Spectral characteristics of confined photonic and plasmonic nanostructures

S.M. Kachan*, A.N. Ponyavina

Institute of Molecular and Atomic Physics
National Academy of Sciences of Belarus
F. Skaryni Ave. 70, 220072 Minsk, Belarus

ABSTRACT

The transmission and reflection spectra of 1D photonic crystals based on close-packed silver nanosphere monolayers separated by thin solid dielectric films are investigated in the frame of the statistical theory of multiple scattering of waves. In order to realize jointed electron and photonic confinement we choose intermonolayer film thickness so that the photonic band gap and metal nanoparticle surface plasmons are realized at close frequencies in the visible region. Photonic stopband formation is studied under these conditions at different particle sizes, concentrations and geometrical parameters of the system with regard to size dependence of metal nanoparticle dielectric function. The red shift of plasmon resonance with packing factor increasing due to the lateral coupling between close-packed metal nanoparticles within a monolayer is shown. One-dimensional ordering of monolayers gives rise to the formation of the photonic stopband in the vicinity of a plasmon absorbency resonance. The appearance of a doublet structure of attenuation spectra and narrowed reflection peak has been established.

Keywords: metal nanoparticles, collective effects, 1D photonic crystals, surface plasmon

1. INTRODUCTION

Now it is well known that different types of composites formed by metal nanocrystals embedded in transparent hosts are promising materials for linear and non-linear optics, laser physics, optoelectronics[1]. Considerable advance in fabrication of these nanocompounds is achieved[2,3] and their electrical and optical properties are actively studied over the last years[3,4].

A wide variety of interesting effects demonstrating unique physical properties of metal-dielectric nanocompounds have been revealed. Among the optical effects the most interesting are, for instance, high optical nonlinearity due to strong local fields into metal nanostructures[5], "supertransmission" of thin metal films perforated with nanoholes[6], the growth of the detection efficiency for thin-film photodetectors covered with metal islands[7], the enhancement of Raman scattering and luminescence of organic molecules and ions adsorbed on the nanostructural metal surface or imbedded into dielectric matrix together with some quality of metal nanoparticles[8]. It is worthwhile to note that the great majority of these effects take place in the spectral region close to the surface plasmon frequency of concerned metal nanoparticles.

The nature of nanoparticle surface plasmons (NSP) is connected with the collective oscillations of conduction electrons confined by the nanoparticle surface. NSP existence together with size dependence of the nanoparticle dielectric

* e-mail: lirp@imaph.bas-net.by

function determines the considerable distinctions of ultradisperse metal phase optical properties from those for the corresponding bulk metal[9]. It is known that absorption and scattering by metal nanoparticles are resonantly enhanced in the plasmon frequency region. The typical NSP frequencies for metals lie in the UV and in the visible. In the common case NSP characteristics are extremely dependent on particle sizes, shapes, concentration, matrix refractive index and may be controlled by these parameters changing[10].

In our opinion, there is an additional way to control spectral properties of a metal-dielectric nanostructure. One can reach it by particle array space ordering in a different manner. For example, by forming a stack of close-packed metal nanoparticles monolayers separated by solid dielectric intermediate films. On the other hand, the system formed in this way is a kind of 1D photonic crystals (PC) due to dielectric function 1D periodicity. It is common knowledge that such a structure behaves in respect to photons in the same manner as the ordinary crystal behaves in respect to electrons[11,12]. In particular, there have to be some spectral ranges where photon propagation through PC is prohibited and, consequently, the photon band gap (PBG) are formed.

In the present paper we consider the situation when PBG and NSP are realized at the near frequencies, i.e. when electron and photon confinement are revealed simultaneously. As a model for theoretical investigation we choose a structure like a stack of close-packed monolayers of spherical metal nanoparticles separated by dielectric films with the thickness comparable to the NSP wavelength. This type of structures can be fabricated, for example, by means of the pulsed excimer laser ablation of metal and dielectric targets alternatively[13].

2. CALCULATION METHOD

To calculate transmission and reflection coefficients of the layer-periodic systems of metal ultradisperse monolayers we have applied the approach based on the statistical theory of multiple scattering of waves (STMWS)[14]. The approach allows taking into account electrodynamic coupling as an interference of the waves multiply scattered into the partially-ordered particle array both into each close-packed monolayer and between different monolayers too. The efficiency of this approach has been already demonstrated at the description of spectral properties of 3D opal-based PC[15] and so-called stratified IR scattering filters[16].

