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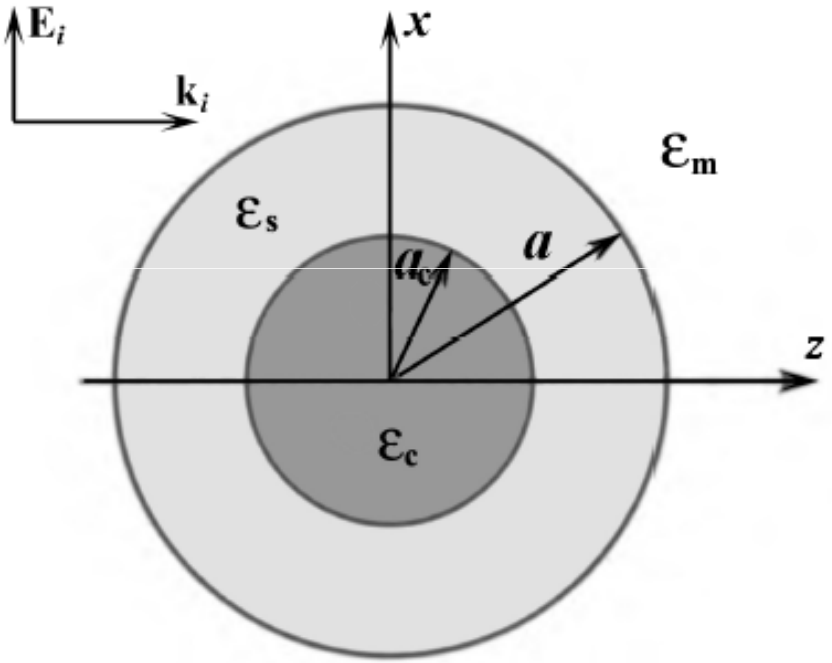
Surface plasmons in core-shell and non-spherical metal nanoparticles. Plasmonic crystals

1. SPR in core-shell nanoparticles (nanoshells)



Core-shell nanoparticles with dielectric core and metal shell – metal nanoshell.

dipole polarizability of core-shell spherical nanoparticle

$$\alpha = a^3 \frac{(\varepsilon_s - \varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + \beta(\varepsilon_m + 2\varepsilon_s)(\varepsilon_c - \varepsilon_s)}{(\varepsilon_s + 2\varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + 2\beta(\varepsilon_s - \varepsilon_m)(\varepsilon_c - \varepsilon_s)} \qquad \beta = (a_c/a)^3$$

$$\sigma_{abs} = 4\pi k_m \operatorname{Im}\alpha$$

- absorption cross-section

$$\sigma_{sca} = \frac{8\pi}{3} k_m^4 |\alpha|^2$$

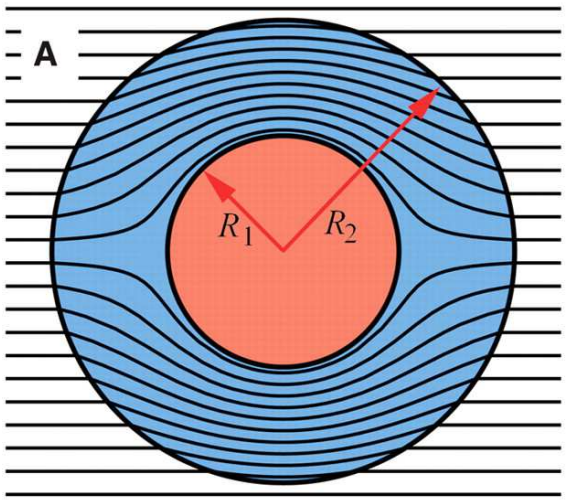
- scattering cross-section

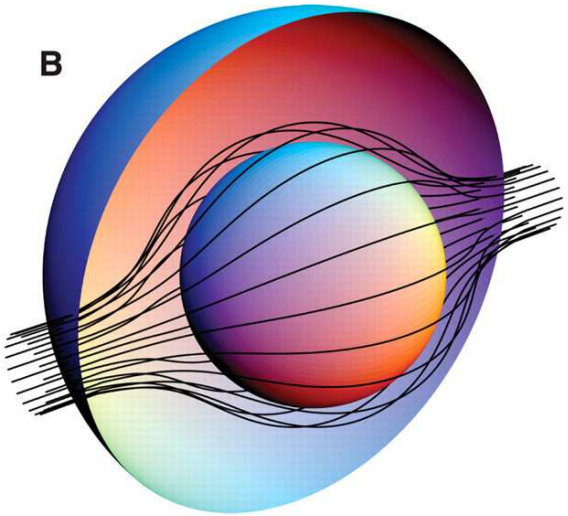
Plasmonic “invisibility cloak” by core-shell particles

The core-shell NP parameters can be selected to achieve its zero polarizability – **NP becomes invisible**:

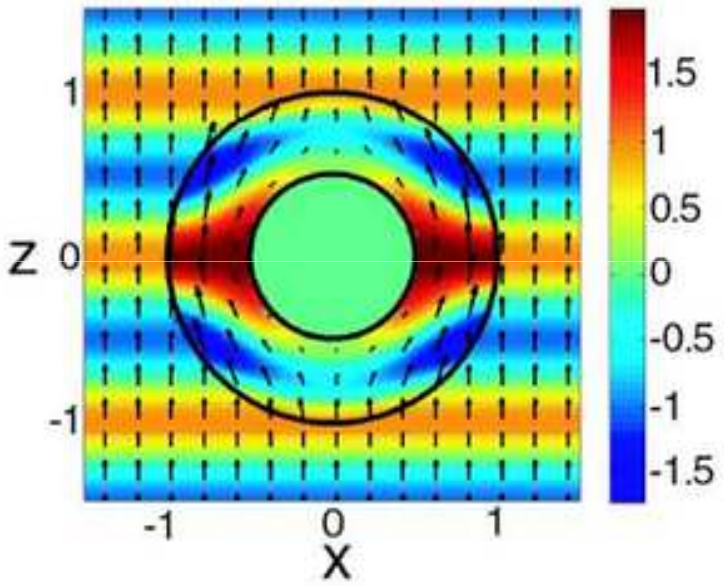
$$\alpha = a^3 \frac{(\varepsilon_s - \varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + \beta(\varepsilon_m + 2\varepsilon_s)(\varepsilon_c - \varepsilon_s)}{(\varepsilon_s + 2\varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + 2\beta(\varepsilon_s - \varepsilon_m)(\varepsilon_c - \varepsilon_s)} = 0$$

$$\beta \frac{\varepsilon_c - \varepsilon_s}{\varepsilon_c + 2\varepsilon_s} = \frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + 2\varepsilon_s}$$ - condition of the particle invisibility





EM-waves bending the invisible core-shell NP



Field distribution near invisible core-shell NP

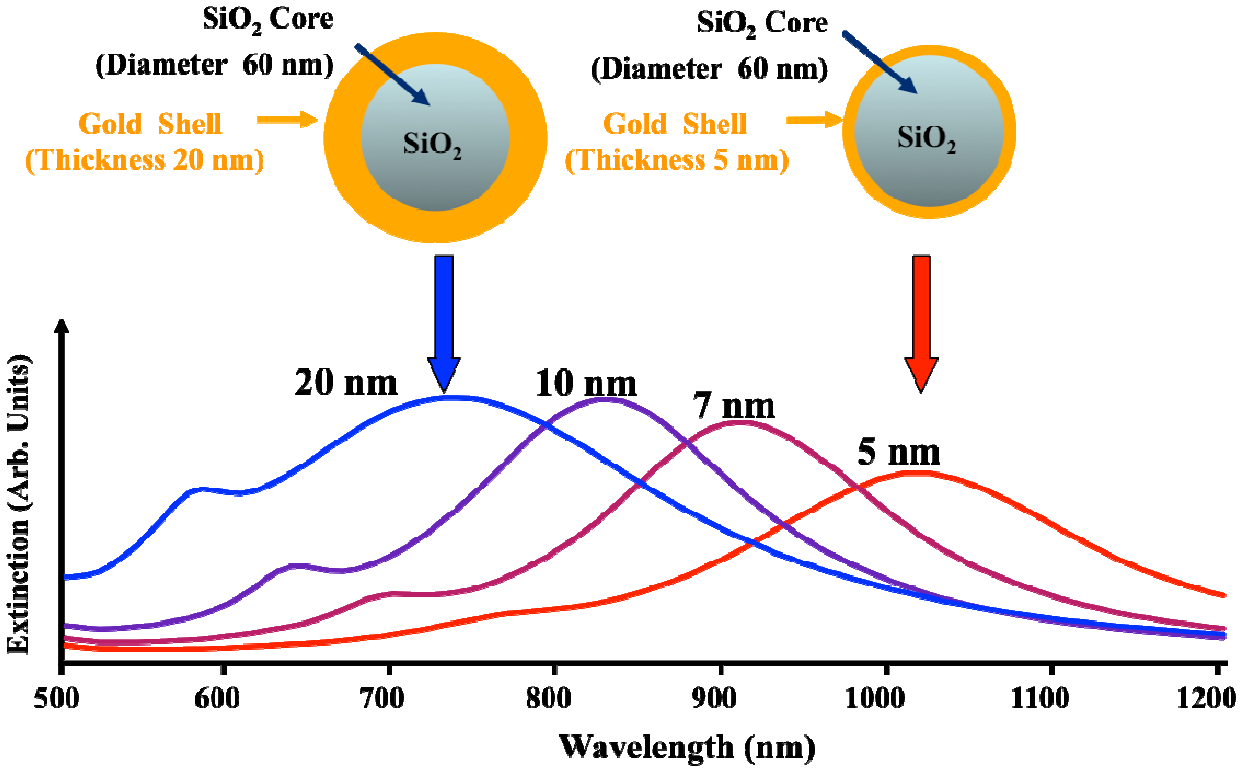
Wide spectral range tuning of optical spectra of metal nanoshells

$$\varepsilon_s = -\frac{5+4\beta}{4(1-\beta)} \pm \frac{3\sqrt{1+8\beta}}{4(1-\beta)}$$

