Total light absorption in ultrathin size-gradient metal-dielectric nanostructures

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ABSTRACT

We propose ultrathin plasmonic nanocoatings that can absorb more than 90% of visible light in a broad (exceeding 100 nm) wavelength range, reaching almost total absorption at the surface plasmon resonance (SPR) wavelength. Such a coating contains only two monolayers of metal nanoparticles (with smaller nanoparticles in the first monolayer and larger nanoparticles in the second monolayer) separated by a dielectric film with quarter-wave thickness. We analytically derive spectral characteristics of two-monolayer systems and explore the regimes, which must be satisfied for realization of high-absorptive coatings at the SPR range.

Keywords: surface plasmon resonance, multilayer, gradient nanostrucutures, absorption

1. INTRODUCTION

Metallic nanostructures are now considered as promising photonic materials for a wide variety of applications at optoelectronics, biosensing and diagnostics. Their unique optical properties allow effective light manipulating. These properties are fundamentally based on the localized surface plasmon resonances, which are determined by collective oscillations of the conduction electrons in metallic nanoparticles. The SPR features can be effectively controlled by changing the nanoparticle metal, size, shape and matrix material.

Close contact of nanoparticles in dense arrays gives rise to appearance of coupled plasmons, that are high sensitive to spatial arrangement of metallic nanoparticles. Indeed, large opportunities to control the SPR modes are already demonstrated for close-packed or regular monolayers of nanoparticles and multilayers consisting of polymer-linked several monolayers [1]. Currently developed physical and chemical techniques for preparation of the metal-dielectric multilayers [2-6] allow controlling both topology of ultradisperse metallic layers and thickness of dielectric films. Emphasize that subwavelength periodicity leads to strong plasmonic-photonic intermonolayer coupling that causes the dramatic change in optical properties of metal-dielectric nanocomposites [2-3]. Such subwavelength layer-periodic structures may be considered as quasi-one-dimensional metallic photonic crystals, where the photonic bandgap occurs under simultaneous realization of electronic and photonic confinements. Tailoring the multilayer optical properties is made by matching the thickness of separating dielectric films to the SPR wavelength of metal nanoparticle monolayer.

In [2-3] we have theoretically and experimentally considered the multilayer nanostructured systems, which are the stacks composed of identical metallic nanoparticle monolayers separated by dielectric films of equal thickness. Thus, we stacked a number of close-packed layers of metallic nanoparticles with identical particle's material, size, concentration and other monolayer parameters. It was shown that the choice of the quarter-wave thickness of dielectric films (see Fig. 1) leads to destructive multibeam interference and provides us with strong absorption over the SPR spectral range due to reducing both transmission and reflection. In [7] we suggested that efficiency of destructive interference in quarter-wave systems can be enhanced by getting comparable in intensity beams reflected from the neighboring monolayers. For this purpose, to compensate the increasing light attenuation at its penetration into the multilayer, one should enhance the reflectance of each next monolayer. It can be reached by using a gradient change of the monolayer parameters, for example (i) by changing the nanoparticle sizes from monolayer to monolayer (so-called size-gradient nanostructures, see

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Fig. 2) and (ii) by changing the nanoparticle concentrations from monolayer to monolayer (so-called concentration-gradient nanostructures).

In the present paper we provide a more detailed analysis of the size-gradient nanostructures which demonstrate some important advantages relatively to concentration-gradient nanostructures [7]. Here we focus on the systems consisting of only two monolayers to make the absorbing coating as thin as possible. In contrast to [7] we analyze two-monolayer size-gradient systems by taking into account a real spectral dependence of phase shifts of waves transmitted and reflected from monolayers at the surface plasmon frequency.

The paper is organized as follows. In Section 2 we briefly describe the calculation method applied to obtain spectral properties of a partially-ordered monolayer of metallic nanoparticles and multilayers consisting of such nanoparticle monolayers. In Section 3 we analyze a two-monolayer gradient system and deduce the conditions of simultaneous realization of reduced reflection and enhanced absorption compared with non-gradient systems. Optical properties of optimized in this way size-gradient two-layer systems made of silver nanoparticles are presented and discussed in Section 4.

