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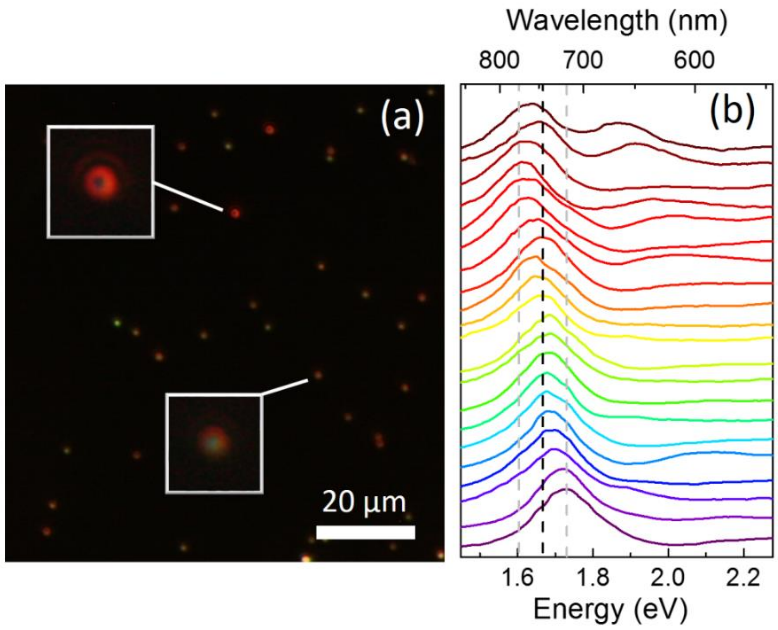
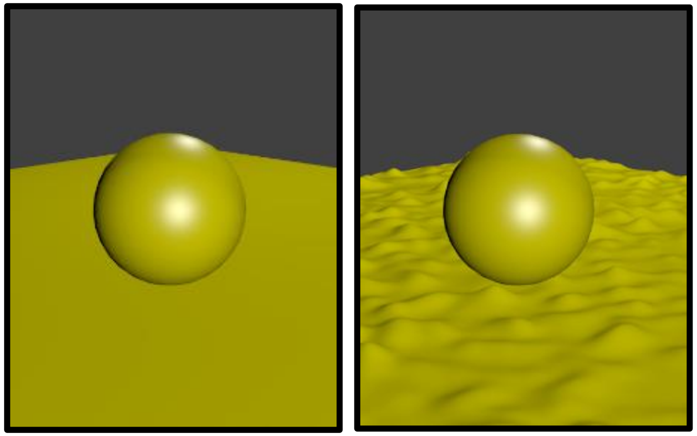
Effect of nanoscale surface roughness on surface-tuned nanoparticle plasmon resonances

Chatdanai Lumdee and Pieter G. Kik

CREOL, the College of Optics and Photonics, UCF, Orlando, FL, USA





Outline

- Introduction: substrate-coupled metal nanoparticles
  - Attractiveness
  - Resent studies

- All inorganic substrate-coupled gold nanoparticles
  - Resonance control using Al_2O_3 coatings
  - Stability under laser irradiation

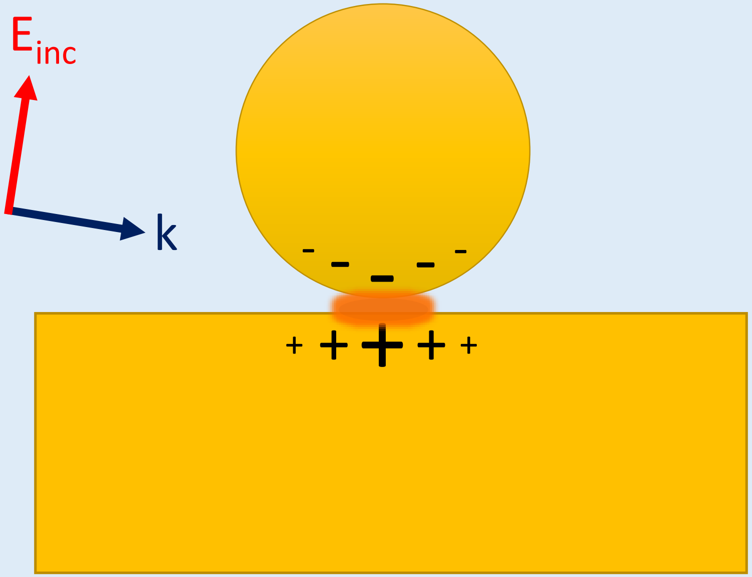
- Effect of surface roughness on gold nanoparticle resonances
  - Observations
  - Experiment
  - Model and simulation

- Summary

Introduction

Substrate-coupled nanoparticles: attractiveness

- High field enhancement in the gap



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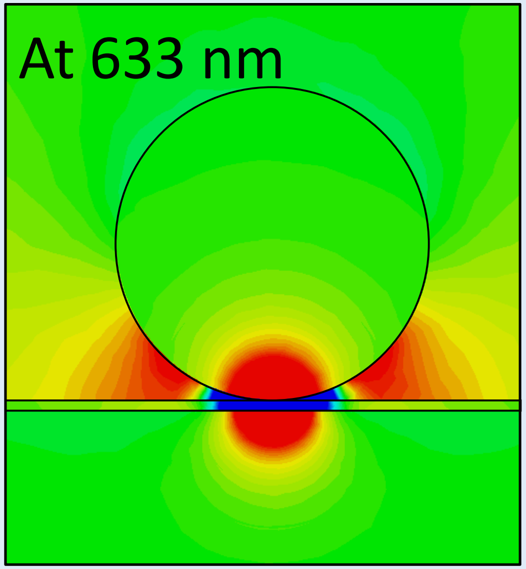
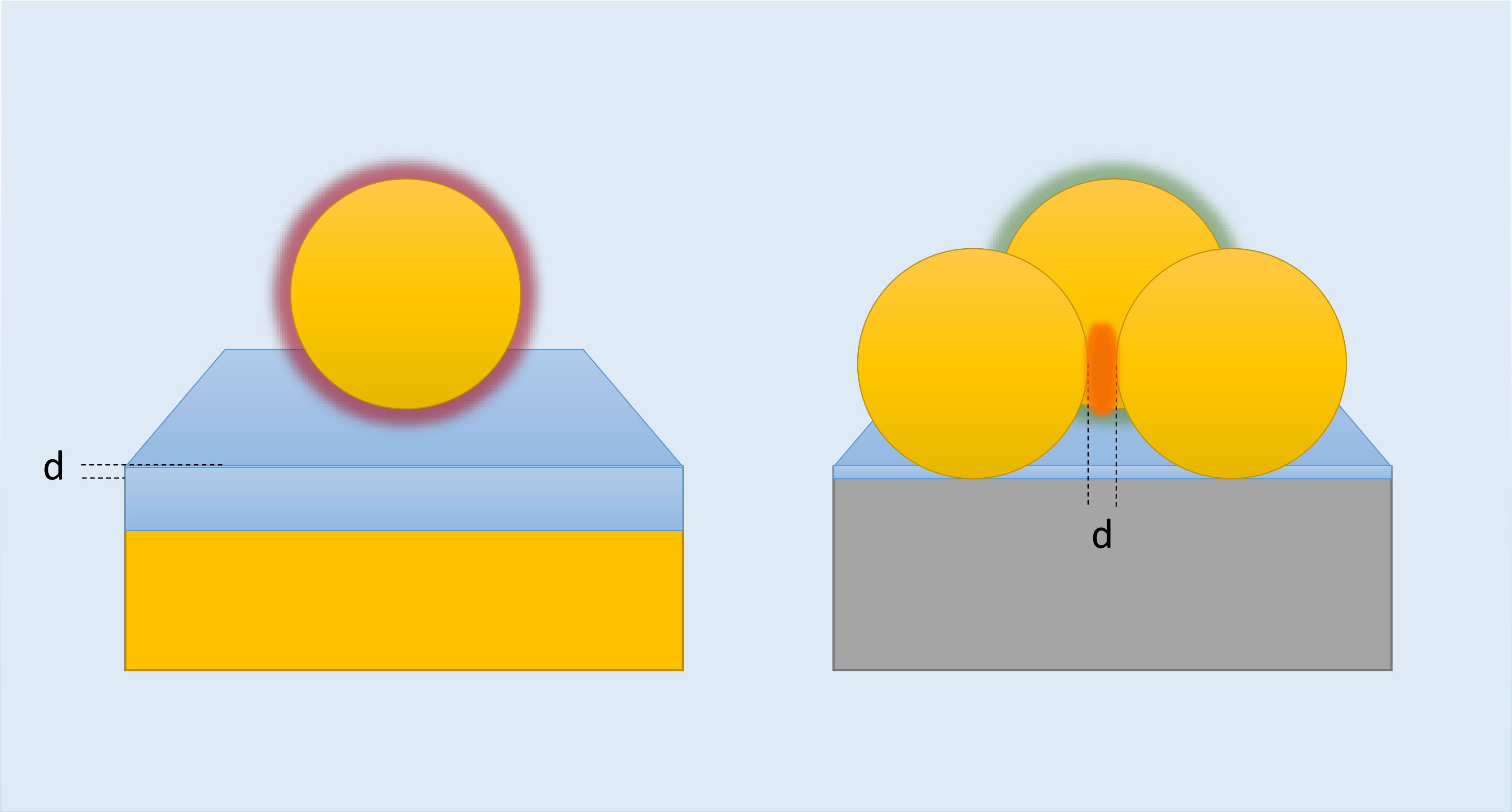


60 nm diameter Au NP
on Al_2O_3 coated Au film

Introduction

Substrate-coupled nanoparticles: attractiveness

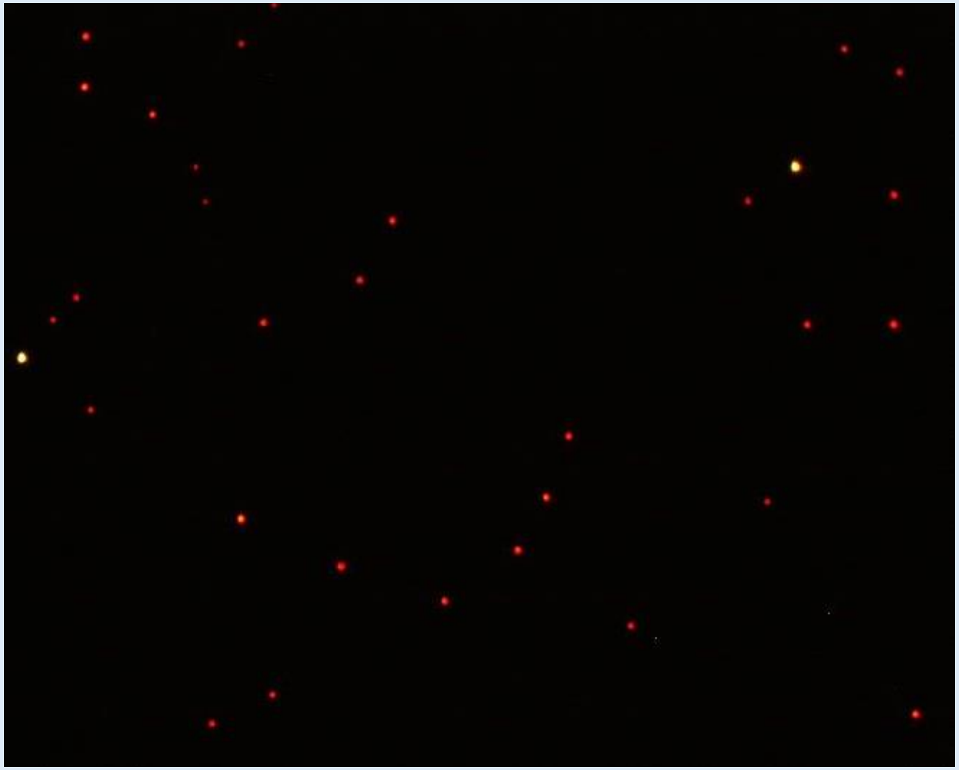
- High field enhancement in the gap
- Easy to control coupling strength

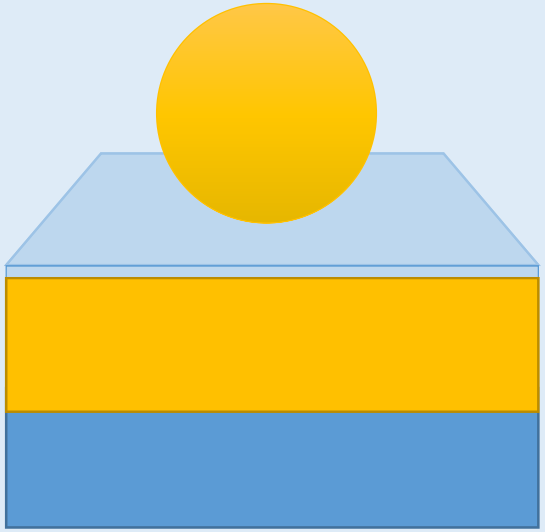


Introduction

Substrate-coupled nanoparticles: attractiveness

- High field enhancement in the gap
- Easy to control coupling strength
- Robust, reproducible, simple, and inexpensive



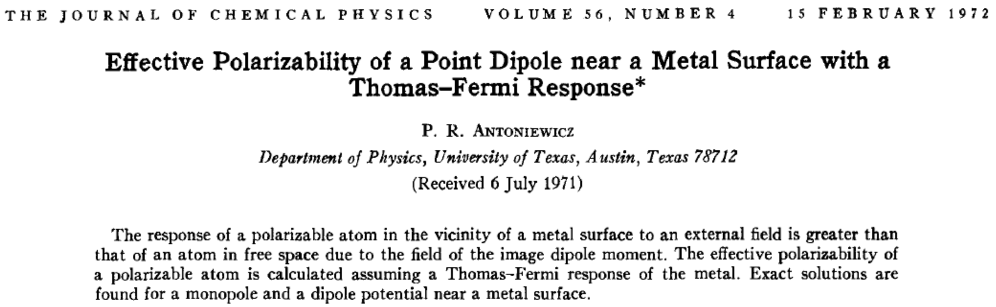


60 nm diameter Au NPs on 3.4 nm Al_2O_3 coated gold film

(Not very) Recent studies

substrate-coupled nanoparticles

- Effective polarizability of a point dipole near a metal surface
  P. R. Antoniewicz, J. Chem. Phys. 1972, 56 (p.1711)



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 56, NUMBER 4 15 FEBRUARY 1972

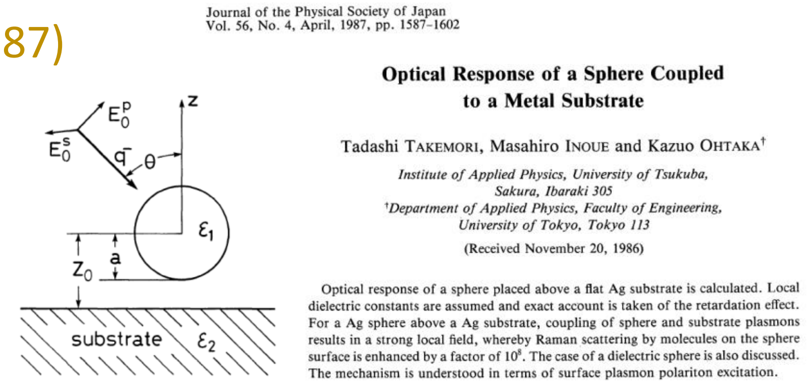
Effective Polarizability of a Point Dipole near a Metal Surface with a Thomas–Fermi Response*

P. R. Antoniewicz
Department of Physics, University of Texas, Austin, Texas 78712

(Received 6 July 1971)

The response of a polarizable atom in the vicinity of a metal surface to an external field is greater than that of an atom in free space due to the field of the image dipole moment. The effective polarizability of a polarizable atom is calculated assuming a Thomas–Fermi response of the metal. Exact solutions are found for a monopole and a dipole potential near a metal surface.

