Dissertation Defense



Nanoscale Control of Gap-Plasmon Enhanced Optical Processes



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Outlines



Introduction

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

Project 1: Enhanced scattering and resonance control

Project 2: Gap-plasmon enhanced photoluminescence

Project 3: Alternative gap-plasmon supporting structure



Create

Read Edit View



Nanophotonics

From Wikipedia, the free encyclopedia

Nanophotonics or Nano-optics is the study of the behavior of light on the nanometer scale, and of the interaction of nanometer-scale objects with light. It is a branch of optics, optical engineering, electrical engineering, and nanotechnology. It often (but not exclusively) involves metallic components, which can transport and focus light via surface plasmon polaritons.

Thanks Wikipedia!

Introduction – Nanophotonics



Nanophotonics? What can it do?

Tons. For example ...



Broadband circular polarizer

Nature Mat. 10, 631 (2011)



Gas sensor

Nature Nano. 10, 429 (2015)



3D imaging

Nano Letters 10, 1537 (2010)



Nanodisk resonators

OPN, June 2015



More ...



Nanophotonics? What can it do?

Tons. For example ...

What's a common element?

Near-field and in some cases optical resonances by metallic nanostructures (plasmons)



Simplest form \rightarrow nanosphere

ACS Nano 7, 11064 (2013)





Electrostatic approximation Particle << wavelength

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

(Homogeneous)

Boundary conditions

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

Perfect metal: $\epsilon_{in} = -\infty$ $E_{in} = 0$ $E_{out} = -3E_{inc}$ (just have a small particle!) Real metal: $\epsilon_{in}(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ E_{in} and $E_{out} \to \infty$ when $\epsilon_{in} + 2\epsilon_{out} = 0$ (resonance frequency)





50 nm diameter Au NP nm diameter in water



Frequency domain finite-element simulation

Perfect metal: $\epsilon_{in} = -\infty$ $E_{in} = 0$ $E_{out} = -3E_{inc}$

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

Near-field $\propto \frac{1}{r^3}$ Decays quickly \rightarrow localized in a nm³ volume (nanophotonics)





50 nm diameter Au NP nm diameter in water



Frequency domain finite-element simulation

Perfect metal: $\epsilon_{in} = -\infty$ $E_{in} = 0$ $E_{out} = -3E_{inc}$

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

Question: How do we observe resonance in far-field? Answer: Scattering

$$C_{sct} \propto \omega^4 \left| \frac{\epsilon_{in} - \epsilon_{out}}{\epsilon_{in} + 2\epsilon_{out}} \right|^2$$





50 nm diameter Au NP nm diameter 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?



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!

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 \rightarrow Gap-plasmon resonance (mode volume \Box gap size)

Optical wavelength \Box 440 nm in water at this frequency

NP dimer in free space



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



Frequency domain finite-element simulation

Gap plasmon resonance \rightarrow 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?



NP on metallic film



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



Introduction – Optical Near-field



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



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 \Box dimer \rightarrow Gap plasmon at the junction!

Much easier and cheaper to fabricate than dimers

This presentation will focus on this structure.

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- Different applications require different working frequencies
- Can we precisely control gap-plasmon resonance frequency?

Project 2: Gap-plasmon enhanced photoluminescence

Project 3: Alternative gap-plasmon supporting structure

<u>Goal</u>: 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 \rightarrow organic background, not robust

Our structure: Gold nanoparticles on an aluminum film Aluminum can be oxidized to grow Al₂O₃ spacer













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



Simple and low-cost \rightarrow Good!

Question: How do we grow Al_2O_3 thickness?

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Answer: Anodization.

Overall reaction: $2AI + 3H_2O \rightarrow AI_2O_3 + 3H_2$



Increase the

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



Answer: Darkfield microscopy and single particle spectroscopy





Answer: Darkfield microscopy and single particle spectroscopy





Darkfield microscopy image of an as-deposited sample



Very well separated scattering spots \rightarrow can do <u>single particle</u> 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)



Darkfield microscopy and single particle spectroscopy after each anodization step





From single NP!

Thinner AI_2O_3 = redder the NPs Less loss = Stronger scattering



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?



Question: Can we get a larger tuning range?



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

Thinner oxide \rightarrow more red-shift \rightarrow larger tuning range

Question: Can we get a larger tuning range? Answer: Yes, but we need to change the substrate material.



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

Thinner oxide \rightarrow more red-shift \rightarrow larger tuning range

Gold does not oxidize!





