Optical transparency of mesoporous metals

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Abstract

We examine the optical properties of metals containing a periodic arrangement of nonoverlapping spherical mesopores, empty or filled with a dielectric material. We show that a slab of such a porous metal transmits light over regions of frequency determined by the dielectric constant of the cavities and the fractional volume occupied by them, with an efficiency which is many orders of magnitude higher than predicted by standard aperture theory. Also, the system absorbs light efficiently over the said regions of frequency unlike the homogeneous metal.

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Recently, optical transmission experiments [1] have shown that periodic arrays of cylindrical holes in metallic films display a transmission efficiency, at wavelengths much larger than the hole diameter, which is orders of magnitude higher than predicted by standard aperture theory [2]. Such intriguing optical properties may have important technological applications in photolithography, in near-field microscopy, in flat-panel displays, and in novel active filter devices [1,3]. Similar enhanced optical transmission occurs in metallic gratings with very narrow slits [4], and it has been recognized that the physical mechanism behind this phenomenon relies on resonant transmission through coupled surface-plasmon modes.

It has long been known that when metals are bombarded with energetic particles such as neutrons or ions over a sufficiently long time, regular arrangements of vacancy clusters may form, such as three-dimensional (3D) lattices of

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spherical voids or bubbles. The lattice of voids or bubbles is isomorphic to the microscopic lattice of the metallic matrix, with a lattice constant which is typically 100 to 1000 times larger than that of the matrix lattice (see, e.g., Ref. [5] and references therein). Nowadays, considerable advances are being made in the template-assisted assembly of macroporous and mesoporous metals: a 3D template is assembled from a self-organizing material and impregnated with the desired metal; then, the template is removed, resulting in an array of pores that reflects the structure of the template [6]. In this paper we predict some extraordinary optical transmission effects in such mesoporous metals. We show that these properties can be understood in a systematic manner on the basis of exact calculations, which at the end provide a transparent model of the underlying physics.

We consider, to begin with, a single spherical cavity, of radius $S$, in a metal characterized by a Drude-like relative dielectric function

$$\epsilon = 1 - \omega_p^2/\omega^2,$$

where $\omega_p$ is the bulk plasma frequency, and we have neglected damping for now. The electromagnetic (EM) field at frequency $\omega$ is described by its electric-field component $E(r; t) = \text{Re}[E(r) \exp(-i\omega t)]$, where $E(r)$ is written as follows (see, e.g., Ref. [7]). Inside the cavity ($r < S$)

$$E(r) = \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left[ \frac{i}{\kappa_s} a'^E_{lm} \nabla \times j_l(\kappa_s r) X_{lm}(\hat{r}) + a'^H_{lm} j_l(\kappa_s r) X_{lm}(\hat{r}) \right],$$

where $\kappa_s = \omega/c$, $c$ being the velocity of light in vacuum; $j_l$ is a spherical Bessel function; and $X_{lm}(\hat{r})$ is a vector spherical harmonic. We need not write down the associated magnetic-field component of the EM wave. Outside the cavity ($r > S$)

$$E(r) = \sum_{l=1}^{\infty} \sum_{m=-l}^{l} \left[ \frac{i}{\kappa} a'^E_{lm} \nabla \times j_l(\kappa r) X_{lm}(\hat{r}) + a'^H_{lm} j_l(\kappa r) X_{lm}(\hat{r}) \right. + \left. i a'^{+E}_{lm} \nabla \times h^+_l(\kappa r) X_{lm}(\hat{r}) + a'^{+H}_{lm} h^+_l(\kappa r) X_{lm}(\hat{r}) \right],$$

where $h^+_l$ is a spherical Hankel function corresponding to an outgoing wave. The first two terms in the above equation describe an incident wave and the last two terms a scattered wave. The wavenumber $\kappa$ for a medium with negative dielectric function, as is the case to be considered here ($\omega < \omega_p$), is a purely imaginary number: $\kappa = iq = i\omega\sqrt{-\epsilon/c}$.

