Electric properties of hemispherical metal nanoparticles: influence of the dielectric substrate

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Abstract. We calculated surface plasmon resonance position for gold and silver hemispheres placed on a dielectric substrate and covered with a thin dielectric layer. The results are applicable in metal islands film enhanced Raman spectroscopy.

1. Introduction
Surface plasmon resonance (SPR) in differently shaped metal nanoparticles is under extensive studies during last decades. This is because of both academic interest in general behavior of the SPR and its applications in optical polarizers and filters [1], nonlinear optics [2], and surface enhanced Raman scattering (SERS) [3]. A very special case of metal nanoparticles corresponds to the nanoislands forming a metal islands film (MIF) which are being widely used in SERS measurements [4]. These nanoislands are often hemispherically shaped [5], especially if they made using out-diffusion technique [6], and their SPR position determines the spectral range of SERS observations. In spite of the conventional use of MIFs in SERS the resonant properties of metal hemispheres deposited on a dielectric, conventionally glass, substrate have not been properly studied by now, but a red shift of plasmonic resonance of hemispheres deposited on a dielectric surface relatively to the SPR position in spheres deposited on the same substrates was mentioned [7]. Several research papers related to the problem were concentrated on comprehensive theoretical and numerical analysis of the SPR in an isolated metal hemisphere surrounded by the air [8], spheroids deposited on a dielectric substrate [9] and a nanosphere combined of two conjoined hemispheres of different materials, one of them being plasmonic [10]. Below we present an analytical study of the SPR in metal hemispheres placed on a dielectric substrate. We also use the developed theory to calculate the position of SPR in hemispherical metal nanoparticles on a soda-lime glass surface and the shift of the SPR vs the substrate permittivity.

2. Theory
Let us consider a metal hemisphere of radius \( a \) placed on a dielectric semi-infinite substrate with dielectric constant \( \varepsilon_{\text{sub}} \)(Fig.1). To examine the polarizability of the hemisphere it is common to use
spherical geometry, where two separate components of polarizability exist: the axial one, $\alpha_\parallel$, when the external field is normal to the substrate and parallel to $z$ axis, $E_\parallel z$, and the transverse component, $\alpha_\perp$, when the external field is parallel to the substrate surface and transverse to $z$ axis, $E_\perp z$. The latter case corresponds to the normal incidence of light.

If the object is small compared to the wavelength of light the quasistatic approximation can be used. In this case to determine the electric response of the hemisphere one has to find the potential which should satisfy the Laplace equation $\Delta \phi = 0$ throughout the space.

Developing the approach proposed in [8] we divided the space into four regions (Fig.1): the hemisphere with dielectric permittivity $\varepsilon_1$, so-called double hemisphere in the substrate with the dielectric permittivity of the substrate $\varepsilon_2$, the upper media (3, $\varepsilon_{out}^3 = 1$), and the substrate (4, $\varepsilon_{out}^4$). To describe the problem under consideration the dielectric permittivity of the double hemisphere should be the same as the substrate permittivity: $\varepsilon_2^3 = \varepsilon_4^4$. The potential corresponding to the external field parallel to the substrate (transverse case) could be written as [8]:

$$\phi = -Er \sin \theta \cos \varphi = -Er P_1^1 (\cos \theta) \cos \varphi,$$

where $P_1^1$ is the associated Legendre polynomial of the first order. To satisfy the Laplace equation in and outside the hemisphere, the potential should be written as the series of associated Legendre polynomials:

$$\phi_1 = \sum_{n=0}^{\infty} A_n^1 r^n P_n^1 (\cos \theta) \cos \varphi,$$

$$\phi_2 = \sum_{n=0}^{\infty} A_n^2 r^n P_n^1 (\cos \theta) \cos \varphi,$$

$$\phi_3^3 = \sum_{n=0}^{\infty} D_n^3 r^{-(n+1)} P_n^1 (\cos \theta) \cos \varphi - Er P_1^1 (\cos \theta) \cos \varphi,$$

$$\phi_4^4 = \sum_{n=0}^{\infty} D_n^4 r^{-(n+1)} P_n^1 (\cos \theta) \cos \varphi - Er P_1^1 (\cos \theta) \cos \varphi.$$

