

Photonic crystals of coated metallic spheres

A. MOROZ(*)

FOM Institute AMOLF - Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

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Abstract. – It is shown that simple face-centered-cubic (fcc) structures of both metallic and coated metallic spheres are ideal candidates to achieve a tunable complete photonic bandgap (CPBG) for optical wavelengths using currently available experimental techniques. For coated microspheres with the coating width to plasma wavelength ratio $l_c/\lambda_p \leq 10\%$ and the coating and host refractive indices n_c and n_h , respectively, between 1 and 1.47, one can always find a sphere radius r_s such that the relative gap width g_w (gap width to midgap frequency ratio) is larger than 5% and, in some cases, g_w can exceed 9%. Using different coatings and supporting liquids, the width and midgap frequency of a CPBG can be tuned considerably.

Introduction. – Photonic crystals are characterized by a periodically modulated dielectric constant. Some of such structures occur in nature, for instance, opals and nanostructured colour wings of butterflies [1]. There is a common belief that in the near future photonic crystals will give us the same control over photons as ordinary crystals give us over electrons [2]. At the same time, photonic structures are of great promise to become a laboratory for testing fundamental processes involving interactions of radiation with matter in novel conditions. This promise originates from the fact that, in analogy to the case of an electron moving in a periodic potential, certain photon frequency modes within a photonic crystal can become forbidden, independent of the photon polarization and direction of propagation—a complete photonic bandgap (CPBG) [3, 4]. Consequently, the density of states (DOS) and the local DOS (LDOS) of photons are significantly changed compared to their vacuum value (see [5] for the exact results in one-dimensional photonic crystals). If the LDOS is sufficiently smooth, the spontaneous emission (SE) rate Γ of atoms and molecules embedded in a photonic crystal is directly proportional to the LDOS [6]. On the other hand, if the LDOS exhibits sharp features (as a function of frequency and position in the unit cell), one expects the Wigner-Weisskopf approximation [7] to break down and novel phenomena to occur, such as non-Markovian behaviour and nonexponential SE accompanied by the change of the spectrum from a single Lorentzian peak into a two-peaked structure [8, 9].

Unfortunately, the problems in the fabrication of three-dimensional CPBG structures increase rapidly with decreasing wavelengths for which a CPBG is required—mainly because of

(*) Present address: Faculty of Physics and Astronomy, Debye research Institute, Utrecht University, P.O. Box 80000, 3508 TA Utrecht, The Netherlands. www.amolf.nl/research/photonic_materials_theory

the simultaneous requirements on the modulation (the total number and the length of periodicity steps) and dielectric contrast. In order to achieve a CPBG below infrared wavelengths, the modulation is supposed to be on the scale of optical wavelengths or even smaller and, as for any CPBG structure, has to be achieved with roughly ten periodicity steps in each direction, a task currently beyond the reach of reactive ion and chemical etching techniques. Fortunately, such a modulation occurs naturally in colloidal crystals formed by monodisperse colloidal suspensions of microspheres. The latter are known to self-assemble into three-dimensional crystals with excellent long-range order on the optical scale [10], removing the need for complex and costly microfabrication. They form a face-centered-cubic (fcc) or (for small sphere filling fraction) a body-centered-cubic (bcc) lattice [10]. Thus, it comes as no surprise that the best photonic crystals in the visible (although without any CPBG) are colloidal based fcc structures [11]. The latter are purely dielectric structures composed of spheres with dielectric constant ε_s embedded in a host with the dielectric constant ε_h . For such structures the dielectric contrast δ is defined as $\delta = \max(\varepsilon_h/\varepsilon_s, \varepsilon_s/\varepsilon_h)$. Then $\delta \gtrsim 8.2$ is required to open a CPBG [12, 13]. Colloidal crystals suffer from the same kinds of defects as ordinary electronic crystals. Therefore, practical crystals should have such a dielectric contrast which for an ideal crystal yields a CPBG with the gap width to midgap frequency ratio (the relative gap width), $g_w = \Delta\omega/\omega_c$, of at least 5% —to leave a margin for gap edge distortions due to impurities and yet to have a CPBG useful for applications. Then, for an fcc structure, $\delta \gtrsim 12$ is required [12, 13], which makes fabrication of photonic crystals with an operational CPBG at optical wavelength seemingly hypothetical [14]. The requirements on δ are less restrictive (although still rather strong in the visible) for colloidal crystals with a diamond structure [3]. The latter, however, have yet to be fabricated. As a result of the above, no three-dimensional CPBG structures below the infrared wavelengths [14, 15] have been fabricated thus far.

