

Title	Erasing diffraction orders: Opal versus Langmuir-Blodgett colloidal crystals
Authors	Romanov, Sergei G.;Bardosova, Maria;Whitehead, D. E.;Povey, Ian M.;Pemble, Martyn E.;Torres, C. M. Sotomayor
Publication date	2007
Original Citation	Romanov, S. G., Bardosova, M., Whitehead, D. E., Povey, I. M., Pemble, M. and Torres, C. M. S. (2007) 'Erasing diffraction orders: Opal versus Langmuir-Blodgett colloidal crystals', Applied Physics Letters, 90(13), pp. 133101. doi: 10.1063/1.2714198
Type of publication	Article (peer-reviewed)
Link to publisher's version	http://aip.scitation.org/doi/abs/10.1063/1.2714198 - 10.1063/1.2714198
Rights	© 2007 American Institute of Physics.This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP Publishing. The following article appeared in Romanov, S. G., Bardosova, M., Whitehead, D. E., Povey, I. M., Pemble, M. and Torres, C. M. S. (2007) 'Erasing diffraction orders: Opal versus Langmuir-Blodgett colloidal crystals', Applied Physics Letters, 90(13), pp. 133101 and may be found at http://aip.scitation.org/doi/abs/10.1063/1.2714198
Download date	2024-04-25 07:29:42
Item downloaded from	https://hdl.handle.net/10468/4380

Erasing diffraction orders: Opal versus Langmuir-Blodgett colloidal crystals

S. G. Romanov, M. Bardosova, D. E. Whitehead, I. M. Povey, M. Pemble, and C. M. Sotomayor Torres

Citation: *Appl. Phys. Lett.* **90**, 133101 (2007); doi: 10.1063/1.2714198

View online: <http://dx.doi.org/10.1063/1.2714198>

View Table of Contents: <http://aip.scitation.org/toc/apl/90/13>

Published by the [American Institute of Physics](#)



Erasing diffraction orders: Opal versus Langmuir-Blodgett colloidal crystals

S. G. Romanov,^{a)} M. Bardosova, D. E. Whitehead, I. M. Povey, M. Pemble, and C. M. Sotomayor Torres

Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Ireland

(Received 29 November 2006; accepted 13 February 2007; published online 26 March 2007)

The optical transmission of photonic crystals self-assembled from colloidal nanospheres in opals and assembled from two-dimensional colloidal crystals in a periodic stack by the Langmuir-Blodgett technique has been compared. Elimination of all related zero order diffraction resonances other than that from growth planes and broadening and deepening of the remaining one-dimensional diffraction resonance have been observed for samples prepared by the Langmuir-Blodgett approach, which are explained in terms of the partial disorder of a crystal lattice. © 2007 American Institute of Physics. [DOI: 10.1063/1.2714198]

Three-dimensional (3D) crystals prepared via self-assembly of colloidal particles¹ are proven to be suitable for converting into omnidirectional photonic band gap^{2,3} materials (PBG) and for integration with standard optical elements on a common platform.^{4,5} In spite of a broad variety of assembling techniques explored so far, the most energetically favorable face-centered-cubic (fcc) symmetry dominates the topology of colloidal crystal lattices. In order to overcome this inflexibility, forced construction is currently the only alternative. Such approaches use templates to direct the self-assembly,⁶ micromanipulation for deterministic particle-by-particle assembling a lattice,⁷ or the Langmuir-Blodgett (LB) technique^{8–10} for stacking a one-dimensional (1D) lattice from monolayers of prepacked two-dimensional (2D) colloidal crystals. Among these the LB method is arguably the only method which possesses a clear prospect for large-scale implementation.

The LB approach has a distinct advantage over other methods of self-assembly for systems where only few monolayers are required as, for example, in photonic crystal (PhC) superlattices. However, the precise structure of LB colloidal crystals remains unclear. Scanning electron microscopy cannot resolve the cross section of LB crystals, because the film cleavages look relatively chaotic.¹¹

In order to clarify the structure of LB colloidal crystals and to evaluate the in pros and cons as potential PhCs, it would be instructive to compare their optical properties with that of opals. Recently we demonstrated that LB crystals can be described as (2+1)D PhCs.¹² This approach conveniently allows the separation of the spectral range into two parts. The 1D part spans over the wavelength range $\lambda \leq 2D$, where D is the diameter of spheres. The 2D part comes into effect if $\lambda \approx D$.