To find the unknown coefficients $A_n$ and $D_n$, one should use the boundary conditions:
\[ \theta = \frac{\pi}{2} \begin{cases} \phi^1_m = \phi^2_m, & \phi^3_m = \phi^4_m \\ \varepsilon^1_m \frac{\partial \phi^1_m}{\partial \theta} = \varepsilon^2_m \frac{\partial \phi^2_m}{\partial \theta}, & \varepsilon^3_m \frac{\partial \phi^3_m}{\partial \theta} = \varepsilon^4_m \frac{\partial \phi^4_m}{\partial \theta} \end{cases} \] \tag{4}\]

\[ r = a: \begin{cases} \phi^1_m = \phi^3_m, & \phi^2_m = \phi^4_m \\ \varepsilon^1_m \frac{\partial \phi^1_m}{\partial r} = \varepsilon^3_m \frac{\partial \phi^3_m}{\partial r}, & \varepsilon^2_m \frac{\partial \phi^2_m}{\partial r} = \varepsilon^4_m \frac{\partial \phi^4_m}{\partial r} \end{cases} \] \tag{5}\]

Due to the special features of the Legendre polynomials \( P^k_0(0) = 0 \) for odd \( n \) and \(-\frac{d}{d\theta} P^k_0(0) = 0 \) for even \( n \) the boundary condition (4) leads to the relation between the coefficients \( A_m \) and \( D_m \):

\[ A^1_n \eta^1_n = A^2_n, \text{where } \eta^1_n = \begin{cases} 1, & n - \text{odd} \\ \varepsilon^2_m, & n - \text{even} \end{cases} \] \tag{6a}\]

\[ D^3_n h^3_n = D^4_n, \text{where } h^3_n = \begin{cases} 1, & n - \text{odd} \\ \varepsilon^4_m, & n - \text{even} \end{cases} \] \tag{6b}\]

Let us use the normalized radius \( \rho = r/a \) and the notations \( c_n = A^1_n \varepsilon_a \) and \( b_n = D^3_n \varepsilon_a \) for the potential inside and outside the hemisphere, respectively. Then, in accordance with (6):

\[ \phi^1_m = \sum_{0}^{\infty} a^n c_n \eta^1_n \rho^n P^1_n(\cos \theta) \cos \varphi, \] \tag{7}\]

\[ \phi^4_m = \sum_{0}^{\infty} a^{-(n+1)} b_n h^4_n \rho^{-(n+1)} P^4_n(\cos \theta) \cos \varphi - Er P^1_1(\cos \theta) \cos \varphi, \] \tag{8}\]

where \( \eta^2_n = 1 \) and \( h^4_n = 1 \).

To match the boundary conditions at the surface of the sphere, \( r = a \) (Eq.5), equations (7) and (8) should be multiplied by \( P^k_n(\cos \theta) \) for the angle \( \pi/2 \leq \theta \leq \pi \) and \( 0 \leq \theta \leq \pi/2 \), respectively. Using the calculations made in [8] for the integration of the Legendre polynomials, one obtains:

\[ \int_{-1}^{0} P^1_n(\xi) P^1_1(\xi) d\xi = (-1)^{n+1} \int_{0}^{1} P^1_n(\xi) P^1_1(\xi) d\xi, \] \tag{9}\]

where \( \xi = \cos \theta \). Further we will use the following notation:

\[ U^1_{nl} = \int_{0}^{1} P^1_n(\xi) P^1_1(\xi) d\xi. \]

Finally, the whole set of the equations could be written as:

\[ \sum_{n} b_n U^1_{nl} [\eta^1_n \varepsilon^1_l + (-1)^{n+1} \varepsilon^2 l + (n + 1) (\eta^2_n \varepsilon^2_n + (-1)^{n+1} \varepsilon^3)] = U^1_{ll} \{(-1)^{n+1} (1 - l) \varepsilon^2 + \eta^1_l - l \varepsilon^2 \}. \] \tag{10}\]
where the calculations of $U_{nl}$ are described in [11]. The solution of (10) is to be found numerically. This requires solving $N$ equations and using $N \times N$ matrix.

In the far field the polarizability is defined by the dipole term of the series (3) for the potential outside the sphere:

$$\varphi_{n=1}^3 = b_3 a^2 \varepsilon_0 \rho^2 \gamma_1 \propto (\cos \theta) \cos \varphi = b_3 a^3 E r^{-2} \sin \theta \cos \varphi.$$  \hspace{1cm} (11)

By comparison of (11) with the standard expression for the potential of the dipole moment $p$,

$$\varphi_{dip} = \frac{pr}{r^3},$$  \hspace{1cm} (12)

one obtains:

$$p_\perp = b_3 a^3 E = \alpha_\perp E.$$  \hspace{1cm} (13)

Sometimes it is convenient to introduce normalized transverse polarizability, that is

$$\alpha_\perp = \frac{\alpha_\perp}{V} = \frac{3}{\pi}.$$  \hspace{1cm} (14)

The calculations above were done for the transverse case when the external field is perpendicular to the substrate. The approach can be easily extended to the case of the axial field, $E||z$.