The STMWS approach supposes that at interaction of electromagnetic radiation with an ensemble of particles the resulting field in some point of space is the sum of fields corresponding to different waves multiply scattered to the point with considering wave phase relations. In addition each particle is not acted by an incident wave field $\mathbf{E}_0$ but it is irradiated by some effective field also obtained as a result of summing all waves multiply scattered in the particle disposition area by all other particles from the array.

Averaging on different configurations of a particle ensemble leads to the chain of equations for all moments of a random field. To break this chain one must make some assumption concerning to the particle space distribution. The most w... using quasicrystalline approximation[17] (QCA) implies that fixing locations of any two particles gives us the information about the whole particle ensemble. It is evidently, the more regular the particle array, the better this assumption holds. Correspondingly, in the QCA the basic correlation function is the binary (or so-called radial distributional) function $g(|\mathbf{R}-\mathbf{R}'|)$. The radial distribution function characterizes the probability of location of two particles at the points $\mathbf{R}$ and $\mathbf{R}'$. For statistically isotropic and uniform media it depends only on the modulus $|\mathbf{R}-\mathbf{R}'|$. This function can be calculated by using the model of solid spheres from the solution of the Percus-Yevick equation[18]. For a close-packed system of particles the g(R) function has sharply pronounced maxima for R values associated to the most probable distances between particles. This behavior of g(R) reflects the short-range ordering in the close-packed disperse system.

The calculation scheme we used is divided into two parts[15,16]. The first step is calculation of the monolayer scattering amplitude as well as transmission and reflection coefficients with the use of the quasicrystalline approximation of the STMWS:

$$T_M = \left|1 - \frac{\pi}{k^2}\sum_l \rho(2l+1)(c_l + d_l)\right|^2$$

$$R_M = \left|-\frac{\pi}{k^2}\sum_l \rho(-1)^l(2l+1)(c_l - d_l)\right|^2,$$

Here c_l and d_l are the complicated functions of the radial distributive function g(R), surface particle concentration ρ, complex particle refractive index $\tilde{m}$ and single particle scattering parameters; k is the wavenumber.

On the second step we regard electrodynamic coupling between different monolayers within the stack by means of a kind of the self-consistent procedure. We should note, that in the case of layer-periodic systems namely this interference determines the PBG formation.

For a system of parallel monolayers displaced with equal distances l_M between the centres of nearest ones it is necessary to consider an addition contribute of fields scattered by particles of the other monolayer to the averaged field. The coherent field of such system made of N statistically independent monolayers can be written as:

$$\langle \mathbf{E}(\mathbf{z})\rangle = \exp(ikz)\left(\mathbf{e} + \sum_{j=1}^{N}\mathbf{G}_j^{+}\right)$$

$$\langle \mathbf{E}(-\mathbf{z})\rangle = \exp(ikz)\left(\sum_{j=1}^{N}\mathbf{G}_j^{-}\exp\{(j-1)2ikl_M\}\right),$$

Here $\mathbf{G}_j^{\pm}$ are the amplitudes of scattering forward and backward for j monolayer in the presence of the other monolayers.

Thus having determining the coherent field we can obtain coefficients of coherent transmission $T_S = |\langle \mathbf{E}(\mathbf{z})\rangle|^2$ and reflection $R_S = |\langle \mathbf{E}(-\mathbf{z})\rangle|^2$ of a stack.

3. RESULTS AND DISCUSSION

The calculation of the silver nanoparticle monolayer and stack coherent transmission and reflection has been made with the help of the above stated algorithm. The monolayer overlap parameter $\eta = \rho\pi d^2/4$ was varied over the range η =0.02÷0.6, diameter of particles d=2÷10 nm.

Size dependence of metal nanospheres optical constants has been taken into account in the frame of the model proposed in Ref. 19. The principle of the model is that the limitation of electron mean free path due to collisions with the spherical particle bounding surface causes an additional collision damping. Thus, the size-corrected collision damping for metal spherical nanoparticles which should be used in the Drude-Lorentz-Sommerfeld free-electron model is:

$$\gamma_d = \gamma_0 + \frac{2v_F}{d}$$

where v_F is the electron velocity on the Fermi level, γ_0 is the bulk damping constant.

We used the scheme, described in Ref. 19, to calculate the size-dependent optical constant of Ag nanospheres. Metal permittivity was subdivided into two parts associated with the contributions of free and bound electrons respectively.

The part of permittivity, which defined by free electrons, was considered as size-dependent. Its values were calculated using the following parameters: plasma frequency $\omega_p = 1.38 \cdot 10^{16} s^{-1}$, $v_F = 1.4 \cdot 10^{6} m \cdot s^{-1}$, $\gamma_0 = 0.27 \cdot 10^{14} c^{-1}$.