Recently we have shown [16] that a way to avoid the requirements on δ is to use spheres with a Drude-like behaviour of the dielectric function

$$\varepsilon_s(\omega) = 1 - \omega_p^2/\omega^2, \quad (1)$$

where ω_p is called the plasma frequency [17]. In the following, r_s is the sphere radius and $\lambda_p = 2\pi c/\omega_p$ the plasma wavelength, c being the speed of light in vacuum. For notational simplicity we often refer to the spheres having such a dielectric function (1) as metallic spheres, although we are aware that i) not all metals show a Drude-like behaviour and ii) such a behaviour can also be found in certain semiconductors [18] and in new artificial structures [19]. Fcc structures of metallic spheres exhibit several exceptional properties [16]. For frequencies within $0.6\omega_p \leq \omega \leq 1.1\omega_p$, where the bulk metal absorption can be negligible [20], a CPBG opens in the spectrum with g_w up to $\approx 10\%$, and that already for a host dielectric constant $\varepsilon_h = 1$. Moreover, up to *four* CPBGs can open in the spectrum. A CPBG with $g_w \approx 5\%$ can be achieved for sphere filling fractions from $f = 0.56$ till the close-packed case ($f \approx 0.74$). For the wavelengths λ within the CPBGs the size parameter of spheres $x = 2\pi r_s/\lambda$ satisfies $x \geq 5$. Consequently, absorption is governed entirely by the bulk absorption, since the so-called plasmon-induced absorption is negligible [17]. Another unexpected feature is that for some values of r_s/λ_p , for example $r_s/\lambda_p = 1.35$, extremely narrow almost dispersionless bands “within a bandgap” appear. These bands can to a certain extent perform many functions of an impurity band [2] since they involve photons with extremely small group and phase velocities (less than $c/200$) [16].

Motivation. – In this letter we study the question how the photonic-bandgap structure is affected by coating monodisperse metallic microspheres with a semiconductor or an insulator. This question is not only of theoretical but also of significant experimental interest. Coating

can actually facilitate the preparation of photonic colloidal crystals made up from metallic spheres because it can i) stabilize metallic microparticles by preventing, or, at least, by significantly reducing their oxidation; ii) prevent aggregation of metallic particles by reducing Van der Waals forces between them. In the latter case, a coating of roughly 30 nm is required. Also a suitable coating can enlarge some of the stop gaps (gaps in a fixed direction of propagation) by as much as 50% [13]. From the application point of view, optically nonlinear Bragg diffracting nanosecond optical switches have been fabricated by doping silica (SiO_2) shell with an absorptive dye [21]. On the other hand, coating with an optically nonlinear material can reduce the required intensity for the onset of optical bistability [22] due to the enhancement of local fields near the surface-plasmon resonance. Last but not least, using a semiconductor coating may allow a matching of the photonic and electronic bandgaps, which is important for many applications involving photonic crystals [2].

Let r_c be the core radius and l_c be the coating width, *i.e.*, $r_s = r_c + l_c$. We assumed that the refractive indices n_c and $n_h = \sqrt{\epsilon_h}$ of the coating material and host, respectively, are constant within the frequency range considered. The latter was taken to be roughly $0.55\omega_p \leq \omega \leq 1.1\omega_p$, where the bulk absorption of the metal is assumed to be small. This is a good approximation, for instance, for structures made of silica-coated silver microspheres [23]. For silver $\lambda_p = 328$ nm and the bulk absorption is rather small in the region 310–520 nm [20]. The dependence of the refractive index of silica on frequency in this frequency region is very weak and is described by a Cauchy model. The actual value of n_c depends on the method used to synthesize silica. We took $n_c = 1.47$. In view of their experimental relevance, we only investigated simple fcc structures. Band-structure calculations were performed using a photonic analogue [24] of the familiar Korringa-Kohn-Rostocker (KKR) method [25]. Compared to the plane-wave method, dispersion does not bring any difficulties to the KKR method and computational time is the same as without dispersion. In order to ensure precision within 0.1%, spherical waves were included with angular momentum up to $l_{\max} = 10$. Further discussion of convergence and errors can be found in [13]. The values of the angular frequency are, unless otherwise stated, in the units $2c/A$, where A is the length of the conventional unit cell of a cubic lattice (not to be confused with the lattice spacing [18]).