3. Calculation results

To calculate the polarizability for a metal hemisphere we used experimental data on dielectric functions of Ag and Au [12]. As it was shown in [8], for positive permittivity of a hemisphere or for the permittivity ‘negative enough’ ($\varepsilon_{in}^3 < -10\varepsilon_{out}^3$) the accuracy of the simulation using the described approach is of the order of $10^{-5}$. However, the SPR in hemispherical particles is expected to be close to that in spherical particles, that is at $\varepsilon_{in}^3 = -2\varepsilon_{out}^3$. Thus, the solution can be unstable in the spectral region near the SPR resonance.

![Figure 2](image_url)

*Figure 2.* Real part of the coefficient $b_1$ for silver hemisphere on the glass in the transverse (a) and axial (b) case.

We calculated the transverse and axial polarizabilities of silver and gold hemispheres placed on a glass ($\varepsilon_{out}^2 = 2.25$) surface for different series number $N$ (Fig.2). As it was expected, the SPR position
is very close to the instability region, however, for the transverse case (Fig.2a) the curves for different $N$ converge. For the axial component (Fig.2b) the region of the singularity starts right from the wavelength of the SPR, so that the calculations are not correct near plasmon resonance position. For the case of gold hemisphere, the imaginary part of the permittivity is much larger than that for silver, and, as followed, the accuracy of calculations is higher (Fig.3).

The other advantage of the model presented is the possibility to use only the dipole mode to describe the response of the hemisphere at the distance greater than $2a$ from the center and to neglect the influence of the other modes (quadruple mode etc.). To demonstrate this we calculated the dipole potential and the potential from the other components in series (the full potential) in dependence of the normalized distance from the hemisphere center. The results of the calculations for the transverse case are presented in Fig.4. It is seen that at distances longer than $2a$ the difference between the dipole and full potential can be neglected. However, in the vicinity of the hemisphere the higher modes should be accounted for. Spectral dependence of the potential curves is presented in Fig.5. At the position of the SPR resonance the dipole mode dominates that makes it possible to use the dipole approximation for the calculations in this spectral region.

**Figure 3.** Gold hemisphere on the glass substrate: real part of the coefficient $b_1$ in the transverse case (a) and imaginary part in the axial case (b).

**Figure 4.** Dependence of the silver hemisphere potential on the distance from the center for the dipole mode (solid line), the full potential (dashed line), and the difference between them (dash dot). Wavelength of light 401 nm, glass substrate.

**Figure 5.** Spectral dependence of the silver hemisphere potential for the dipole mode (solid line) and the difference between full and dipole potentials (dash dot). Distance from the center $r=2a$, glass substrate.
The SPR position dependence on the substrate dielectric constant is presented in Fig.6 for silver and gold hemispheres. It is seen that the dependence is almost linear, and the resonance position can be tuned in a wide range by choosing substrates with different index. In the case of soda-lime glass SPR is at 445 nm for silver and at 565 nm for gold hemisphere these wavelengths are longer than for silver and gold nanospheres embedded in a glass matrix [6].

![Figure 6. The SPR position of an isolated metal hemisphere on a dielectric substrate vs the substrate dielectric permittivity.](image)

4. Conclusions
We have proposed a novel approach to analytically calculate the SPR position of a metal hemisphere on a dielectric substrate and to find its dependence on the substrate permittivity. The calculation showed that the SPR position differs from that of an isolated hemisphere and shifts towards longer wavelengths with the increase of the substrate. Dipole approximation can be successfully used to calculate the potential outside the hemisphere at distances exceeding the hemisphere diameter. These results can be used in the design of MIF substrates for SERS applications.

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References
[1] Heger Pet al 2004 Proc. Conf. Advanced in Optical Thin Films(SPIE)1 pp 21-28.
[2] Tsutsui Y, Hayakawa T, Kawamura G, Nogami M 2011 Nanotechnology22p 275203
[3] AndoJ,Taka-aki Yano,Fujita K andKawata S 2013Phys. Chem.15pp 13713-13722
[4] Dieringer J Aet alFaraday Discuss132pp 9–26
[5] Gupta Get al 2009Nanotechnology20 025703
[6] Zhurikhina Vet al A 2012Nanoscale Research Letters7p 676.
[7] Albella P 2011 et alNano Lett.11pp 3531–3537
[8] Kettunen H, Wallén H, and Sihvola A2008 J. Appl. Phys.103 p 094112.
[9] Fedotov V, Emel’yanov V, MacDonald K, and Zheludev N 2004 J. Opt. A: Pure Appl. Opt.6pp 155–160.
[10] Alù A and Engheta N, 2009 New J. Phys.11p 013026.
[11] Kettunen H, Wallén H, and Sihvola A 2007 J. Appl. Phys.102 044105
[12] Johnson P and Christy R 1972 Phys. Rev. B.6 12