2. CALCULATION METHOD

As it was noted above, the considerable distinctions between optical spectra of metal nanostructures and the corresponding bulk metal emerge from the existence of surface modes (plasmon resonances) on metal nanoparticles. Besides, electron confinement in metal nanoparticles leads to size dependence of their optical constants. For close-packed nanoarrays these effects are of the collective nature because of strong coupling between partially-ordered nanoparticles. Initiated coherent multiple scattering of waves within the array has a dramatic effect on its optical properties. The most convenient theoretical approach considering these coherent interactions for arrays with short-range ordering is the statistical theory of multiple scattering of waves [8], especially the quasicrystalline approximations (QCA). This approach considers electrodynamic coupling of spatially correlated scatterers by means of interference summation and subsequent averaging of fields scattered by all nanoparticles. It supposes the advance information about statistical structural parameters and scattering properties of a single particle. In the frame of the QCA the particle spatial ordering is described by the radial distribution function. For random close-packed structures with short-range ordering we used the solid-sphere approximation. Single scattering characteristics of metal nanospheres are determined by means of the Mie theory.

In order to calculate the coefficients of the direct light transmission and specular reflection for metal-dielectric multilayer nanostructures considered in this paper we combine the QCA applied for calculations of the transmission properties of individual monolayers with the transfer-matrix technique (QCA-TM) used for subsequent calculations of the transmission properties of multilayer structures as described in [7].

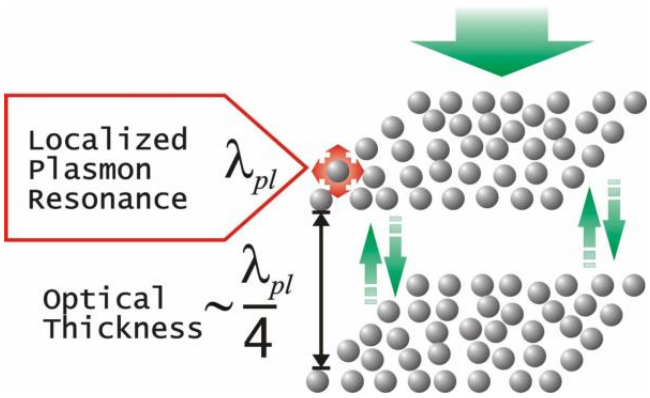

Fig. 1. Schematic illustration of a quarter-wave nanostructure made of metallic nanoparticle monolayers.

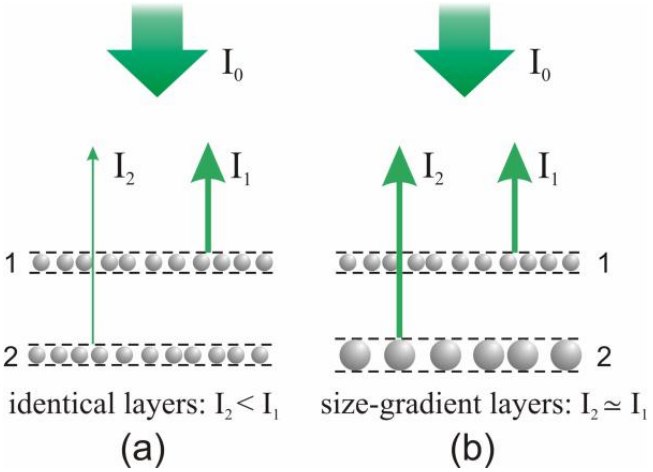

Fig. 2. Schematic comparison of the beam intensities reflected from the monolayers in (a) non-gradient and (b) size-gradient two-monolayer nanostructures.

