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Ordered layers of monodispersive colloids

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We discuss both organic and inorganic monodispersive colloids having diameters of the order of a few hundred nm. The use of emulsion polymerisation and the Stober technique to produce organic and inorganic particles respectively is described. The application of ordered layers of such particles in photonics is discussed with particular reference to obtaining a photonic bandgap and the theoretical treatments of this question are briefly reviewed. There follows a review of the principal methods which have been employed to form good ordered multilayers of these materials. The so called inverted structures made by filling the interstices of these multilayers with another compound and then etching out the original particles are described. The results of some of the more important optical studies of both original multilayers and inverted multilayers are given.

Introduction

The first preparation of monodispersive colloids appears to have been made in the laboratories of the Dow Chemical Company in 1947 though, curiously enough, there was no publication of this work and one depends on other papers in the literature (see for example Krieger *et al.*, 1968[1]) for this information. These initial colloids consisted of polystyrene and were presumably made by emulsion polymerisation. This technique was, at that date, very poorly understood and it is thus likely that the correct conditions to produce a monodispersive preparation were found by trial and error. The first publication to illustrate the monodispersive nature of such a preparation used electron microscopy and was made by Backus and Williams[2] in 1948. Over the years many groups have used emulsion polymerisation and related techniques to produce monodispersive specimens of polystyrene, poly(methyl methacrylate), polyacrylate and several related copolymers.

In 1968 Stober *et al.*[3] published a paper describing a method of producing a monodispersive preparation of SiO_2 particles. This method has been extended and applied by other groups more recently.

It should be pointed out that by using the word monodispersive we refer to families of particles whose diameters only vary by one or two percent and, in all these cases, we are considering diameters of a few hundred nm. In the case of those specimens which we have examined by TEM and SEM we have been unable to find any measurable deviation from a spherical structure.

The importance and interest of these particles lies in the fact that it is possible to induce them to coalesce in a close packed structure analogous to an ordinary close packed crystal. It is possible to obtain repeat distances large enough so that radiation in the optical region can be diffracted from them just as X-rays are diffracted from an ordinary crystal. One of the earliest papers which described this phenomenon in some detail was published by Alfrey *et al.*[4] in 1954 and a further study was made by Krieger *et al.*[1] in 1968. The behaviour of electromagnetic radiation in these structures is also analogous to the behaviour of electrons in a crystal which can be described by the band theory of solids. In principle it would be possible to obtain an energy bandgap similar to the bandgap in semiconductors and use this to trap radiation locally and a substantial amount of work has been carried out in this field over the last few years. We will return to this topic later in this article. It should be pointed out that other techniques for the formation of 3D structures which might lead to an optical bandgap have also been explored and that, in the mm wavelength region, success has been obtained. However, clearly, real interest lies in wavelengths in the optical region and in the near infrared and here several papers have been published which claim the production of a bandgap.

Curiously enough other articles on this general topic have avoided a discussion of the problem of producing monodispersive colloids, a matter on which the whole topic depends. The production of monodispersive polymer particles, which are usually referred to as latexes, makes use of emulsion polymerisation and we believe that many readers will only have a vague idea of this technique and thus we should explain it briefly giving particular attention to its application to our topic.

Emulsion polymerisation

This technique has been employed for over fifty years but it is only in the last twenty years that it has become well understood and that it has been possible to relate theoretical predictions to experimental results in a meaningful way. A general discussion of this topic has been given by Gilbert.[5]

Most emulsion polymers are made by the addition polymerisation of vinyl compounds. Much of the basic research on the topic has made use of styrene and we will thus give a typical laboratory recipe used to polymerise this compound:
625 g of water
300 g of styrene
10.5 g of sodium dodecyl sulfate (as a surfactant)
1.0 g of $K_2S_2O_8$ (as an initiator)
1.0 g $NaHCO_3$ (as a buffer to control the pH).

Polymerisation is carried out at 90 °C and the mixture is vigorously stirred. Initially the surfactant stabilises small particles of the styrene monomer and much of the remaining surfactant forms micelles.

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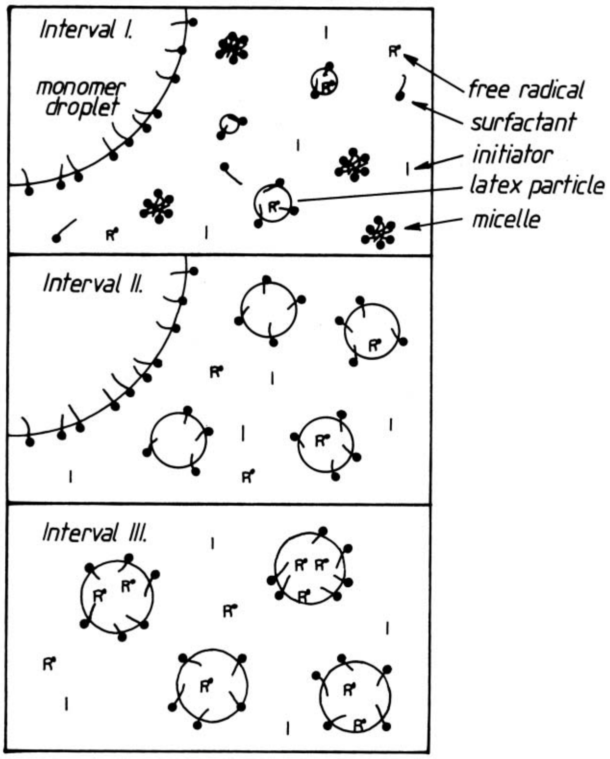

Fig. 1 Schematic diagram illustrating the process of emulsion polymerisation. For further explanation see the text.