The aim of the present letter is to discover what are the consequences in terms of optical properties imposed by the LB crystal topology as compared to those of an opal. We restrict our consideration to the wavelength range of the two lowest order PBGs of the opal.

Silica spheres of diameter $D=250$ nm grown by the Stöber method¹³ were rendered hydrophobic using 3-(tri-

methoxysilyl)propyl methacrylate. Opals were prepared from these spheres by controlled evaporation from an ethanol solution on a glass substrate with the [111] growth axis of the fcc lattice along the substrate normal.¹⁴ LB crystals were deposited on a glass substrate from doubly distilled deionized water subphase.¹⁵ A barrier speed of 6 cm²/min was used during the compression of monolayers to allow spheres to form a hexagonal lattice.¹⁰ The pressure at which the films were deposited was 4 mN/m. Subsequent layers were deposited after drying the deposited ones. The LB film studied was 20 layers thick. The thickness of opal film was made nearly equal to this by adjusting weight fractions of a solution during the controlled evaporation process to facilitate the comparison.

Angle-resolved transmission spectra were acquired at different angles of incidence θ from 0° to 80° with respect to the film normal. A collimated light beam of 1 mm in diameter from a tungsten halogen lamp was delivered through a prism polarizer to allow for polarization-dependent measurements. The transmitted light was collected from a solid angle of 2°. A quarter-wavelength plate was used in front of the entrance slit of the spectrometer to transform the linear polarized signal into circularly polarized light.

Along the film normal, $\theta=0^\circ$, the transmission spectrum of the opal film shows one minimum centered at $\lambda_0=555$ nm, while that of the LB crystal shows a corresponding minimum at 600 nm [Fig. 1(a)]. At the oblique light incidence, $\theta=55^\circ$, the transmission spectrum of the opal film contains two minima at 436 and 531 nm [Fig. 1(a)]. These minima correspond to the gaps between 1-4 and 5-6 eigenmodes in the PBG structure of the opal.¹⁶ These minima show the losses of the incoming beam due to its coupling to the diffraction orders of a 3D grating. As illustrated in Fig. 1(b), two minima in the transmission spectra from 3D lattice are accounted for by zero order light diffraction at two different sets of crystal planes. Without loss of generalization, only two sets of planes are shown with three corresponding diffraction orders in transmission (01T and 02T) and reflectance (01R and 02R). This is not the case in the LB crystal, where only one broad minimum centered at 480 nm is observed at $\theta=55^\circ$.

Summarizing transmission spectra obtained at different incidence angles in one plot [Figs. 2(a) and 2(b)], two

^{a)} Author to whom correspondence should be addressed; electronic mail: sergei.romanov@tyndall.ie

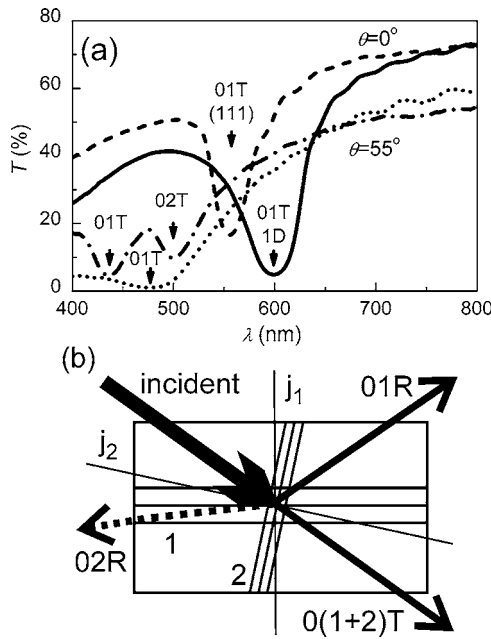


FIG. 1. (a) Transmission spectra of opal at $\theta=0^\circ$ and 55° (dashed and dash-dotted lines, respectively) and LB crystal at the same angles (solid and dotted lines, respectively) in the s -polarized light. Arrows indicate transmission minima and labeled in accord with schematic representation of zero order diffraction in a 3D lattice (b). Considering two different lattice plane sets 1 and 2 with corresponding normals j_1 and j_2 , the incident light intensity is spread between three zero order diffracted beams, denoted by solid and dashed lines for plane sets 1 and 2, respectively. Set 1 corresponds to (111) planes in the opal film and to construction planes in the LB film. Diffraction orders in transmission and reflectance are labeled as 0(1+2)T and 01R, 02R, respectively, for sets 1 and 2.