In illustration, Fig.3 demonstrates calculated by the QCA spectral dependences of optical characteristics of single close-packed monolayers at nanoparticle size changing. Packing density of monolayers indicated in terms of the overlap parameter η, which gives the fraction of area occupied by nanoparticles. From Fig. 3(a) and 3(b) one can see that the growth of nanoparticle sizes leads to a decrease in transmittance and, simultaneously, increase in reflectance of a close-packed monolayer in the SPR region. Thus, in order to realize the efficient destructive interference in a quarter-wave size-gradient system, we should sequentially enlarge the nanoparticle size in each next monolayer on the way of the incident beam.

Fig. 3 (c,d) shows the spectral dependence of the QCA phase shifts φ_i^t and φ_i^r of waves transmitted and reflected from a monolayer, correspondingly. One can see that for different nanoparticle diameters the phase shifts are vanishing at the SPR wavelength λ_{pl}. This feature will be taken into account in Section 3 for analysis and optimization of systems made of two absorbing monolayers.

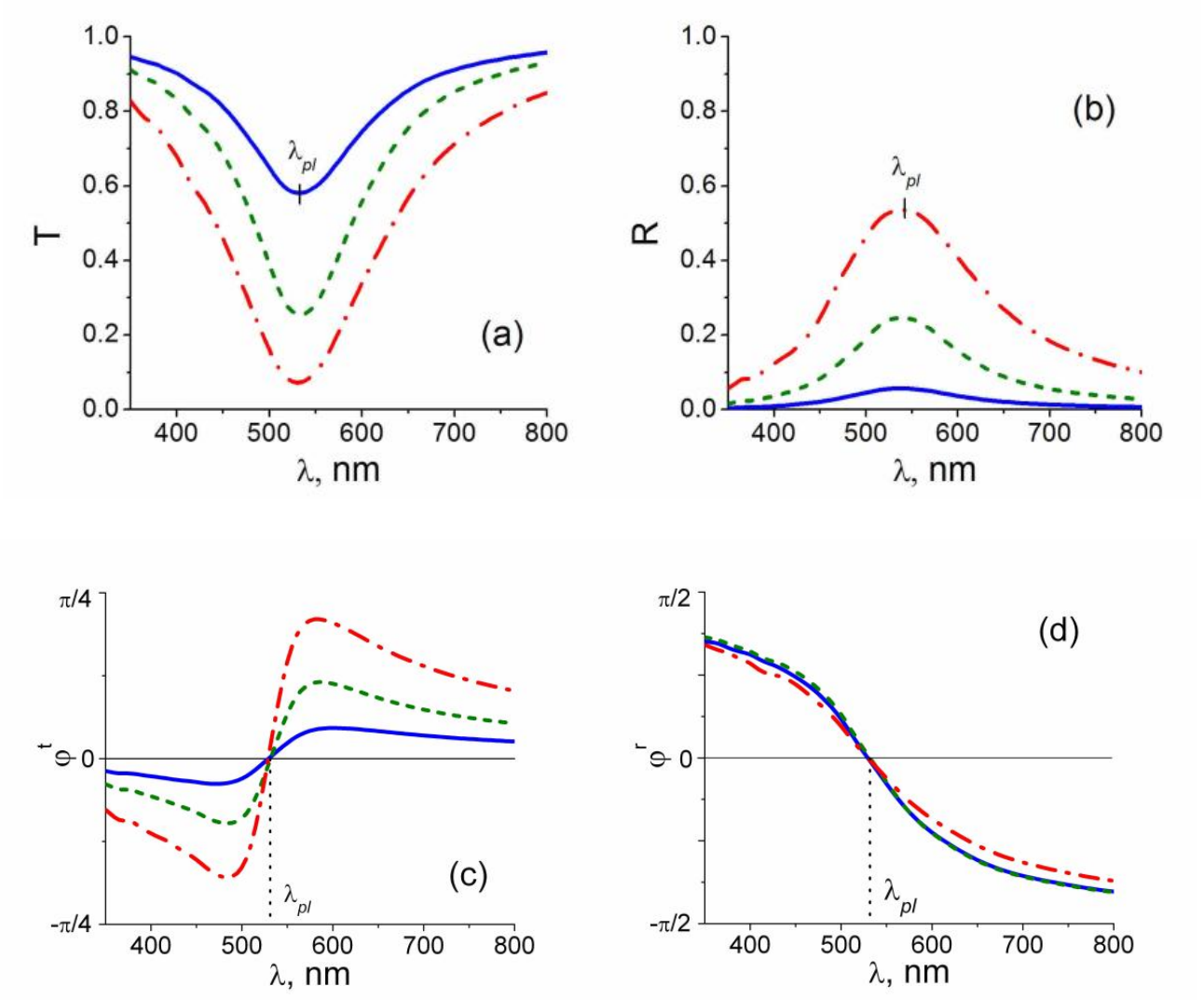

Fig. 3. Spectral dependences of transmission (a) and reflection (b) coefficients, as well as phase change at transmission (c) through and reflection (d) from the close-packed monolayers with different size of Ag nanoparticles *d* at fixed overlap

parameter η=0.5 (Al_2O_3 matrix): solid lines correspond to d=5 nm, dashed lines – d=10 nm and dot-dashed lines – d=20 nm

3. ANALYSIS OF A SYSTEM MADE OF TWO ABSORBING MONOLAYERS

