

Optical scattering resonances of metal nano particles and related structures

(PhD course: Optical at the nanoscale)

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Outline:

Gold coated spherical polystyrene particles

Alloys and other geometries

Metal nano strip resonators

Quasistatic approximation

$$\nabla \times \mathbf{E} = \mathbf{0} \quad , \quad \nabla \cdot (\epsilon \mathbf{E}) = 0 \quad , \quad \mathbf{E}_{inc} = \hat{z} E_0 = -\nabla(-E_0 r \cos \theta)$$

$$\mathbf{E}_i = -\nabla \Phi_i \quad , \quad \Phi_i = A_i r \cos \theta + B_i \frac{1}{r^2} \cos \theta$$

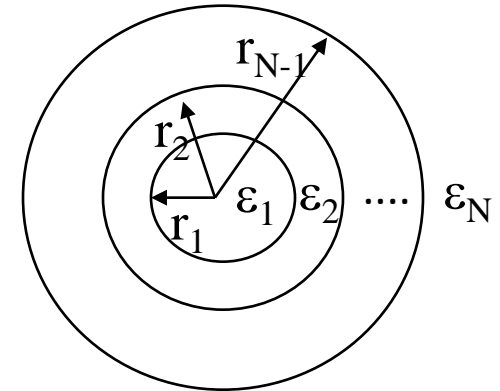
Boundary conditions

$$B_1 = 0 \quad , \quad A_N = -E_0$$

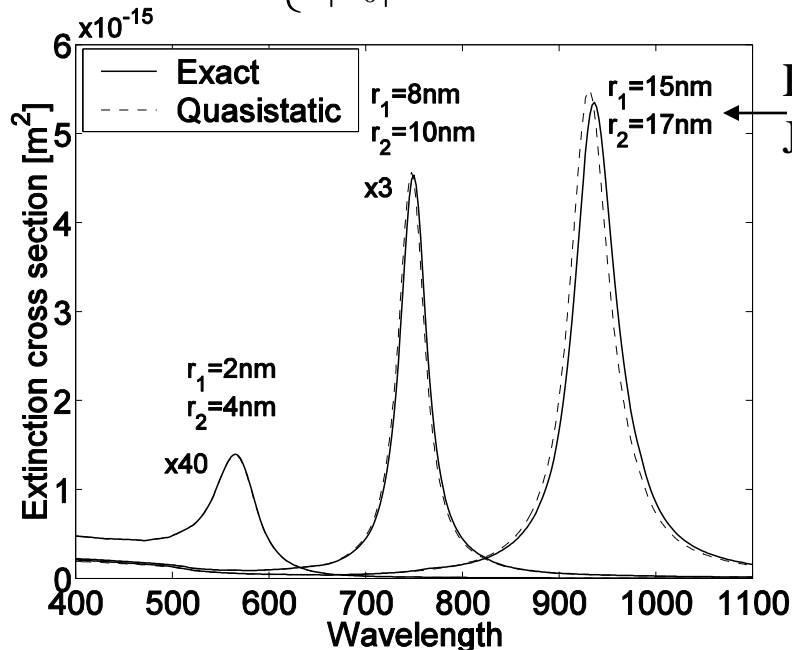
$$\hat{\theta} \cdot \nabla \Phi_i(r_i) = \hat{\theta} \cdot \nabla \Phi_{i+1}(r_i)$$

$$\epsilon_i \hat{r} \cdot \nabla \Phi_i(r_i) = \epsilon_{i+1} \hat{r} \cdot \nabla \Phi_{i+1}(r_i)$$

$$C_{ext} = \text{Im} \left\{ \frac{k_0 \sqrt{\epsilon_N}}{|E_0|^2} \int (\mathbf{E}_{inc})^* \cdot \frac{\epsilon(r) - \epsilon_N}{\epsilon_N} \mathbf{E}(\mathbf{r}) d^3 r \right\}$$

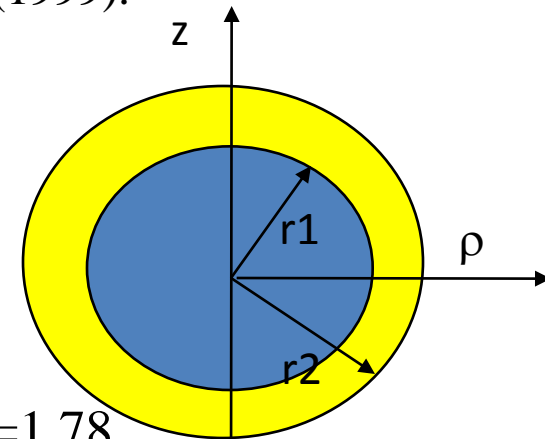


The incident field is oriented along the z-axis.



Reproduced from Averitt et al.,
 JOSA B **16**(10), 1824-32 (1999).

- = Au_2S
- = Au
- = liquid with $\epsilon = 1.78$



Exact calculation that includes retardation

$$\mathbf{E}_{inc} = \hat{x}E_0 e^{ikz} = E_0 \sum_{n=1}^{\infty} (-i)^n \frac{2n+1}{n(n+1)} \left(\mathbf{m}_{o1n}^{(1)} + i\mathbf{n}_{e1n}^{(1)} \right)$$

$$\mathbf{E}_j = E_0 \sum_{n=1}^{\infty} (-i)^n \frac{2n+1}{n(n+1)} \left(a_{n,j}^{(1)} \mathbf{m}_{o1n}^{(1)} + a_{n,j}^{(3)} \mathbf{m}_{o1n}^{(3)} + ib_{n,j}^{(1)} \mathbf{n}_{e1n}^{(1)} + ib_{n,j}^{(3)} \mathbf{n}_{e1n}^{(3)} \right)$$

$$\mathbf{B}_j = - \left(\frac{E_0}{c/\sqrt{\epsilon_j}} \right) \sum_{n=1}^{\infty} (-i)^n \frac{2n+1}{n(n+1)} \left(b_{n,j}^{(1)} \mathbf{m}_{e1n}^{(1)} + b_{n,j}^{(3)} \mathbf{m}_{e1n}^{(3)} - ia_{n,j}^{(1)} \mathbf{n}_{o1n}^{(1)} - ia_{n,j}^{(3)} \mathbf{n}_{o1n}^{(3)} \right)$$

$$\mathbf{m}_{e1n}^{(1,3)} = \pm \frac{1}{\sin\theta} z_n^{(1,3)}(kR) P_n^1(\cos\theta) \cos\phi \hat{\theta} - z_n^{(1,3)}(kR) \frac{dP_n^1(\cos\theta)}{d\theta} \frac{\sin\phi}{\cos\phi} \hat{\phi}$$

$$\mathbf{n}_{e1n}^{(1,3)} = \frac{n(n+1)}{kR} z_n^{(1,3)}(kR) P_n^1(\cos\theta) \frac{\sin\phi}{\cos\phi} \hat{r} + \frac{1}{kR} \left[kR z_n^{(1,3)}(kR) \right] \frac{dP_n^1(\cos\theta)}{d\theta} \frac{\sin\phi}{\cos\phi} \hat{\theta}$$

$$\pm \frac{1}{kR \sin\theta} \left[kR z_n^{(1,3)}(kR) \right] P_n^1(\cos\theta) \cos\phi \hat{\phi}$$

$P_n^1(\mathbf{x})$ is a legendre function

$z_n^{(1)}(kR)$ is a spherical Bessel function

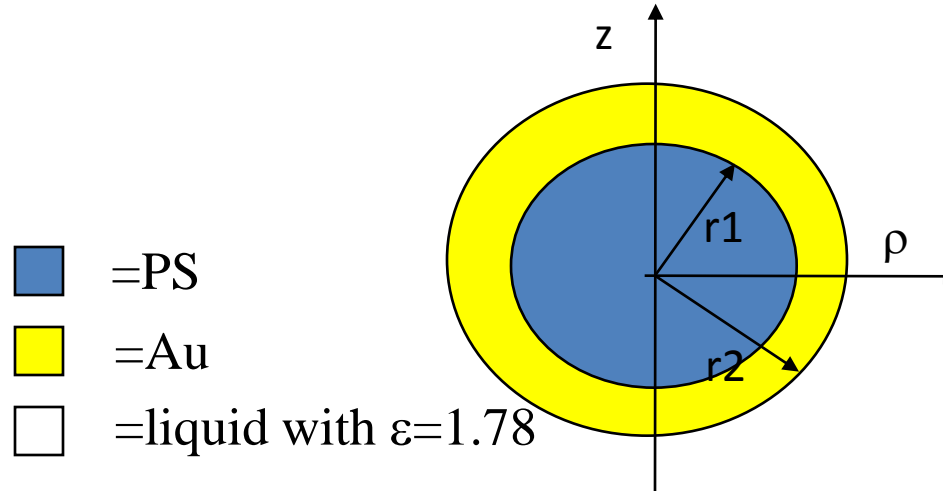
$z_n^{(3)}(kR)$ is a spherical Hankel function

References:

Aden and Kerker, J. Appl. Phys. 22 (10), 1242-46 (1951).

J.A. Stratton, *Electromagnetic theory*, McGraw-Hill, 1941

Gold coated polystyrene spheres



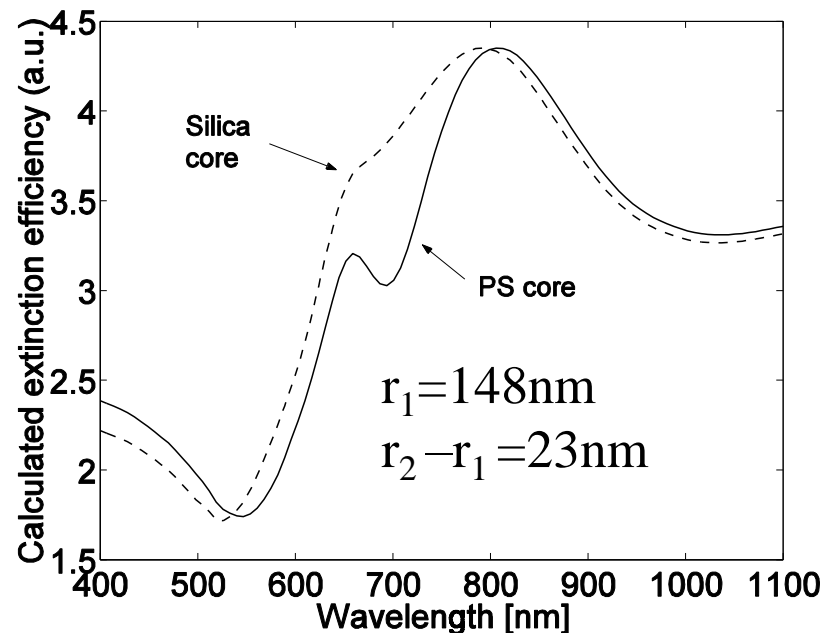
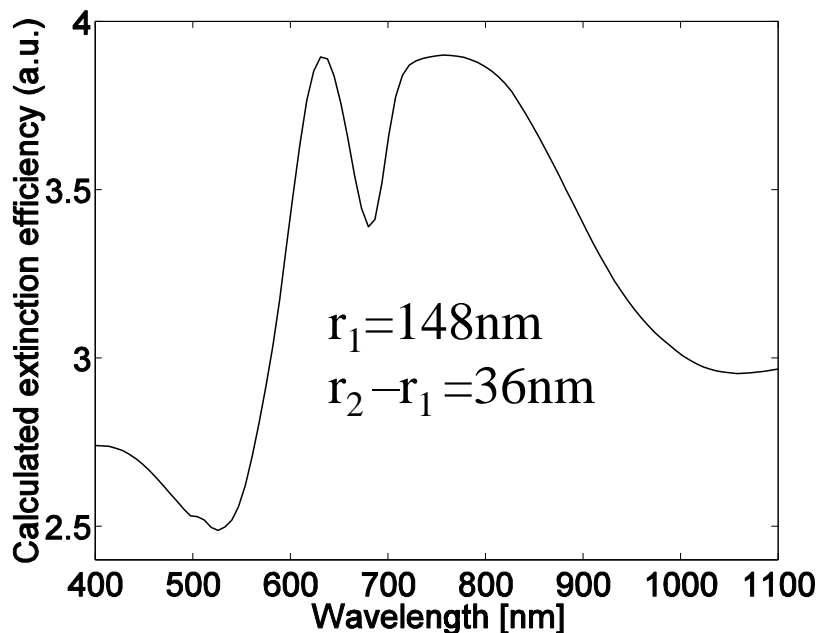
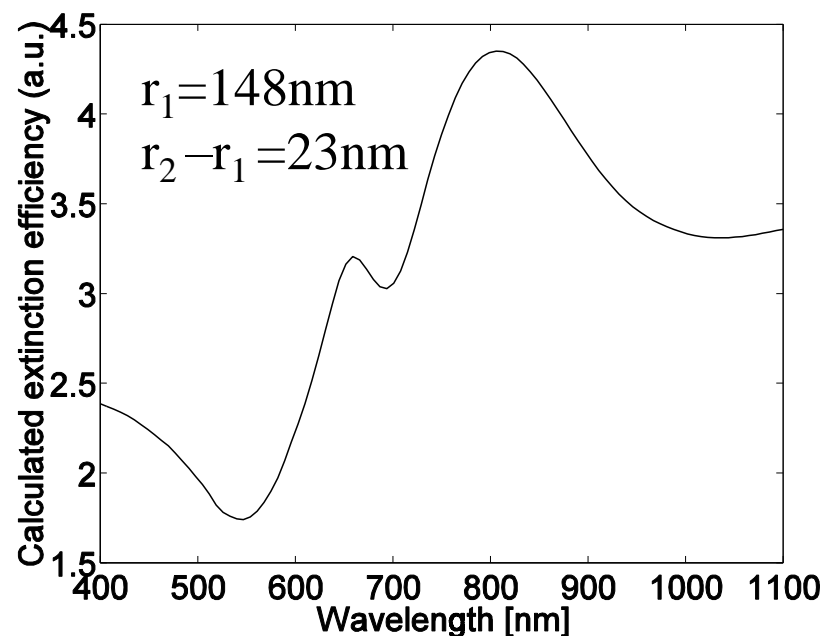
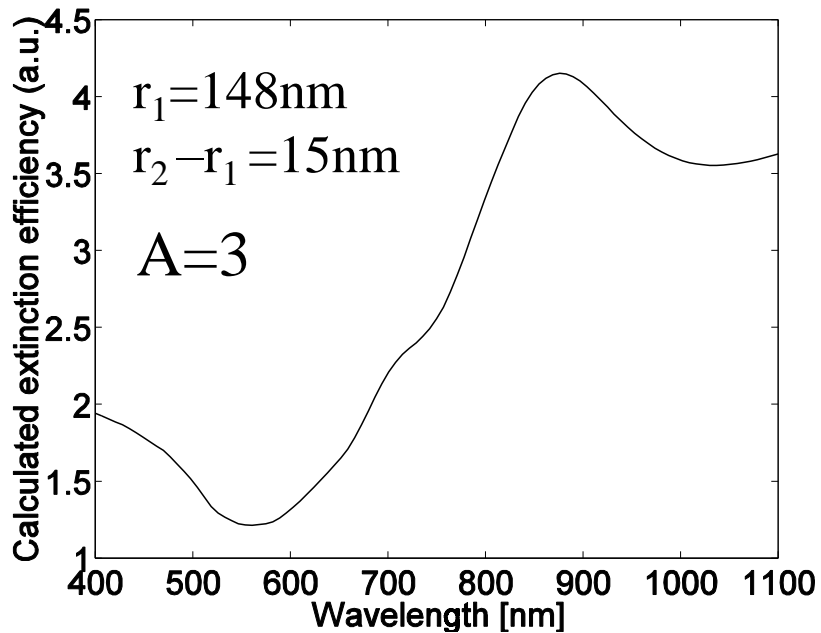
The finite thickness of the gold layer will result in additional loss due to surface scattering of electrons. This is sometimes taken into account to some extent in models by modifying the gold dielectric constant in the following way

$$\epsilon(\omega) = \epsilon_{bulk}(\omega) + \left(\frac{\omega_p^2}{\omega^2 + i\omega\gamma_{bulk}} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} \right)$$

$$\Gamma = \gamma_{bulk} + A \frac{v_F}{(r_2 - r_1)}$$

$$\omega_p = 1.37 \cdot 10^{16} \text{ rad/s}, \quad v_F = 1.4 \cdot 10^6 \text{ m/s}, \quad g = 3.33 \cdot 10^{13} \text{ s}^{-1}$$