branches of minima in the spectra of the opal in contrast to the one 1D branch for the LB crystal can be revealed. In order to identify the differences in topology between an opal and a LB colloidal crystal, it is instructive to compare the angle dispersions $\lambda_0(\theta)$ of observed transmission minima [Fig. 3(a)]. These dispersions were examined against the Bragg law $\lambda_{0hkl} = 2d_{hkl}n_{\text{eff}}\sqrt{1 - \sin^2 r_{hkl}}$, where d_{hkl} is the interplane distance along the $[hkl]$ direction, n_{eff} is the effective refractive index (RI) and r_{hkl} is the internal angle between the incident beam and the $[hkl]$ direction. The external angle of incidence θ is related to the internal angle r_{hkl} via Snell's law: $n_{\text{eff}} \sin(r_{hkl}) = n_{\text{air}} \sin(\theta)$.

In the case of the opal, the descending dispersion branch of 01T minimum is well approximated by the Bragg diffraction from the (111) planes. An interplane distance $d = 211$ nm and the effective RI $n_{\text{eff}} = 1.324$ were extracted from the Bragg fit. Assuming that the spacing between planes is $d = 0.816D$, as expected for an fcc lattice, the sphere diameter in the lattice is calculated to be $D = 258$ nm. The ascending branch of 02T diffraction minimum was fitted using parameters of (200) and $(\bar{1}11)$ planes of the fcc lattice. Neither of these branches fit the experimental data particularly well, but they encompass the range of data location. This uncertainty can be explained by mixing different lattice orientations due to the polycrystallinity of the opal film. Exceptions from the diffraction model occur in the angle range from 40° to 50° , where multiple diffraction takes place.¹⁶ This phenomenon is well explained in the PBG model of the opal.¹⁷

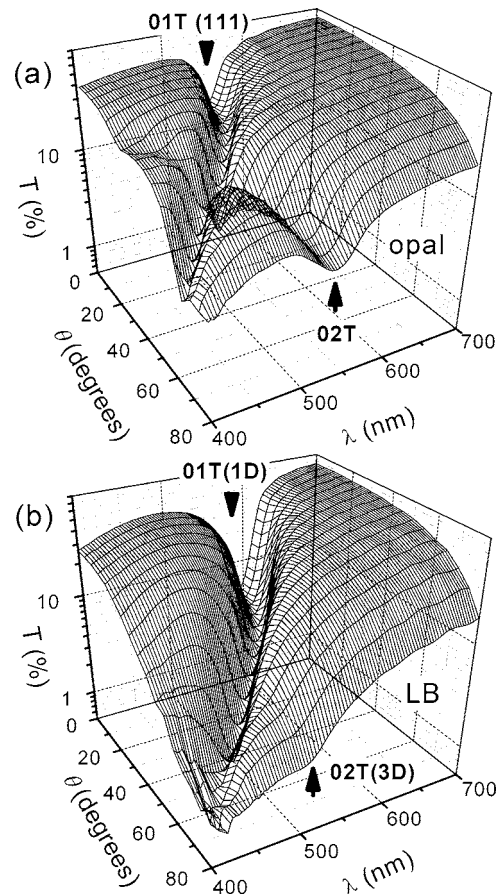


FIG. 2. Transmission spectra in s -polarized light of the opal (a) and the LB crystal (b) assembled from 250 nm spheres. Arrows indicate transmission minima labeled according to diffraction orders.

The dispersion of the 01T transmission minimum in the spectra of the LB crystal obeys the same law as the (111) diffraction branch of the opal (Fig. 3). Applying the sphere diameter $D = 258$ nm, the grating period $d = 229$ nm and the RI $n_{\text{eff}} = 1.315$ can be extracted. This produces interplane spacing $d = 0.89D$ vs $0.816D$ in the opal. No deviation from the diffraction model was observed in the LB crystal, indicating its 1D PBG structure in this wavelength range. Since the sphere monolayers in LB crystals are well ordered,¹² the loss of all but one zero diffraction order in the LB crystal can be explained by the absence of a 3D ordering in its lattice [Fig. 1(b)].

It is worth noting that another 02T branch of very weak attenuation appears consistently at high angles of beam propagation [Fig. 2(b)]. A Bragg fit to this branch gives an interplane spacing $d = 203$ nm and the angle of 64° with respect to construction planes [Fig. 3(a)]. This branch resembles the diffraction in a 3D lattice, i.e., it points to a weak intermonolayer correlation in a LB stack, allowing one to segregate a system of planes spaced by $d_2 = 0.79D$.

