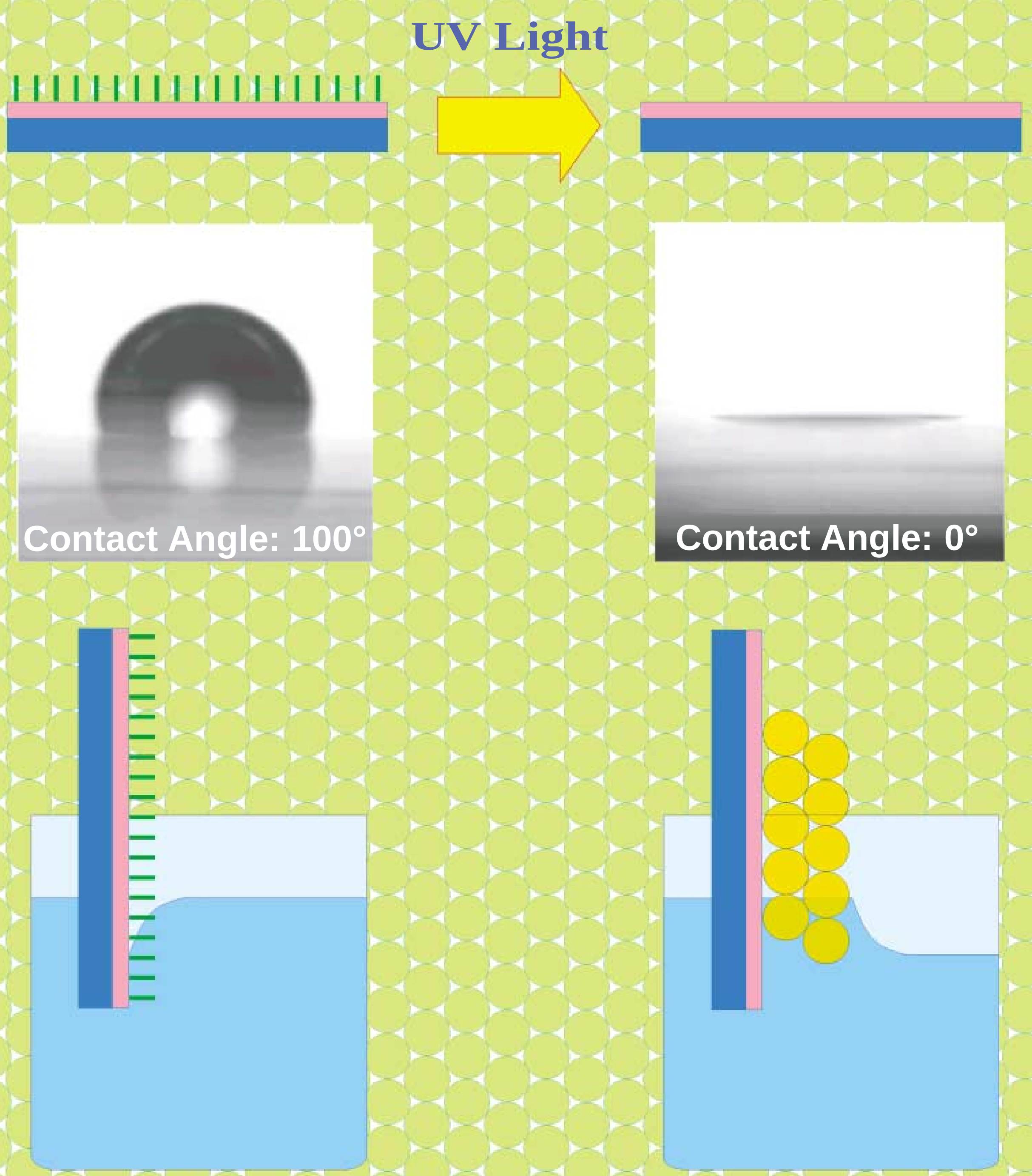
A new approach is proposed for the patterning of colloidal crystal films by taking advantage of the photocatalytic and photoinduced super-hydrophilic properties of titanium dioxide. The substrate used for the patterning of the colloidal crystal film was glass coated with titanium dioxide which was treated with fluoroalkylsilane to render the surface hydrophobic.