The process is usually considered as taking part in three stages which are illustrated schematically in Fig. 1. The initiator generates a free radical and this is denoted by $R^\bullet$.

Interval I: The initial polymerisation forms small latex particles.

Interval II: The particle nucleation has largely stopped. Initiator molecules diffuse through the water and become trapped in latexes (which consist of a mixture of the monomer and polymer chains) and thus bring about further polymerisation. At this stage the determination of polymer formation rate is governed by the availability of initiator molecules. There is a natural monomer/polymer ratio within the latexes and monomers are so freely available that their arrival is not rate determining. Successful mathematical theories of emulsion polymerisation assume that, at this stage, individual latexes contain either no initiator or actively growing polymer or, at the most, one of these.

Interval III: The monomer droplets have now all been consumed and the remaining initiator molecules gradually enter the existing latexes bringing about further polymerisation and increasingly reduce the number of monomers contained in them.

When this process has been completed some form of purification of the system is used if a scientific study of the final product is to be made. Centrifugation followed by the process of redispersing the product is one possibility.

One must now consider how it is possible to bring about a largely monodispersive system. If there is a large initial free-radical flux particles form rapidly and, at an early stage, become so numerous that they will capture all the free radicals in the aqueous phase before they can lead to the creation of new particles. The large free radical flux can be brought about both by the concentration of free radicals and also by working at a relatively high temperature. If very few new free particles are formed and the existing particles all grow at about the same rate an approximately monodispersive system will be produced.

This topic is discussed at length in Chapter 5 of Gilbert's book.[5]

The Stober method

Stober *et al.*[3] were the first group to make a monodispersive preparation of SiO_2 particles which could be used to form synthetic opals. Subsequently many papers have appeared describing variations and improvements of this technique and making attempts to explain the detailed mechanism of this process which depends on the hydrolysis of alkyl silicates or, more often, silicon alkoxides. Most recent papers describe the use of tetraethylorthosilicate (TEOS). Initially water, an alcohol (usually ethanol) and ammonium hydroxide are mixed and stirred, subsequently TEOS is added and the stirring continued. The relative proportions of the compounds employed vary widely depending on the diameter of the particles to be made and on the point of view of the group carrying out the work. However a typical concentration of the TEOS when it is first added to the solution is 0.28 mol l^{-1}.

One recent paper on this topic whose recipe we have ourselves made use of was published by Ballato and James.[6] They used an initial solution of:

168 ml of ethanol
51.2 ml of ammonium hydroxide
100 ml of distilled water

which were mixed by a magnetic stirrer in an Erlenmyer flask.

20 ml of tetraethoxisilane was added during 1 min and the solution was stirred for 48 hours. Cleaning of the product was realised by repeated use of a centrifuge followed by sonication in ethanol.

In such a system many reactions can occur but those of most importance are given below.

$$\equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \leftrightarrows \equiv\mathrm{Si{-}OH} + \mathrm{ROH} \qquad (1)$$

$$\equiv\mathrm{Si{-}OR} + \equiv\mathrm{Si{-}OH} \leftrightarrows \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{ROH} \qquad (2)$$

$$\equiv\mathrm{Si{-}OH} + \equiv\mathrm{Si{-}OH} \leftrightarrows \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \qquad (3)$$

where R is an alkyl group of the form C_xH_{2x+1}.

The question of real interest is why this process should lead to a largely monodispersive product. Many speculative papers have put forward possible explanations for this phenomenon but we will confine our attention to the work of Bogush and Zukoski.[7,8] These authors suggest that, after the initial formation of small particles by the reactions shown above, the formation of larger particles takes place largely by the aggregation of these smaller particles. In their second paper[8] they derive a complex mathematical expression for the interaction of these small particles in solution and obtain a result (see figure 2 of reference 7) which indicates that there is a repulsive force between these small particles which must be overcome by thermal forces before the particles become close enough to undergo a strong mutual attraction. The positive peak in the curve of energy *versus* separation becomes larger for larger particles and thus small particles are more likely to coalesce than are larger ones. From this result it is obvious that, if the growth of particles is dominated by aggregation, the final product will be largely monodispersive. More recent examinations of the aggregation theory and comparisons with other theories[9,10] give strong support to this picture.