Results. – At first glance it seems that coating destroys the CPBGs. For example, if one begins with noncoated metallic spheres with $\omega_p = 9.5$ and filling fraction $f = 0.6$, one finds two CPBGs with $g_w \approx 4.07\%$ and 2.94% at midgap frequencies $\omega_c \approx 0.874\omega_p$ and $0.813\omega_p$, respectively. As the coating width l_c for $n_c = 1.47$ increases from zero till the spheres are close-packed, the two CPBGs steadily decrease to zero. Nevertheless, when also the host refractive index is allowed to vary, one can recover almost all the exceptional features of the photonic band structure of noncoated metallic spheres. Generically, three CPBGs open in the spectrum (see fig. 1), *i.e.*, one less than for noncoated metallic spheres, however, still two CPBGs more than for purely dielectric structures [3, 12, 13]. The relative gap width g_w can exceed 9%. Figure 2 shows how the CPBGs of the close-packed fcc lattice of silica-coated metallic spheres with a coating width $l_c/\lambda_p \approx 9.15\%$ (corresponding to $l_c = 30$ nm for silver) change when the host refractive index n_h is varied between 1 and the coating refractive index $n_c = 1.47$. Data on the right y -axis correspond to the case where n_h matches n_c , *i.e.*, they are identical to those for an fcc structure of purely metallic spheres embedded in the host n_h . It is clear from fig. 2 that the answer to the question whether coating enhances the relative gap width g_w of a CPBG strongly depends on n_h and r_s/λ_p .

Let us denote ω_r as the midgap to plasma frequency ratio, *i.e.*, $\omega_r = \omega_c/\omega_p$. Surprisingly enough, the ratio ω_r (for the CPBGs shown in fig. 2) as a function of n_h can be described

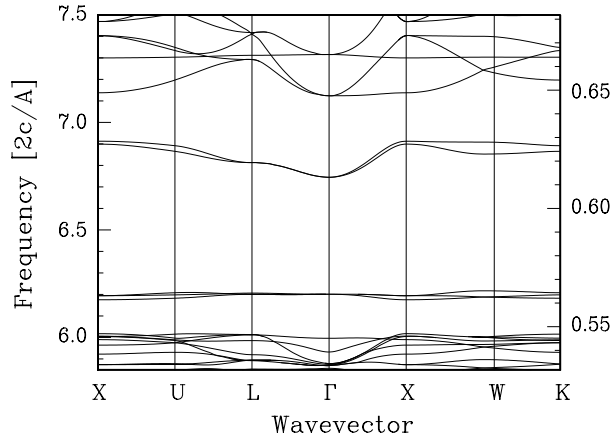


Fig. 1 – Calculated photonic-band-structure of a close-packed fcc lattice of silica-coated ($n_c = 1.47$) metallic spheres embedded in a host dielectric with refractive index $n_h = 1.4$ for $\omega_p = 11$ ($r_s/\lambda_p \approx 1.238$). For convenience, on the right y -axis the angular frequency is shown in units ω_p . The coating width l_c to the sphere radius ratio is $l_c/r_s \approx 7.39\%$ ($l_c/\lambda_p \approx 9.15\%$). This corresponds to a metallic (core) filling fraction of $f_m \approx 0.588$ (to be compared with the fcc close-packed filling fraction $f \approx 0.7405$). Note that there are three CPBGs, one with $g_w = 3.2\%$ at midgap frequency 7.01, the second with $g_w = 8.4\%$ at midgap frequency 6.47, and the third with $g_w = 2.59\%$ at midgap frequency 6.1.