Photoirradiation with ultraviolet light through a photomask transforms the irradiated surface of the substrate from hydrophobic to hydrophilic in character. A subsequent dipping process causes patterns of colloidal crystal films to deposit on the hydrophilic surface of the substrate. For more information see the following pages.

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Patterning of a Colloidal Crystal Film on a Modified Hydrophilic and Hydrophobic Surface[**]

Zhong-Ze Gu, Akira Fujishima, and Osamu Sato*

Structural color-change mechanisms play an important role in the protective and warning coloration of animals.[1] These structural color changes originate from the diffraction and scattering of light by microstructures on the surface of the animal's body, and are therefore very different from coloration phenomena that are brought about by the absorption of dyes. Structural color changes have been extensively investigated recently, since they are not only important for biological systems, but also play a role in the study of photonic crystals.[2] It is important to note that the application of photonic crystals has been proposed for the next generation pigments and optical devices.[3–6] For practical applications of photonic crystals with a three-dimensional microstructure it is essential to be able to fabricate photonic crystal films onto substrates with specific patterns both simply and cheaply, and this is still proving to be a challenge.[7–11] Herein we discuss a new technique for the fabrication of colloidal crystal films on specific areas of substrates that takes advantage of the photocatalytic and photoinduced superhydrophilic properties of TiO_2. We show that this approach makes possible the practical application of colloidal crystals as pigments and optical devices.

A patterned colloidal crystal film was fabricated onto a glass substrate that had been treated by procedures a) and b) in Figure 1. The glass substrate was first coated with a thin film of TiO_2 using the sol–gel method (the coating solutions used are NDH-500A and NDH-510C, which were bought from Nippon Soda, Co. Ltd.). The surface of the TiO_2 film was then modified with fluoroalkylsilane ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, made by Toshiba Silicone, Japan) by using a self-assembly method. The surface of the substrate becomes hydrophobic after the treatment with fluoroalkylsilane, and the contact angle of water was measured as 100°. The substrate was irradiated with ultraviolet light through a photomask to make a pattern with different degrees of wettability on different areas. This changed the contact angle of water on the irradiated surface to 0°, while no change occurred for the un-irradiated surface. The change in the contact angle of the irradiated part derives from the photocatalytic and photoinduced superhydrophilic properties of TiO_2. TiO_2 is a unique photocatalyst that does not exhibit irreversible photocorrosion, but which does display photoinduced superhydrophilic properties.[12, 13] When a film of TiO_2 is irradiated with UV light, active oxygen is generated on the surface of the TiO_2 film as a result of a photo redox reaction. These photogenerated chemical species, which have a very strong redox potential, decompose the fluoroalkylsilane that is adsorbed on the TiO_2 surface. In addition, the UV irradiation creates surface oxygen vacancies on the TiO_2, which renders the surface favorable for the adsorption of dissociative water. This in turn causes the surface of the TiO_2 to become superhydrophilic.[12, 14] Consequently, the unique properties of the TiO_2 allow the easy and precise patterning of the surface to give a large contrast in wettability.

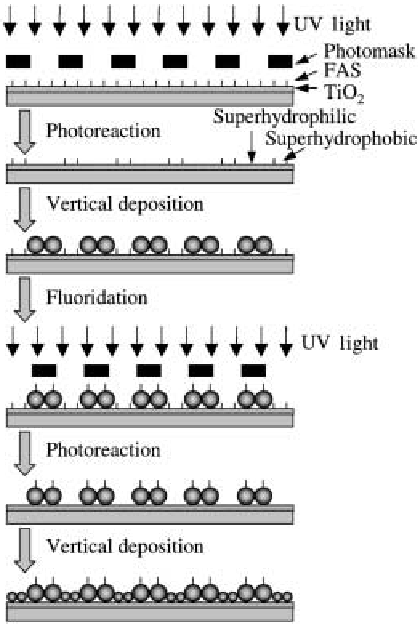

Figure 1. The process of patterning with colloidal crystal films.