The possibility of an optical bandgap

Though ordered films of monodispersive colloids were first made several decades ago they took on a new and important interest when Yablonovitch[11] suggested that a three dimensional periodic structure having a periodicity of a few hundred nm might behave in such a way that there would be a region of wavelengths in which light would be confined and would be unable to propagate. This phenomenon would not only be of intrinsic scientific interest but would also be of technical importance. For example it would be possible to trap fluorescent radiation and thus make a new kind of laser. Though Yablonovitch's paper is usually quoted as the origin of these ideas it is worth pointing out that Ohtaka[12] first discussed the possibility of photonic bandgaps in 1979.

The theory of photonic band structure in three dimensional structures is analogous to the theory of electronic band structure in ordinary crystals which is discussed in many textbooks on the theory of solid state structures. However the Schrodinger equation deals with a scalar variable whereas the Maxwell equations deal with a vector quantity. Thus the results of some of the early theoretical treatments of this problem, in which the vector nature of the variable was ignored, can be misleading and, indeed, even some of the early theories incorporating the vector nature of the variable were subsequently shown to be incorrect. Many papers in this general field have been published but we will restrict our discussion to those dealing with an ordered structure of spherical particles having a compound with a different refractive index occupying the interstices between the spheres. The first rigorous treatment of this problem of which we are aware was published by Sozuer *et al.*[13] in 1992. Subsequently Moroz and Sommers[14] obtained equivalent results by a more elegant method.

Before discussing these results it is important to define exactly what we mean by a bandgap. A periodic structure will always have one or more bandgaps such that there is a discontinuity of wave energy plotted as a function of the wave vector. These discontinuities occur on planes to which lines from the origin to points in the reciprocal lattice are normals and which bisect these lines Thus there will be regions of wave energy which do not correspond to any possible values of the wave vector (and hence of wavelength) and so, in these regions, wave propagation is not possible. However, if radiation is produced corresponding to one of these regions of energy by, for example, fluorescence, it will be trapped and correspond to a localised wave rather than a travelling wave. In a three dimensional structure the situation is more complex as, to produce a three dimensional photonic bandgap, there must exist a region of energy over which it is not possible to produce a travelling wave in any direction. It is questionable whether a true three dimensional bandgap has as yet been produced using a simple structure consisting of dielectric spheres. The theoretical results reported in references 13 and 14 explain why this should be. However several papers have been published in which the behaviour of systems based on such a structure which have, however, been modified in some way, have been described and a true bandgap has been produced. We will return to this topic later in this paper.

The important results of reference 14 can be summarised as follows for the case of a face-centred cubic (close packed) lattice. Let n_s be the refractive index of the material of which the spheres are made and n_i be the refractive index of the material in the interstices. Then if $n_s > n_i$ no gap is found in the spectrum. If $n_s < n_i$ a gap appears between the eighth and ninth bands. These results are, of course, only applicable to a structure consisting of close packed dielectric spheres. It is worth noting that Yablonovitch *et al.*[15] were able to construct a macroscopic face centred cubic structure in which the "atoms" were non-spherical which did give a true photonic bandgap in the microwave region. A useful general review of this topic was given by Yablonovitch[16] in 1994.

While discussing diffraction we will give the expression which leads to the Bragg condition for the first order reflection from the 1 1 1 surface of a face centred cubic structure of dielectric spheres having a diameter, *D*. This can be obtained by using the ordinary Bragg condition for the first order peak,

$$\lambda = 2d\sin\alpha \qquad (4)$$

where λ is the wavelength of the radiation, d is the layer spacing and α is the angle between the direction of incidence of the radiation and the planes from which diffraction is observed. $d = (2/3)^{1/2}D$. We note that $n\lambda = \lambda_0$ where n is the mean refractive index of the material and λ_0 is the wavelength in free space. We must also take account of Snell's law to relate the angle of propagation in free space and in the material. Simple algebraic manipulation gives

$$\lambda_0 = 2(2/3)^{1/2}D(n^2 - \sin^2\theta)^{1/2} \qquad (5)$$

where θ is the angle between the normal to the plane and the direction of incidence of the radiation.

This simple expression is useful in checking if one has succeeded in producing an ordered close packed structure having the 1 1 1 planes parallel to the substrate on which the material has been deposited.

Synthetic opals

References 1 and 4 are early descriptions of the formation of ordered structures made from SiO_2 spheres. The study of such synthetic opals has recently interested a number of groups as a result of the concept of photonic bandgaps. Of particular interest is the work of the Madrid group[17–21] who used sedimentation to assemble spheres made by the Stober[3] method. They used a concentration of about 10^{10} spheres per cm^3 in water and allowed sedimentation to take place over a period of up to several weeks onto a smooth poly(methyl methacrylate) surface. The films so formed were then removed from the solution and allowed to dry. They were studied by AFM and by SEM and regular close packed structures were observed as shown in Fig. 2. By cleaving the films and studying the edges by SEM they were able to show that the structure of the films was face centred cubic and the 1 1 1 faces were parallel to the substrate surface. The structures produced in this way have little mechanical strength. However it is possible to remove the substrate and sinter the resultant film at temperatures of the order of 900 °C. This has the effect of forming a solid neck joining adjacent particles. The temperature was increased at a rate of 1 °C min^{-1} and the final temperature was maintained for a period of 3 hours. They show[21] that the lattice parameter can be reduced by as much as 10% depending on the sintering temperature. The optical properties of these structures were studied by reflectance, making use of eqn. (4), and also by examining the transmission spectra. Typical reflectance results are shown in Fig. 3. The films could be as thin as 7 µm or as thick as 3 mm. In the best films domain sizes up to 50 × 50 µm were obtained.