First of all, let us consider scattering of a plane wave by a nanostructure consisting of two different nanostructured metal-dielectric monolayers separated by a dielectric film with thickness h, as it is shown on Fig. 4. Neglecting interaction of scattered by monolayers evanescent waves, we can write amplitudes of transmission and reflection for the 1-st and 2-nd monolayers as $t_1 = |t_1| \exp\left(i\varphi_1^t\right)$, $r_1 = |r_1| \exp\left(i\varphi_1^r\right)$ and $t_2 = |t_2| \exp\left(i\varphi_2^t\right)$, $r_2 = |r_2| \exp\left(i\varphi_2^r\right)$, correspondingly. Here φ_i^t and φ_i^r are phase shifts at transmission and reflection by i-th monolayer. Here we assume a normal incidence of the plane wave and identical dielectric with refractive index n_m both between and outside the monolayers.

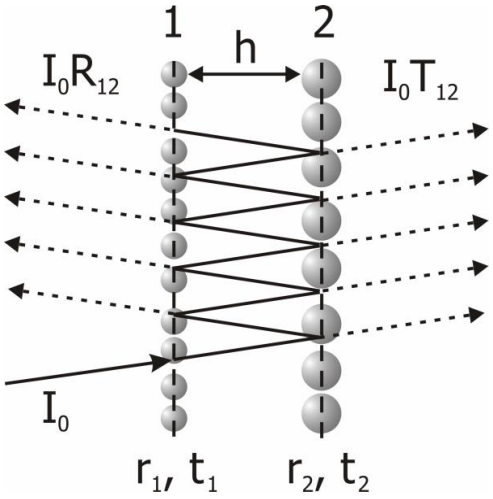

Fig. 4. Interference scheme of plane wave interaction with a two-monolayer size-gradient system

Taking into account multiple coherent scattering of light waves between the first and the second monolayers of nanoparticles, the amplitudes of light transmission and reflection by two-monolayer nanostructure take the form:

$$t_{12} = \frac{t_1 t_2 \exp(ikh)}{1 - r_1 r_2 \exp(2ikh)},\ r_{12} = r_1 + \frac{r_2 t_1^{\,2} \exp(2ikh)}{1 - r_1 r_2 \exp(2ikh)}. \tag{1}$$

Note that these expressions can be reduced to the Airy's formula [9] for a thin dielectric film in the case when (a) the absorption in monolayers can be neglected, and (b) $r_1 = -r_2$ due to π-jump of a complex phase for the reflection from optically more dense medium at the interface film/matrix.