Reproduction of Fig. 11 of Shi et al., Langmuir 2005, 21, 1610-17

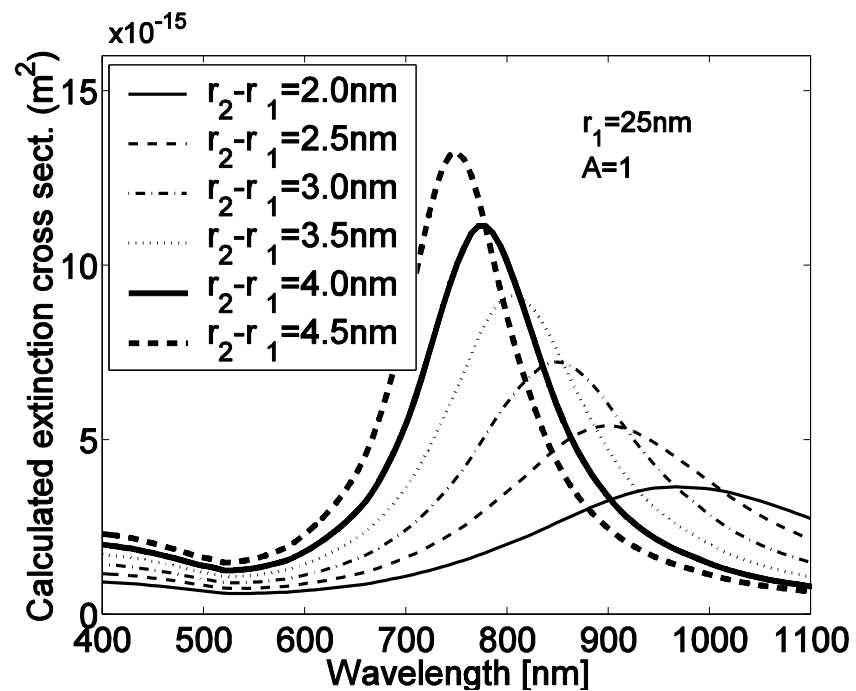
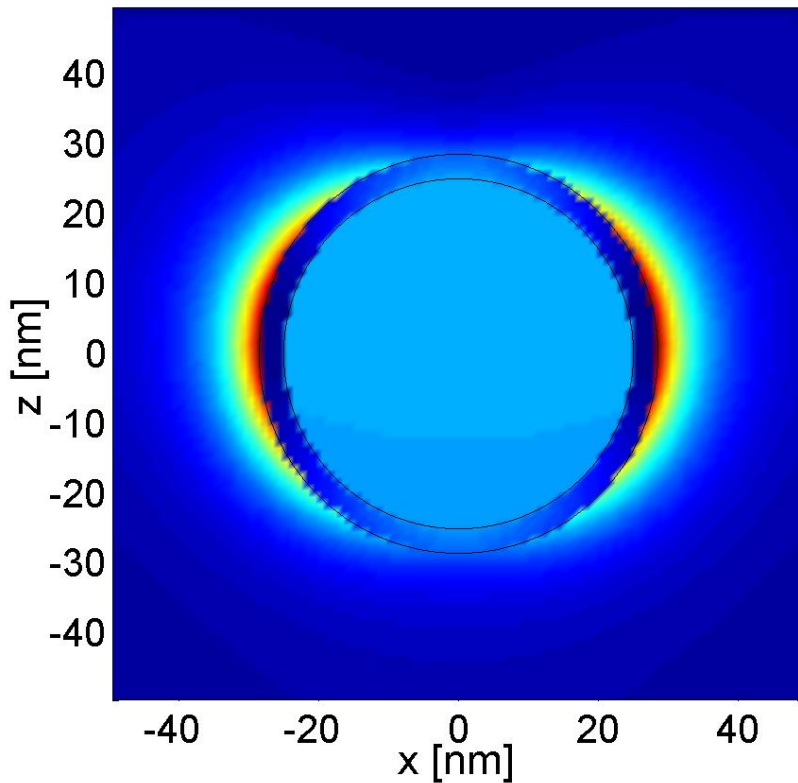


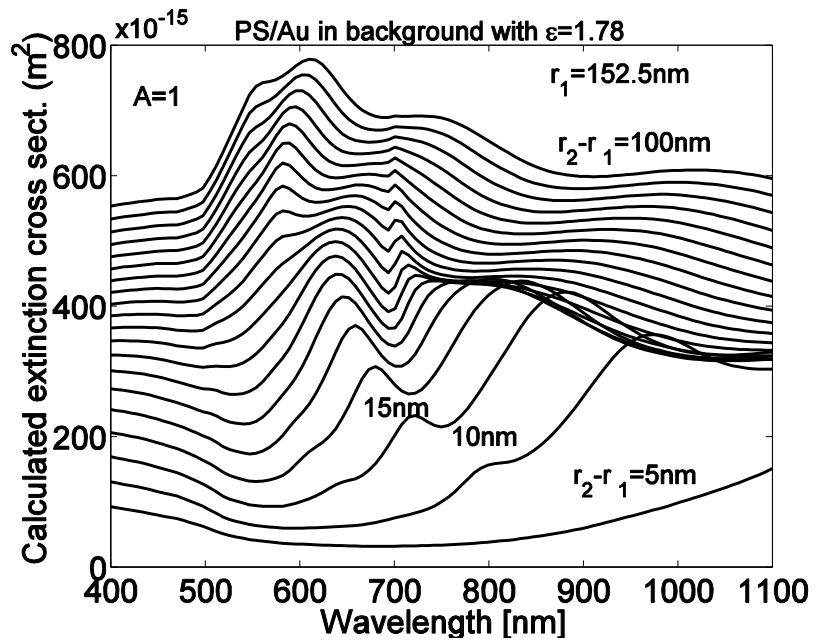
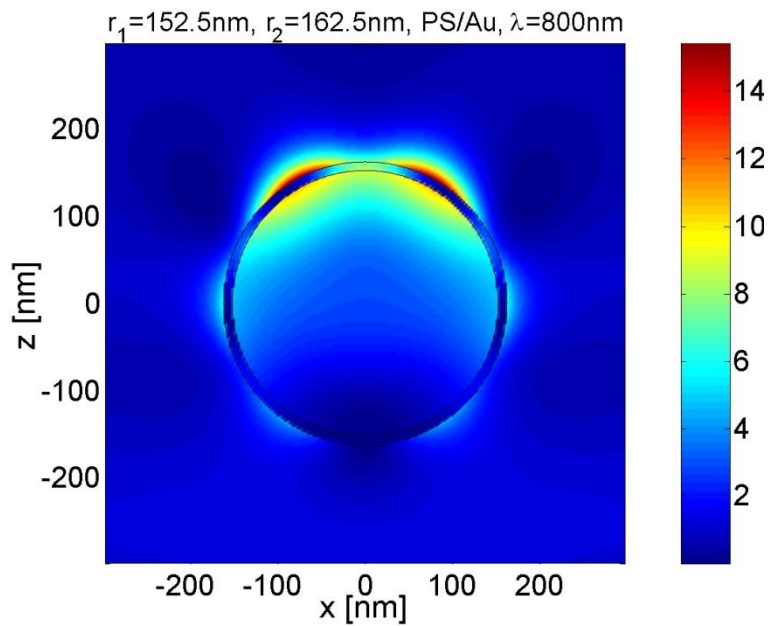
Gold coated polystyrene spheres

PS diameter = 50nm

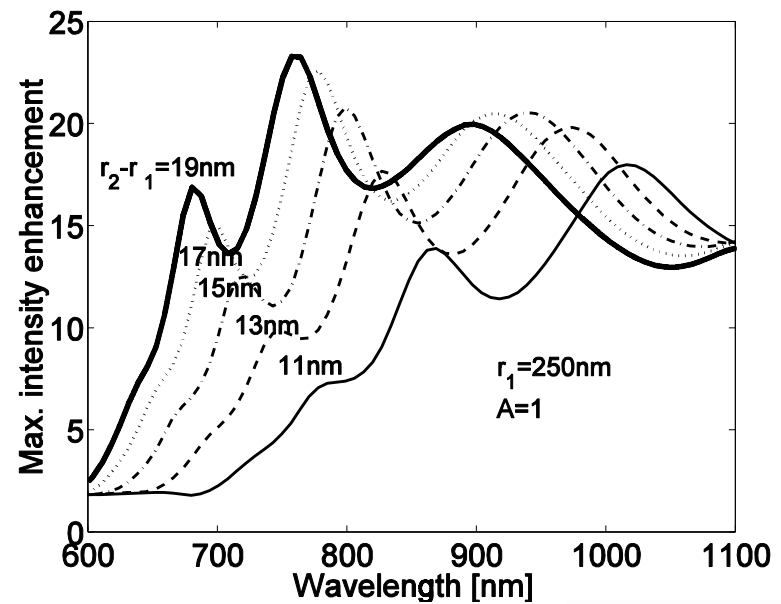
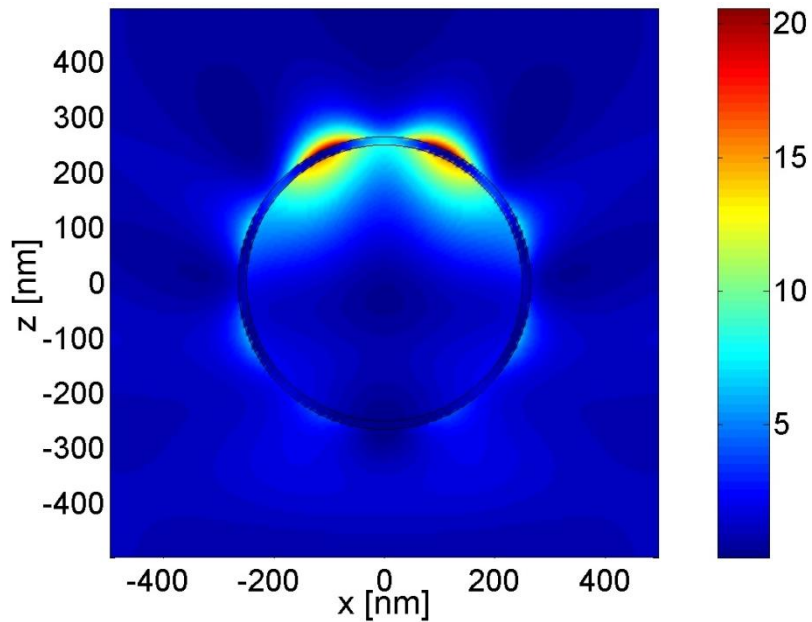
Extinction cross section resonance found for gold layer of 3.5nm at the wavelength 800nm

$r_1=25\text{nm}$, $r_2=28.5\text{nm}$, $\lambda=800\text{nm}$





$r_1=250\text{nm}$, $r_2=265\text{nm}$, $\lambda=800\text{nm}$



Spherical particles made of an alloy of gold and silver

3530 *J. Phys. Chem. B, Vol. 103, No. 18, 1999*

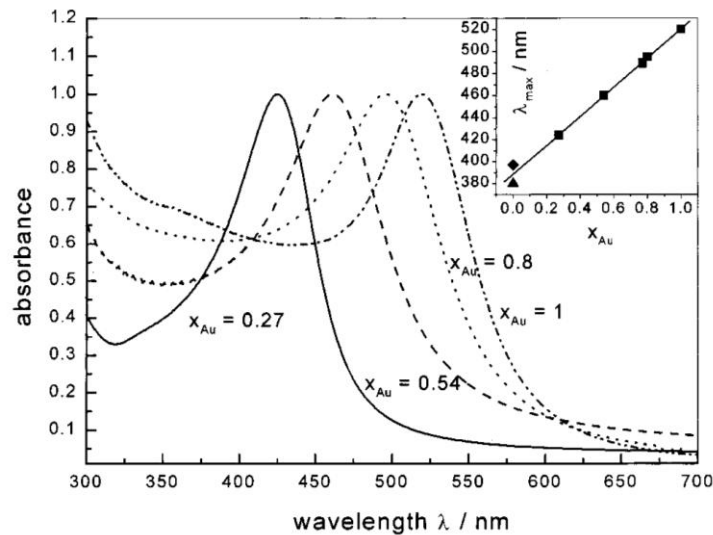
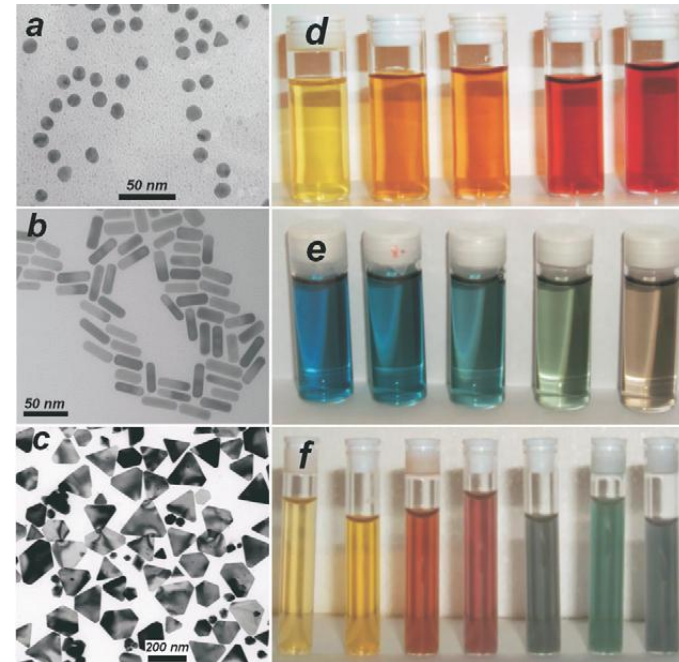


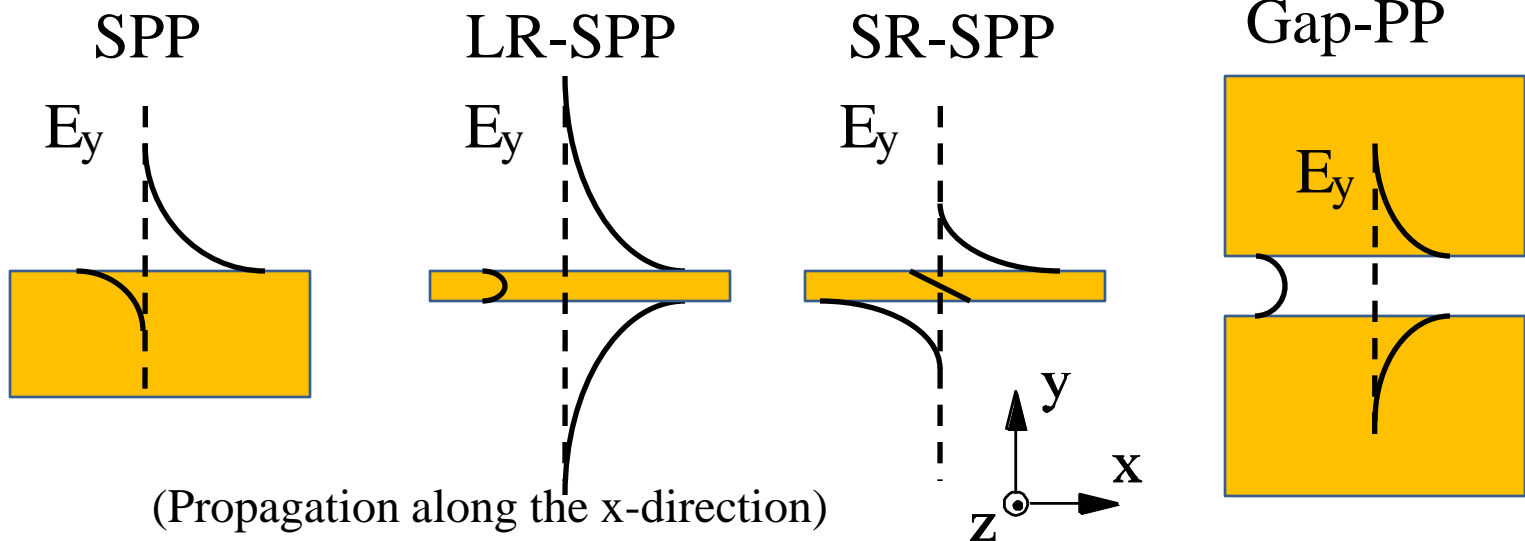
Figure 1. UV-vis absorption spectra of gold and gold-silver alloy nanoparticles with varying gold mole fractions x_{Au} . The spectra have been normalized at the plasmon absorption maximum. The inset shows how the absorption maximum of the plasmon band depends on the composition. The solid line is a linear fit of the absorption maximum to the gold mol fraction x_{Au} . The squares correspond to the experimental data while the triangle and diamond are two literature values for pure silver nanoparticles.^{29,34}

