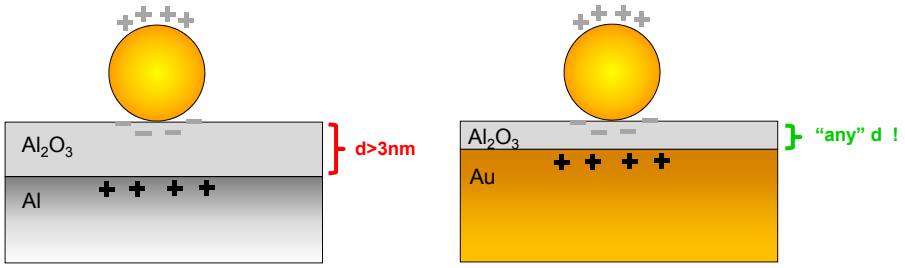




## Part 2: Gold nanoparticle scattering on $Al_2O_3$ coated Au film

**Goal**: increase the tuning range while maintaining thermal and chemical stability



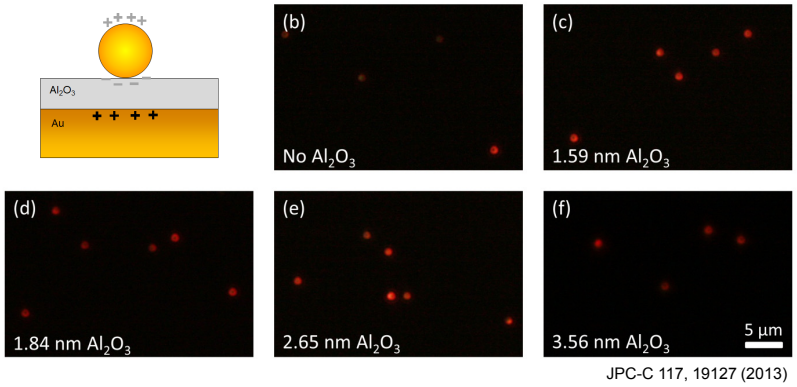

**Approach**: deposit Au film, deposit Al film in vacuum, expose to air → $Al_2O_3$ spacer

**Benefit**: oxide thickness set by initial Al thickness, NOT by native oxide thickness

**Next**: dark-field microscopy

## Dark-field microscopy

**Result**: immediate success! Same particles above Au substrate all look deep red



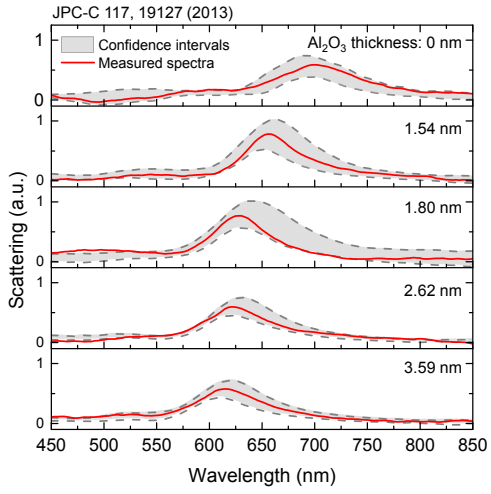

JPC-C 117, 19127 (2013)

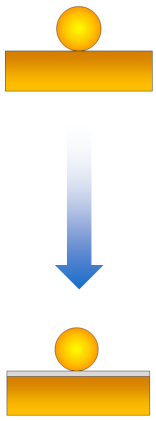
**Question**: All particles look red.. ⇒ no frequency control?

