Total resonant absorption of light by plasmons on the nanoporous surface of a metal

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We have calculated light absorption spectra of planar metal surfaces with two-dimensional lattice of spherical nanovoids right beneath the surface. It is shown that nearly total absorption of light occurs at the plasma resonance in void lattice in the visible when the inter-void spacing and the void deepening into the metal are thinner than the skin depth, which ensures optimal coupling of void plasmons to external light. We conclude that the absorption and local-field properties of this type of nanoporous metal surfaces can be effectively tuned by nano-engineering the spherical pores and they constitute a very attractive system for various applications in future submicron light technology.

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1. Introduction

In general, planar metal surfaces absorb light very poorly. The reason is their high free-electron density, which reacts to the incident light by sustaining strong oscillating currents that, in turn, efficiently re-radiate light back into the surrounding medium, whereas the light intensity inside the metal remains weak. Actually, the same phenomenon takes place when light excites plasma oscillations in metallic particles, and light absorption is inhibited as a result at the plasma resonances. In other words, the local-field enhancement inside or near the metallic particle appears to be quite moderate even at the plasma resonance. Local-field enhancement factors up to 15 have been reported for spherical metallic nanoparticles [1,2].

In apparent contradiction with the above arguments, sharp and deep (down to –20 dB) resonant dips in the reflectivity spectra of light from nanoporous gold surface have been recently observed [3], which points to strong resonant light absorption on such a surface.

It was presumed in [3] that this phenomenon is related to the excitation of plasmon modes in spherical nanocavities inside the metal, which couple much more effectively to the light than those in metallic spheres. As an intuitive explanation of their observations, the authors of [3] employed a simple model of plasmon modes supported by a spherical void in an infinite metallic medium. Although that model gives the eigen-frequency values that somehow can be fitted to the frequencies of the resonances in the measured reflectivity spectra, it can not describe the coupling between plasmon modes in nanocavity and the external radiation field. The reason is that the plasmon modes in a void are non-radiative because their electromagnetic field cannot radiate into an infinite metal having a negative permittivity. However, the huge resonant dips in the reflectivity spectra observed in [3] suggest strong coupling of nanocavity plasmons to the incident light. Therefore, a better understanding of the effect of coupling between plasmons in metallic nanocavities and external radiation becomes of great importance.

On the other hand, it has been shown in [4–6] that the spectra of plasma oscillations in spherical metallic nanoparticles with inner voids (nanoshells) are much richer than those in metallic nanospheres. Both sphere-like plasmons (those mainly bound to the outer surface of the shell) and void-like plasmons (those mainly bound to the inner surface of the shell) can be excited in such a particle. Optical properties of a single metallic nanoshell and nanoshell clusters can be effectivelly tuned by nano-engineering their geometry. As it has been theoretically shown in [6], the local-field enhancement factor at the void-like plasmon resonance can reach ultra-high values for specific values of the metallic wall thickness in nanoshell: local-field enhancement factors exceeding 60 and 150 in gold and silver nanoshells, respectively, have been predicted, and this field enhancement is accompanied by sharply enhanced light absorption at the resonance.

In this paper, we study the optical properties of nanoporous metal surface. We start with a simple model of the resonant surface in order to examine the essential physics underling strong light absorption on such a surface. Then we calculate the reflection/absorption spectra of nanoporous metal surfaces in the framework of a rigorous electromagnetic scattering-matrix approach [7], taking into account the actual porous structure of the surface.

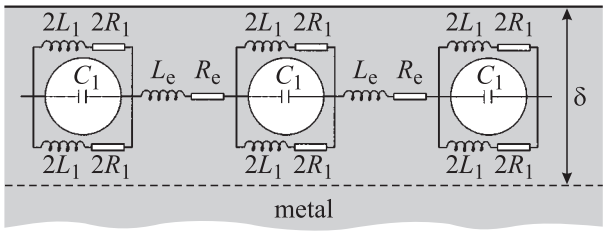

Figure 1. Nanoporous surface of metal and its equivalent circuit.