- A sphere couple to a metal substrate
  T. Takemori, et al. J. Phys. Soc. Jpn. 1987, 56 (p.1587)



Journal of the Physical Society of Japan
Vol. 56, No. 4, April, 1987, pp. 1587–1602

Optical Response of a Sphere Coupled to a Metal Substrate

Tadashi Takemori, Masahiro Inoue and Kazuo Ohtaka[†]
Institute of Applied Physics, University of Tsukuba, Sakura, Ibaraki 305
[†]Department of Applied Physics, Faculty of Engineering, University of Tokyo, Tokyo 113

(Received November 20, 1986)

Optical response of a sphere placed above a flat Ag substrate is calculated. Local dielectric constants are assumed and exact account is taken of the retardation effect. For a Ag sphere above a Ag substrate, coupling of sphere and substrate plasmons results in a strong local field, whereby Raman scattering by molecules on the sphere surface is enhanced by a factor of 10^8. The case of a dielectric sphere is also discussed. The mechanism is understood in terms of surface plasmon polariton excitation.

- Absorption by a small sphere above a substrate
  R. Ruppin, Phys. Rev. B 1992, 45 (p.5663)

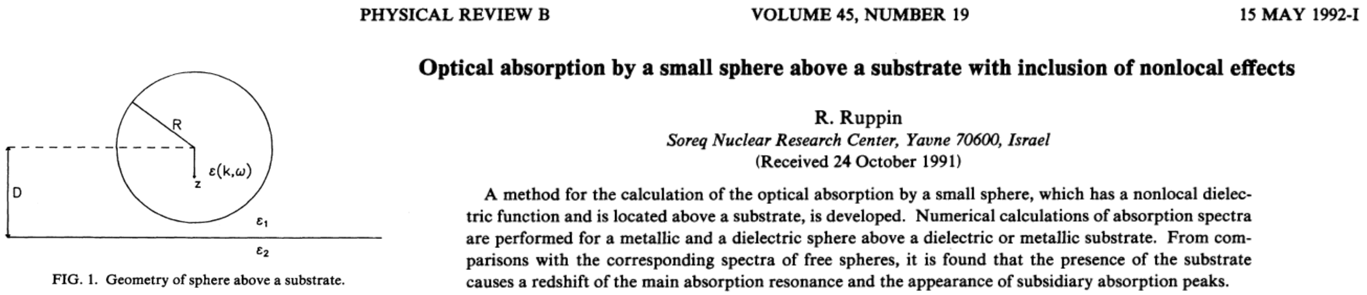


FIG. 1. Geometry of sphere above a substrate.

PHYSICAL REVIEW B VOLUME 45, NUMBER 19 15 MAY 1992-I

Optical absorption by a small sphere above a substrate with inclusion of nonlocal effects

R. Ruppin
Soreq Nuclear Research Center, Yavne 70600, Israel

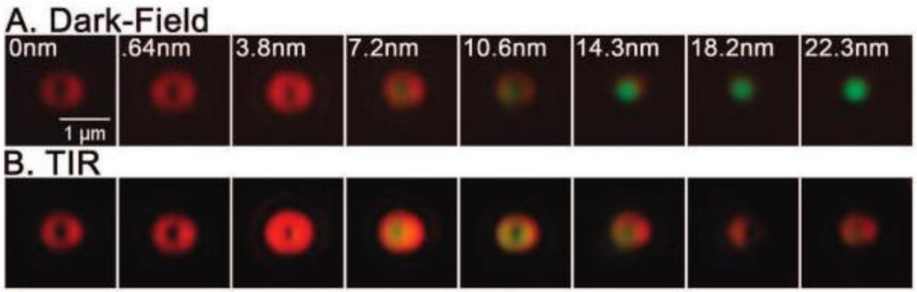
(Received 24 October 1991)

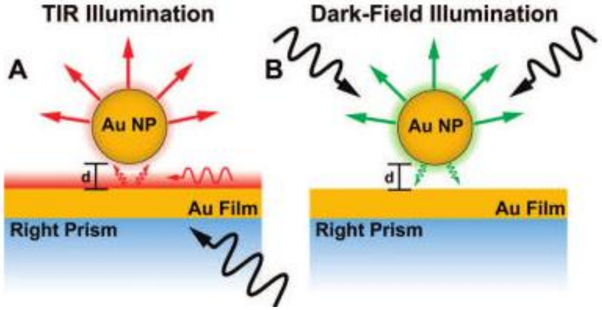
A method for the calculation of the optical absorption by a small sphere, which has a nonlocal dielectric function and is located above a substrate, is developed. Numerical calculations of absorption spectra are performed for a metallic and a dielectric sphere above a dielectric or metallic substrate. From comparisons with the corresponding spectra of free spheres, it is found that the presence of the substrate causes a redshift of the main absorption resonance and the appearance of subsidiary absorption peaks.

Recent studies

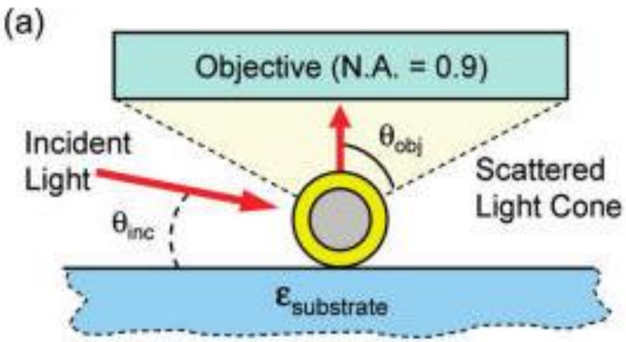
substrate-coupled metal nanoparticles (examples)

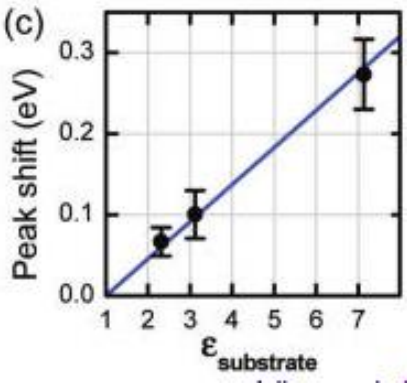
- Distance-dependent plasmon resonant coupling between a gold nanoparticle and gold film
  J. J. Mock, et al. Nano Lett. 2008, 8 (p.2245)





- Substrates matter: Influence of an adjacent dielectric on an individual plasmonic panoparticle
  M. W. Knight, et al. Nano Lett. 2009, 9 (p.2188)





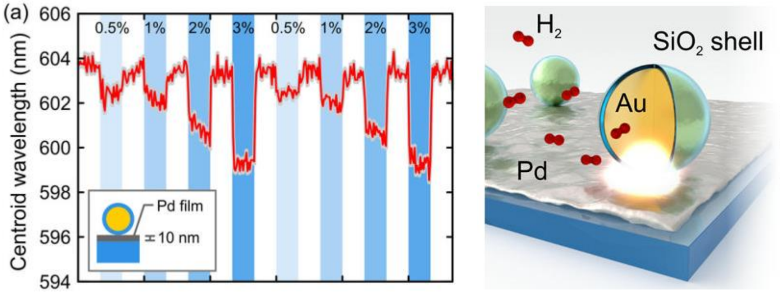
Recent studies

substrate-coupled metal nanoparticles (examples)

- *Sensors*

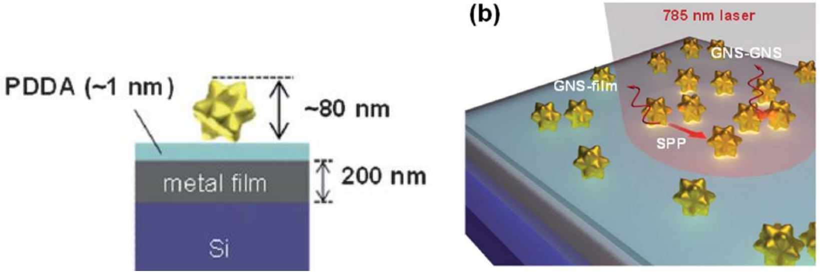
Plasmonic smart dust for probing local chemical reactions

A. Tittl, et al. Nano Lett. 2013, 13 (p.1816)



Tailoring surface plasmons of high-density gold nanostar assemblies on metal films for surface enhanced Raman spectroscopy

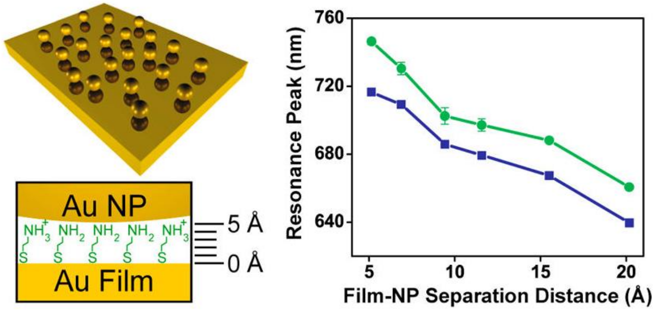
J. Lee, et al. Nanoscale 2014, 6 (p.616)



- *Plasmonic ruler*

Plasmon ruler with angstrom length resolution

M. W. Knight, et al. ACS Nano 2012, 6 (p.9237)



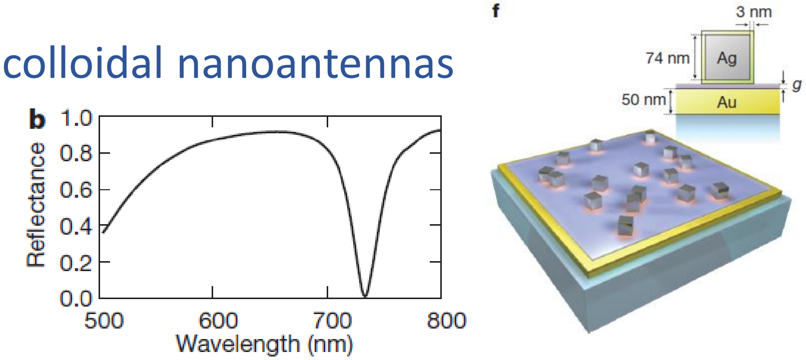
Recent studies

substrate-coupled nanoparticles (examples)

- *Plasmonic absorber*

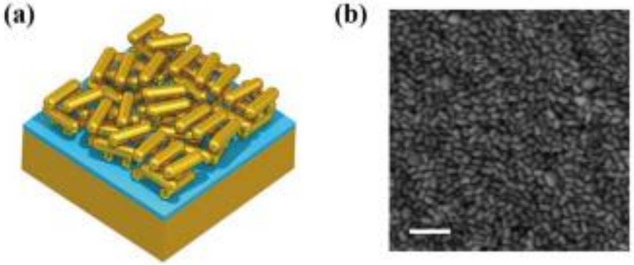
Controlled-reflectance surfaces with film-coupled colloidal nanoantennas

A. Moreau, et al. Nature 2012, 492 (p.86)



Near-infrared broadband absorber with film-coupled multilayer nanorods

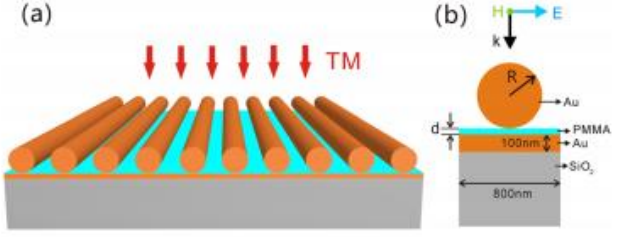
X. Chen, et al. Optics Letters 2013, 38 (p.2247)



- *Nonlinear optics*

Plasmon gap mode-assisted third-harmonic generation from metal film-coupled nanowires

K. Li, et al. Applied Physics Letters, 104, 2014 (p.261105)



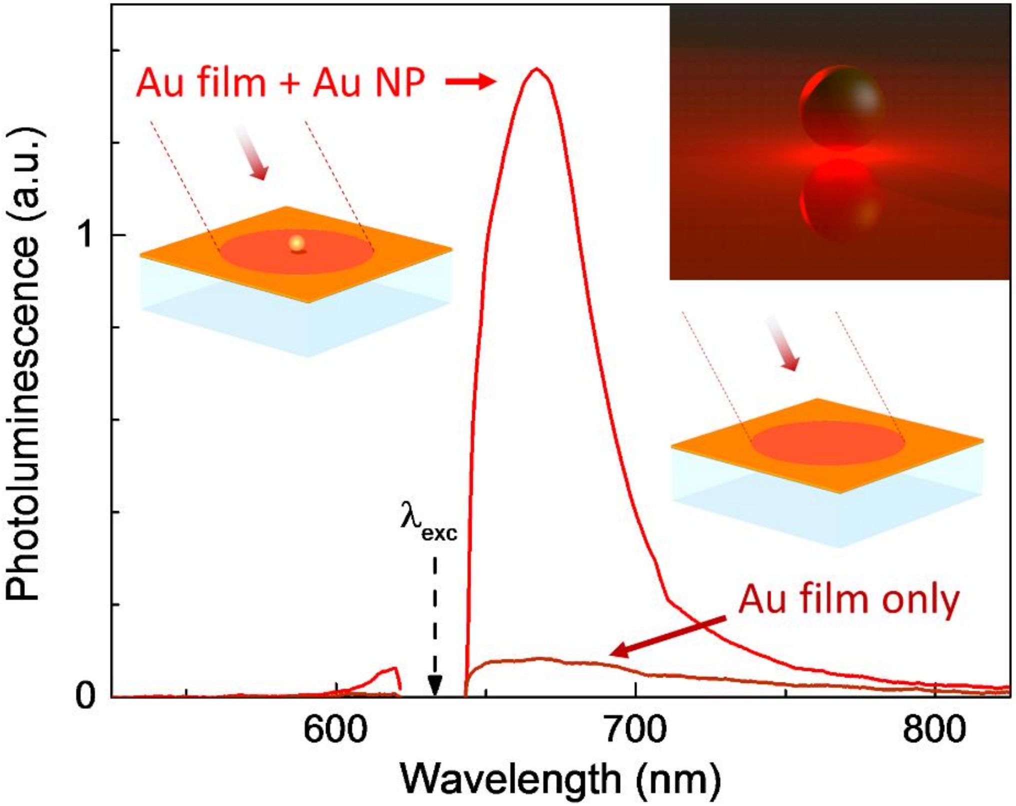
Recent studies

substrate-coupled nanoparticles (examples)