In a general case, the energetic coefficients of transmission T_{12} and reflection R_{12} of the two-monolayer system take the form:

$$T_{12} = |t_{12}|^2 = \frac{T_1 T_2}{1 + R_1 R_2 - 2\sqrt{R_1 R_2}\cos\beta} \tag{2}$$

$$R_{12} = |r_{12}|^2 = R_1 + \frac{T_1\left(R_2 T_1 + 2\sqrt{R_1 R_2}\cos(\alpha - \beta) - 2R_1 R_2 \cos(\alpha)\right)}{1 + R_1 R_2 - 2\sqrt{R_1 R_2}\cos(\beta)} \tag{3}$$

where we introduced for convenience phase parameters

$$\alpha = 2(\varphi_1^r - \varphi_1^t),$$
$$\beta = 2kh + \varphi_1^r + \varphi_2^r, \tag{4}$$

here $T_i = |t_i|^2$ and $R_i = |r_i|^2$ are energetic coefficients of direct transmission and specular reflection of *i*-th monolayer.

We can neglect diffuse light scattering by monolayers of dipole metallic nanoparticles and thus calculate light absorption in *i*-th monolayer according to the equation:

$$A_i = 1 - T_i - R_i. \tag{5}$$

Correspondingly, absorption will completely determine optical losses in the two-monolayer system:

$$A_{12} = 1 - T_{12} - R_{12}. \tag{6}$$

Substituting expressions (2) and (3) into (6), we can rewrite absorption A_{12} of two-monolayer system in the form

$$A_{12} = 1 - R_1 + \frac{T_1\left(A_2 + R_2\left(A_1 + R_1\right) - 1 - 2\sqrt{R_1 R_2}\cos\left(\alpha - \beta\right) + 2R_1 R_2\cos\left(\alpha\right)\right)}{1 + R_1 R_2 - 2\sqrt{R_1 R_2}\cos\left(\beta\right)} \tag{7}$$

As one can see from Eqs. (2), (3) and (7), the phase parameters α and β determined by the phases φ_i^t and φ_i^r of the transmission and reflection amplitudes of individual monolayers have an important influence on the optical properties of two-monolayer system. In Fig. 3 we show the spectral dependence of φ_i^t and φ_i^r for several different diameters of nanoparticles and their concentration inside a single monolayer. As it is evident from this figure, phase shifts for both, transmission and reflection, are vanishing in the vicinities of the volume plasmon resonance ω_p and collective surface plasmon resonance ω_{pl} for metallic nanoparticles in the quaststatic regime at arbitrary concentrations of nanoparticles:

$$\varphi_i^r \approx \varphi_i^t \approx 0. \tag{8}$$

However, for frequencies outside the resonance frequencies ω_p and ω_{pl} relation between transmission and reflection phases φ_i^t and φ_i^r approach the same form as for the interface of two dielectrics:

$$\varphi_i^r \approx \varphi_i^t \pm \frac{\pi}{2}. \tag{9}$$

An additional parameter which determines optical properties of two-monolayer system is the thickness *h* of a dielectric film, entering into Eqs. (2), (3), (7) via the parameter β. As can be easily seen, all spectral characteristics of two-monolayer system are periodic functions of the thickness *h*. In particular, the transmission coefficient T_{12} is always minimal for $\beta = \pi \pm 2\pi m$ and maximal for $\beta = \pm 2\pi m$, where *m* is an arbitrary integer.

For dipole particles, when in according to Eqs. (4), (8)-(9) $\alpha \approx 0$ and $\beta \approx 2kh = 4\pi\tau / \lambda_{pl}$ at the SPR frequency (while far away from the resonance $\alpha \approx \pm\pi$ and $\beta \approx 2kh \pm \pi = 4\pi\tau / \lambda_{pl} \pm \pi$), the analysis of second derivatives of spectral functions T_{12}, R_{12}, A_{12} with respect to β shows that all of them have extrema for quarter-wavelength and half-wavelength (relative to plasmon wavelength λ_{pl}) optical thickness $\tau = hn_m$.