- condition of dipole SPR in hollow metal nanoshell

$$\omega_{sp,1\pm} = \omega_p \left[\frac{1}{2}\left(1 \pm \frac{\sqrt{1+8\beta}}{3} \right) \right]^{1/2}$$

- existence of two SP modes: large red shift of low-energy mode and slight blue shift of high-energy mode when the shell becomes thinner



2. Surface plasmons in non-spherical metal nanoparticles

Unlike to spherical metal NPs, the **NPs with non-spherical shape have several SP-modes**. Number of SP-modes is equal to number of non-equivalent axes of symmetry of NP.

$$K(\omega) = \frac{f\varepsilon_m^{3/2}\omega}{3c}\sum_{j=1}^{3}\frac{\frac{1}{P_j^2}\varepsilon_2}{\left(\varepsilon_1 + \frac{1-P_j}{P_j}\varepsilon_m\right)^2 + \varepsilon_2^2}$$

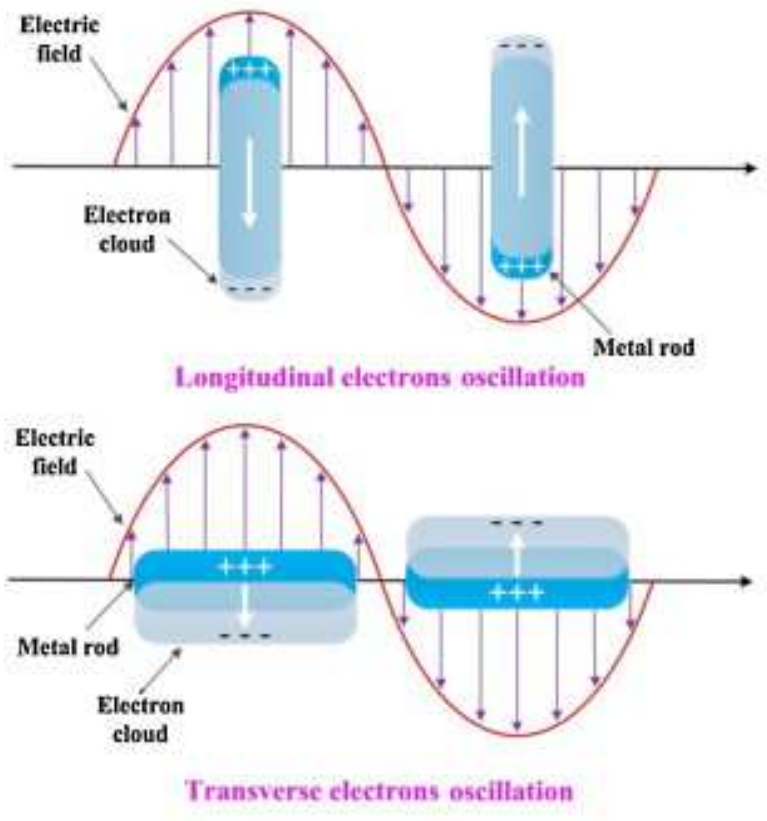
- absorption coefficient of nanocomposite containing the non-interacting non-spherical NPs

$$\varepsilon_1 = -\frac{1-P_j}{P_j}\varepsilon_m$$

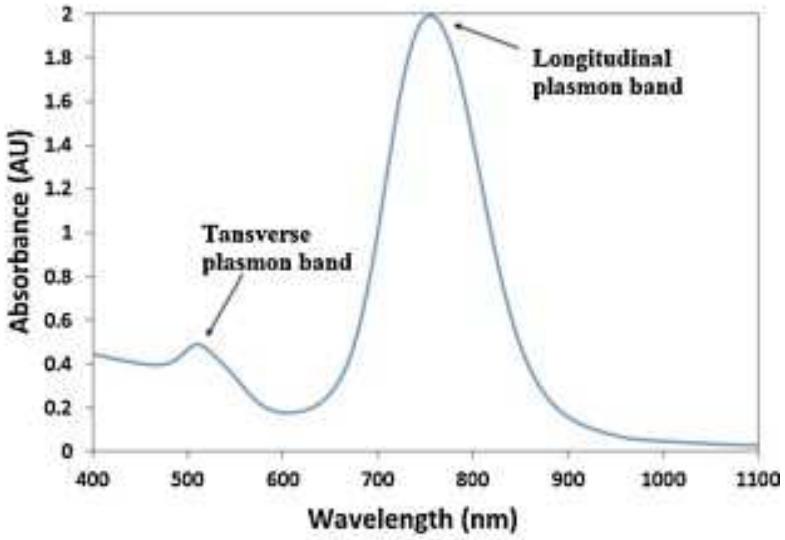
- condition of the excitation of j-th dipolar SP-mode in the non-spherical NP (P_j - geometrical factor of j-th axis of symmtery)

Variation of the shape parameters of NP allows to tune the plasmonic absorption and scattering spectra in very wide spectral range.

2.1. Surface plasmons in metal nanorods and elongated 2-axes ellipsoids



(a)



(b)

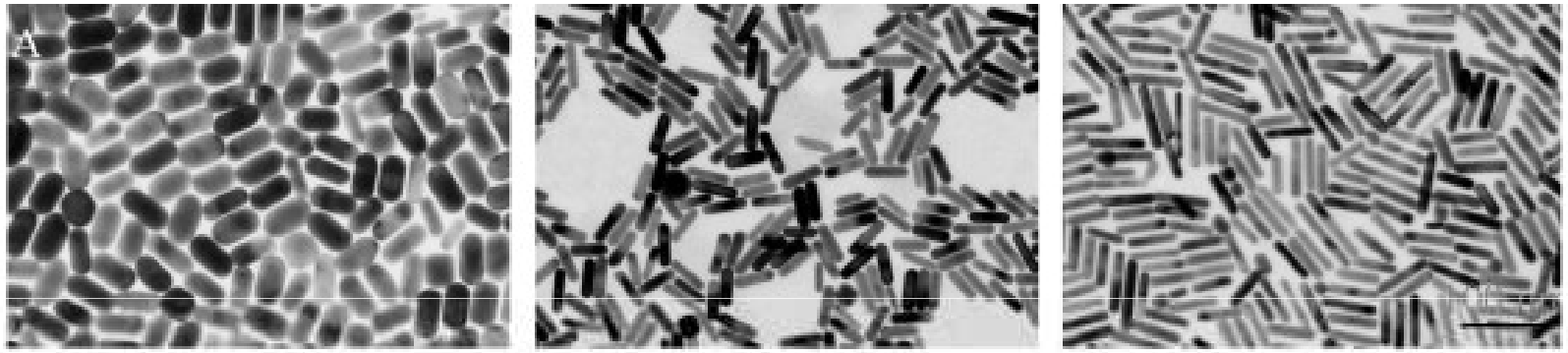
$$P_1 = \frac{1-e^2}{e^2}\left[\frac{1}{2e}\ln\frac{1+e}{1-e} - 1\right] \qquad P_2 = P_3 = \frac{1-P_1}{2}$$