- Photoluminescence enhancement

Gap-plasmon enhanced gold nanoparticle photoluminescnece

C. Lumdee, et al. (submitted)



Recent studies

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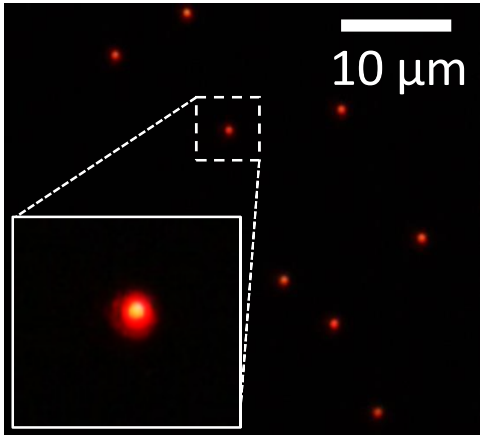
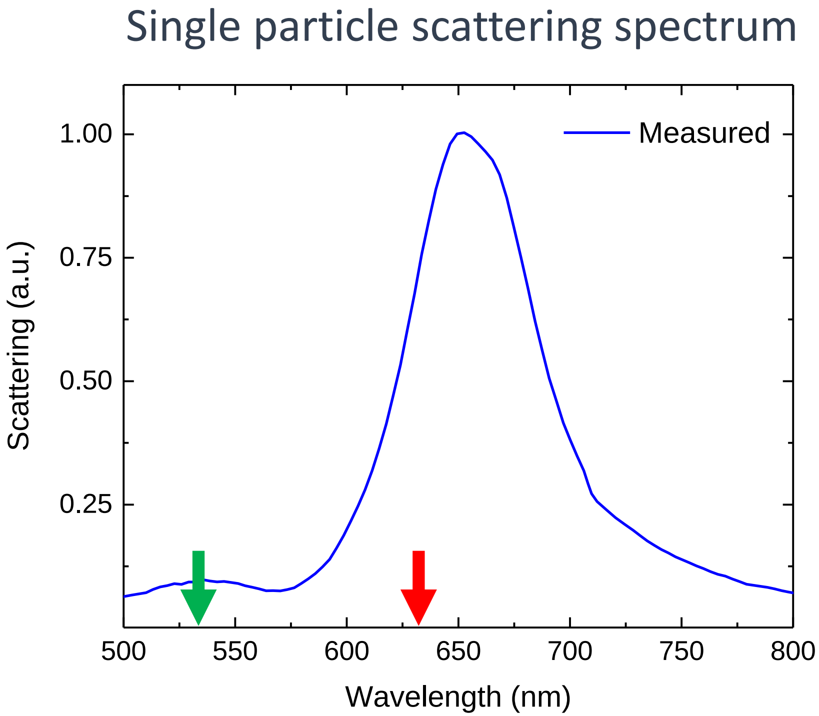
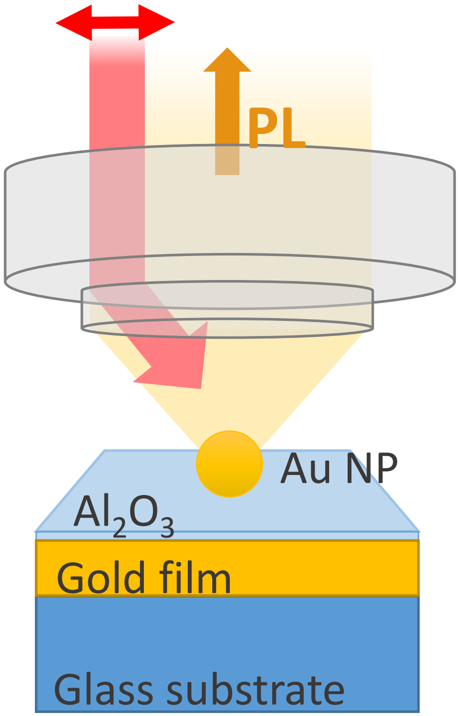



Single particle scattering spectrum



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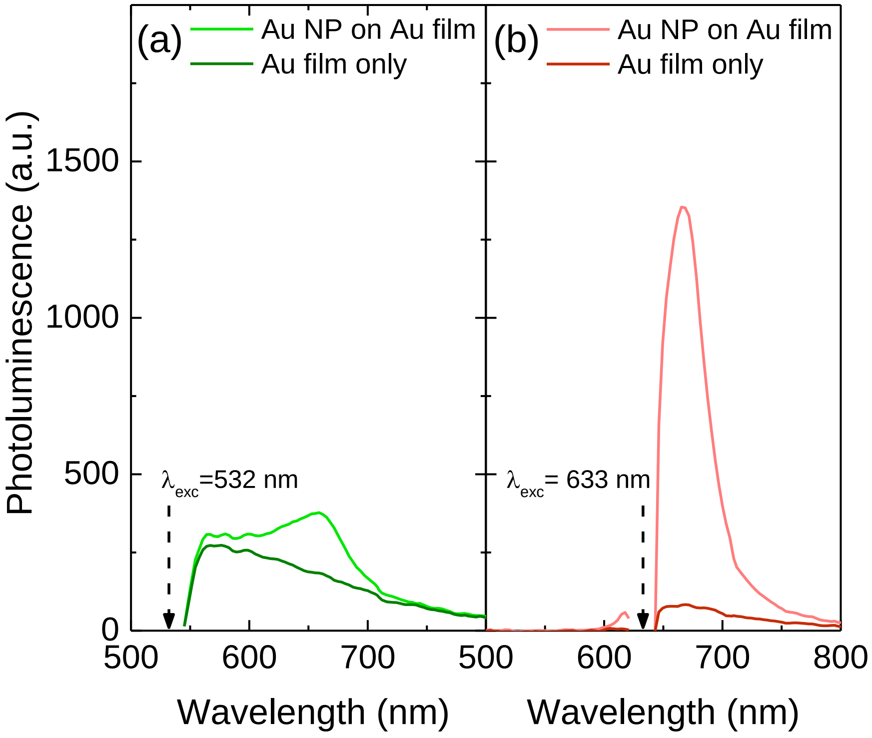
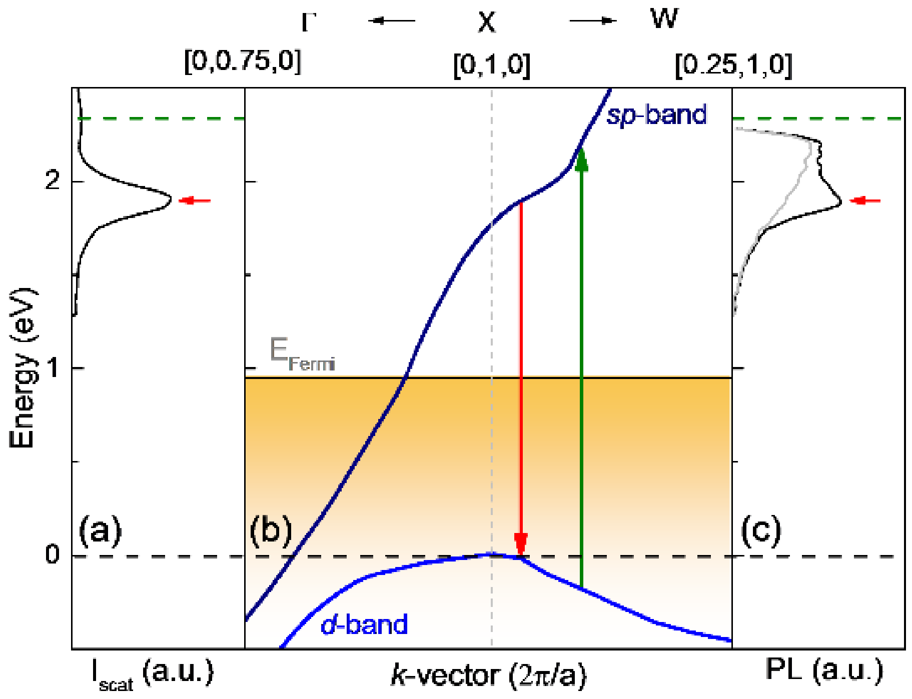


> 4 orders of magnitude enhancement



Very fun!

Want to know more? Meet after the talk

Outline

- Substrate-coupled metal nanoparticles
    - Attractiveness (simple, robust, reproducible)
    - Resent studies

- All-inorganic substrate-coupled gold nanoparticles
    - Resonance control using Al_2O_3 coatings
    - Stability under laser irradiation

- Effect of surface roughness on gold nanoparticle resonances
    - Observations
    - Experiment
    - Model and simulation

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- Substrate-coupled metal nanoparticles
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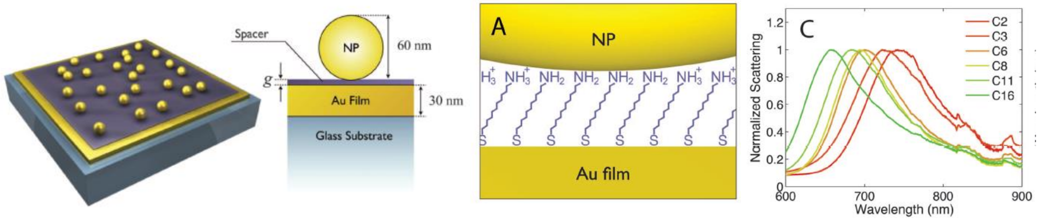
All-inorganic substrate-coupled gold nanoparticles

Why?

Previous attempts

- → Organic molecule spacer layer
- → Organic background
- → Possibly not very stable

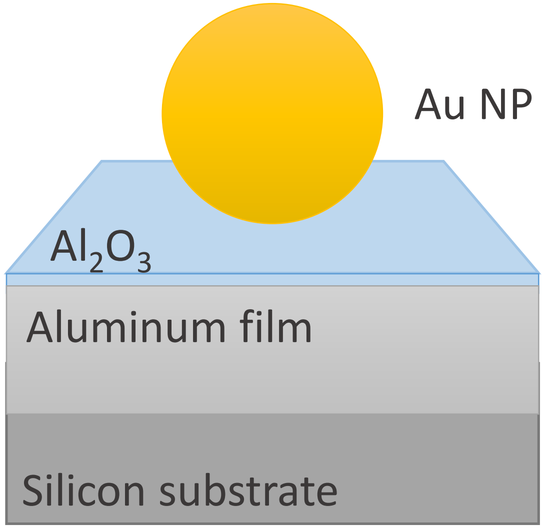
C. Ciraci, et al. Science 2012, 337, p. 1072

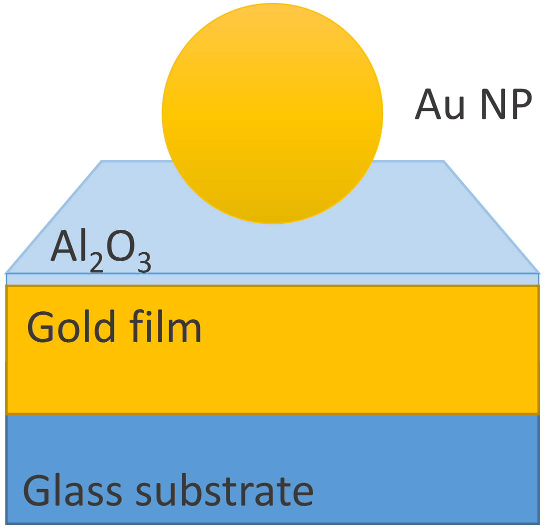


Our structure

Gold nanoparticles on aluminum and gold film

- → Stable Al_2O_3 coating on the surface





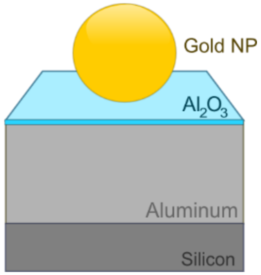
All-inorganic substrate-coupled gold nanoparticles

C. Lumdee, et al. ACS Nano 2012, 6(7), p. 6301–6307

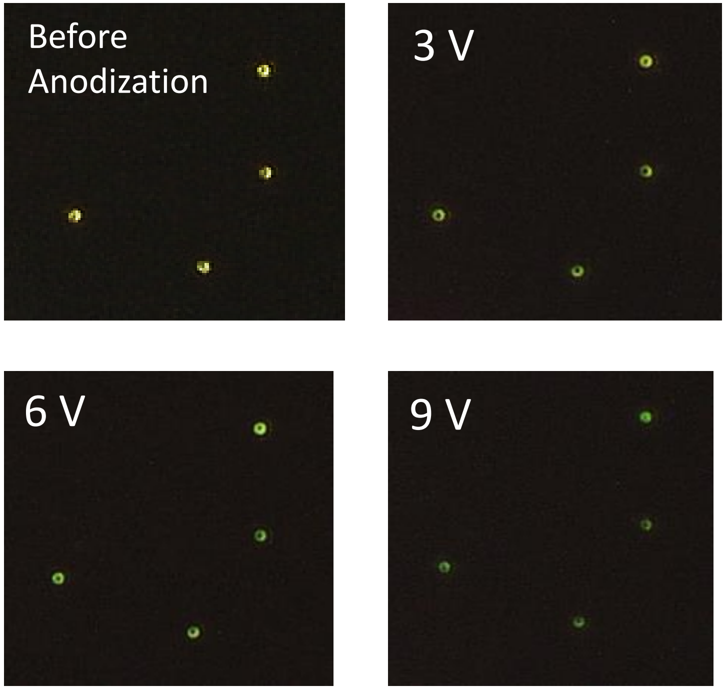
Gold nanoparticles on aluminum film

→ Anodizing aluminum to control Al_2O_3 thickness

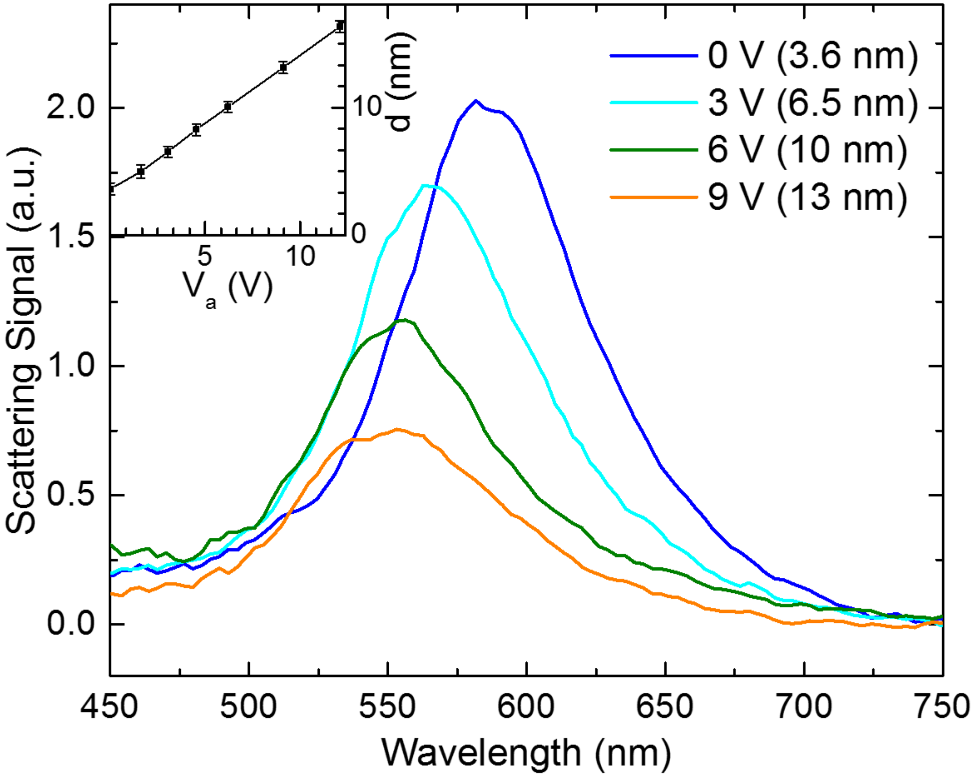
→ NP-to-NP resonance tuning range from 580 – 550 nm



