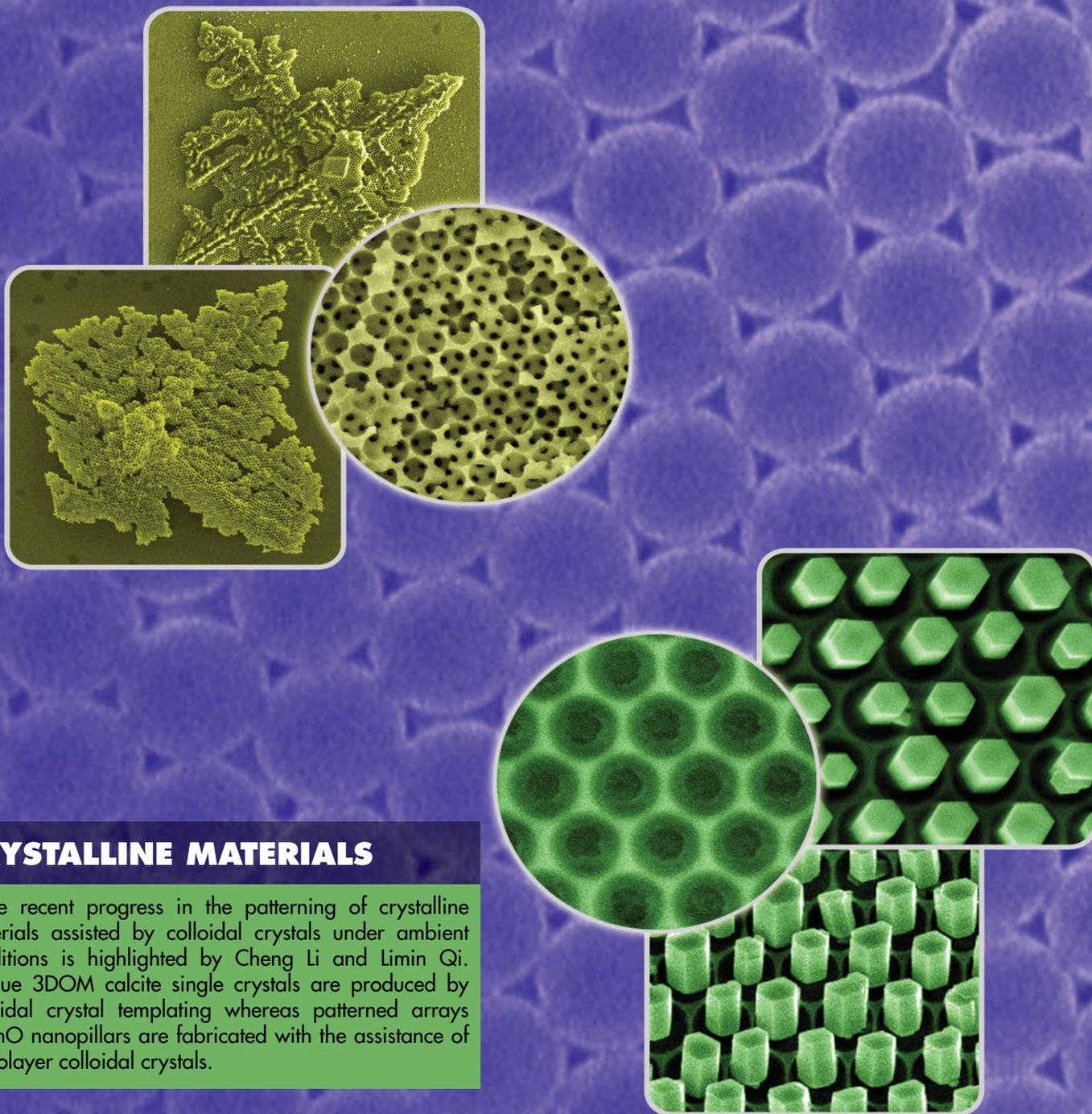


ADVANCED MATERIALS



CRYSTALLINE MATERIALS

Some recent progress in the patterning of crystalline materials assisted by colloidal crystals under ambient conditions is highlighted by Cheng Li and Limin Qi. Unique 3DOM calcite single crystals are produced by colloidal crystal templating whereas patterned arrays of ZnO nanopillars are fabricated with the assistance of monolayer colloidal crystals.