2. Model of a resonant surface

Let us consider an electromagnetic plane wave incident from vacuum normally onto a planar surface of metal with a two-dimensional lattice of voids just underneath the surface (Fig. 1). In order to examine the essential physics of energy transformation in the system we elaborate a simple equivalent model describing the resonant surface by its effective surface impedance Z_{eff} defined by the relation $\mathbf{E}_\tau = Z_{\text{eff}}(\mathbf{n} \times \mathbf{B}_\tau)$, where $\mathbf{E}_\tau$ and $\mathbf{B}_\tau$ are the tangential components of the total electric and magnetic fields, respectively, and $\mathbf{n}$ is the external normal to the planar metal surface. Making use of the impedance boundary condition [8] and solving Maxwell's equations in the surrounding medium, it is easy to obtain the complex amplitude reflection coefficient $r = (Z_{\text{eff}} - Z_0)/(Z_{\text{eff}} + Z_0)$, where Z_0 is the free-space impedance.

We describe plasma oscillations in the lattice of voids by an equivalent *RLC* circuit (Fig. 1) composed of the equivalent areal capacitance $C_l = |f_l|^2 \delta \varepsilon_0$, where δ is the thickness of the nanoporous surface layer, ε_0 is the electrical constant, $|f_l|^2$ is the dimensionless phenomenological form-factor characteristic of a given lth multipole plasmon mode, connected in parallel to $R_l - L_l$ series (Fig. 1). The equivalent areal electronic resistance and kinetic inductance are defined as $R_l = m\nu_l/(e^2 \Delta_l N_e)$ and $L_l = m/(e^2 \Delta_l N_e)$, respectively, where ν_l is the damping of the lth plasmon mode due to all dissipative processes except radiative damping, N_e is the total areal free-electron density in the surface skin layer, Δ_l is the fraction of free electrons participating in the plasma oscillations at the lth mode, and e and m are the electron charge and mass, respectively.

With this considerations, we can easily obtain the equivalent surface impedance in the form

$$Z_{\text{eff}} = \frac{m}{e^2 N_e}(\nu_e - i\omega) - i\frac{m}{2e^2}\sum_{l=1}^{\infty}\frac{|\beta_l|^2}{\Delta_l N_e}\frac{\omega_l^2}{\omega_l - \omega - i\nu_l}, \tag{1}$$

where

$$\omega_l = \sqrt{\frac{e^2 \Delta_l N_e}{|f_l|^2 \delta \varepsilon_0 m}} \tag{2}$$

is the frequency of the lth plasmon mode, and $|\beta_l|^2 < 1$ is the phenomenological coefficient of coupling between the external light and the lth plasmon mode. The first term in Eq. (1), where ν_e is the free-electron scattering rate, describes the Drude response of a homogeneous metal surface within inter-void regions to incident light by the equivalent electronic resistance $R_e = m\nu_e/(e^2 N_e)$ and kinetic inductance $L_e = m/(e^2 N_e)$ (Fig. 1). In the vicinity of the lth plasma resonance, $\omega \simeq \omega_l$, the lth term of the summation dominates the right hand side of Eq. (1) and we have

$$Z_{\text{eff}} \approx -i\frac{m|\beta_l|^2}{2e^2 \Delta_l N_e}\frac{\omega_l^2}{\omega_l - \omega - i\nu_l}. \tag{3}$$

The surface impedance given by Eq. (3) leads to the following expression for the absorbance of light in the neighborhood of the lth plasma resonance

$$A = 1 - rr^* \approx \frac{4\nu_l \gamma_l}{(\omega_l - \omega)^2 + (\nu_l + \gamma_l)^2}, \tag{4}$$

where

$$\gamma_l = |\beta_l|^2 \frac{m\omega_l^2}{2Z_0 e^2 \Delta_l N_e} \tag{5}$$

is the radiative damping of the lth plasmon mode. It should be noted that the line of the absorption resonance given by Eq. (4) has a Lorentzian shape with the full width at half maximum (FWHM) of $2(\nu_l + \gamma_l)$. Free parameters $|f_l|^2/\Delta_l$, and $|\beta_l|^2/\Delta_l$ can be obtained by fitting the resonance frequency and FWHM yielded by this simple model to those yielded by a rigorous electromagnetic modeling, which is done in the next section of this paper.