Microscopy images



Scattering spectra (from one NP)

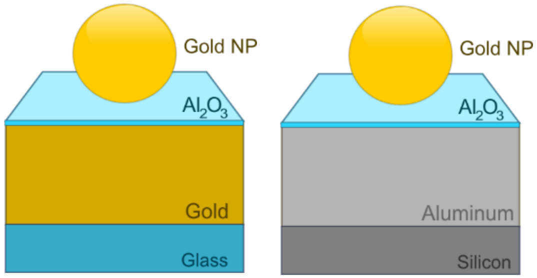


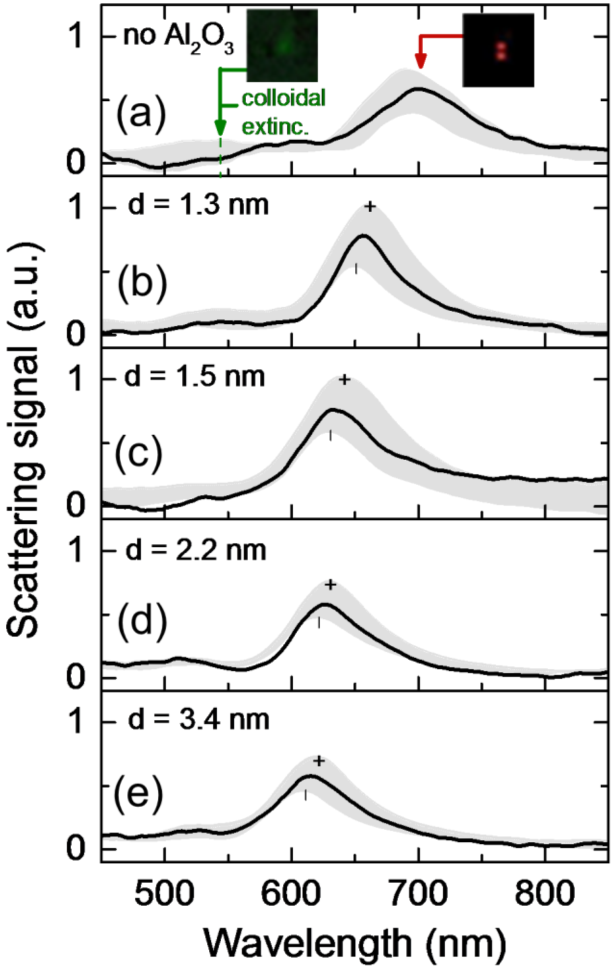
All-inorganic substrate-coupled gold nanoparticles

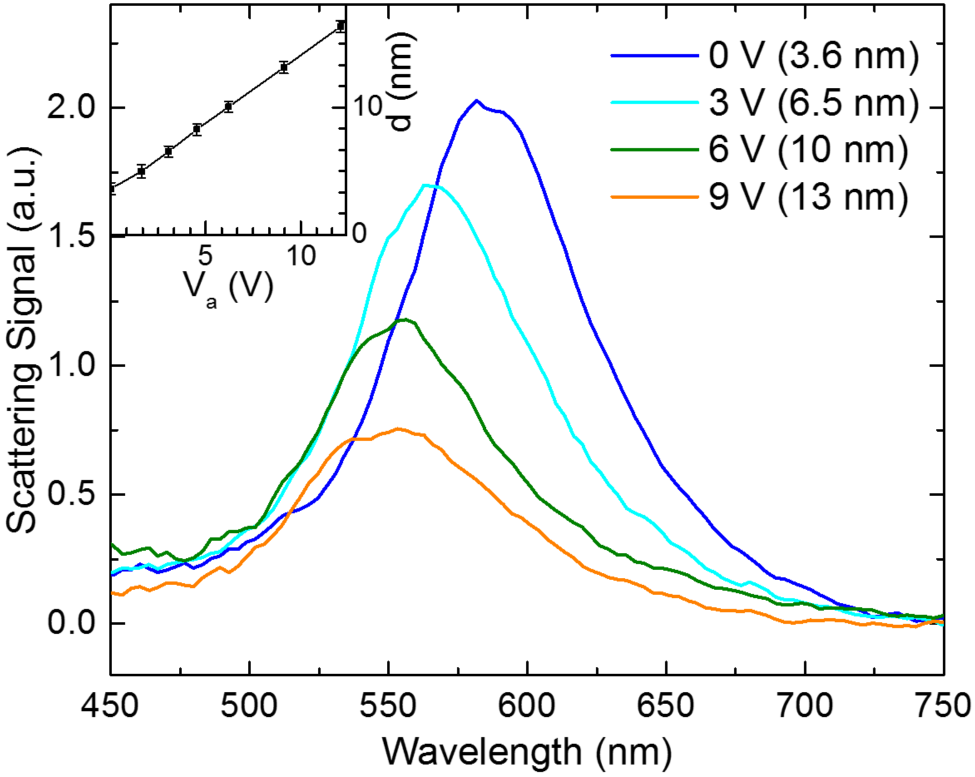
C. Lumdee, et al. J. Phys. Chem. C 2013, 117(37), p. 19127−19133

Gold nanoparticles on aluminum film

- → Improve tuning range limited by 3.6 nm native Al_2O_3
- → Tuning range from 690 – 610 nm for 0 – 3.4 nm Al_2O_3



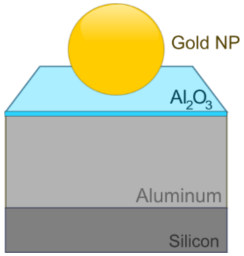


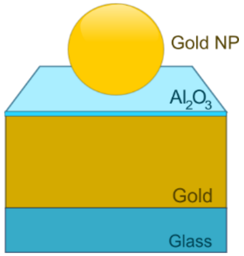


All-inorganic substrate-coupled gold nanoparticles

Gold nanoparticles on Al_2O_3 coated substrates

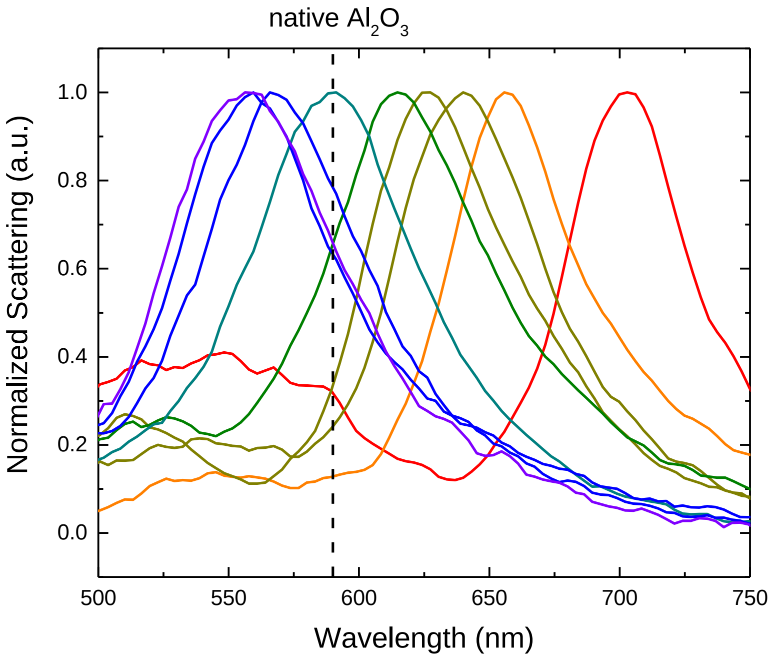
→ Wide tuning range of 140 nm (690-550 nm = far red to green)

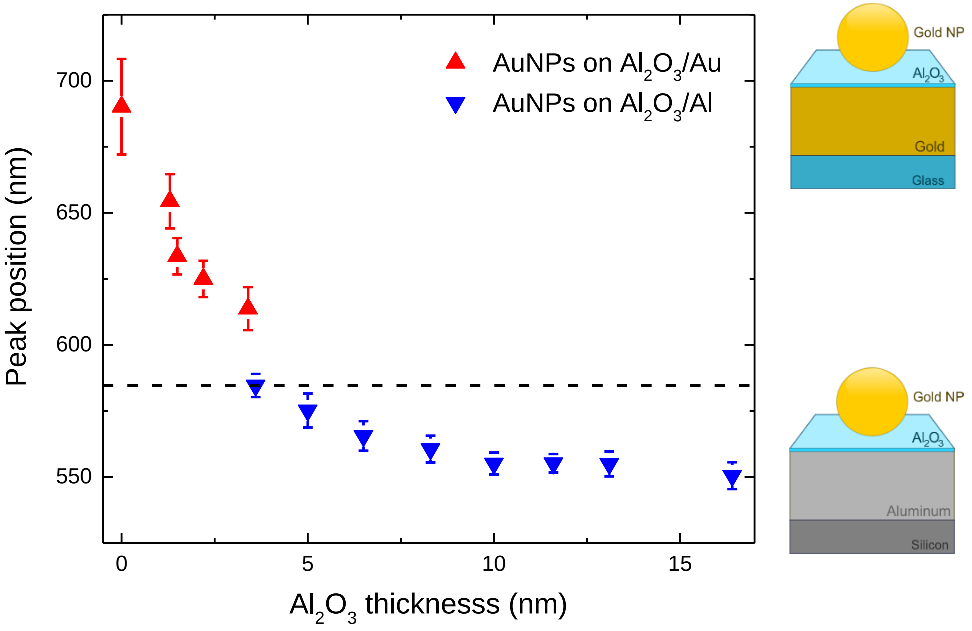




C. Lumdee, et al. ACS Nano 2012, 6(7), p. 6301–6307

C. Lumdee, et al. J. Phys. Chem. C 2013, 117(37), p. 19127–19133

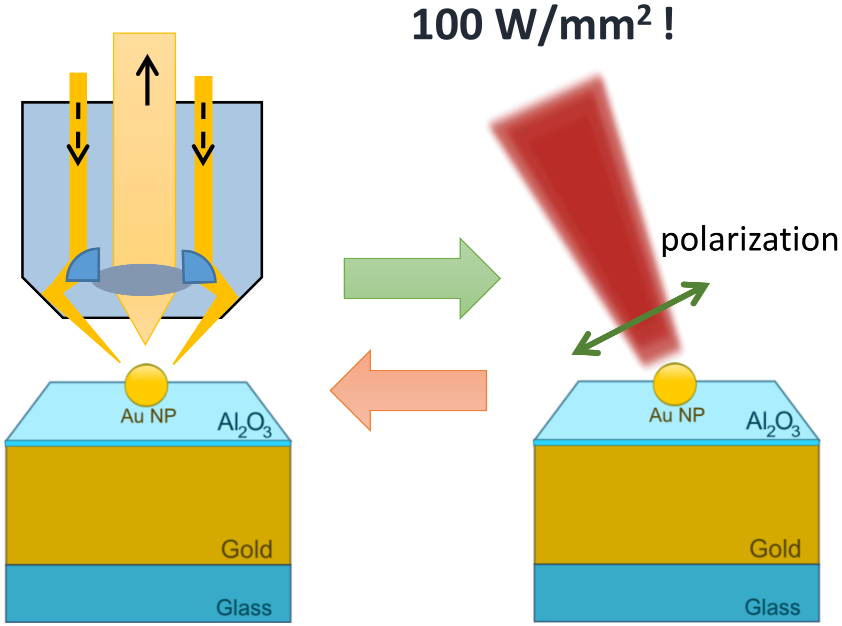


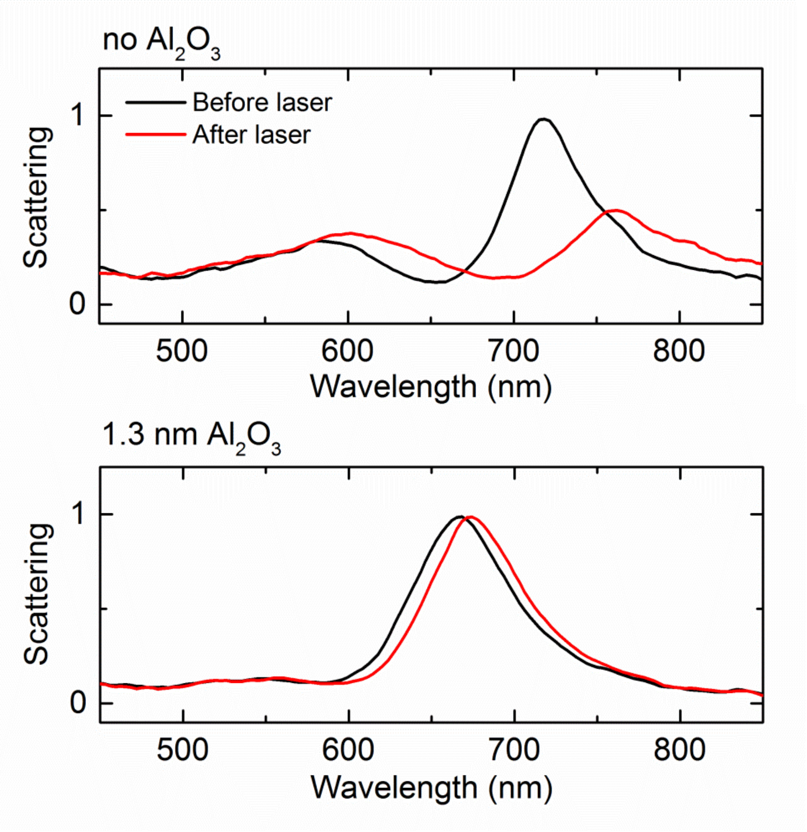


All-inorganic substrate-coupled gold nanoparticles

Gold nanoparticles on Al_2O_3 coated substrates stability

C. Lumdee, et al. J. Phys. Chem. C 2013, 117(37), p. 19127–19133





Stable structure → good for applications e.g. sensing and photoluminescence

Outline

- Substrate-coupled metal nanoparticles
  - Attractiveness (simple, robust, reproducible)
  - Resent studies – applications need resonance control

- All inorganic substrate-coupled gold nanoparticles
  - Resonance control using Al_2O_3 coatings
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Effect of surface roughness on gold nanoparticle resonances

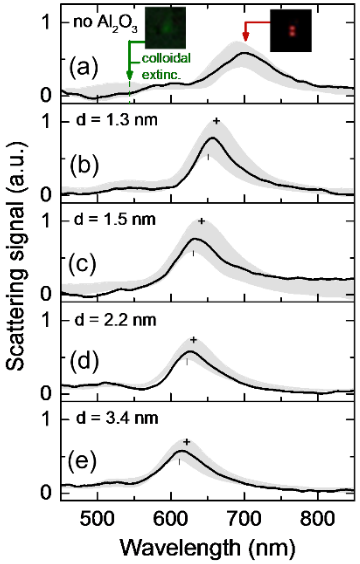
C. Lumdee, et al. J. Phys. Chem. C 2013, 117(37), pp 19127−19133

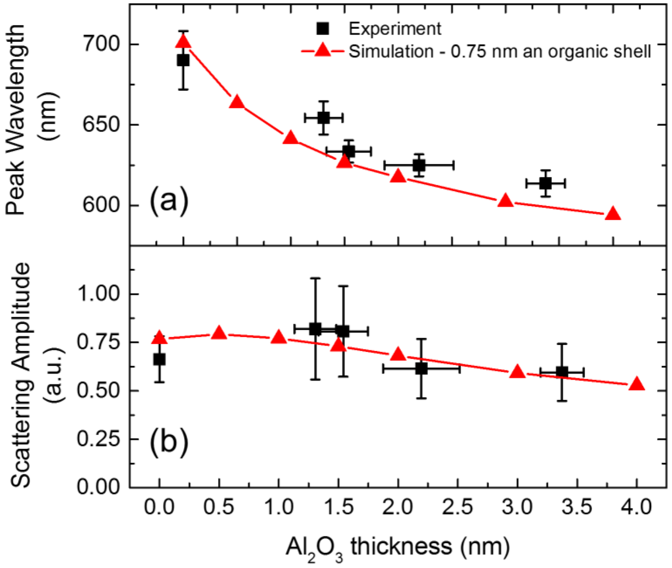
Why?

