Self-Organized Hybrid Materials

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Photoimaging of Self-Organized $CaCO_3$/Polymer Hybrid Films by Formation of Regular Relief and Flat Surface Morphologies**

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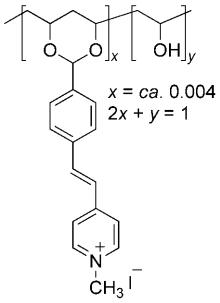
Bioinspired inorganic/organic hybrids have attracted much attention because of their large potential as new functional materials.[1,2] For example, the development of self-organized hybrid materials based on calcium carbonate ($CaCO_3$) crystals has been studied extensively.[2–4] $CaCO_3$ is one of the most abundant minerals in biological inorganic/organic hybrids. A variety of morphologies has been obtained by synthetic methods for the preparation of $CaCO_3$.[2–5] However, it is not easy to manipulate the morphology of $CaCO_3$ synthetically. Previously, the use of self-assembled monolayers resulted in the control of order and arrangement of $CaCO_3$ crystals.[5] In addition, arrays of oriented crystals on a micrometer length scale were obtained.[5] A few examples of ON (crystallization)/OFF (inhibition) control for $CaCO_3$ crystallization were reported.[5,6] However, imaging of different crystal morphologies, that is “ON (morphology A)/ON (morphology B)” control by external stimuli such as light has not yet been achieved for $CaCO_3$ crystal systems. Herein, we report on the photocontrol of crystallization, which results in the imaging of thin-film crystals by two morphologies of periodically patterned and flat surfaces.



Scheme 1. Structure of poly(vinyl alcohol) derivative bearing a 4-styrylpyridinium moiety (PVA–SbQ).

A photoreactive poly(vinyl alcohol) (PVA) derivative that bears 4-styrylpyridinium groups (PVA–SbQ; Scheme 1)[7] forming hydrogels was used for photoimaging matrices. The styrylpyridinium (SbQ) moiety is photoreactive and forms a dimer on UV irradiation.[7] PVA–SbQ was synthesized according to previously reported procedures.[7] The PVA–SbQ matrices were prepared by spin-coating of the polymer solution on glass substrates and by the subsequent UV irradiation using a photomask with checkered pattern. The matrices were immersed in an aqueous solution of calcium chloride (10 mM) that contains poly(acrylic acid) (PAA; 2.5 × 10^{-3} wt %). The photo-crosslinked PVA–SbQ formed hydrogels in aqueous solution.[7]

$CaCO_3$ was crystallized by slow diffusion of ammonium carbonate vapor into the calcium chloride solution at 30 °C. The scanning electron micrographs of the crystals are shown in Figure 1 a. The thin-film $CaCO_3$ crystals grown on the UV-irradiated areas are observed as bright squares, while the nonirradiated areas are represented by the darker squares of the thin film. The surface morphologies of the $CaCO_3$/polymer hybrid films differ a lot between the irradiated and nonirradiated areas (Figure 1 a, middle); the flat film has grown on the irradiated area (Figure 1 a, bottom left). In contrast, the film crystals with self-organized regular surface-relief structures are developed on the nonirradiated areas of the matrix (Figure 1 a, bottom right). The periodicity of the regularly patterned structures is about 1 μm and the cross-sectional micrograph shows that the height of the relief structures on the nonirradiated area is about 150 nm (Figure 1 b).

The photoimage formation of $CaCO_3$ films with different crystal morphologies has been achieved even on a micrometer scale (Figure 2). The minimum width of the thin-film crystals with tunable surface morphologies is about 4 μm (Figure 2, left). The photoimaging of complex structures also induces the sharp morphological changes of the $CaCO_3$ films (Figure 2, right).

The polarizing optical micrographs of the obtained thin-film $CaCO_3$/polymer hybrids are shown in Figure 3. In the optical micrographs under crossed polarizers, the darker square areas are the $CaCO_3$ film crystals formed on the UV-irradiated areas of the PVA–SbQ matrix, while the brighter squares are the film crystals formed on the nonirradiated areas. The FTIR spectra for the film crystals with the checkered pattern show that both the crystals formed on the irradiated and the crystals formed on nonirradiated areas are in the vaterite polymorph (see the Supporting Information, Figure S6). The vaterite films on the irradiated areas show mosaic extinction patterns (Figure 3 b, left side). The darker parts in the mosaic texture remain darker on the rotation of the sample under crossed polarizers, which suggests that the *c* axes of the $CaCO_3$ crystals are perpendicularly aligned with respect to the substrate (see the Supporting Information, Figure S7).[8] The *c* axes of the crystals grown on the non-irradiated areas (Figure 4 b, right side) are oriented in parallel with the radial directions of the thin-film vaterite, which is