The intrinsic misalignment of sphere monolayers in the LB crystal follows its layer-by-layer construction in contrast to opal self-crystallization, which incorporates spheres immediately in a 3D lattice. Since LB 2D crystals are fully formed before deposition, there is no adequate force to align monolayers in a 3D lattice. The larger monolayer spacing manifests the departure from the equilibrium packing.

The lack of lateral alignment between sphere monolayers affects the transparency of the LB film. Along the film

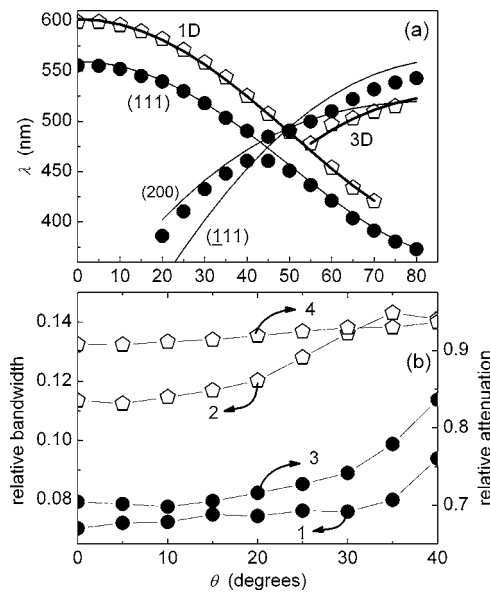


FIG. 3. (a) Dispersion of the transmission minima for the opal (circles) and the LB (pentagons) films. The thin and thick solid lines show fits of experimental data to the Bragg law for the opal and the LB crystal, respectively. Fitting parameters for the opal are chosen in accord with the symmetry of the fcc lattice. (b) Relative resonance bandwidth (curves 1 and 2) and relative light attenuation (3 and 4) of the (111) and 1D diffraction resonance in the opal (circles) and LB (pentagons) films.

normal, the transmission T decreases as $T \sim \lambda^{0.61}$ in the LB sample and as $T \sim \lambda^{0.36}$ in the opal. At $\theta = 80^\circ$ the exponent grows to 1.7 in the LB film spectrum while remaining at 0.6 in the opal spectrum. Nevertheless, the transparency decrease remains much below the rate attributed to the Rayleigh scattering, indicating that the diffuse scattering regime was not approached.

The thickness of the opal film was estimated from the period of Fabry-Pérot oscillations, ΔE [eV], which are superimposed on the transmission spectrum measured along the film normal in the spectral region of the PhC transparency, using the expression $t = 1239/2n_{\text{eff}}\Delta E$ [nm]. Thus the estimated film thickness is 4350 nm, corresponding to 20–21 monolayers of spheres comprising the opal film. Similarly, the thickness of the LB film is 4500 nm, corresponding to the 20 layers deposited during the 20 deposition cycles. This allows quantitative comparison of transmission minimum parameters in opal and LB crystals.

At $\theta = 0^\circ$ the 01T for the LB film is about twice as broad as the similar (111) minimum for the opal, and the relative bandwidth $\Delta\lambda/\lambda_0 \approx 0.13$ vs 0.07 applies, where $\Delta\lambda$ is the full width at the half minimum. Moreover, this difference is preserved over the angle range from 0° to 40° [Fig. 3(b)]. Slight broadening of the resonance with the increase of the angle θ can be a consequence of the lattice disorder.

The relative attenuation $\Delta I/I_0$, where ΔI is the depth of the minimum in transmission spectrum and I_0 is the transmission at the same wavelength projected from the transparency region, appears stronger in the 1D minimum of the LB crystal than in the (111) minimum of the opal; $\Delta I/I_0 = 92\%$ vs 71% at $\theta = 0^\circ$ applies [Fig. 3(b)]. Increase of this parameter along the angle increase is a consequence of the multiple diffraction in the opal.

