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Surface Effects from Nanostructure

Structural Color and the Lotus Effect[**]

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The study of biological microstructure is one of the most important research areas in biomimicry.[1–3] Microstructure plays many important roles in living things.[2,3] For example, the charming blue color of the *Morpho sulkowskyi* butterfly originates from light diffraction and scattering, which results from the ordered microstructure of its scales. This form of color is usually known as structural color, which is utilized by animals both for protection and as a warning. Today, the study of structural color has been extended from biology to optics.[4–6] As well as affecting coloration, microstructure also plays an important role in self-cleaning.[2,7] For the butterfly, the specific nanostructure enhances the hydrophobicity of its wings, which allows droplets of water to be dispersed more easily. During this process, dust particles on the surface of the wings are removed. This phenomenon is known as the "lotus effect", which is not only very useful for natural species, but also for materials applications, such as for decoration where a natural force might be used to clean a surface. It would be interesting to discover whether it is possible to design a material that incorporates both structural color and the lotus effect, thus mimicking the wings of a butterfly. Such a material should be of great biological and technological importance. In this paper, we will show one approach to fabricating such a biomimetic decorative material by taking advantage of a nanostructured inverse opal surface.

Inverse opal is a solid material that consists of a three-dimensional network.[6,8–10] Ordered monodisperse air spheres throughout the network contribute to an optical stop band, the position of which can be tuned by careful control of the periodicity of the air spheres. Colors can be observed by the naked eye when the stop band falls in the visible region. As a consequence of its unique optical properties, inverse opal has been regarded as a new-generation decorative material, in addition to its application as a photonic crystalline material.[6,11] Recently, we realized that inverse opal might also be incorporated into the design of a hydrophobic material. The solid material network of inverse opal contributes a rough surface composed of well-ordered meshes. According to the Cassie–Baxter law, the intrinsic wettability of the solid material can be greatly reduced.[12] Such a decorative material, which exhibits both structural color and the lotus effect, would be environmentally friendly and energy-efficient.

For practical applications, a convenient method of fabricating a uniform inverse opal film over a large area is required. In addition, the rough inverse opal surface needs to be further optimized to imbue the surface with superhydrophobic character. We describe here the development of a dipping method that can be used to meet these criteria, and which can derive uniform inverse opal films with a nanostructured surface. The procedure for the fabrication is as follows: First, submicron-sized monodisperse polystyrene spheres and nanosized particles were ultrasonically dispersed into deionised water. A glass substrate was then immersed into the solution and withdrawn at a constant speed. It is known that a mixture of spheres with different sizes cannot be used to fabricate colloidal crystals with long-range structural order by such a deposition method,[13–15] as phase separation occurs, or an amorphous structure is formed. In our experiment, we found that this conclusion is only partially correct. A structure with long-range order can be derived when the ratio of the diameters of the spheres falls into a particular regime. Figure 1a shows an image of a structure composed of monodisperse spheres, while Figure 1b–d displays three images of structures composed of spheres of two sizes, with diameter ratios of 0.94, 0.34, and 0.07, respectively. The structure formed by the spheres of varying size depends on the diameter ratio. A structure with long-range order can be observed in films composed of monodisperse spheres, however, such order is absent in films composed of spheres of two sizes, where the diameter ratio is larger than 0.15. Usually, the particles form a structure with discernible separation when the ratio between the two types of sphere is larger than 0.5 (Figure 1b), while the domains formed by different types of particles are separated when the ratio is smaller than this value (Figure 1c). When the diameter ratio between the

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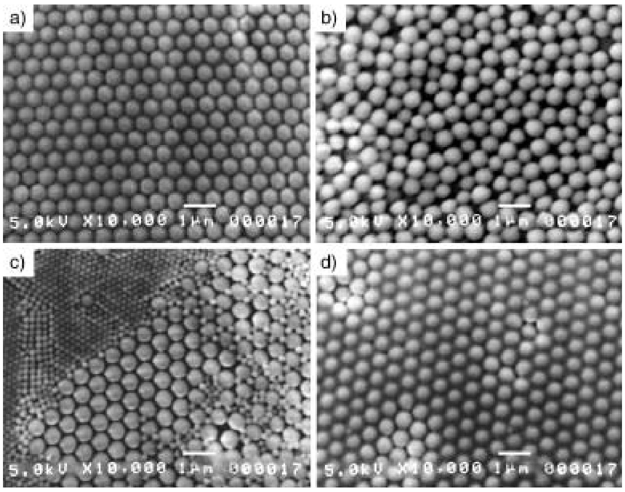

Figure 1. a) SEM image of a film composed of polystyrene spheres with a diameter of 680 nm; b–d) SEM image of a film composed of polystyrene spheres of two sizes. The diameter of the larger spheres is 680 nm in each case. The diameters of the smaller spheres are 580 (b), 230 (c), and 48 nm (d).