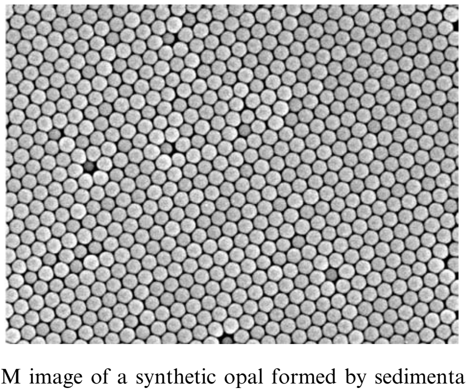

Fig. 2 SEM image of a synthetic opal formed by sedimentation. The particles have a mean diameter of 415 nm. We wish to thank Dr C. Lopez, Professor F. Meseguer and Dr H. Miguez for kindly providing this figure.

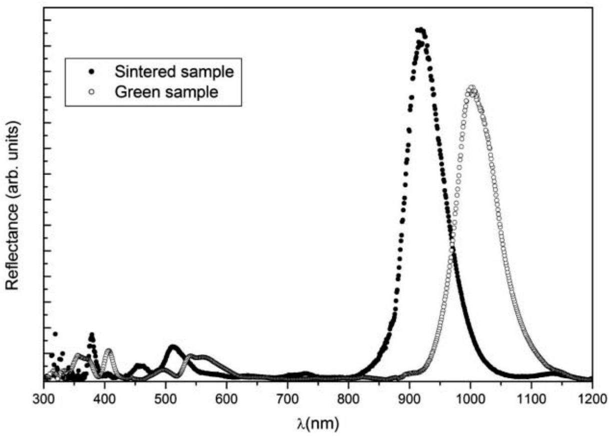

Fig. 3 Reflection spectra from the synthetic opal shown in Fig. 2. The "Green" sample had been directly obtained by sedimentation and the other sample had been sintered at 900 °C. We wish to thank Dr C. Lopez, Professor F. Meseguer and Dr H. Miguez for kindly providing this figure.

In order to obtain layers with true long range order van Blaaderen *et al.*[22] deposited their silica spheres on a template. This consisted of a 500 nm thick fluorescent polymer layer with holes made by electron beam lithography. This thickness is close to the particle radius (525 nm) which they employed. The inter particle forces were made hard-sphere-like by matching the refractive index of the solvent mixture to that of the spheres and thus minimising the effect of van der Waals forces and also by increasing the ionic strength so that double layer repulsion occurred over distances much smaller than the particle radius. Not only could this group obtain true long range order by this method but, by a suitable template pattern, they could grow crystals having the 1 0 0 planes parallel with the substrate.

Jiang *et al.*[23] prepared solutions of SiO_2 spheres in ethanol. They deposited layers of 3-(trimethoxysilyl)propyl methacrylate on silica microslides and placed them in clean scintillation vials the planes of the microslides being vertical. 15 ml of the solution were added and allowed to evaporate. Depending on the concentration of the solution different film thicknesses were obtained. By careful purification of the original material and the use of a vibration free support they obtained high quality films which they studied by SEM and other techniques. They claim that the crystallographic directions can be shown to remain constant over a region of about one square centimetre. As will be seen in reference 51 this is probably the best way of obtaining a highly ordered opal structure which has so far been published.

The difficulty of the sedimentation method of deposition is that the rate of sedimentation depends simply on gravity and the effect of viscosity so that the velocity with which the particles descend is proportional to the square of their diameter. For particles having a diameter less than about 300 nm the process is excessively slow whereas particles having a diameter greater than 550 nm descend so fast as to prevent a proper ordered structure being formed. However silica particles have a negative surface charge when in water unless the pH is less than 2.5. Thus, if a positive electrode is placed at the upper end of the sedimentation tube and a negative electrode at the lower end, the rate of sedimentation can be decreased. Conversely an electric field in the opposite direction increases this rate. Holgado *et al.*[24] exploited this fact. They used a silicon wafer sputtered with titanium as the lower electrode and a platinum upper electrode and could observe the rate of sedimentation by watching the progress of the interface between the suspension and the clear water above. This method of controlling the sedimentation rate proved completely satisfactory.