Colloidal-Crystal-Assisted Patterning of Crystalline Materials

By Cheng Li and Limin Qi*

Colloidal crystals have shown great potential as versatile templates for the fabrication of patterned micro- and nanostructures with complex architectures and novel properties. The patterning of functional crystalline materials in two and three dimensions is essential to the realization of their applications in many technologically important fields. This article highlights some recent progress in the fabrication of 2D and 3D patterned crystalline materials with the assistance of colloidal crystals. By combining a bioinspired synthetic strategy based on a transient amorphous phase with a colloidal-crystal templating method, unique 3D ordered macroporous (3DOM) calcite single crystals can be created. Moreover, patterned arrays of regular ZnO nanopillars with controlled size, shape, and orientation can be fabricated via a facile wet chemical approach by using masks derived from monolayer colloidal crystals (MCC).

1. Introduction

Colloidal crystals are generally two- or three-dimensionally close-packed arrays of monodisperse colloidal particles.^[1] The long-range ordered structures possessed by colloidal crystals have made them of great interest in several research aspects of advanced materials. The periodic alternation in the dielectric constant on the submicrometer length scale endows colloidal crystals with promising applications as bottom-up self-assembled photonic bandgap (PBG) materials, which has triggered intensive studies aimed at improving the structural perfection and optical quality of colloidal crystals.^[2,3] Another thriving application of colloidal crystals is their use as hard templates for the fabrication of inversely replicated functional materials such as 3D ordered macroporous (3DOM) materials, which are considered to be more promising as PBG materials than bare colloidal crystals. This templating strategy employing colloidal crystals is often referred to as colloidal-crystal templating (CCT) and great successes have been achieved in this research area.^[4] In the past decade, nanosphere lithography (NSL), which basically employs 2D colloidal crystals or monolayer colloidal crystals

(MCC) as the lithographic mask, has been established as an alternative patterning technique to conventional lithography. In conjunction with techniques such as deposition and etching, 2D patterned nanostructured arrays of various types have been successfully fabricated on different substrates.^[5]

Until now, various structural patterns have been produced by using the colloidal-crystal templating method, but they usually consist of either amorphous or polycrystalline units. The fabrication of patterned crystalline materials through wet chemical routes is relatively difficult while the patterning of amorphous materials is quite easy. In particular, the patterning of single-crystalline materials remained a formidable

challenge until recently. In this Research News article, we describe the recent progress in the patterning of crystalline materials assisted by colloidal crystals via bottom-up crystal growth under ambient conditions. Firstly, we introduce the bioinspired approach in conjunction with the CCT method that led to the formation of 3DOM single crystals. Then, we describe how to use MCC as a versatile template to precisely control the 2D patterned growth of crystalline nanoarrays.

2. Bioinspired Fabrication of 3DOM Calcite Single Crystals

The direct fabrication of single crystals with patterns on the micro- and nanometer length scale is of great technological significance, as these patterned structures are constituent parts in the construction of devices used in electronics, optics, and sensors.^[6] Particularly, single crystals with 3D ordered macropores might be promising candidates for highly desirable photonic crystals with full photonic bandgaps and birefringent photonic crystals with optical tunability because of their anisotropic refractivity.^[7] However, the 3DOM materials prepared are mostly polycrystalline or amorphous because it is very difficult to maintain the complex structural features on the micro- and nanometer scale without losing the single-crystalline nature.^[4] Therefore, the bottom-up fabrication of 3DOM single crystals with well-defined structure and pore sizes remains a great challenge.

