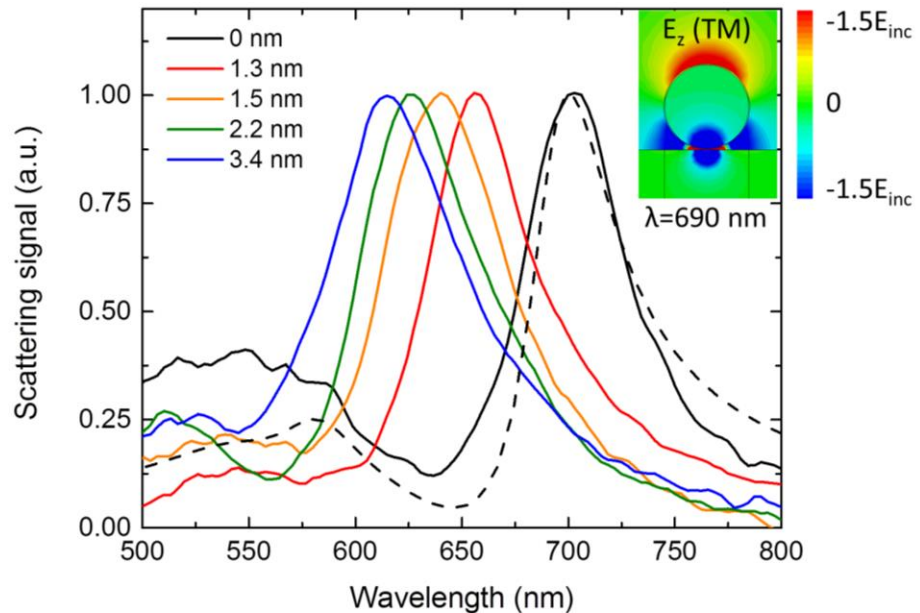
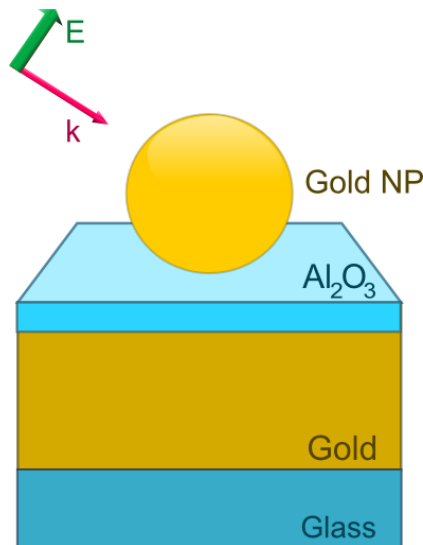


Wide-band Spectral Control of Au Nanoparticle Plasmon Resonances on a Thermally and Chemically Robust Sensing Platform

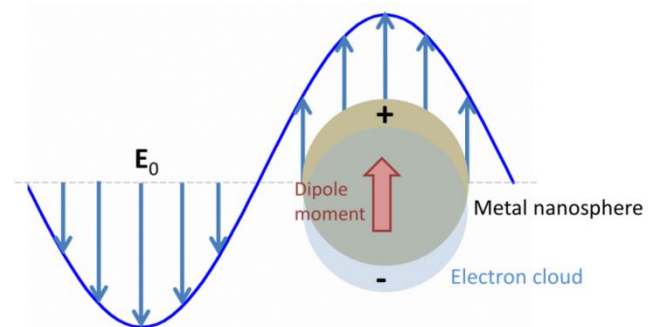
Chatdanai Lumdee, Binfeng Yun, and Pieter G. Kik

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



Introduction

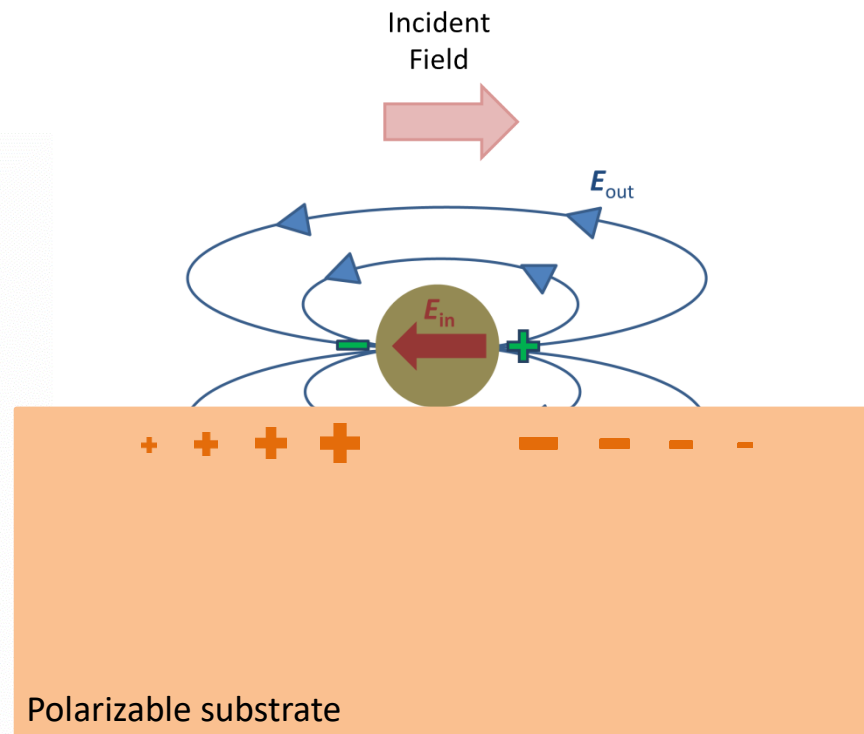
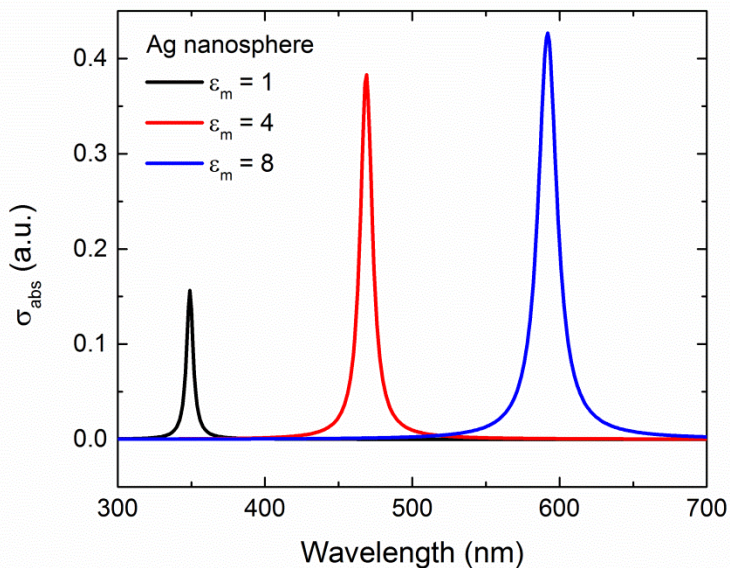
- Localized Surface Plasmon Resonance (LSPR)
 - Provide a strong field enhancement
 - Application:
 - SERS, non-linear enhancement, solar cell, etc.



Introduction

- Localized Surface Plasmon Resonance (LSPR)
 - Provide a strong field enhancement
 - Application:
 - SERS, non-linear enhancement, solar cell, etc.