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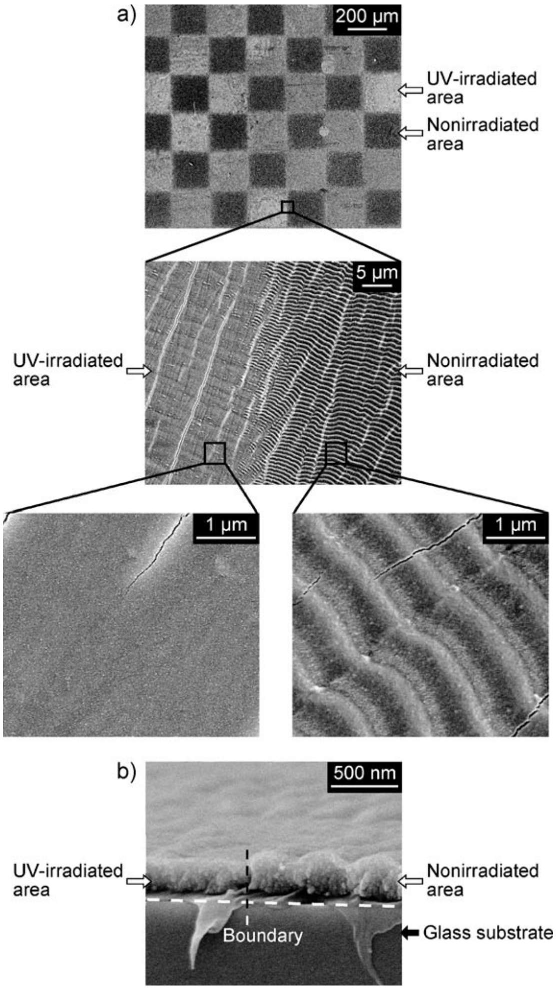

Figure 1. a) Top: scanning electron micrograph of the thin-film $CaCO_3$ crystals formed on the photoimaged PVA–SbQ matrix in the presence of PAA (2.5×10^{-3} wt%). Middle: scanning electron micrograph for the boundary part of the $CaCO_3$ between the UV-irradiated (left side) and the nonirradiated (right side) areas. Bottom: scanning electron micrographs of the $CaCO_3$ crystals on the irradiated area of the matrix (left) and on the nonirradiated area of the matrix (right). b) Scanning electron micrograph for the cross section of the thin-film $CaCO_3$ on the boundary area.

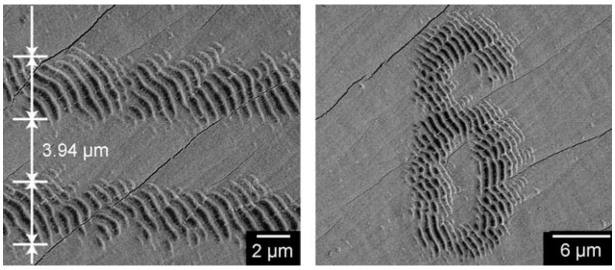

Figure 2. Scanning electron micrographs of the $CaCO_3$ crystals formed on the photoimaged PVA–SbQ matrix in the presence of PAA.

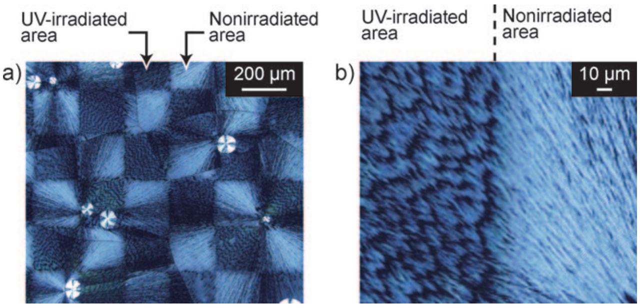

Figure 3. Polarizing optical micrographs of the $CaCO_3$ crystal film formed on the photoimaged PVA–SbQ matrix in the presence of PAA: a) overall view; b) magnified image of the boundary area.

revealed by the crossed extinction pattern of the film (see the Supporting Information, Figure S7). Even for the finer and more complex imaging by photoirradiation, this orientation behavior is observed (see the Supporting Information, Figure S8).