**Check**: take single particle spectra for all samples



## Scattering spectra vs. $Al_2O_3$ thickness

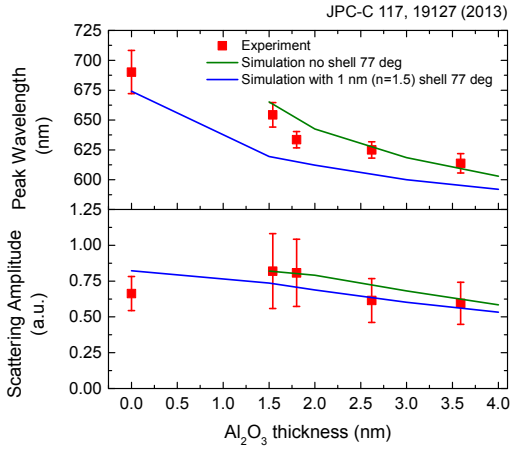


**Observed**: some spectral variation, consistent tuning ('typical spectra' actually typical)

**Next**: collected spectral data vs. spacer thickness, comparison with simulation

## Summary of experimental and numerical results



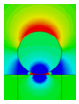

**Conclusion**: All trends understood; residual coating on NP can have huge effect!

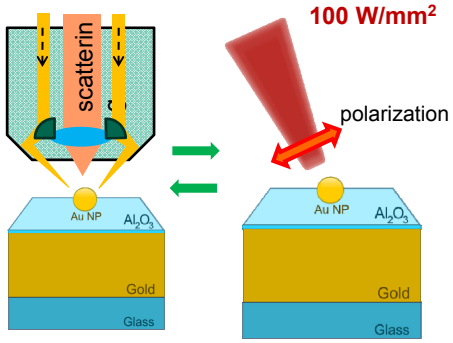
**Ultimate goal**: frequency tuned and **stable**?



## Stability under laser irradiation

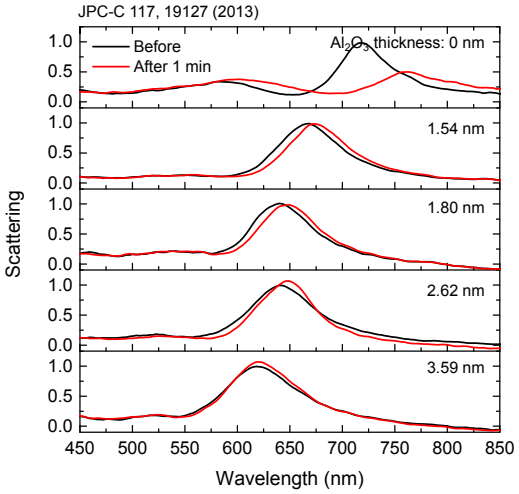
Surface coupled plasmons ('gap modes') provide large field enhancement, strong confinement in reproducible and structure. Stability?

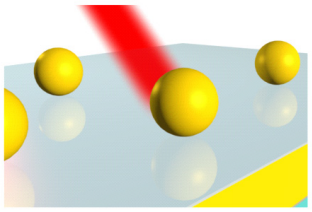




## Spectral stability under high power irradiation

Excite single NP with HeNe, measure scattering spectrum before and after irradiation



CW irradiance: **100 W/mm²**

J. Phys. Chem C. **117**, 19127 (2013)

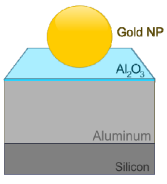
**Success!** On all $Al_2O_3$ coated substrates Au NP survive high power irradiation

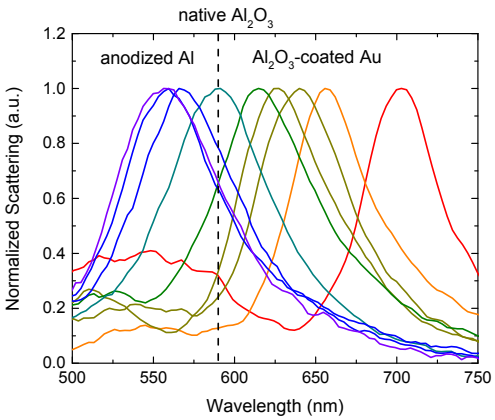


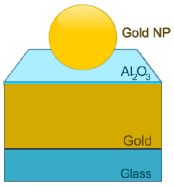
## Summary Part 1+2

Au NP on oxidized Al: limited tuning range due to 'large' native oxide thickness

Au NP on $Al_2O_3$-coated Au : 'arbitrarily thin' spacer layer




**Result**: tuning range extended to NIR using inorganic, stable spacer layer

**Coming up**: stability allows investigation of Au NP photoluminescence

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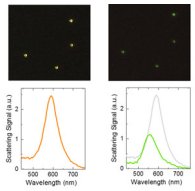