Other geometries of particles made of pure gold or silver



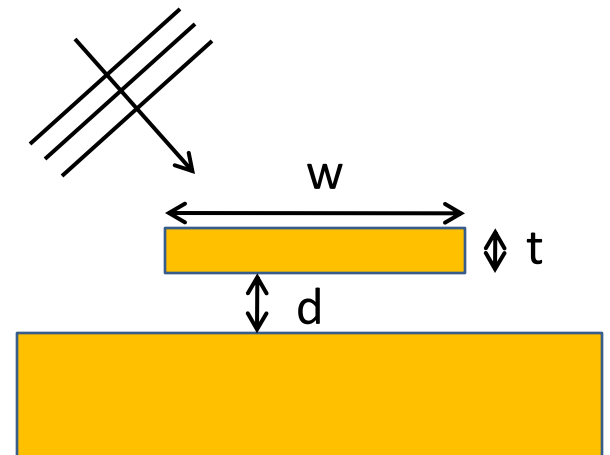
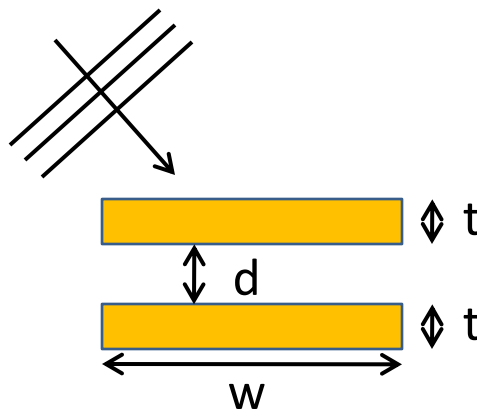
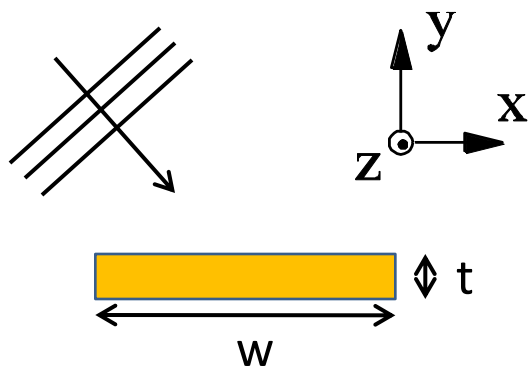
[1] Luis M. Liz-Marzán, "Nanometal: formation and color", materials today, 26-31, (Feb. 2004).

Introduction to surface plasmon polaritons



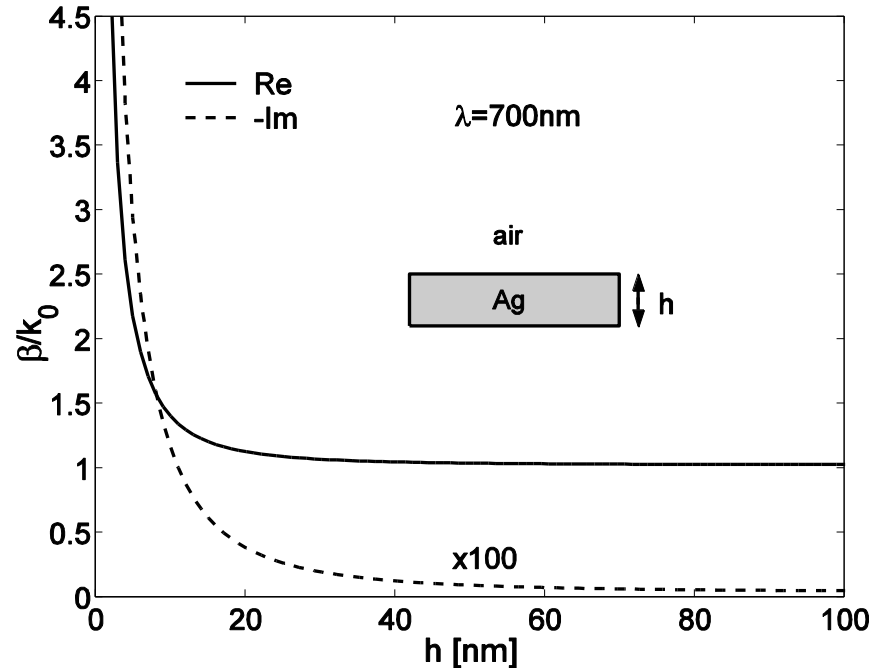
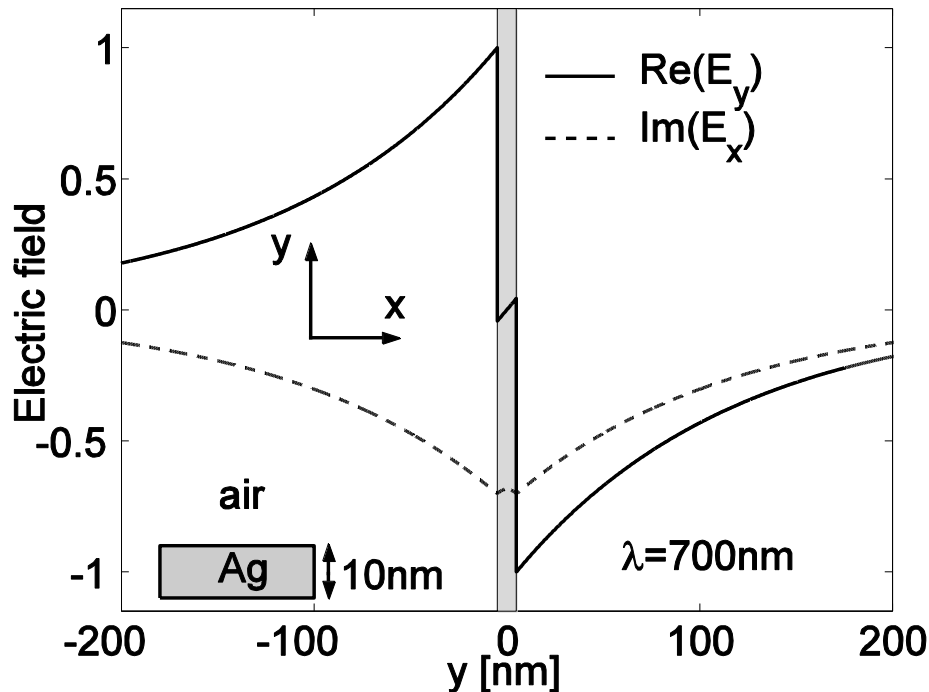
Metal nano-strip resonator

Gap-plasmon resonators



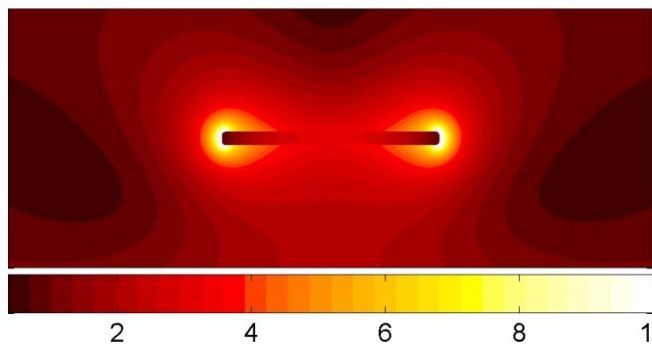
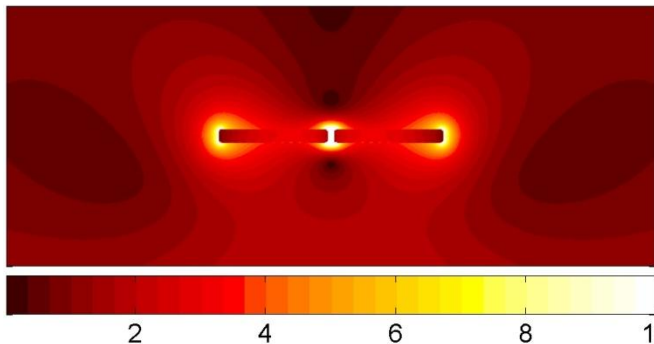
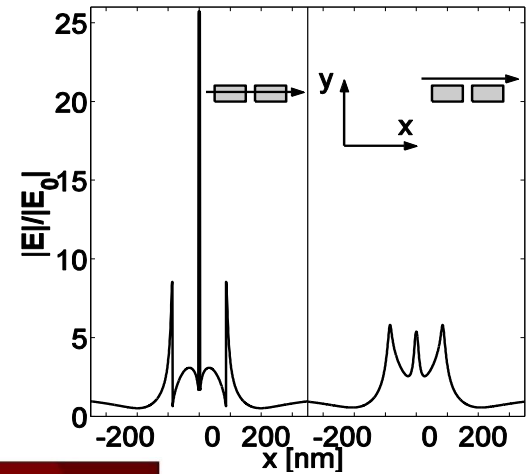
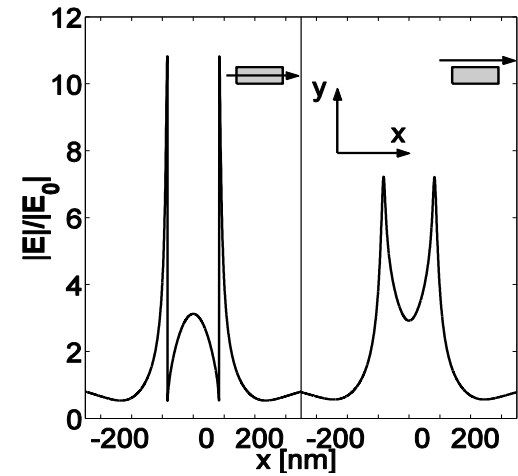
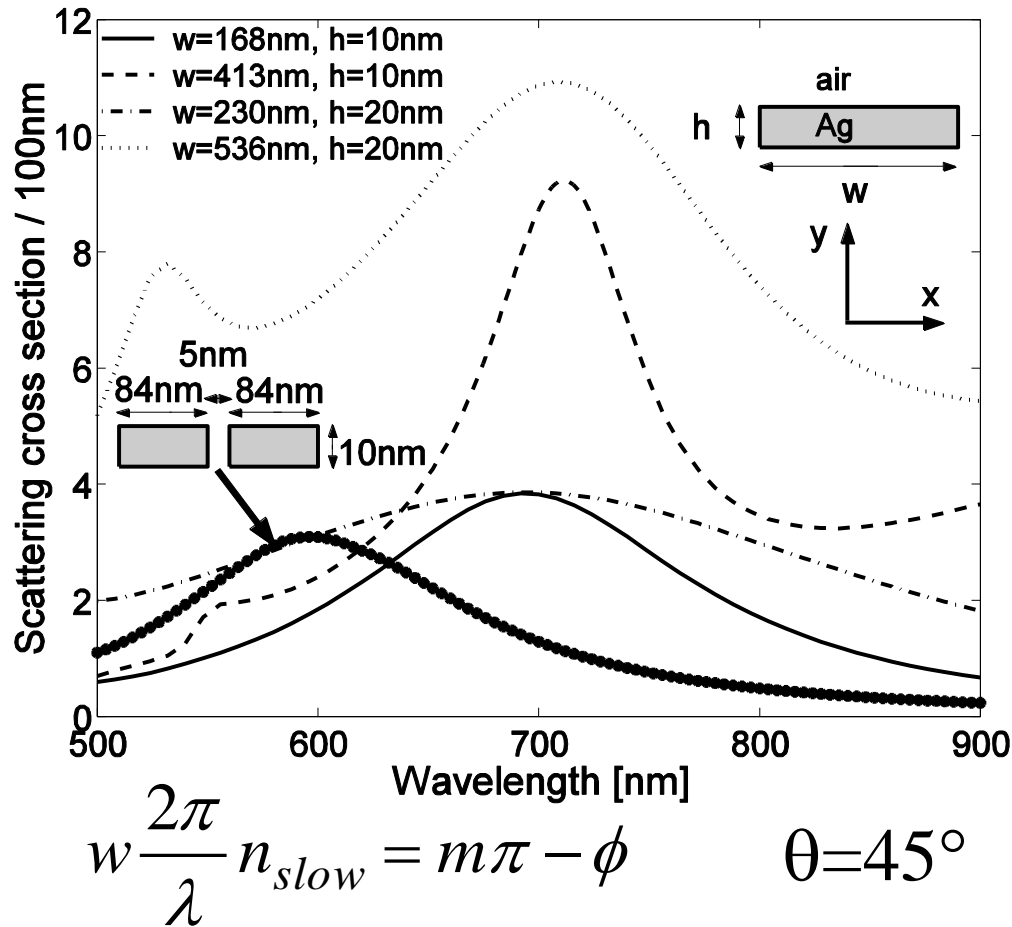
Metal nano-strip resonators