On the other hand, natural organisms have provided us with excellent examples of beautifully sculpted single crystals, for

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example, the calcite skeletal plates of echinoderms and coccoliths. Such patterned single crystals show unique material behavior endowed by the single crystallinity. For instance, sophisticated arrays of microlenses formed by brittlestars as skeletons are made of birefringent calcite single crystals, which improve the optical performance of the lenses and retain the excellent mechanical strength of the skeletons. These micropatterned single crystals represent a remarkable example of a multifunctional biomaterial that fulfills both mechanical and optical functions.^[8] Until now, a few key mechanisms have been recognized in the mineralization process of these organisms. One concerns the inorganic–organic interface where insoluble organic matrices and soluble acidic proteins co-mediate the nucleation and orientation of the depositing minerals.^[9] Another evolving mechanism is based on the increasing evidence of an amorphous phase as the precursor in the formation of mineral parts with non-equilibrium shapes in many organisms.^[10,11] One of the advantages to use this amorphous-to-crystal transition strategy lies in the fact that amorphous phases such as amorphous calcium carbonate (ACC) can be molded arbitrarily into any shape thanks to their isotropic nature.^[12] Inspired by these biomineralization principles, Aizenberg et al. succeeded in fabricating large-area micropatterned calcite single crystals by controlling the crystallization of the pre-molded ACC precursor.^[13] Nevertheless, the experimental procedure was relatively complex and only 2D patterns on the length scale of some tens of micrometers were incorporated into the as-obtained single crystals.

Recently, we developed a facile, bioinspired strategy to create 3DOM calcite single crystals, which was achieved by infiltration of freshly prepared transient ACC dispersions into colloidal-crystal templates with the assistance of vacuum suction.^[14] The transient ACC was prepared by rapidly mixing solutions containing calcium and carbonate ions without any organic stabilizers. The liquid ACC granules solidified and crystallized into a single crystal soon after their infiltration through the interstices of the colloidal-crystal template. The applied vacuum suction during the infiltration of ACC guaranteed the rapid feeding of the transient phase to crystallization sites, thus avoiding direct nucleation on the top surface of the template. The carboxylate groups of the poly(styrene-methyl methacrylate-acrylic acid) colloidal-crystal template provided a strong affinity for the ACC phase and hence enhanced the filling of ACC into the interstices. Figure 1 shows typical scanning electron microscopy (SEM) images of the obtained 3DOM calcite single crystals. It can be seen that each crystal exhibits a dendritic morphology with symmetric dendrites spreading along the two diagonals of the top rhombus of the {104} oriented calcite core (Fig. 1a). The microstructure of the colloidal-crystal template was perfectly replicated inversely by the calcite crystal (Fig. 1b–d). While the calcite crystal was thoroughly perforated by 3D interconnected ordered macropores, it turned out to be single crystalline as demonstrated by the electron-diffraction and polarized light microscopy measurements. Figure 2 illustrates the possible formation process of the 3DOM calcite single crystals on the basis of the experimental observations. The molded ACC went through a single nucleation process initiated by an evolving rhombohedral-shaped calcite core formed from an initial amorphous “tuber”. Subsequent growth at the expense of ACC under non-equilibrium conditions led to its lateral expansion into a

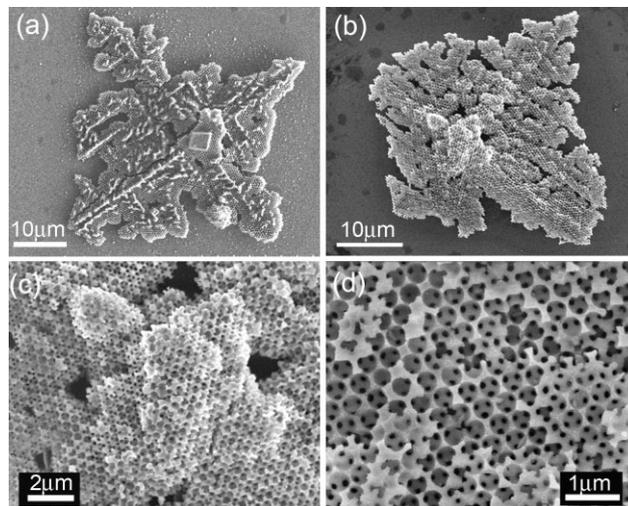


Figure 1. SEM images of 3DOM calcite single crystals: a) top view; b–d) bottom view. Reproduced with permission from [14].