Compounds in the opal interstices

Numerous papers have been published describing the study of synthetic opals the interstices of which have been filled or partly filled with other compounds. Yates *et al.*[25–27] introduced indium phosphide into opals by metal-organic chemical vapour deposition (MOCVD). The reactants which they employed were trimethylindium and phosphine. The opals were initially heated to 400 °C in a nitrogen atmosphere to dehydrate them. The opals were then alternately exposed to the two reactants in a hydrogen atmosphere (at atmospheric pressure) starting with trimethylindium. They studied the resultant materials by SEM, optical diffraction, AFM and observed their luminescent properties. It appears that, though the indium phosphide was crystalline, it consisted of many tiny crystals adhering to the silica spheres. The refractive index of opal is approximately 1.5 whereas the refractive index of indium phosphide is in excess of 3.5 in the visible and near infrared region. The effect of introducing this high refractive index compound into the opal interstices is to increase the intensity of the Bragg reflections by a factor of 2. However, as would be expected from the theoretical considerations discussed above, a photonic bandgap was not observed. Romanov *et al.*[28,29] have carried out similar experiments in which gallium phosphide was deposited in the interstices of synthetic opals.

Several other inorganic compounds have been deposited in opal interstices including tin oxide[30] and barium titanate.[31] However the study which provided some evidence for a near photonic bandgap was made by Blanco *et al.*[32] using cadmium sulfide. They studied the photo-luminescence of an opal impregnated with this compound and found a marked reduction in luminesence in the wavelength region where a bandgap might be expected to appear. Clearly they had not produced a full bandgap but the reduction in luminescence indicates that the motion of photons in this region was inhibited.

Eradat *et al.*[33] impregnated synthetic opals with various metals and studied their optical properties. Needless to say, all the metals they employed had low melting points but unfortunately they do not give any details of the method they used to introduce the metals. To a large extent this study deals with the modification of the reflectivity of the metals by the presence of the opal structure and thus is not really relevant to our present discussion.

It is not surprising that a number of workers have introduced various organic compounds into the opal interstices. Petrov *et al.*[34] used a mixture of methyl methacrylate and a fluorescent dye which they introduced into the opal interstices and then photo-polymerised. They irradiated their samples with 337.1 nm light from a pulsed laser and compared the fluorescent spectra obtained from a simple film of dye and PMMA formed without the opal. Results are shown in Fig. 4. Further results from such systems have been reported by this group and their collaborators.[35–37] Such behaviour is what would be expected from the face centred cubic colloid lattice which leads to a partial but imperfect optical bandgap. Related studies were made by Yoshino *et al.*[38]

Just as the presence of the opal lattice can influence the behaviour of the compound in the interstices so the diffraction brought about by the opal can be tuned by the presence of a suitable compound in the interstices. In particular this effect can be brought about by the insertion of liquid crystal materials. A striking change in the position of the Bragg peak can be observed as the material is heated through the transition from the nematic phase to the isotropic phase. However what is of more interest is the fact that the orientation of the liquid crystal can be aligned by the application of an electric field and that the relative orientation to the direction of propagation of light in the system brings about a change in the position of the Bragg diffraction peaks thus producing a true tuneable system.

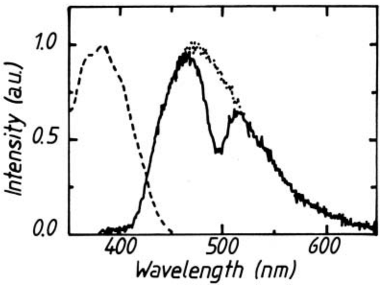

Fig. 4 Fluorescent results from reference 34. The solid line corresponds to the fluorescence obtained from a synthetic opal the interstices of which contain a dye and PMMA. The dotted line corresponds to the fluorescence obtained from a film of the dye and PMMA without the presence of the opal and the hatched line represents the excitation spectrum. The dip in the solid line at about 500 nm corresponds to an incomplete bandgap. We wish to thank Professor Petrov and the editor of *Phys. Rev. Lett.* for permission to reproduce these results.

The biphenyl liquid crystals are more polarisable along their axes than normal to it and the components of their dielectric constant are thus greatest when the electric component of the light is in this direction. Thus the velocity of light in them is greatest when the direction of propagation is along the direction of the liquid crystal molecular axes. The possibility of this effect seems to have occurred simultaneously to several individuals and a number of papers have appeared dealing with this topic.[39–46]

Inverted photonic crystals

The expression "inverted photonic crystals" is rather misleading but, as it has become accepted in the literature, we employ it. Such structures are made by filling the interstices of a synthetic opal or similar material with a substance which has a high refractive index and can be formed into a stable solid and then etching away the opal. The result is an ordered array of air spheres embedded in a substance which has a high refractive index. Theoretical work had shown[13,14] that such a structure would exhibit a definite photonic bandgap provided that the substance used had a high refractive index. More recent theoretical papers by Doosje *et al.*[47] and Busch and John[48] have shown that suitable inverted structures which can be derived in this way should show a definite photonic bandgap.

