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Sensitivity of the optical sensor based on the local plasmons in the layers of nanoparticles depending on size and shape of the particles

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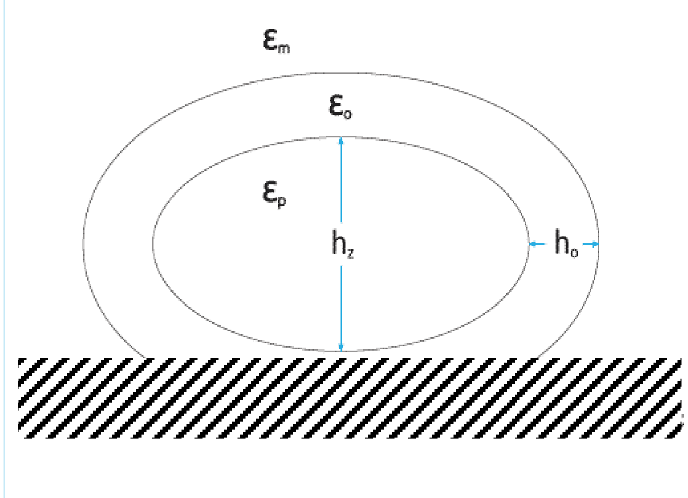
Introduction

Optical sensors based on the localized plasmons in nanoparticles of noble metals represent the layer of metallic nanoparticles on the substrate.



Localized plasmon resonance appears when collective oscillations of free electrons at the nanoparticles are excited by incident light.

Introduction

Such kind of sensor is used since 1996*

- Application
    - Chemical
        - Detection of nanolayers of chemical substance
    - Biological
        - detection of biomolecules
        - DNA

Such optical sensors are perspective devices as they are simple in use.

*Mirkin C.A., Letsinger R.L., Mucic R.C., Storhoff J.J. Nature, 1996, v. 382, p. 607—609.

Problem

Theoretical modeling of the behavior of such sensors

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- It is necessary to calculate the optical response of a system of nanoparticles
  - The account of interparticle interactions is important for this purpose* (Standart models like EMA are 3-dimensional and don’t account direct interparticle interactions).

*Persson, B. N. J., “Lateral interactions in small particle systems,” J. de Physique (suppl.) **44**(C10), 409-419 (1983).

Calculation of the response of a sub-monolayer of interacting nanoparticles by the Green function method

- **Lipman-Swidenger equation** determines the local field at any point of the system, which is the sum of the incidence field and the field generated by self-consistent dipole moments of other particles.

$$E_i(\vec{R},\omega) = E_i^{(0)}(\vec{R},\omega) - k_0^2 \sum_{\alpha}{}' G_{ij}(\vec{R}-\vec{R}',\omega)\tilde{\chi}_{\alpha jl}(\omega)E_l(\vec{R}',\omega)$$

where E and $E^{(0)}$ are total and external fields correspondingly, G- Green function of the medium, χ is the polarizability of the inclusions, $k_0=w/c$ where ω is the frequency and c is the speed of light.

Calculation of the response of a sub-monolayer of interacting nanoparticles by the Green function method

Solution of the equation

$$X_{ji}(\vec{k}_{\parallel}, z_{\alpha}, \omega) = n\left[\left(\tilde{\chi}_{ij}(\omega)\right)^{-1} + nk_0^2 G_{ij}(\vec{k}_{\parallel}, z_{\alpha}, z_{\alpha}, \omega)\right]^{-1}$$

