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Resonance absorption spectra of composites containing metal-coated nanoparticles

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Abstract

The possibility of controlling the selective absorbance of composites containing nanoparticles with a metallic shell is investigated. The dependence of spectral position and absolute value of surface plasmon extinction maximum on the particle radius and material of core and shell are analysed in the visible region. The effect of absorbed energy redistribution between external and internal surface plasmons is established to be a change in the ratio of dielectric core/matrix refractive indices.

Keywords: Metalline nanoparticles; Spectral characteristics; Surface modes

1. Introduction

In recent years, during the development of new nonlinear materials, effective optical emitters, detectors and transformers, considerable attention has been given to metal nanoparticle systems due to their unique properties close to plasma resonance frequencies [1,2].

For colloids made of silver and gold nanoparticles, near the frequencies of plasma resonances corresponding to surface modes on such nanoparticles, the strong optical nonlinearity stipulated by considerable amplification of an internal field in metallic nanoparticles is established experimentally [3]. Recent works [4,5] have shown that detection efficiency of thin-film photodetectors can be increased by over an order of magnitude (in a limited wavelength range) if the surface is covered with metal islands. The enhancement of europium luminescence in thin layers of compounds deposited onto a silver island film and in glass upon embedding of silver nanoinclusions was also observed [6,7]. To realize these effects, the overlapping of ion spectral bands and absorption bands of metallic nanoparticles surface plasmon is necessary.

As it is known, the spectral position of a plasma resonance for homogeneous metallic particle is determined by their size and ratio of permittivities of particle and environment materials. The use of inhomogeneous particles, for example, metal nanoparticles with a dielectric shell, opens up additional capabilities to control the spectral position, intensity and half-width of plasma resonances due to the variation of a metal volume fraction f of particle and the use of shell materials with different index of refraction [8]. In that case, when the metal is localized in a shell of double-layered particles with a dielectric core, there are two types of plasma resonances corresponding to

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electronic density vibrations on internal and external shell surfaces (see, for example, Ref. [9]).

The purpose of this paper is to investigate the basic dependencies for resonance plasmon absorption of metal-coated nanoparticles with a dielectric or metal core.

2. Method of calculation

In the case of low particle volume concentration c, composite resonance absorption is determined by plasmon modes of single nanoparticles. Then extinction coefficient of a composite is $\beta = 0,75cQ_\lambda/R$, where Q_λ is the particle extinction efficiency factor [8]. The calculations have been performed on the basis of the rigorous solutions of the light diffraction problem for a coated sphere [10], which permit Q_λ to be obtained by expanding into infinite series on parameters depending on the radii of concentric spheres and the component permittivities.