The self-organization behavior of $CaCO_3$ crystals on the PVA–SbQ matrix is depicted in Figure 4. For nonirradiated areas, the aggregated nonreacted SbQ groups may function as physical crosslinking points of the nonirradiated area in the PVA–SbQ film because of hydrophobic and ionic interactions[7] (Figure 4 and the Supporting Information, Figure S2,S3). These polymers form swollen hydrogels in aqueous solution. We previously reported that the physical hydrogel matrices of cholesterol-bearing pullulan[9a,b] induced self-organization of $CaCO_3$ films with regular relief structures. It is assumed that these crystals with periodic structures are formed by competition between precipitation and ion diffusion.[8–10] The minimum width for photoimaging may be the limitation for the occurrence of competition between them. In contrast, the flat $CaCO_3$ films are grown on the irradiated areas of the PVA–SbQ matrix (Figure 1 a). These areas bear SbQ groups that are chemically dimerized by the photoinduced cycloaddition reaction. Conversion of the photoreactive moieties has been confirmed by optical spectra of the PVA–SbQ film (see the Supporting Information, Figure S4).[7] For the polymer film after 5 min of UV irradiation (365 nm), the conversion ratio of the SbQ groups was approximately 0.7, which was monitored by the decrease in absorption of conjugated aromatic rings at 350 nm. The increase of the absorption band at around 270 nm may also correspond to the progress of the photodimerization.[7] With the photoinduced formation of the covalent crosslinking points, the polymer film becomes less swellable. The dense polymer network suppresses ion diffusion and affects the structures of the crystals formed on/in the gel matrices[9,11] because the ion diffusion rate is a key factor for the self-organization processes of the patterned crystals.[10]

For the 2D arrangement of $CaCO_3$ and $BaCO_3$ crystals,[5,6] microstructured substrates formed through microcontact printing and photolithography techniques have been used. The microarrays of $CaCO_3$ crystals are controlled by using micropatterned self-assembled monolayers (SAMs) and multilayered polymer films.[5] Volkmer and co-workers reported that the microstructured calcite films were fabricated from amorphous calcium carbonate stabilized by patterned poly(methacrylic acid) brushes.[6a] A photoreactive amphiphilic block copolymer was used as the microstructured substrate

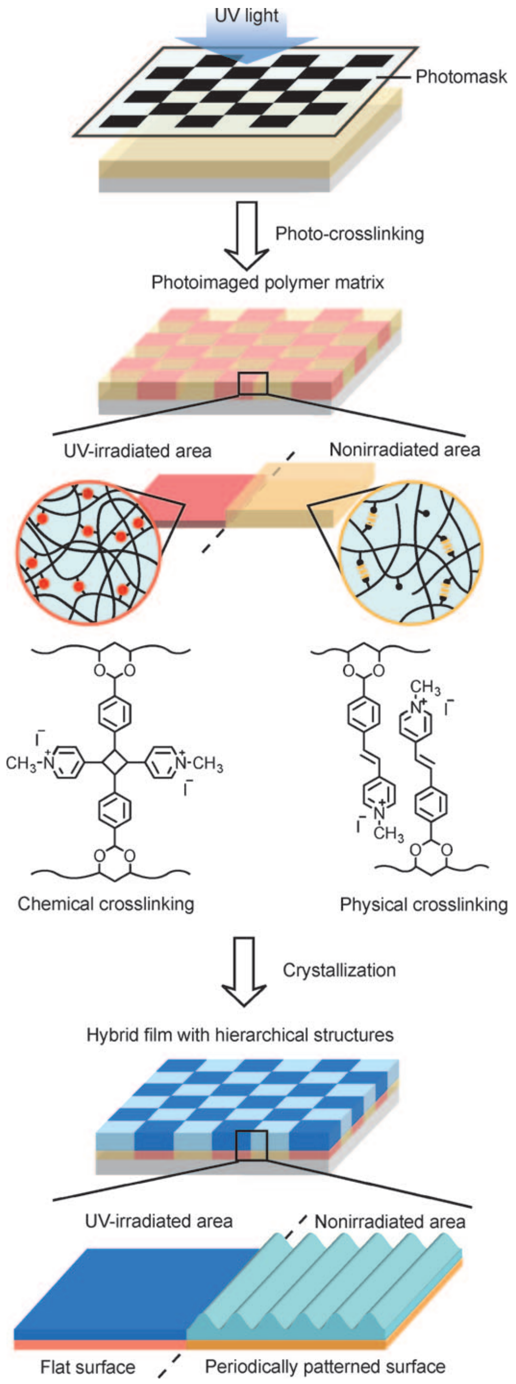

Figure 4. Schematic illustration of the self-organization of the $CaCO_3$ hybrid film with hierarchical structures on the PVA–SbQ matrix.

for controlled crystallization.[6b] The organosilane stamped on the surface also gave the 2D arrangement of the crystals.[6c] However, these approaches are the ON/OFF control for the crystallization and are mainly useful for the fabrication of ordered structures on a tens of micrometers length scale. Our method shown herein can be used to prepare ordered structures with remarkable regularity on a one micrometer length scale on the designed areas through the ON (flat surface)/ON (patterned surface) control. The self-organization on a photoimaged gel matrix is a novel method for the formation of hierarchically ordered crystals.