Because of the spherical symmetry of the scatterer we obtain
\[ a_{lm}^+ E = T_l^E a_{lm}^0 \]
\[ a_{lm}^+ H = T_l^H a_{lm}^0 , \]  

(4)

where

\[ T_l^E(\omega) = \left[ \frac{j_l(\kappa sr) \frac{\partial}{\partial r}(r j_l(\kappa sr)) - j_l(\kappa sr) \frac{\partial}{\partial r}(r j_l(\kappa sr)) \epsilon}{h_l(\kappa sr) \frac{\partial}{\partial r}(r j_l(\kappa sr)) \epsilon - j_l(\kappa sr) \frac{\partial}{\partial r}(r h_l(\kappa sr))} \right]_{r=S} \]

(5)

with a corresponding expression for \( T_l^H(\omega) \) [7]. In the case of a single cavity in a homogeneous medium of negative dielectric function there can be no incident wave: \( a_{lm}^0 E = a_{lm}^0 H = 0 \) and, therefore, non-trivial states of the EM field, of given \( l \), will exist if

\[ T_l^E(\omega) = \infty \quad \text{or} \quad T_l^H(\omega) = \infty . \]

(6)

It can be shown that the second of the above equations does not obtain a real frequency solution in the region from 0 to \( \omega_p \). The first equation, for any \( l \), has a solution in this frequency region; we denote it by \( \tilde{\omega}_l \). For a small cavity, using the appropriate asymptotic expansions of the spherical Bessel and Hankel functions for small arguments [8] in Eq. (5), we obtain

\[ \tilde{\omega}_l \simeq \omega_p \sqrt{(l + 1)/(2l + 1)} , \quad l = 1, 2, 3, \ldots . \]

(7)

Taking for instance \( S \omega_p/c = 0.4 \), which for \( \omega_p = 10 \) eV corresponds to a radius \( S = 7.5 \) nm, Eq. (7) approximates \( \tilde{\omega}_l \) with an accuracy better than 1%. The eigenmodes of the EM field obtained at \( \tilde{\omega}_l \) define the \( 2l \)-pole plasma oscillations at the surface of the cavity.

Let us now ask whether it is possible for a system of small spherical cavities in a metal to be transparent. For a crude, qualitative description of the optical properties of the composite system, we can use its effective dielectric constant, \( \varepsilon \), as given by the Maxwell Garnett (MG) effective-medium theory [9]

\[ \frac{\varepsilon - \varepsilon_s}{\varepsilon + 2\varepsilon} = f \frac{\varepsilon_s - \varepsilon}{\varepsilon_s + 2\varepsilon} , \]

(8)

where \( f \) is the fractional volume occupied by the cavities (\( \varepsilon_s = 1 \)) and \( \varepsilon \) is the relative dielectric function of the metal given by Eq. (1). Eq. (8) gives a positive \( \varepsilon \) over the range of frequencies from \( \omega_{\text{min}} = \omega_p \sqrt{2(1-f)/3} \) to \( \omega_{\text{max}} = \omega_p \sqrt{2+f)/3} \). In other words, in the above frequency region, there is a band of propagating states of the EM field in the porous metal, the width of which, \( \omega_{\text{max}} - \omega_{\text{min}} \), increases with \( f \). As \( f \to 0 \), \( \omega_{\text{max}} \to \omega_{\text{min}} \to \omega_p \sqrt{2/3} \) which,
according to Eq. (7), is the resonance frequency, $\tilde{\omega}_1$, associated with the dipole plasma oscillations at the surface of a single small cavity. Clearly the above band (for $f > 0$) arises from the interaction between dipole plasma modes localized on neighboring cavities and can therefore be understood in the spirit of the tight-binding approximation [10]. Its bandwidth will be larger the larger the spatial overlap between the wavefields associated with neighboring spheres which in turn increases with $f$.

The entire band can be shifted to lower frequencies by filling the pores with a dielectric material. One can show that the resonance frequencies of a single small sphere of dielectric constant $\epsilon_s$ in a metal described by Eq. (1) are given by

$$\tilde{\omega}_l \simeq \omega_p \sqrt{(l + 1)/(l\epsilon_s + l + 1)}.$$  

Therefore, with $\epsilon_s \approx 10$, $\tilde{\omega}_1$ of the isolated sphere and the corresponding band of the porous metal are found in the optical region.