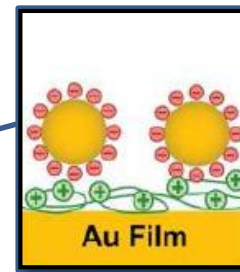
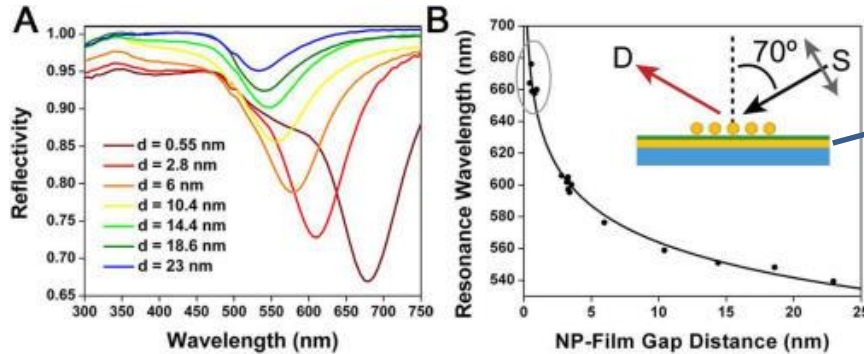
- Plasmon Resonance Tuning
 - Resonance wavelength is crucial



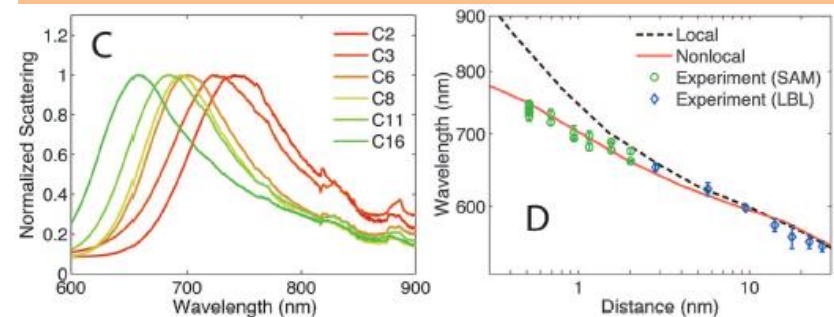
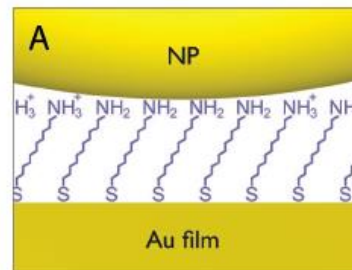
Substrate based Resonance Tuning

- Controlling particle-substrate interaction
 - Using Organic layers – e.g. polyelectrolyte (PE) layers, amine-terminated alkanethiol

J. J. Mock, et al. Nano Lett. 2012, 12(4), pp 1757–1764



C. Ciraci, et al. Science 2012, 337, pp 1072–1074

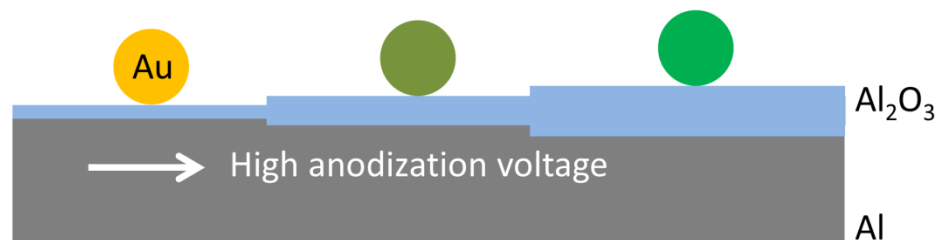
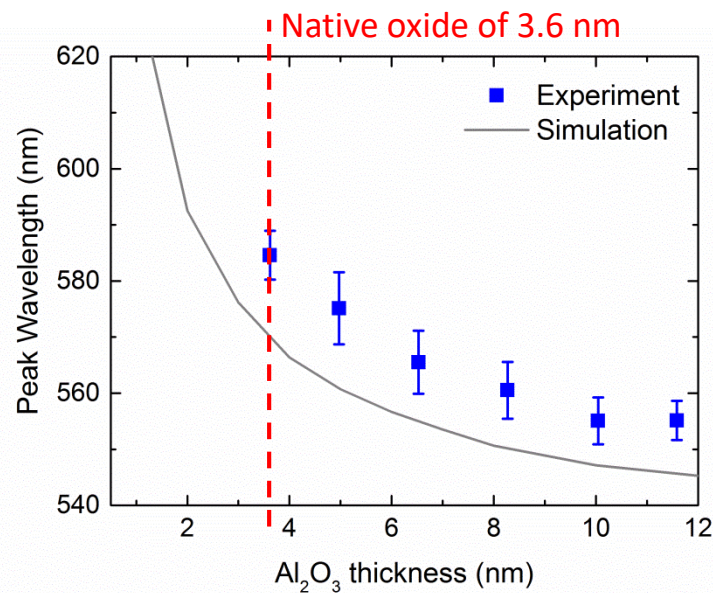
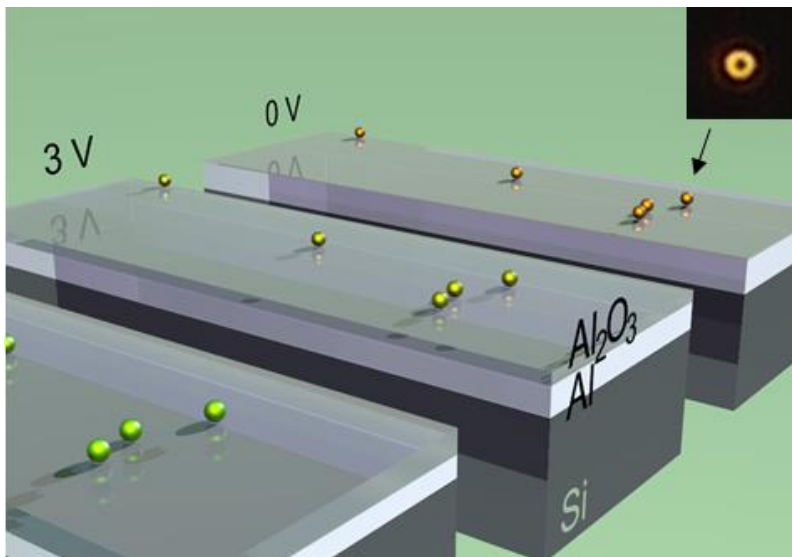


- Challenges: background signal, thermal/chemically stability

Substrate based Resonance Tuning

- Controlling particle-substrate interaction
 - Single particle resonance tuning using metal oxide film

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

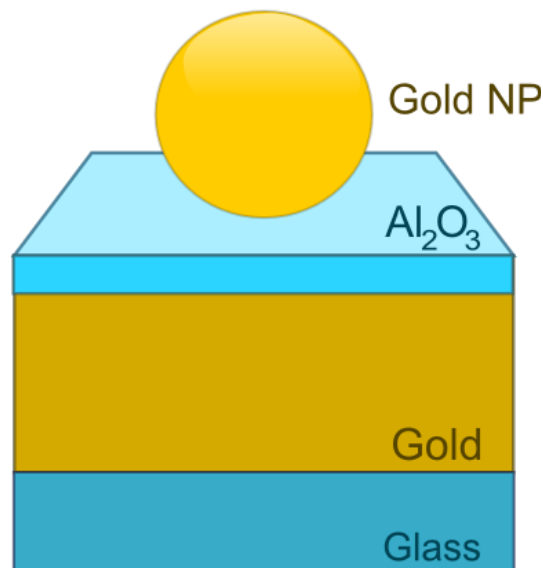


- Challenges: small resonance tuning range

Gold nanoparticle on Al_2O_3 coated gold film

- Challenges:
 - background signal, thermal/chemically stability
 - small resonance tuning range