The substrate was inserted vertically into an aqueous suspension containing either monodispersed silica spheres or polystyrene to fabricate a pattern consisting of a colloidal crystal film. The liquid surface is concave above the hydrophilic surface, while it is convex over the hydrophobic area. The substrate was then extracted from the liquid at a constant rate, which ranged from 2 to 8 $\mu m\,s^{-1}$. Colloidal crystals form over the hydrophilic areas during the lifting process, whilst no film was observed on the hydrophobic regions. The reason for this selective formation of the film can be explained as follows:[15, 16] The solution forms a meniscus on the hydrophilic surface of the substrate with an angle smaller than 90°. Such a meniscus contributes to the generation of a capillary force, which causes the spheres to assemble on the surface. The slope of the meniscus over the hydrophobic surface increases to an angle of greater than 90°, and the capillary force responsible for the assembly of the spheres disappears.

Figure 2 shows pictures of a colloidal crystal film fabricated on a glass substrate with a fish-shaped hydrophilic pattern.

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[*] Dr. O. Sato, Dr. Z.-Z. Gu
Kanagawa Academy of Science and Technology
KSP Bldg., East 412, 3-2-1 Sakado
Takatsu-ku, Kawasaki-shi, Kanagawa 213-0012 (Japan)
Fax: (+81) 44-819-2070
E-mail: sato@fchem.chem.t.u-tokyo.ac.jp

Dr. Z.-Z. Gu
National Laboratory of Molecular and Biomolecular Electronics
Southeast University, Nanjing 210096 (China)

Prof. A. Fujishima
Department of Applied Chemistry
School of Engineering, The University of Tokyo
7-3-1 Hongo Bunkyo-ku, Tokyo 113-8565 (Japan)

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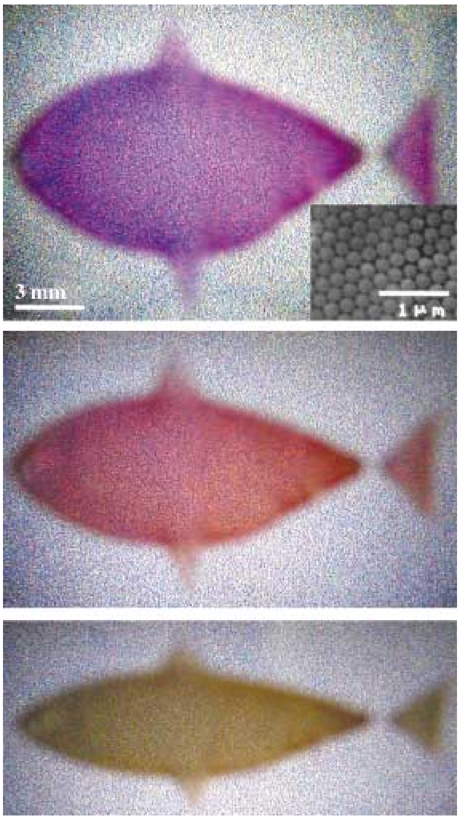

Figure 2. The fish-shaped pattern observed from different angles. The inset shows the arrangement of polystyrene spheres in the film.

Monodispersed polystyrene spheres with a diameter of 230 nm form films on the fish-shaped hydrophilic regions, while no film was observed in the region where the substrate was hydrophobic. Uniform colors can be observed at different glancing angles and are caused by diffraction induced by the ordered monodispersed spheres. A hexagonal arrangement of spheres can be observed over a wide area.