We note that the MG theory is based on the electric-dipole approximation and, therefore, cannot describe $2^l$-pole states with $l > 1$. There is of course an infinite number of bands corresponding to the $2^l$-pole plasma modes of the individual spheres. These modes, according to Eq. (9), extend approximately from $\omega_p \sqrt{1/(\epsilon_s + 1)}$ to $\omega_p \sqrt{2/(\epsilon_s + 2)}$. It is therefore clear that there are no frequency bands below a cutoff frequency at about $\omega_p \sqrt{1/(\epsilon_s + 1)}$. This is what one expects of a metal (a system with DC conductivity at any temperature including zero), and the system under consideration possesses DC conductivity because the metallic component of it forms a continuous network [11]. It is understood, however, that at low frequencies ($\omega\tau < 1$) Eq. (1) must be replaced by Eq. (10) below, which takes into account the damping of conduction-band electrons. We note that, in a system consisting of nonoverlapping metallic spheres in a dielectric medium, there are propagating modes of the EM field at low frequencies with a free-photon-like dispersion [12], reflecting the fact that the system is an insulator at $\omega = 0$.

An accurate analysis of the optical properties of porous metals can be efficiently carried out using the method we developed for the calculation of the optical properties of photonic crystals consisting of nonoverlapping spheres in a homogeneous host medium. The details of the method and a computer program for its implementation can be found elsewhere [13,14]. Here we need only say that in the present case, of a metallic host medium, where only evanescent EM waves exist below the plasma frequency, the $\Omega$-matrices (as defined in Ref. [14]) must be calculated by a direct summation over the space lattice; a few terms in the relevant lattice sums give adequate convergence.
We consider a system of nonoverlapping, identical silicon spheres ($\epsilon_s = 11.9$), centered at the sites of a fcc lattice of lattice constant $a$, in a metallic host medium whose dielectric function is given by Eq. (1). The radius, $S$, of the spheres equals one fifth of the first-neighbor distance, $a_0$, which corresponds to a fractional volume occupied by the spheres $f = 4.74\%$. We view the crystal as a stack of layers (planes of spheres) parallel to the fcc (001) surface. For given $k_\parallel$, the reduced component of the wavevector parallel to the fcc (001) surface, we calculate, as functions of $\omega$, the frequency lines $k_z = k_z(\omega; k_\parallel)$ corresponding to generalized Bloch wave solutions of the EM field. $k_z(\omega; k_\parallel)$ is the $z$ component [normal to the (001) plane] of the wave vector of a generalized Bloch wave with the given $\omega$ and $k_\parallel$; and there are many such waves corresponding to different values of $k_z$. The regions of $\omega$ over which at least one $k_z$ is real define corresponding frequency bands and regions over which all $k_z$ are complex define frequency gaps, for the given $k_\parallel$.

In Fig. 1a we show the frequency bands for $k_\parallel = 0$ [dispersion curves along the normal to the (001) plane] of the above crystal, which arise from the $2l$-pole states of the individual spheres for $l = 1, 2, 3$. We see that these bands develop about the corresponding resonance frequencies given by Eq. (9), and that their width decreases with $l$. Apparently the spatial extent of the wavefield around a sphere decreases with increasing $l$, thus leading to a weaker hybridization between the higher $2l$-pole states of the spheres and, consequently, to a smaller bandwidth. The bands shown by the black solid lines in Fig. 1a are doubly degenerate and couple with light incident normally on a slab of the crystal parallel to the (001) surface. The black broken line shows the dipole band (doubly degenerate) as obtained in the MG approximation. The bands shown by the gray solid lines are nondegenerate and do not couple with normally incident light. The existence of these optically inactive modes at high-symmetry points and along symmetry lines has been noted by a number of authors [13,15]. Fig. 2 shows more clearly all frequency bands corresponding to $l = 2$ and $l = 3$. One can see that the total number of bands associated with a given $l$ equals $2l + 1$ as expected from the $(2l + 1)$-degeneracy of the corresponding state of the isolated sphere. The degeneracy of the bands and the symmetry properties of the corresponding eigenmodes is what one expects from a group-theoretical analysis [16]. Next to the frequency band structure, in Fig. 1b, we show by the solid line the transmission coefficient of light incident normally on a slab of the crystal consisting of 16 planes of spheres parallel to the (001) surface, assuming that the medium on either side of the slab is air. As expected, the transmittance practically vanishes for frequencies within the frequency gaps of the infinite crystal and exhibits the well-known Fabry-Pérot-type resonances over the regions of the optically active frequency bands [12]. The broken line shows the transmittance as evaluated in the MG approximation.