- Proposed system:
 - Gold nanosphere and $\text{Al}_2\text{O}_3 \rightarrow$ stable, no background
 - Spacer layer $<$ native Al_2O_3



Numerical Simulation

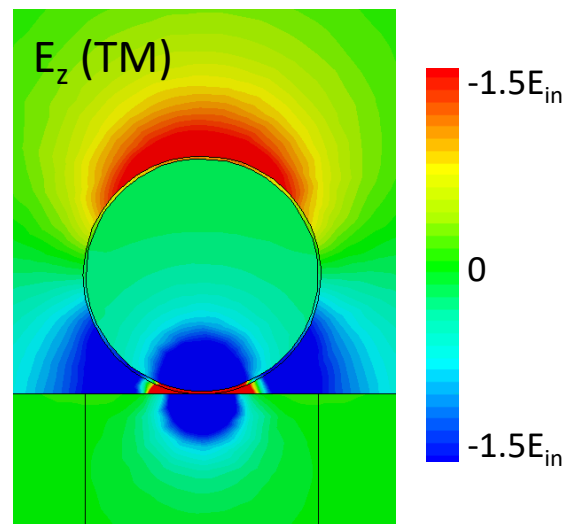
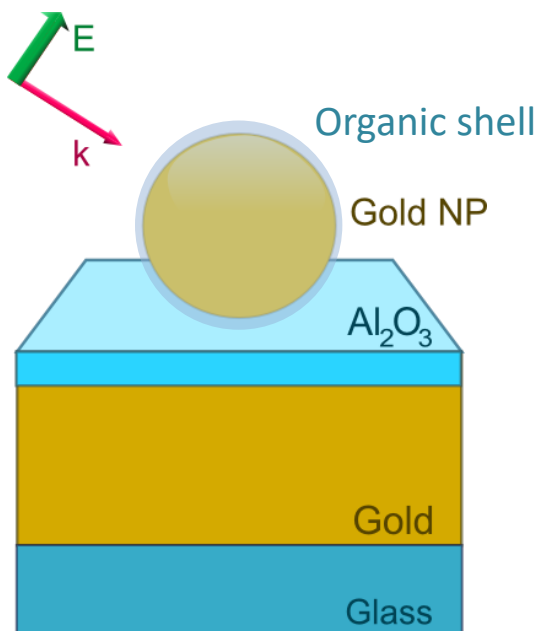
- Gold nanoparticle (60 nm diameter) on Al₂O₃ coated gold film
 - Frequency domain finite integration technique (CST microwave studio®)

- Dipole moment summation

$$\vec{\mu}_{NP} = \epsilon_0 \int_V \chi \vec{E}(\vec{r}) d\vec{r}$$

- Assume electric dipole radiation

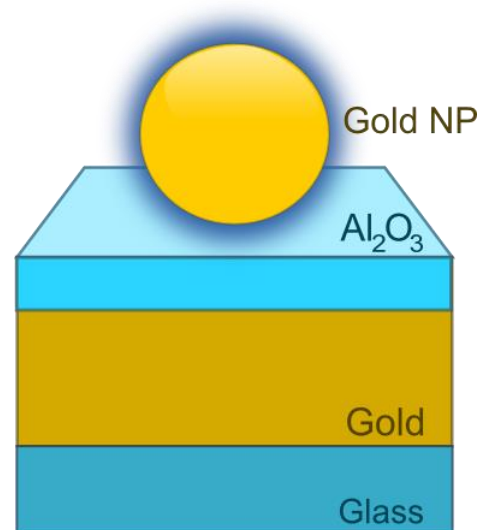
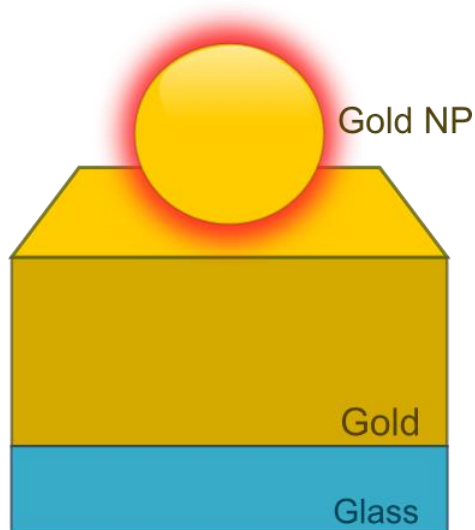
$$I_{scat} \propto |\vec{\mu}_{NP}|^2 \omega^4$$



$\lambda = 690 \text{ nm}$

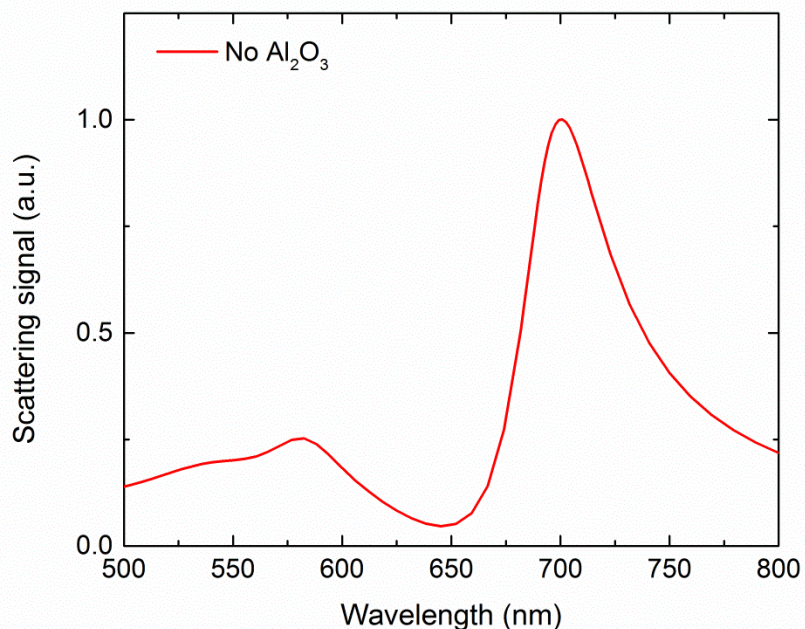
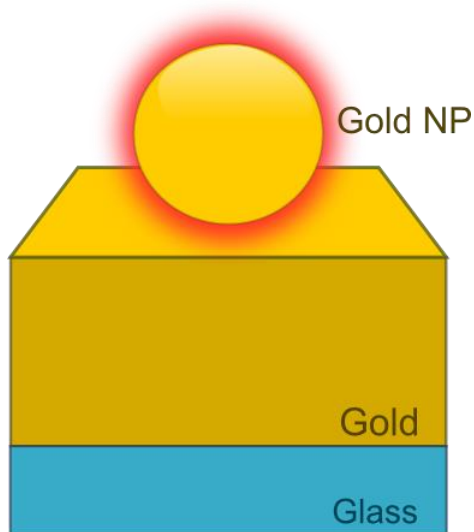
Numerical Simulation

- Gold nanoparticle (60 nm diameter) on Al_2O_3 coated gold film
 - AuNP on gold films without and 4 nm Al_2O_3 coating
 - Multi-resonance modes
 - Tuning range ~ 100 nm