In conclusion, we have demonstrated that hierarchically ordered $CaCO_3$/polymer hybrid materials are obtained by using the cooperation between the photoreactive polymer matrix and PAA. For the first time, we have succeeded at photoimaging of $CaCO_3$ film crystals by forming different morphologies of the film. The periodically patterned film crystals and the flat surfaces are self-organized on the nonirradiated and UV-irradiated areas of the matrix, respectively. The materials with controlled relief structures are sought for in various fields, such as optics, microfluidics, and cellular engineering. Moreover, our present results suggest that the combination of bottom-up and top-down methods is one of the most promising approaches for the development of inorganic/organic hybrid materials with hierarchically ordered structures.

Experimental Section

PVA–SbQ was prepared according to the previously reported procedures.[7] Details can be found in the Supporting Information. PVA–SbQ matrices were prepared by spin coating of a 4 wt% dimethylsulfoxide solution onto glass substrates. They were annealed for 40 min at 90 °C to remove the solvent. UV irradiation for the dried PVA–SbQ film was performed with a high-pressure mercury lamp (365 nm, 15 mW cm^{-2} for 5 min).

Purified water from an Auto pure WT100 purification system (Yamato, Japan, maximum relative resistivity $1.8\times10^7\ \Omega$cm) was employed for crystallization of calcium carbonate. Poly(acrylic acid) ($M_w = 2.0\times10^3$) was added to an aqueous calcium chloride solution ([Ca^{2+}] = 10 mM). The solution was transferred to vessels that contained the photoimaged PVA–SbQ matrices. The vessels were then placed in a closed desiccator together with a vial of ammonium carbonate.[9] An incubator (Fukushima, Japan) was used to maintain a constant crystallization temperature (30 °C).

Scanning electron microscope images were obtained using a Hitachi S-900S field-emission SEM, a Hitachi S-4700 field-emission SEM, and a Keyence VE-9800 SEM operated at 5–6 kV. SEM samples were platinum-coated by using a Hitachi E-1030 ion sputter. Optical micrographs were taken with an Olympus BX51 polarizing optical microscope. FTIR spectra were recorded on a JASCO FT/IR-660 Plus spectrometer connected to an Irtron IRT-30 microscope unit.

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[1] a) E. Dujardin, S. Mann, *Adv. Mater.* **2002**, *14*, 775–788; b) S. I. Stupp, P. V. Braun, *Science* **1997**, *277*, 1242–1248; c) C. Ritchie, G. J. T. Cooper, Y.-F. Song, C. Streb, H. Yin, A. D. C. Parenty, D. A. MacLaren, L. Cronin, *Nat. Chem.* **2009**, *1*, 47–52.

[2] a) F. C. Meldrum, H. Cölfen, *Chem. Rev.* **2008**, *108*, 4332–4432; b) N. A. J. M. Sommerdijk, G. de With, *Chem. Rev.* **2008**, *108*, 4499–4550; c) S. Weiner, L. Addadi, *J. Mater. Chem.* **1997**, *7*, 689–702; d) S.-F. Chen, J.-H. Zhu, J. Jiang, G.-B. Cai, S.-H. Yu, *Adv. Mater.* **2010**, *22*, 540–545; e) T. Kato, T. Sakamoto, T. Nishimura, *MRS Bull.* **2011**, *35*, 127–132; f) F. C. Meldrum, *Int. Mater. Rev.* **2003**, *48*, 187–224; g) H. Imai, Y. Oaki, A. Kotachi,

Bull. Chem. Soc. Jpn. **2006**, *79*, 1834–1851; h) T. Kato, A. Sugawara, N. Hosoda, *Adv. Mater.* **2002**, *14*, 869–877.