Slow plasmon polaritons in a silver film



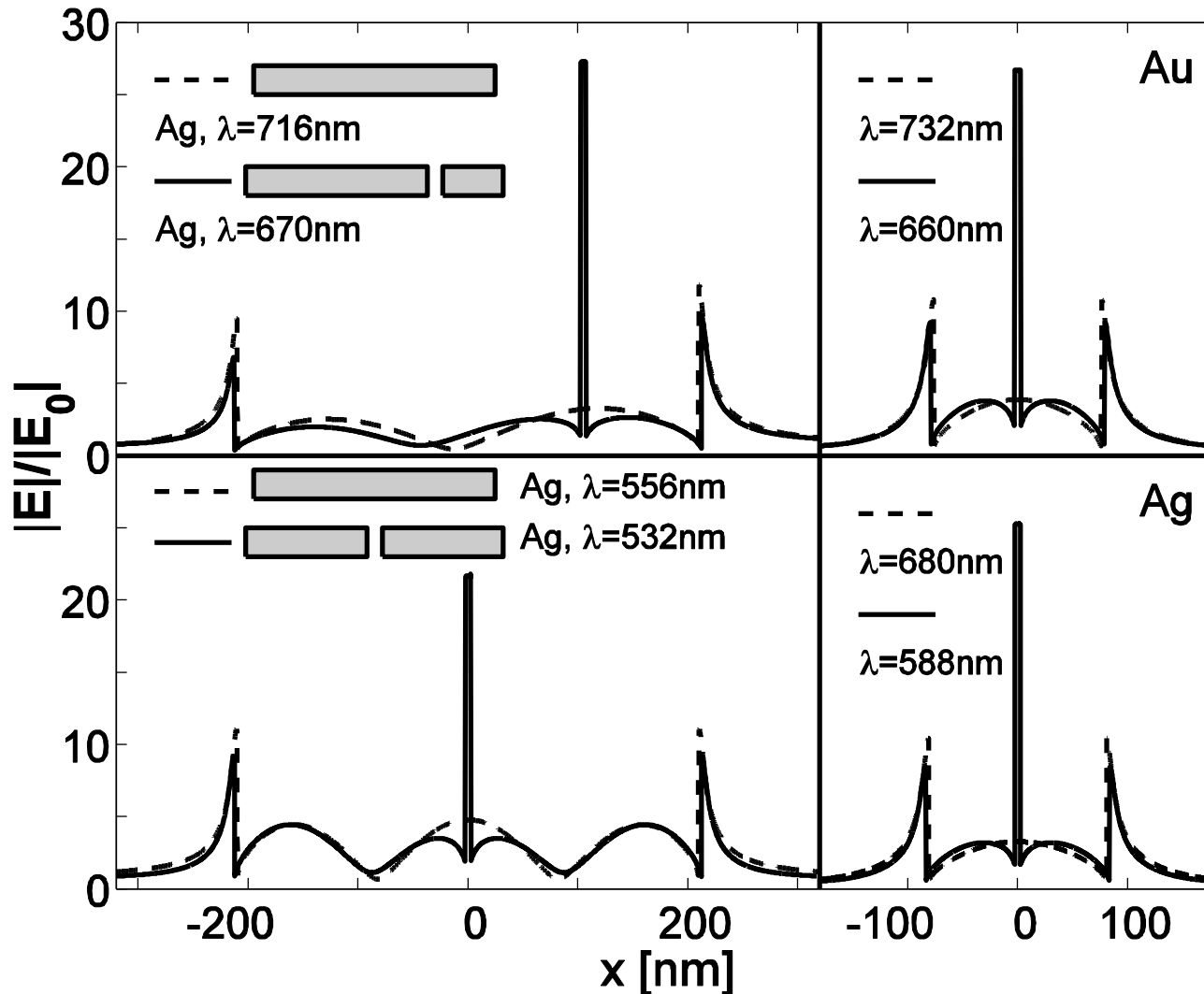
$$\mathbf{E}(\mathbf{r}) = \mathbf{E}(y)e^{-i\beta x} \quad k_0 = \frac{2\pi}{\lambda}$$

- The x-component of the electric field dominates inside the metal film
- The x- and y-components of the field are out of phase
- The mode becomes less strongly bound as the film thickness increases

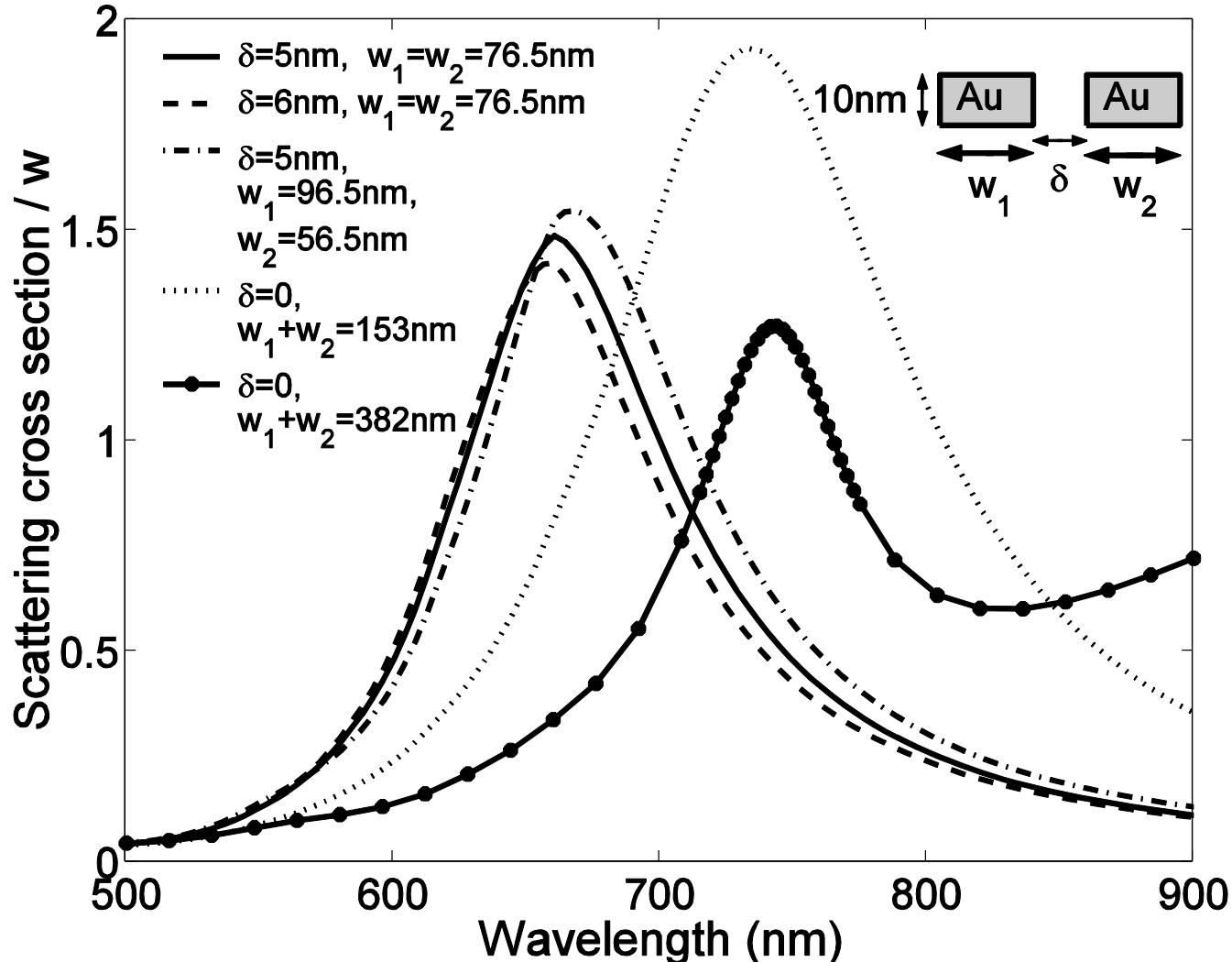


Electric field magnitude enhancement (values >10 are set to 10)

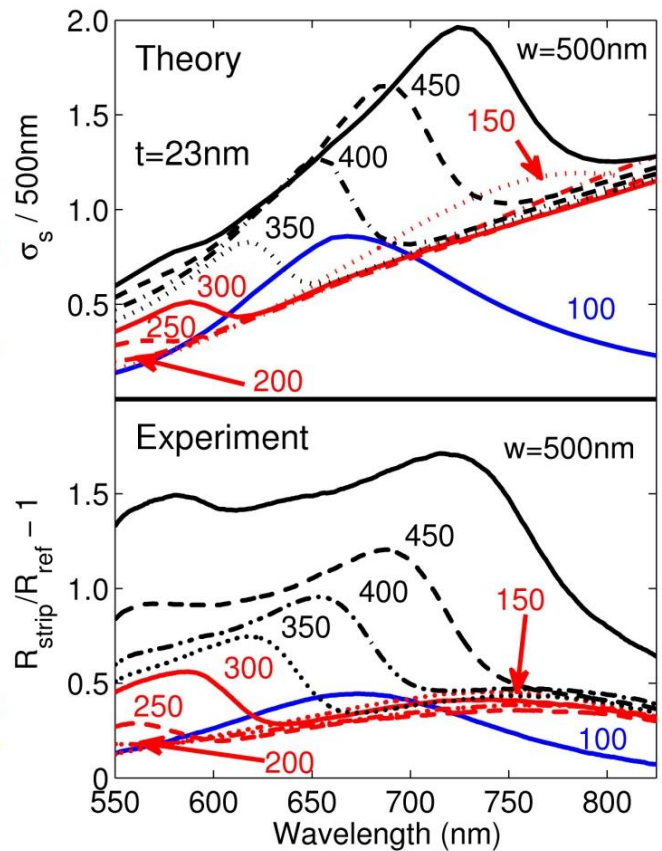
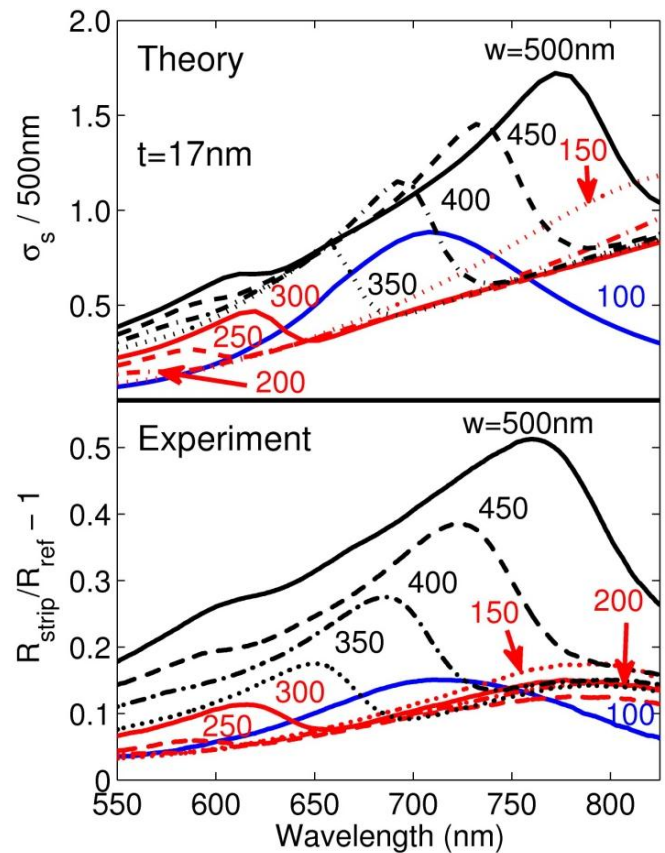
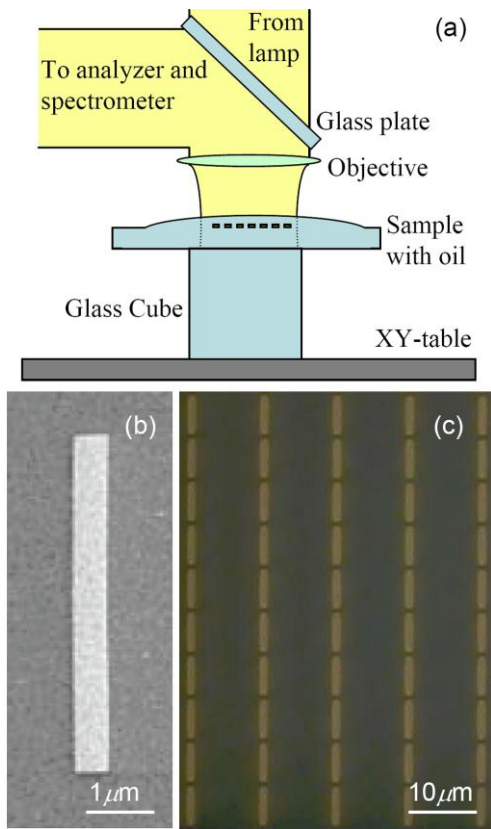
Cross section of resonant fields through the center of the metal strips



The resonance is robust towards a 20% increase in δ ($\delta=5 \rightarrow 6\text{nm}$) and towards shifting the position of the 5nm gap by 20nm



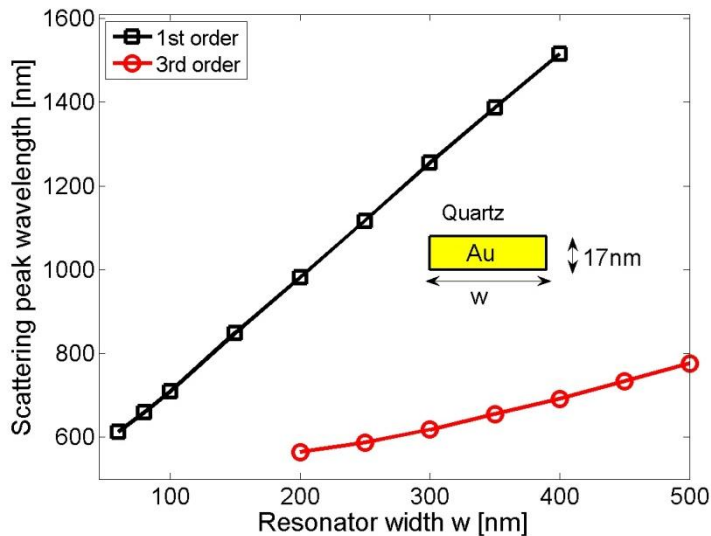
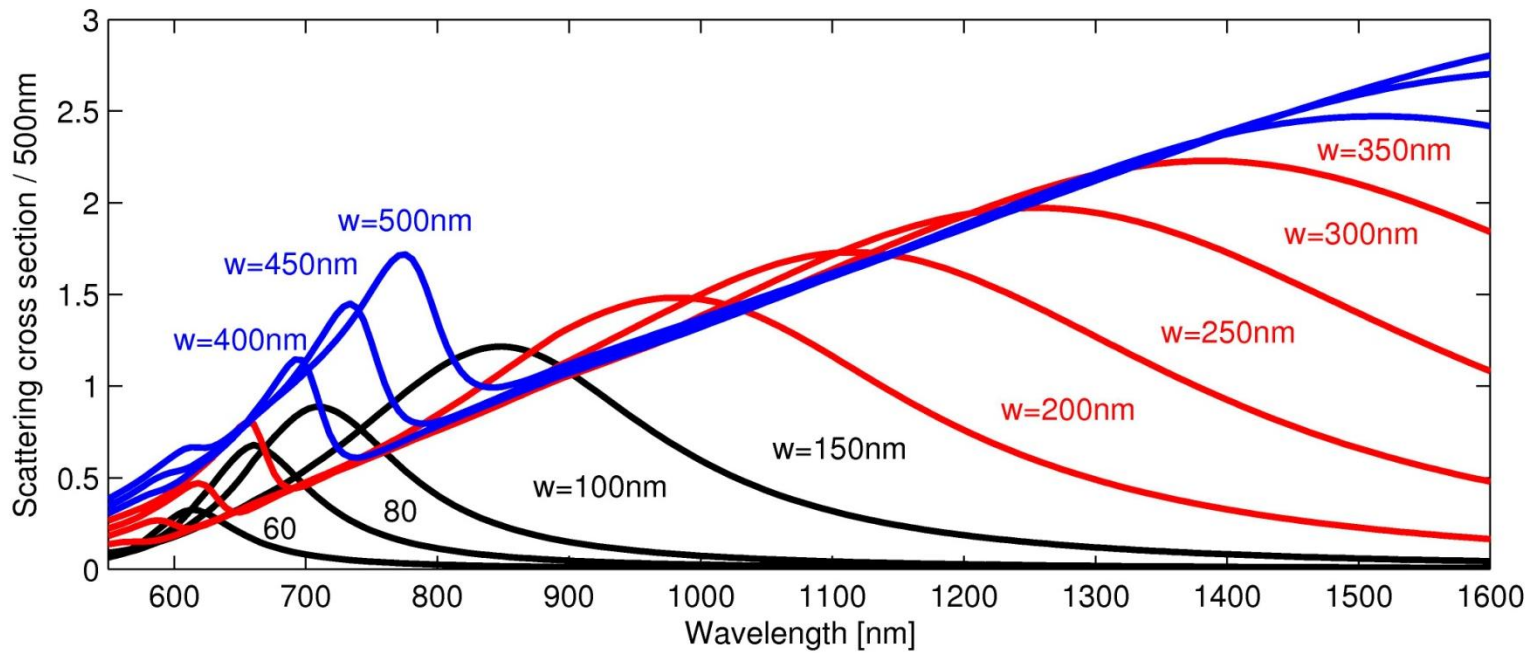
Gold nano-strip optical resonators: theory and experiment



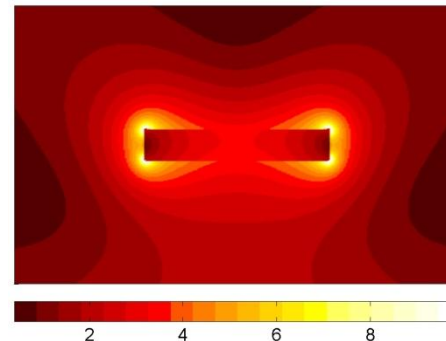
Fabrication: A. Boltasseva
 Measurements: J. Beermann

$$w \frac{2\pi}{\lambda} n_{\text{slow}} = m\pi - \phi$$

Ref.: T. Søndergaard, J. Beermann, A. Boltasseva, and S.I. Bozhevolnyi, Phys. Rev. B 77, 115420 (2008).