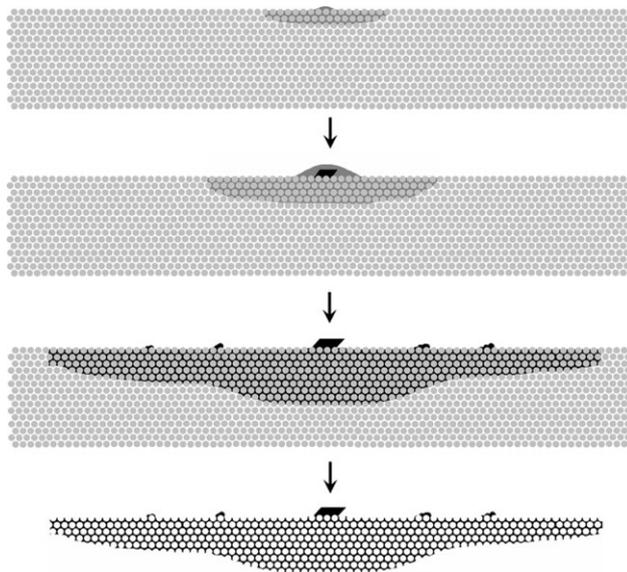


Figure 2. Schematic illustration of the formation process of the 3DOM calcite single crystal. Reproduced with permission from [14].

dendritic crystal while retaining the crystallographic orientation. Accidentally, this nucleation and crystallization process resembles the initial formation process of the sea urchin larval spicule.

The amorphous precursor pathway was found to be crucial for the formation of 3DOM calcite single crystals in this approach. As commented by Dr. Cölfen: “The application of amorphous precursor phases for the infiltration of an organic template with subsequent crystallization is an important transfer of biomineralization principles into the realm of synthetic materials.”^[15] Our approach may be a significant step towards large 3DOM single crystals since it combines several desirable features of easy and versatile syntheses using amorphous precursor particles.

However, efficient approaches remain to be developed to obtain larger (macroscopic) 3DOM single crystals with controllable thickness and crystal orientation, which is essential to their application in optical devices. If the crystallization could be tuned to proceed slowly enough (for example, at lower temperatures) a delicate balance between maintaining a single nucleation event for the production of a large oriented single crystal and the necessary supply of enough material for growth could be achieved. In this way the precursor solution flow and thus the amount of added ACC could be tuned to replicate even macroscopic templates, leading to the formation of 3DOM calcite single crystals with desired bulk shapes. Such large 3DOM calcite single crystals with a combination of good mechanical properties, remarkable anisotropic refractivity, and unique photonic bandgaps would be promising for the fabrication of high-performance optical devices that could find applications in displays, optical waveguides, lasers, sensors, and so on. Since colloidal crystals represent a topologically complex confinement with a resolution at the nanometer scale, this approach may represent a general strategy for the design and fabrication of functional single-crystalline materials with desired nanopatterns, orientations, and shapes. For example, this approach could be applied to other nanopatterned templates to obtain calcite single crystals patterned with even smaller features, which has lately been demonstrated by Steiner and coworkers.^[16] Furthermore, this strategy could be expanded to other crystalline systems as amorphous precursor phases are known for a number of organic and inorganic crystals.