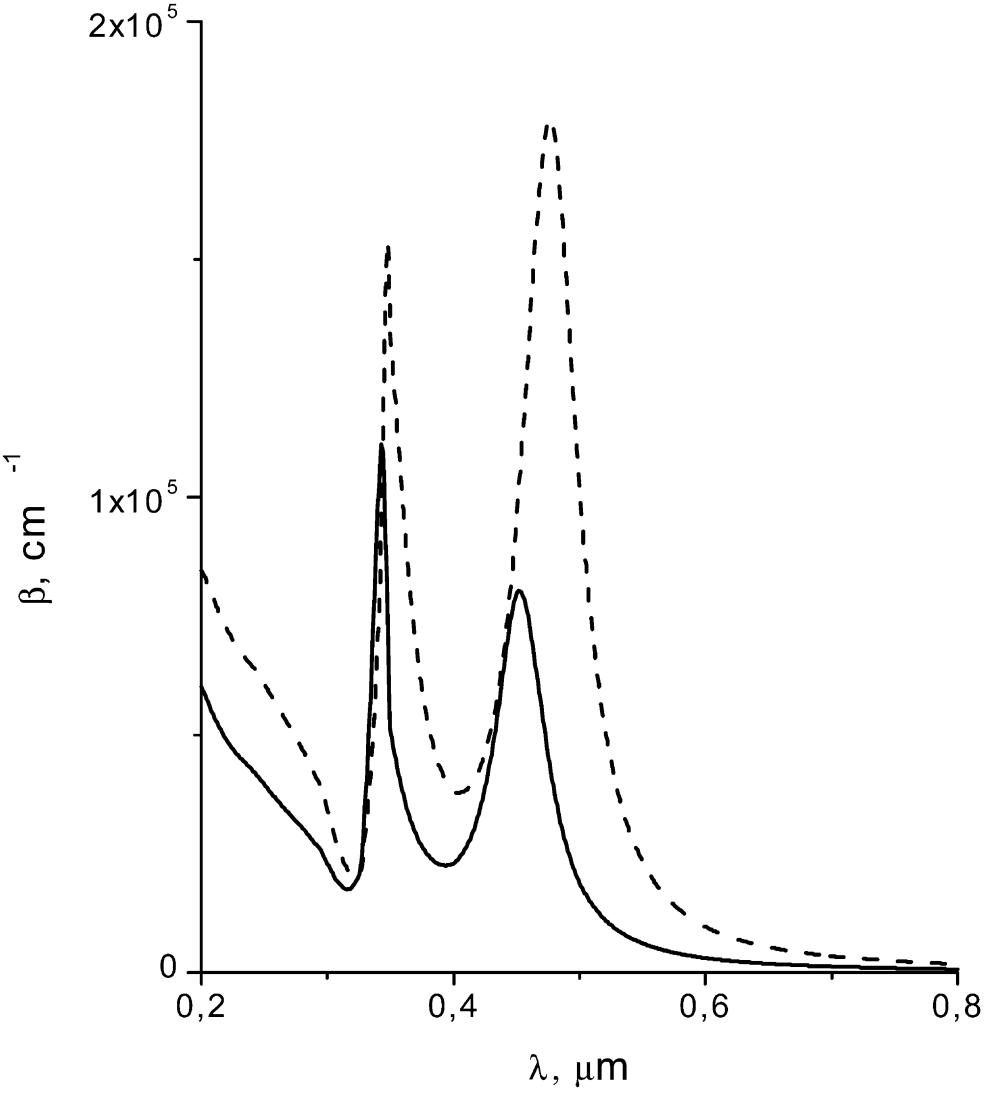

Fig. 1. Absorption spectra of composites made of nanospheres with a nonabsorbing dielectric core ($n = 2.7$) covered by Ag shell and at a changing of medium refractive index n_m ($R = 5$ nm; $c = 0.1$; $f = 0.9$). Solid line — $n_m = 1.0$; dashed line — $n_m = 1.3$.

