

Determination of the Optical Properties of Individual Gold Nanorods through Numerical Modeling and Experiment

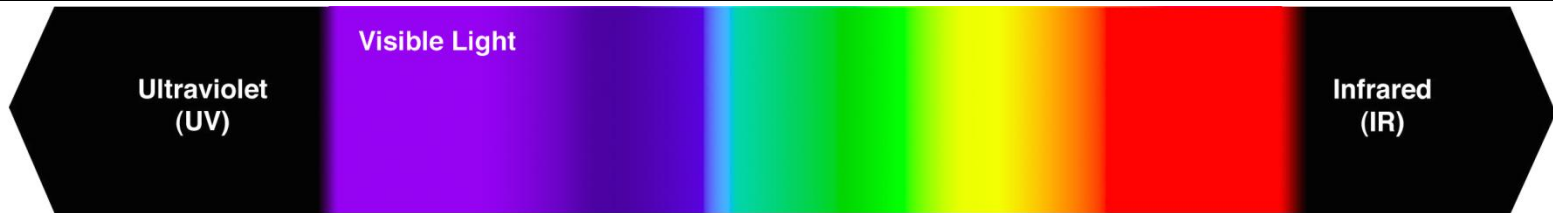
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The Lycurgus Cup. Late Roman Empire 4th Century AD.