Finally, at resonance ($\omega = \omega_l$), one finds

$$A_{\text{res}} \approx \frac{4\nu_l \gamma_l}{(\nu_l + \gamma_l)^2}$$

and it is readily seen that nearly total light absorption by the lth plasmon mode (i. e., $A_{\text{res}} \approx 1$) occurs when $\gamma_l = \nu_l$. The radiative damping γ_l may be conceived as the coupling coefficient that controls the strength of interaction between the plasmon mode and light. For small γ_l (i. e., $\gamma_l \ll \nu_l$) the coupling is weak and the plasmon mode absorbs light only weakly. In the opposite limit, $\gamma_l \gg \nu_l$, the strong plasma oscillation currents flowing on the metal surface re-radiate incident light back into the surrounding medium, which again reduces absorption drastically. Therefore, it is possible to realize the condition of total light absorption by plasmons on nanoporous metal surface by varying the coupling coefficient $|\beta_l|^2$. The optimal value of $|\beta_l|^2$ can be easily realized for void-like plasmon modes in the spherical voids buried in a metal substrate. For example, the condition $\gamma_l = \nu_l$ can be easily satisfied for void-like plasmons in a nanoshell by choosing a specific value of the shell-layer thickness, as shown in [6].

3. Self-consistent electrodynamic modeling

Let us consider a periodic two-dimensional hexagonal lattice of spherical voids with the lattice vectors $\mathbf{a}$ and $\mathbf{b}$, where $|\mathbf{a}| = |\mathbf{b}|$ and $\mathbf{a} \cdot \mathbf{b} = |\mathbf{a}|^2 \cos\alpha$ with $\alpha = 60°$. We

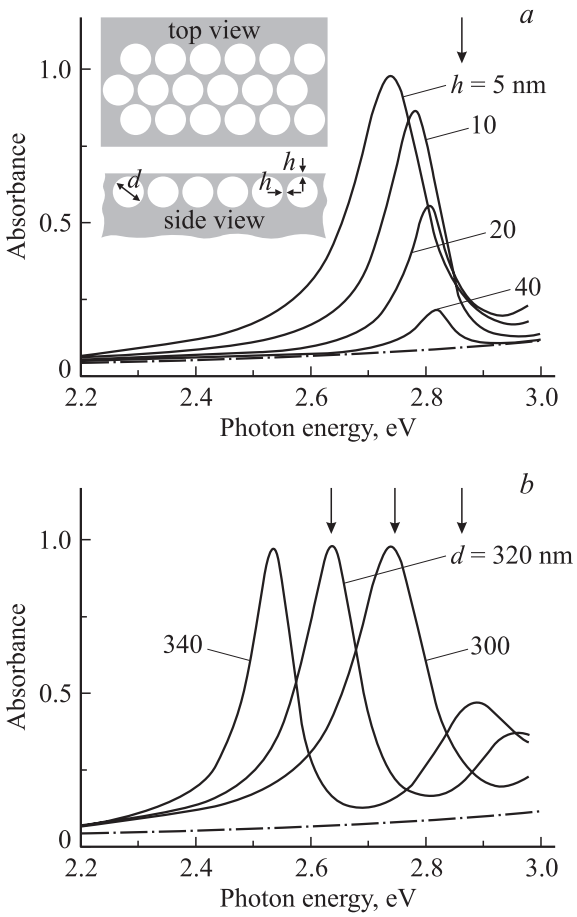

Figure 2. Absorption spectra of light incident normally onto a planar silver surface with a lattice of spherical voids right beneath it (see inset). *a* — variation of the spectra with the inter-void spacing *h*, which is chosen to be equal to the void deepening, for the void diameter $d = 300$ nm. *b* — variation of the spectra with the voids diameter for the inter-void spacing $h = 5$ nm also taken to be equal to the void deepenigh. The absorption of light on the surface of bulk silver is shown by dash-dotted curve. Vertical arrows mark the energies of the fundamental plasmon modes ($l = 1$) of a single void in bulk silver.