In Fig.1 one can see the spectra of coherent transmission in the visible for close-packed monolayers of 2 nm silver particles in gelatin (n_m=1.4) with different values of a particle concentration. It confirms the experimentally established[20] tendency to the red NSP shift as a particles concentration increases in a monolayer. This shift may be defined not only by the short-range electrodynamic interactions, connected with particle aggregation and, consequently, with a change of the nearest particle surrounding. Besides, it may be caused by the effective field modification as a whole when the particle concentration grows. Apparently, a single inclusion is excited by a wave propagating in some effective medium associated with the average coherent field and characterized by the effective refractive index.

In opposite, for sparse systems of the same particles there is not any plasmon frequency changing when an overlap parameter increases (see dashed curves, corresponding to calculations with using the Bouger law[9] $T_B = \exp(-\eta Q)$, where Q is the efficiency extinction factor of single particle).

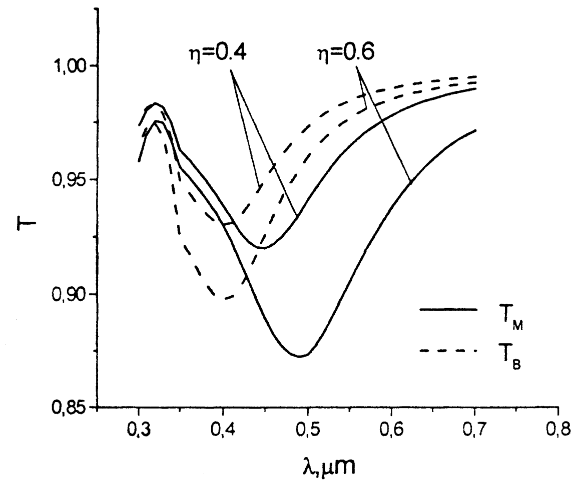

Figure 1. Coherent transmission T_M of monolayers made of Ag spheres with a diameter d=2 nm imbedded into matrix with the refractive index n_m=1.4 at different monolayer overlap parameters η and transmission of a sparse system of the same particles T_B

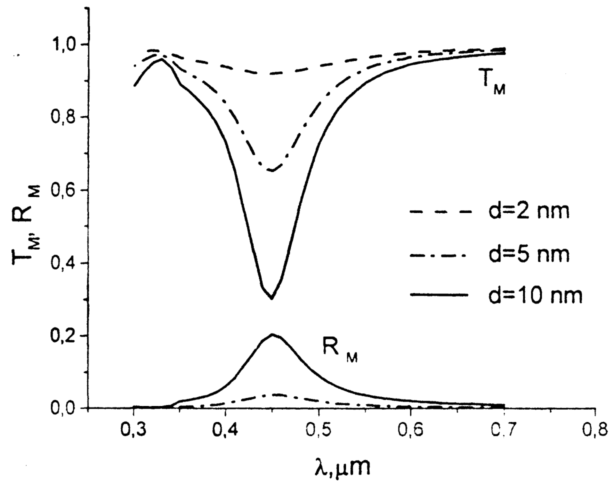

Figure 2. Coherent transmission and reflection of monolayers made of Ag spheres (η=0.4, n_m=1.4)

The particle size influence on collective NSP characteristics is shown in Fig. 2. The growth of particle diameters over the considered range of Rayleigh scattering (d<10 nm) is accompanied by amplification and narrowing the plasmon attenuation peak with the resonance spectral position defined only by the particle concentration value. It is interesting that selective reflectance in the NSP spectral region is enhanced significantly when the particle size increases. For example, for Ag monolayers with η=0.4 maximal reflectance increases from 5% to 20% when particle diameter changes from 5 nm to 10 nm (see Fig. 2).Thus, using the treated above algorithm to calculate coherent transmission T_S and reflection R_S, we have shown that the coherent collective effects in close-packed monolayers of silver particles result to a red shift (in relation to isolated particles) of a surface plasmon resonance frequency and the NSP peak amplification and broadening. The lateral electrodynamic coupling transforms a structure of plasmon resonances and effects on their spectral position.In the case of a stack of close packed Ag nanospheres monolayers with the appropriate thickness l_m of solid dielectric intermediate films (refractive index n_m=1.4) there is a stopband in the visible corresponding to the formation of the PBG due to 1D ordering of the nanoparticle system. In Fig. 3 one can see a comparison of spectral characteristics for three different realisations of the same monolayers. The first case (dashed curves) corresponds to a close-packed stack, when monolayers lie on each other. Two other cases correspond to special choice of intermonolayer optical distances. It equals to a half and to a quarter of the plasmon peak wavelength λ_0

(l_m=175 nm and 90 nm, respectively). Obviously, there is an additional extinction in the region of collective plasmon absorption due to interference of waves scattered in a periodic system of monolayers. For the half-wavelength intermonolayer distances we can note a strong narrowed reflection peak as well as some broadening and a doublet structure of transparency spectra in the NSP vicinity. The case of quarter-wavelength films corresponds to stopband spectral position at the collective plasmon resonance frequency. In this case one can see minimised transmission and reflection.