Due to vanishing of α in the vicinity of the SPR frequency (see Eqs. (4) and (8)) the resonant transmission T_{12} and reflection R_{12} coefficients of two-monolayer system *simultaneously* reach maximum at $\tau = \lambda_{pl} / 2$ and minimum at

$\tau = \lambda_{pl} / 4$. Accordingly, resonant absorption A_{12} is a contrast function of β, with the minimum at $\tau = \lambda_{pl} / 2$ and the maximum at $\tau = \lambda_{pl} / 4$.

In the last case of the maximal light absorption at the SPR frequency (at $\tau \approx \lambda_{pl} / 4$) the spectral characteristics (2), (3), (7) take the form:

$$T_{12} = \frac{T_1 T_2}{\left(1 + \sqrt{R_1 R_2}\right)^2}; \tag{10}$$

$$R_{12} = \left[\frac{\sqrt{R_1} + \sqrt{R_2}\left(R_1 - T_1\right)}{1 + \sqrt{R_1 R_2}}\right]^2; \tag{11}$$

$$A_{12} = A_1 + \frac{T_1\left(A_2 + A_1 R_2 + 4\sqrt{R_1 R_2}\left(1 + \sqrt{R_1 R_2}\right)\right)}{\left(1 + \sqrt{R_1 R_2}\right)^2} \tag{12}$$

In contrast, far away from the resonance frequency, when according to Eqs. (4) and (9) $\alpha \approx \pm\pi$, the transmission T_{12} and reflection R_{12} coefficients exhibit counter-phase behavior with varying the parameter β: for $\tau = \lambda_{pl} / 4$ transmission reaches maximum but reflection reaches minimum, while for $\tau = \lambda_{pl} / 2$ we observe an opposite behavior. Such a counter-phase change of T_{12} and R_{12} leads to the smoothing of the modulations of the absorption coefficient in two-monolayer system. In this case the spectral characteristics (2), (3), (7) of quarter-wavelength system can be written as presented in [7]:

$$T_{12} = \frac{T_1 T_2}{\left(1 - \sqrt{R_1 R_2}\right)^2} \tag{13}$$

$$R_{12} = \left[\frac{\sqrt{R_1} - \sqrt{R_2}\left(1 - A_1\right)}{1 - \sqrt{R_1 R_2}}\right]^2 \tag{14}$$

$$A_{12} = A_1 + \frac{T_1\left(A_2 + A_1 R_2\right)}{\left(1 - \sqrt{R_1 R_2}\right)^2} \tag{15}$$

4. RESULTS AND DISCUSSIONS

In the previous Section we analyzed light absorption in two-monolayer systems in terms of the spectral characteristics of the monolayers: their transmittance $T_i(\lambda)$, reflectance $R_i(\lambda)$, and absorptance $A_i(\lambda)$. We have shown that the maximal absorption in such systems is achieved at the SPR frequency using the quarter-wavelength thickness of the dielectric film separating two monolayers. Quantitatively this absorption is described by Eq.(12), where T_i, R_i, and A_i are taken at the plasmon frequency. To complete the analysis, we should know how these spectral parameters depend on the diameters and concentration of nanoparticles in monolayers.

In contrast to [7], here we shall consider only size-gradient two-monolayer system characterized by a common concentration η of particles in both monolayers but different diameters d_1 and d_2 of the nanoparticles in the first and the second monolayers, correspondingly. The advantage of such system is that in the quasistatic regime (nanoparticle diameters up to 20 nm) the wavelength of the plasmon resonance λ_{pl} is determined by only overlap parameter η being

very weakly sensitive to the particles diameter. Therefore, for every given concentration η we can find (with the QCA method) T_i, R_i, and A_i at the plasmon resonance frequency $\lambda_{pl} = \lambda_{pl}(\eta)$ as functions of the particles diameters d_i. Then, substituting such functions into Eq.(12), we can find the maximally achievable at the given diameters d_1 and d_2 resonant light absorption by a two-monolayer system.