X- effective polarizability of the unit area of the layer of particles

$$X_{ji}(\vec{k}_{\parallel}, z_p, \omega) = n\begin{vmatrix} \frac{1}{D}\left[\frac{1}{\chi_{\perp}} + 2\pi ni\frac{k^2}{\varepsilon_a k_{\perp}}\left(1+\overline{R}_p\right)\right] & 0 & \frac{1}{D}2\pi ni\frac{k}{\varepsilon_a}\overline{R}_p \\ 0 & \left[\frac{1}{\chi_{\parallel}} + 2\pi ni\frac{k_0^2}{k_{\perp}}\left(1-\overline{R}_s\right)\right]^{-1} & 0 \\ -\frac{1}{D}2\pi ni\frac{k}{\varepsilon_a}\overline{R}_p & 0 & \frac{1}{D}\left[\frac{1}{\chi_{\parallel}} + 2\pi ni\frac{k_{\perp}}{\varepsilon_a}\left(1-\overline{R}_p\right)\right] \end{vmatrix}$$

where $$D = \left[\frac{1}{\chi_{\perp}} + 2\pi ni\frac{k^2}{\varepsilon_a k_{\perp}}\left(1+\overline{R}_p\right)\right]\left[\frac{1}{\chi_{\parallel}} + 2\pi ni\frac{k_{\perp}}{\varepsilon_a}\left(1-\overline{R}_p\right)\right] + 4\pi^2 n^2\frac{k^2}{\varepsilon_a^2}\overline{R}_p^2$$

Calculation of the response of a sub-monolayer of interacting nanoparticles by the Green function method

In the case of a spheroidal particle covered by a shell with the dielectric function ε_2

$$\chi_i = V\frac{(\varepsilon_2-\varepsilon_a)\left[\varepsilon_2+(\varepsilon_p-\varepsilon_2)(L_i^1-fL_i^2)\right]+f\varepsilon_2(\varepsilon_p-\varepsilon_2)}{\left[\varepsilon_2+(\varepsilon_p-\varepsilon_2)(L_i^1-fL_i^2)\right]\left[\varepsilon_a+L_i^2(\varepsilon_2-\varepsilon_a)\right]+fL_i^2\varepsilon_2(\varepsilon_p-\varepsilon_2)}$$

where *V* is the volume of the particle with the shell, V_p is the volume of the particle core, $f=V_p/V$.

Two depolarizing factors are included here – L^1 for the inner and L^2 for the outer spheroids.