Previous works

→ Resonance tuning of Au NPs on all inorganic substrates

→ Spectral variations





Q1: What causes this?

A1: Particles, size and shape.

Q2: What about surface of substrate?

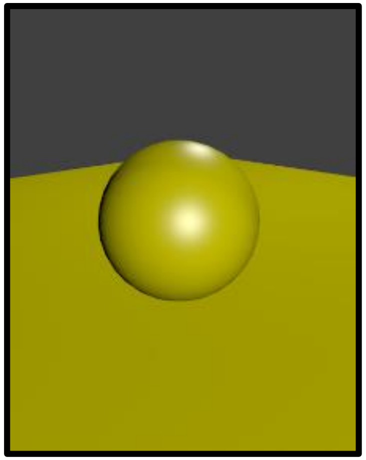
This study

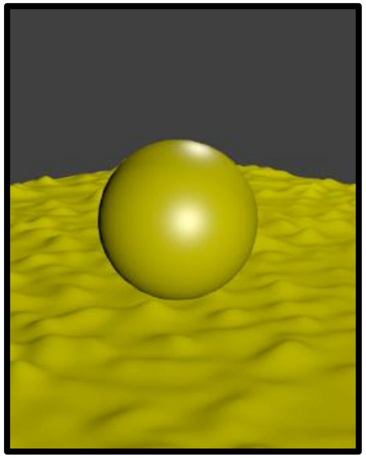
Gold nanoparticles on a gold film

→ Mapping local surface roughness

→ Simulate particle's scattering spectra

→ Compared predicted and measured spectral variations

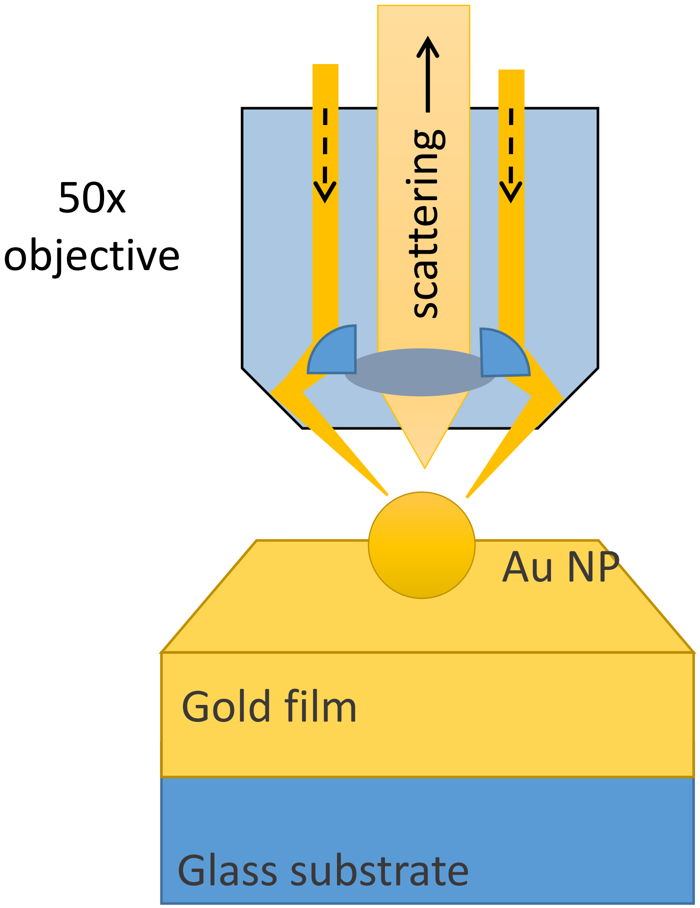


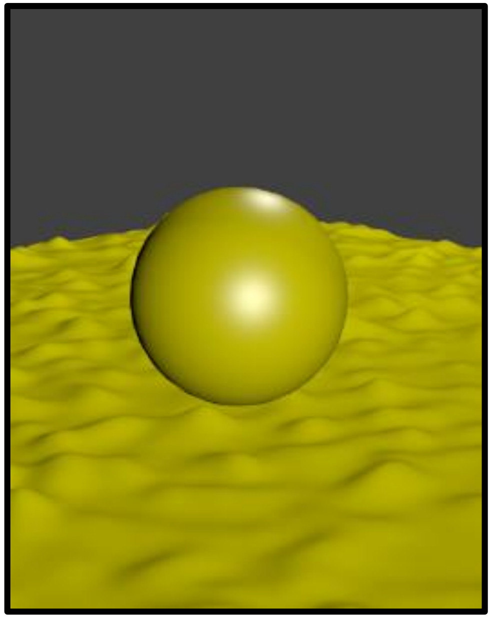


Effect of surface roughness on gold nanoparticle resonances

How?

Dark-field microscopy and spectroscopy





Effect of surface roughness on gold nanoparticle resonances

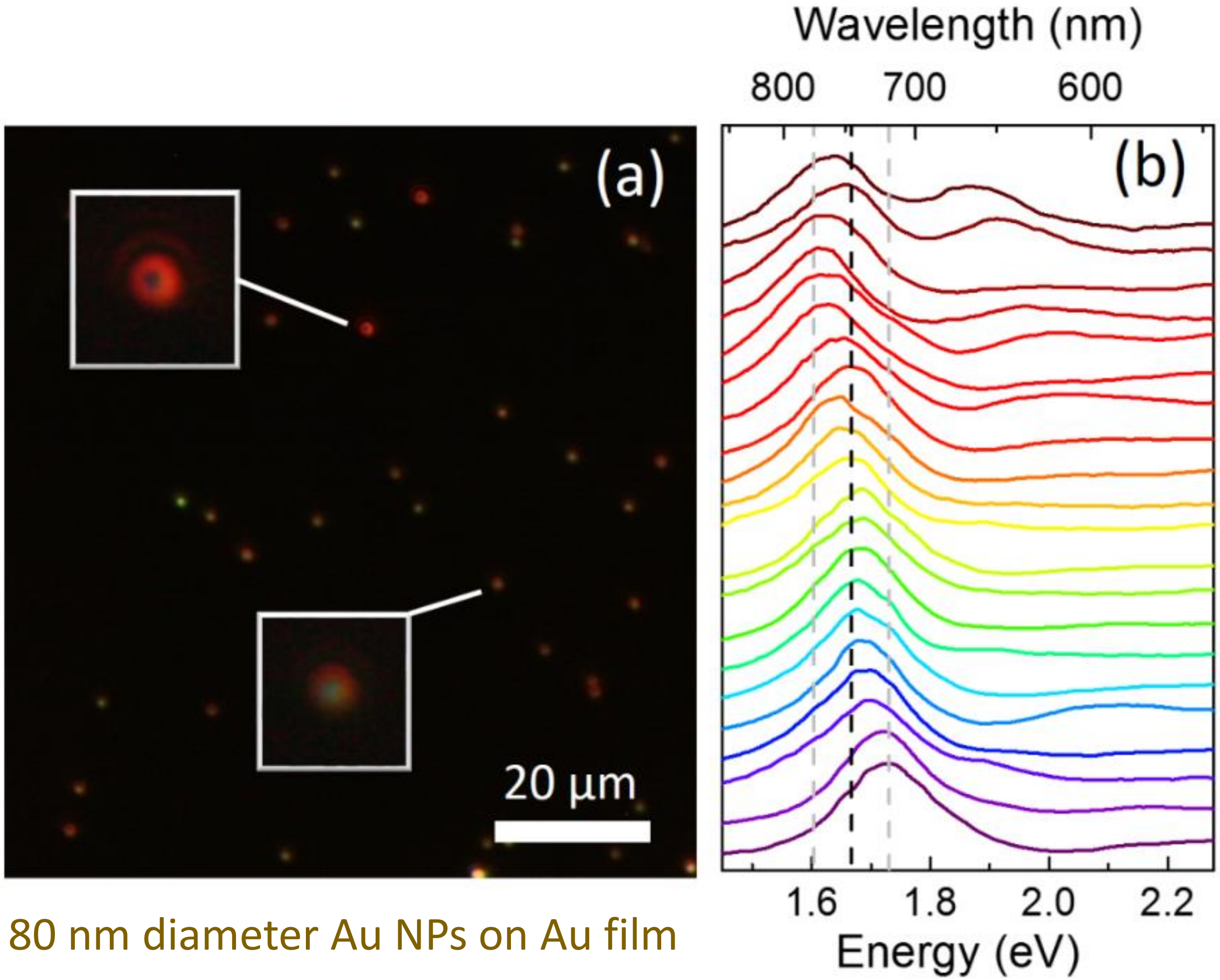
What causes this?

Size variation cannot make this!

How we model surface roughness???

Results

Single gold nanoparticle scattering spectra



80 nm diameter Au NPs on Au film

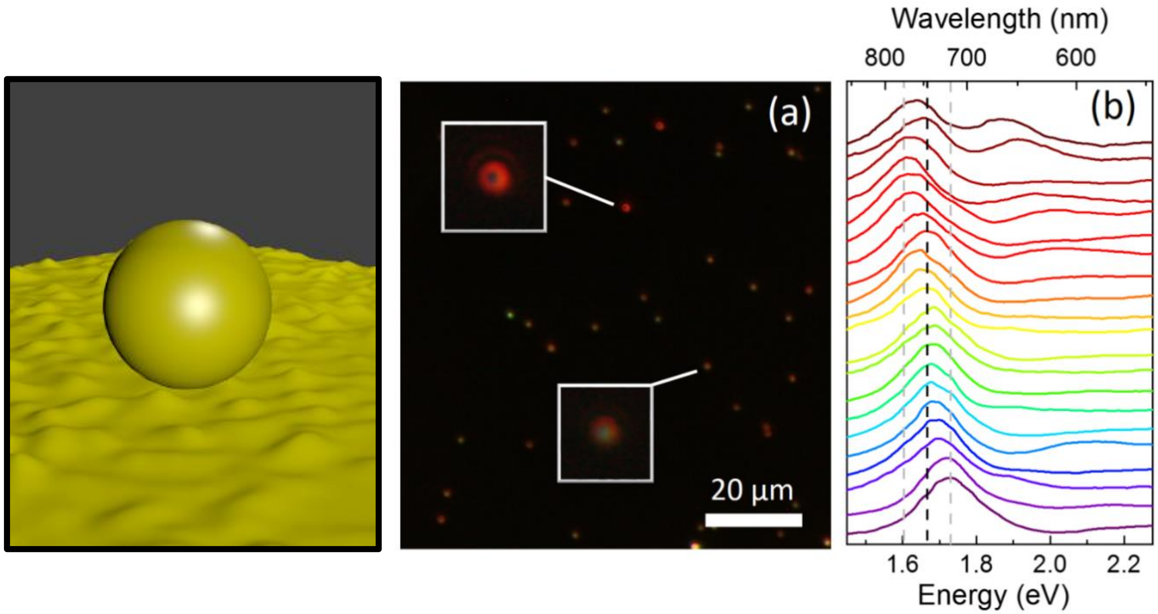
Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

Challenges

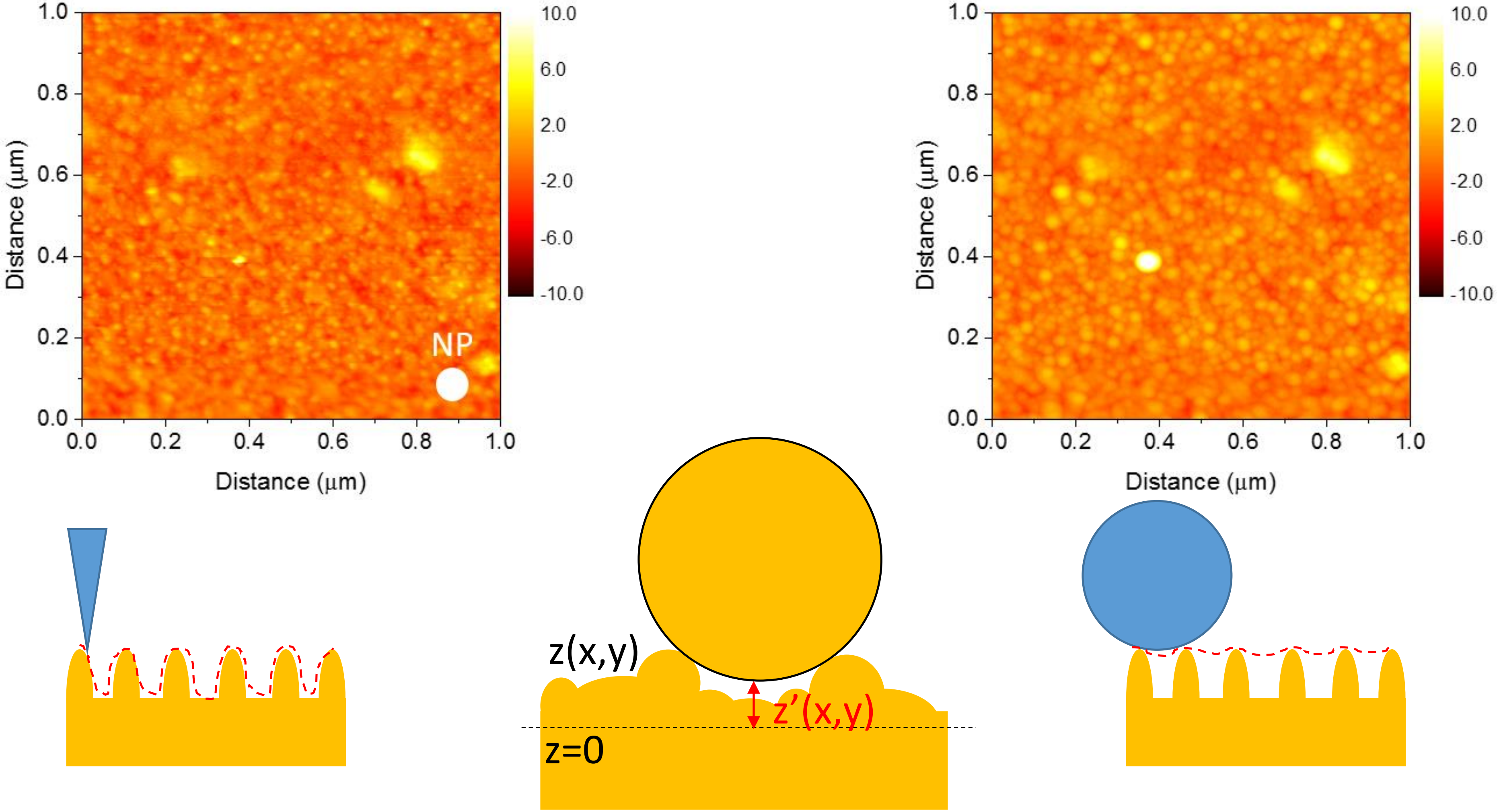
1) Accessing local surface near each nanoparticle
2) Randomness of surface morphology and particle locations
3) Infinite number of possible scenarios → infinite simulations?