In Fig. 5 we plot the corresponding resonant absorption in a system of two close-packed monolayers of silver nanoparticles separated by a quarter-wavelength Al_2O_3 film, for two different particles concentrations: η=0.3 (for which λ_{pl} = 490 nm) and η=0.7 (for which λ_{pl} = 610 nm). As we see, the dependence of A_{12} on d_1 and d_2 is qualitatively identical for all concentrations: it always grows with increasing d_2 (over the size range under investigation) but changes non-monotonically with d_1. Thus, there is the maximum of A_{12}, which is located at some relatively small (indicated by black arrows in Fig. 5) value of d_1, determined by the concentration, and large (around 20 nm or even larger) value of d_2. The larger is the nanoparticle concentration, the higher is the maximally achievable resonant absorption value A_{12} (reaching 93% for η=0.3 and 99% for η=0.7). The optimal diameter d_1 corresponding to this maximal absorption decreases with increasing η (d_1=8.8 nm for η=0.3 and 4.7 nm for η=0.7). So, one can see that almost total absorption can be reached for a size-gradient system of two monolayers with high packing density of nanoparticles.

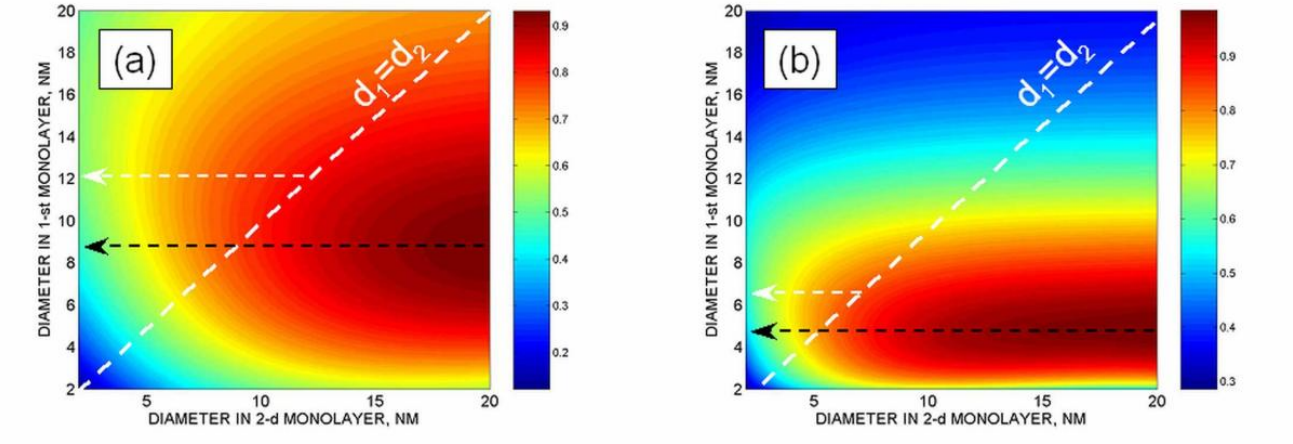

Fig. 5. Resonant absorption in a two-monolayer size-gradient system (Ag nanoparticles/quarter-wave Al_2O_3 film) as function of nanoparticle size in the first and second monolayers at different overlap parameters: (a) η=0.3 (λ_{pl}=490 nm); (b) η=0.7 (λ_{pl}=610 nm).