Here we discuss a few of the more successful attempts to apply this idea, starting with an opal structure and also refer to a similar system which started with a polystyrene lattice in the next section of this paper. Jiang *et al.*[49] infiltrated an opal lattice with monomers and polymerised them *in situ* to form either polystyrene or polyurethane and then etched away the opal material. Scanning electron microscopy showed that a good regular structure had been obtained. The air spheres were connected by pores the diameter of which depended on the polymerisation temperature. The optical properties of the structures made in this way agreed well with those predicted theoretically . However the refractive indices of these polymers were not sufficiently great to bring about a bandgap. Germanium with a refractive index of 4.01 and silicon with a refractive index of 3.42 (both in the mid visible region) seem ideal substances to inject into the opal voids and both have been studied.

Blanco *et al.*[50] succeeded in introducing silicon into opal interstices and then etching out the opal particles. The silicon was grown by placing the opals in an atmosphere of disilane gas at a pressure of 200 Torr and the temperature was varied between 250 °C for low filling fractions to 350 °C for high filling fractions. The reaction time was 24 hours. It was possible to obtain 100% filling. After silicon growth the samples were heated to 600 °C in order to improve the semiconductor crystallisation and to allow diffusion of silicon inside the void structure. The silica template was subsequently removed using a fluoride based etching procedure designed to minimise the dissolution of the macroporous silicon structure. They used microscope Raman spectroscopy to show that crystalline silicon had been produced. They also used SEM and AFM to show that good quality specimens had been obtained. They made calculations based on the work of Busch and John[48] which predicted the region where a bandgap would appear and compared this result with the reflection which they observed from their specimens. Their results are shown in Fig. 5. Clearly the experimental and theoretical results agree well. However, the authors claim to have obtained a complete bandgap, in which case surely one would expect a higher reflectivity than 80%. Vlasov *et al.*[51] also infiltrated silicon and etched out the silica but used the method of Jiang *et al.*[23] to grow the original opals. This provided better long range order and thus a more convincing bandgap. To the best of our knowledge, this is the most convincing example of a real bandgap originating from an ordered colloid structure so far published.

Miguez *et al.*[52] grew germanium crystals in opal voids by the following method. Bare sintered opals are placed in a vacuum of 10^{-2} Torr and are then immersed in tetramethoxygermane (TMOG). When the TMOG has impregnated the opal it becomes translucent as the SiO_2 and the TMOG have nearly equal refractive indices. The material is then placed in a flow of water vapour in nitrogen which hydrolyses the TMOG to GeO_2 and subsequently *in vacuo* to remove the remaining methanol resulting from the reaction. The GeO_2 is now reduced by placing the specimen in an atmosphere of hydrogen at a temperature of 550 °C. The opal interstices are now only partly full and the whole process needs to be repeated five times in order to fill the interstices. SEM studies were made to prove that the interstices were largely filled. Finally the material is etched in a 1 wt% solution of hydrofluoric acid in water which removes the SiO_2. The authors used SEM studies of their materials cleaved along various planes to show that a good face centred cubic structure had been maintained. Inverse opal structures produced in this way were studied by Ozin *et al.*[53]

Organic colloids

Ordered structures made from polystyrene colloids have been made over a number of years starting with the work of Backus and Williams[2] and we will not attempt to refer to the many papers on this topic but select those which illustrate particular aspects of this work. One must distinguish between two basically different approaches to this problem. On the one hand a concentrated aqueous solutions of charged polystyrene particles is formed which is found to diffract light in a manner which one would expect from a face centred cubic

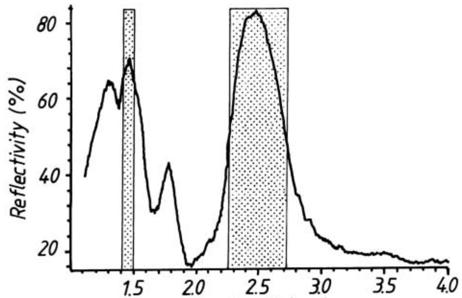

Fig. 5 Results from reference 50 showing the reflection spectrum from an inverse silicon opal. The shaded regions at 2.5 μm and 1.5 μm show the calculated positions of the first stop band and the complete photonic bandgap, respectively. Reprinted by permission of *Nature*, **405**, page 439, copyright 2000, and with the kind permission of Professor John and his fellow authors.

lattice. Clearly the structure can only be inferred from optical measurements as electron microscopy could not be used. This is a technique pioneered by Asher[54] and his associates who have published a number of papers on the topic. Tarhan and Watson[55] made a careful study of the diffraction from such a structure. We will not discuss this work further here as it could never lead to stable permanent structures.