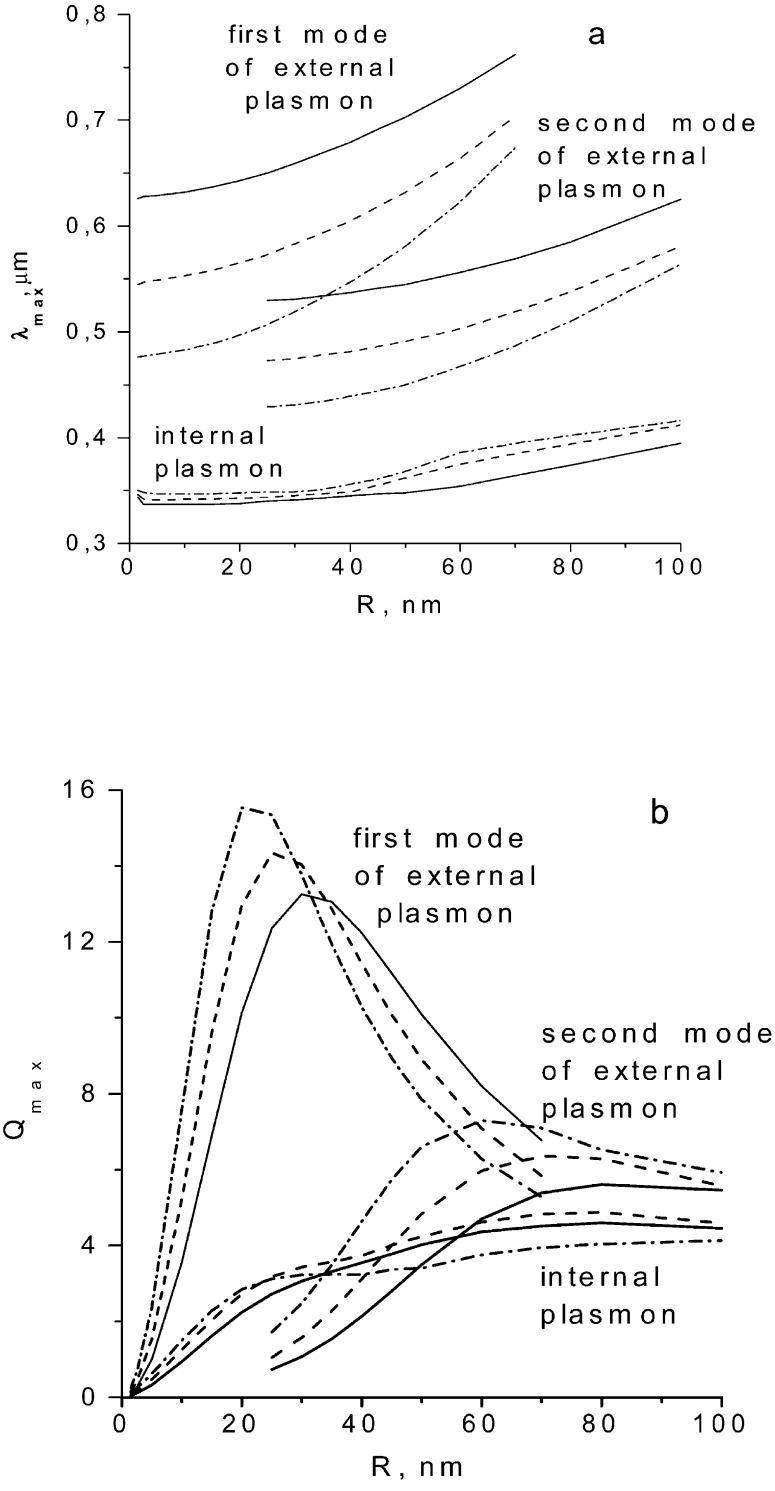

Fig. 2. Dependence of the wavelength (a) and the absolute value (b) in a plasma extinction maximum on the radius of sphere with Ag shell and dielectric core at different f ($n_c = 2.2$, $n_m = 1.4$). Solid line — $f = 0.6$; dashed line — $f = 0.75$; dash dot line — $f = 0.9$.