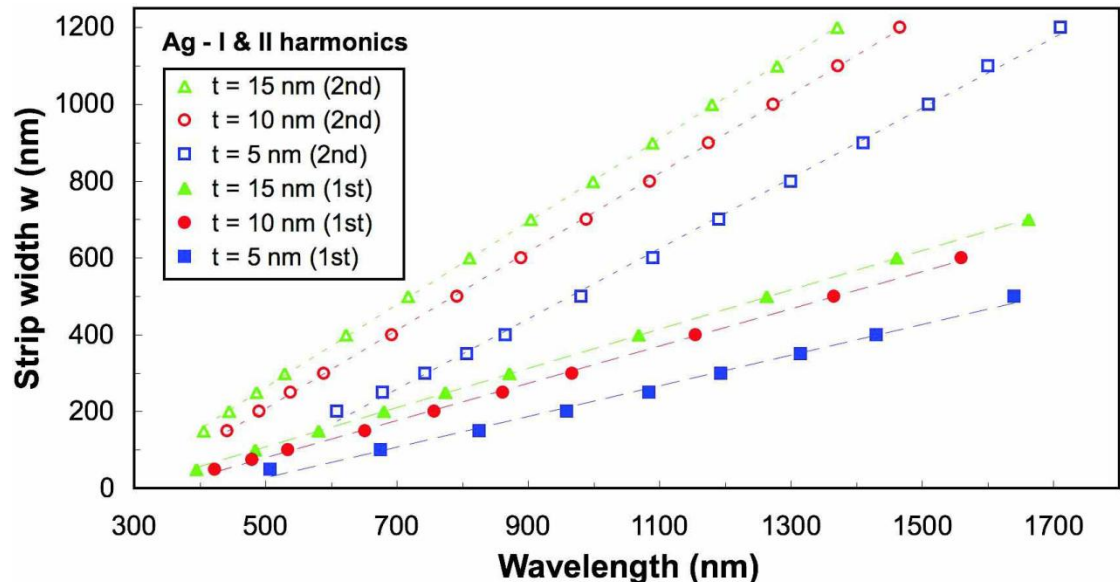
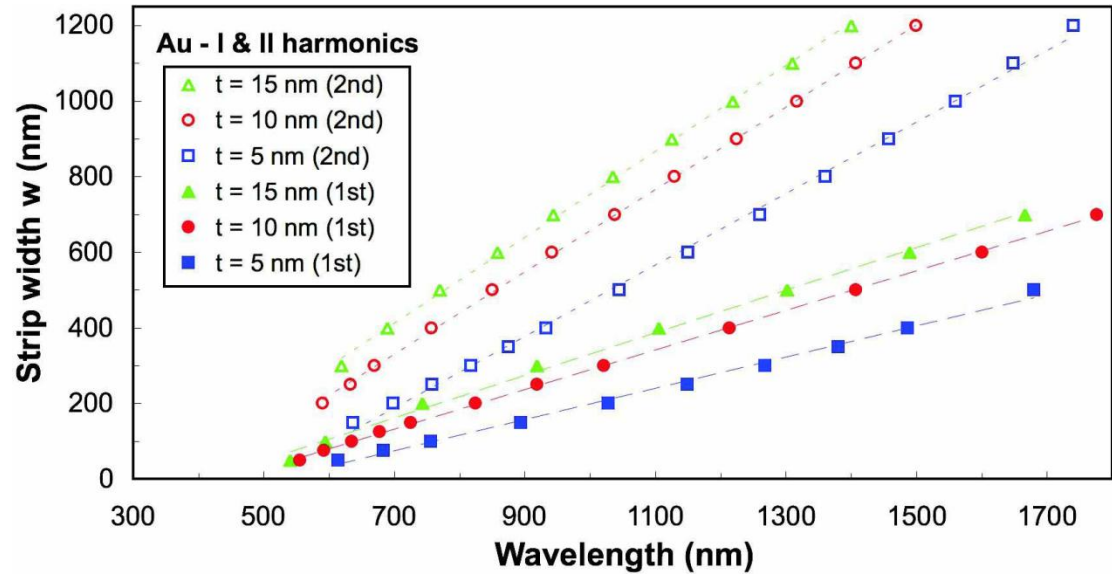
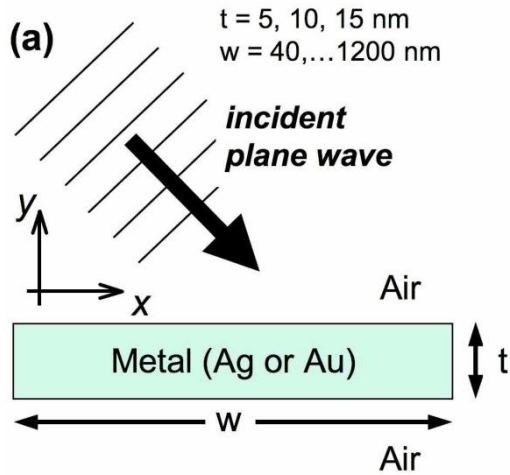


$$\lambda = \left(\frac{2\pi}{m\pi - \phi} n_{slow} \right) w$$

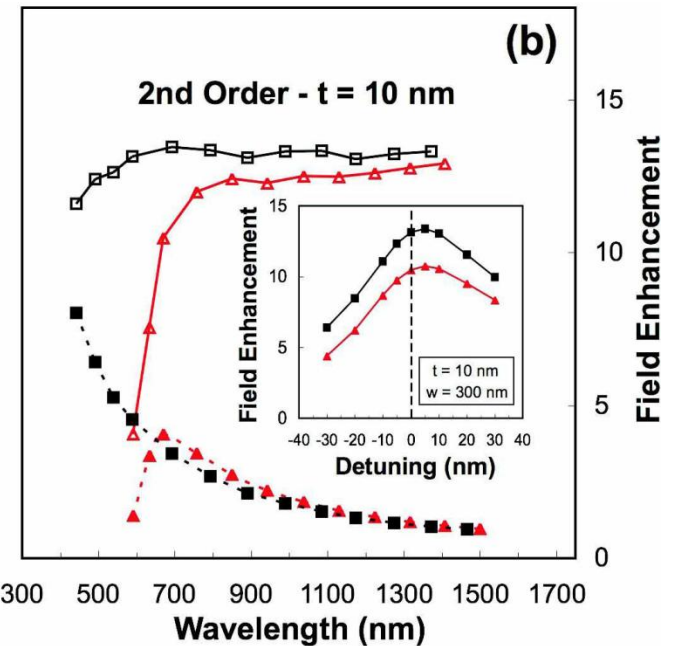
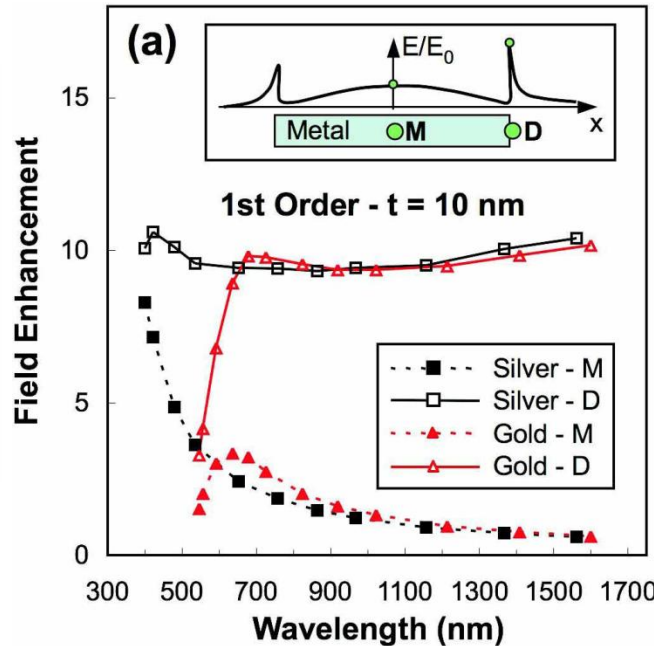
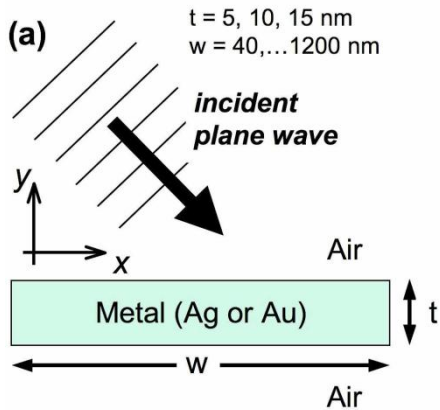
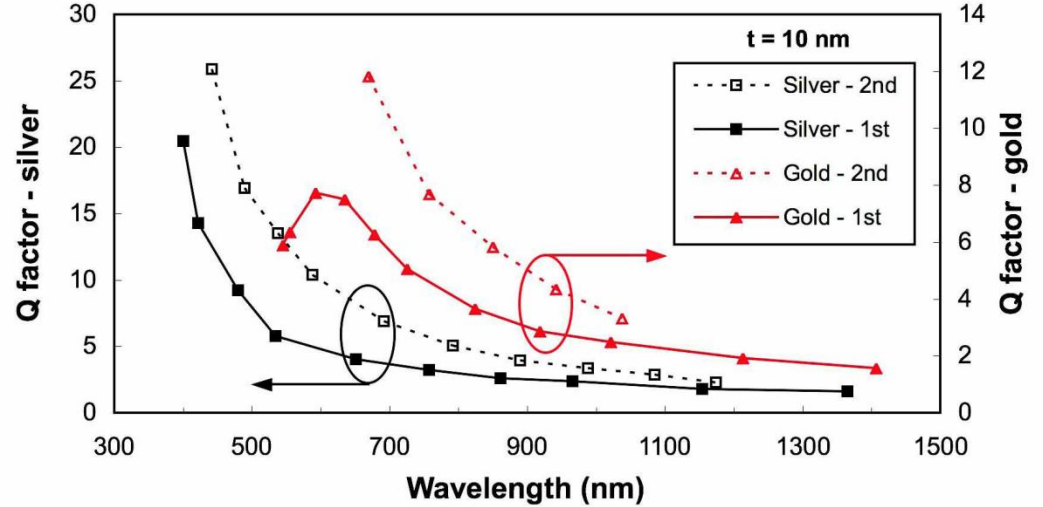
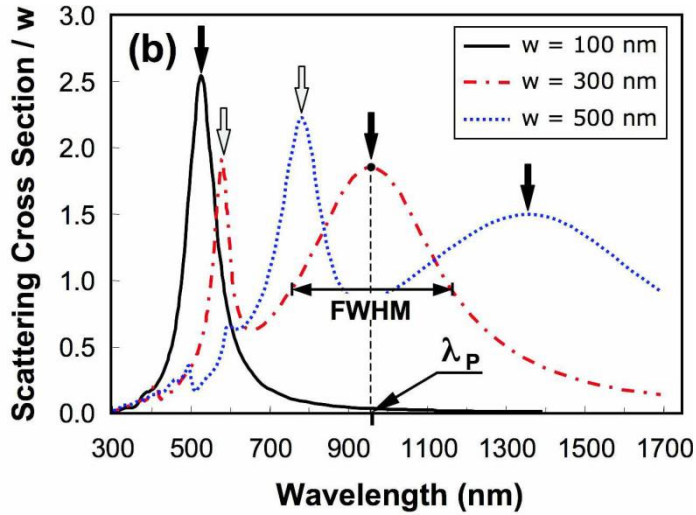


$w=100\text{nm}$, $l=708\text{nm}$,
Bottom-illuminated
(Field magnitudes > 10
have been set to 10).

Design of single-nano-strip optical resonators

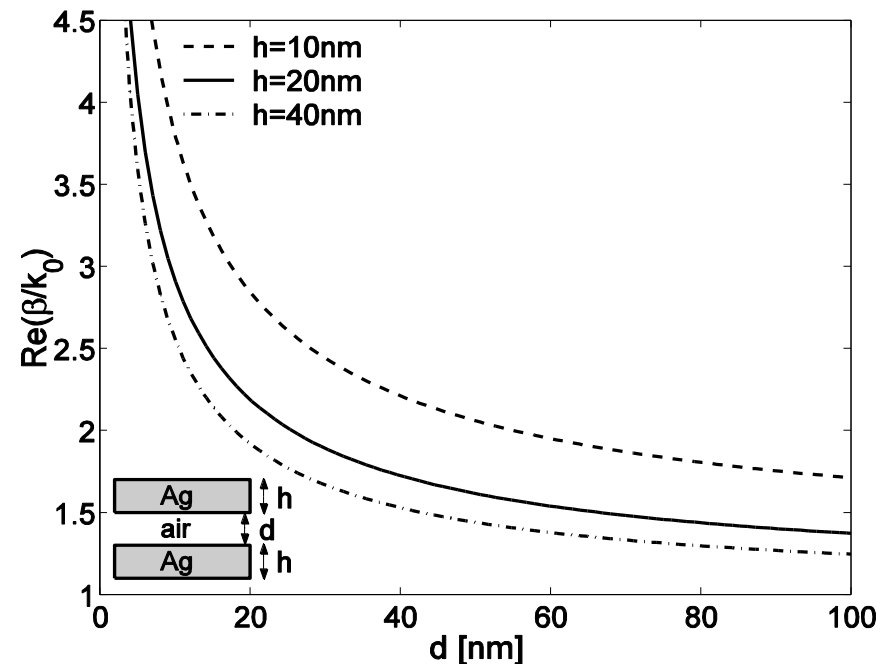
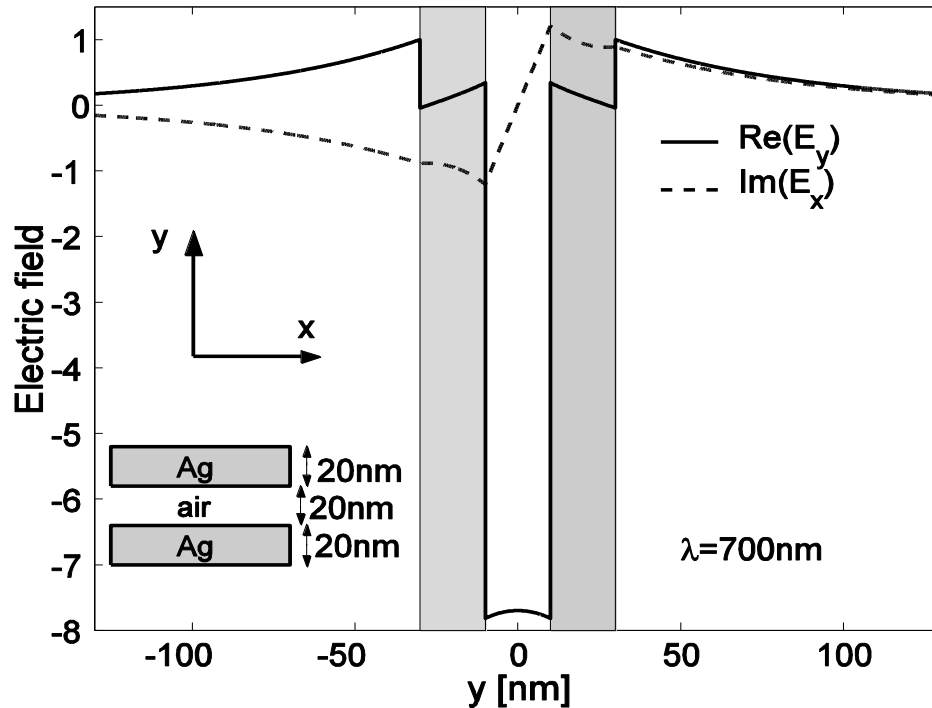


Q-factor and field enhancement



Ref.: G. Della Valle, T. Søndergaard, and S.I. Bozhevolnyi, Optics Express **16**, 6867 (2008).