…



Effect of surface roughness on gold nanoparticle resonances

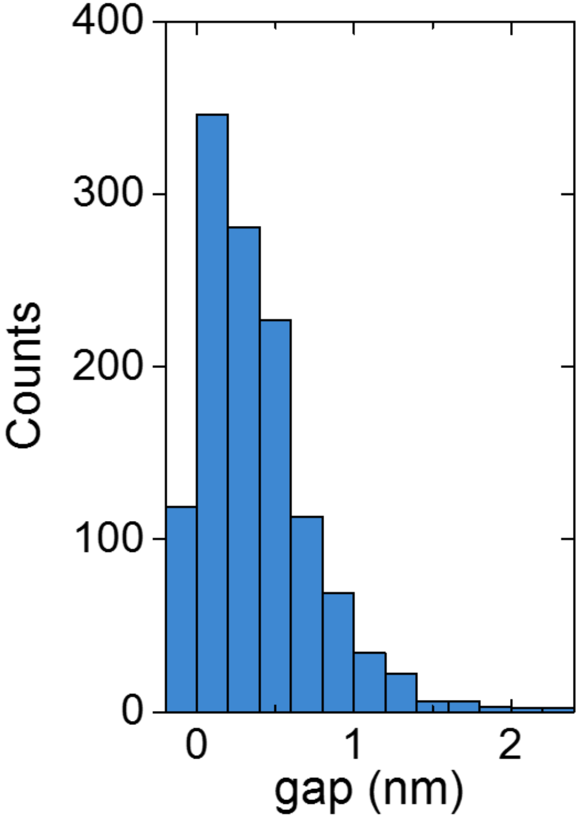
How? – Modeling surface roughness

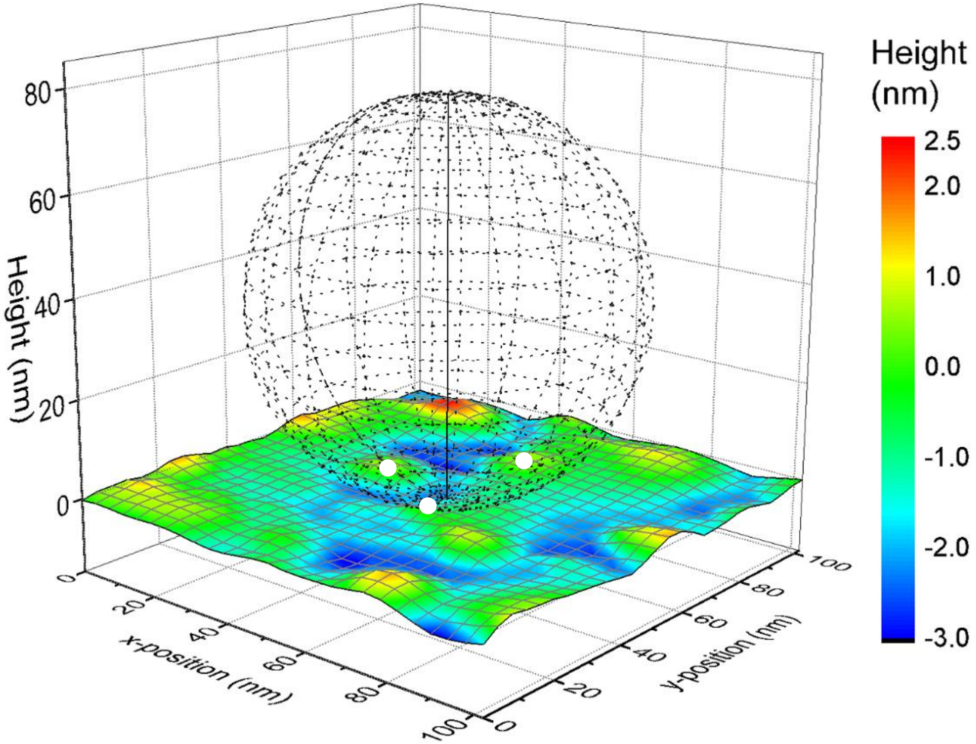


Finding local height seen by a nanoparticle

Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness



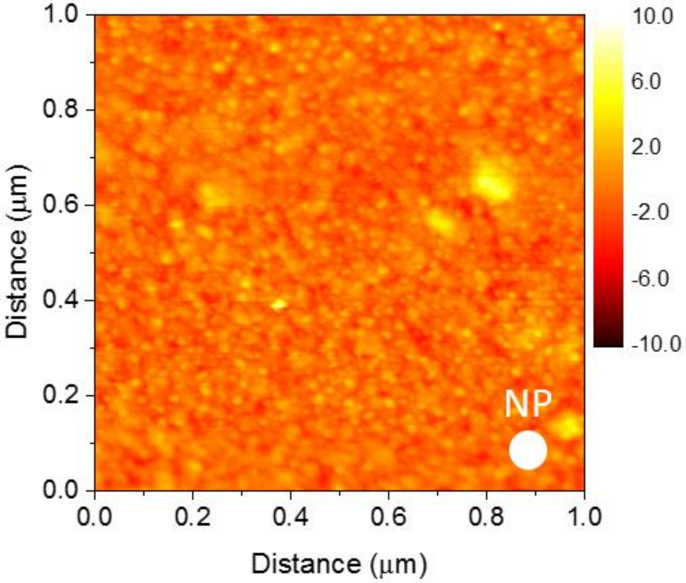


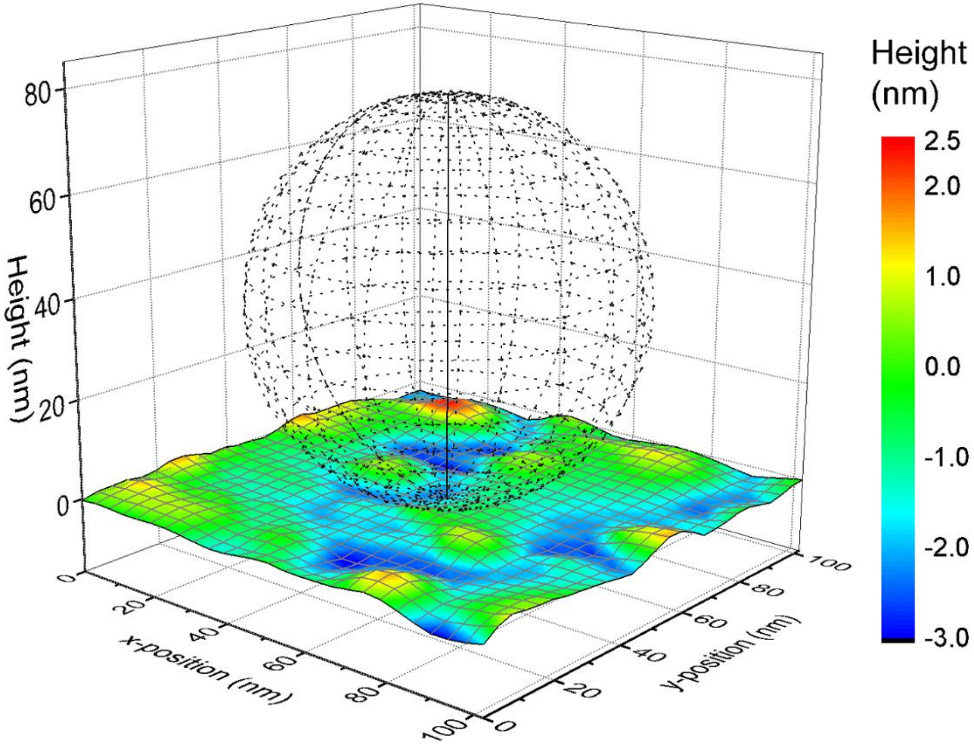
What to defined in simulation?

Roughness period, roughness radius of curvature and height

Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness





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How? – Modeling surface roughness

Roughness period (P) = 25 nm,
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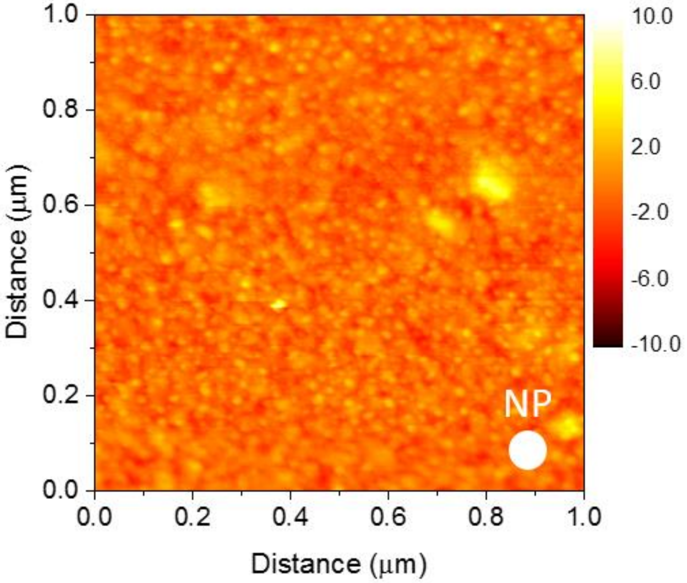
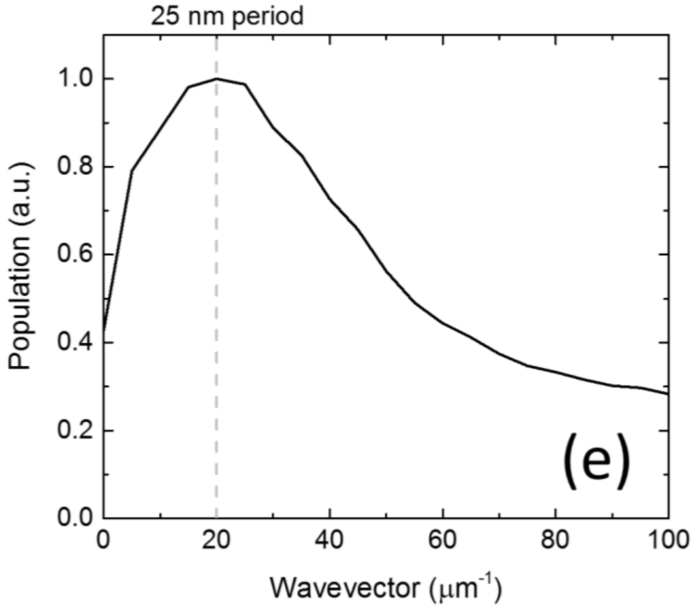


2D-FFT
Angular integral



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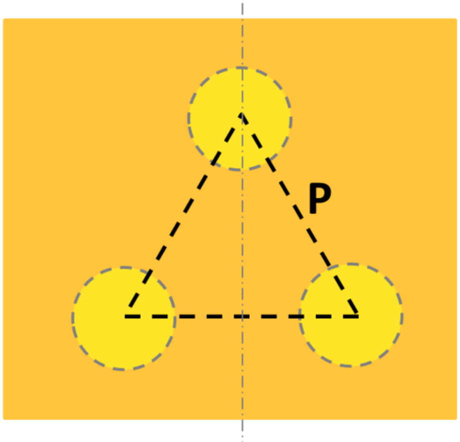