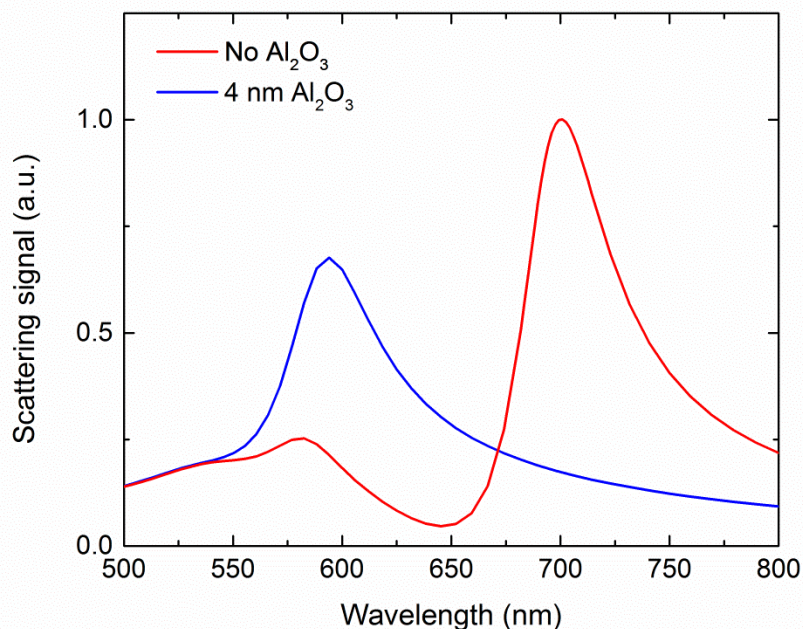
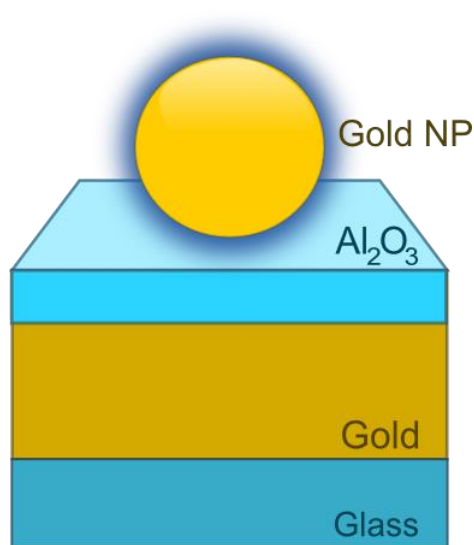
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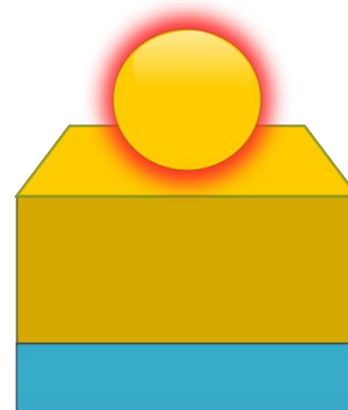
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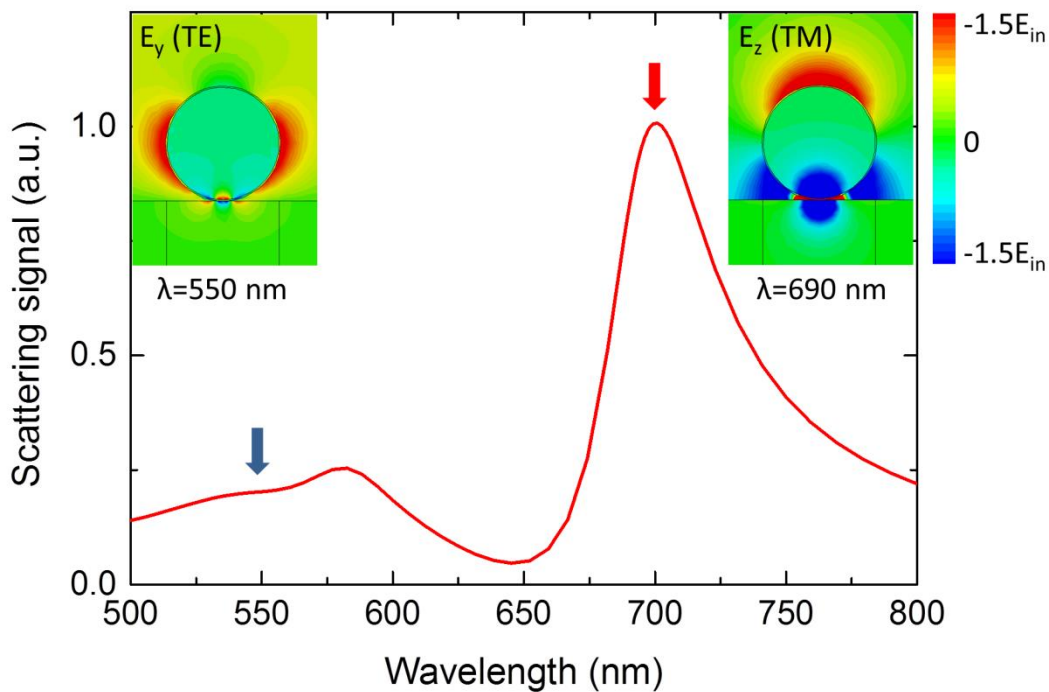
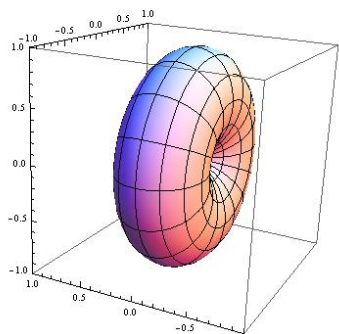
Numerical Simulation

- Resonance modes

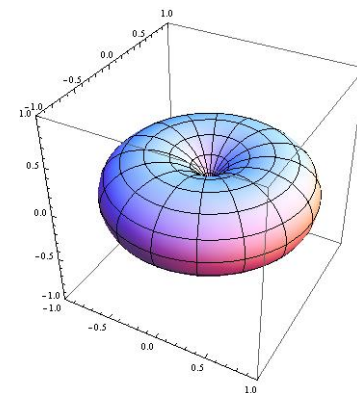
- Lateral mode – weak coupling
- Vertical mode – stronger coupling
 → redshift, strong enhancement



