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A NEW METHOD OF FORMING SYNTHETIC OPALS

M. Bardošová[a,b,1], **P. Hodge**[a], **V. Šmatko**[c], **R.H. Tredgold**[a], **D. Whitehead**[d]
[a] *Department of Chemistry, University of Manchester, Manchester, UK*
[b] *Institute of Informatics, Slovak Academy of Sciences, Bratislava, Slovakia*
[c] *Electrotechnical Institute, Slovak Academy of Sciences, Bratislava, Slovakia*
[d] *Department of Chemistry, University of Salford, Salford, UK*

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A new method is described to deposit synthetic opal films by using the Langmuir-Blodgett (LB) technique. We show that, using a NIMA two compartment trough, good quality films can be formed if the substrate is maintained in a horizontal position during the drying period between dips. The first layers to be deposited consists of a number of highly ordered domains which make good contact with one another but which have differing crystal orientation. With the deposition of further layers the domain structure gradually disappears but these further layers have a good degree of order with regions which are as regular in structure as the domains.

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1 Introduction

Recently there has been considerable interest in the formation of synthetic opals as they have important possible applications in optoelectronics. These applications have been reviewed by Bardošová and Tredgold [1] and in more detail by Lopez [2]. These authors also discuss the various methods which have been employed to form ordered thin films of these materials. The method most often made use of is sedimentation. One of the difficulties of this method and of the other methods so far employed is that it is not possible to obtain films which consist of an exact number of layers of the particles employed. There are, moreover, difficulties in obtaining long range order over distances sufficiently large so as to form efficient devices. Last year Reculusa and Ravaine [3] and Bardošová *et al.* [4] showed that the Langmuir-Blodgett method could be applied to this problem with some success but, even then, it would be desirable to improve the degree of order obtained. (For a general discussion of the Langmuir-Blodgett (LB) technique and its applications to the formation of ordered multilayers of amphipilic organic molecules see the books by Tredgold [5] and Ulman [6]).

For optical applications the individual spheres from which the opals are formed have to have a diameter of a few hundred nanometres, the exact diameter depending on the wave length of the

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[1] E-mail address: upsybard@savba.sk

light which is used. Clearly the volume and mass of such particles are many orders of magnitude larger than those of the molecules usually deposited by the LB method and it is thus not surprising that they behave rather differently to ordinary molecules. We have thus been attempting to find out how to overcome the difficulties arising from these differences and believe that we have made significant progress.

Before discussing our own experiments we wish to draw attention to some earlier work involving the study of large hydrophobic colloid particles at the air/water interface. Clint and Taylor [7] and Aveyard *et al.* [8] obtained isotherms of such particles and attempted to obtain information about the contact angles at the particle surfaces from the nature of the isotherms.

Van Duffel *et al.* [9] used [3-(trimethoxysilyl)-propyl]trimethylammonium chloride to render opal particles hydrophobic. After purification they made a suspension of these particles in a sodium dodecylsulfate chloroform/ethanol solution and were able to obtain good isotherms which collapsed at a surface pressure of about 20 mNm^{-1}. However, without the use of this latter compound in the spreading suspension, they were unable to obtain stable films indicating that the particles were not truly hydrophobic. They were able to deposit Langmuir-Blodgett monolayers which had some degree of order but did not apparently make any attempt to form multilayers. More recently this group together with two Hungarian collaborators (Szekeres *et al.* [10]) studied the behaviour of silica particles rendered hydrophobic using the same compound employed in [9] and making use of various different surfactants added to the spreading solution. They also studied the behaviour of bare silica particles spread in a methanol/chloroform solution containing several different possible surfactants. Their extensive results can not be further summarised here except to say that the collapse pressures obtained when using treated particles were usually about 10 mNm^{-1}and about 5 mNm^{-1}when using untreated particles. Using treated particles they were able to deposit up to 6 successive monolyers but the degree of order they obtained was not high. In a further paper [11] these authors showed that, using extensive treatment with methanol, it was possible to form stable films of silica particles at the air/water interface without the use of any surfactant and to deposit monolayers of this material on glass slides. It is curious that, though their particles must have been rendered hydrophobic in order to remain at the air/water interface, they nevertheless prepared hydrophilic surfaces to deposit them on. Reculusa and Ravaine [3] also used a hydrophilic substrate.