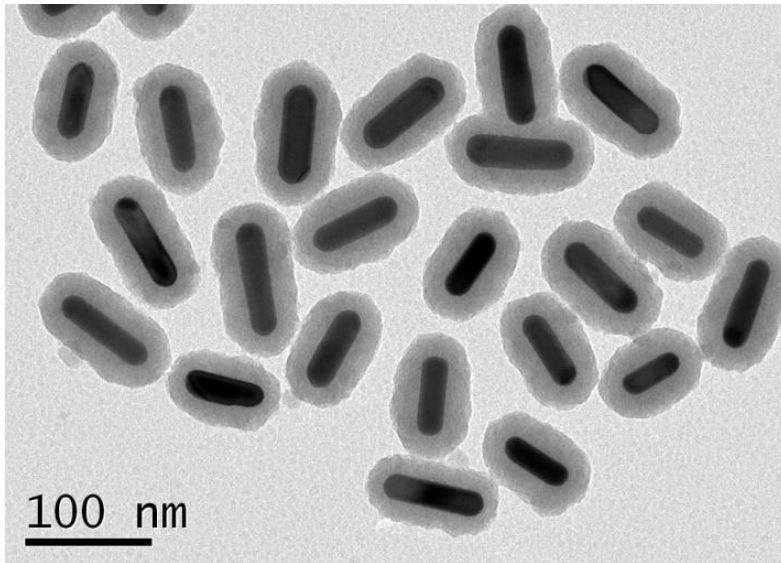
400 nanometers

500 nanometers

600 nanometers

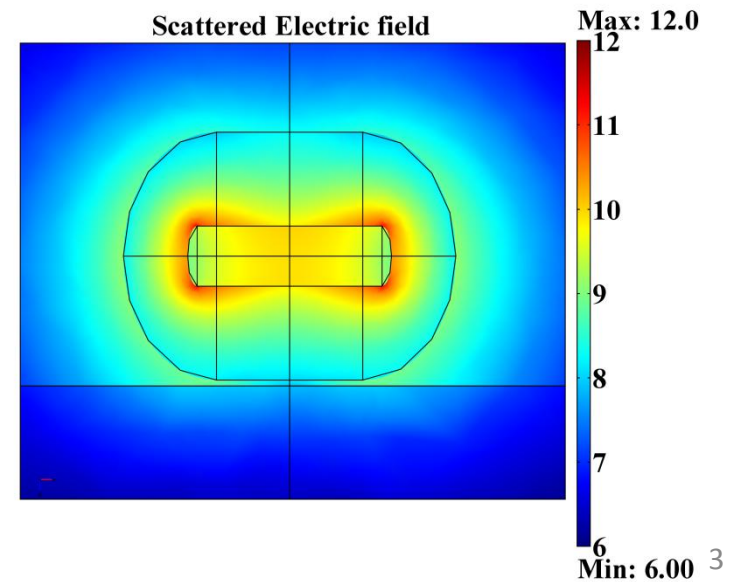
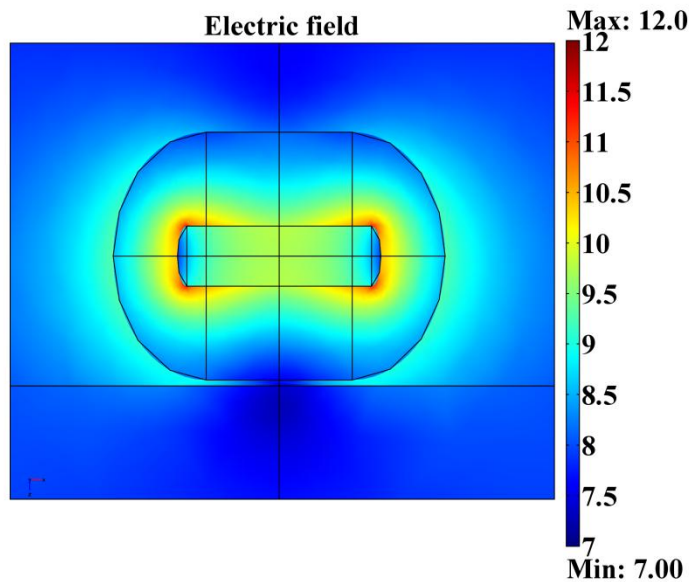
700 nanometers

Optimization of Optical Properties of GNPs through FE Modeling



Optical properties to optimize:

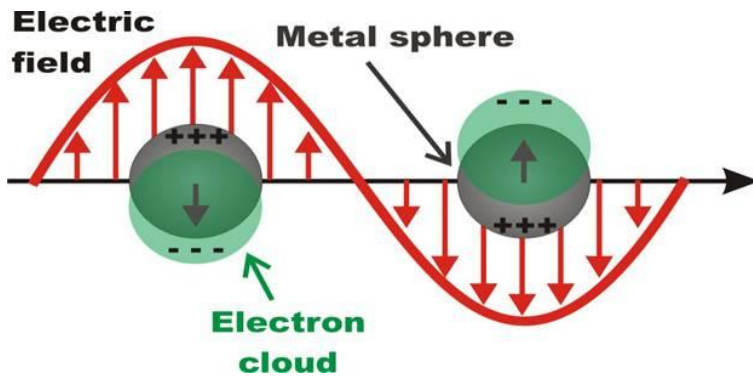
- Absorption
- Scattering
- E field Enhancement
- Etc.