Lateral (x and y) dipole oscillation



Vertical (z) dipole oscillation

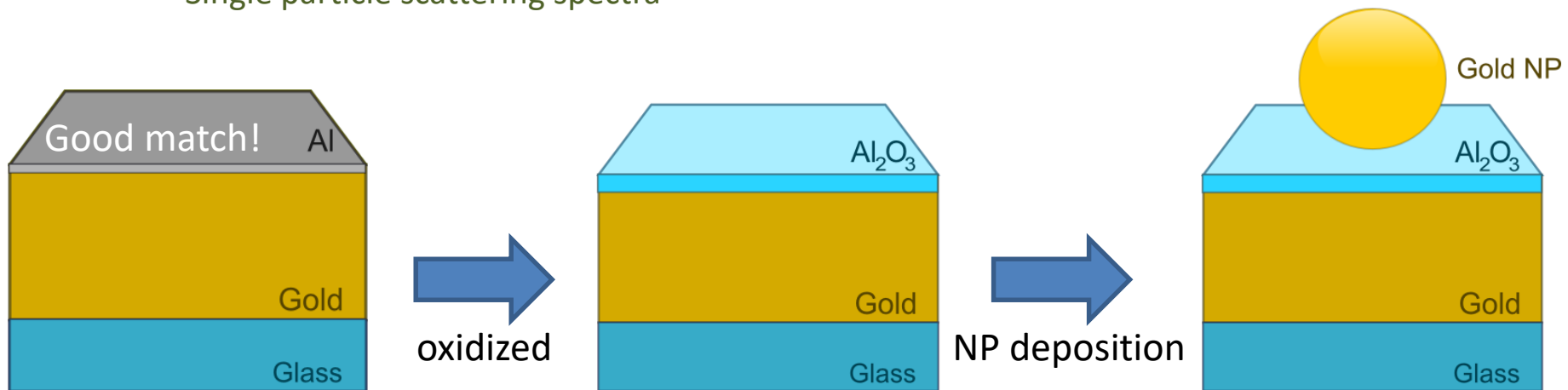


Experimental Process

- **Simulation**
 - Resonance tuning range ~ 100 nm, two resonance modes

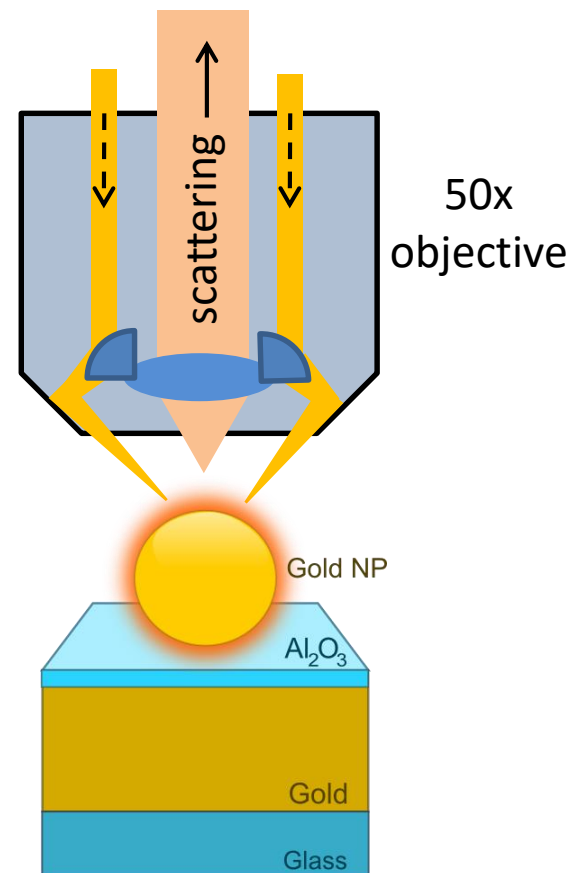
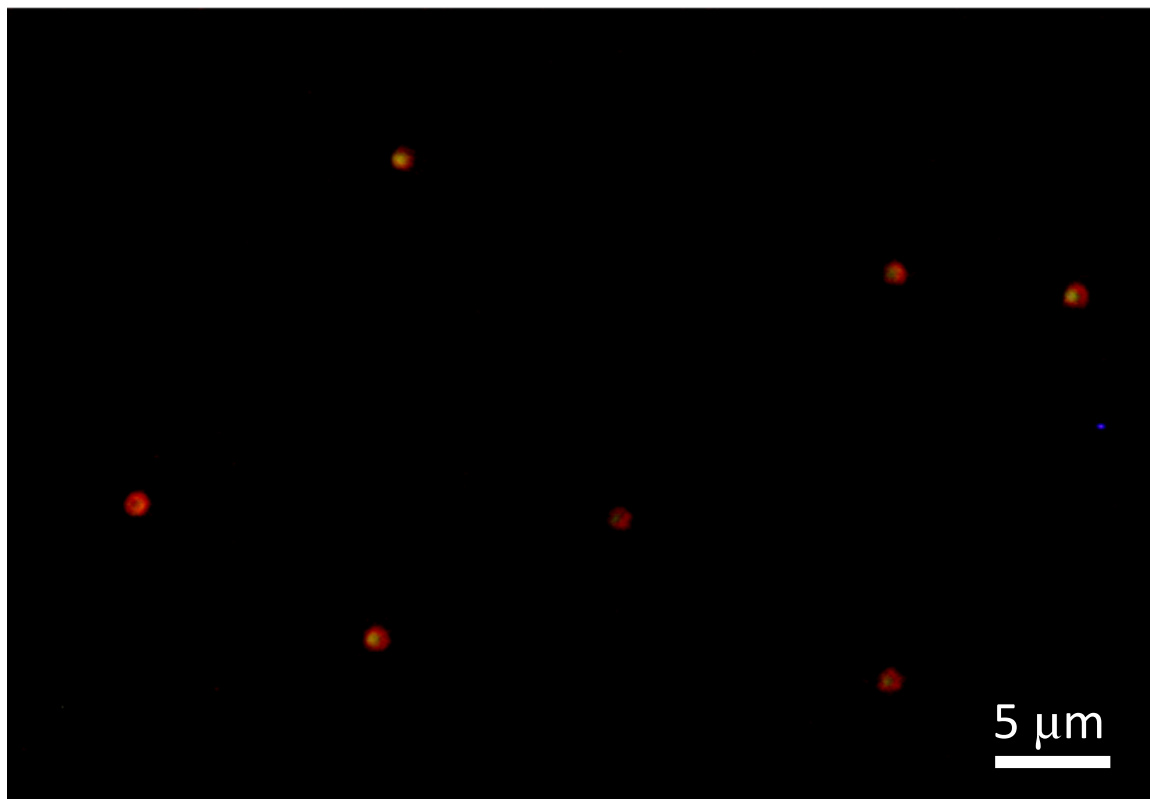
- **Sample**
 - A thin Al layer on top of a Au film (base pressure $< 10^{-5}$ mbar)
 - The Al film gets oxidized entirely \rightarrow Al_2O_3 coating layer
 - Au nanoparticles deposition

- **Measurements**
 - Ellipsometry \rightarrow Al_2O_3 thicknesses,
 - Darkfield microscopy images,
 - Single particle scattering spectra



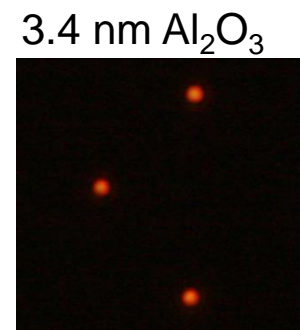
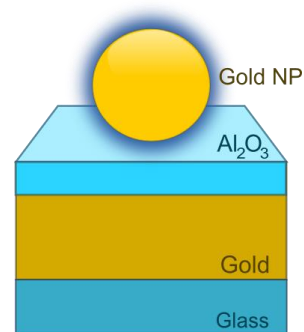
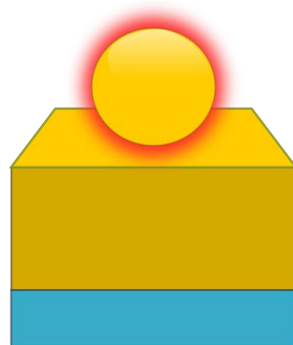
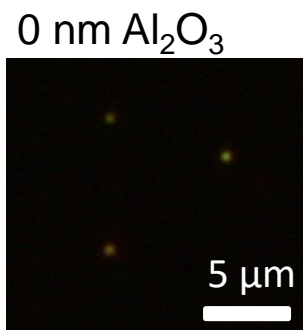
Dark-field Microscopy Images