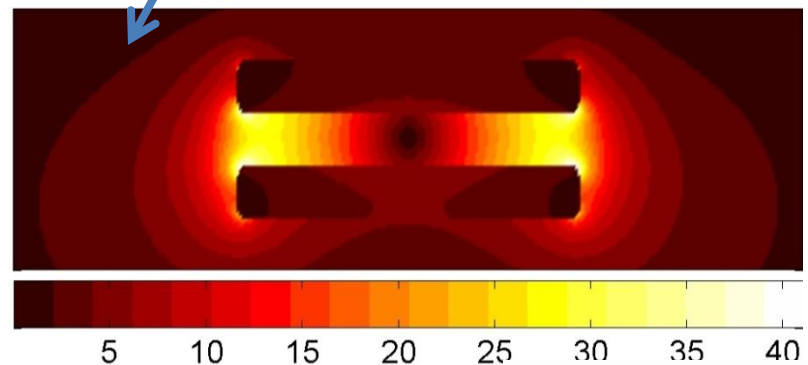
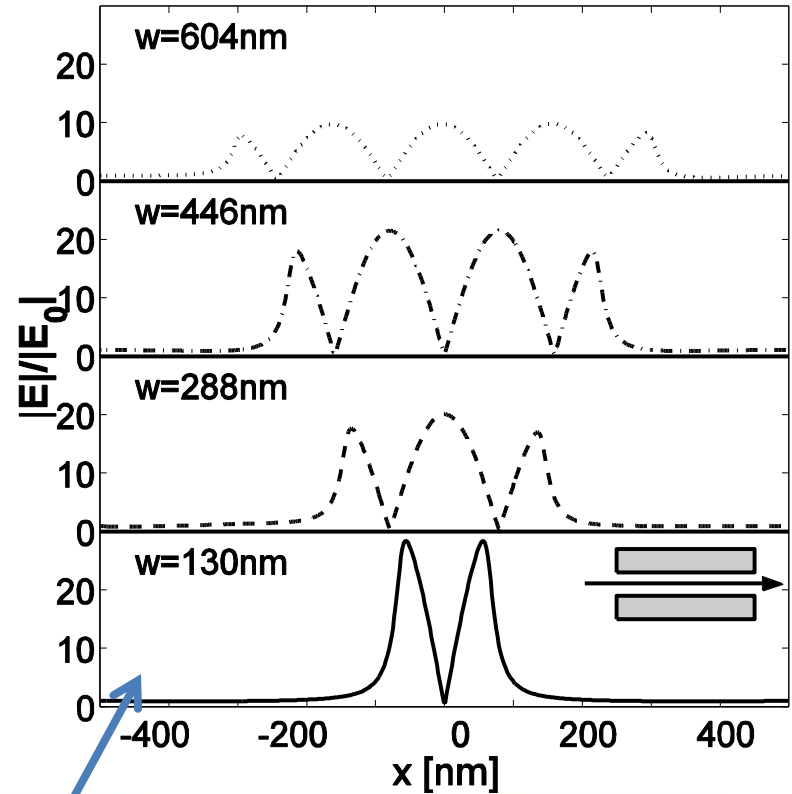
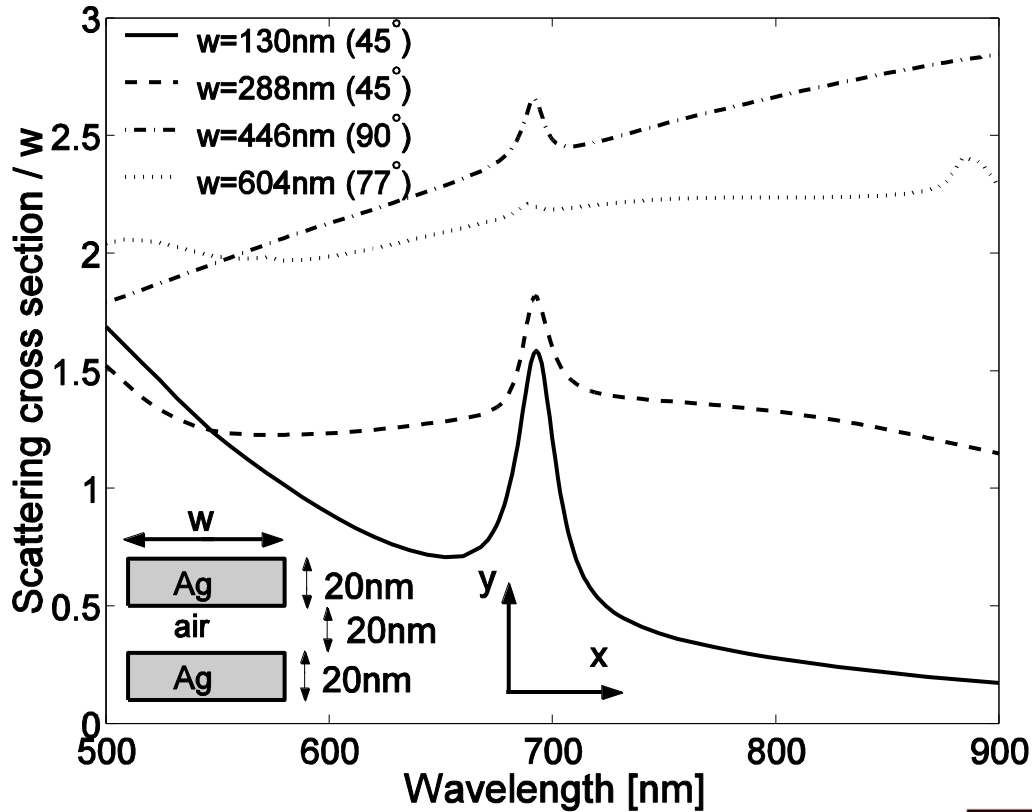
Gap plasmon polaritons between two metal films



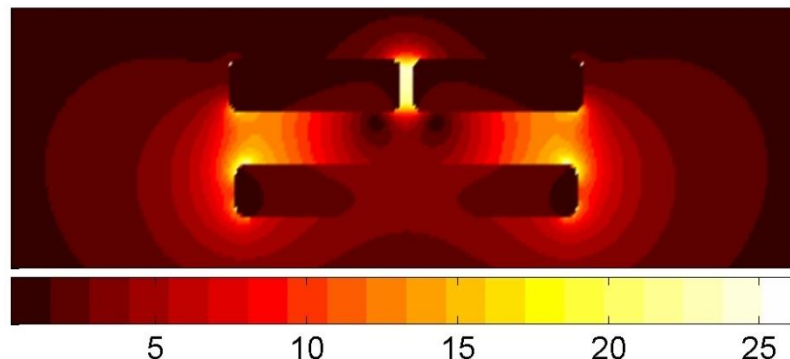
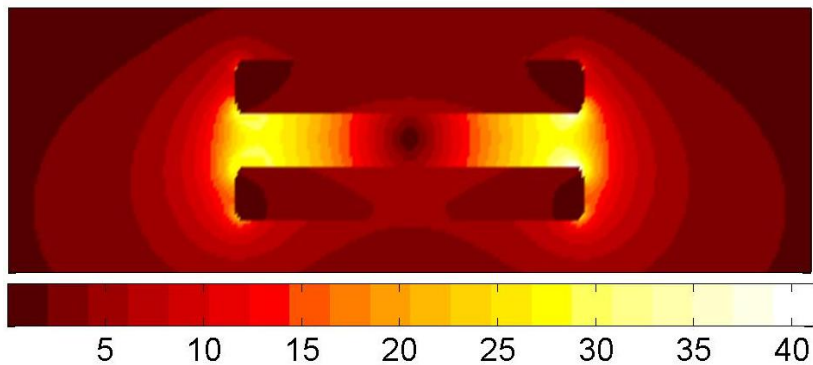
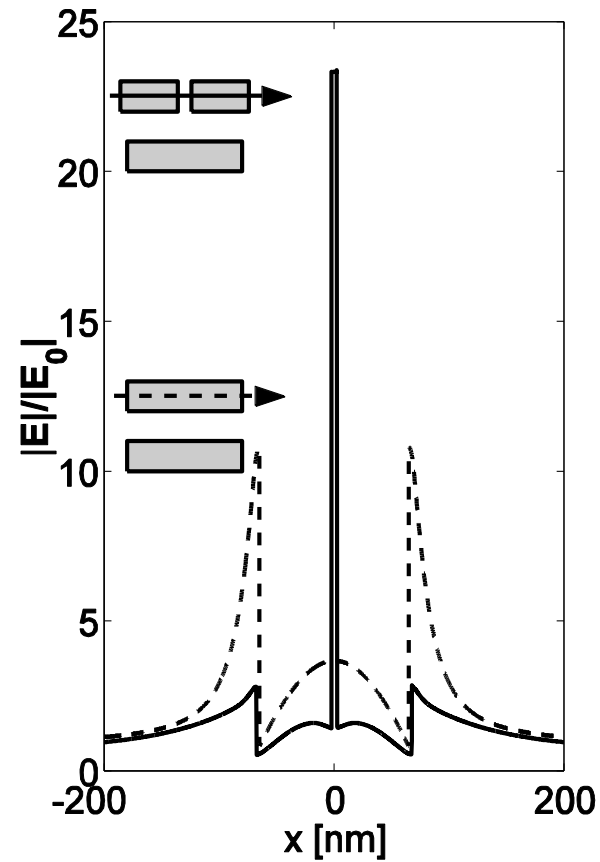
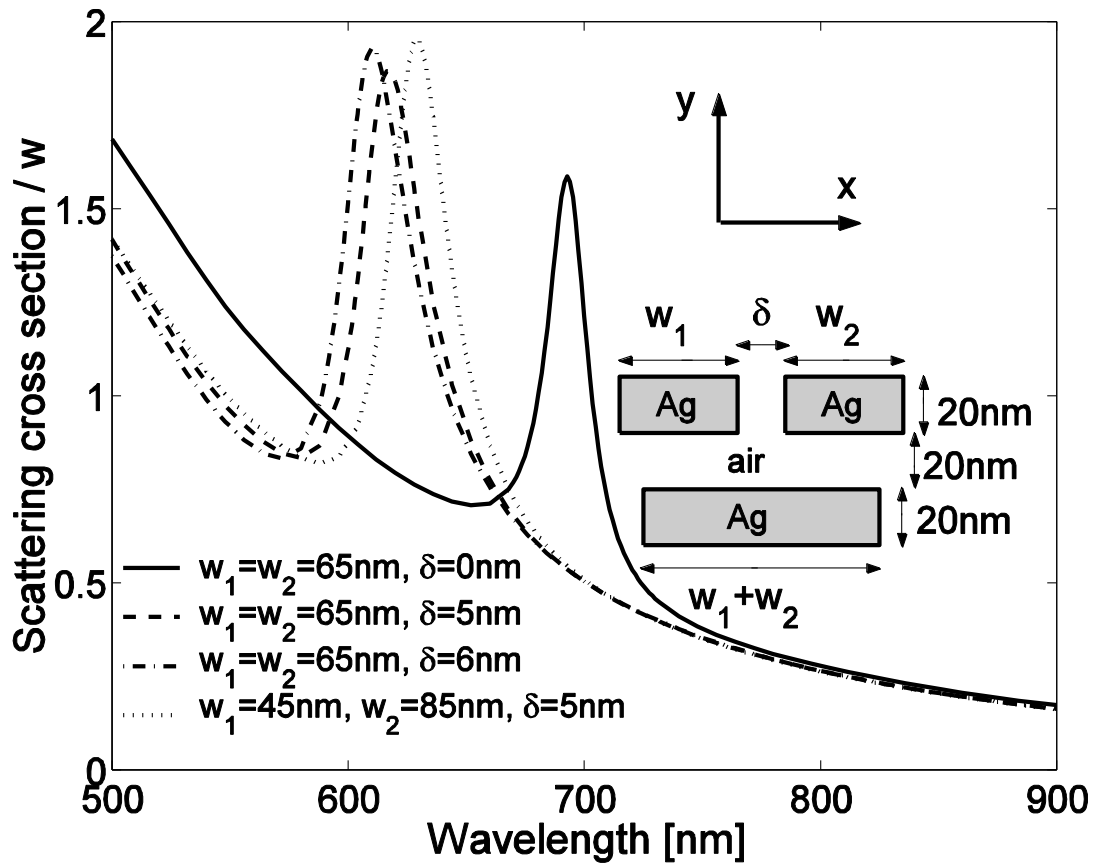
$$\mathbf{E}(\mathbf{r}) = \mathbf{E}(y)e^{-i\beta x}$$

- The x-component of the electric field dominates inside the metal films
- The mode index is larger compared to the single film and increases with decreasing gap and decreasing film thickness