On the other hand it is possible to form lattices of both polystyrene and PMMA particles from which all the water has been removed and which are analogous to the synthetic opals which we have already discussed. The first paper describing such films was published by Alfrey *et al.*[4] The simplest way of making such films is to spread an aqueous solution of the colloids on a clean flat surface such as glass or silicon and allow the water to evaporate. Subsequent mild heating to a temperature of about 65 °C is needed to drive off the remaining water. Reasonably good monolayers and multilayers can be produced in this way but they tend to be polycrystalline as islands of ordered structure nucleate at a variety of points and eventually make contact. The low density of these organic colloids makes sedimentation impossible.

Many papers have been published describing methods of obtaining relatively large single crystal areas but they all fall into two categories. One is the physical confinement of the particles an example of which was describes by Park *et al.*[56] They used photo-resist technology to form a number of narrow channels on a glass sheet which was maintained parallel to another glass sheet which was a chosen distance (of the order a few tens of microns) from it. The depth of the channels was always less than the diameter of the polystyrene particles. A dispersion of the particles in water was injected by a syringe through a glass tube which penetrated the upper glass sheet. The channels encouraged the water to flow between the sheets and to leave *via* an opening at one end of the structure. As thermal activation would be too small to encourage the particles to form a crystalline structure sonication was used.

The top plate was eventually removed and the structure dried at 65 °C. SEM was used to characterise the resultant film and the authors claim that they could make a single crystalline structure as large as 12 μm × 0.5 cm × 2 cm. Gates *et al.*[57] studied the effect of heating on films formed in this way. Though they may not have achieved a full photonic bandgap there is a wavelength region where the optical transmittance is very small. Heating at temperatures below 93 °C, the glass transition temperature of polystyrene, had very little influence on the transparency but heating to 100 °C moved the region of decreased transparency to shorter wavelengths and decreased the effect. This result would be expected as the polystyrene spheres deform and their centre to centre distance decreases.

Another way of increasing the long range order of polystyrene films is by using a suitable template. We are not aware of an exact analogy of the work of van Blaaderen et al.[22] who used a template having the periodicity of the required lattice to form ordered layers of SiO_2 but several groups have formed patterns on their substrates having a larger scale repeat distance and have induced polystyrene to conform to this pattern. Guo *et al.*[58] decorated a mica surface with gold squares. Using 90 nm polystyrene particles in pure water the particles were selectively deposited on the mica surface. However, when they used a dilute surfactant (5 mM sodium dodecylsulfate) the reverse arrangement was produced. Xia *et al.*[59] published an account of similar work.

Rogach *et al.*[60] prepared polystyrene particles covered by very small cadmium telluride particles having a diameter of the order of 2.5 to 5 nm. They covered these small particles with 1-mercapto-2,3-propanediol and used alternate layers of these small particles and poly(allylamine hydrochloride) to form a layer round the styrene particles. The surface composite layers were shown by TEM to be 5–8 nm thick. Regular layers of these coated particles were formed in the usual way. Optical transmission and luminescence of these structures are shown in Fig. 6 and it seems possible that a full bangap had been obtained though transmission measurements in one direction only are not sufficient to ensure this result and, in any case, the results may have been boosted by resistive losses.

Muller *et al.*[61,62] have studied the behaviour of films of monodispersive colloids of poly(methyl methacrylate) made by emulsion polymerisation. They claim that their films were made by sedimentation but this is a wrong use of this term as their films were made by spreading an aqueous suspension of the colloid on a glass surface and allowing it to dry very slowly in an atmosphere of high humidity. Clearly, as the density of this material is only 1.2, sedimentation would be impossible. In one of their papers[61] they describe the formation of inverted SnS_2 films. PMMA films were initially formed and placed in a dessicator together with about 0.5 ml of $SnCl_4$ and stored at 0 °C for 3 hours. The dessicator was then evacuated and subsequently filled with H_2S. After 24 hours the films were washed with water and dried. The PMMA was removed by placing the slide for 30 minutes in THF. In their other paper[62] they show that a film of PMMA particles can be used as an e-beam resist. They also incorporated the fluorescent dye, coumarin 6, in PMMA particles which were deposited as ordered structures and observed their fluorescent behaviour.

Subramanian *et al.*[63] formed polystyrene lattices including very finely divided metal oxides in the colloidal suspension they employed. The amount of oxide employed was chosen so as to fill the interstitial voids in the polystyrene lattice. The polystyrene was calcinated at 450 °C leaving an inverted lattice of oxide. These authors used both titanium oxide and silica and it is surprising that the inverted lattices were stable as 450 °C is far too low a temperature to sinter these compounds.