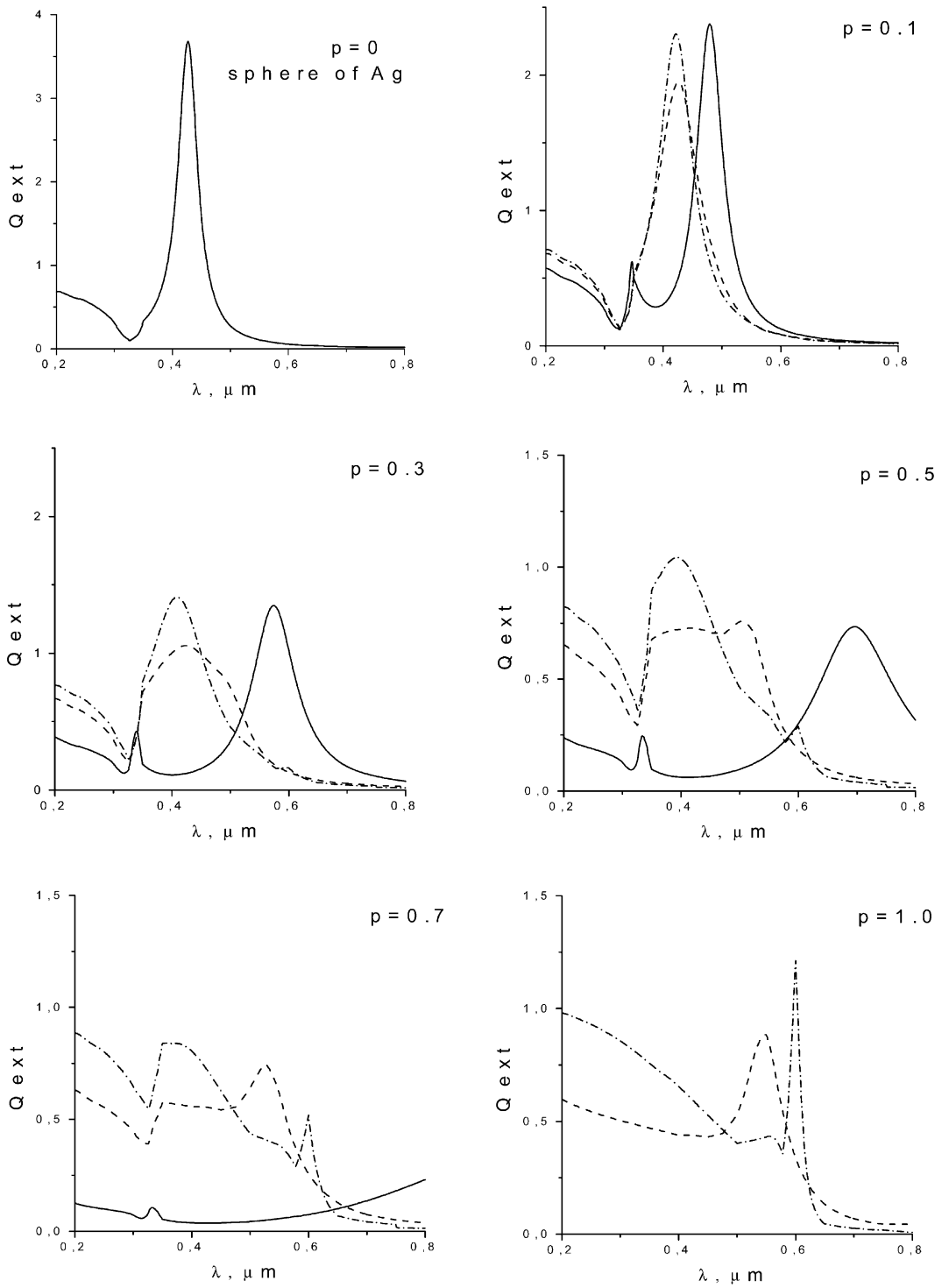

Fig. 3. Extinction efficiency factor of Ag coated nanosphere ($R = 5$ nm); medium refractive index $n_m = 1.4$. Solid line-nonabsorbing dielectric core ($n_c = 2.2$); dashed line — Au core; dash dot line — Cu core.

The size dependence of metal core optical constants has been calculated within the framework of the limitation of electron mean free path model (LEMFP) suggested for homogeneous metal nanoparticles by Kreibig. To obtain an appropriate size-dependent permittivity, one can use the Drude–Lorentz–Sommerfeld free-electron model, where the bulk damping constant is replaced by the size-dependent damping constant due to additional collision processes of conduction electrons with the particle surface [11]. We had also applied this model for metal-coated spheres and have shown that in this case the effective electron mean free path L_S depends on the radius of a particle R as well as on the radius of a dielectric core r [9]:

$$L_S(R,a) = R\left[\frac{1}{1+a^2} - \frac{a}{2} - \frac{1}{4}\frac{(1-a^2)}{(1+a^2)}(1-a)\ln\frac{(1-a)}{(1+a)}\right]$$

where $a = r/R$. The basic manifestation of the LEMFP effect in extinction spectra of the particles with a metal shell and dielectric core is the fact that peaks of extinction associated with surface plasma resonances at the shell boundaries are diminished and spread.