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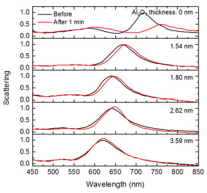

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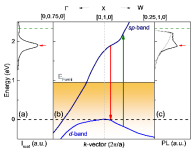


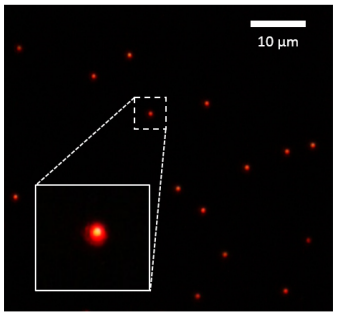


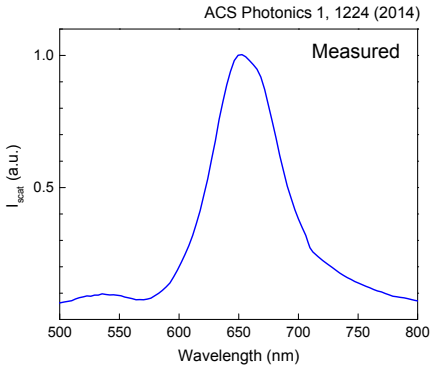
## Dark-field scattering spectroscopy of Au NP on $Al_2O_3$ coated Au

System for PL studies: 80 nm diameter Au NP on 3.4nm thick $Al_2O_3$ coated Au

Larger Au diameter ⇒ more scattering signal, longer resonance wavelength

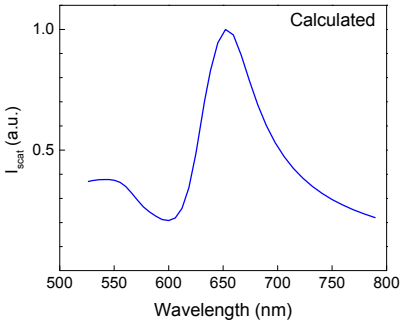
Thicker oxide possible, less sensitive to small thickness variation

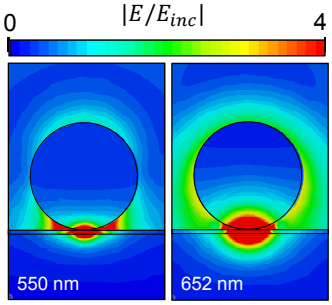



**Next**: identify mode distribution for green and read scattering peaks

## Numerical simulation: resonance identification




ACS Photonics 1, 1224 (2014)

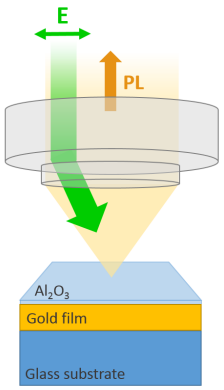
Scattering spectrum determined from net dipole moment

**Note:** - both green and red resonances show field enhancement in gap region
- strong field inside gold on either side of interface

**Next**: photoluminescence measurements



## Green excitation – bulk Au photoluminescence

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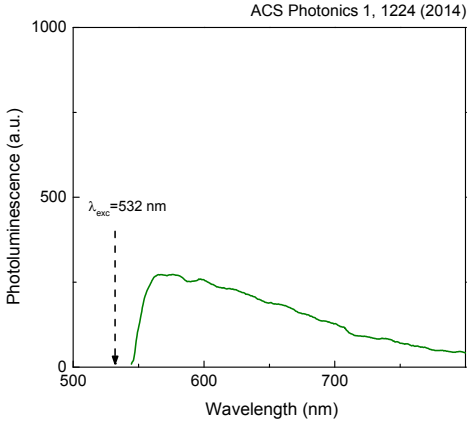