3. Wet Chemical Route to Patterned ZnO Nanopillar Arrays

In recent years, 1D ZnO nanostructures such as nanowires, nanorods, nanobelts, and nanotubes have stimulated intensive interest because of their unique semiconducting and piezoelectric properties.^[17] Moreover, the alignment of these 1D ZnO structures into ordered nanoarrays can bring about improved performances in several promising applications, such as UV lasers, dye-sensitized solar cells, piezo-nanogenerators, and antireflection coatings.^[18] To integrate devices for such applications it is essential to realize rational control over the pattern (e.g., morphology, diameter, orientation, location, and spacing) of the 1D ZnO nanostructure arrays. Until now, various patterning techniques including lithographic methods using UV light, electron beams, polydimethylsiloxane (PDMS) stamps, or laser interference, and templating approaches using anodic aluminum oxide, block copolymers, or colloidal spheres, have been intensively exploited to generate patterned substrates for the selective growth of ZnO nanostructures.^[18]

Nanosphere lithography has proven to be a useful tool to create metal catalyst nanoarrays on a substrate for the patterned growth of 1D ZnO nanoarrays via a vapor-phase process.^[19–21] Although vapor-phase growth methods bear lots of advantages, wet-chemical

approaches are also appealing because of their cost efficiency, environmental friendliness, and compatibility with various substrates. Besides, for the production of uniform devices for applications such as micro-electron beams it is crucial to integrate uniform arrays of individual single-crystal nanowires with controllable diameter and location. Therefore, it remains a great challenge to develop facile solution routes to the individually patterned growth of well-aligned 1D ZnO nanoarrays with good control over both the pattern and the crystal quality.

We recently demonstrated the fabrication of well-aligned, individually patterned, regular ZnO nanopillar arrays assisted by MCC directly on zinc foil from solution.^[22] The experimental process is illustrated in Figure 3. By either inversely replicating or connecting the pristine monolayer colloidal crystals, two kinds of highly ordered masks were derived from MCC, which were denoted as inverted MCC (IMCC) and connected MCC (CMCC), respectively. Figure 4a and 4b show typical microstructures of the as-prepared IMCC and CMCC templates, respectively, revealing arrays of open growth windows on the zinc foil. Individual ZnO nanopillars grew vertically at each growth site and formed arrays that precisely preserved the hexagonal periodicity of the IMCC and CMCC templates, as shown in Figure 4c and 4d. The diameter of the ZnO nanopillars can be controlled in a wide range from 60 to 900 nm by varying the structural parameters of the MCC templates and the growth conditions. With the IMCC template, the width and spacing of the ZnO nanopillar arrays could be readily tuned by varying the colloidal sphere size of the MCC template or by elongating the reaction period. Interestingly, the vertically aligned ZnO nanopillars were also side-oriented, indicating a quasi-epitaxial growth on the zinc substrate (Fig. 4c). With the CMCC template, the size and spacing of the ZnO nanopillars could also be adjusted by changing the aperture size of the CMCC mask and patterned arrays of nanopillars with thinner diameters could thus be obtained. Moreover, by decreasing the reaction solution concentration, a bundle of ZnO nanorods rather than an individual one could be selectively grown at one growth site.

This wet-chemical approach demonstrated a facile and efficient way for the production of individually patterned arrays of well-aligned ZnO nanopillars with a wide range of sizes and spacings. The as-integrated ZnO nanopillar arrays showed lower defect densities and hence a higher optical quality, which promises their potential application in optical devices such as

