The Influence of Dielectric Environment on Spectral Shift of Localized Plasmonic Resonance

O A Tomilina, V N Berzhansky and S V Tomilin
Institute of Physics and Technologies, V.I. Vernadsky Crimean Federal University, Crimea, Simferopol, 295007, Russian Federation

Abstract. In paper the investigation results of dielectric environment influences on spectral shift of localized plasmonic resonance in a system of self-assembled metallic nanoparticles was introduced. It was shown, that the value of spectral shift of localized plasmonic resonance has a linear proportion towards the changes of environment refractive index. For investigated plasmonic system of self-assembled Au nanoparticles the coefficient of proportionality was determined.

1. Introduction
Discrete conducting nanoobjects and nanostructured materials are very perspective for creating sensory plasmonic structures [1–7]. The interaction of the electromagnetic field with metallic nanoobjects is determined by the properties of their electronic subsystem, which is limited by spatial restrictions. In conducting nanoparticles with a band type of the energy spectrum, the conduction electrons are plasma with a certain resonant frequency of plasma oscillations (plasmons) [8]. The absorption of quanta of electromagnetic radiation for resonant excitation of plasmons can be observed on transmission spectra in the form of “dips” at the resonant frequency. In this case, the dielectric environment of the conducting nanoobject has a significant effect on its properties, in particular, on the processes of transfer and relaxation of energy excitations, and as a consequence, on a change in the conditions of localized plasmon resonance (LPR) [9–11]. Therefore, on the basis of various types plasmonic systems the sensors are actively developed and studied to detect changes in the properties of dielectric media, including the medical and biological application [1–7]. Based on the foregoing, the great fundamental and practical importance have investigations of the influence of the dielectric environment on the shift of the LPR resonance frequency in metallic nanoparticles.

In this work, the studied plasmonic system is self-assembled gold nanoparticles (Au(NP)). Gold nanoparticles formed on the dielectric substrate by thermally activated granulation of the initial ultrathin gold film. This design is the simplest and cheapest for realization, and the placing of plasmonic particles on a carrier substrate makes it easy and convenient to change their dielectric environment without violating the integrity of the system. It also allows the use of similar plasmon systems in more complex composites and structures.

2. Model analysis
Let's consider the influence of an environment with dielectric constant $\varepsilon_{\text{env}}$ on the spectral position of localized plasmon resonance in a metallic nanoparticle (MNP). The extinction coefficient for a spherical particle with radius $r_{\text{NP}}$ is described by the expression [9, 12, 13]:

$$Q_{\text{ext}} = 4\pi \text{Im}(\delta).$$  \hspace{1cm} (1)
where \( x = 2\pi \varepsilon_{\text{env}}^{1/2} / \lambda \) is the wave number in the environment (\( \lambda \) is the wavelength), and \( \delta \) is the complex polarizability of the MNP, which is determined by the expression:

\[
\delta = r_{\text{NP}}^3 \frac{\varepsilon'_{\text{NP}} - \varepsilon_{\text{env}}}{\varepsilon'_{\text{NP}} + 2\varepsilon_{\text{env}}} = r_{\text{NP}}^3 \varepsilon^{\text{MNP}},
\]

(2)

Here \( \varepsilon'_{\text{NP}} = \varepsilon_{\text{NP}} + i\varepsilon''_{\text{NP}} \) is the complex dielectric constant of the MNP. Assuming \( \varepsilon_{\text{env}} \) is real (non-absorbing environment), we express \( g \) from (2):

\[
\text{Re}(g) = \frac{(\varepsilon'_{\text{NP}} - \varepsilon_{\text{env}})(\varepsilon'_{\text{NP}} + 2\varepsilon_{\text{env}}) + \varepsilon''_{\text{NP}}^2}{(\varepsilon'_{\text{NP}} + 2\varepsilon_{\text{env}})^2 + \varepsilon''_{\text{NP}}^2},
\]

(3.1)

\[
\text{Im}(g) = \frac{3\varepsilon_{\text{env}}\varepsilon''_{\text{NP}}^2}{(\varepsilon'_{\text{NP}} + 2\varepsilon_{\text{env}})^2 + \varepsilon''_{\text{NP}}^2},
\]

(3.2)

Substituting (3.2) into (1) we obtain an equation for the spectral dependence of the extinction coefficient [14, 15]:

\[
Q_{\text{ext}} = \frac{8\pi r_{\text{NP}}^3 \varepsilon_{\text{env}}^{1/2}}{\lambda} \frac{3\varepsilon_{\text{env}}\varepsilon''_{\text{NP}}^2}{(\varepsilon'_{\text{NP}} + 2\varepsilon_{\text{env}})^2 + \varepsilon''_{\text{NP}}^2},
\]

(4)