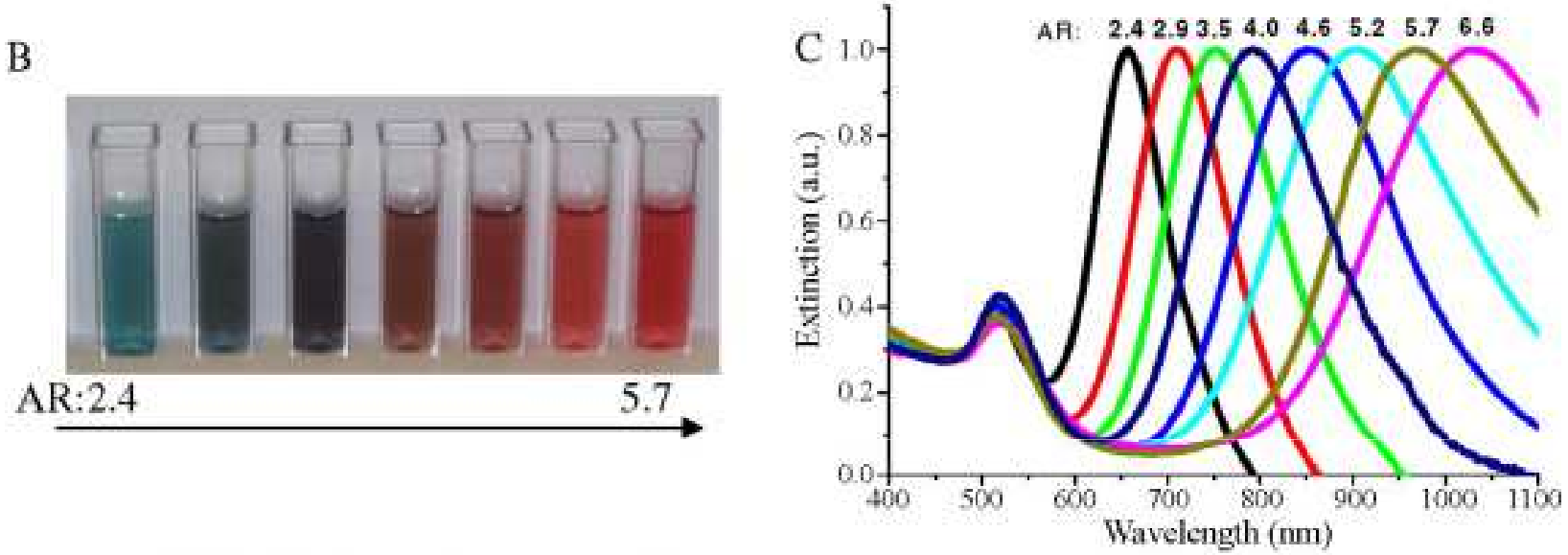
- geometrical factors of symmetry axes of the nanorod

$$e = \sqrt{1-\left(\frac{b}{a}\right)^2} = \sqrt{1-\frac{1}{R^2}}$$ - eccentricity of the nanorod

$$R = \frac{a}{b}$$ - aspect ratio of the nanorod

The nanorod spectrum tuning by variation of its aspect ratio

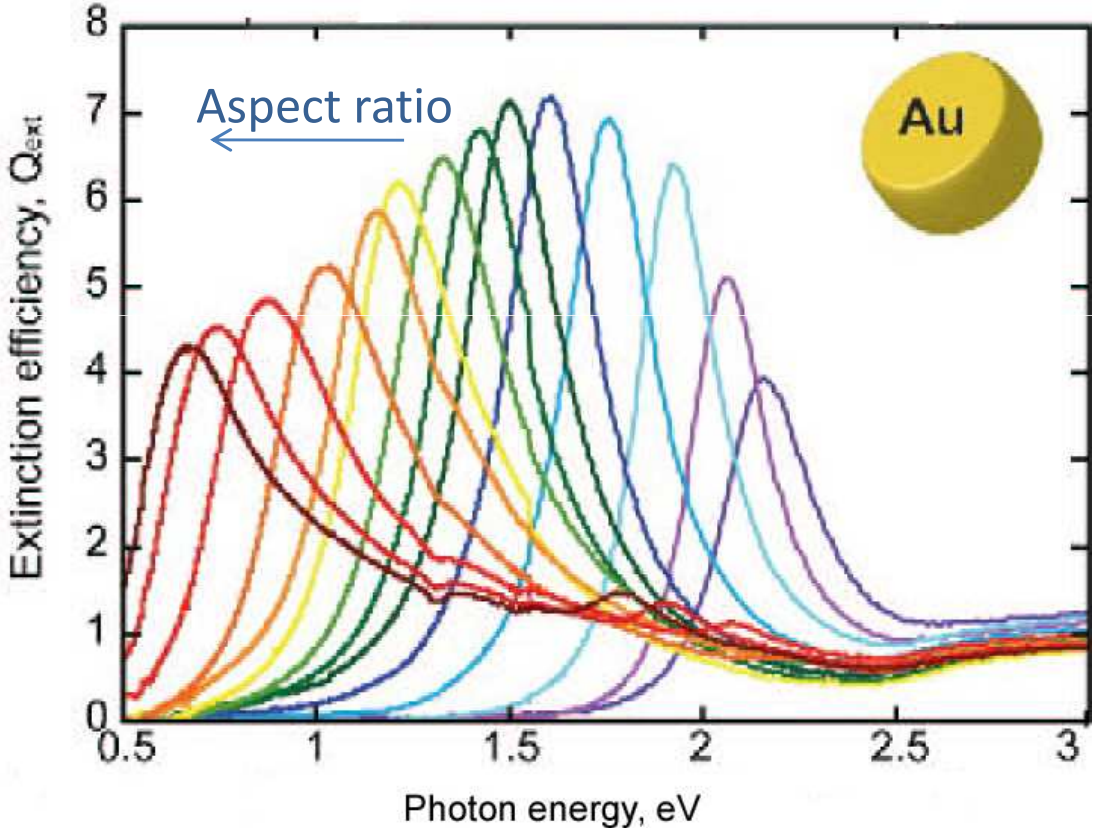




$$\lambda_{\max}\left(R,\varepsilon_m\right)=\left(c_1R+c_2\right)\varepsilon_m+c_3$$

The aspect ratio increase causes the large red shift of low-energy longitudinal (L) SP-mode, while the frequency of high-energy transversal SP-mode almost does not change.

2.2. Surface plasmons in metal nanodisks and oblate ellipsoids



$$R = \frac{a}{c}$$ - aspect ratio of the nanorod

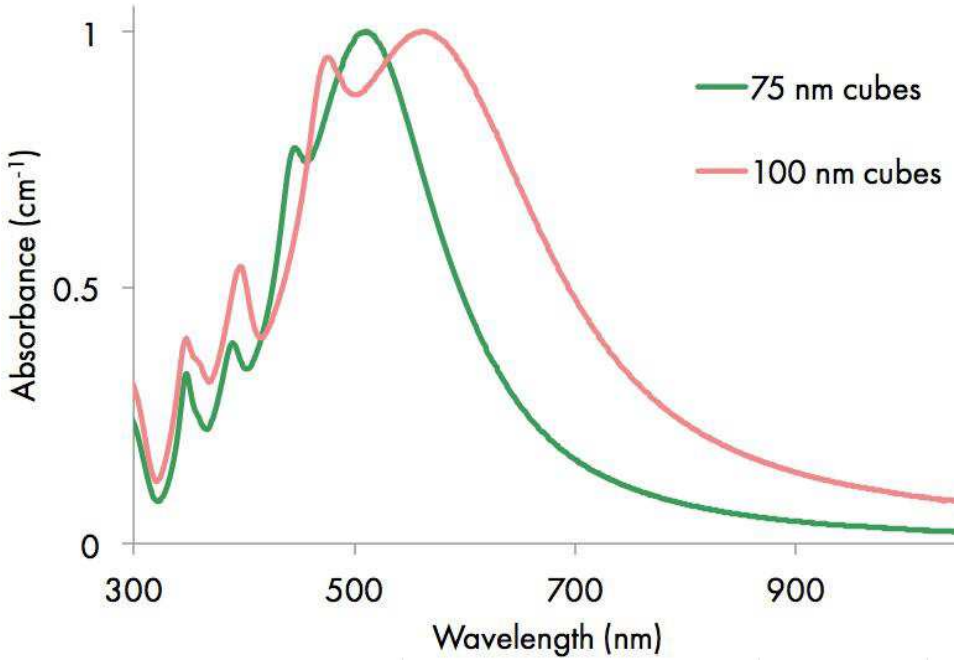
$$P_3 = \frac{g(e)}{2e^2}\left[\frac{\pi}{2} - \operatorname{arctg} g(e)\right] - \frac{g^2(e)}{2} \qquad P_1 = P_2 = \frac{1 - P_3}{2}$$

- geometrical factors of symmetry axes of the nanodisk

$$g(e) = \left(\frac{1-e^2}{e^2}\right)^{1/2}, \quad e = \sqrt{1-\left(\frac{c}{a}\right)^2} = \sqrt{1-\frac{1}{R^2}}$$