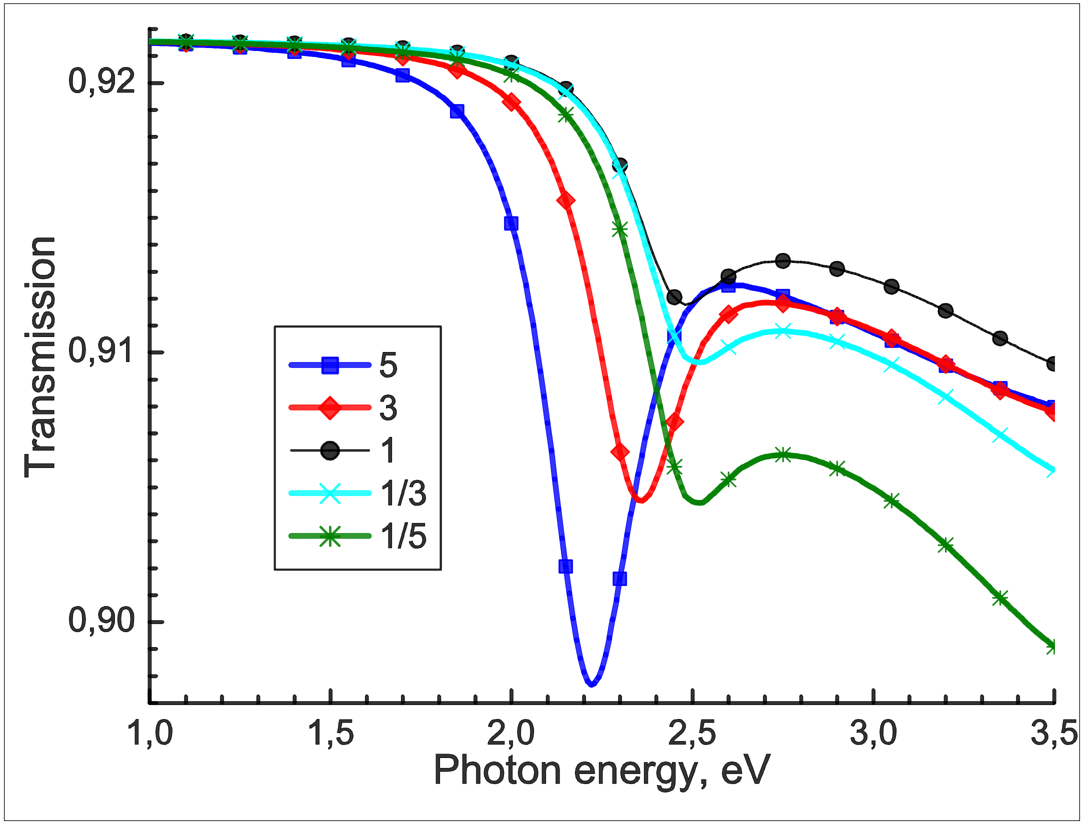
Modeling

- System of gold spheroidal nanoparticles on a glass surface.
- Refractive index of substrate **n=1.5**.

- Refractive index of the particles` shell: **n=1.3** (like water), **n=1.5** (like organic) or **n=1.7**(like polymers).

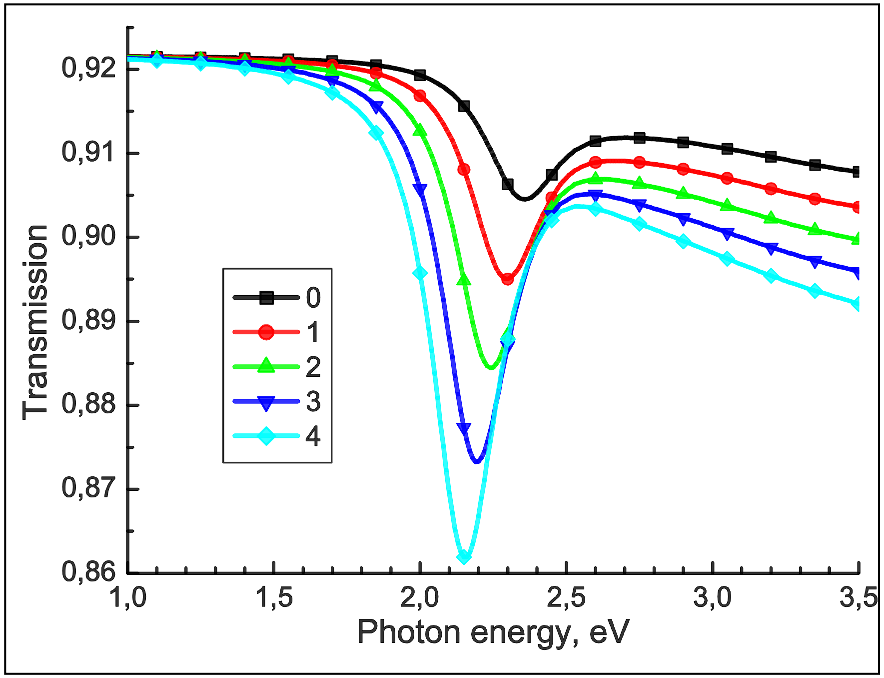
- Calculations were mainly performed for particles with the gold core of the constant volume equal to the volume of the sphere with the radius **10nm** and the particles concentration on the surface was also constant – $\mathbf{4 \bullet 10^{14}\ m^{-2}}$ that corresponds to the noticed spherical particles with no shell to about 13% of the surface coverage.
- All particles in the layer are considered to be similar.