Fulda *et al.* [12, 13] attempted to make LB multilayers from polymer colloidal spheres with some degree of success.

2 Experimental Procedures

The individual particles were prepared using the Stober [14] method and generally as in our earlier paper [4]. The compounds used to make the particles hydrophobic were 3-(trimethoxysilyl)-propyl methacrylate (TPM), as in our previous paper [4], and allyltrimethoxysilane, as used by Reculusa and Ravaine [3]. We did not find that films formed using this latter material were better than those made in our original way and thus continued in the use of TPM. Unlike the work discussed in references [9 – 11] we did not add any surfactants to the spreading suspension which was based on chloroform.

For the LB dipping procedure we used a NIMA double compartment trough. It is possible to programme this instrument so that, after a substrate has been immersed and withdrawn from

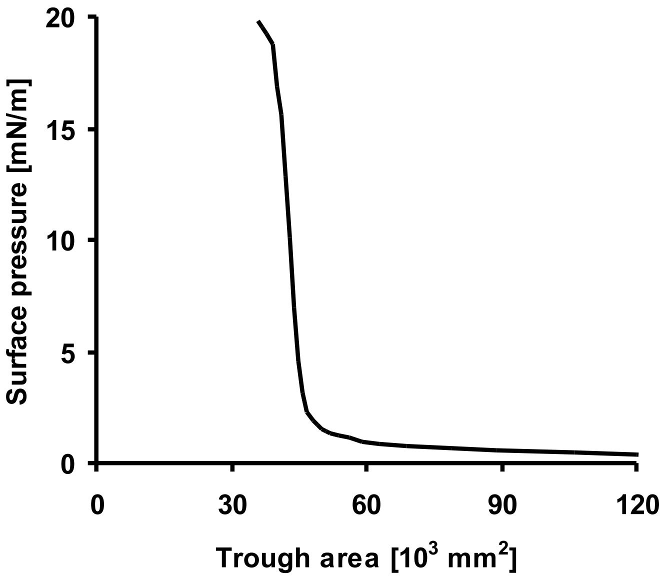

Fig. 1. Isotherm for colloidal particles (diameter 540 nm) in chloroform taken over a subphase of a pure doubly distilled deionised water at 25 ° C.

the subphase, it can be rotated so that the surface is horizontal and maintained in this position for any chosen time while the excess water evaporates.

To deposit multilayers, glass substrates were used after a standard cleaning procedure which consisted of refluxing microscopic slides first washed in sulfochromic acid in ethyl acetate. Such substrates were then either rendered hydrophobic by a several hours of exposure to hexamethyldisilazane vapours or used without a delay for LB deposition thus remaining hydrophilic. Independently of the treatment of the substrates, we always obtained what would in Langmuir-Blodgett literature be called Z-deposition, i.e. the deposition occurred during the upward movement of the substrate only.

We used chloroform as a spreading solution diluting the silica suspensions with it. A suspension was first homogenized in an ultrasonic bath for 15 minutes and, after diluting it with chloroform, for another 15 minutes. After spreading, the monolayer was left for 15 minutes to evaporate the chloroform and to stabilize. The film was then compressed with the slowest barrier speed that the NIMA 622 trough allows (3 mm/min) resulting in an decrease of the trough area by $\sim$ 600 mm^2/min. An isotherm (see Fig. 1) was taken at least 3 times and the results were only accepted if the curves differed by a small amount only.