- Dark-field microscopy
 - Canon EOS 450D digital camera
 - Well separated scatterers



Dark-field Microscopy Images

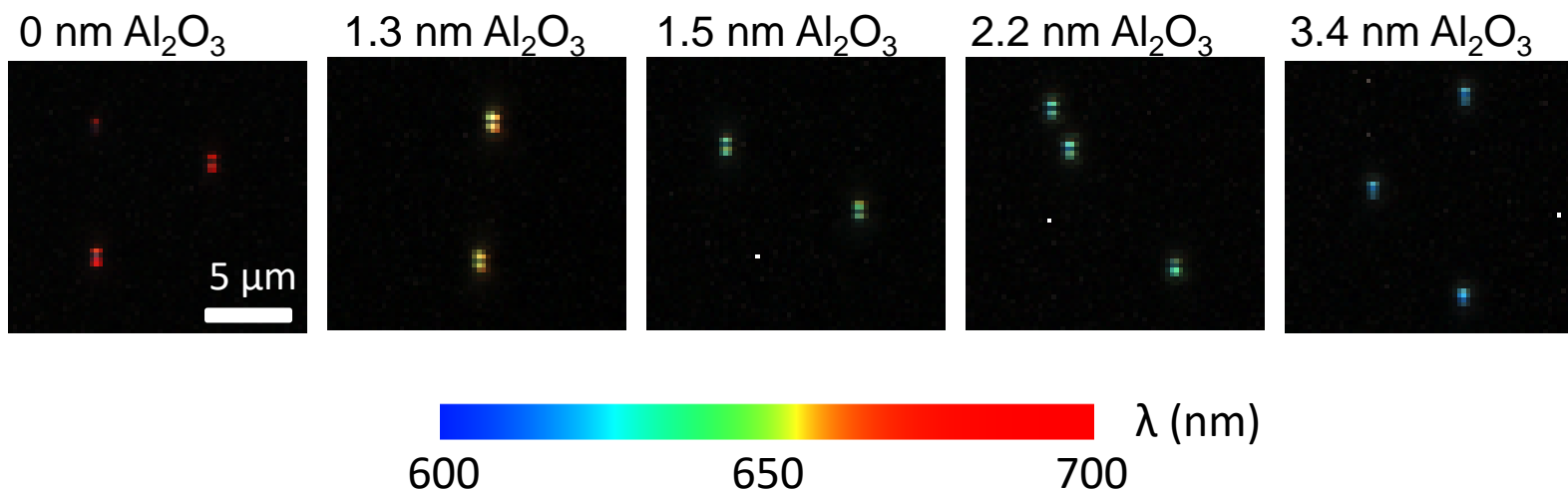
- Dark-field microscopy
 - Canon EOS 450D digital camera
 - **Green** central and **Red** ring scattering



Not what we expected!!!

Dark-field Microscopy Images

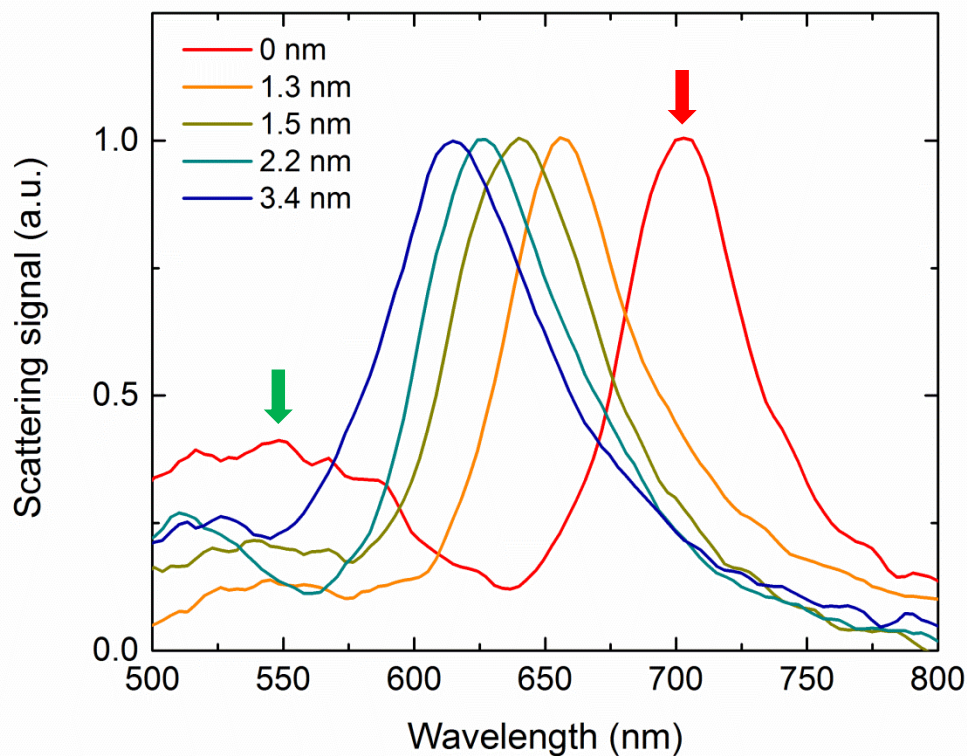
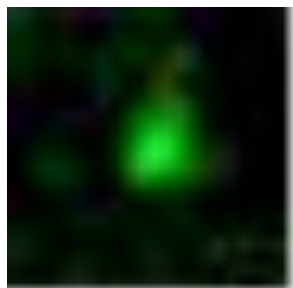
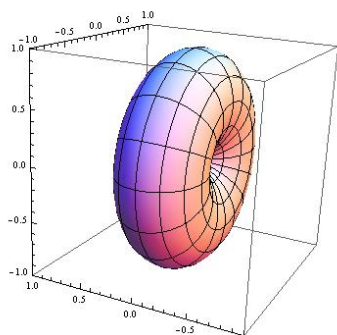
- Dark-field microscopy
 - Canon EOS 450D digital camera
 - **Green** central and **Red** ring scattering
 - HSi-440C Hyperspectral Imaging System (Gooch & Housego)



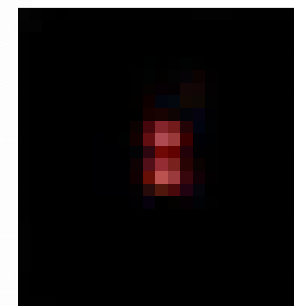
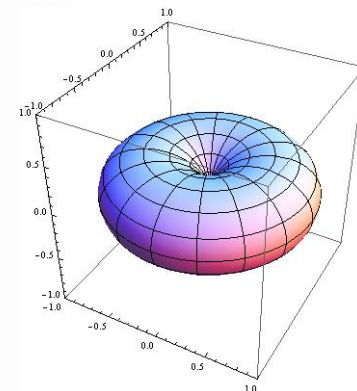
Single Particle Scattering Spectra

- Measured single particle scattering spectra
 - Resonance tuning range ~ 90 nm
 - Two resonance modes (at least)