assume that the lattice of voids is buried inside a metal substrate at distance *h* from the planar metal surface to the top of the voids, therefore we call *h* the void deepening. We also assume that the inter-void spacing along the lattice vectors **a** and **b** is equal to the void deepening *h* (inset of Fig. 2, *a*). We consider that external light shines normally onto the metal surface.

To calculate the light absorption on such a nanoporous surface of metal we use a self-consistent rigorous electrodynamic method based on the scattering-matrix approach with making use of re-expansion of the plane-wave representation of electromagnetic fields in terms of the spherical harmonics [7]. This approach involves the following steps. First of all we define a planar surface layer containing the periodic lattice of voids in such a way that the planar real surface of metal and the imaginary plane located below the voids at distance *h* from the void bottoms form the interfaces between the periodic surface layer and either the surrounding medium or metal substrate, respectively. The total fields in the surrounding medium and in the substrate result from the superposition of propagating and evanescent plane waves with in-plane wavevectors $\mathbf{G}_{pq} = p\mathbf{A} + q\mathbf{B}$, where $\mathbf{A} = 2\pi(\mathbf{b} \times \mathbf{n})/(\mathbf{a} \times \mathbf{b})$ and $\mathbf{B} = 2\pi(\mathbf{n} \times \mathbf{a})/(\mathbf{a} \times \mathbf{b})$ are the principal vectors of the reciprocal lattice, and p and q are integers. It should be noted that at frequencies below the bulk plasma frequency every plane wave in the metal substrate is evanescent. The total field inside the periodic surface layer is represented as a superposition of the incoming plane waves (both propagating and evanescent) and the field scattered from every void. In this way, the multiple light scattering between all voids in the surface layer is self-consistently accounted for. The in-plane summations of fields scattered from different voids performed in our case directly in real space provide a quite fast convergence.

The interaction between the combined electromagnetic field incident upon a given single void and the electromagnetic field scattered from this void is determined by its scattering matrix [9,10]. Because the scattering matrix of a single void is constructed in a spherical-harmonic representation, we decompose the combined field incident upon a given single void into spherical harmonics. Then, we transform the combined self-consistent field scattered from all voids into a plane-wave representation that is expressed as a sum over in-plane wavevectors $\mathbf{G}_{pq}$, and apply the boundary conditions at the interfaces of the planar surface layer containing lattice of voids with the surrounding medium and substrate. As a result we construct the scattering matrix of the entire structure, which allows us to calculate the reflectance, R, and absorbance, $A = 1 - R$, of the porous metal surface. Note that this approach can be straightforwardly extended to model an arbitrary number of layers with periodically arranged spherical voids with the same period but having different void radii in different layers if one wishes. A detailed description of this method can be found in [7].

It is interesting to point out that the propagation of the electromagnetic field between voids is performed through the metal, so that each void interacts directly only with its nearest neighbors, unlike what happens in a dielectric environment. Accordingly, the Bragg resonances controlled by periodicity of the system are not exhibited in the calculated spectra. Therefore, only resonances originated from the excitation of Mie plasmon modes in every single void influenced by nearest void neighbors show up in the spectra.