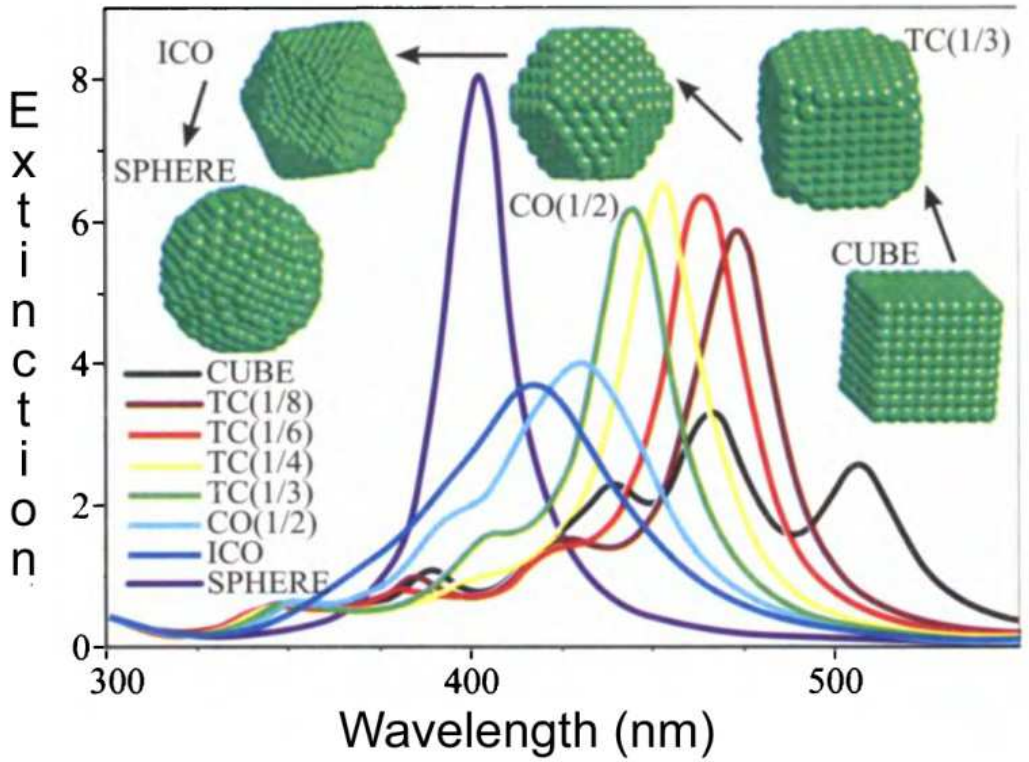
- eccentricity of the nanodisk

2.3. Surface plasmons in metal multi-facet nanoparticles



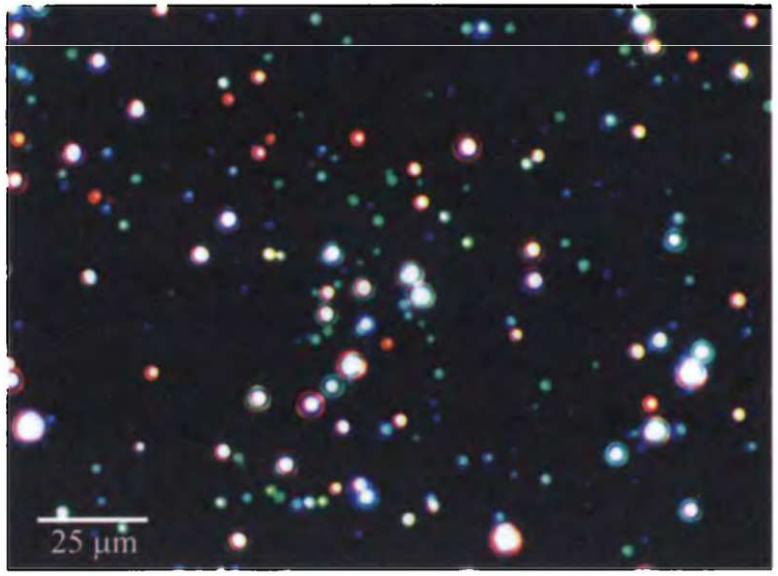
Absorption spectra of gold nanocube

Transformation of plasmonic extinction spectra of multi-facet gold NP from cube to sphere



Conclusion:

1. The variation of parameters of core-shell and non-spherical nanoparticles is very effective and suitable tool for essential controlable tuning of the absorption and scattering spectra that are important for the fabrication of plasmon based nanophotonics devices.



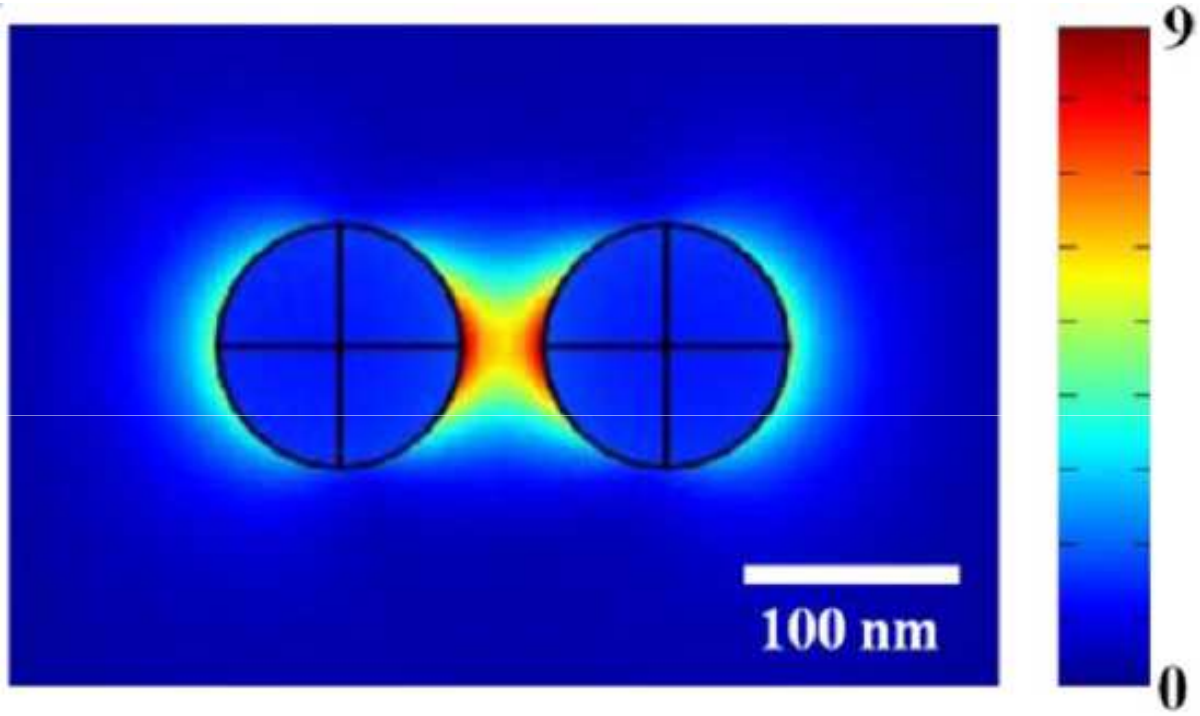
The images of Ag NPs of various shapes and sizes obtained by dark field microscopy.

2. The metal core-shell nanoparticles are perspective material for the fabrication of the metamaterials for coatings with invisibility properties.

3. Surface plasmon coupling in clusters of metal nanoparticles

In clusters containing several metal NPs the coupling of SPs of neighbour NPs leads to collectivization (hybridization) of SPs. The hybridization is the physical mechanism of the formation of collective SP-modes of entire cluster.

3.1. Surface plasmon modes in plasmonic dimer



Plasmonic field distribution in dimer of spherical metal NPs showing the plasmonic coupling . The strong field (hot spot) appears in the gap between the NPs.