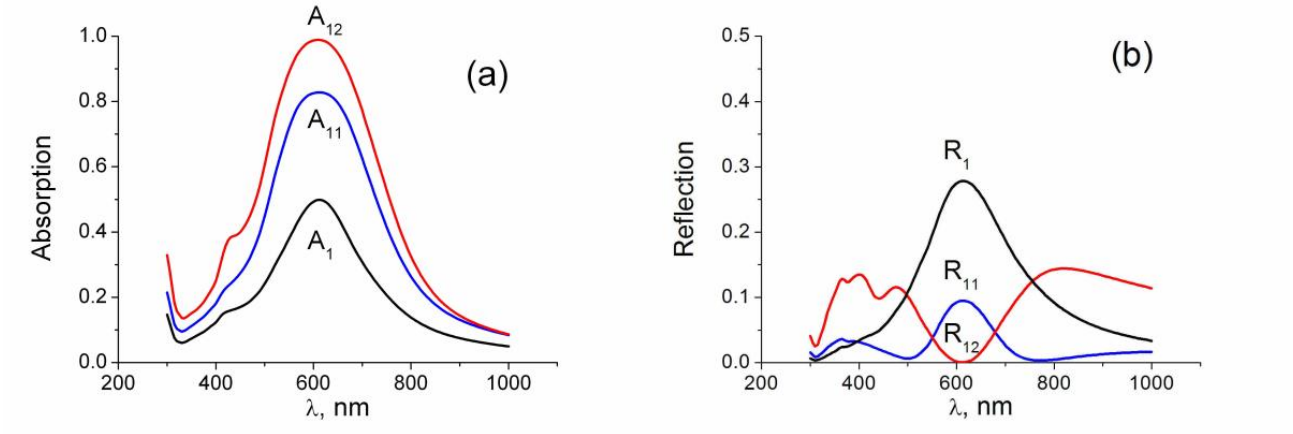

Fig. 6 Absorption (a) and reflection (b) spectra of one monolayer (A_1, R_1), two-monolayer quarter-wave non-gradient (A_{11}, R_{11}) and size-gradient (A_{12}, R_{12}) systems (Ag nanoparticles / Al_2O_3 film, η=0.7) calculated by the QCA-TM for the case of nanoparticle diameters giving the **maximal absorption** for each system: d=8.8 nm for the monolayer; d_1=d_2=6.6 nm for the non-gradient system; d_1=4.7 nm and d_2=20 nm for the size-gradient system.

It should be noted that the maximal resonant absorption in the size-gradient system is significantly higher than it would be possible to achieve in the system of two identical monolayers with $d_1=d_2$ (see white dashed lines and arrows in Fig. 5). Moreover, as one can see from absorption spectra presented in Fig. 6(a), using optimized size-gradient systems provide us not only with the largest peak of plasmon absorption band but also with its widest bandwidth. At the same time, both optimized size-gradient and optimized non-gradient two-monolayer systems have significant advantage in absorption in comparison to an optimized single monolayer with the same overlap parameter. This advantage is determined by minimization of reflection from the two-monolayer systems. As Fig. 6(b) shows, a single monolayer is characterized by very large resonant reflection, while the destructive interference in the quarter-wave two-monolayer systems dramatically reduces the reflection from the system and makes it completely vanishing at the SPR frequency for the optimized size-gradient system.

Briefly, the absorption maximization procedure for a size-gradient system made of dipole nanoparticles is divided in two steps. At first, the choice of the nanoparticle surface density determines the spectral position of the SPR (the more is the nanoparticle surface concentration, the larger is a red concentration shift of the SPR). The next step is concentration-dependent choice of nanoparticle size for the first monolayer. The nanoparticle size for the second monolayer should be taken the largest in the frame of the quasistatic regime (in the case under investigation d_2=20 nm).

5. CONCLUSIONS

In conclusion, we show that the total absorption of light in the vicinity of the SPR can be reached in a size-gradient two-monolayer system of dipole silver nanoparticles. The maximal absorption at any required frequency in the visual and near-IR ranges can be reached by special, concentration-dependent choice of nanoparticle size in the first monolayer and using the larger nanoparticles in the second monolayer. Such optimized size-gradient two-monolayer plasmonic coatings demonstrate the broadband and strong absorptance, having the thickness of a few tens of nanometers.

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