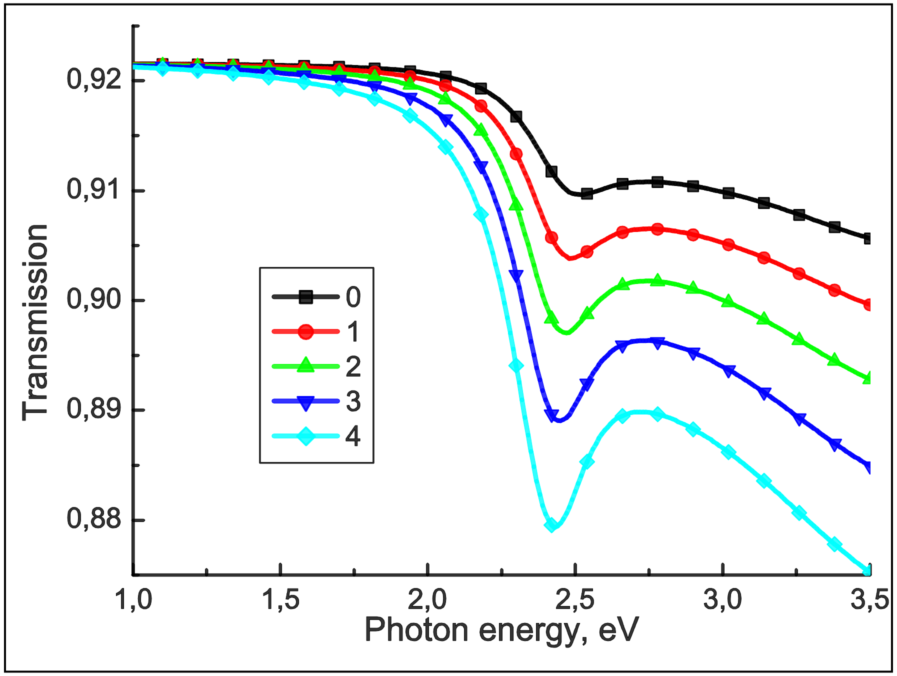
Modeling
(different shapes)



Modeled transmission of layers of bare spheroidal gold nanoparticles of different shapes but the constant mass thickness and concentration.

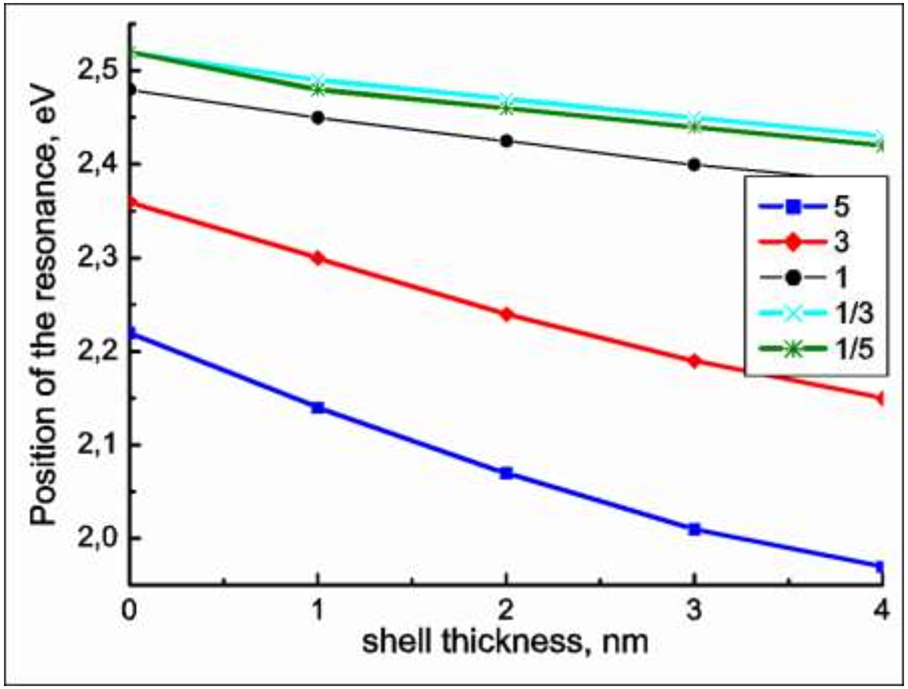
Modeling
(different shapes)