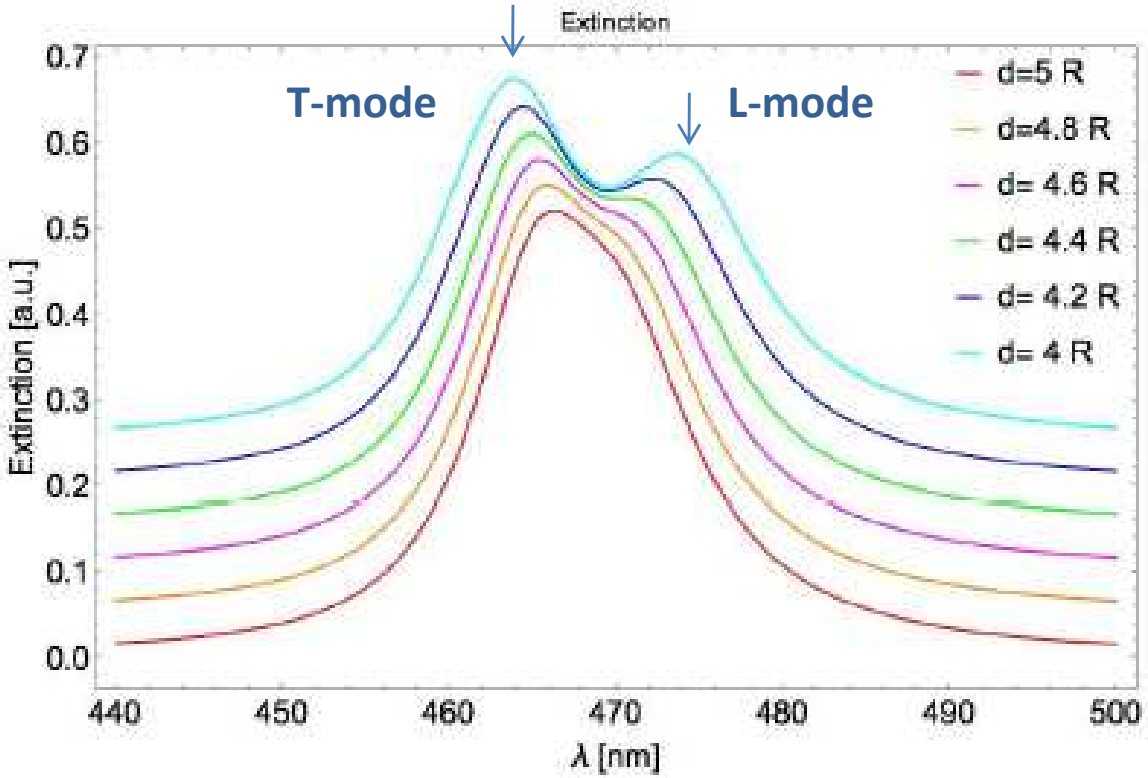
The model of dipole plasmon coupling in plasmonic dimer

Dipole polarizability of isolated NP

$$\alpha_1(\omega) = \alpha_2(\omega) = 4\pi R^3 \frac{\varepsilon(\omega) - \varepsilon_h}{\varepsilon(\omega) + 2\varepsilon_h}$$

Dipole polarizabilities of dimer

$$\tilde{\alpha}_\perp = \frac{\alpha_1 + \alpha_2 - \frac{\alpha_1\alpha_2}{2\pi d^3}}{1 - \frac{\alpha_1\alpha_2}{(2\pi d^3)^2}} \qquad \tilde{\alpha}_\parallel = \frac{\alpha_1 + \alpha_2 + \frac{\alpha_1\alpha_2}{2\pi d^3}}{1 - \frac{\alpha_1\alpha_2}{(2\pi d^3)^2}}$$

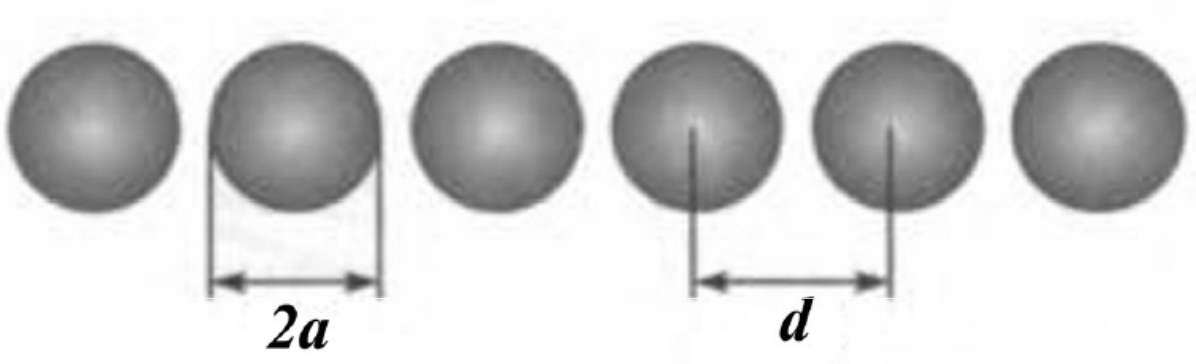


$$\tilde{\alpha} = \frac{1}{2}\left(\tilde{\alpha}_\parallel \cos\theta + \tilde{\alpha}_\perp \sin\theta\right)$$

$$\sigma_{ext} = \frac{2\pi}{\lambda} \operatorname{Im} \tilde{\alpha}$$

Light extinction cross-section

3.2. Collective surface plasmon modes in periodic linear chain of metal NPs (1D plasmonic crystal)



Plasmonic dipole of each NP creates the electric field

$$\mathbf{E} = \mathbf{E}_n + \mathbf{E}_m + \mathbf{E}_f$$

Dipole near field $(r \ll \lambda)$ $\quad E_n \sim 1/r^3$

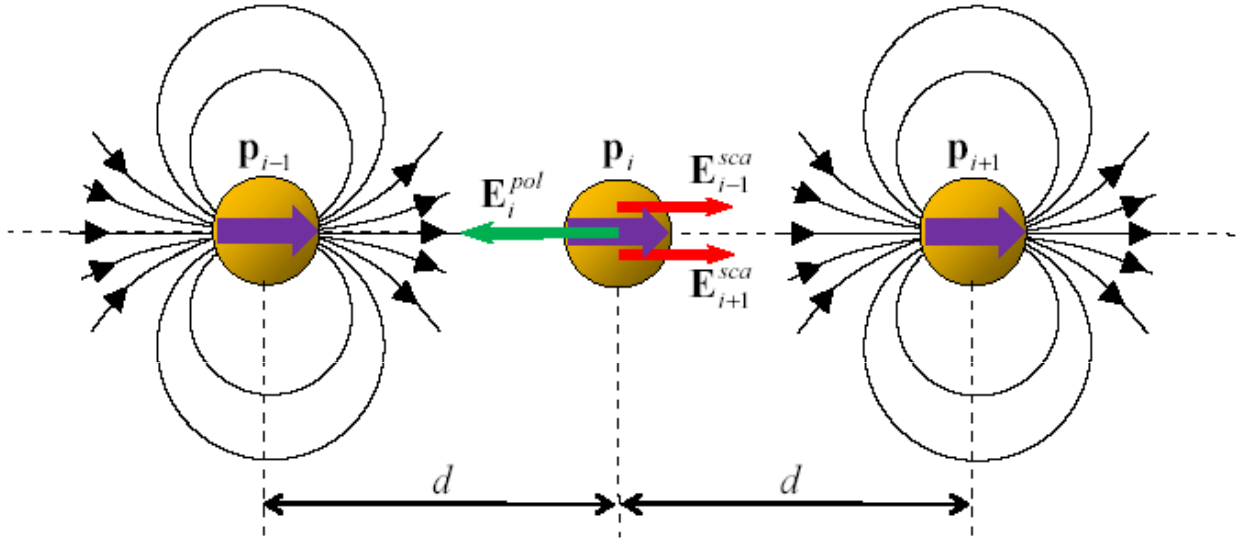
Dipole middle field $(r \approx \lambda)$ $\quad E_m \sim 1/r^2$

Dipole far field $(r \gg \lambda)$ $\quad E_f \sim 1/r$

The near field is most short-acting one. It dominates at small distances between the NPs in the chain:

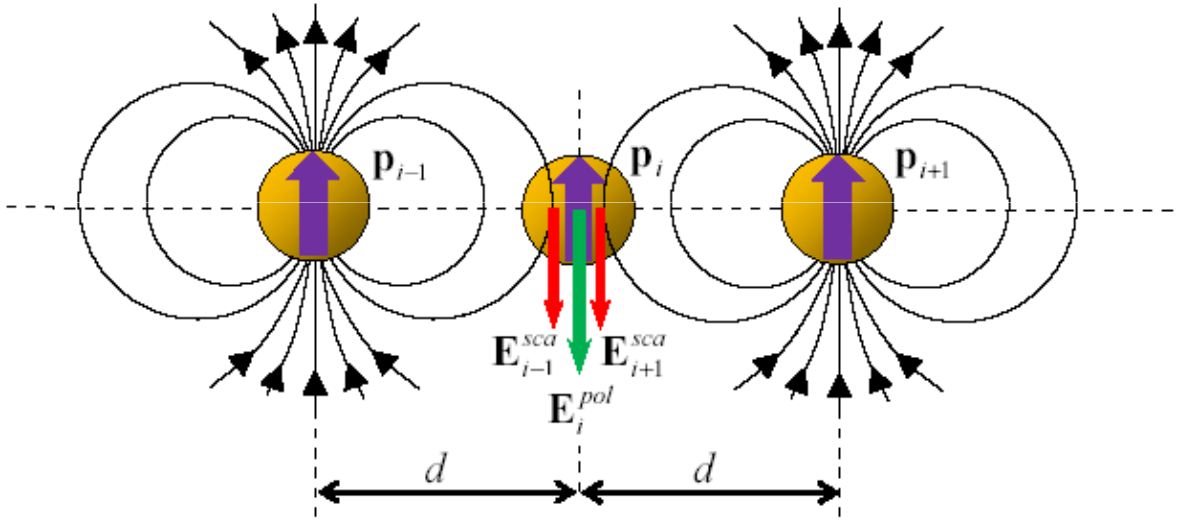
$$\mathbf{E} = \mathbf{E}_n = -\frac{\mathbf{p}}{r^3} + 3\frac{\mathbf{r}(\mathbf{p}\cdot\mathbf{r})}{r^5}$$

Formation of two SP-modes in periodic linear chain: L (dipoles are parallel to the chain) and T (dipoles are perpendicular to the chain)



L-mode

Electrodynamic coupling between two dipoles at small distances ($d << \lambda$) when the SPR oscillations are excited along the axis of the chain.