In this case, the resonance condition is satisfied when the real part of the denominator in (2) is equal to zero [13, 15]:

\[
\text{Re}(\varepsilon_{\text{NP}} + 2\varepsilon_{\text{env}}) = 0.
\]

(5)

If \( r_{\text{NP}} \ll \lambda \), the spectral dependence for \( \varepsilon_{\text{NP}} \) is determined by the expression [15]:

\[
\varepsilon_{\text{NP}} = \varepsilon_{\text{M}} + 1 - \frac{\omega_p^2}{\omega(\omega + i\omega_e)},
\]

(6)

Here \( \varepsilon_{\text{M}} = \varepsilon_{\text{M}}' + i\varepsilon_{\text{M}}'' \) is the frequency (spectral) dependence of the complex dielectric constant for bulk metal. In the case of Au, the spectral dependences for the real and imaginary parts of \( \varepsilon_{\text{M}} \) are shown in figure 1a [16]. In equation (6) \( \omega = 2\pi c / \lambda \) is the frequency of the exciting radiation, and the own plasmon frequency \( \omega_p \) is defined as \( \omega_p = \left( (ne^2) / (\varepsilon_0 m) \right)^{1/2} \), where \( \varepsilon_0 \) is the dielectric constant, \( n \) is the concentration of electrons in the metal, \( e \) and \( m \) are the charge and mass of the electron respectively. The electrons impact frequency \( \omega_e \) is determined from the equation: \( \omega_e = v_F / l + 2v_F / r_{\text{NP}} \), where \( v_F \) is the Fermi velocity, \( l \) is the mean free path of the electron.

On figure 1b the results of calculating the transmission spectra for gold nanoparticles with a radius \( r_{\text{NP}} = 40 \) nm at different dielectric environments are show (the \( \varepsilon_{\text{env}} \) value is indicated in the legend, the choice of values is determined by materials in the experimental part of the work).
Figure 1. The results of modeling the transmission spectra of MNPs with a radius $r_{NP} = 40$ nm: (a) dispersion curves for the real and imaginary parts of the dielectric constant of a bulk Au sample [16]; (b) transmittance spectra of gold MNPs at different dielectric environments ($\varepsilon_{env}$ value is indicated in the legend); (c) the first derivative of the transmittance $dT/d\lambda$.

When modeling, the influence of a gadolinium-gallium garnet substrate (Ga$_3$Gd$_5$O$_{12}$) with a dielectric constant $\varepsilon_{sub} = 4.042$ is taken into account (effective medium model) [17]:
\[ \varepsilon(A, B) = n(A)\varepsilon(A) + [1 - n(A)]\varepsilon(B), \]  

(7)

where \(\varepsilon(A,B)\) is the dielectric constant of the double-component system \(A,B\); \(\varepsilon(A)\) and \(\varepsilon(B)\) are the dielectric constants of each component, respectively; \(n(A)\) is the volume fraction of component \(A\).

For clarity, on figure 1c, the spectral dependence of the first derivative on the transmittance \(dT/d\lambda\) is presented. The insets in figures 1b,c show the spectral areas in the LPR region on an enlarged scale. It can be seen that an increase in the dielectric constant of the external environment leads to a red shift of the LPR. For investigated system a change in \(\varepsilon_{\text{env}}\) by 0.02 leads to a shift of the resonance by 0.5 nm.

3. Methods of samples manufacturing and investigation

In the experimental part of the work, a plasmonic system was synthesized in the form of self-assembled gold nanoparticles \(\text{Au}_{(NP)}\) on a substrate of single-crystal gadolinium-gallium garnet \(\text{Ga}_3\text{Gd}_5\text{O}_{12}\) (GGG). \(\text{Au}_{(NP)}\) nanoparticles were obtained by thermally activated granulation of a continuous gold film with 3 nm thickness (annealing in air at 950°C during 10 min) [18]. The initial Au/GGG film was synthesized by thermal deposition in vacuum (residual pressure is not more than \(4 \times 10^{-4}\) Pa) at a substrate temperature of 150°C.

For investigation, the plasmon system was placed in an optical cell, which was filled with a transparent dielectric medium. Isotropic materials with different dielectric constants \(\varepsilon_{\text{env}}\) were used as a dielectric medium (in increasing order): air, distilled water, an aqueous NaCl solution (with a mass fraction of 4.17%, 7.14%, 11.11%), and glycerin. In addition, a nanocomposite sample was synthesized in which a system of self-assembled Au nanoparticles was coated with a layer of bismuth-substituted ferrite garnet Bi:YIG with 100 nm thickness [19].

The optical and plasmonic properties of self-assembled \(\text{Au}_{(NP)}/\text{GGG}\) system were studied by optical transmission spectrophotometry in the spectral range 400 – 1000 nm.