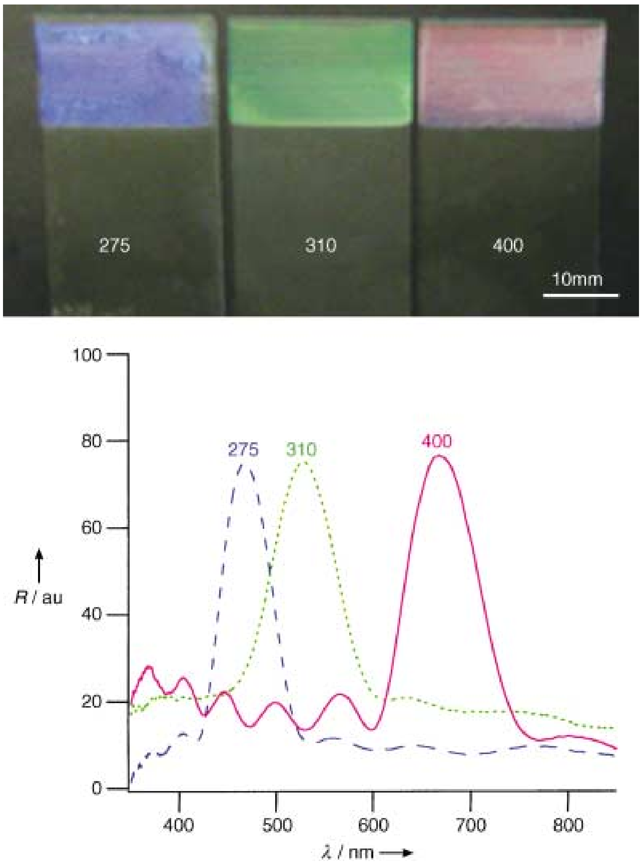

Figure 2. Pictures (top) and transmission spectra (bottom) of three types of inverse opal film with different structural periods. The center-to-center distances between two neighboring holes are 275, 310, and 400 nm, respectively.

spheres is smaller than 0.15, a close-packed cubic structure composed of large spheres is formed, with the small particles located within the voids formed between the large spheres (Figure 1 d). The mechanism for the formation of an ordered structure can be thought of as follows: During the formation of the film, large particles assemble first, followed by the smaller spheres. The face-centered cubic structure formed by the large spheres possesses interconnected voids. The diameter of the smallest voids is approximately 15% of that of the spheres. Thus, when the diameter ratio of the small particles is less than 0.15, the small particles can enter the voids, rather than aggregating around the larger particles. As a result, there is no phase separation.

The inverse opal films were fabricated by taking advantage of the phenomena described above. The suspension used for the fabrication process contained polystyrene spheres and silica nanoparticles. The polystyrene spheres were several hundred micrometers in diameter, while the diameter of the silica nanoparticles was around 6 nm; the concentration of the polystyrene spheres and silica nanoparticles was 2 and 0.3%, respectively. The speed of withdrawal of the glass substrate was 0.4 $\mu m\,s^{-1}$. After the film was formed, it was dried in air and then calcined at 450 °C to remove the polymer and to solidify the silica nanoparticles. Finally, the surface of the substrate was modified with a fluoroalkylsilane ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$) by thermal chemical vapor deposition, to render the surface hydrophobic.

Figure 2 (top) displays the inverse opal films that were deposited onto glass substrates. Uniform colors extend over the whole substrates, which are over 2 cm wide. The color of the inverse opal film derives from microscopically ordered structures, which were observed by scanning electron microscopy (SEM) and which are exhibited in Figure 3. Figure 3 a shows the film as viewed from above. The hexagonal arrangement of the air spheres encircled by the silica networks can be clearly observed, through which the arrangement of the second layer can also be seen. The center-to-center distance between the neighboring air spheres is 275 nm, which is 5% shorter than the distance before calcination. Information on the three-dimensional structure was derived from cross-sectional observations (Figure 3 b), which show that the ordered structure is continuous from the substrate to the top surface. Such a three-dimensionally ordered structure contributes to the stop band. Incident light whose wavelength is the same as the position of the stop band is reflected (Figure 2, bottom), and as a result, inverse opal films exhibit brilliant colors when their stop bands fall into the visible region. The color can be easily engineered to range from blue to red through a change in the size of the polystyrene spheres during the fabrication process.