T-mode

Electromagnetic coupling between spherical nanoparticles for small distances between the particles ($d << \lambda$): the SPR oscillations are perpendicular to the axis of the chain.

The electric field of *j-th (j=L,T)* SP-mode of *m-th* NP in the location of neighbour (m-1)-th and (m+1)-th NPs:

$$E_{m,j}(t)=\frac{\sigma_j p_{m,j}(t)}{\varepsilon' d^3}\,, \quad \sigma_T=1 \text{ and } \sigma_L=-2$$

$p_{m,j}=qx_{m,j}$ - dipole of *j-th* mode of *m-th* NP, q - full charge of free electrons in NP,

$x_{m,j}$ - displacement of full charge of free electrons in NP from equlibrium position

Equation of charge motion – equation for particle dipole:

$$\ddot{p}_{m,j}=-\omega_0^2 p_{m,j}-\gamma_{int}\dot{p}_{m,j}+\frac{\gamma_R}{\omega_0^2}\dddot{p}_{m,j}-\sigma_i\omega_1^2\left(p_{m-1,j}+p_{m+1,j}\right)$$

$\omega_0=\omega_{sp}=\omega_p\Big/\sqrt{1+2\varepsilon'}$ - SPR frequency in isolated NP $\omega_1^2=\left(\frac{a}{d}\right)^3\omega_0^2$

Solution of equation – damping wave of polarization (plasmon polariton) propagating along the chain:

$$p_{m,j}=p_{0,j}\exp\left[-\kappa md+i\left(\omega t\pm kmd\right)\right]$$

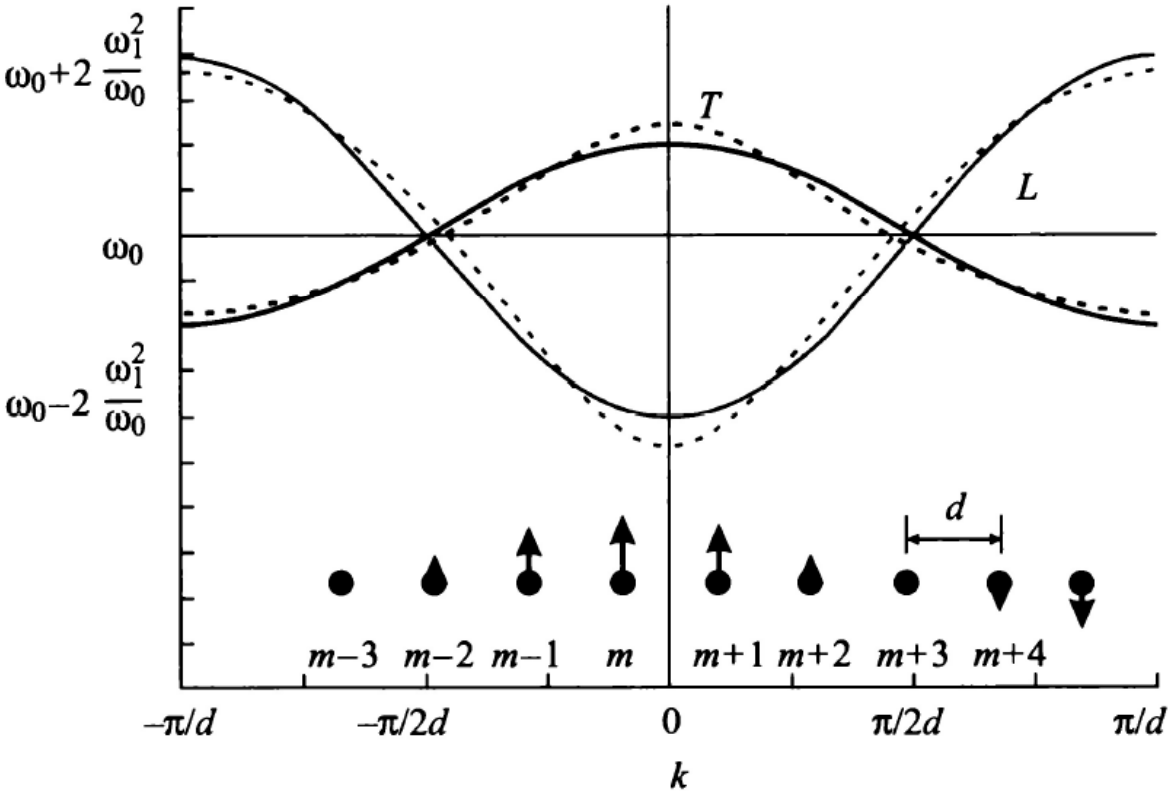
Dispersion relations for L and T-modes:

$$\omega_j^2 = \omega_0^2 + 2\sigma_j\omega_1^2\cos(kd)\,\mathrm{ch}(\kappa d),$$

$$0 = \omega_j\gamma_{int} + \frac{\omega_j^3\gamma_R}{\omega_0^2} + \sigma_j\omega_1^2\sin(kd)\,\mathrm{sh}(\kappa d)$$

at low damping $(\kappa d \ll 1)$

$$\omega_j^2 = \omega_0^2 + 2\sigma_j\omega_1^2\cos(kd)$$



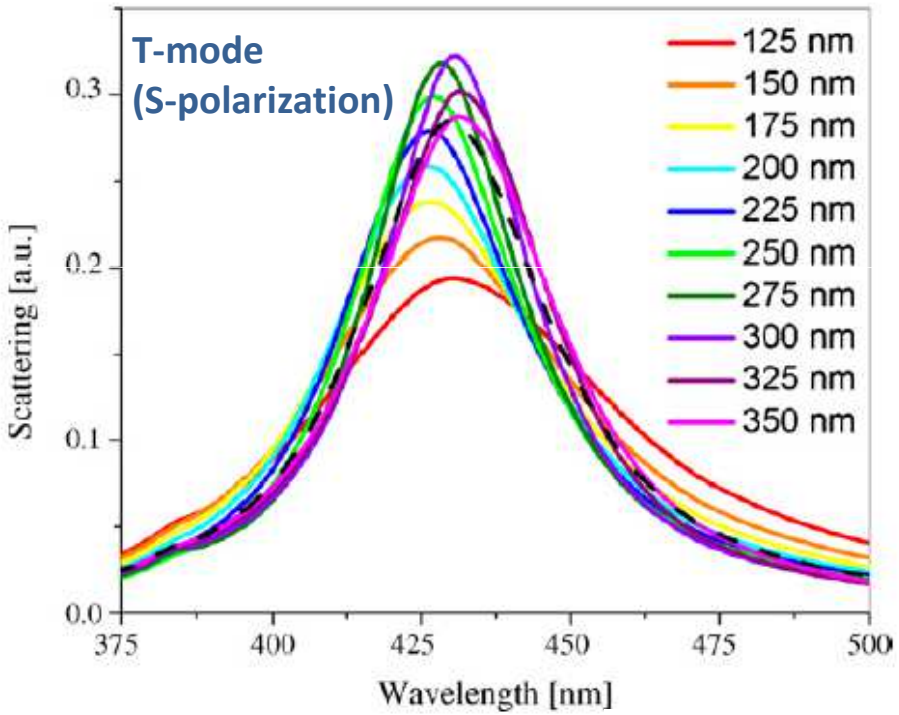
Effective mass of polariton

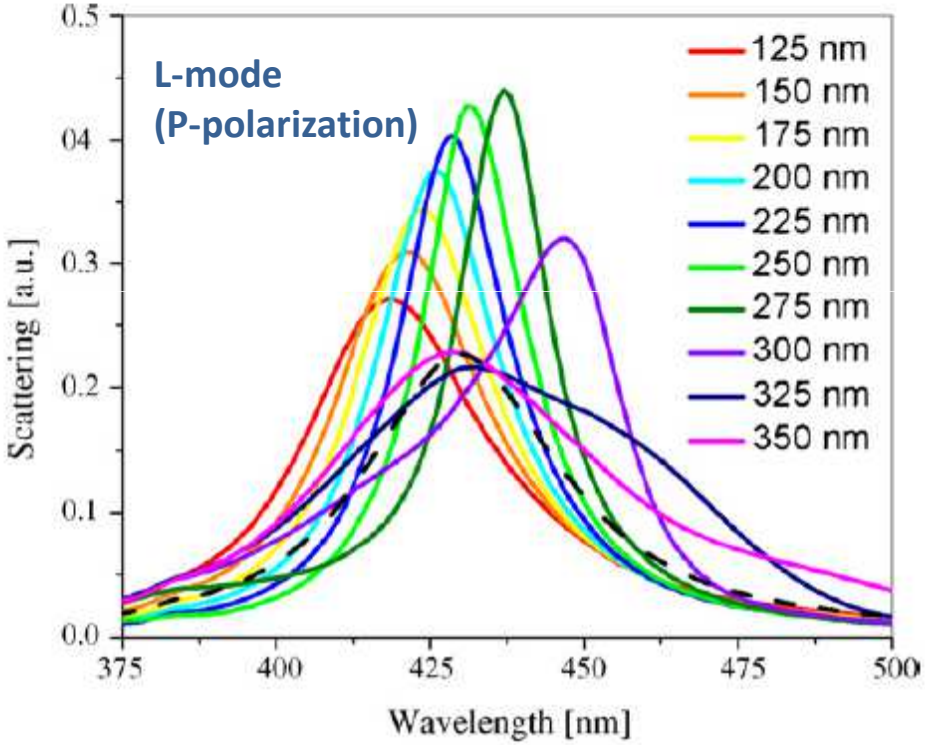
$$m_j^* = \hbar^2\left(\frac{\partial^2 E_j(k)}{\partial k^2}\right)^{-1}$$