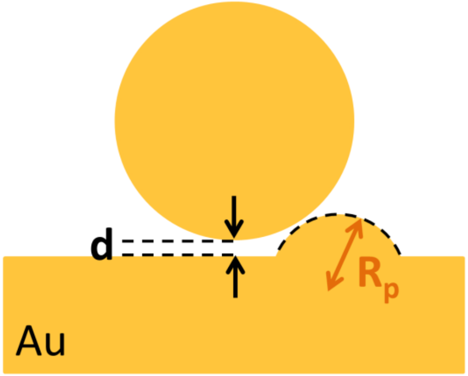

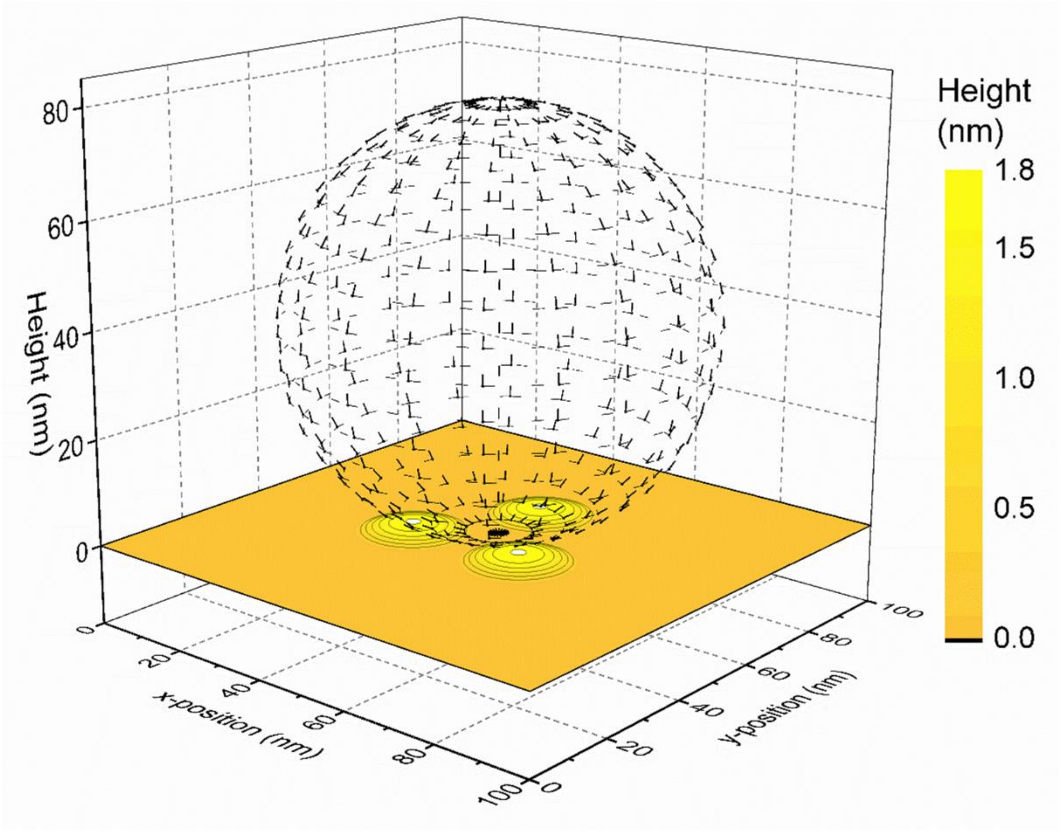

Effect of surface roughness on gold nanoparticle resonances

How? – Modeling surface roughness

Roughness period (P) = 25 nm,
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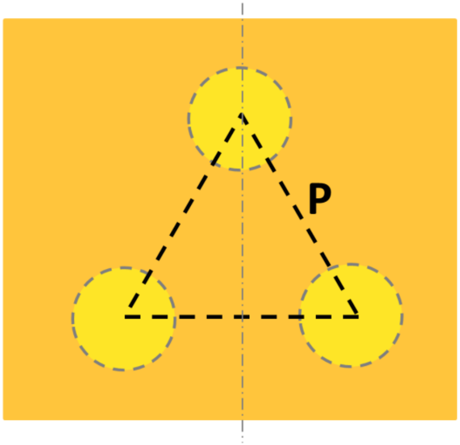
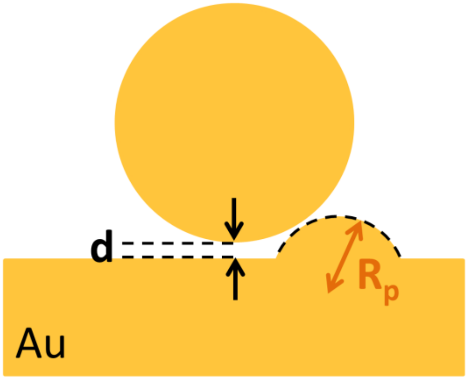
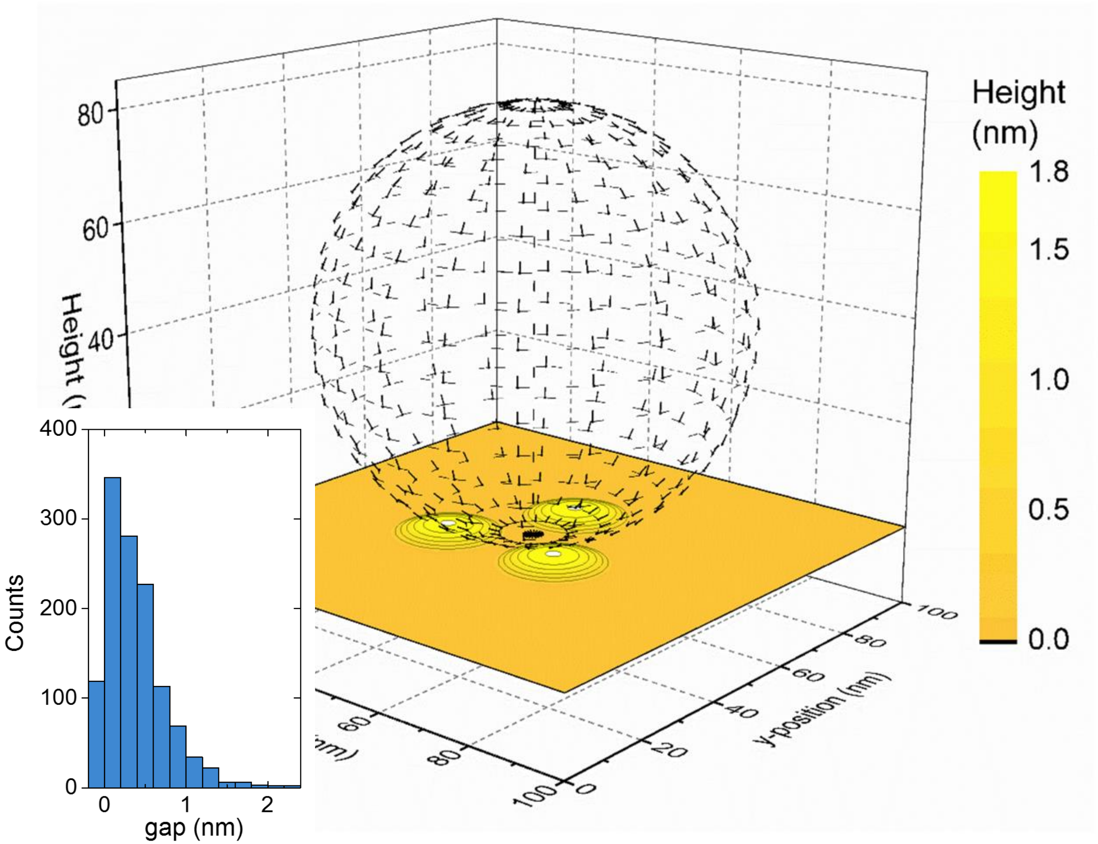
Roughness height is determined by the gap size (d)







Effect of surface roughness on gold nanoparticle resonances

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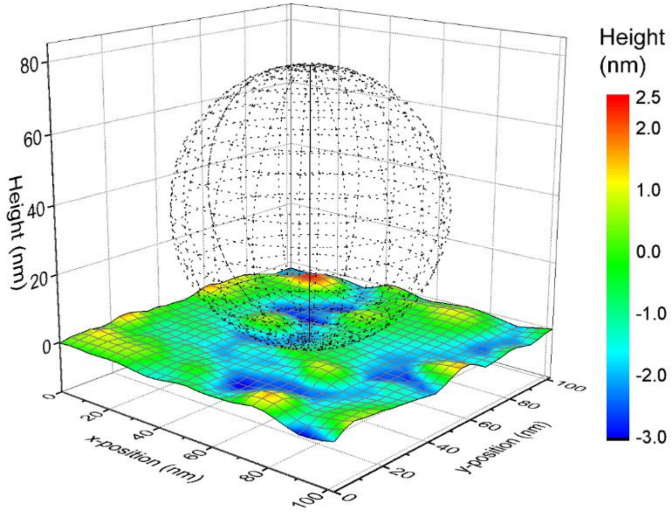
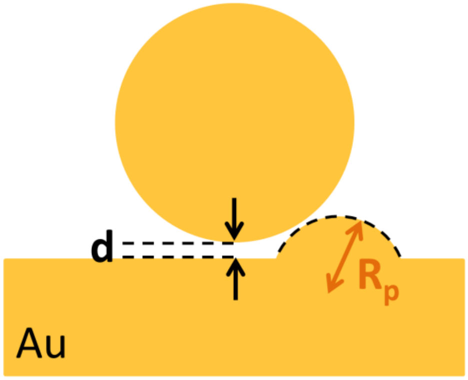
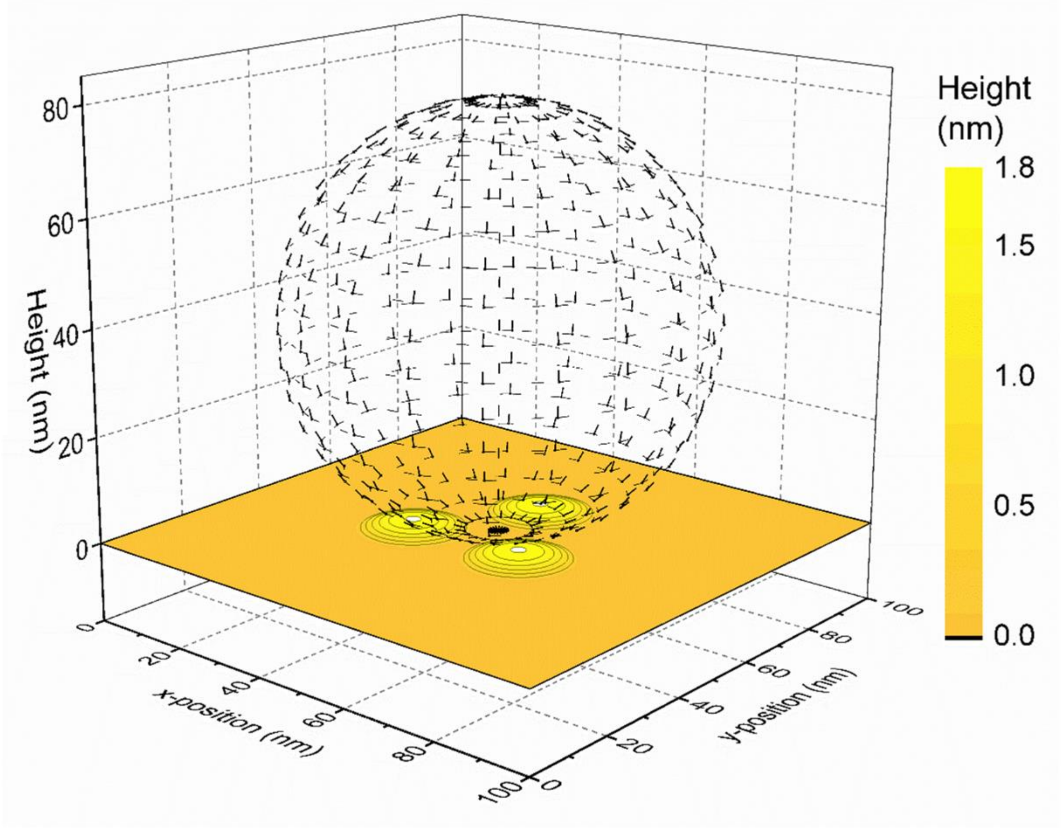
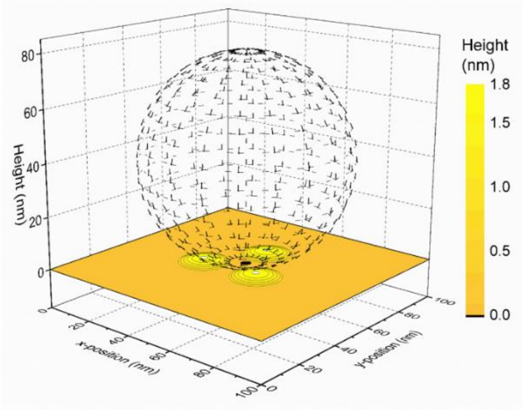


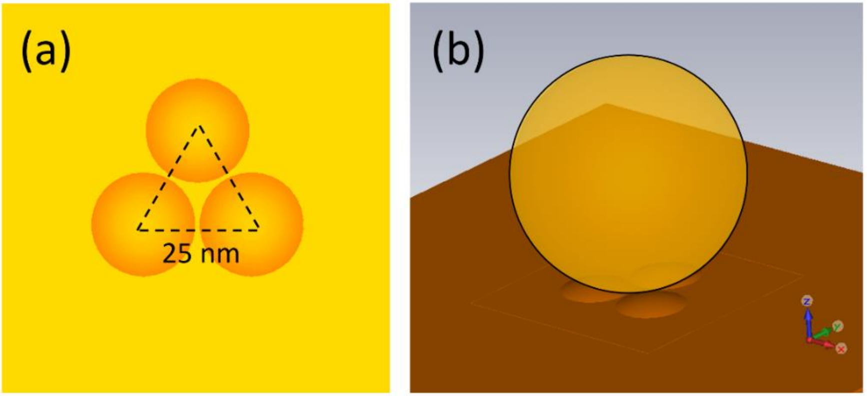


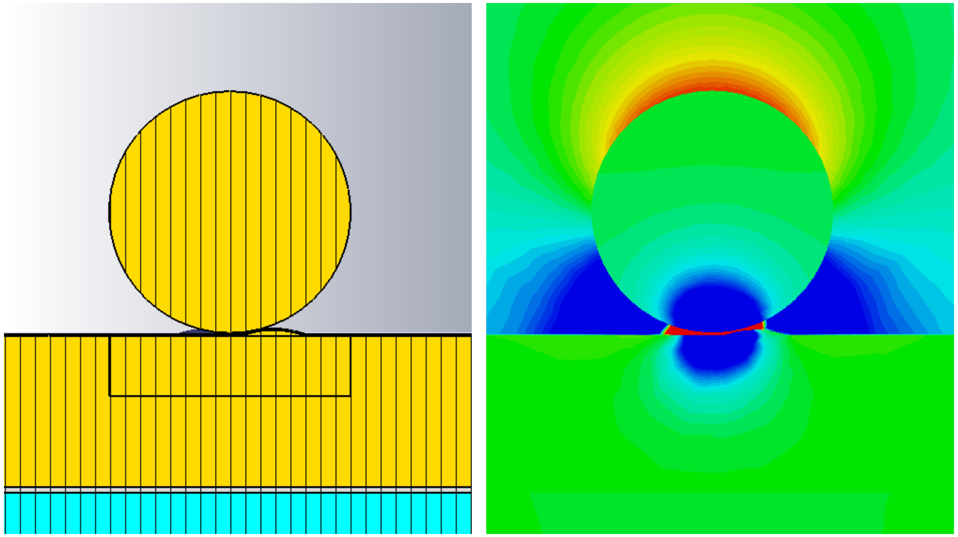


Effect of surface roughness on gold nanoparticle resonances

How? – Numerical simulation







$P_{rad} \propto |\mu_z|^2 \omega^4$

C. Lumdee, et al. ACS Nano 2012, 6(7), pp 6301−6307

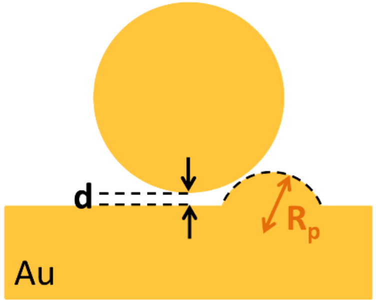
CST Microwave Studio® and Au dielectric function from literature

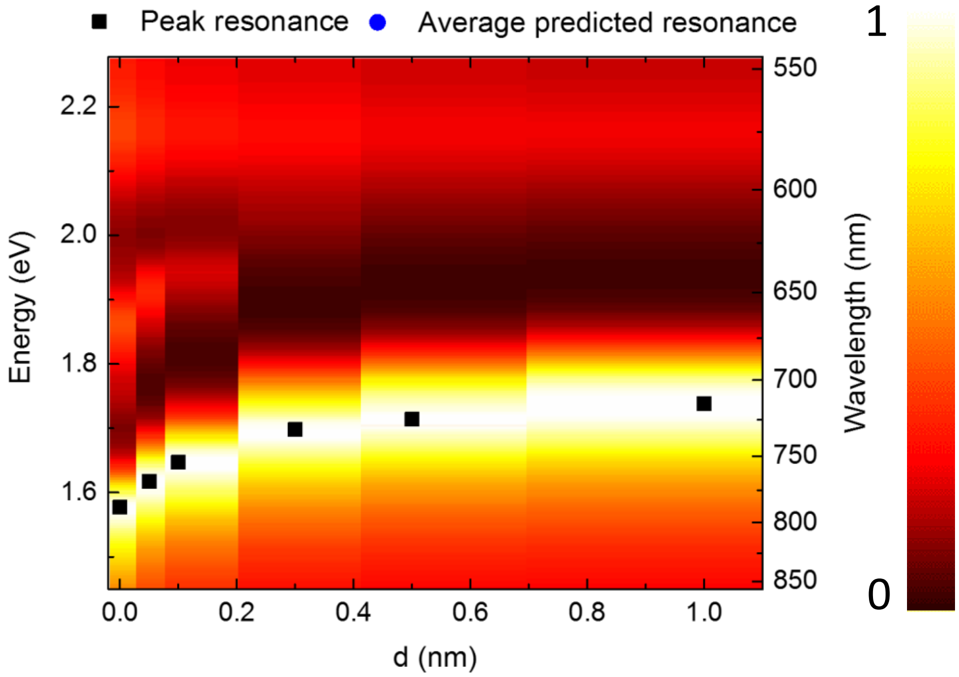
P. B. Johnson, and R. W. Christy, R. W., Phys. Rev. B 1972, 6(12), pp 4370-4379.