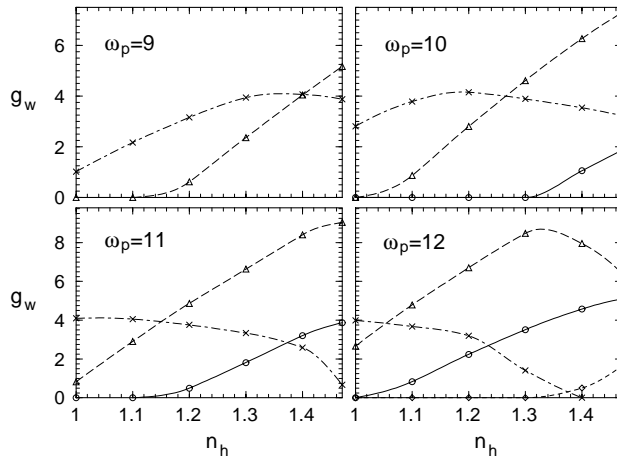


Fig. 2 – The relative gap width g_w of the CPBGs of a close-packed fcc lattice of silica-coated metallic spheres as a function of the host refractive index n_h for $l_c/\lambda_p \approx 9.15\%$ (i.e., $l_c = 30$ nm for silver). For a close-packed fcc lattice, the value of r_s/λ_p can be recovered by multiplying the numerical values of ω_p by $1/(2\pi\sqrt{2})$, i.e., $r_s/\lambda_p = 1.013, 1.125, 1.238,$ and 1.35 for $\omega_p = 9, 10, 11, 12$ in this order. The metallic filling fractions in the same order are $f_m \approx 0.557, 0.574, 0.588,$ and 0.6 . The symbols $\circ, \Delta,$ and \times are for the upper, middle and the lower CPBG, respectively (cf. fig. 3). Data on the right y -axis correspond to the case when n_h matches n_c .

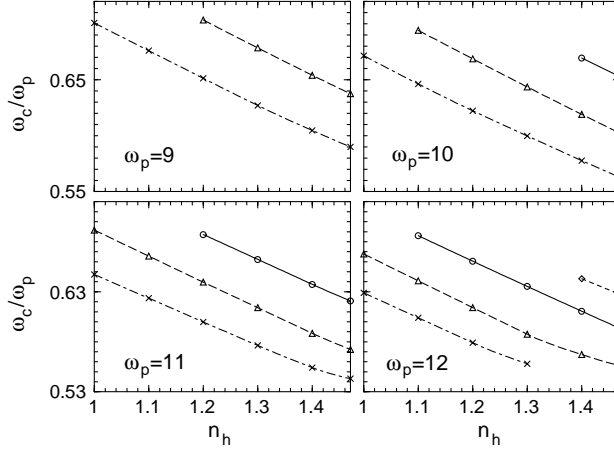


Fig. 3 – The ratio ω_c/ω_p , corresponding to the CPBGs shown in fig. 2, as a function of the host refractive index n_h . With high precision the curves can be described by a simple linear relation (see eq. (2)).

with high precision by a simple linear relation

$$\omega_r(n_h) = \omega_r(n_0) - C(n_h - n_0), \quad (2)$$

with a universal constant $C = 0.2478 \pm 0.0075$. Here n_0 is the lowest host refractive index for which a given CPBG opens in the spectrum and $\omega_r(n_0)$ is the corresponding value of ω_r for $n_h = n_0$. This shows that changing n_h allows one to tune not only the width g_w of a CPBG but also, within $\approx 8\%$, the corresponding midgap frequency.

The tuning of the midgap frequency ω_c by changing n_h is more pronounced in the absence of coating. In the latter case, for example for sphere filling fraction $f = 0.6$, $\omega_p = 9$, and $n_h = 1$, two CPBGs appear with $g_w = 3.27\%$ and $g_w = 2.55\%$ at the midgap frequencies $\omega_c \approx 0.904\omega_p$ and $0.839\omega_p$, respectively. As n_h increases from 1 to 1.47, the midgap frequencies can be tuned down to $\approx 65\%$ of their original values and their respective values reach $\omega_c \approx 0.593\omega_p$ and $0.556\omega_p$. At the same time, the relative gap width gradually increases up to $g_w = 5.1\%$ and $g_w = 6.43\%$, respectively (see figs. 2, 3).