Solving Wave Equation for Arbitrary Shape Objects

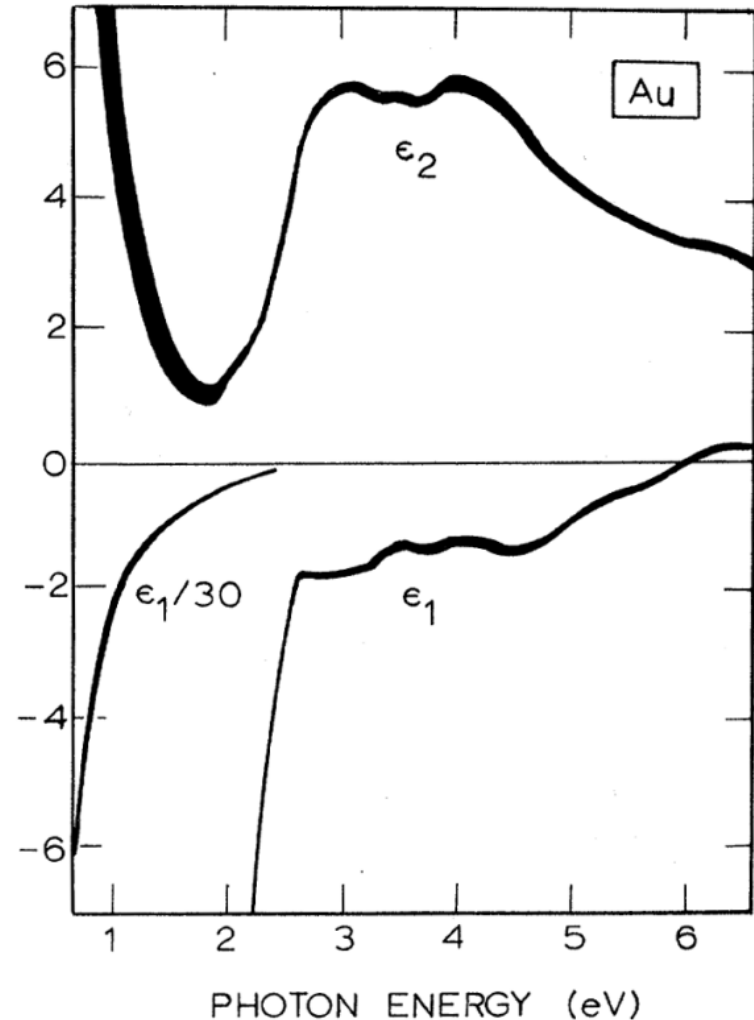


James Clerk Maxwell (1831–1879)



$$\left(\nabla^2 - \mu \tilde{\epsilon}_B \frac{\partial^2}{\partial t^2} \right) \vec{E} = 0$$

$$\tilde{\epsilon}_B = \epsilon_1 + i * \epsilon_2$$



Dielectric Function of Small Clusters

For nanoparticles where $L_{\text{eff}} \leq L_{\infty}$ size correction to $\tilde{\epsilon}_B$ needed

$$\tilde{\epsilon} = \tilde{\epsilon}_B + \Delta\tilde{\epsilon}(\text{Size})$$

$$\Delta\tilde{\epsilon}(\text{Size}) = \frac{\omega_p^2}{\omega^2 + i\omega\gamma_D} - \frac{\omega_p^2}{\omega^2 + i\omega(\gamma_D + \gamma_S + \gamma_R)}$$

$$\omega_p = 1.41 \text{ nm/fs}$$

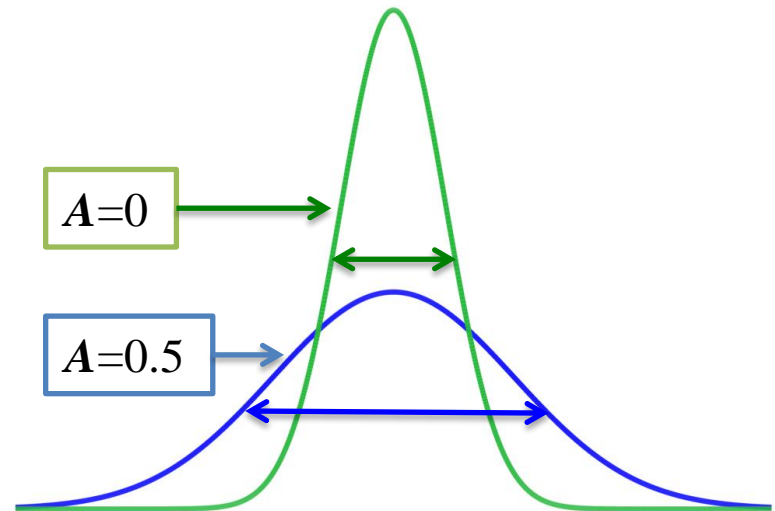
$$\gamma_D = \frac{v_F}{L_{\infty}} = 1.094 \times 10^{14} \text{ 1/s}$$

$$\gamma_S = \frac{A v_F}{L_{\text{eff}}}, \quad L_{\text{eff}} = \frac{4V}{S}, \quad (2R < 40 \text{ nm})$$