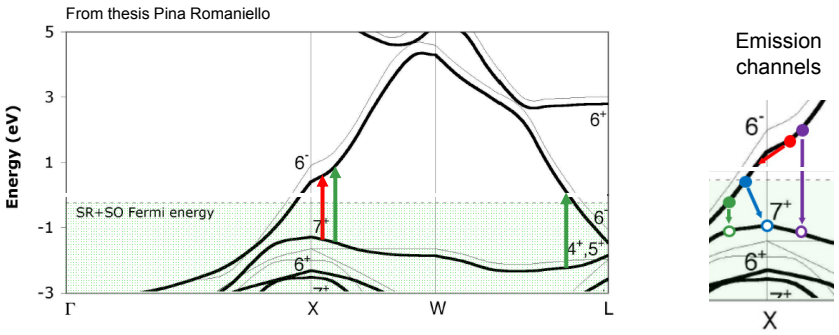

Excitation angle 35° off-normal

Excitation power 100 μW CW at 532 nm, spot size 2.8 μm FWHM

Largely featureless emission spectrum. Origin?

## Gold photoluminescence: link to band structure

Interband absorption options for red (633nm) and green (532nm) light




Low energy excitation: most transitions occur near X-point

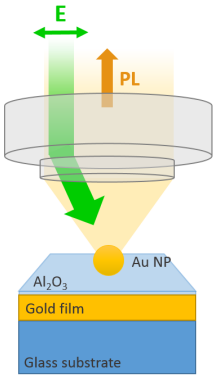
Emission due to recombination of hole in d-band with electron near Fermi level

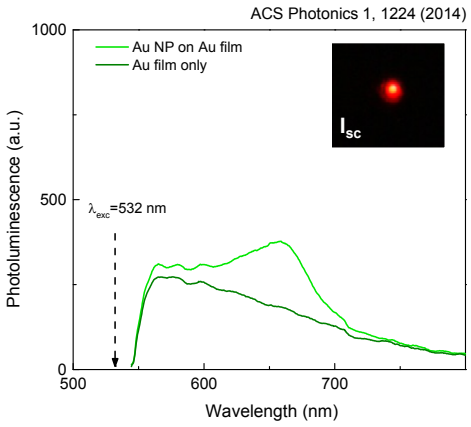
Quantum efficiency for radiative recombination: **~$10^{-10}$**

**Question**: can field enhancement from gap mode also enhance gold PL ?



## Green excitation – gold film + single nanoparticle

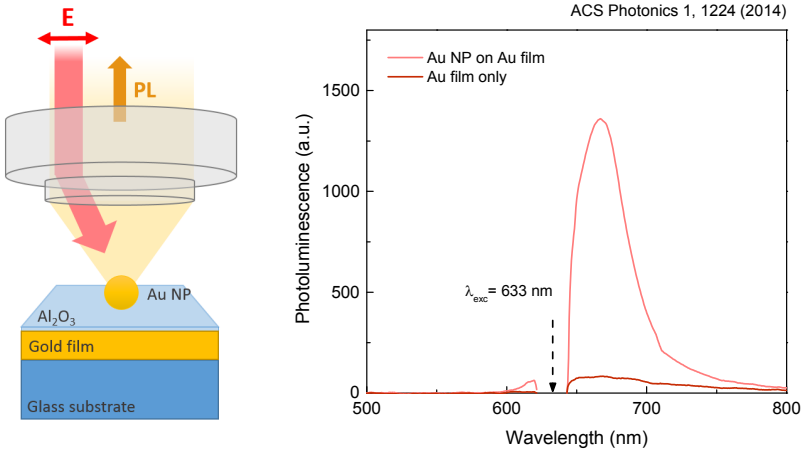



**Note**: incident laser light contains surface-normal field component ⇒ can excite gap mode

**Result**: gold photoluminescence ~doubles near the gap mode wavelength

## Red excitation – gold film + single nanoparticle




**Red excitation**: Au film PL lower, particle enhanced PL stronger compared to green case.

Photoluminescence near emission peak increases by factor 16. Not very large?