The above results are not specific for the case of silica coating when $n_c = 1.47$. For example, for $n_c = 1.4$ and $l_c/\lambda_p \approx 9.15\%$ one can find a region of parameters ($n_h = 1.3$ and $\omega_p = 12$ (the metallic filling fraction $f_m \approx 0.6$)) for which g_w can be as large as 8.9% .

It is important to realize that, because the metallic core size parameter $x = 2\pi r_c/\lambda$ satisfies $x \geq 3.4$ for all wavelengths within a CPBG for all CPBGs considered here in the frequency region $0.55\omega_p \leq \omega \leq 1.1\omega_p$, the absorption is still dominated by bulk properties, *i.e.*, can be negligible [20], since the plasmon-induced absorption becomes relevant only for particle sizes much smaller than the wavelength [17]. One cannot get rid of absorption completely. Nevertheless moderate absorption was shown to cause only a slight perturbation of the band structure calculated in the absence of absorption [26].

It is worthwhile to mention that the exact Drude-like dispersion (1) of ε_s is not necessary to reproduce the exceptional properties of metallo-dielectric photonic crystals. It is enough if, for sufficiently large frequency window, $-15 \lesssim \varepsilon_s(\omega) \leq 0$ [16]. Many of the above features (except for the extremely narrow, almost dispersionless bands “within a bandgap”) can also be reproduced for a constant and sufficiently small negative ε_s [16]. This is important since,

in real systems, a deviation from the ideal Drude behaviour can occur at a proximity of the zero crossing of $\text{Re } \varepsilon$ at some λ_z . If λ_p is the plasma wavelength extracted from the fit (1) to a material data, then λ_z is red-shifted compared to λ_p [20] and the band structure between λ_z and λ_p can be modified compared to the ideal Drude behaviour (1).

Outlook and conclusions. Our calculations show that simple fcc structures of both metallic and coated metallic spheres are ideal candidates to achieve a CPBG for optical wavelengths. For coated microspheres with a coating width $l_c/\lambda_p \leq 10\%$ (up to $l_c = 30$ nm for silver) and coating and host refractive indices n_c and n_h , respectively, between 1 and 1.47, one can always find a sphere radius r_s such that the relative gap width g_w is larger than 5% and, in some cases, g_w can even exceed 9%. This provides a sufficiently large margin for gap-edge distortions due to omnipresent imperfections and impurities to allow both technological and experimental applications involving the proposed structures. Using different coatings and by changing the refractive index n_h of the supporting liquid (this can be easily achieved), one can tune the width and midgap frequency of a CPBG considerably. In principle, the midgap frequency ω_c can be tuned to whatever frequency within a nonabsorptive window ($0.6\omega_p \leq \omega \leq 1.1\omega_p$ for silver [20]). Using a procedure in which fluorescent organic groups are placed inside the silica shell with nm control over the radial position [27] makes it, in principle, possible to perform a precise position-dependent testing of the spontaneous emission within a photonic crystal. By applying an electric field one can switch in ms from an fcc colloidal crystal to a body-centered-tetragonal (bct) crystal: a so-called martensitic transition [28]. Hence, the proposed structures are also promising candidates for the CPBG structures with tunable bandgaps. Last but not least, since metals are known to possess large nonlinear susceptibilities, switching [21] and optical bistability [22] can be studied in the presence of a CPBG. It is interesting to note that many of these ideas also apply to two-dimensional photonic structures [29].

The region of plasma frequencies of conventional materials ranges from the near-infrared to the ultraviolet [17]. However, in a recent interesting paper [19], it has been shown that a whole new class of artificial materials can be fabricated in which the plasma frequency may be reduced by up to 6 orders of magnitude compared to conventional materials, down to GHz frequencies. Correspondingly, the proposed structures can provide CPBG structures from the GHz up to ultraviolet frequencies. Apparently, the main experimental problem in fabricating the proposed photonic structures, using colloidal systems of metallic microspheres, is to synthesize large enough spheres in order to reach the threshold value $r_s n_h / \lambda_p \gtrsim 0.9$ to open a CPBG. However, a method to produce monodisperse gold colloids of several hundred nm radius and larger has been developed [30]. Recent results on the fabrication of such spheres from silver, *i.e.*, material with a Drude-like behaviour of the dielectric function, are promising [31]. The only remaining problem is to control the size polydispersity of spheres and reduce it below 5% to trigger crystallization [10].

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