Lateral (x and y) dipole oscillation

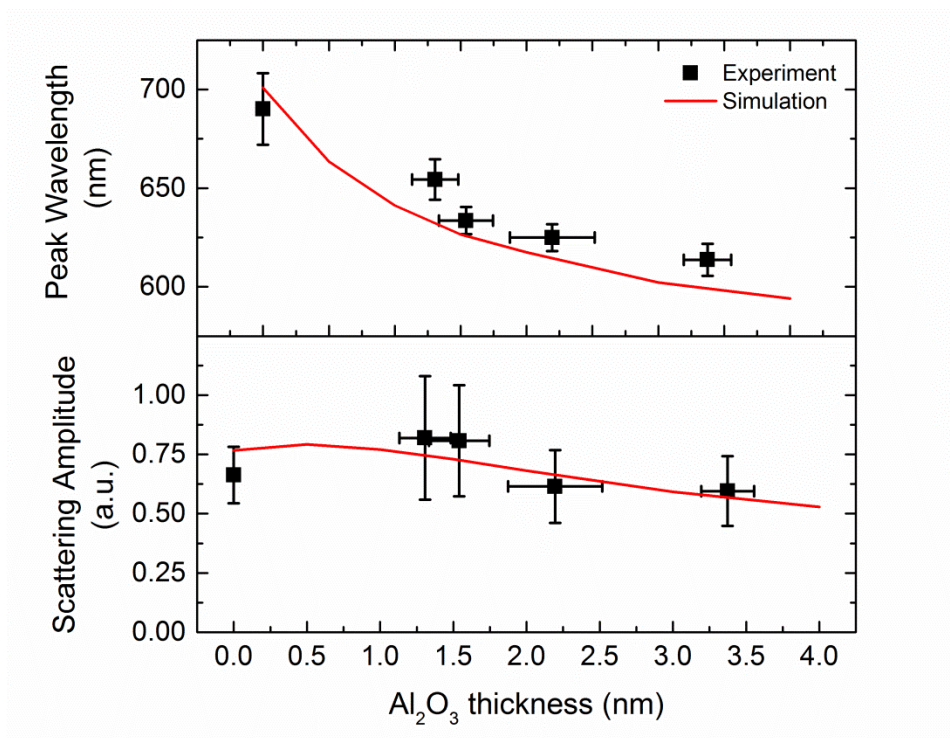


Vertical (z) dipole oscillation



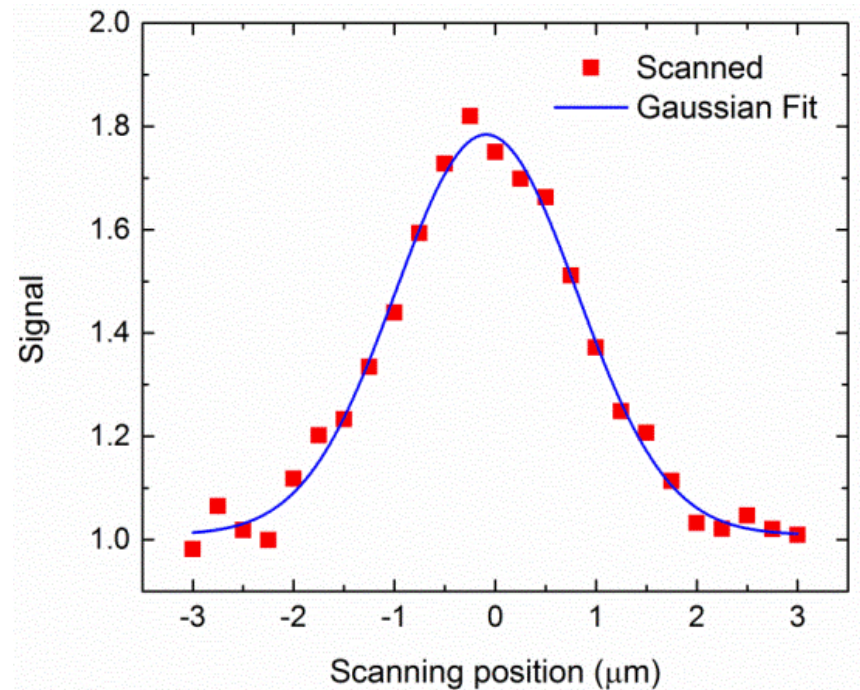
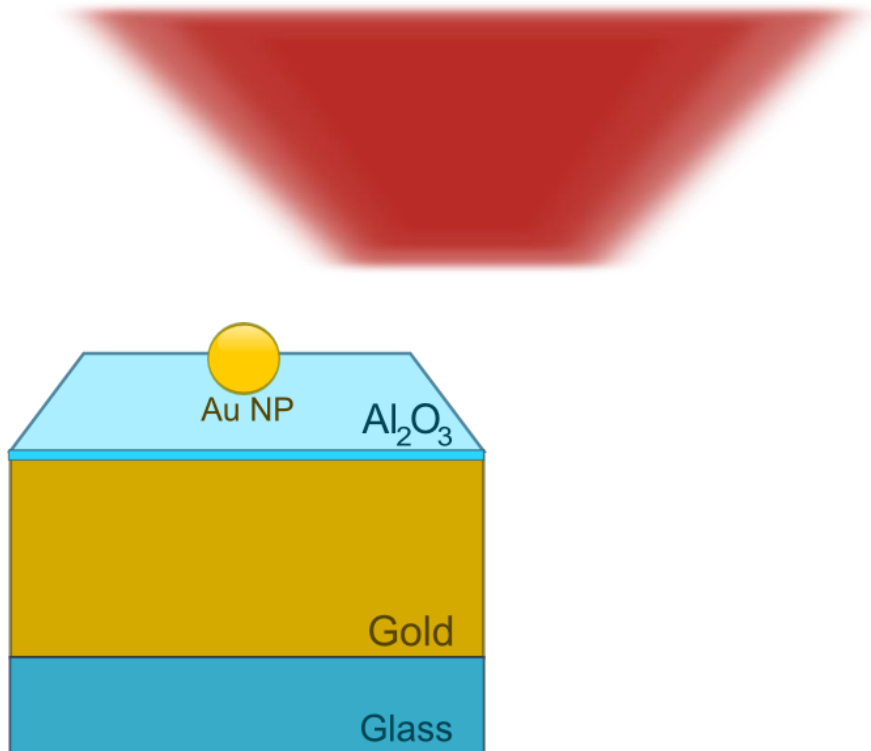
Single Particle Scattering Spectra

- Simulation and measurement (~100 nanoparticles)
 - Scattering peak wavelength – ~100 nm resonance shifting
 - Scattering peak strength – quite stable, slowly gets weaker after $\text{Al}_2\text{O}_3 > 2 \text{ nm}$



Laser Heating and Stability

- Particle probing and alignment
 - Align the NP to the center of the beam by near-field probing
 - Laser irradiation: TM polarization, 15° angle of incidence