Effect of surface roughness on gold nanoparticle resonances

Results

Simulated gold nanoparticle scattering spectra



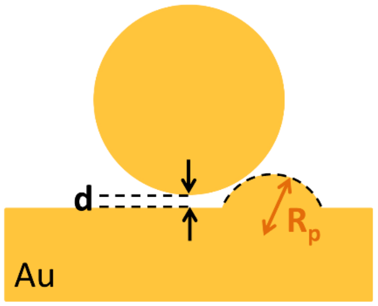


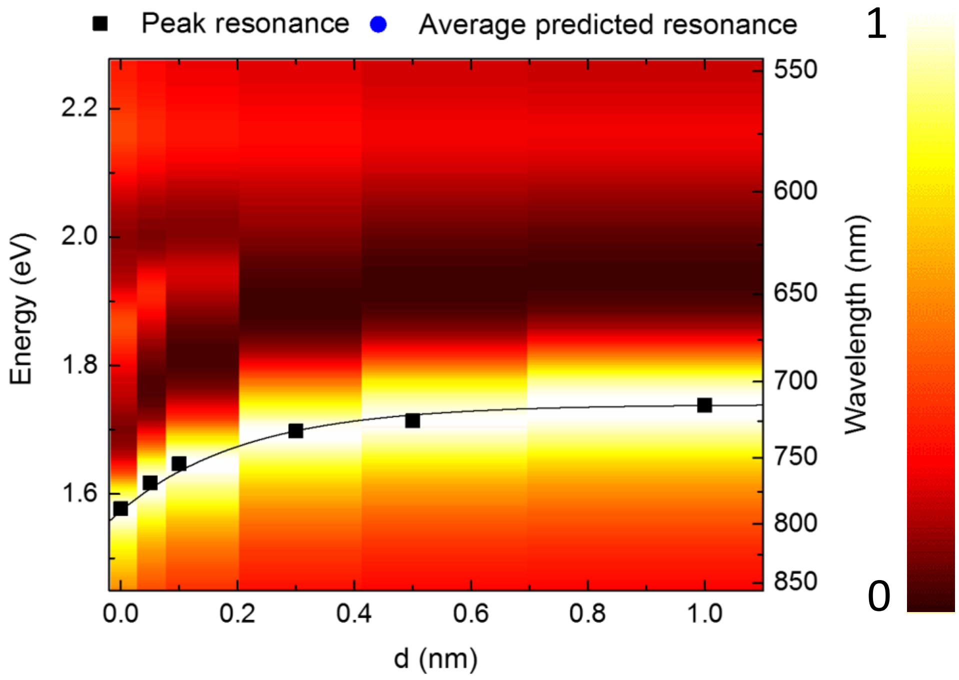
Variation due to surface roughness (gap variation)

Effect of surface roughness on gold nanoparticle resonances

Results

Simulated gold nanoparticle scattering spectra





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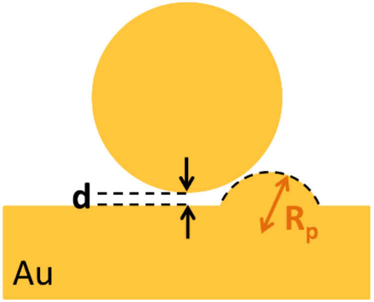
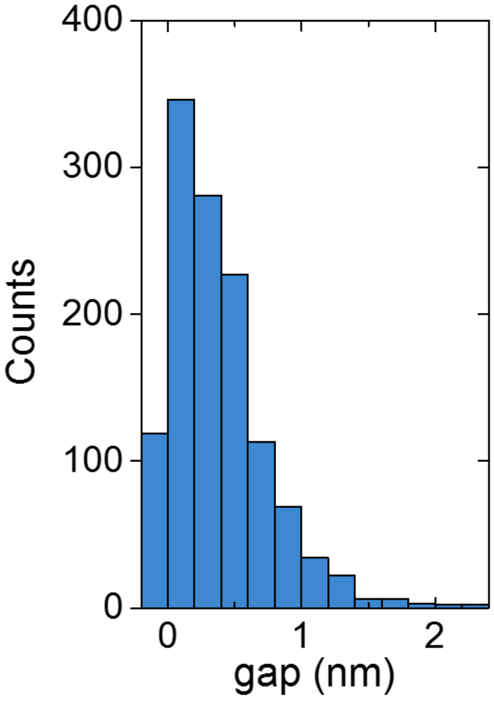
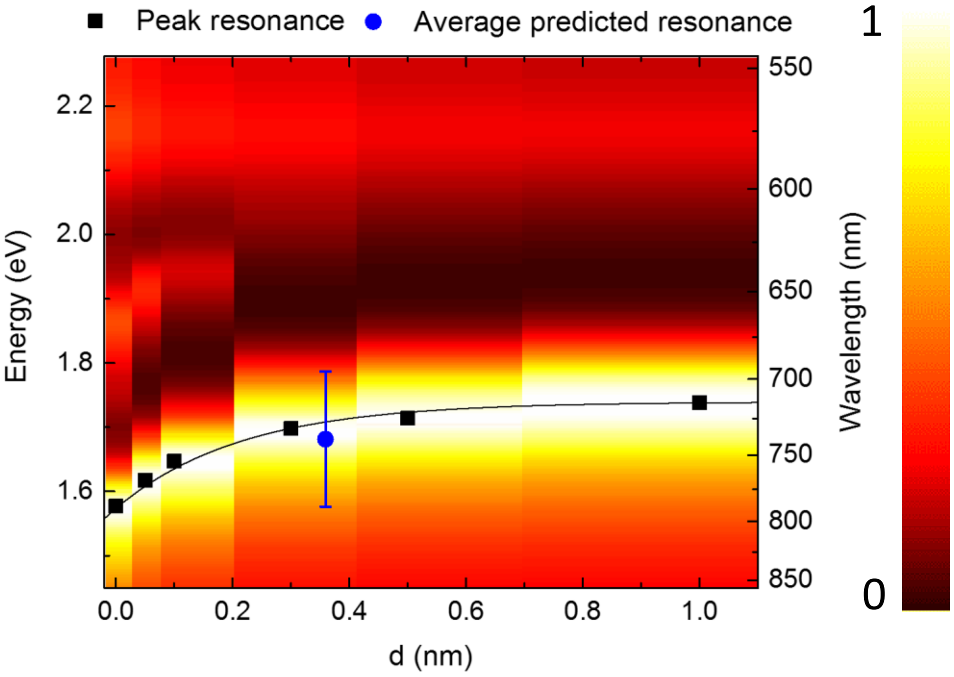




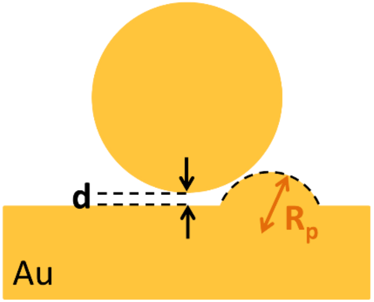


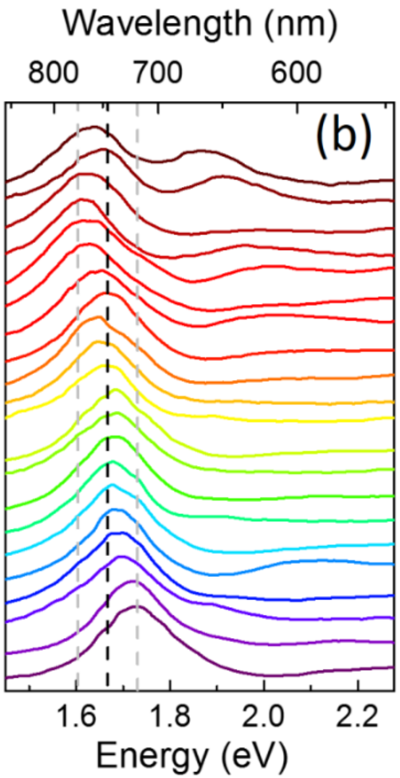
Variation due to surface roughness (gap variation)

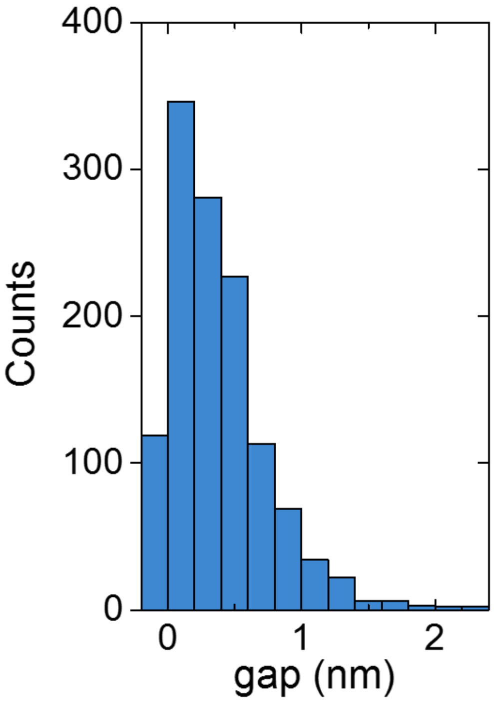
Effect of surface roughness on gold nanoparticle resonances

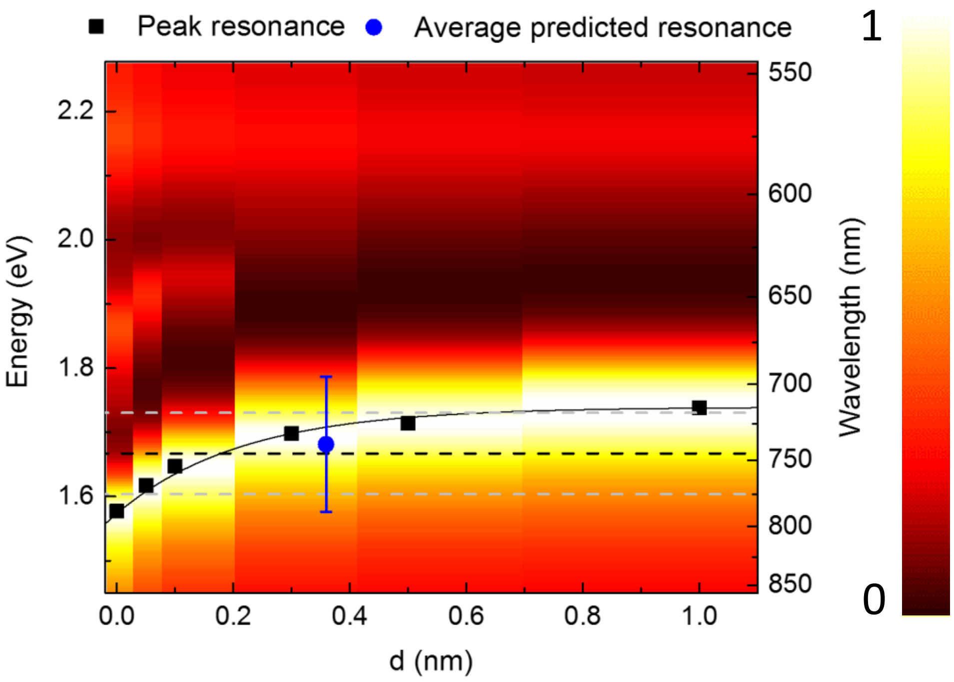
Results

Simulated and measured gold nanoparticle scattering spectra









Variation due to surface roughness (gap variation)

Effect of surface roughness on gold nanoparticle resonances

Summary

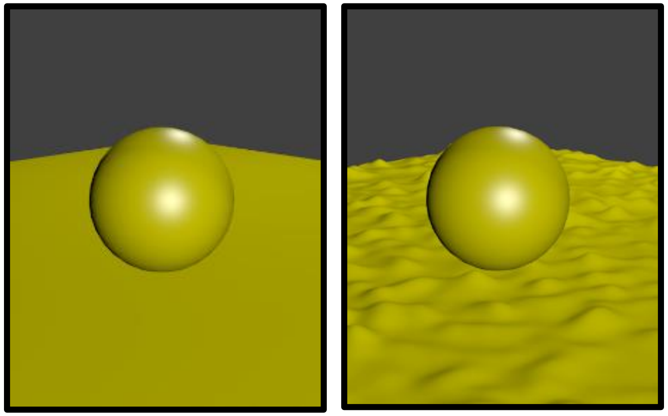
Surface roughness can contribute to spectral variation.

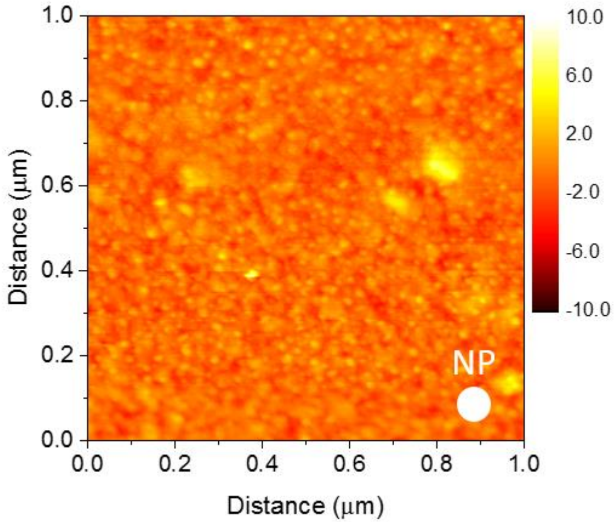
The effect is difficult to estimate due to infinite possible scenarios.

Use an AFM image to predict nanoparticle locations and model local surface.

Statistically calculate scattering spectra and spectral variation of gold nanoparticles on a thermally evaporated gold film.

The calculation seems to be in a good agreement with the measured data.

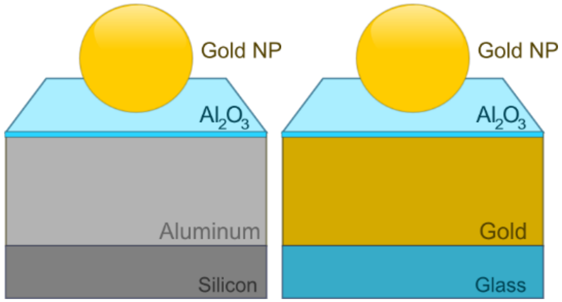


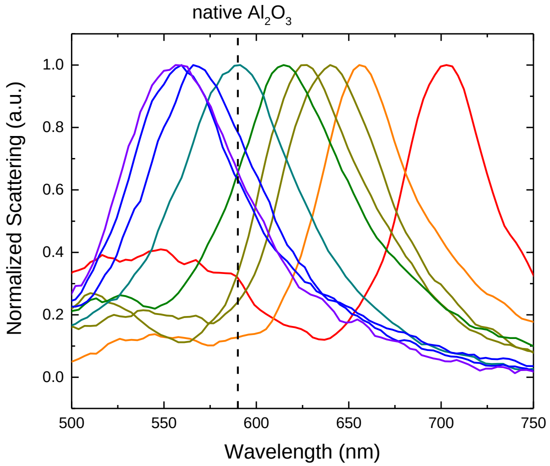


Talk summary

1) Introduction and current studies on substrate-coupled metal nanoparticles

2) All-inorganic substrate-couple resonances → broad tuning range and stable structure





3) Significant part of spectral variation comes from surface roughness.
This spectral variation can be predicted using an AFM image and numerical simulations.