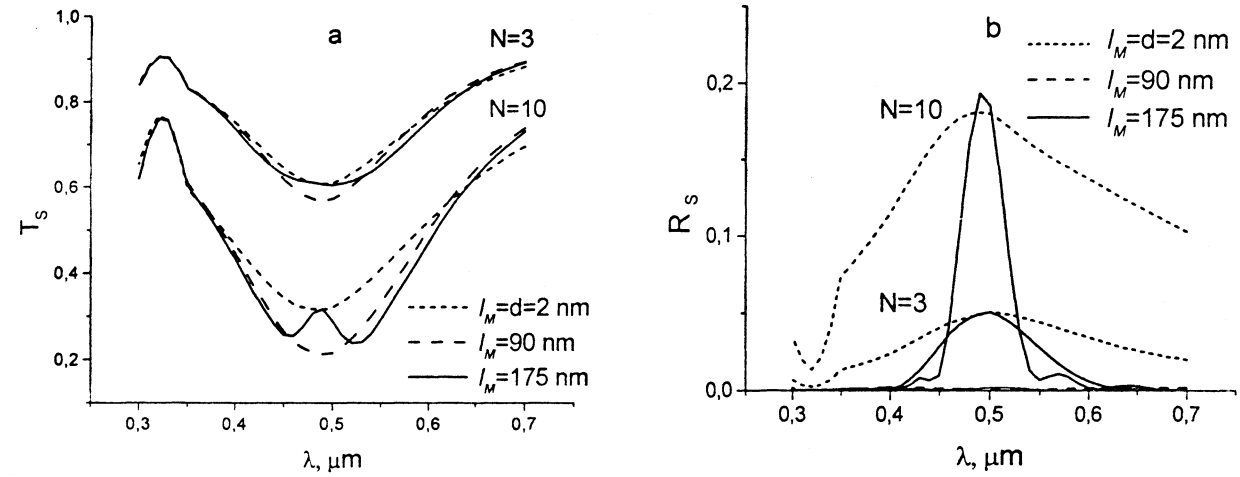

Figure 3. Transmission (a) and reflection (a) of stacks made of monolayers of silver nanoparticles (d=2 nm; η=0.6;n_m=1.4) at different distances between monolayer centers l_M and monolayers quantity N.

Fig.4 shows the transmission spectra of the stacks with several intermonolayers optical distances close to $\lambda_0/2$. As it could be expected, there is a blue shift of a doublet structure at intermonolayer distances decreasing. But simultaneously there is a quite strong dependence of transmission at λ_0 on intermonolayers distances, with the highest transmission for the central case, when l_m=175 nm.

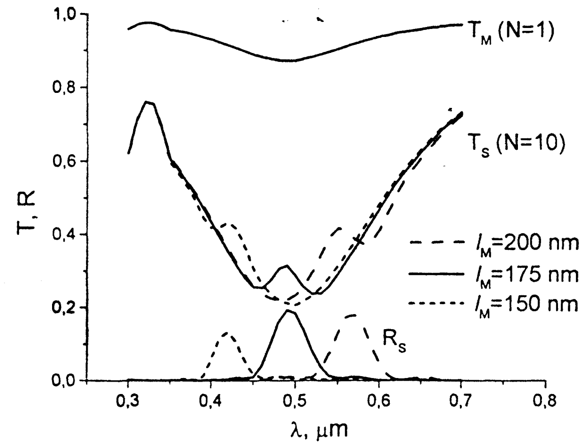

Figure 4. Transmission of stacks made of Ag nanosphere monolayers (d=2 nm; η=0.6; n_m=1.4) separated by dielectric films of different thickness.

Figure 4 also demonstrates a spectral shift of PC reflection peak with being constant its absolute value determined by the particle size, surface concentration and the number of monolayers N. These effects are broken when one moves out of the plasmon peak position. Apparently, the important role in such behaviour belongs to a value of monolayer reflection coefficient R_M, which has a maximum at the monolayer collective plasmon peak.

4.CONCLUSIONS

In this paper we demonstrated that quasicrystalline approximation of the statistical theory of multiple scattering of waves is an efficient method for calculation of PC spectral characteristics. The STMSW gives the most compact and general formalism for calculating moments of field under the condition of electrodynamic coupling the spatial arranged scatterers.