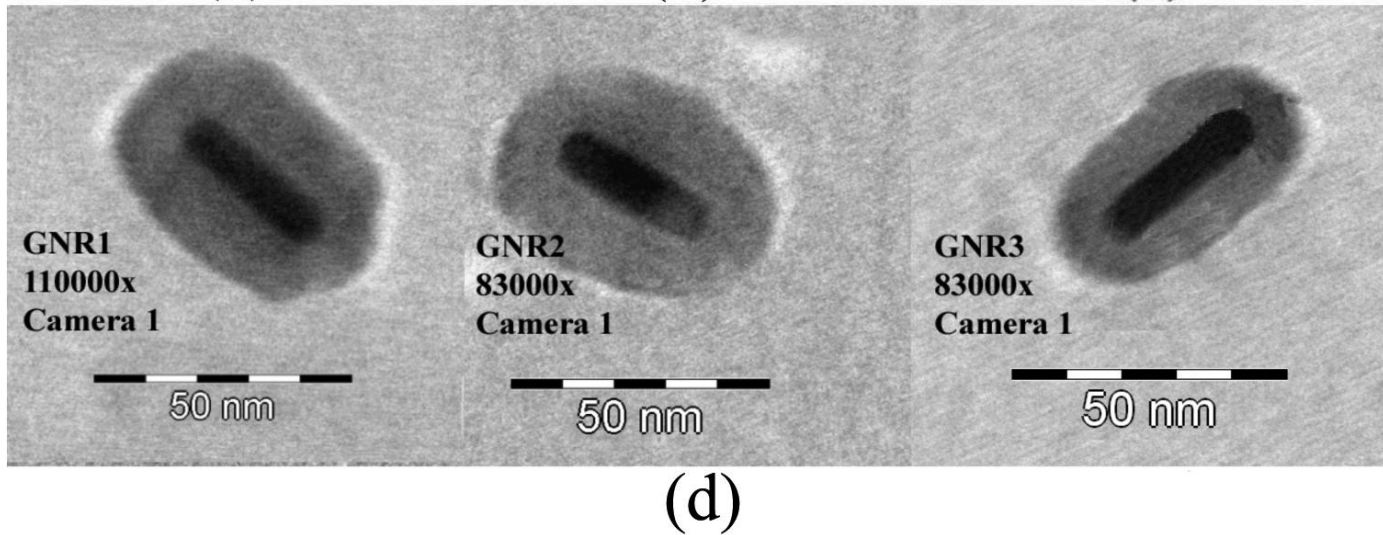
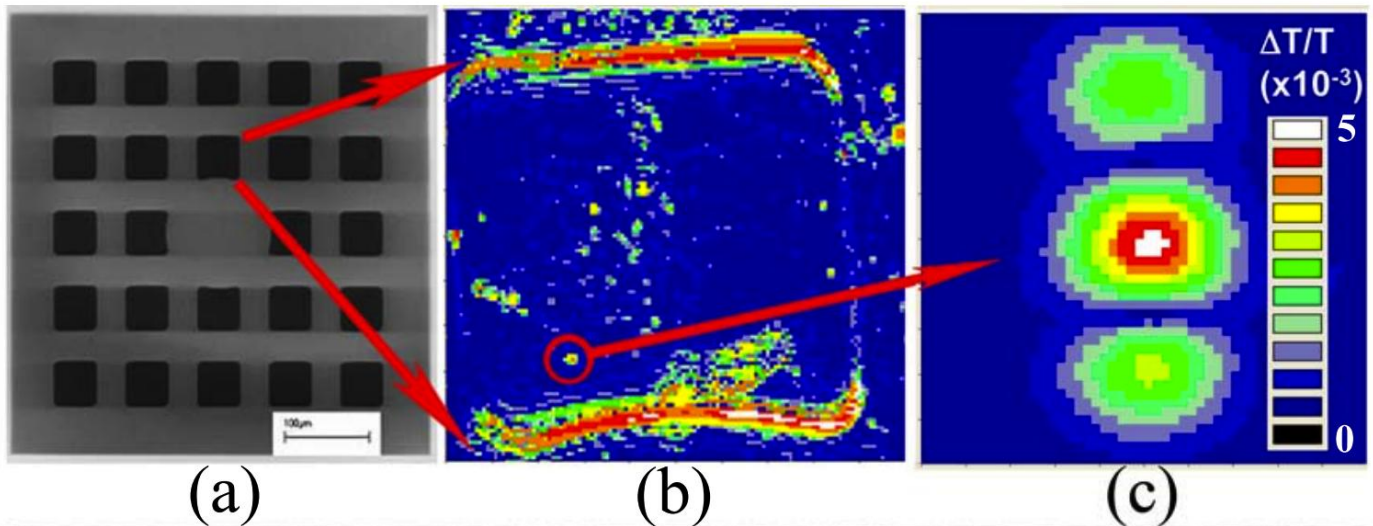
$$\gamma_R = \frac{\eta V}{\pi}, \quad \eta = (5.5 \pm 1.5) \times 10^{-7} \text{ fs}^{-1} \text{ nm}^{-3}$$