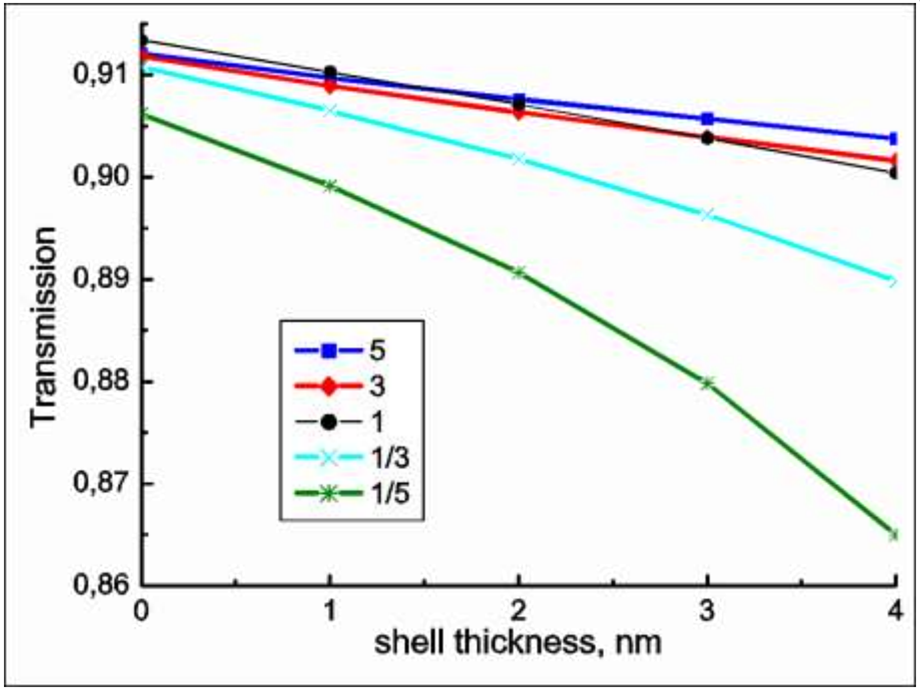




Modeled transmission of layers of oblate e=3 (a) and prolate e=1/3 (b) gold nanoparticles for different thickness of the shell with the refractive index n=1.7.

Modeling
(different shapes)





Dependences of the change in the resonance position (a) and transmission at 2.75eV (b) vs the thickness of the shell with the refractive index n=1.7 for particles of different shapes.

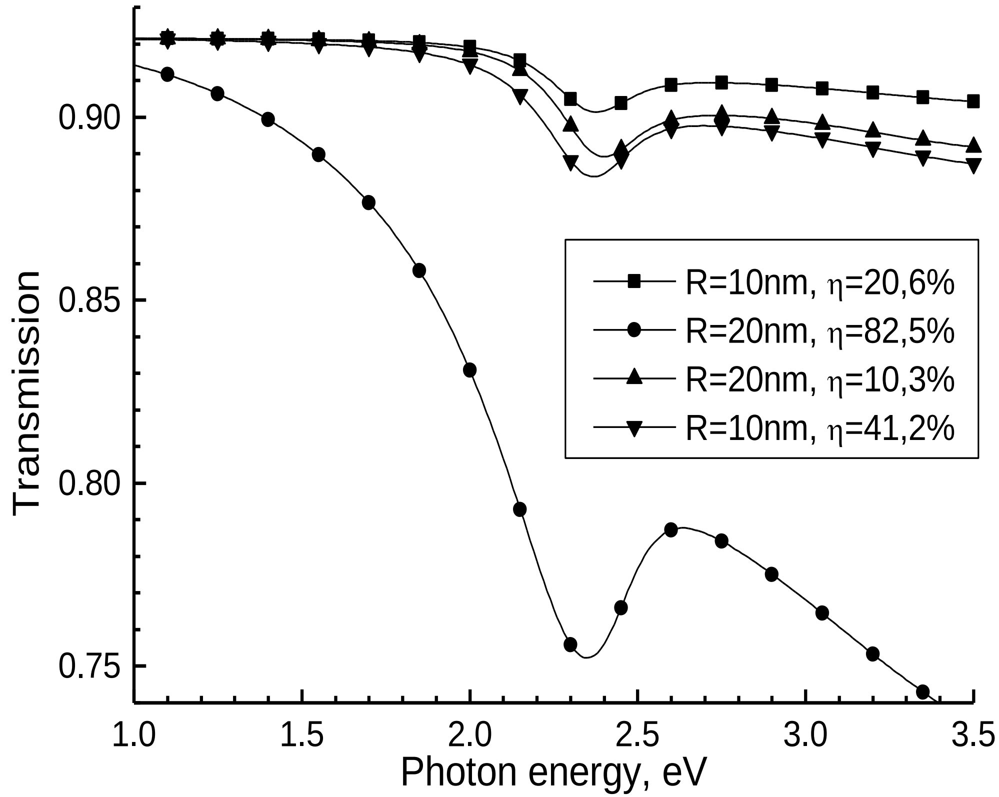
Sensitivity of layers of particles with different shapes to the adsorption of different analytes at different methods of registration.