We have shown, that the lateral electrodynamic coupling in a monolayer of close-packed metal nanoparticles results mainly in a long-wave (in relation to isolated particles) shift of a plasmon resonance frequency. One-dimensional ordering of the nanoparticles array with the appropriate thickness of solid intermediate films gives rise to an appearance of a doublet structure of attenuation spectra and narrowing the reflection peak in the vicinity of a plasmon absorbency resonance in the visible.

It has been shown, that the spectral position of these transparency minima and reflectance maxima can be controllable in the plasmon band spectral region by the intermonolayer distances change. Absolute values of transparency minima and reflectance maxima for this layer-periodical metal nanoparticle system are strong dependent on particle sizes, surface concentration and the number of monolayers.

ACKNOWLEGMENTS

The work was supported by the International Scientific and Technical Centre (Grant # B276) and by the National Foundation for Basic Research of Belarus (Grant no. Ph 01-121).

REFERENCES

1. R. Reisfeld., *Optical and Electronic Phenomena in Sol-Gel Glasses*, Heidelberg, Berlin, 1996.
2. , *Nanostructured Materials and Nanotechnology*, ed. By H.S.Nalwa, Academic Press, New York, 2001.
3. M.P. Pileni, "Self-assemblies of nanocrystals: fabrication and collective properties", *Appl. Surf. Sci.*, **171**, pp.1-14, 2001.
4. R.D.Fedorovich, Naumovets A.G., Tomchuk P.M., "Electron and light emission from island metal films and generation of hot electrons in nanoparticles", *Phys.Rep,*. **328,** pp.73-179, 2000.
5. R.J.Gehr, and R.W. Boyd, "Optical properties of nanostructured optical materials", *Chem. Matt.,* **8**, pp.1807- 1819, 1996.
6. T.W. Ebbesen, H.J. Lezec, H.F. Graemi, T. Thio, and P.A. Wolff, "Extraordinary optical transmission through sub-wavelength hole array", *Nature*, **391**, pp. 667-669, 1998.
7. T.F. Krauss, and R.M. De La Rue, "Photonic crystals in the optical regime-past, present and future", *Progr. Quant. Electronics*, **23**, pp.51-96, 1999.
8. Creighton J.A., in *Surface Enchanced Raman Scattering*, Chang R.K., Furtak T.E., Eds.; Plenum Press, New York, 1982
9. C.Bohren and D.Huffman. *Absorption and Scattering of Light by Small Particles* Wiley, New York, 1983.
10. U. Kreibig, M. Vollmer *Optical Properties of Metal clusters,* Springer, Berlin, 1995.
11. S. John, "Strong localization of photons in certain disordered dielectric superlattices", *Phys.Rev.Lett.*, **58,** pp.2486-2489, 1987.
12. E. Yablonovich, "Inhibited spontaneous emission in solid-state physics and electronics", *Phys.Rev.Lett.*, **58,** pp.2059-2062, 1987.
13. R.Serna, M. Jimenez de Castro, J.A.Chaos, C.N. Afonso and I.Vickridge," The role of Er^{3+} –Er^{3+} separation on the luminescence of Er–doped Al_2O_3 films prepared by pulsed laser deposition", *Appl.Phys.Lett.,* **75**, p. 4073, 1999.
14. A. Ishimaru, *Wave Propagation and Scattering in Random Media,* Academic Press, New York, 1978.
15. V.N. Bogomolov, S.V. Gaponenko, I.N.Germanenko, A.M. Kapitonov, E.P.Petrov, A.V. Prokofiev, A.N.Ponyavina, N.I. Silvanovich, and S.M. Samoilovich, "Photonic band gap phenomenon and optical properties of artificial opals", *Phys. Rev. E*, **55**, pp.7619-7625, 1997.

16. A.N. Ponyavina, N. I. Sil'vanovich, "Interference effects and spectral characteristics of multilayer scattering media", *Opt. Spektrosk.*, **76**, pp.648-655, 1994.
17. M.Lax, "The effective field in dense systems", *Phys. Rev.*, **58**, pp.621-629, 1952.
18. J.Ziman, *Models of Disorder,* Cambridge University Press, Cambridge, 1979.
19. U.Kreibig, C.v.Fragstein, "The limitation of electron mean free path in small silver particles", *Z. Phys.*, **224**, p. 307, 1969.
20. H. Hovel, S.Fritz, A.Hilger, U.Kreibig, and M.Vollmer, "Width of cluster plasmon resonances: Bulk dielectric functions and chemical interface damping", *Phys. Rev. B,* **48,** pp.18148-18187, 1993.