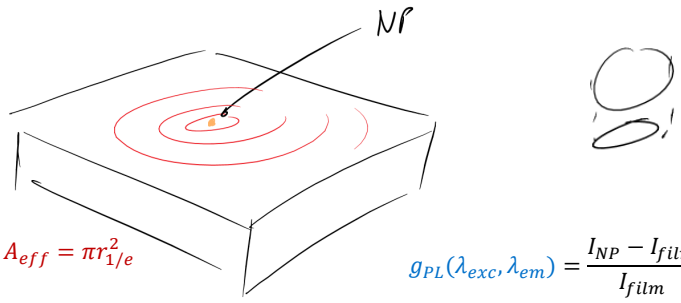


## Nanoparticle photoluminescence enhancement factor

Consider laser spot area and particle cross section:

Laser spot FWHM ~2.8 um, nanoparticle diameter 80 nm.

Particle cross-section is factor $(2.8 / 0.080)^2$ = 1225 smaller than laser spot! (less than 0.1%)




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

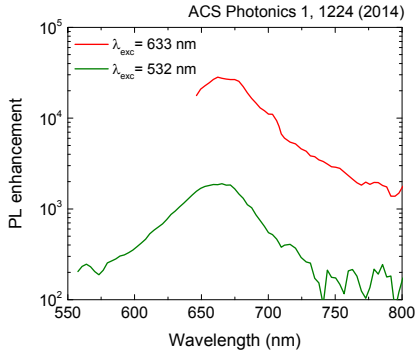
Define **enhancement $g_{PL}$** as PL added by NP / PL from Au film with same area

Benefit: can easily be used by fellow researchers, provides 'on-sample' reference data

**Next**: use this definition determine $g_{PL}$ for green and red excitation

## Nanoparticle PL enhancement factor – experimental result

Single particle enhancement factor after spot size correction: up to **28000** and **1900**




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

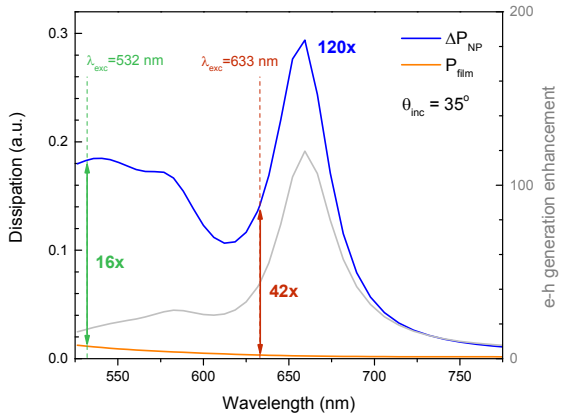
**Note**: line-shape and peak position very similar

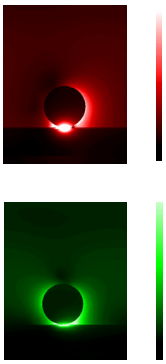
**Question**: can we quantitatively understand the magnitude and spectral dependence of $g_{PL}$

**First contribution**: excitation enhancement



## Simulation - comparison of power dissipation



Dissipated power in film without particle: smooth function vs. frequency

Adding NP : power dissipation increases for all frequencies

Ratio is the enhancement of e-h pair generation rate: 16x and 42x (vs. $g_{PL}$ = 1900 and 28000)

Possibly: gap mode also enhances emission rate (radiative recombination rate)

## Model assumptions

1) Radiative *e-h* recombination in the gold film is highly inefficient (measured ~$10^{-10}$)

   ⇒ emission remains inefficient even for large emission enhancement

2) Reciprocity: emission probability from e-h pair at location **r** into a given angular range is linearly proportional to $|E(\mathbf{r})|^2$ under plane wave excitation at an angle in that range

3) The collected PL spectrum dominated by large-angle emission (simulate single emission angle)