The absorption of light by the material, which we have neglected so far, is of course a quantity of great importance. We account for it by inserting, as
usual, a damping term in the relative dielectric function given by Eq. (1). We write

\[ \epsilon = 1 - \frac{\omega_p^2}{\omega(\omega + i\tau^{-1})}, \]  

(10)

where \( \tau \) is the relaxation time of the conduction-band electrons, with a typical value \((\omega_p\tau)^{-1} = 0.001\). Absorption is mainly associated with the resonantly oscillating multipoles of the spheres and, therefore, is appreciable only in the region of the frequency bands. This is demonstrated in Fig. 3a, for light incident normally on a slab of the crystal consisting of 16 planes of spheres parallel to the (001) surface. We see that absorption is considerable; the corresponding absorbance of a homogeneous metallic slab of the same thickness is of the order of \(10^{-3}\). In Fig. 3b we show the transmission coefficient of light for the same system; transmission occurs in the frequency region of the dipole band. It is somewhat reduced, due to absorption, but it is extraordinarily high: the corresponding transmittance of a homogeneous metallic slab of the same thickness is of the order of \(10^{-9}\), while a single hole of diameter \(d\) in a metal film transmits light of wavelengths \(\lambda >> d\) with an efficiency proportional to \((d/\lambda)^4\) [2] and in our case we have \(d/\lambda \approx 0.02\).

In addition to the above, the results shown in Figs. 1 and 3 indicate that though the MG approximation gives a reasonable estimate of the transmittance and absorbance of the system in the frequency region of the dipole band, it differs significantly from the exact picture. And of course, it fails to reproduce all features associated with the higher \(2^l\)-pole resonances (see also Ref. [12]). Finally, it appears that the position of the frequency bands (and consequently the range of frequencies over which a high transmission and absorption occurs) depends mostly on the characteristics of a single sphere in the metal host and on the fractional volume occupied by the spheres, and less so on the specific arrangement of the spheres. We should also emphasize that though our results have been obtained for a metallic component described by Eqs. (1) and (10), what really matters is that the dielectric function of the host medium is such that solutions of Eqs. (6) exist at appropriate frequencies; and as long as this remains true, similar results will be obtained.

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Fig. 1. (a) The photonic band structure normal to the (001) surface of a fcc crystal of silicon spheres in a nonabsorbing Drude metal \( (\omega_0 \omega_p/c = 1, \; S \omega_p/c = 0.2) \). The solid lines (black lines: doubly degenerate bands, gray lines: nondegenerate bands) are exact results; the broken line is the MG result. (b) The corresponding transmittance curve for light incident normally on a slab of the above crystal consisting of 16 lattice planes parallel to the (001) surface. The solid (broken) lines are exact (MG) results.

Fig. 2. The frequency bands associated with the \( l = 2 \) (a) and \( l = 3 \) (b) states of an isolated sphere, for the system described in Fig. 1.
Fig. 3. Absorbance (a) and transmittance (b) of light incident normally on a slab of 16 lattice planes parallel to the (001) surface of a fcc crystal consisting of silicon spheres in a Drude metal \[ a_0 \omega_p/c = 1, \quad S \omega_p/c = 0.2, \quad (\omega_p \tau)^{-1} = 0.001 \]. The solid (broken) lines are exact (MG) results.