Particle shape	Refractive index of the shell	Sensitivity of the transmission at 2.75eV to 1nm of the shell thickness	Sensitivity of the resonance position in meV to 1nm of the shell thickness	Sensitivity of the transmission at the resonance position to 1nm of the shell thickness
e=1/5 (2.5eV)	n=1.3	-0.0043	-25	-0.0055
	n=1.7	-0.0059	-35	-0.0078
	n=1.7	-0.0071	-40	-0.0096
e=1/3 (2.5eV)	n=1.3	-0.0027	-20	-0.0034
	n=1.5	-0.0036	-30	-0.0047
	n=1.7	-0.0043	-40	-0.0058
e=1 (2.4eV)	n=1.3	-0.0022	-5	-0.0032
	n=1.5	-0.0027	-15	-0.0044
	n=1.7	-0.0031	-30	-0.0054
e=3 (2.3eV)	n=1.3	-0.0028	-27	-0.0080
	n=1.5	-0.0030	-44	-0.0100
	n=1.7	-0.0029	-60	-0.0113
e=5 (2.15eV)	n=1.3	-0.0029	-40	-0.0132
	n=1.5	-0.0027	-61	-0.0158
	n=1.7	-0.0024	-82	-0.0168

Sensitivity of layers of particles with different shapes to the adsorption of different analytes at different methods of registration.

- The sensitivity of sensors with oblate particles is higher, so it’s better to use particles of this shape in such sensors.
- The region of the optimal measurements of the transition coincides with the region of localized resonances.
- Measurements of the transmission with the band-pass filter 2-2.5eV will cover area of resonances for any shape of particles, so we don’t have to use expensive optical equipment.

Modeling
(different sizes)



Transmission spectra of films of bare gold nanoparticles with the eccentricity e=2 for different sizes and surface concentrations.

Sensitivity of layers with different coverages of oblate particles of different sizes and the constant eccentricity e=2 to the adsorption of an analyte like dense polymer with n=1.7.

Layer parameters	Sensitivity of the transmission at 2.75eV to 1nm of the shell thickness	Sensitivity of the resonance position in meV to 1nm of the shell thickness	Sensitivity of the transmission at the resonance position 2.3eV to 1nm of the shell thickness
R=10nm, h=20,6%	-0.0029	-40	-0.0094
R=20nm, h=82,5%	-0.0137	-23	-0.0216
R=20nm, h=10,3%	-0.0030	-23	-0.0092
R=10nm, h=41,2%	-0.0056	-40	-0.0148

Smaller size and higher but still moderate concentration of oblate nanoparticles is preferable for the optimization of the sensitivity of optical sensors on localized plasmons

Conclusions

- The developed model allows to calculate parameters of optical transmission sensors based on localized plasmons in layers of nanoparticles depending on their size and shape with the account of interparticle interactions.
- Such an analysis allows to find optimal parameters of the layer of particles to obtain maximal sensitivity of such kind of sensor.

Thank you
for your
attention!