Another application of polystyrene spheres deposited as a monolayer was made by Bartlett *et al.*[64] They deposited the spheres on a gold surface and then were able to use electrochemical deposition *via* the interstices to form ordered

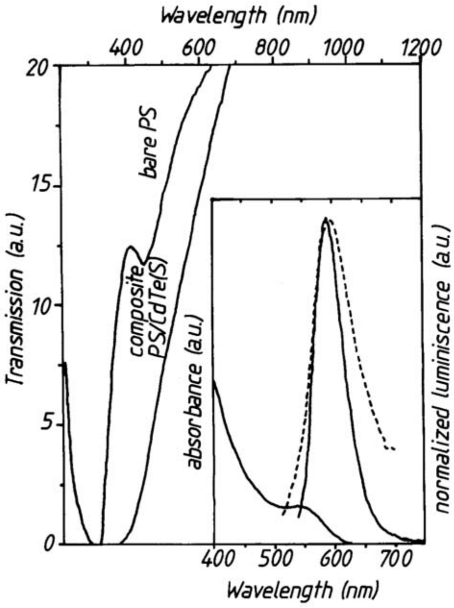

Fig. 6 Results from reference 60. Transmission spectra of 3D colloidal crystals made from uncoated 0.2 μm diameter polystyrene latex spheres and from the same spheres coated with a polyelectrolyte/CdTe nanocrystal shell. Inset: absorbance and photoluminescence spectra of CdTe nanocrystals in aqueous solution (solid lines) and photoluminescence of colloidal crystals made from the composite particles (dashed line). Reprinted with permission from *Adv. Mater.*, 2000, **12**, 335, and with the kind permission of Professor Weller and his fellow authors.

hexagonal arrays of voids surrounded by walls of platinum, palladium and cobalt. The polystyrene was removed by soaking the films in toluene for 24 hours.

Opal structures can be made rigid by sintering as we have already discussed but this process is clearly not possible in the case of multilayers of polystyrene. None of the authors of papers on this topic appear to have observed interpenetration. Foulger *et al.*[65] have incorporated compounds capable of photo-polymerisation into the interstices of their multilayers and subsequently used UV light to bring about polymerisation, thus producing a rigid structure. Their overall procedure is a little complicated and will not be discussed in detail here.

Langmuir–Blodgett deposition of colloidal layers

The success of the deposition method employed by Jiang *et al.*[23] as exemplified by Vlasov *et al.*[51] shows that the gradual movement of a colloidal suspension down a vertical surface can produce exceptionally long range order in the resulting film. This result suggests that the Langmuir–Blodgett method of deposition (see for example Tredgold[66]) might be useful in forming good well ordered films.

Fulda and Tieke[67,68] used emulsion polymerisation to form monodispersive preparations of polystyrene containing small amounts of either acrylic acid or 2-acryloxyethyltrimethylammoniun chloride, the initiators being either potassium peroxodisulfate or 2,2′-azobis(2-amidinopropane) hydrochloride. The particles were dispersed in ethanol and spread at the air/water surface. They used the Langmuir–Blodgett dipping method to deposit monolayers on a glass support and studied them by SEM. They examined the influence of the pH of the subphase on the behaviour of the layers at the air/water interface and on deposition. They obtained reasonably good films but failed to achieve long range order.

Bardosova *et al.*[69] made opal particles by the method of Bellato and James[6] which were then made hydrophobic by a method described by Liz-Marzan *et al.*[70] The reagent employed was 3-(trimethoxysilyl)propyl methacrylate and the suspension was purified by the repeated use of a centrifuge and re-dispersal of the material using sonication and magnetic stirring, first in denatured alcohol, then in pure ethanol and finally in chloroform. The suspension was stored in chloroform from which it was spread at the air/water interface using a Nima Langmuir–Blodgett trough and deposited on glass slides which had been rendered hydrophobic by exposure to hexamethyldisilazane vapour. The initial layer was formed by the Langmuir–Schaefer method in which the glass substrate is slowly moved upward in a nearly horizontal position. Subsequent layers were deposited by the normal Langmuir–Blodgett method. Good highly ordered layers were formed and an SEM picture of one such layer is shown in Fig. 7. It is hoped that an extension of this technique could lead to highly ordered multilayers wherein the number of layers is precisely determined.

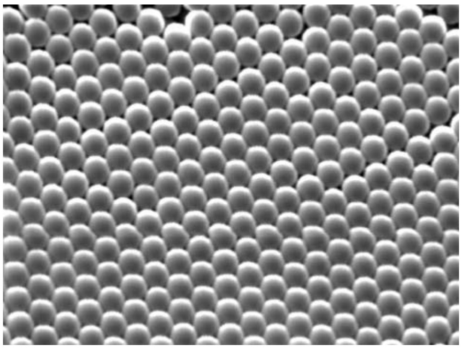

Fig. 7 SEM image of a synthetic opal formed by the Langmuir–Blodgett technique obtained by the present authors in collaboration with Dr L. Pach and Dr V. Smatko. The particles have a diameter of approximately 300 nm.

Conclusions

Using the techniques which we have discussed it has been found possible to form highly ordered layers of monodispersive colloids. By filling the interstices of these layers with compounds which have a high refractive index and then etching away the original colloid, structures have been made which have an optical bandgap in the visible region. Such structures could form the basis of a new kind of laser.

Liquid crystals have been introduced into the interstices of ordered layers and an electric field used to change the position of the principal peak in the diffraction spectrum thus producing a tuneable system.

It thus seems likely that structures produced in these ways will eventually have a practical application in optoelectronics.

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