4) Since radiative recombination may lead to *s*- and *p*-polarized emission, we take into account simulated fields $E_{TM}(\omega_{em})$ and $E_{TE}(\omega_{em})$

5) Carrier motion during the *e-h* recombination time is negligible relative to the spatial extent of the excitation field (no nonlocal effects, no need to convolute excitation and emission fields)

$$R_{PL}(\omega_{exc},\omega_{em}) \propto \varepsilon''_{IB}(\omega_{exc})\left|\vec{E}(\omega_{exc})\right|^2 \times \gamma(\omega_{exc},\omega_{em})\left[\left|\frac{E_{TE}(\omega_{em})}{E_0(\omega_{em})}\right|^2 + \left|\frac{E_{TM}(\omega_{em})}{E_0(\omega_{em})}\right|^2\right]$$

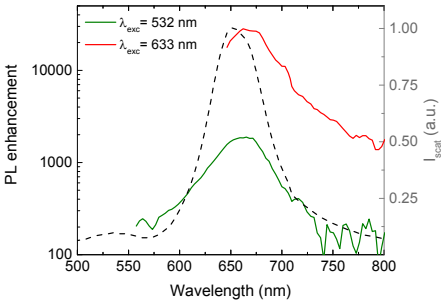


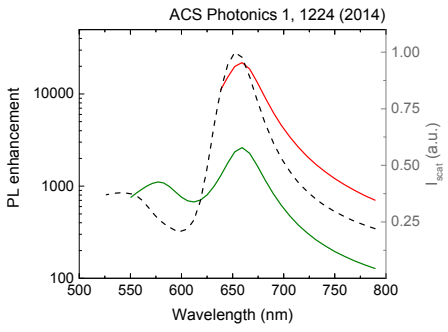
## Comparison of experimental and simulated enhancement

Integration of $R_{PL}$ throughout Au in simulation volume ⇒ prediction of enhancement

$$R_{PL}(\omega_{exc},\omega_{em}) \propto \varepsilon''_{IB}(\omega_{exc})\left|\vec{E}(\omega_{exc})\right|^2 \times \gamma(\omega_{exc},\omega_{em})\left[\left|\frac{E_{TE}(\omega_{em})}{E_0(\omega_{em})}\right|^2 + \left|\frac{E_{TM}(\omega_{em})}{E_0(\omega_{em})}\right|^2\right]$$

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

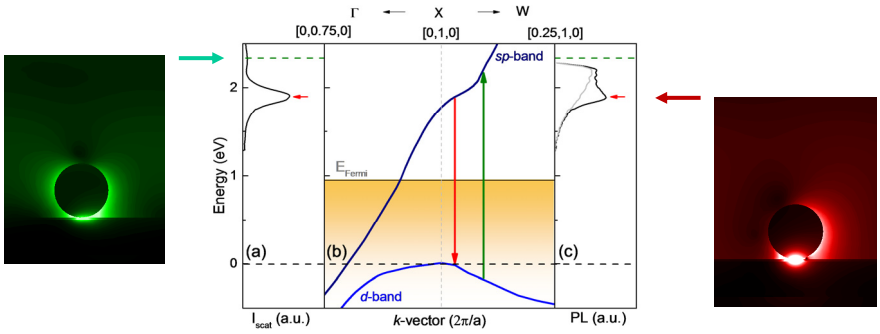



Magnitude of PL enhancement predicted correctly without any free parameters

We appear to have a reasonable model description

## Complete PL enhancement process




Laser excitation near resonance: enhanced e-h generation rate

Generated holes recombine with electron before leaving hot spot

Oscillatory dipole moment associated with e-h recombination couples to gap mode

Gap mode field couples partly to free space

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## Final thoughts: magnitude of the effect – reasonable?