Films were compressed to the deposition pressure with the slowest speed available. The deposition started when the film did not show signs of collapse (inward movement of barriers less than 600 mm^2 per 5 minutes). We have used both a conventional dipper and an alternate

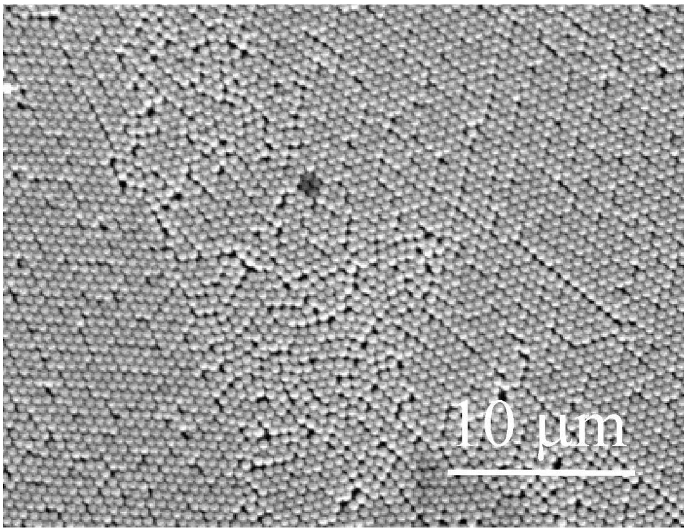

Fig. 2. SEM images of colloidal particle LB films (10 layers thick) covered with a 15 nm layer of sputtered gold. The domain structure is clearly visible though the domains are now much smaller than was the case when only a single layer had been deposited.

dipper available with the NIMA 622 trough. The quality of samples deposited by the alternate dipper was considerably better then when using the conventional dipper. We found that leaving the sample on the top position of the alternate dipper (the substrate being horizontal) and allowing it a sufficient time for drying makes it possible to deposit multilayers of any desired thickness (we produced samples up to 20 layers thick).

We deposited opaline samples which were up to 20 layers thick at 18 mN/m. Using the alternate dipper we found that samples exhibit a shiny homogeneous surface but starting from a monolayer thickness there is a domain structure visible to the naked eye; the domains being of a fraction of mm to mm size. They exhibit a hexagonal symmetry.

Scanning electron microscopy (SEM) was carried out using a Tesla BS 340 instrument in the reflection mode. The surface was covered by a sputtered layer of gold about 15 nm thick and beam energies of between 4 keV and 10 keV were employed.

Analysing the SEM photographs one can see that the domains are in fact clusters of spheres having a uniform orientation and that there are defects between neighbouring domains. Subsequent layers deposit independently of previous ones and the domain structure fades as more layers are deposited. (See Fig. 2.)

The reflectance spectra were measured by an Aquila Instruments nkd-7000 scanning reflectance and transmittance spectrometer. The instrument allows the transmittance and reflectance to be measured on exactly the same part of the sample simultaneously. Reflectance spectra presented in Fig. 3 show that the structure is relatively well organized and there are several side maxima in reflectance intensity for thicker samples. For samples thicker than 8 layers the value of the main maximum decreases but the peak becomes sharper and more side maxima appear.