[3] a) Y. Oaki, A. Kotachi, T. Miura, H. Imai, *Adv. Funct. Mater.* **2006**, *16*, 1633–1639; b) E. M. Pouget, P. H. H. Bomans, J. A. C. M. Goos, P. M. Frederik, G. de With, N. A. J. M. Sommerdijk, *Science* **2009**, *323*, 1455–1458; c) J. Aizenberg, A. Tkachenko, S. Weiner, L. Addadi, G. Hendler, *Nature* **2001**, *412*, 819–822; d) H. Gong, M. Pluntke, O. Marti, P. Walther, L. Gower, H. Cölfen, D. Volkmer, *Colloids Surf. A* **2010**, *354*, 279–283; e) Y.-Y. Kim, L. Ribeiro, F. Maillot, O. Ward, S. J. Eichhorn, F. C. Meldrum, *Adv. Mater.* **2010**, *22*, 2082–2086.

[4] a) T. Kato, *Adv. Mater.* **2000**, *12*, 1543–1546; b) A. Sugawara, T. Nishimura, Y. Yamamoto, H. Inoue, H. Nagasawa, T. Kato, *Angew. Chem.* **2006**, *118*, 2942–2945; *Angew. Chem. Int. Ed.* **2006**, *45*, 2876–2879; c) T. Nishimura, T. Ito, Y. Yamamoto, M. Yoshio, T. Kato, *Angew. Chem.* **2008**, *120*, 2842–2845; *Angew. Chem. Int. Ed.* **2008**, *47*, 2800–2803; d) Y. Yamamoto, T. Nishimura, T. Saito, T. Kato, *Polym. J.* **2010**, *42*, 583–586; e) M. Suzuki, K. Saruwatari, T. Kogure, Y. Yamamoto, T. Nishimura, T. Kato, H. Nagasawa, *Science* **2009**, *325*, 1388–1390.

[5] a) C. Lu, L. Qi, J. Ma, H. Cheng, M. Zhang, W. Cao, *Langmuir* **2004**, *20*, 7378–7380; b) I. Lee, S. W. Han, S. J. Lee, H. J. Choi, K. Kim, *Adv. Mater.* **2002**, *14*, 1640–1643; c) J. Aizenberg, A. J. Black, G. M. Whitesides, *Nature* **1999**, *398*, 495–498; d) J. Aizenberg, A. J. Black, G. M. Whitesides, *J. Am. Chem. Soc.* **1999**, *121*, 4500–4509.

[6] a) S. Tugulu, M. Harms, M. Fricke, D. Volkmer, H.-A. Klok, *Angew. Chem.* **2006**, *118*, 7619–7623; *Angew. Chem. Int. Ed.* **2006**, *45*, 7458–7461; b) D. C. Popescu, E. N. M. van Leeuwen, N. A. A. Rossi, S. J. Holder, J. A. Jansen, N. A. J. M. Sommerdijk, *Angew. Chem.* **2006**, *118*, 1794–1799; *Angew. Chem. Int. Ed.* **2006**, *45*, 1762–1767; c) J.-H. Zhu, J.-M. Song, S.-H. Yu, W.-Q. Zhang, J.-X. Shi, *CrystEngComm* **2009**, *11*, 539–541.

[7] a) K. Ichimura, S. Watanabe, *J. Polym. Sci. Polym. Lett. Ed.* **1980**, *18*, 613–617; b) K. Ichimura, S. Watanabe, *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 1419–1432.

[8] a) A. Sugawara, A. Oichi, H. Suzuki, Y. Shigesato, T. Kogure, T. Kato, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 5153–5160; b) T. Sakamoto, A. Oichi, Y. Oaki, T. Nishimura, A. Sugawara, T. Kato, *Cryst. Growth Des.* **2009**, *9*, 622–625.

[9] a) A. Sugawara, T. Ishii, T. Kato, *Angew. Chem.* **2003**, *115*, 5457–5461; *Angew. Chem. Int. Ed.* **2003**, *42*, 5299–5303; b) T. Sakamoto, A. Oichi, A. Sugawara, T. Kato, *Chem. Lett.* **2006**, *35*, 310–311; c) T. Sakamoto, A. Oichi, T. Nishimura, A. Sugawara, T. Kato, *Polym. J.* **2009**, *41*, 522–523.

[10] a) Z. Wang, G. C. Alfonso, Z. Hu, J. Zhang, T. He, *Macromolecules* **2008**, *41*, 7584–7595; b) A. Volford, F. Izsák, M. Ripszám, I. Lagzi, *Langmuir* **2007**, *23*, 961–964; c) T. Wang, A.-W. Xu, H. Cölfen, *Angew. Chem.* **2006**, *118*, 4561–4566; *Angew. Chem. Int. Ed.* **2006**, *45*, 4451–4455.

[11] Y. Oaki, H. Imai, *Cryst. Growth Des.* **2003**, *3*, 711–716.