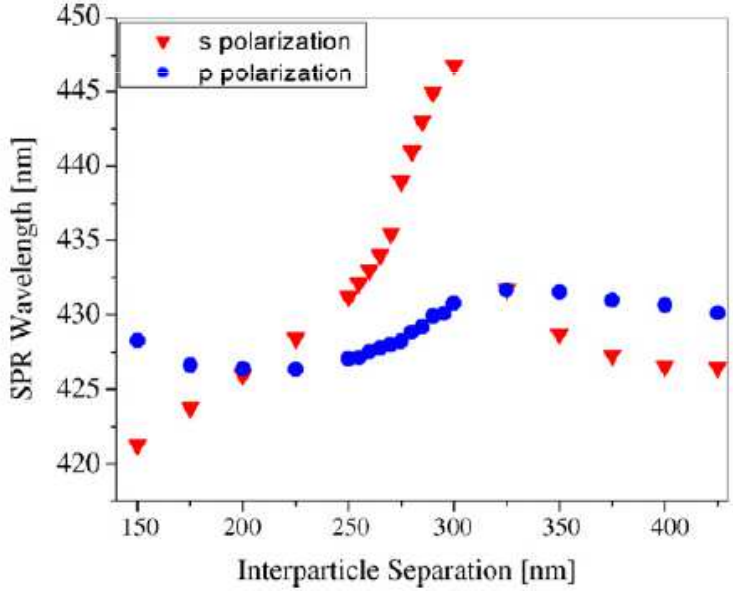
Group velocity of polariton

$$v_{g,j} = \left|\frac{d\omega_j}{dk}\right| = \left|\frac{\sigma_j\omega_1^2\sin(kd)}{\omega_j}\right|$$

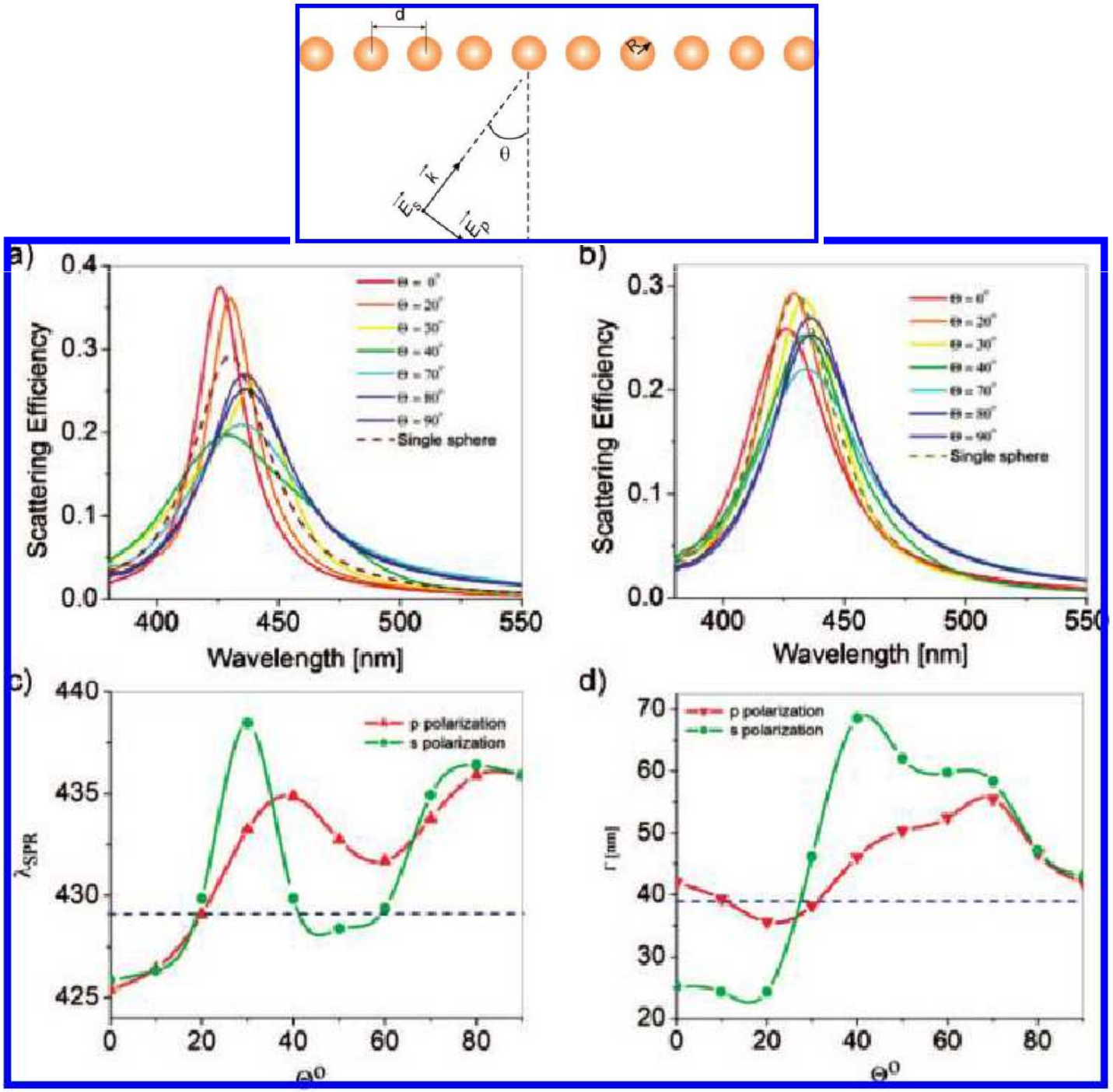
Plasmonic extinction spectra of linear chain of metal NPs: dependence on interparticle distance