The wettability of an inverse opal film was studied by measuring the angle of a water drop on the substrate. Figure 4 shows a picture of a water drop on an inverse opal film modified with the fluoroalkylsilane (top), where the contact angle was measured at 155°. This compares to a contact angle of only 100° for a glass substrate modified with the fluoroalkylsilane (Figure 4, bottom), and displays that the surface had been made superhydrophobic after coating it with the inverse opal. The reason for the great enhancement in the hydrophobicity depends on the surface morphology of the inverse opal film, which was studied by atomic force micros-

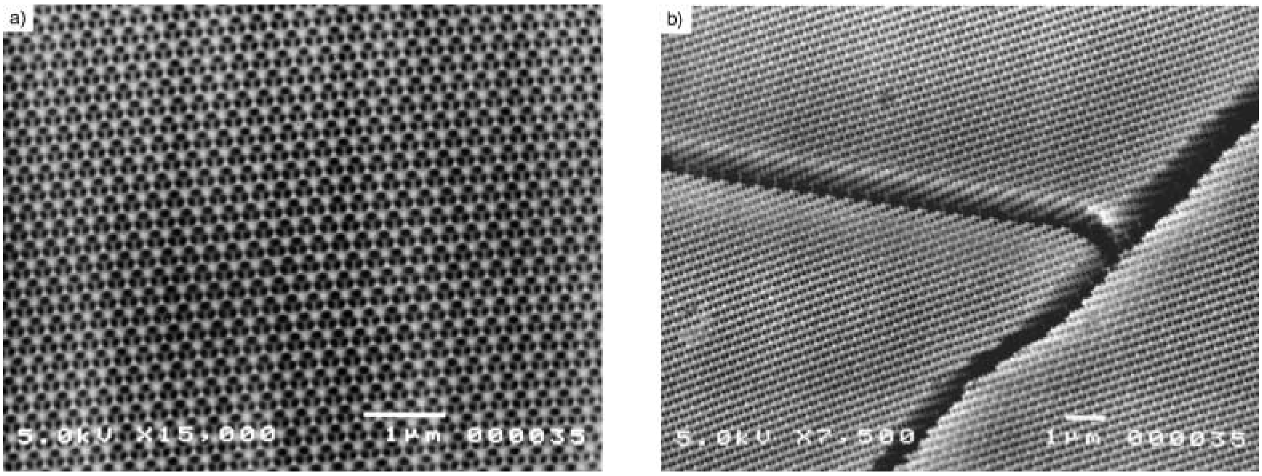

Figure 3. SEM image of an inverse opal film with a center-to-center distance between neighboring holes of 275 nm. a) Plan-view image; b) cross-sectional image.

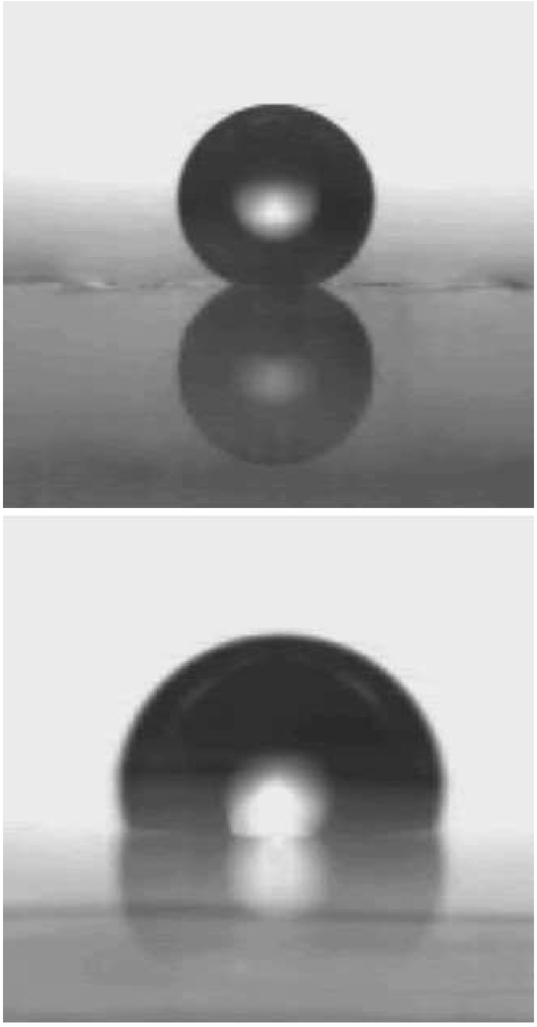

Figure 4. Water drops on a flat glass substrate (bottom) and an inverse-opal coated glass substrate (top) modified with a fluoroalkylsilane, which displays the enhanced hydrophobic character of the inverse opal film.