(40 < 2R < 150 nm)

A - unknown

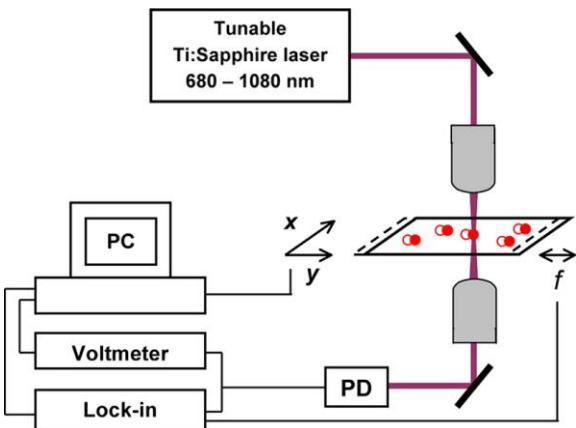


Experimental Approach: Spatial Modulation Spectroscopy with TEM on a Single Particle

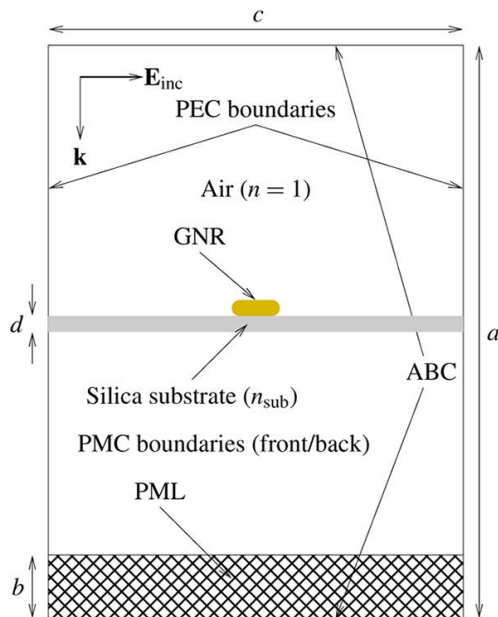


Modeling SMS Experimental Setup

SMS

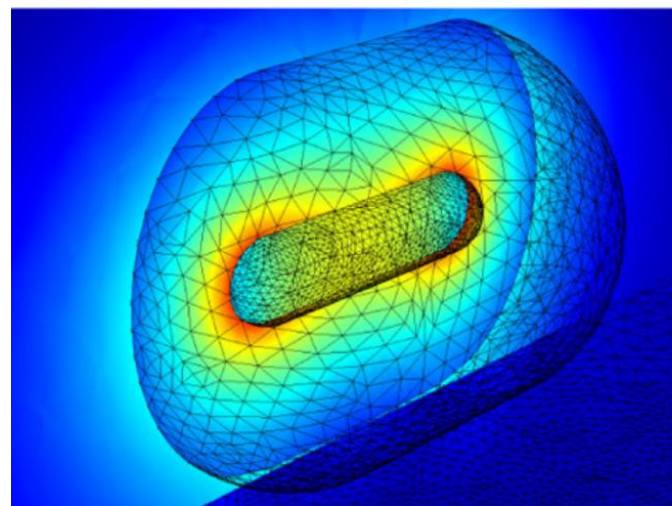


FEM (COMSOL 3.5a)



(a) Computational geometry.