NP solution drop coating

Question: If gold does not oxidize, how do we control Al₂O₃ thickness Answer: Regular thin-film deposition



Very thin Al \rightarrow Entire Al film oxidizes and becomes Al₂O₃

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



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



Wavelength (nm)

More redshift compared to Au NPs on anodized Al

Al₂O₃ thickness (nm)



Question: What is the total tuning range we achieved? Answer: > 140 nm, from green to red (good range for Raman measurements)



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

Mission accomplished!

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

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Project 2: Gap-plasmon enhanced (Raman?) photoluminescence

- Gap-plasmon resonance = very strong and confined = good for Raman (SERS)
- But we observed something else?

Project 3: Alternative gap-plasmon supporting structure



Goal: Gap-plasmon mediated SERS measurement (Surface Enhanced Raman Scat.)



60 nm diameter Au NPs

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



Frequency domain finite-element simulation

Question: What is the setup for SERS measurement?

Project 2: Gap-plasmon enhanced photoluminescence

Question: What is the setup for SERS measurement? Answer: Same system as scattering, add a laser







Surprising SERS result!

4-methylbenzenethiol (4-MBT)



Narrow lines on small background

A few Raman lines on huge background The background moves with resonance freq.!

Question: The strong background is not Raman, but what is it?



Answer: Photoluminescence (PL) \rightarrow Light emission as a result of photoexcitation of carriers



But it was very strong in the measurement and it moved!

 \rightarrow gap-plasmon enhanced gold PL!

<u>Goal</u>: Gap-plasmon mediated SERS measurement (Surface Enhanced Raman Scat.) **NEW** <u>**Goal**</u>: Explain the process of gap-plasmon enhanced photoluminescence

Project 2: Gap-plasmon enhanced photoluminescence



Back to the structure without Raman coating, and take a scattering spectrum



Single NP scattering spectrum

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

Project 2: Gap-plasmon enhanced photoluminescence







Photoluminescence spectra



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



Photoluminescence spectra



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

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



Photoluminescence enhancement



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



Photoluminescence enhancement spectra



PL = *Light emission as a result of photoexcitation of carriers*

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

Both green and red excitations show max. PL enhancement [] resonance wavelength (650 nm) Suggests \rightarrow Gap-plasmon enhanced emission 40















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

Goal: Explain the process of gap-plasmon enhanced photoluminescence

Mission accomplished!

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- We observe gap-plasmon enhanced gold PL (while doing SERS)
- A numerical model is developed to explain the phenomenon



Project 3: Alternative gap-plasmon supporting structure

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Project 3: 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?



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



Normal incidence excitation Unhindered hot-spot

Question: How do we make it?



Question: How do we make it? Answer: Nanosphere lithography + NP self-assembly

(i) PS bead deposition









Question: How do we make it? Answer: Nanosphere lithography + NP self-assembly





Darkfield microscopy image





Question: How do we make it? Answer: Nanosphere lithography + NP self-assembly



Darkfield microscopy image











(iii) PS bead removal and native Al_2O_3 formation









Question: How do we make it? Answer: Nanosphere lithography + NP self-assembly



Darkfield microscopy image





Question: How do we make it? Answer: Nanosphere lithography + NP self-assembly



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



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)



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)



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



HiO has a gap-plasmon mode 🗆 650 nm



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



HiO has a gap-plasmon mode 🗆 650 nm

SEM shows that the NP is off-center \rightarrow Polarization dependent study



HiO darkfield microscopy and single particle spectroscopy: polarization study





HiO darkfield microscopy and single particle spectroscopy: polarization study



DF – Rotating analyzer



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



HiO darkfield microscopy and single particle spectroscopy: polarization study



Question: Didn't we want normal incidence excitation?



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

After NP deposition







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



Question: Didn't we want normal incidence excitation? Answer: Yes, we did. And we had it!



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

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



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?



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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Project 3: 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

Project 1: Enhanced scattering and resonance control

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

Project 2: Gap-plasmon enhanced gold photoluminescence

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

Project 3: Hole-in-One structure

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









Publications



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.

S. Toroghi, C. Lumdee, and P. G. Kik, "Heterogeneous Plasmonic Trimers for Enhanced Nonlinear Optical Absorption," Appl. Phys. Lett. 2015, 106, 103102.

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

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.

<u>CONFERENCE PRESENTATIONS</u> (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.

S. Toroghi, C. Lumdee, and P. G. Kik, "Extreme Plasmon Resonant Field Enhancement in Multi-material Nanoparticle Trimers," FTh3C. 3 (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.

S. Toroghi, C. Lumdee, and P. G. Kik, "Cascaded Plasmon Resonances Multi-material Nanoparticle Trimers for Extreme Field Enhancement," Proc. 8809-88091M (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.

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Kik group (Oct 2012)



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Thai Student Association(s)





UCF Badminton Club