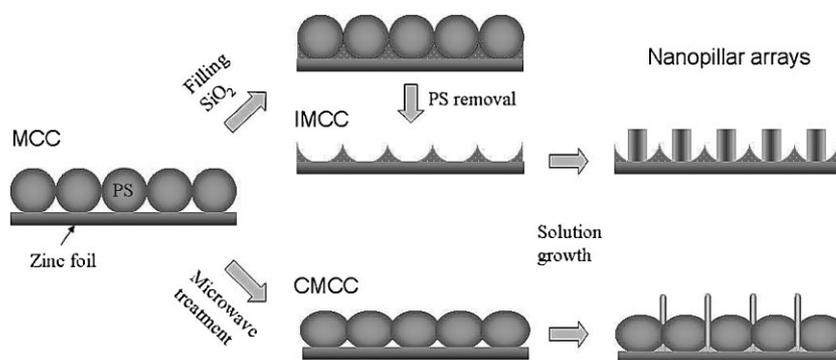


Figure 3. Schematic illustration of the MCC-assisted patterning of ZnO nanopillar arrays. Reproduced with permission from [22]. Copyright 2009, American Chemical Society.

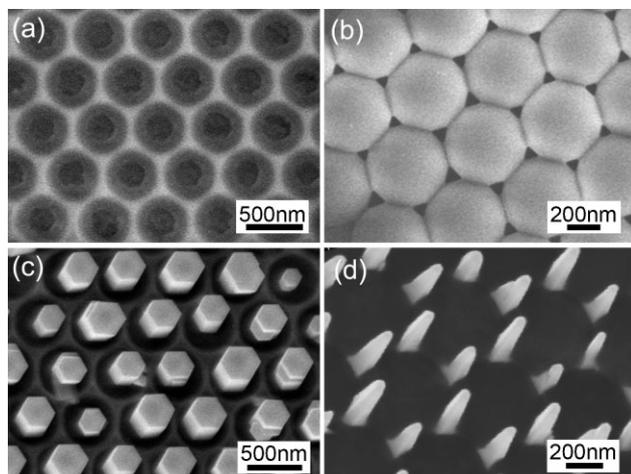


Figure 4. SEM images of a) IMCC and b) CMCC masks and c,d) the as-grown ZnO nanopillar arrays. Images (c) and (d) show ZnO nanoarrays grown using the masks in (a) and (b), respectively. Reproduced with permission from [22]. Copyright 2009, American Chemical Society.

stimulated emitters and lasing cavities. What is more, the highly ordered IMCC and CMCC masks may prove to be useful for the nanopatterning of other functional materials.

4. Conclusions

Colloidal crystals have proven to be a type of versatile templates for the patterning of crystalline materials with submicrometer- and nanometer-sized features in three or two dimensions. Inspired by biomineralization mechanisms, 3DOM single crystals of calcite can be created by infiltration of the colloidal-crystal template by a transient amorphous precursor and its spontaneous crystallization at room temperature. Here the colloidal crystal not only acts as a structural template but also provides the specific surface functional groups needed in the infiltration process. Based on the structure of MCC, two kinds of highly ordered masks could be constructed by either inversely replicating or connecting the colloidal spheres. As a demonstration, these masks were used to precisely control the patterned growth of 1D ZnO nanoarrays from solution, which are important semiconductor structures.

A lot of work still needs to be carried out to explore the great potential of the colloidal-crystal templating method in the patterning of crystalline materials. In this regard, the optimization of the available approaches towards 3D patterned single crystals is required to obtain large single crystals with desirable size, pattern, and crystal orientation. Effective wet-chemical approaches should be developed to realize inexpensive large-area fabrication of patterned arrays of various 1D semiconductor nanostructures with enhanced functional performance. Moreover, it is still a challenge to explore novel routes towards patterned micro- and nanostructures with promising applications by delicately manipulating the colloidal crystals. For example, most of the reported templating processes are conducted on solid substrates. Recently, monolayer colloidal crystals were used at the air/water interface in combination with photochemical reactions to produce hollow-sphere arrays.^[23] We are currently exploiting

the interfacial reactions assisted by nanosphere lithography at the gas/liquid interface to obtain highly regular crystalline nanonets and trying to establish a facile and general procedure for the fabrication of such structures for a variety of materials. Furthermore, colloidal crystals consisting of binary particles and colloidal crystals assembled by anisotropic particles^[24] could be employed to fabricate functional materials with even more complicated micro- and nanopatterns.

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