A complex pattern composed of different types of monodispersed spheres can be fabricated by repeating the processes of fluoridation and photodecomposition. Figure 3a shows a pattern of alternate lines composed of two different types of silica spheres. The green lines are films composed of spheres of 275-nm diameter, between which are films composed of spheres with a diameter of 195 nm. The difference in colors comes from the change in the wavelength of the diffraction peaks (Figure 3b). The fabrication details for this sample are outlined in Figure 1 as procedures a)–e). Firstly, a linear colloidal crystal film pattern composed of silica spheres with a diameter of 275 nm was deposited onto a substrate by following the same procedure as described above (procedures a) and b)). Then, the substrate was again modified with fluoroalkylsilane (procedure c)). The subsequent irradiation with UV light decomposes the molecules of fluoroalkylsilane on the surface of the TiO_2, while those on the surface of the silica spheres remained unchanged (procedure d)). Therefore, the surface of the TiO_2 becomes hydrophilic, while the surface of the colloidal crystal, which is composed of silica spheres, is hydrophobic. The final vertical deposition, procedure e), causes the silica spheres with a diameter of 195 nm to form crystals only between the lines of the colloidal crystals composed of 275-nm silica spheres.

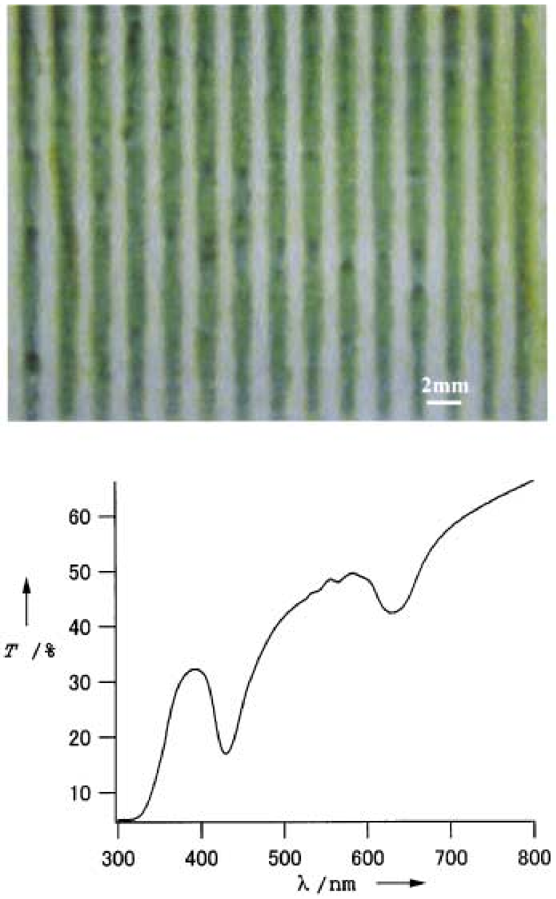

Figure 3. Top: Lines composed of different silica spheres. Bottom: Transmission spectrum of the line pattern. The two peaks can be assigned to lines composed of spheres with diameters of 195 nm and 275 nm, respectively.

In conclusion, a method of controlling wettability has been developed for the patterning of colloidal crystal films. Films composed of different types of spheres can be deposited simply onto the substrate step by step. Since the materials used for patterning are very cheap and readily commercially available and the fabrication process is very simple, it can be anticipated that the approach exhibited here would enable the application of colloidal crystals to a new generation of decorative materials and optical devices. In addition, this method also provides a new approach for the study of the crystallization of colloidal particles onto a surface with modified wettability, which is important in the fields of colloids and biological films.

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An Inverted Metal-Organic Framework with Compartmentalized Cavities Constructed by Using an Organic Bridging Unit Derived from the Solid State**

Giannis S. Papaefstathiou and
Leonard R. MacGillivray*

Porous crystalline solids that employ metal-organic components as building blocks, where a rigid, linear organic bridge propagates the coordination geometry of a metal node in one-, two-, or three-dimensions, are attracting much interest.[1–3] Such metal–organic frameworks (MOFs) are designed to exhibit properties that mimic, and improve upon, more conventional porous solids, such as zeolites[4] and mesoporous materials (MCMs).[5] Many porous MOFs, however, have fallen short, in contrast to zeolites and MCMs, as robust porous solids.[2, 6] Interpenetration[6] and framework fragility[2] have hampered progress such that host cavities tend to self-include while guest removal often results in a collapse of host structure. Recently, however, such problems of interpenetration and framework fragility have been largely circumvented by using metal clusters, as secondary building units (SBUs), for host design.[7] SBUs (e.g. metal carboxylates) reduce the likelihood of interpenetration owing to their large sizes which can preclude filling of void spaces,[8] producing stable, porous solids able to support inclusion and catalysis.[1a–c]