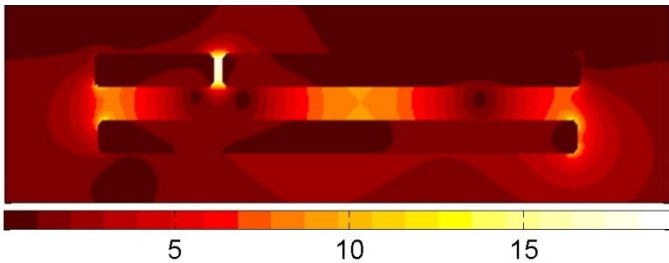
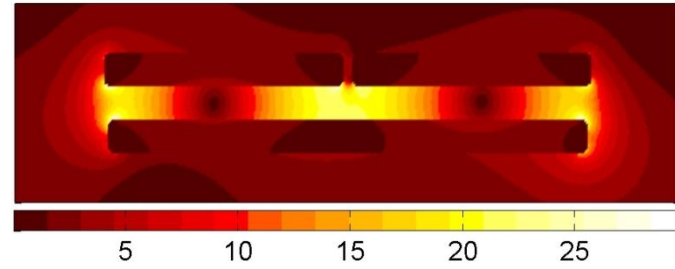
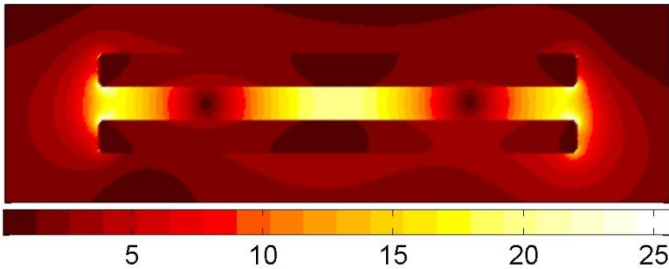
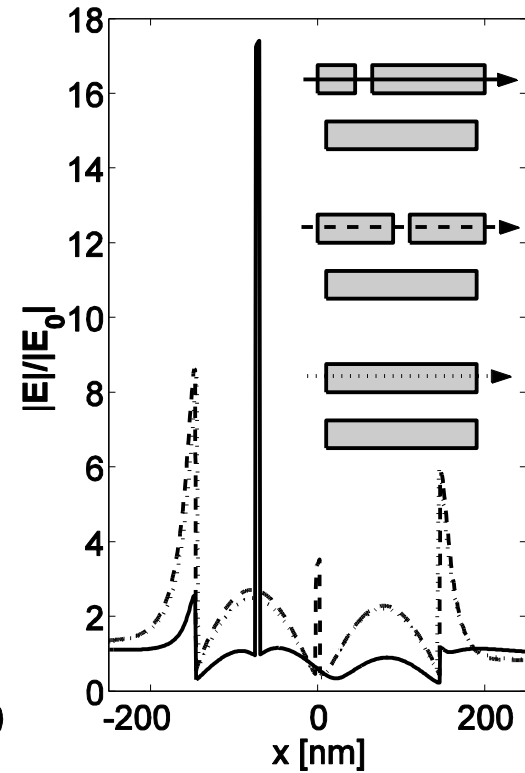
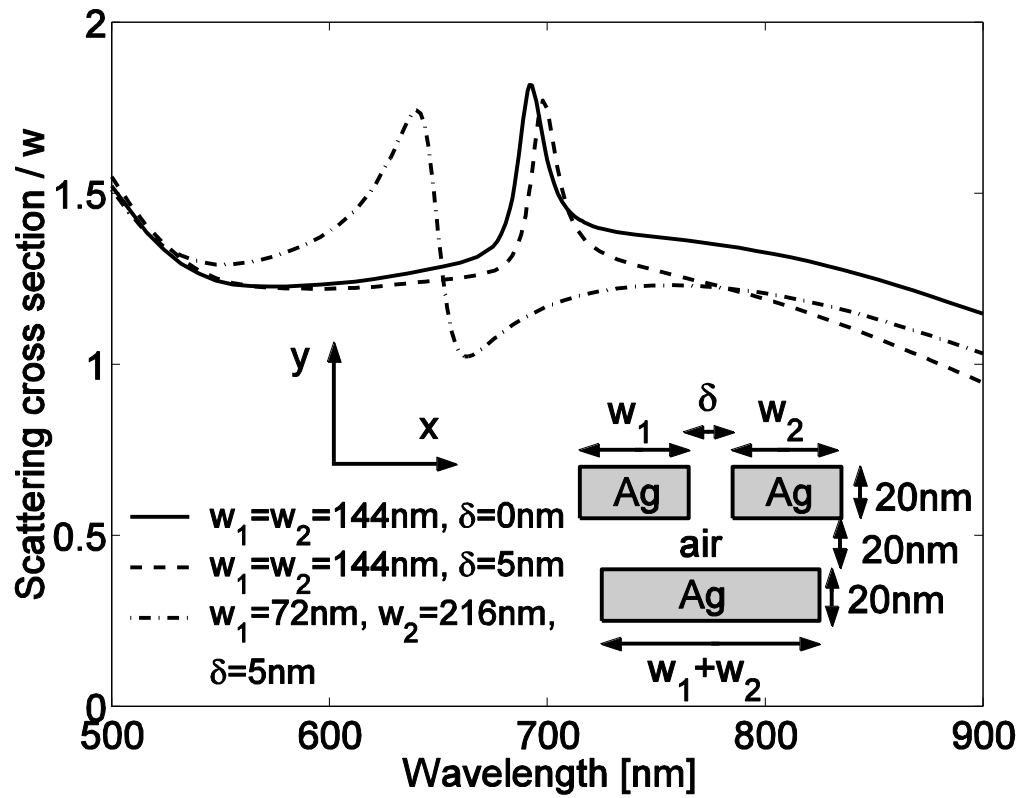
Gap plasmon polariton resonator



$$w \frac{2\pi}{\lambda} n_{slow} = m\pi - \phi$$

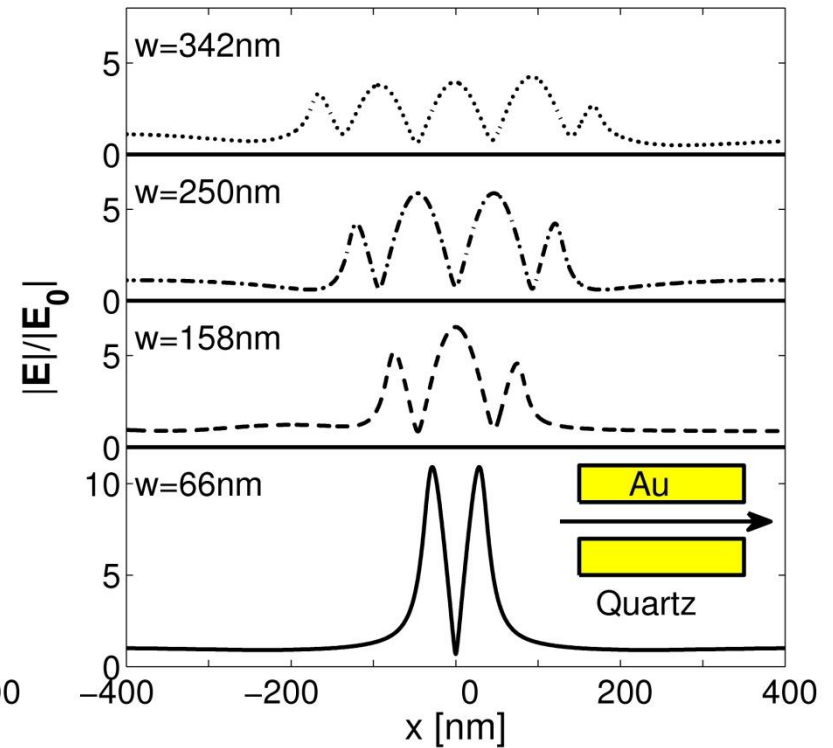
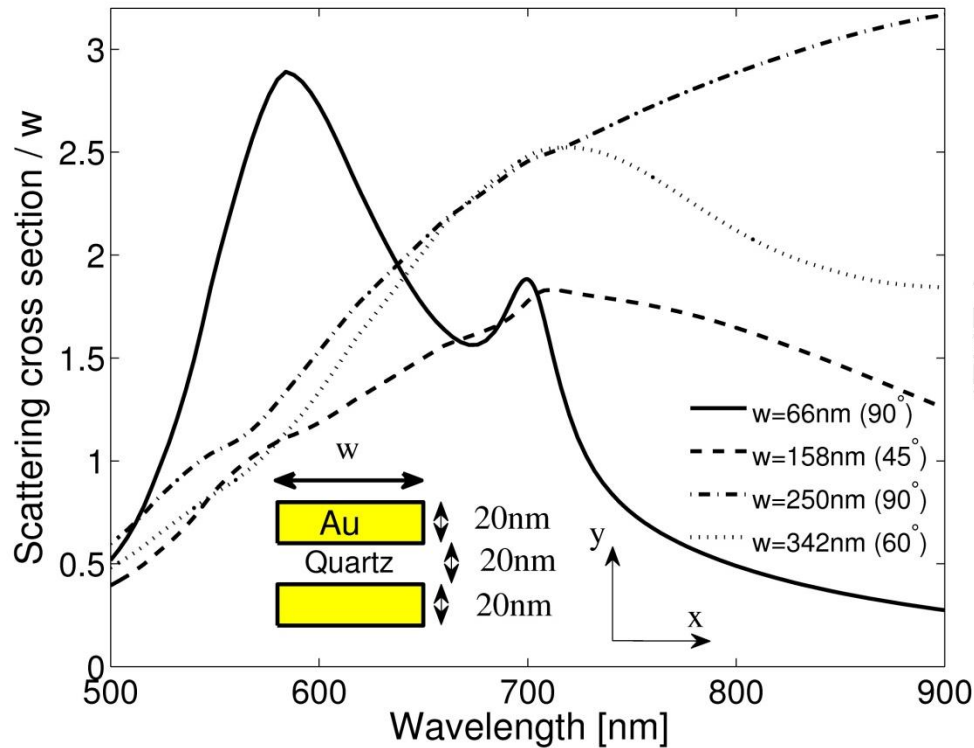


Ref.: T. Søndergaard, and S.I. Bozhevolnyi, Phys. Stat. Sol. (b) **245**, 9-19 (2008).



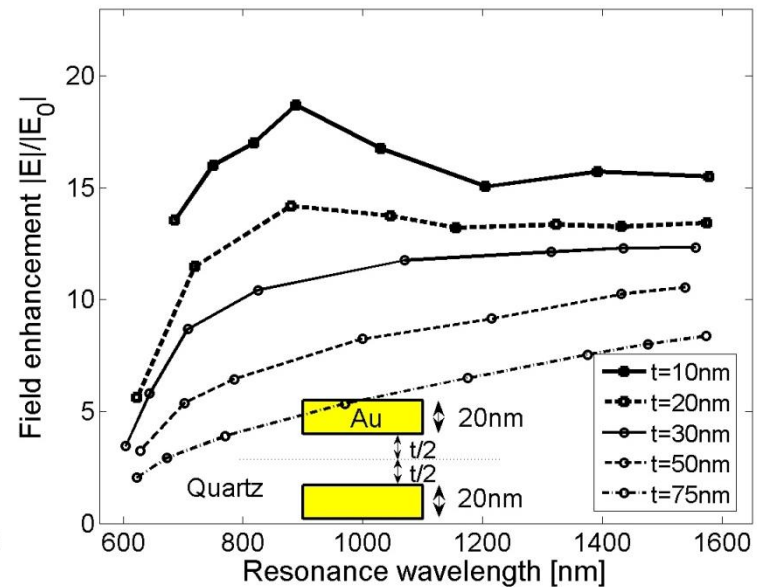
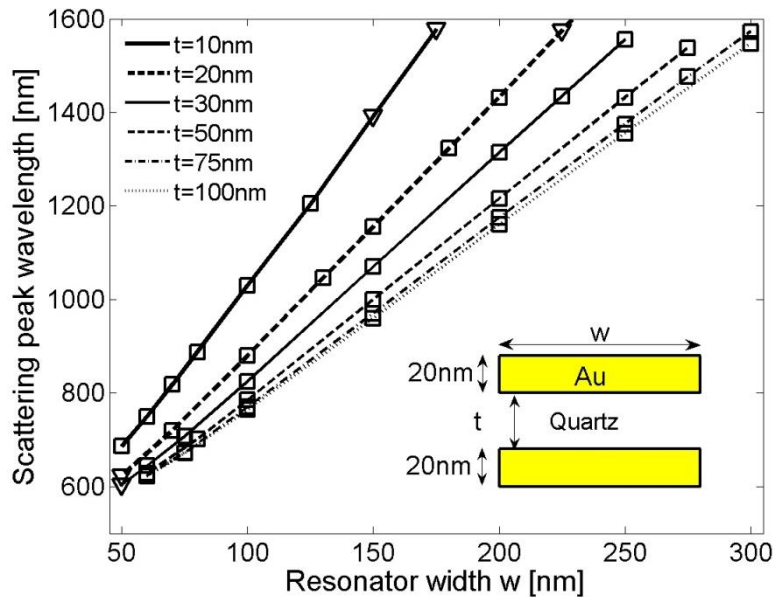
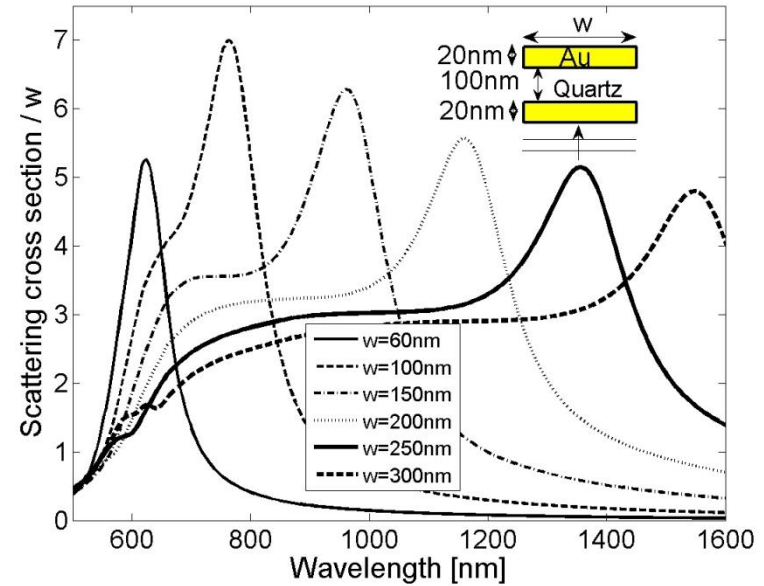
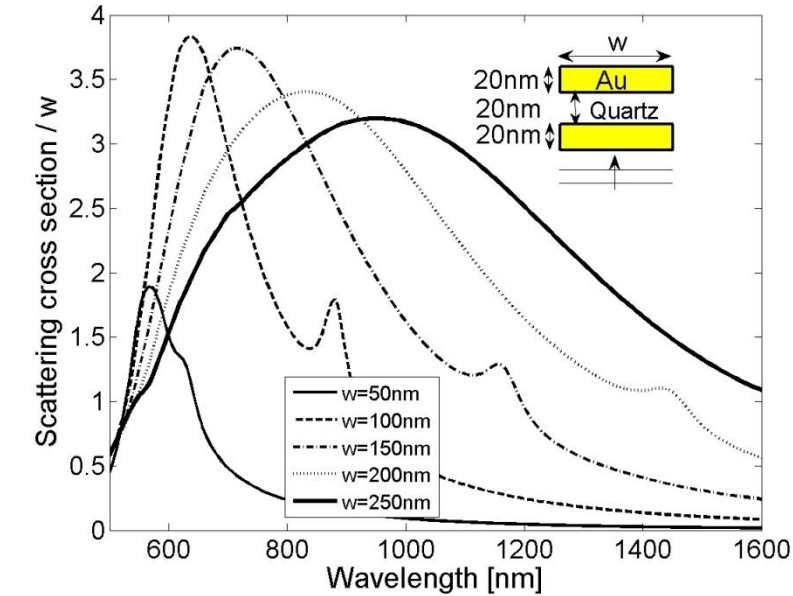
Ref.: T. Søndergaard, and S.I. Bozhevolnyi,
 Phys. Stat. Sol. (b) **245**, 9-19 (2008).