4. Experimental results and it's discussion

On figure 2a the SEM-image of synthesized \(\text{Au}_{(NP)}/\text{GGG}\) plasmonic system is shown (REM-106, SELMI).

It can be seen that self-assembled \(\text{Au}_{(NP)}\) nanoparticles have a nearly spherical shape, and the size distribution of nanoparticles is well described by the normal distribution (figure 2b) with the most probable size of 78 nm (diameter) and standard deviation of 27 nm.

![Figure 2. SEM-image of self-assembled gold nanoparticles Au_{(NP)}/GGG (a); size distribution of Au nanoparticles (b), columns — experimental data, curve — approximation by Gaussian.](image-url)
The results of investigating the influence of the dielectric environment on the optical transmission of the plasmonic system Au(NP)/GGG are presented on figure 3a. It can be seen on figure, that the transmittance spectra of the Au(NP)/GGG plasmonic system have spectral minima that correspond to energy absorption for resonant excitation of localized plasmons in self-assembled nanoparticles Au(NP) [20]. The width increasing of the experimentally obtained resonance peaks compared with the calculated peaks is due to the size dispersion of the synthesized MNPs.

It can be seen that an increase in the dielectric constant of the environment \( \varepsilon_{\text{env}} \) leads to a “red” shift of plasmonic resonance. But at small changes in \( \varepsilon_{\text{env}} \) (for example, distilled water and aqueous NaCl solutions) the observation of a plasmonic resonance shift is difficult due to the “smooth” bottom of the LPR resonance peak. For convenience of observing the spectral shift of plasmon resonance on figure 3b the spectral dependences of the first derivative on the transmittance \( \frac{dT}{d\lambda} \) are shown, where the point of the curve intersection with the abscissa axe corresponds to the resonant wavelength of the LPR.

![Figure 3](image)

**Figure 3.** Spectral dependence of the transmittance of plasmonic system Au(NP)/GGG in various dielectric environments (a) and its derivative \( \frac{dT}{d\lambda} \) (b)

Table 1 presents a comparison of experimental results and model calculations about the influence of \( \varepsilon_{\text{env}} \) on the spectral shift of the LPR in Au(NP) nanoparticles. To determine the dielectric constant of NaCl solutions, an effective medium model for a homogeneous isotropic system was used (7).
Table 1. Resonance wavelength of the LPR in the plasmonic system Au(NP)/GGG at different $\varepsilon_{\text{env}}$.

| Dielectric environment   | $\varepsilon_{\text{env}}$ | $\lambda_{\text{LPR}}$(model), nm | $\lambda_{\text{LPR}}$(exper), nm |
|--------------------------|-----------------------------|-----------------------------------|----------------------------------|
| Air                      | 1.001                       | 616                               | 617                              |
| H$_2$O                   | 1.777                       | 632                               | 636.5                            |
| H$_2$O+NaCl (4.17 mas. %)| 1.802                       | 633                               | 637.5                            |
| H$_2$O+NaCl (7.14 mas. %)| 1.820                       | 633.5                             | 639                              |
| H$_2$O+NaCl (11.11 mas.%)| 1.844                       | 634                               | 640                              |
| Glycerin                 | 2.220                       | 639                               | 647                              |
| Bi:YIG (100 nm)          | 8.011                       | 735                               | 733                              |

On figure 4 shows the dependence of the shift of the LPR resonance wavelength in the plasmonic system Au(NP)/GGG on the change in the refractive index of the environment $n_{\text{env}}$. It is assumed that for a nonmagnetic isotropic medium $n_{\text{env}} = \varepsilon_{\text{env}}^{1/2}$.

![Figure 4. Dependence of the LPR resonant wavelength in the plasmonic system Au(NP)/GGG on the refractive index of the environment (squares — simulation results, circles — experimental data, inset — equation of the approximating line for the experiment data).](image)

As can be seen from figure 4, the dependence of the LPR spectral shift on the refractive index of the environment is approximate to linear ($\lambda_{\text{LPR}} = 63.64 \cdot n_{\text{env}} + 552.68$), which is also confirmed by the theoretical and experimental results [9, 13]. For the investigated plasmonic system Au(NP)/GGG, the $\lambda_{\text{LPR}}$ shifting proportionality coefficient with respect to the $n_{\text{env}}$ change is 63.64 nm, i.e. a change in the refractive index by 0.016 leads to a spectral shift of the LPR by 1 nm.

5. Conclusions

Thus, it was shown in the work that an increase in the dielectric constant of the environment leads to a red spectral shift of the localized plasmon resonance in the system of self-assembled Au nanoparticles. The dependence of the shift of the LPR resonant wavelength on the environment refractive index is linear, and for the investigated plasmonic system Au(NP)/GGG a change in $n_{\text{env}}$ by 0.016 leads to LPR spectral shift by 1 nm.

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