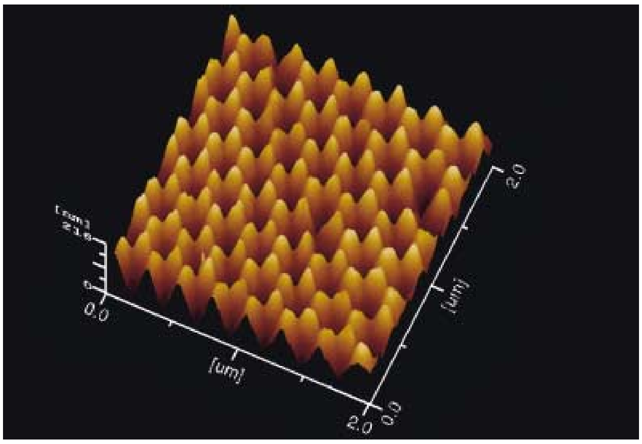

Figure 5. AFM image of the surface topography of an inverse opal film.

copy (AFM). Figure 5 is an AFM image of an inverse opal film with a center-to-center distance of 275 nm. From the AFM image it can be shown that the surface of the silica network encircling the air holes is not a flat surface but a collection of well-ordered bumps. Each air hole is surrounded by six distinct bumps, each with a diameter of approximately 100 nm, and which are located between three neighboring air holes. According to the Cassie–Baxter law, such a topography can greatly enhance the hydrophobicity, and even contribute to superhydrophobicity.[12,16]

In conclusion, we have demonstrated a convenient method of fabricating a uniform inverse opal film with a nanostructured surface. Both structural color and superhydrophobicity were derived simultaneously. Such films are anticipated to become a new generation of decorative materials. In addition, as the surface of the inverse opal fabricated by this method is composed of two dimensionally ordered nanosized dots, the fabrication method exhibited here might be a new approach for the preparation of a quantum dot array. Applications in the fields of nanomaterials, optical devices, and biology are anticipated.

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Liquid-Crystal Molecular Design

Ionic Quaterrylenebis(dicarboximide): A Novel Mesogen and Long-Wavelength Polarizing Material**

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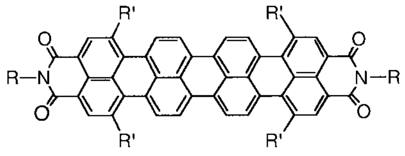
Within the broad scope of supramolecular chemistry,[1,2] the construction of materials and devices through self-assembly and self-organization processes is becoming one of the premier frontiers.[3–11] In the last decade, there has been extensive research on the interplay between molecular architecture, molecular order, and macroscopic properties.[12] In this paper, we report the aggregation and liquid-crystalline properties of a novel ionic quaterrylenebis(dicarboximide) **1** in aqueous solution. More importantly, by exploiting the self-organizing properties of **1**, unprecedented control of the molecular orientation of the quaterrylenebis(dicarboximide) in thin solid films was achieved, which produces a novel linear polarizer of light at long wavelengths.



1, R' = H, R = $(CH_2)_2NEt_2H^+$ $HCOO^-$
2a, R' = H, R = $C_{12}H_{25}$,
2b, R' = H, R = C_6H_3-2,6-*i*Pr_2,
2c, R' = OC_6H_4-4-*t*Bu, R = C_6H_3-2,6-*i*Pr_2

Nonionic quaterrylenebis(dicarboximide)s **2a–c** are known to absorb light at long wavelengths. In chlorinated organic solvents, the absorption maxima of **2b** and **2c** are at 764 nm and 781 nm, respectively.[13,14] These thermally and photochemically stable dyes can potentially be used in optical applications in conjunction with commercially available GaAlAs lasers that emit at 780 nm. Near-infrared (NIR) absorbing and emitting dyes have potential use in high-technology applications such as optical recording, thermally written displays, laser printers, laser filters, infrared photography, and fiber-optic communications.[15,16] However, the solubility of **2a–c** in chlorinated solvents is only about 10^{-2} M.[13,14] The design and synthesis of more-soluble quaterrylenebis(dicarboximide) derivatives will allow greater convenience in the processing of such materials. In addition, because of the intrinsic anisotropy in the molecular optical properties of quaterrylenebis(dicarboximide)s, the development of techniques for controlling their orientation on a macroscopic scale in the solid state will lead to novel anisotropic materials and broaden their utility. For instance, NIR polarizers have applications as optical isolators that are used in conjunction with semiconductor lasers and fiber optics.[17]

In the structural design of **1**, we anticipated that the functionalization of the hydrophobic quaterrylenebis(dicarboximide) core with cationic pendant groups would impart amphiphilicity, which would render it soluble in aqueous solution. Aggregation of these molecules in an aqueous medium is expected because of π-stacking among the "plank-shaped" aromatic molecules and the entropy-driven hydrophobic interactions. Furthermore, it was expected that the introduction of flexible alkyl chains would enhance the formation of lyotropic (solvent-dependent) liquid-crystalline phases by hindering regular close-packing of the molecules into a crystalline phase. Although liquid-crystalline phases are only of short-range structural regularity, induced alignment of the self-organized ensembles under an external force can increase the degree of orientational order over a substantially longer range in thin liquid films.[18] By preserving this long-range anisotropic order during the transition from the liquid to the solid state, desirable structural regularity and aniso-

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