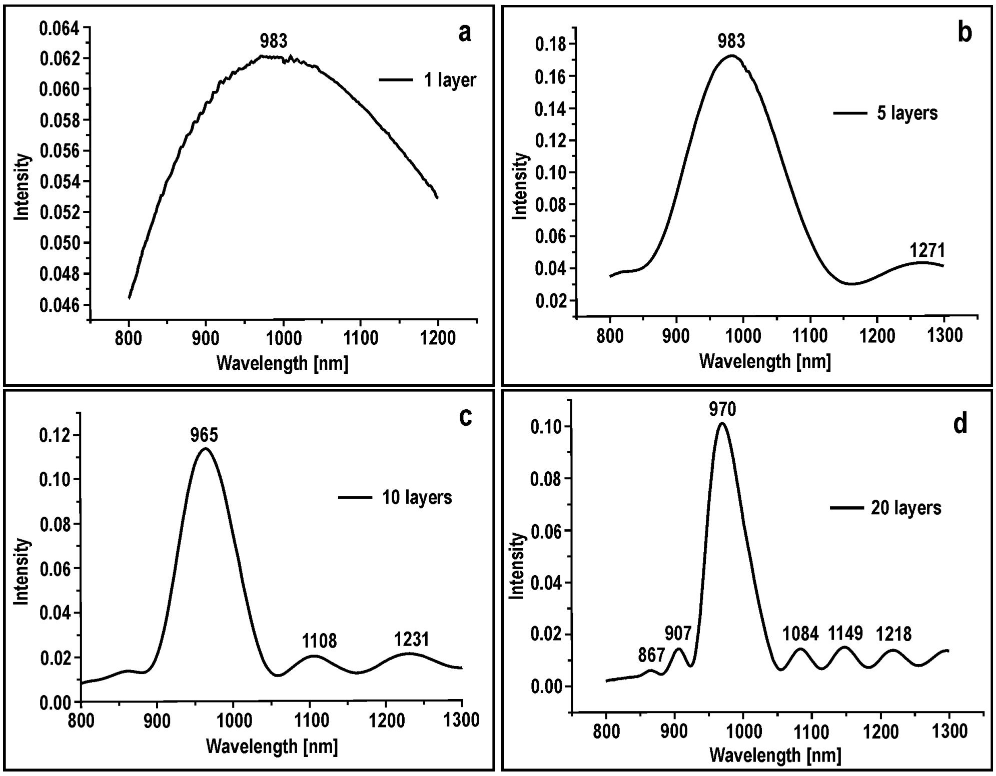

Fig. 3. Bragg reflection data of the LB films of silica particles coated with octyltrimethoxysilane (particle diameter 540 nm) deposited on a glass substrate. The radiation impinged on the sample at 30 ° with respect to the normal to the plane. The thickness of the films were as follows: (a) 1 layer, (b) 5 layers, (c) 10 layers, and (d) 20 layers.

3 Discussion and Conclusions

When only a few layers of the spheres have been deposited SEM studies show that the film consists of highly ordered domains which fit together well but do not all have the same crystal orientation. After the deposition has proceeded to 5 or 6 layers the domain structure tends to disappear though it is still possible to select areas of the films which are highly ordered.

We have found that, in order to obtain well ordered films, it is important that the drying process between dips should take place with the substrate surface in a horizontal position. This result is in contrast with the behaviour of ordinary Langmuir-Blodgett films. As far as we are aware the only type of trough with which this process is possible is the NIMA model 622 which is designed for the deposition of alternate layers.

It is interesting that, even with highly hydrophobic balls, deposition only occurs in the Z manner, that is to say when the substrate is being moved in an upward direction. We have found this to be the case in our present work and it was also observed by Reculusa and Ravaine [3] and by Bardosova *et al.* [4]. However, if one considers the behaviour of highly hydrophobic spheres at the air/water interface, the origin of this result becomes understandable. In a first approximation let us ignore the line tension effect which has been discussed, for example, by Drelich [15]. Then one may use the expression obtained by Clint and Taylor [7] for the energy necessary to remove a sphere from the air/water interface in an upward direction

$$E_{\mathrm{OUT}} = \pi R^2 \gamma_{\mathrm{LA}} (1 + \cos\theta)^2, \tag{1}$$

where R is the radius of the sphere, γ_{LA} is the liquid to air interfacial tension and θ is the obtuse angle between the tangent to the spherical particle at the water surface and the plane of this surface. They also showed that the energy needed to force the sphere into the liquid phase is

$$E_{\mathrm{IN}} = \pi R^2 \gamma_{\mathrm{LA}} (1 - \cos\theta)^2. \tag{2}$$

Thus

$$\frac{E_{\mathrm{OUT}}}{E_{\mathrm{IN}}} = \cot^4(\frac{\theta}{2}) \tag{3}$$

which becomes a very small quantity when θ approaches the value π.

Thus it is very much easier to remove a sphere from the air/water interface in an upward direction than in a downward direction. Thus, if the layer of spheres at the air/water interface is pressed against the substrate when it is being moved in an upward direction it will be easy for the particles to move upward with the substrate. Conversely, it will be difficult to move a sphere in a downward direction when the substrate is being moved downwards.

It is our tentative conclusion that to form really large domains, it may be necessary to apply a variation of the method introduced by van Blaaderen *et al.* [16] who used a template having the periodicity of the required lattice to form ordered layers of SiO_2 spheres. However, as we are using the Langmuir-Blodgett technique, it might only be necessary to use a narrow strip template in the region where the films start to form.

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