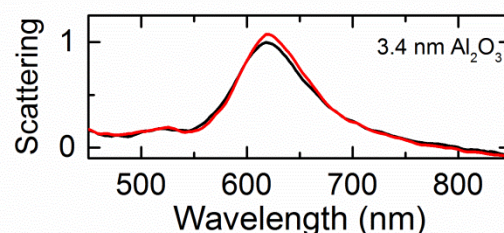
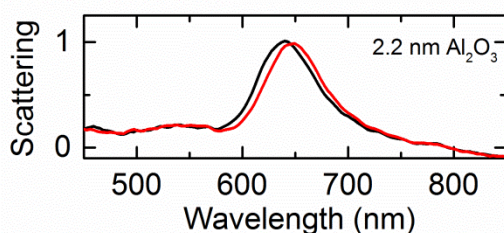
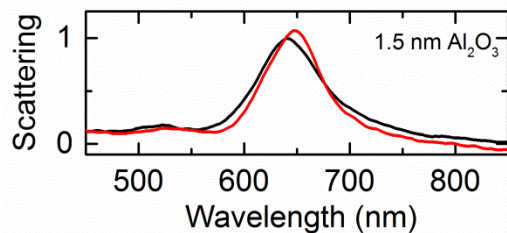
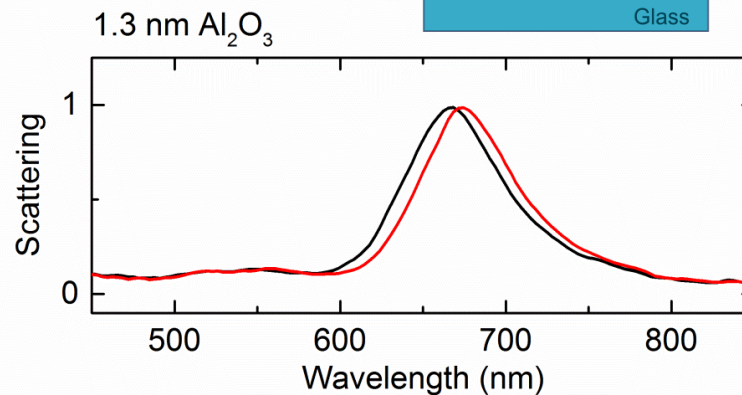
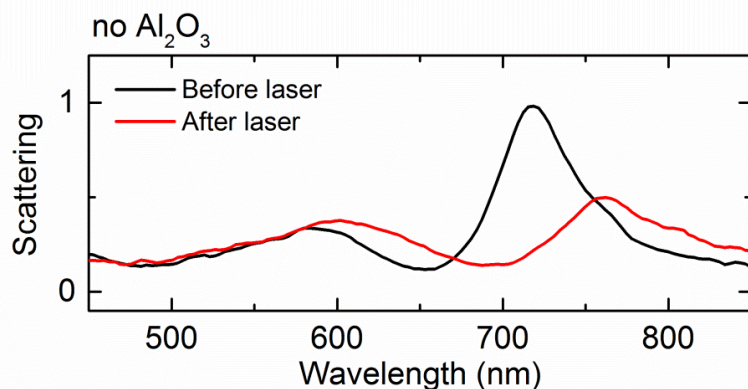
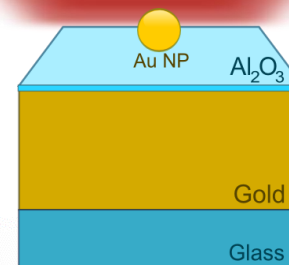


Laser Heating and Stability

■ Observation

- No $\text{Al}_2\text{O}_3 \rightarrow$ spectrum drifts upon irradiation
- with $\text{Al}_2\text{O}_3 \rightarrow$ survive the irradiation

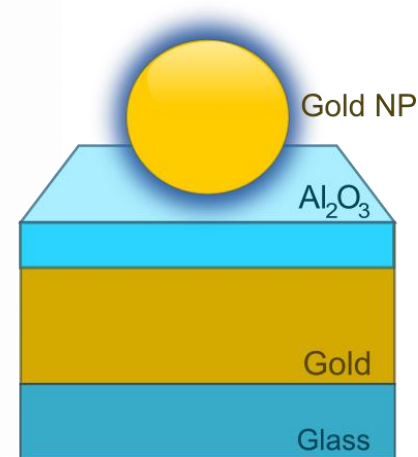
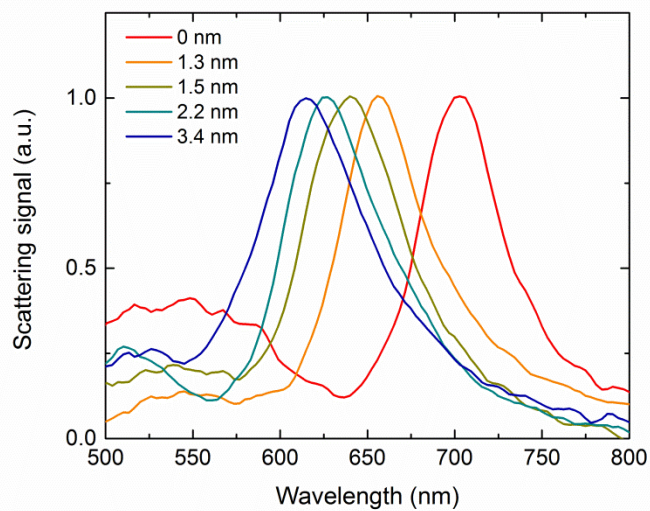
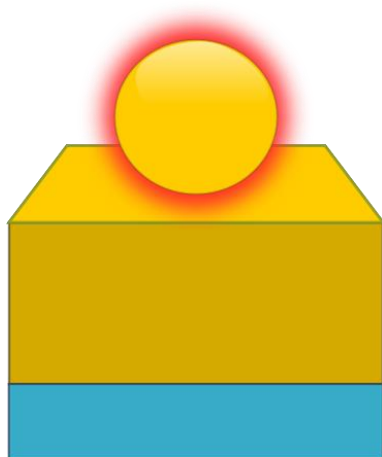
peak irradiance $\sim 100 \text{ W/mm}^2$



Summary

- Al₂O₃ coated gold film

→ Tuning range ~100 nm **(3 times improvement)**



Summary

- Al₂O₃ coated gold film

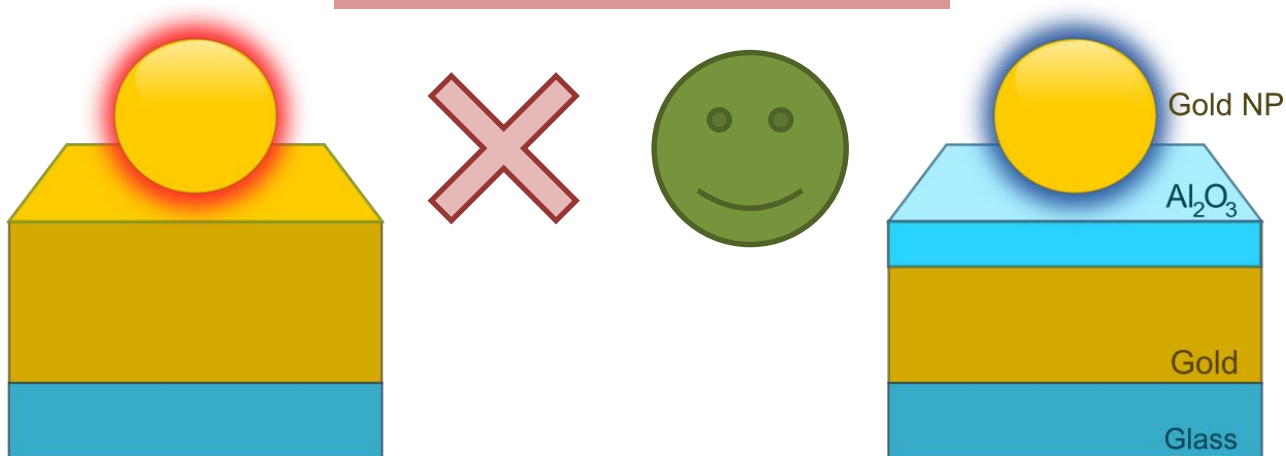
Challenges solved!

Just accepted – Journal of Physical Chemistry C

[DOI: 10.1021/jp4056522](https://doi.org/10.1021/jp4056522)

- Tuning range ~100 nm **(3 times improvement)**
- Irradiation tolerance > polymer based substrate tuning
- No organic background --- good for sensing application

Laser irradiation



Thank you!

■ Q & A