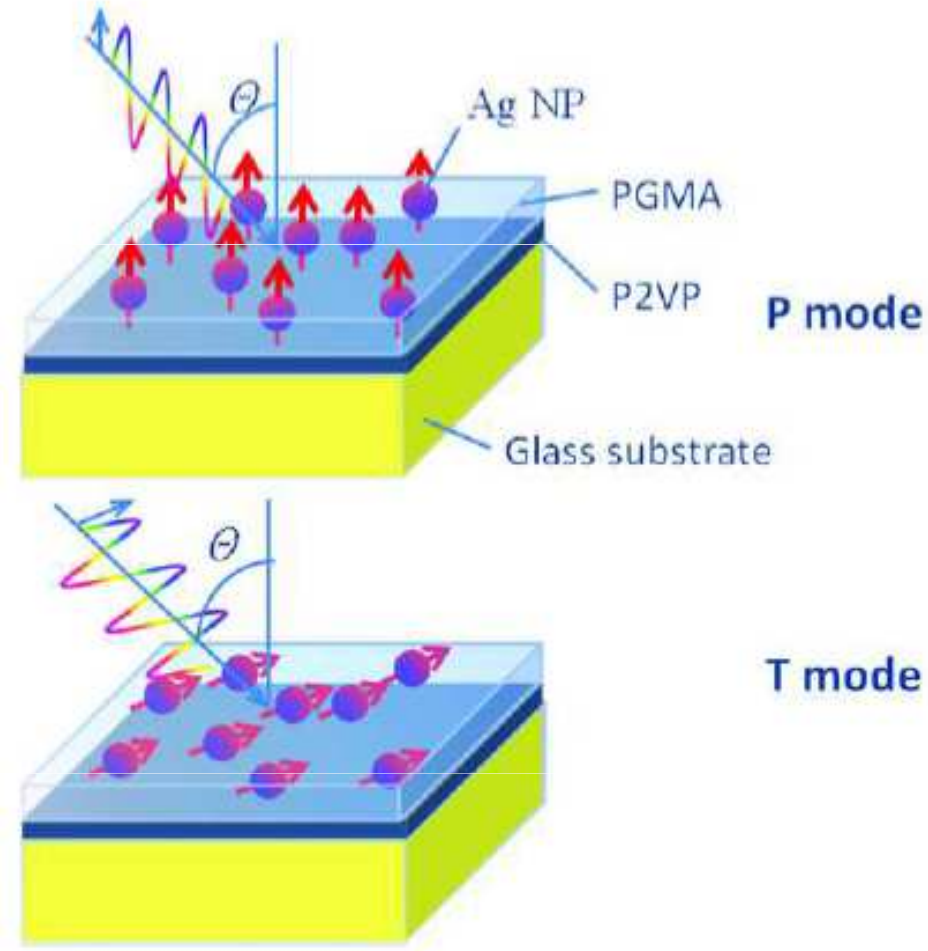




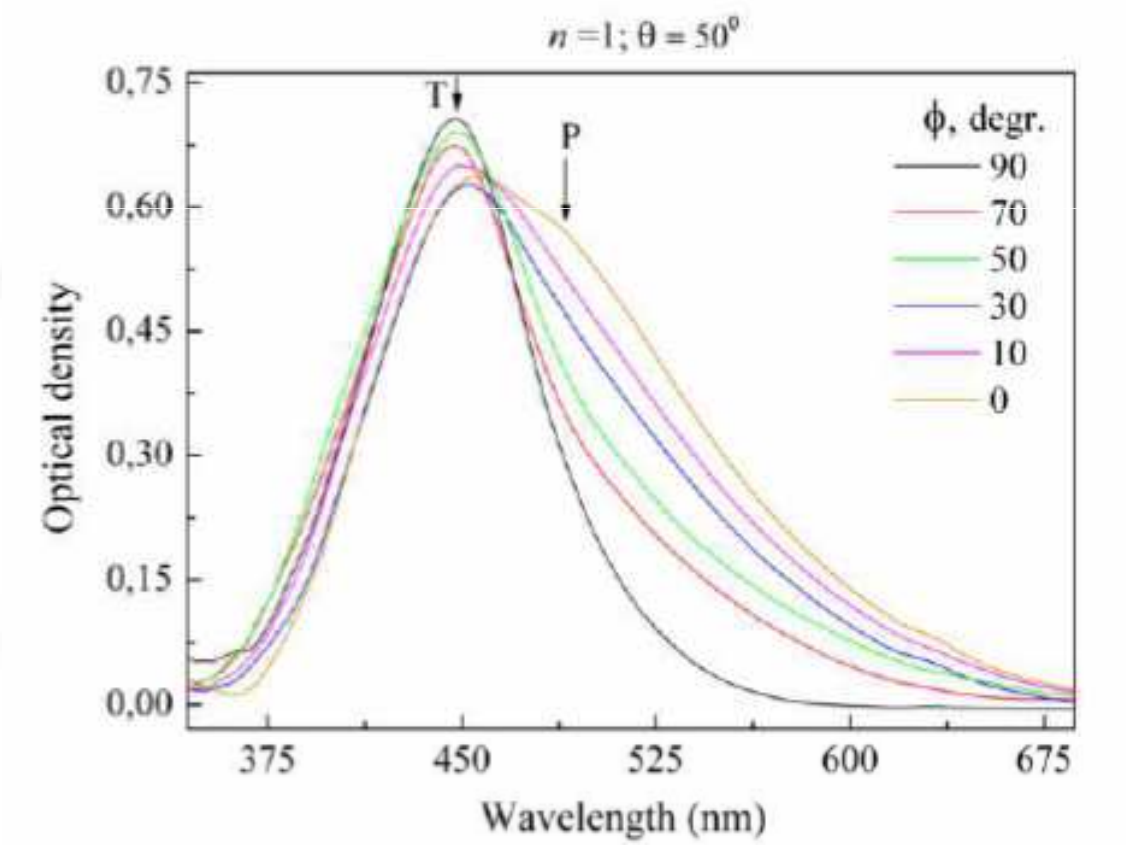
Plasmonic extinction spectra of linear chain of metal NPs: dependence on angle of incidence and polarization



3.3. Collective surface plasmon modes in 2D arrays of metal NPs

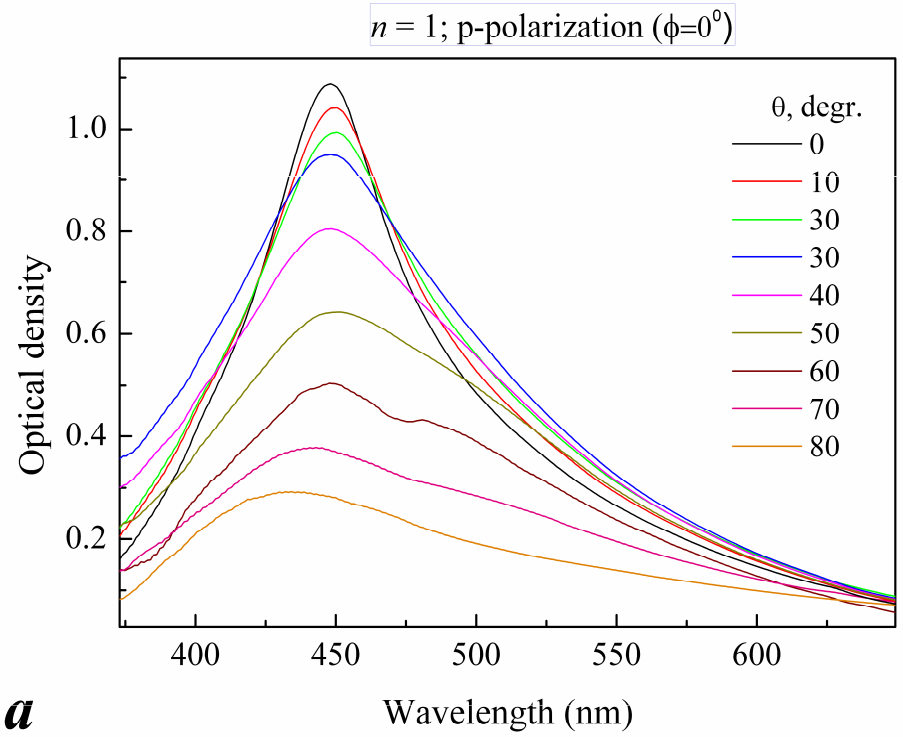


Formation of collective P and T modes



Polarization dependence of extinction spectrum of dense 2D array of 110 nm silver NPs

Dependence of extinction spectrum of dense 2D array of 110 nm silver NPs on incidence angle



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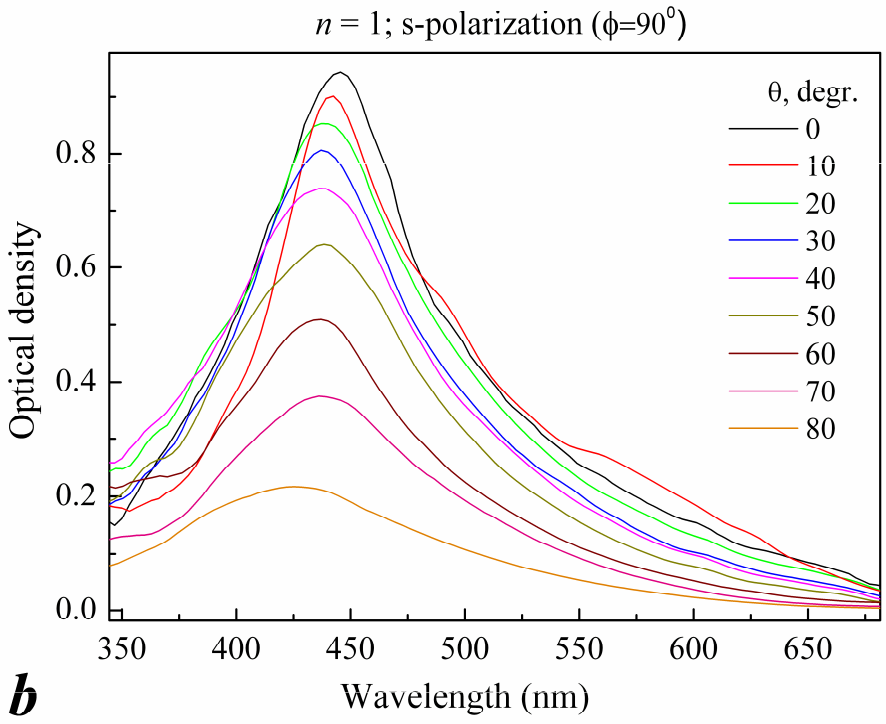

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Conclusion:

The variation of the interparticle distance in the clusters of metal nanoparticles as well as polarization and incidence angle of exciting light allows an essential controlable tuning of their absorption and scattering spectra that are important for the development of new plasmon based nanophotonics devices.

THANK YOU
FOR ATTENTION !