Although SBUs have been successfully employed for the construction of MOFs with stable pores, it can be difficult, in contrast to MCMs,[5, 9] to line the interiors of such solids with organic groups since an elaborate covalent synthesis of a linear organic bridge is often required to introduce simple (e.g. -Me) and diverse (e.g. chiral) functional groups. With this in mind, it has occurred to us that one way to circumvent this problem may be to invert the structural role[10] of the SBU and linear organic bridge such that the SBU serves as a linear bridge and the organic ligand serves as a node. In this design, the bonds of the SBU that support the framework are minimized (i.e. two) such that the remaining coordination sites of the SBU may be filled with organic ligands that decorate the interior of the framework. Moreover, such an inverted metal-organic framework (IMOF) would enable the second sphere of a SBU to line the walls of a host, in contrast to a covalent synthesis, supramolecularly[11] where convergent[12] terminal groups may be tailored to define structure and recognition properties of the solid.

Herein, we describe initial results of a strategy for the construction of such a porous IMOF that employs a molecule derived from a template-directed[13] solid-state [2+2] photodimerization[14] as the node (Figure 1). Owing to the presence of divergent and multiple Lewis-base functional groups, we anticipated that the product of this solid-state approach, *rctt*-tetrakis (4-pyridyl)cyclobutane[15] (4,4′-tpcb), upon reaction with the Cu paddle-wheel complex $[Cu_2(O_2CR)_4L_2]$,[16] would serve as a 4-connected node, propagating the dimetal complex, as a linear SBU through axial coordination, within a porous 2D IMOF.[17] Moreover, in contrast to a planar organic node (e.g. 4,4′-bipyridine),[18] the ligand derived from the solid-state synthesis was anticipated to produce cavities with deepened interiors owing to enforced twisting of the

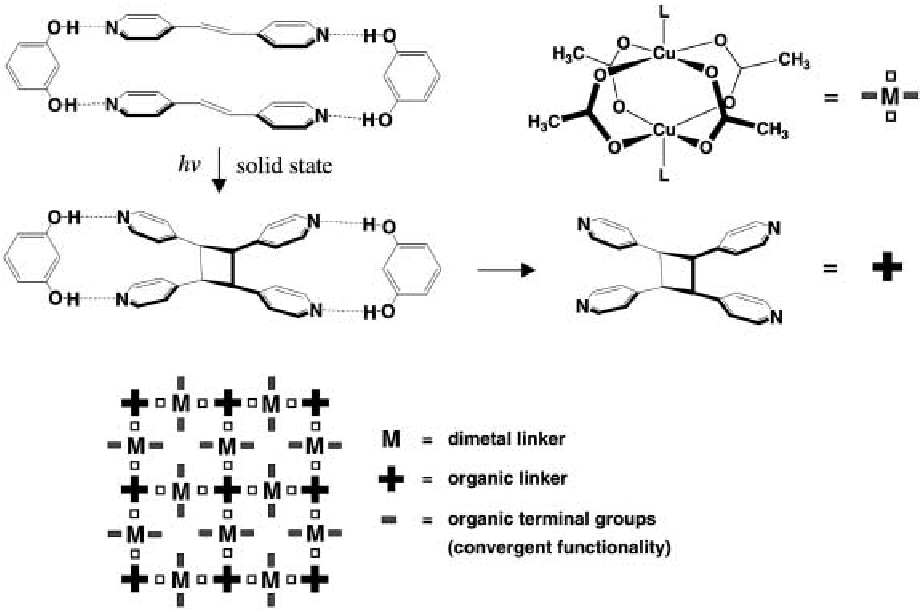

Figure 1. Construction of a porous inverted metal-organic framework (IMOF).

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[*] Prof. L. R. MacGillivray, G. S. Papaefstathiou
Department of Chemistry
University of Iowa
Iowa City, IA 52242-1294 (USA)
Fax: (+1) 319-335-1270
E-mail: len-macgillivray@uiowa.edu

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