Silica-coated GNR

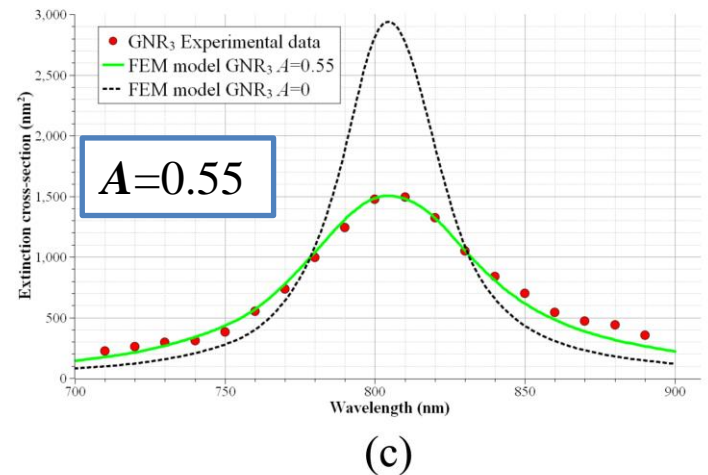
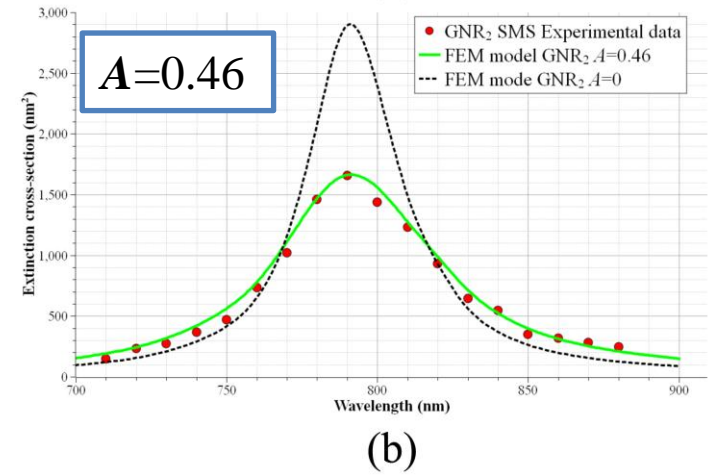
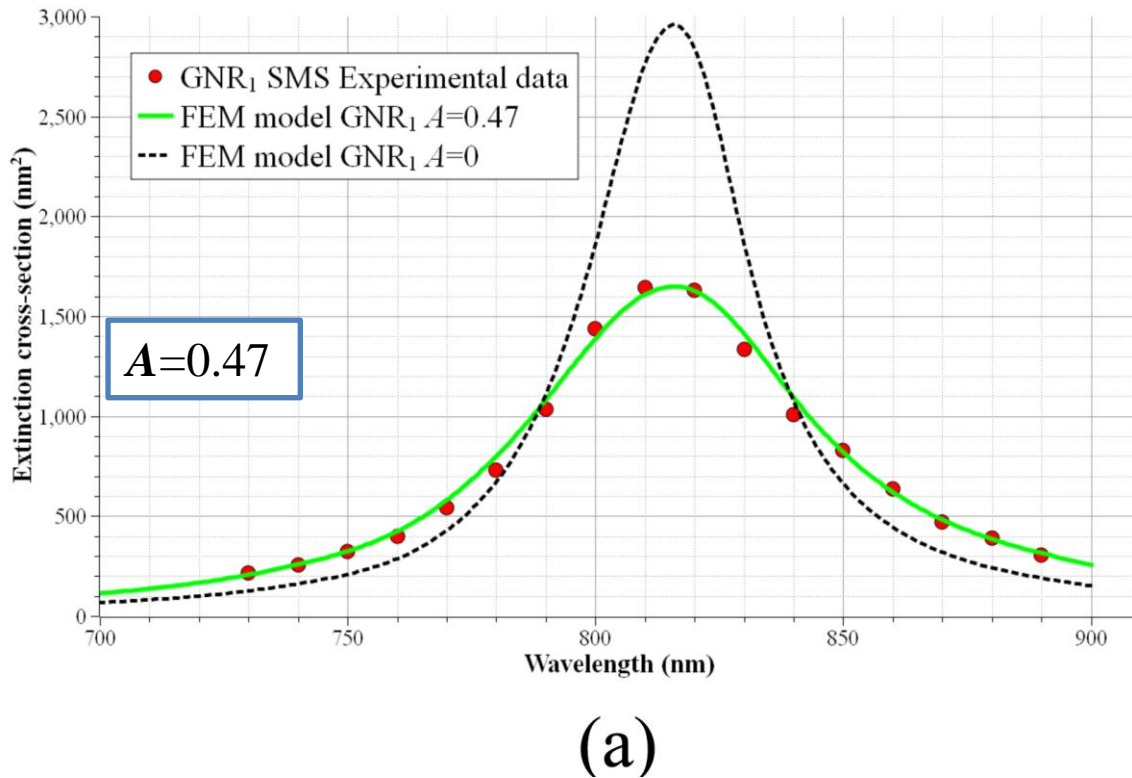