3. Results and discussion

Using theoretical scheme described above, we studied double-layered nanoparticles (various combinations of Ag, Au, Cu) embedded in non-absorbing dielectric matrix with refractive indices n_m changed from 1 to 3. The particle radius R has been extended from 5 to 100 nm. The basic results of calculations of resonance absorption spectra are shown in Figs. 1–3.

As can be observed from Fig. 1, the change of the medium refractive index, with the other parameters kept constant, of a composite system allows redistribution of absorbed energy between external and internal plasmons. The increase of n_m results in a displacement of both plasmons in low energy area. However, the greater the value of the core refractive index is, the greater is the spectral shift for an internal plasmon, and less for an external one.

If R exceeds 20 nm, the composite extinction spectrum has a second mode and at $R > 60$ nm, it has a third surface mode of an exterior boundary of a shell, respectively. The spectral position of external plasmons of a different order is displaced in the long-wave area of the spectrum with increasing R at constant f, and with reduction of the metal fraction in a particle with its radius constant (see Fig. 2). The spectral position of an internal plasmon in the wavelength range in question is practically constant for particles with radius not exceeding 40 nm at any ratio of the core and shell sizes. For particles of greater size, the shift of an internal plasmon in long-wave area is observed.

The dependence of extinction in the band maximum Q_{max} on a particle radius is non-monotonic both for external and for internal resonances. With an increase of the metal fraction in a particle, Q_{max} increases and corresponds to smaller R.

An extinction spectrum of a bimetallic particle transforms between a homogeneous sphere made of a shell material and a sphere made of a core material, whereas core volume fraction p ranges from 0 to 1 (see Fig. 3). When the volume fractions of both the metals of the bimetallic nanoparticle are compared, there is a two-peak structure in the absorbance spectra of the compound. To make such two-peaks structure more pronounced, two conditions have to be satisfied simultaneously: a pair of metals should be characterized by (i) close values of Q_λ of homogeneous particles of definite size and (ii) a significant difference of corresponding plasmon maxima spectral positions. At intermediate p, a peak spectral positions depend, in a complicated manner, on core and shell permittivities relation and on particle and core radii. The absorbance peak positions may be estimated by an electrostatic approach from the condition of Frolich mode excitation [8]: $(\varepsilon_2 + 2\varepsilon_m)(\varepsilon_1 + 2\varepsilon_2) + p(2\varepsilon_2 - 2\varepsilon_m)(\varepsilon_1 - \varepsilon_2) = 0$. Here ε_m, ε_1 and ε_2 are complex permittivities of medium, core and shell, respectively.

The obtained regularities can be used to control the optical characteristics of composite systems based on metal-coated nanoparticles as well as for optical diagnostics of the interior structure of small metalline double-layer particles.

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References

[1] R. Reisfeld, Optical and Electronic Phenomena in Sol–Gel Hasses, Heidelberg, Berlin, 1996.
[2] R.J. Gehr, R.W. Boyd, Chem. Mater. 8 (1996) 1807.
[3] F. Hache, D. Richard, C. Flytzanis, J. Opt. Soc. Am. B3 (1986) 1647.
[4] H.R. Stuart, D.G. Hall, Appl. Phys. Lett. 69 (1996) 2327.
[5] H.R. Stuart, D.G. Hall, Phys. Rev. Lett. 80 (1998) 5663.
[6] D.A. Weitz, S. Garoff, C.D. Hanson, et al., J. Lumin. 24/25 (1981) 83.
[7] G.A. Denisenko, V.A. Oleinikov, Malashkevich, et al., J. Appl. Spectrosc. 62 (1995) 1093.
[8] C. Bohren, D. Huffman, Absorption and Scattering of Light by Small Particles, Wiley, New York, 1983.
[9] S.M. Kachan, A.N. Ponyavina, Reviews and Short Notes to Nanomeeting'99, 1999, pp.103.
[10] A.L. Aden, M. Kerker, J. Appl. Phys. 22 (1951) 1242.
[11] U. Kreibig, C.v. Fragstein, Z. Phys. 224 (1969) 307.