The gold gap plasmon metal nano-strip resonator

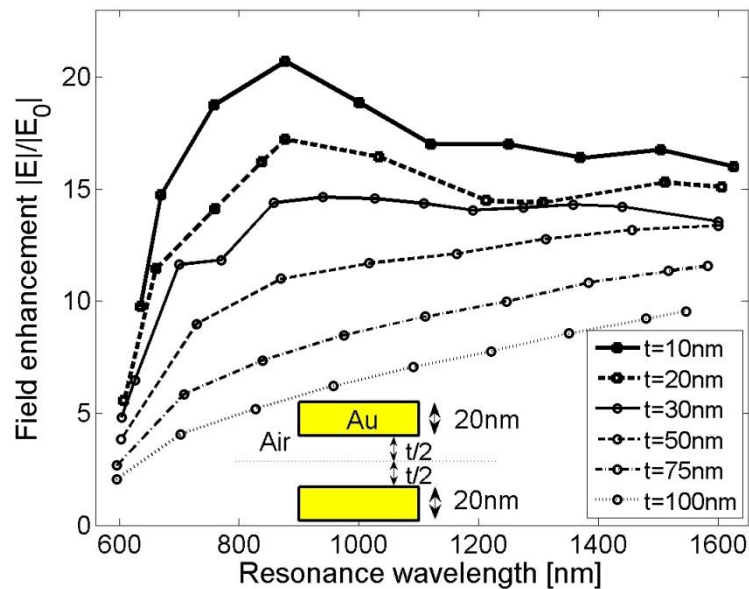
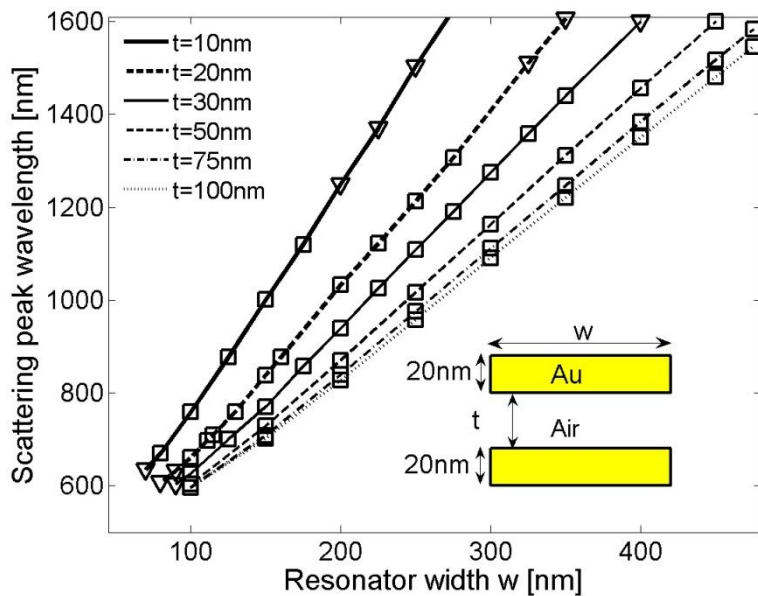
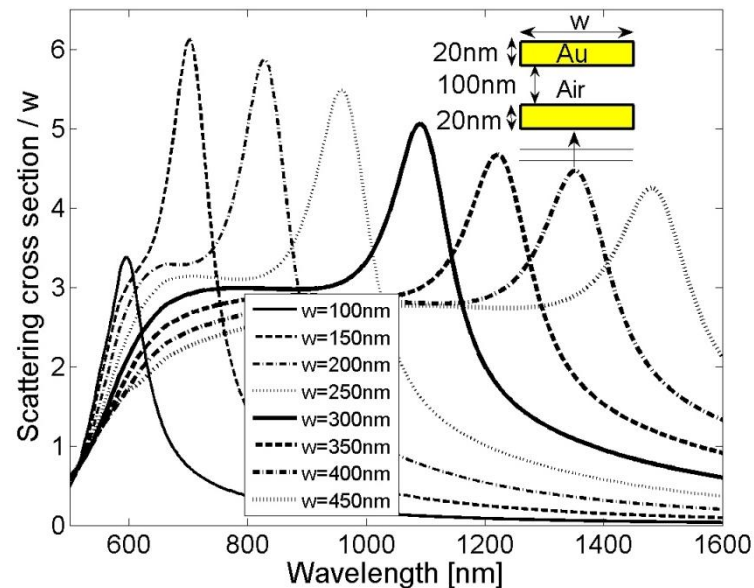
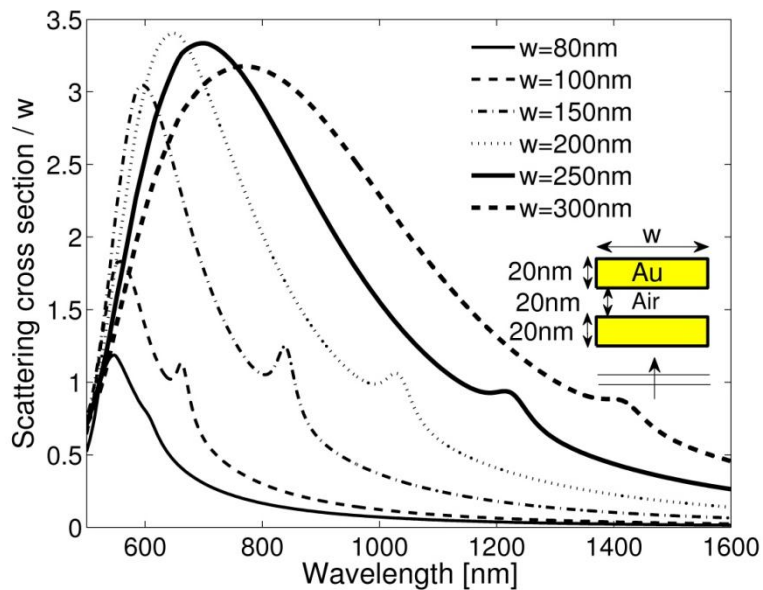


- Contrary to using silver the scattering peaks are hardly observable for the 3rd and 4th order resonances.
- Standing-wave fields are still clearly seen

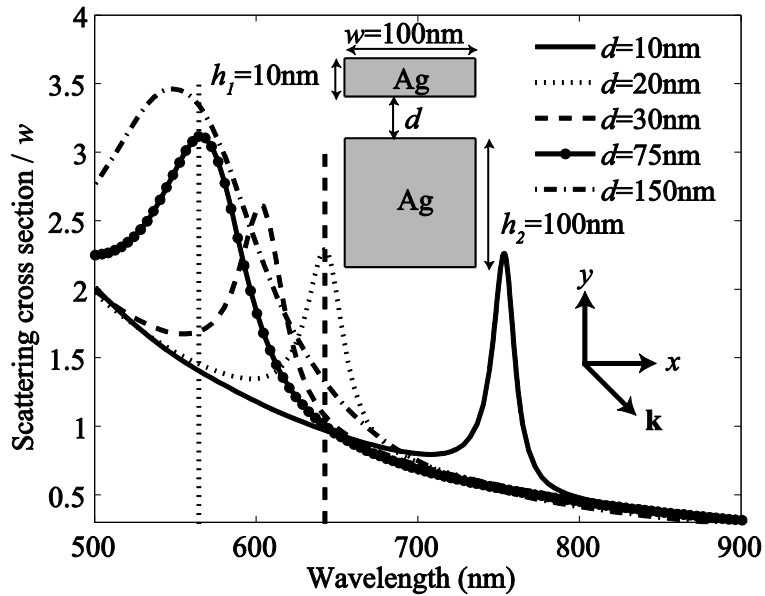
The gold gap plasmon metal nano-strip resonator



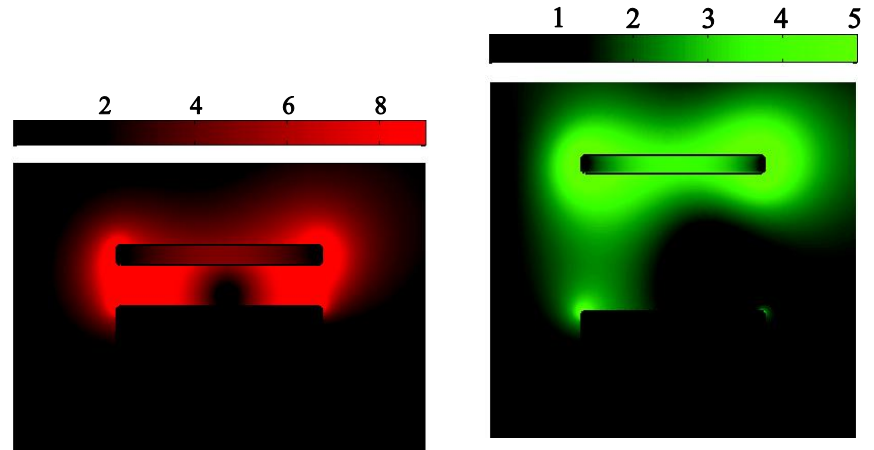
The gold gap plasmon metal nano-strip resonator



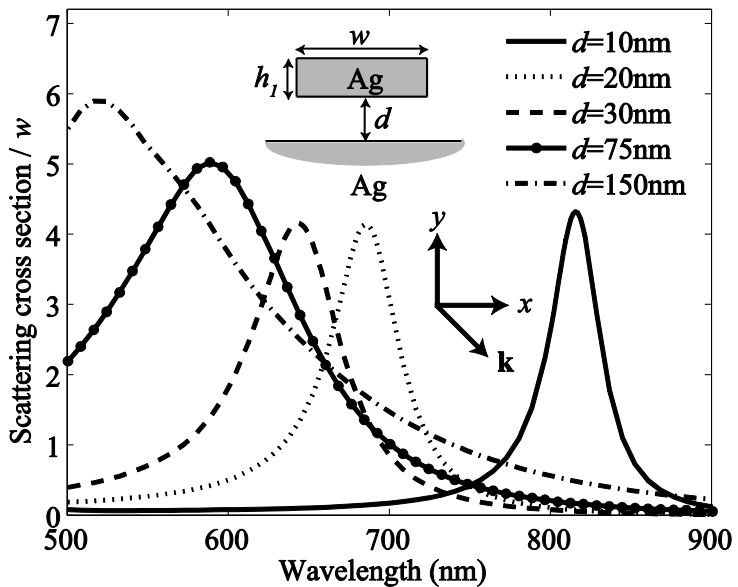
Single strip close to a thick metal block



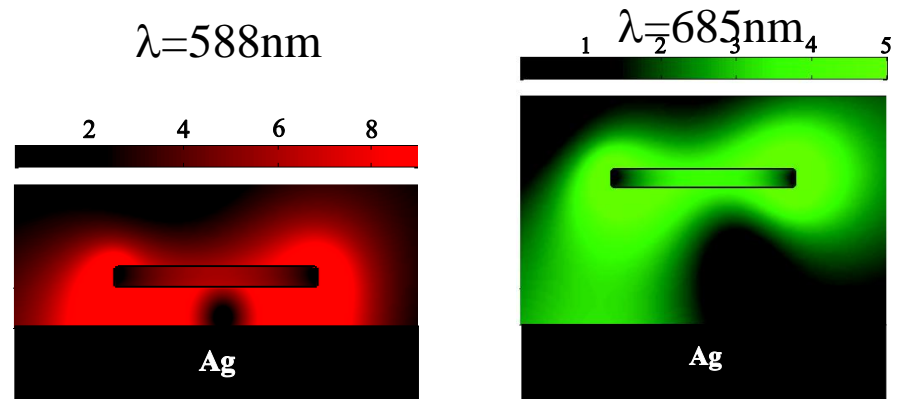
Electric field magnitude



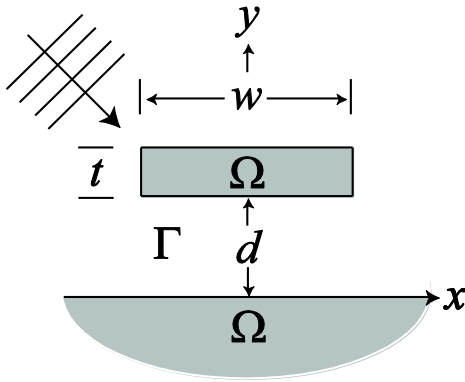
Electric field magnitude



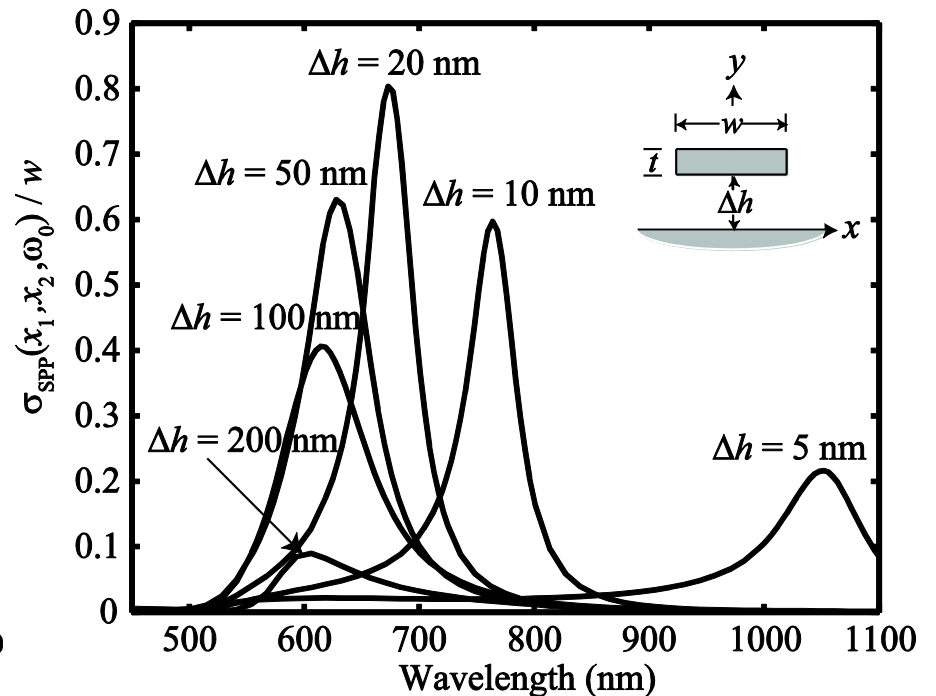
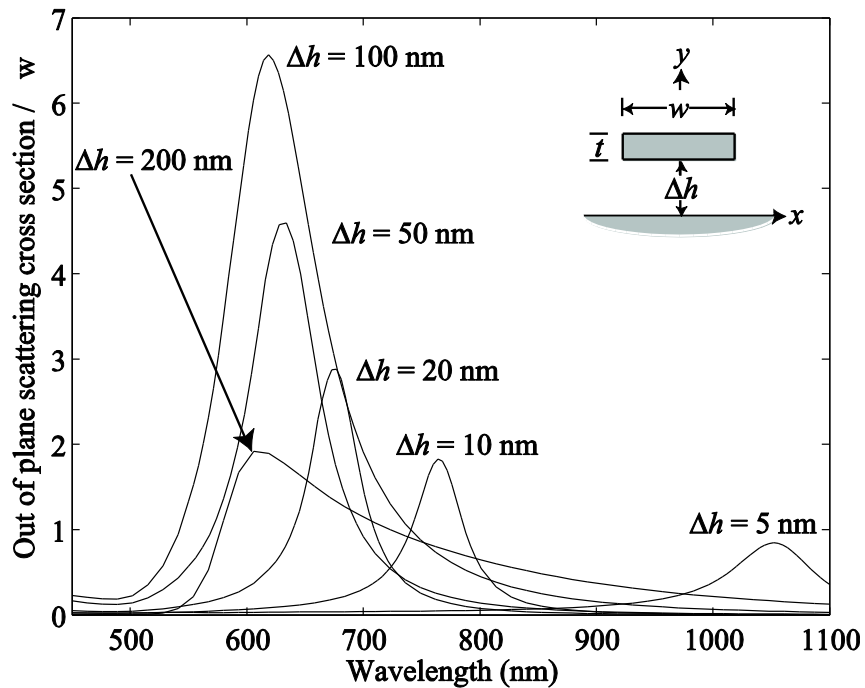
$\lambda=588\text{nm}$



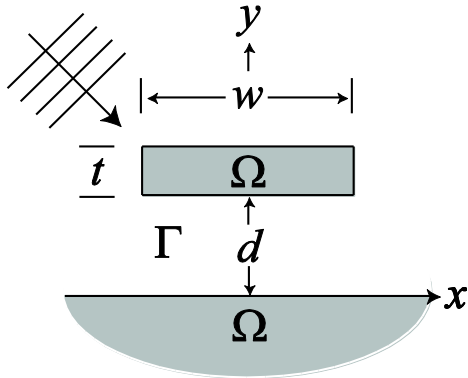
Gold-air gap plasmon resonators



In this case we also use the Green's function surface integral equation method. However, we avoid the surface integral over the infinite surface by using a specially constructed Green's function.



Special construction of Green's function



$$g_{\Gamma}(\mathbf{r}, \mathbf{r}') = \frac{1}{4i} H_0^{(2)}\left(k_0 \sqrt{\varepsilon_{\Gamma}} |\mathbf{r} - \mathbf{r}'|\right) - \frac{i}{2\pi} \int_{\kappa_x=0}^{\kappa_x=\infty} \frac{1}{\sqrt{k_0^2 \varepsilon_{\Gamma} - \kappa_x^2}} \cos(\kappa_x (x - x')) r^{(p)}(\kappa_x) e^{-i\sqrt{k_0^2 \varepsilon_{\Gamma} - \kappa_x^2} (y + y')} d\kappa_x$$

, $y, y' > 0$

Conclusion on metal nanostrip resonators

- Optical scattering resonances for metal nano-strip resonators is due to excitation of counter-propagating slow surface plasmon polaritons
- We can exploit the electromagnetics boundary conditions to obtain large field magnitudes.
- Robust enhancement of the magnitude of the electric field by a factor $\sim 20-30$.
- Excellent match of calculated and measured scattering spectra
- Near-linear relation between resonance wavelength and strip width for both strip and gap plasmon resonators

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