The medium inside the domain was air, and the GNR support layer on the TEM grid was modelled as a 40 nm thick silica substrate. In the computational model $a = 2.4 \mu\text{m}$, $b = 0.4 \mu\text{m}$, $c = 1.4 \mu\text{m}$, and $d = 40 \text{ nm}$. The domain in the front-to-back direction had a size equal to c . **Mesh: 540k tetrahedral elements, 4M degrees of freedom**

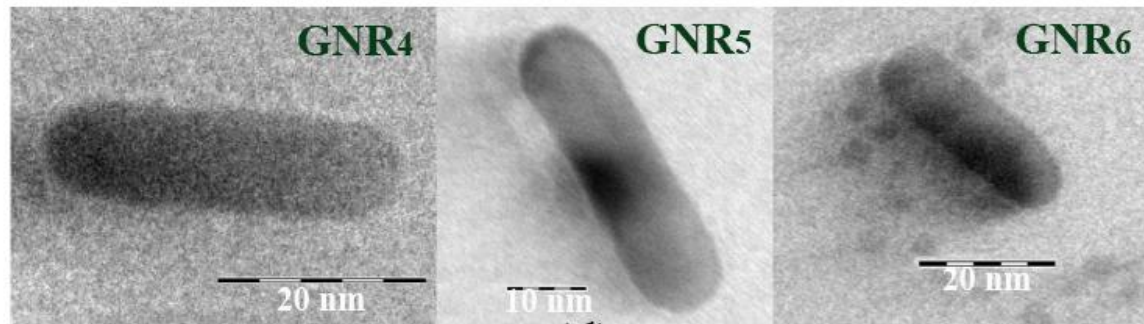
Results: Silica Coated GNRs

Fitting procedure:

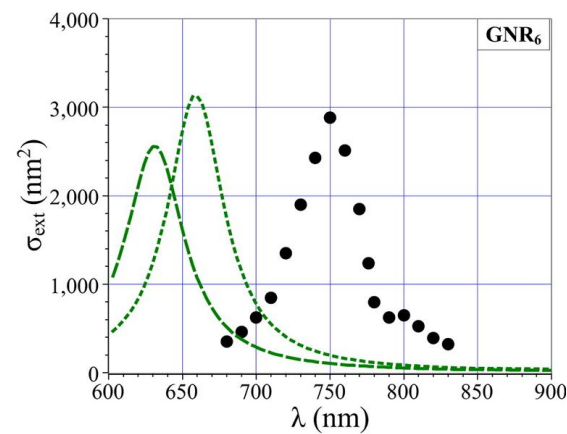
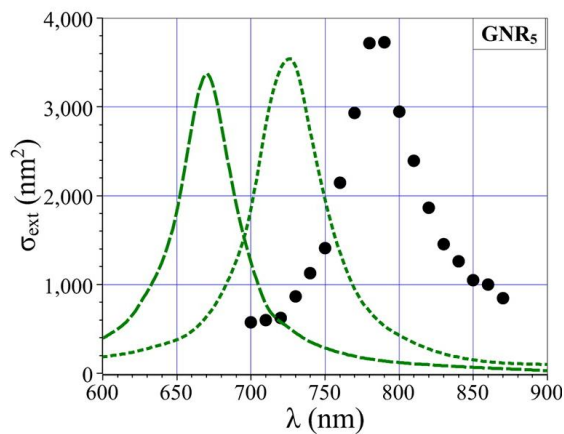
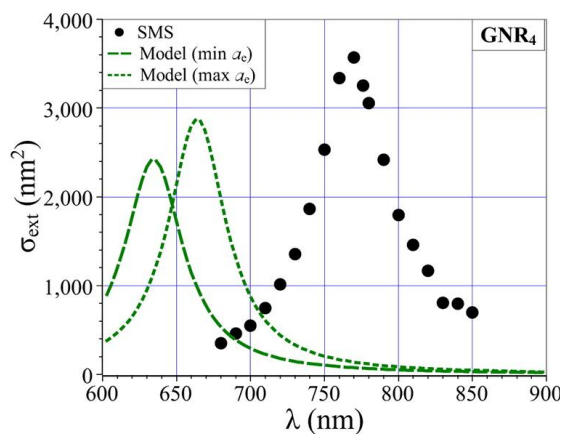
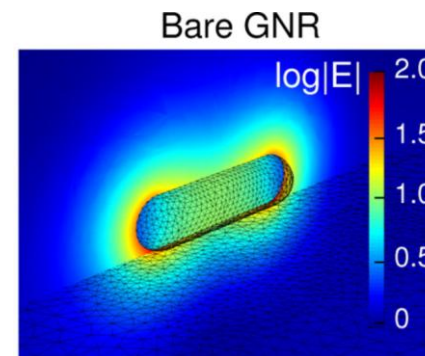
- GNR dimension within TEM uncertainty (± 0.5 nm)
- A parameter to obtain longitudinal SPR FWHM within 1% of experimental value