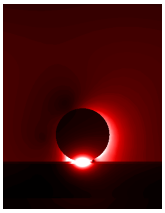
**Surprise**: e-h generation rate enhancement $\propto |E|^2$ 'only' produced factor ~40

Common assumption: emission enhancement, Raman enhancement $\propto |E|^4$

**But**: $40^2 = 1600$, far less than observed PL enhancement of > 20000

**Reason**: factor 40 is volume integrated

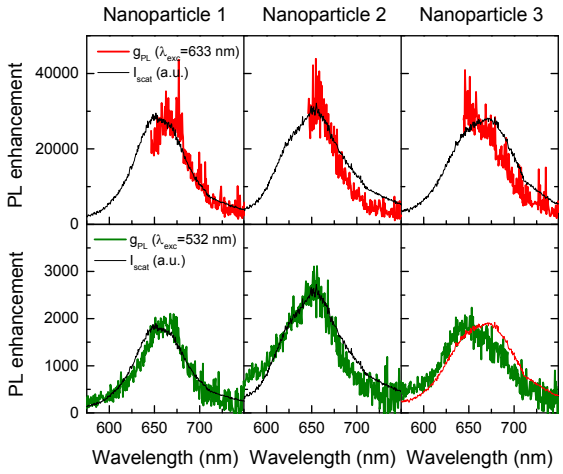
**Model**: integrates $|E_{exc}|^2 |E_{em}|^2$ throughout volume



"*Emission enhancement happens most strongly at at locations where excitation enhancement occurs as well*"

Mathematically: $\int |\vec{E}(\omega_{exc})|^2 |E(\omega_{em})|^2 dV \gg \int |\vec{E}(\omega_{exc})|^2 dV \times \int |E(\omega_{em})|^2 dV$

## All this work on one particle? Does this reproduce? (yes)

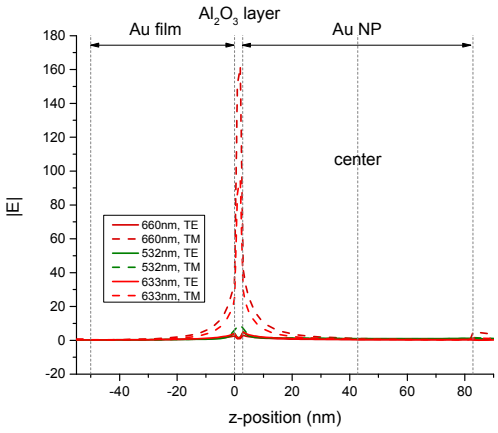


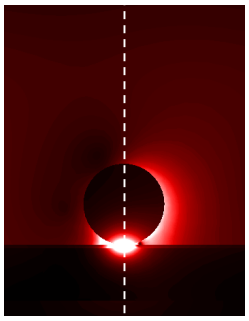

$$g_{PL}(\lambda_{exc}, \lambda_{em}) = \frac{I_{NP} - I_{film}}{I_{film}} \frac{A_{eff}}{\sigma_{NP}}$$

Results sensitive to field enhancement, yet highly reproducible



## Linearity of enhancement: reasonable?



Maximum simulated internal field enhancement: ~42

Predicted maximum emission rate enhancement: ~1800

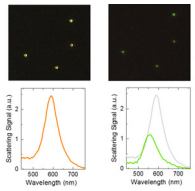
Estimated maximum Au PL quantum efficiency within NP: $10^{-7}$

## Summary

1. Gold nanoparticle scattering on anodized Al film

   - single particle spectroscopy
   - voltage control of NP resonance
   - polarization selectivity, reproducibility

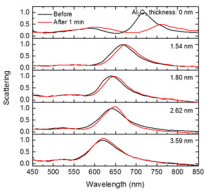
   ACS Nano 6, 6301 (2012)



2. Gold nanoparticle scattering on $Al_2O_3$ coated Au film

   - thinner oxides, larger tuning range
   - all-inorganic structure
   - stable against radiation

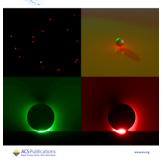
   JPC-C 117, 19127 (2013)




3. Gold photoluminescence enhancement using gap plasmons

   - excitation frequency dependence
   - numerical model, enhancement of excitation and emission
   - photoluminescence as indirect probe of field enhancement

   ACS Photonics 1, 1224 (2014)

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