Broadening and deepening of the 01T transmission minimum in LB crystals compared to that in opals can be considered as the PBG enhancement. The volume fraction of

silica spheres in a LB film is significantly lower than that in an opal, and, consequently, monolayers become better geometrically resolved. Reduction of the volume fraction of a “heavy dielectric” while maintaining the RI contrast leads to the PBG broadening.¹⁸ Since the minimum broadening is accompanied by a higher attenuation, inhomogeneous broadening is an unlikely mechanism. The lateral randomization of sphere planes in the LB crystal lattice cannot itself be a reason for a PBG enhancement in analogy to disordered opals. According to theoretical predictions, stacking faults in the fcc lattice, which are represented by a random ...ABACAB... plane sequence instead of regular one will not generate band broadening along the [111] axis.¹⁹

In summary, we have found that the lattice of a LB crystal is far from being that expected under in equilibrium self-assembly conditions. However, a weak 3D ordering is present in a LB crystal, the reason for which is not clear at the moment. The specificity of a LB crystal appears as follows: (i) the 1D periodicity in the LB crystal brings well-defined zero order diffraction at construction planes, (ii) the misalignment of monolayers erases all but construction plane zero order diffractions in contrast to a 3D diffraction in opals, (iii) the coexistence of order and disorder strengthens the zero order diffraction resonance, and (iv) the intrinsic disorder of the LB lattice reduces the sample transparency.

The authors gratefully acknowledge the support from Science Foundation Ireland, the EU project “PHAT,” and NoE PHOREMOST.

¹Y. Xia, B. Gates, Y. Yin, and Yu Lu, Adv. Mater. (Weinheim, Ger.) **12**, 693 (2000).

²A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader, and H. M. van Driel, Nature (London) **405**, 437 (2000).

³Y. A. Vlasov, X.-Z. Bo, J. C. Sturm, and D. J. Norris, Nature (London) **414**, 289 (2001).

⁴S. M. Yang, H. Miguez, and G. A. Ozin, Adv. Funct. Mater. **12**, 425 (2002).

⁵P. Ferrand, M. Egen, B. Griesebeck, J. Ahopelto, M. Muller, R. Zentel, S. G. Romanov, and C. M. Sotomayor Torres, Appl. Phys. Lett. **81**, 2689 (2002).

⁶J. Zhang, A. Alsayed, K. H. Lin, S. Sanyal, F. Zhang, W.-J. Pao, V. S. K. Balagurusamy, P. A. Heiney, and A. G. Yodh, Appl. Phys. Lett. **81**, 3176 (2002).

⁷F. Garcia-Santamaria, H. T. Miyazaki, A. Urquia, M. Ibisate, M. Belmonte, N. Shinya, F. Merseguer, and C. Lopez, Adv. Mater. (Weinheim, Ger.) **14**, 1144 (2002).

⁸B. van Duffel, R. H. A. Ras, F. C. De Schryver, and R. A. Schoonheydt, J. Math. Chem. **11**, 3333 (2001).

⁹S. Reculosa and S. Ravaine, Chem. Mater. **15**, 598 (2003).

¹⁰M. Bardosova, P. Hodge, L. Pach, M. E. Pemble, V. Smatko, R. H. Tredgold, and D. Whitehead, Thin Solid Films **437**, 276 (2003).

¹¹P. Masse and S. Ravaine, Colloids Surf., A **270–271**, 148 (2005).

¹²S. G. Romanov, M. Bardosova, M. Pemble, and C. M. Sotomayor Torres, Appl. Phys. Lett. **89**, 043105 (2006).

¹³W. Stober, A. Fink, and E. Bohn, J. Colloid Interface Sci. **26**, 62 (1968).

¹⁴P. Jiang, J. F. Bertone, K. S. Hwang, and V. L. Colvin, Chem. Mater. **11**, 2132 (1999).

¹⁵M. Bardosova, P. Ode, V. Smatko, R. H. Tredgold, and D. Whitehead, Acta Phys. Slov. **54**, 1 (2004).

¹⁶S. G. Romanov, T. Maka, C. M. Sotomayor Torres, M. Muller, R. Zentel, D. Cassagne, J. Manzanares, and C. Jouanin, Phys. Rev. E **63**, 056603 (2001).

¹⁷A. Reynolds, F. Lopez-Tejeda, D. Cassagne, F. J. Garcia Vidal, C. Jouanin, and J. Sanchez-Dehesa, Phys. Rev. B **60**, 11422 (1999).

¹⁸K. M. Ho, C. T. Chan, and C. M. Soukoulis, Phys. Rev. Lett. **65**, 3152 (1990).

¹⁹V. Yannopoulos, N. Stefanou, and A. Modinos, Phys. Rev. Lett. **86**, 4811 (2001).