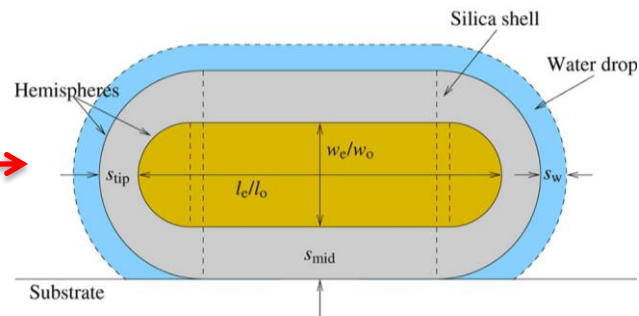
Results: Bare GNRs



(d)

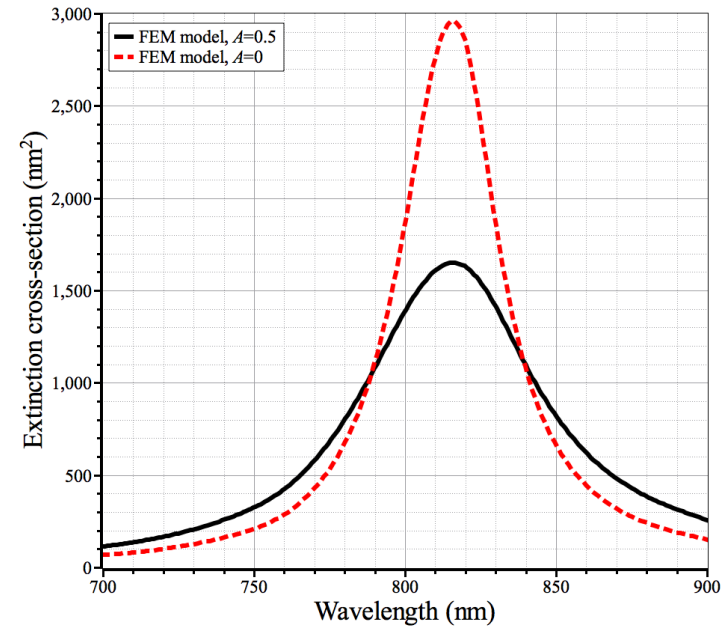


Environmental factors:
water, humidity, surfactant molecules



Discussions

- Realistic FE model of experimental SMS setup
 - * Silica substrate
 - * GNR geometry
 - * GNR dimensions
 - * Size corrected dielectric function of gold
- Determination of A (broadening parameter), consistent values for 3 silica coated GNRs



Remaining questions:

- FE model didn't work for bare GNRs (environmental factors)
- Will A parameter work for other GNR sizes
- Dependence of $L_{\text{eff}}=4V/S$ not tested.

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