Fig. 2 shows the calculated absorption spectra of light incident normally onto a nanoporous silver surface for the case of a single periodic layer of close-packed voids buried inside the silver substrate (the inset of Fig. 2, *a*). We use experimental optical data [11] to describe the dielectric function of silver to electric field in our calculations. The light absorption exhibits resonant enhancement at the frequencies of plasma resonances in nanovoids. Almost

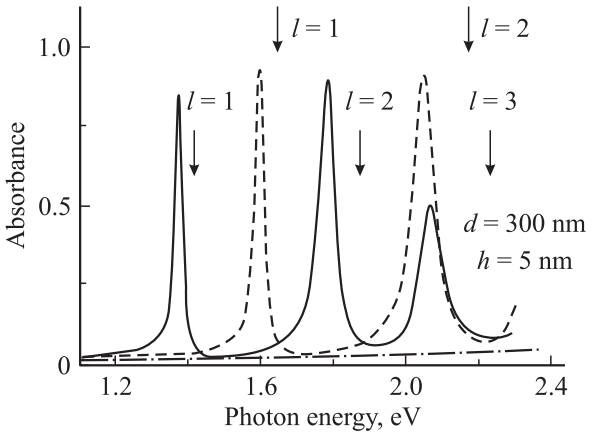

Figure 3. Absorption spectra of light incident normally onto a silver surface with spherical inclusions of a material with dielectric constant $\varepsilon = 4.5$ (solid curve) and $\varepsilon = 3.3$ (dashed curve). The absorption of light on the surface of bulk silver is shown by dash-dotted curve. Vertical arrows mark the energies of the fundamental ($l = 1$), second ($l = 2$), and third ($l = 3$) plasmon modes of a single void in bulk silver.

total resonant light absorption (the effect of „black silver“) occurs when the lattice of voids is buried in the silver substrate at distance smaller than the skin depth (the latter is about 23 nm for silver). Although the frequency of the plasma resonance on the porous metal surface is close to the frequency of the fundamental (with the orbital quantum number $l = 1$) Mie plasmon mode of a single spherical void in an infinite metallic medium, they do not coincide. As clearly seen in Fig. 2, *a*, the shift between these two frequencies grows with decreasing the inter-void spacing, which shows that the reason for such a shift is the coupling of plasmons in adjacent voids. Note that the spectra are independent of the polarization for normally incident light due to the symmetry of the void lattice, $|\mathbf{a}| = |\mathbf{b}|$.

Now we can estimate free parameters $|f_l|^2/\Delta_l$ and $|\beta_l|^2/\Delta_l$ introduced in the previous section by fitting Eqs. (2) and (5) to the resonance frequency and FWHM in the case of total light absorption. In this case the FWHM is equal to $4\gamma_l$ as shown in the previous section. We obtain free parameters $|f_l|^2/\Delta_l \approx 1$ and $|\beta_l|^2/\Delta l \approx 0.1$ for every resonance shown in Fig. 2, *b*.

Fig. 2 depicts the resonant absorption caused by the excitation of the fundamental plasmon mode ($l = 1$) in voids. The frequencies of high-order plasma resonances fall within the interband absorption spectra (at frequencies higher than 3.5 eV for silver [11]) and, therefore, these resonances can hardly be observed in the reflectivity spectra. The frequencies of plasmon resonances on a nanoporous metal surface can be reduced by filling the pores with a dielectric material. Fig. 3 shows the calculated absorption spectra of light incident normally onto a silver surface with filled spherical nanopores. In this case the second and the third plasmon resonances along with the fundamental plasma resonance show up in the visible. A giant light absorption can also be achieved at high-order plasma resonances by choosing the appropriate parameters of the porous layer (Fig. 3).

In conclusion, we have shown theoretically that nearly total light absorption on a nanoporous surface of metal can be achieved at the plasma resonance. This phenomenon occurs when the lattice of spherical voids is buried in the metal substrate at a specific distance from the metal surface, which ensures optimal coupling of plasmons in the voids to the external light. Based upon a simple model, corroborated by detailed calculations later on, we have found a physical criterion for the optimal coupling, which reads that the radiative broadening of the plasma resonance must be equal to its dissipative broadening in order to produce total light absorption at the resonance. It is worth mentioning that the resonant light absorption must be accompanied by high local-field enhancement near or inside the voids, and this could be used to trigger non-linear effects. The frequencies of absorption resonances can be easily tuned by varying the diameter of the voids or by filling them with dielectric materials. This makes this type of nanoporous metals very attractive for variety of applications from nanophotonics to biophysics.

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